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Remediation of lead-, arsenic-, and cesium-contaminated soil using consecutive washing enhanced with electro-kinetic field

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Abstract

Purpose Extensive deposition of Pb, As, and Cs in soils may damage ecosystems and human's health. Soil washing is the most conventional remediation method, and its efficiency depends on metal solubility in soil. This study aims to optimize operating variables of electro-kinetic field (EKF)-enhanced soil washing procedures.

Materials and methods Soil samples from a Mississippi River Delta rice field were homogeneously spiked with Pb, As, and Cs, and contaminated soil was aged for 3 months. The remediation involved a first stage electro-kinetic process, followed by a soil washing procedure. Soil pH changes under EKF were studied. Effects of citric acid and reversed EKF were investigated for alleviating possible alkaline precipitation. In the washing procedure, soil washing time and cycles with different extractants were examined. The overall EKF-enhanced soil washing efficiencies were discussed as well.

Results and discussion The implement of EKF offered an acidic soil environment around the anode areas for solubilizing metal(loid)s. Combined with EKF, citric acid was more conductive to desorb metal(loid)s. In addition, the reversed EKF effectively alleviated metal(loid) precipitation caused by alkalization in the first stage cathode areas. The EKF significantly enhanced metal(loid) extractions in the anode area

of soils using Na_2EDTA, $CaCl_2$, and citric acid at pH of 2. The most preferable removal of Pb (80–98 %), As (48–63 %), and Cs (10–13 %) was achieved with three extractants. $CaCl_2$ and citric acid were proved to be suitable alternatives to Na_2EDTA for Pb extraction. A washing process of 2 h extraction with double washing cycles was optimized.

Conclusions Soil washing time and cycles were major factors governing the metal(loid) removal from soil. Washing process of 2 h extraction with double cycles was optimized for further extraction based on higher washing efficiency. The EKF effectively improved washing efficiency while some electrical parameters need further studies for cost performance consideration.

Keywords Consecutive soil washing · Electro-kinetic field · Extraction efficiency · Metal(loid) remediation

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1 Introduction

Soil contamination caused by heavy metal(loid)s is an increasing global concern due to their persistence, high toxicity, and potential carcinogenic characteristics (Han et al. 2004; Adriano 2001). Anthropogenic activities such as coal burning, combustion of leaded gasoline, mining, and production of electronics and ceramics have led to a significant building up of lead (Pb) and arsenic (As) which are the most common contaminants in soils (Shotyk et al. 1997; Adriano 2001; Mandal 2002; Han et al. 2007; Salazar and Pignata 2014). On the other hand, nuclear power plant accident and nuclear weapon testing largely released radioactive contaminants such as cesium (Cs) into soils (Giannakopoulou et al. 2007). Extensive deposition of Pb, As, and Cs in soils may damage ecosystems (Tyler et al. 1989). In addition, they may cause acute or chronic illnesses by damaging humans' nervous,

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cardiovascular, and reproductive systems via food chain accumulation (Adriano 2001; Duruibe et al. 2007; Wuana and Okieimen 2011). Therefore, proper remediation and cleaning up of contaminated soils are important in keeping a healthy ecosystem and decreasing the human exposure.

Soil washing has been developed as one of the *ex situ* traditional remediation methods for heavy metal-polluted soils (Dermont et al. 2008). It is a process of dissolving metals/metalloids with extractants and of concentrating them into a small volume via particle size separation (Maturi and Reddy 2008). It has been proved to be effective on soils with higher permeability (Chaiyaraksa and Sriwiriyanuphap 2004). Successful soil washing is usually dependent on three factors: the nature of contaminants, soil washing parameters, and soil properties (Zou et al. 2009). The nature of contaminants includes the speciation of metals/metalloids and their concentrations, distributions, and solubility in soils (Lim et al. 2004). Soil washing parameters consist of the type and concentration of extracting solutions, solution pH, liquid/soil (L/S, mL g^{-1}) ratios, washing time, and cycles (Zou et al. 2009). Soil properties, which are significant for metal mobility, mainly include soil pH, organic and inorganic matter content, cation exchange capacity, oxidation-reduction potential, etc. (Reed et al. 1996; Nowack et al. 2006b).

For certain polluted soils, soil washing parameters and soil properties are two variables available for improving the efficiency and decreasing the cost of the remediation. The extractant type is the most important soil washing parameter since it affects dissolution capacity of different heavy metals (Lim et al. 2004). Ethylenediaminetetraacetic acid (EDTA) is the most commonly used extractant due to its strong chelating ability to a variety of heavy metals in soil (Han et al. 2004; Labanowski et al. 2008; Tsang et al. 2007). Previous studies have shown great remediation effects on Pb- and As-contaminated soils with EDTA (Gabos et al. 2009; Sun et al. 2009; Virkutyte et al. 2002). However, EDTA is not an ideal extractant since it is quite persistent and less biodegradable in the soil environment, which may result in the secondary pollution in groundwater (Egli 1988). Additionally, relatively expensive cost may restrict its large-scale applications (Barona et al. 2001). Thus, environmentally friendly and biodegradable extractants such as calcium chloride (CaCl$_2$) and citric acid have received more interest as alternatives to EDTA (Suzuki et al. 2014). The extracting solution with a high extractant concentration and L/S ratio may damage soil structure by preferentially dissolving indigenous oxides, carbonates, and organic matter (Zhang et al. 2010). Therefore, diluted extracting solutions with moderated L/S ratios are preferred for both ecological and economical considerations. In addition, the release and dissolution of liable metal fractions are closely related to their contact duration in extraction procedures. However, concentration and L/S ratios of those environmentally friendly solutions for soil washing need

to be determined. Similarly, washing time and cycles are required to be optimized for high washing efficiency (Zou et al. 2009).

Most recently, electro-kinetic field (EKF) has been developed to enhance the remediation of contaminated soils (Finzgar and Lestan 2007; Giannis et al. 2009; Kim et al. 2011; Ng et al. 2014). Many extraction solutions such as diluted salt or diluted acid only dissolve a limited portion of the liable metals and metalloids in contaminated soils (Zhang et al. 2010). Recent studies reported that the EKF, as an assisted method, was effective on promoting the release of heavy metals from solid-phase components and reducing the usage of washing solution (Giannis et al. 2009; Ng et al. 2014). The electro-kinetic process involves introducing EKF by inserting the electrodes into the contaminated soils (Shen et al. 2007). The H$^+$ and OH$^-$ ions from water electrolysis are generated around the anode and cathode electrodes, respectively. As a result, acidification caused by the elevated H$^+$ enhances the desorption of metals from soil surface as well as facilitates the dissolution of precipitated metals around the anode areas (Li and Li 2000). The electro-kinetic process increases soil washing efficiency via lowering soil pH at the anode region. However, alkalization caused by the elevated OH$^-$ also results in the precipitation of metals around the cathode areas which may reduce the remediation efficiency (Gidarakos and Giannis 2006). In order to alleviate alkaline precipitation, organic acid such as citric acid may be applied near the cathode electrode. Citric acid desorbs metals from solid-phase components and neutralizes OH$^-$ to some extent (Lestan et al. 2008). Moreover, the reverse of anode and cathode electrodes is another approach alleviating alkaline precipitation. The reversed electrical field efficiently eliminated OH$^-$ and lowered the pH around the first stage cathode area which made the precipitated metals re-dissolving (Bi et al. 2011). Nevertheless, electrical parameters such as electrical field intensity and stimulation duration which are correlated to washing effectiveness and cost performance are not studied in detail (Cameselle et al. 2013).

In the present study, consecutive *ex situ* washing were conducted on Pb-, As-, and Cs-contaminated soils after the first stage and reversed electro-kinetic processes. The objective of this study was to determine the soil pH changes affected by the first stage and reversed electro-kinetic processes and to optimize the contact time and cycles for soil washing with CaCl$_2$, citric acid, and Na$_2$EDTA solutions. The overall EKF-enhanced soil washing efficiencies for Pb-, As-, and Cs-contaminated soils were discussed as well.

2 Materials and methods

2.1 Soil

The surface paddy soil samples (0–20 cm) were collected from below a rice field in the Mississippi River Delta. All

samples were air-dried at room temperature and grounded to pass the 2-mm sieve.

The physicochemical characteristics of collected soils were shown in Table 1. The total contents of native Pb, As, and Cs were determined by a 16-h acid digestion using 4 M HNO_3 at 80 °C with a soil-HNO_3 ratio of 1:25 (g:mL). The mixture was then centrifuged for 10 min at 8000 rpm. The supernatant was filtrated through a 0.45-μm filter and diluted tenfold before analyzing. The concentrations of Pb, As, and Cs in supernatants were then determined by inductively coupled plasma mass spectrometry (ICP-MS) (Han and Banin 1997). Soil pH was determined by using a 1:1 soil to water ratio with a pH meter. The organic matter (OM) content was measured by potassium dichromate titration method (Jackson 1958).The distribution of soil particle size was determined with hydrometer method after mechanical sieving (Blake and Harte 1986).

Chemical grade lead nitrate ($Pb(NO_3)_2$), sodium arsenite ($NaAsO_2$), and cesium chloride (CsCl) were used as extraneous sources of Pb, As, and Cs. The Pb, As, and Cs salts were added to soils at levels of 1000, 40, and 40 mg kg^{-1}, respectively. The salts were grounded and homogeneously mixed with air-dried soils and then were aged for 3 months with field capacity moisture regime.

2.2 Electro-kinetic processes

The electro-kinetic processes were performed in plastic pots of 15 cm diameter and 14 cm height. A DC power supplier (0–60 V, 0–3 A) was used as electrical power source. Graphite electrode rod (0.95 cm diameter, 30.5 cm length) was used as both anode and cathode due to its low cost and inertness. A pair of graphite electrode rods were vertically inserted into both sides of each pot with a distance of 12 cm between the anode and cathode. The copper wires were used to connect the electrodes with the power source. The areas with a 3-cm radius around the anode, the middle of the pot, and the cathode were defined as the anode, middle, and cathode areas, respectively. EKF of 0 (control), 2, and 4 V cm^{-1} were introduced to

soils in order to investigate the effect of different EKF intensities on altering soil pHs. Citric acid was applied in the cathode area of soils under 4 V cm^{-1} EKF for evaluating the effect of citric acid on lowering soil pH around the cathode. For each electro-kinetic test, approximately 600 mL water was added to 1800 g of dry soil per 48 h. For treatments amended with citric acid, 0.4 M citric acid was added in the cathode areas in the equal amount of water. The EKF was initially implemented on contaminated soils for 48 h (first stage EKF process) and then applied for another 48 h with reversed current (reversed EKF process). The surface soil samples (0–5 cm) were collected after the first stage and reversed EKF process. The soils at 1 and 2, 5 and 6, and 10 and 11 cm from the anode were collected as the samples of the anode, middle, and cathode areas, respectively. All the tests were performed in duplicates, and the average contents of Pb, As, and Cs and pH values were measured.

2.3 Washing procedures

The washing procedures were conducted in 50-mL Teflon tubes. The 0.01-M Na_2EDTA, $CaCl_2$, and citric acid solutions were prepared, and their pH values were adjusted to 2. The tubes containing 1.0 g soil and 20 mL extracting solution were agitated in a shaker at a speed of 110 rpm at room temperature for a certain period. Suspensions were centrifuged at 8000 rpm for 10 min and then filtered through a 0.45-μm membrane for analysis with ICP-MS (Han and Banin 1999). All the washings were performed in duplicates.

Samples collected from the anode area of soils under 4 V cm^{-1} EKF and citric acid-treated cathode area were used for determination of washing variables. Washing time of 0.5, 1, 2, 4, 6, 8, and 12 h were used for kinetic study to determine the optimized washing duration. In another experiment, six consecutive extractions were conducted with optimal washing time. The suspension was centrifuged and the solution was renewed in each washing cycle. Cumulative removal rates of Pb, As, and Cs with $CaCl_2$ and citric acid solutions were calculated and compared with those of Na_2EDTA. The removal efficiency was calculated from the equation:

$$\text{Removal Percent } (\%) = \frac{\text{Co} - \text{Ct}}{\text{Co}} \times 100$$

where C_0 was the first stage metal content in soil and Ct was the metal content that remained in soil after the experiment (Ng et al. 2014).

Extraction procedures with optimized operating variables were applied for further investigation of soil washing enhanced by EKF. The washing was conducted on soils under 0 (CK), 2, and 4 V cm^{-1} EKF and soil under 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area. The removal efficiency of metals from the first stage anode, middle, and

Table 1 Physicochemical characteristics of the soil sample

Metal	
Pb (mg kg^{-1})	22.3
As (mg kg^{-1})	7.3
Cs (mg kg^{-1})	1.4
Soil components[a]	
pH	6.6-7.0
OM (g kg^{-1})	15
Sand (g kg^{-1})	320
Silt (g kg^{-1})	490
Clay (g kg^{-1})	480

[a] From Han et al. 2007

cathode regions were calculated and compared with those after the reversed electro-kinetic process.

2.4 Statistical analysis

The data were processed, and averages and standard deviations were calculated with Microsoft Excel. SPSS 11.5 software was used for statistical analyses. Duncan's multiple range tests were applied for significant analysis of pH changes and metal(loid) removal efficiency under EKF ($P < 0.05$).

3 Results and discussion

3.1 Soil pH changes influenced by EKF

The pH changes of Pb-, As-, and Cs-contaminated soils after electro-kinetic processes were shown in Table 2. The pH of polluted soils without EKF (CK) was around 6.6 which was almost the same as that of unpolluted soils. This suggests that distribution of metal(loid)s in MS Delta paddy field soil had no influence on soil pH.

After the 48-h EKF process of the first stage, the pH values of treated soils were significantly polarized upon the electrical current. Sub-region soil pHs near the anode and cathode areas were around 0.6–1.5 and 11–12, respectively, which significantly changed compared with those without EKF. As supported by the present study, EKF seemed an effective technique to lower the pH of soil with lower buffer capacity (Puppala et al. 1997). The H$^+$ ions generated by the electrolysis of water

caused soil acidification in the vicinity of the anode region (Kim et al. 2010). They were transported towards the cathode through electromigration and electroosmosis, while OH$^-$ generated from the cathode area was transported to the anode (Kim et al. 2010). Basically, the traveling velocity of H$^+$ is 1.8 times faster than that of OH$^-$ (Kim et al. 2011). However, the pH values observed in the middle region of soils were approximately the same to those of CK. This indicates that the H$^+$ had not reached the middle region which might be due to the low permeability of soils or short duration of the electro-kinetic process (Kim et al. 2008). Low soil pH values around 1.2–1.5 were achieved in the anode region of soils under 2 V cm^{-1} EKF, and slight decreases were obtained as the EKF increased to 4 V cm^{-1}. This indicates that the higher voltage input accelerated the efficiency of water electrolysis (Park et al. 2009). H$^+$ enhanced the desorption of heavy metals from soil solid-phases through ion exchange while OH$^-$ decreased the metal solubility via alkaline precipitation (Altin and Degirmenci 2005). Therefore, it is essential to keep an acidic environment to avoid alkaline precipitation around the cathode (Iannelli et al. 2015). The addition of acid such as HCl, HNO$_3$, and citric acid has been applied. As a weak acid, citric acid is not as effective as strong acid (Yeung and Gu 2012). Nevertheless, it is biodegradable and lowers soil pH to some extent without the risk of secondary pollution to groundwater (Yeung and Gu 2011). In this study, 200 mL 0.4 M citric acid was applied in the cathode area of soils under 4 V cm^{-1} EKF. The effect was not obvious, and the pH values (11–12) were close to those without addition of citric acid. This may indicate that the amount of citric acid for neutralizing OH$^-$ was not enough.

Table 2 Effect of EKF on pH changes of Pb-, As-, and Cs-contaminated soils

Soil pH

Metal(loid)		First stage anode		Middle region		First stage cathode	
		First stage EKF	Reversed EKF	First stage EKF	Reversed EKF	First stage EKF	Reversed EKF
Pb	CK			6.6 ± 0.07	6.6 ± 0.07		
	2 V cm^{-1}	1.5 ± 0*	6.6 ± 0.5	6.9 ± 0.3	7.5 ± 0	12 ± 0.3*	6.6 ± 0.2
	4 V cm^{-1}	1 ± 0.5*	10 ± 1.8*	6.6 ± 0.4	7.5 ± 0.5	11 ± 0.1*	1.8 ± 0*
	4 V cm^{-1} + citric acid	0.9 ± 0.3*	11 ± 0*	6.6 ± 0.1	7.5 ± 0	11 ± 0.1*	1.7 ± 0.4*
As	CK			6.8 ± 0.2	6.8 ± 0.2		
	2 V cm^{-1}	1.2 ± 0.3*	8.5 ± 0	6.3 ± 0.5	7.9 ± 0.3	11 ± 0.1*	5.6 ± 0.1
	4 V cm^{-1}	0.9 ± 0.4*	11 ± 0*	7 ± 0	7.2 ± 1	12 ± 0*	2.9 ± 0*
	4 V cm^{-1} + citric acid	0.6 ± 0.1*	9 ± 0	6.6 ± 0.7*	5.9 ± 0.4	11 ± 0.9*	2.3 ± 0*
Cs	CK			6.8 ± 0.1	6.8 ± 0.1		
	2 V cm^{-1}	1.2 ± 0.7*	6.6 ± 0	6.9 ± 0.2	8.1 ± 0.1	12 ± 0*	7.2 ± 0
	4 V cm^{-1}	0.9 ± 0.8*	12 ± 0*	6.3 ± 0.7	7.2 ± 0.5	11 ± 0.1*	2 ± 0*
	4 V cm^{-1} + citric acid	0.7 ± 0.8*	10 ± 0*	6.1 ± 0.5*	7 ± 0	11 ± 0.1*	1.7 ± 0*

Treatments were implemented under 2 and 4 V cm^{-1} EKF and 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area, respectively. Treatments without EKF were set as the control (CK). The EKF was initially implemented for 48 h (first stage EKF) and then applied for another 48 h with reversed electrical current direction (reversed EKF). Means followed by the asterisk (*) were statistically different to the control (CK) at $P < 0.05$

The reverse of anode and cathode electrodes is another approach of alleviating alkaline precipitation in the cathode. With elevated H$^+$, initial generated OH$^-$ was effectively eliminated in the first stage cathode area under EKF with a reversed current. The reversed electro-kinetic process with the same EKF intensities as the first stage one was implemented for 48 h. Soil pHs in the first stage cathode areas under reversed 2 V cm^{-1} EKF were recovered to around 6.6 while those under reverse 4 V cm^{-1} EKF were decreased to around 2. Results implied that the reverse of anode and cathode electrodes was more efficient than adding citric acid for neutralizing initial OH$^-$. However, electrical parameters such as electrical field intensity and stimulation duration need to be further studied for cost performance consideration (Zhou et al. 2004).

3.2 Determination of washing time and cycles

Soil washing efficiency is dependent on washing parameters such as type of extractant, L/S ratio, washing time, and washing cycles (Zou et al. 2009). As Na$_2$EDTA, CaCl$_2$, and citric acid all at 0.01 M were determined with L/S ratios of 20 mL g^{-1}, the washing efficiency was directly related to washing time and cycles.

Extraction time is significant for soil washing since the desorption of metal(loid)s is a kinetic equilibrium process (Zou et al. 2009). Kinetic study is shown in Fig. 1. The results suggested that Na$_2$EDTA, CaCl$_2$, and citric acid solutions induced a two-step desorption process: rapid desorption of Pb, As, and Cs within the first hour, followed by a slow extraction process. Metal(loid)s in the most labile forms were firstly desorbed while recalcitrant species were slowly removed (Barona et al. 2001). More metals/metalloids were removed as contact duration increases with extracting solution. In our study, relative higher removal percentages of Pb, As, and Cs were achieved at 2 h with Na$_2$EDTA, CaCl$_2$, and citric acid. The removal process reached a plateau after 4–8 h and changed little with further contact. The results indicated that the initial release of metals/metalloids was dominated by the soluble fractions, while the subsequent release was determined by the replenishment of soluble fractions from the solid-phase fractions including exchangeable fraction (Kirpichtchikova et al. 2006). Therefore, a duration of 2 h was the optimal washing time for this study.

On the other hand, soil metal(loid)s usually could not be totally removed by a single washing cycle. According to the previous study, the efficiency of successive washing using extractants at low concentration was higher than single washing with concentrated extractants (Finžgar and Leštan 2007). In order to remove more metal(loid)s, six consecutive washing cycles (2 h/cycle) were conducted (Fig. 2). The fresh extracting solutions were replaced in each washing cycle. Comparing the sixth with the first extraction cycle, the removal percentages using Na$_2$EDTA, CaCl$_2$, and citric acid were
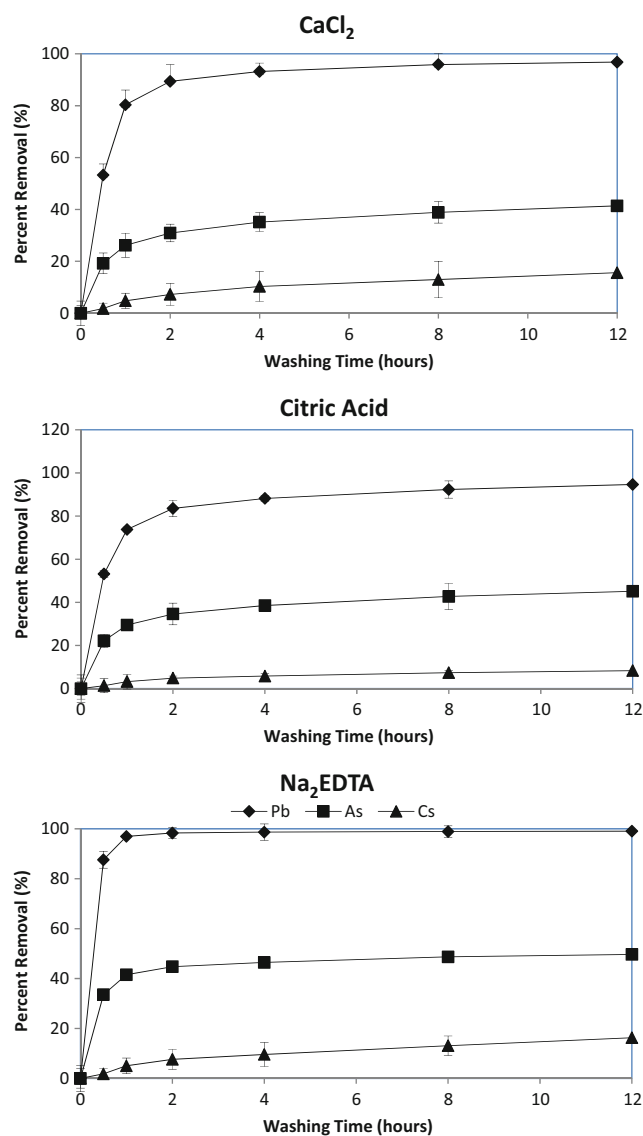
Fig. 1 Kinetic of Pb, As, and Cs extraction from contaminated soils with CaCl$_2$, citric acid, and Na$_2$EDTA (0.01 M, L/S ratio = 20 mL g^{-1}, pH = 2). Soil was polluted with 1000 mg kg^{-1} Pb, 40 mg kg^{-1} As, and 40 mg kg^{-1} Cs. Samples were collected in the anode area of soils under 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area

increased respectively by 9, 17, and 38 % for Pb; 17, 26, and 28 % for As; and 12, 10, and 9 % for Cs. The increase in the removal of metals/metalloids in the continuous washing cycle may be partly due to the dissolution of some residual metal chelates trapped in soil pore solutions (Sun et al. 2001). Additionally, it removed a large amount of competitive cations in initial steps which was beneficial for metal desorption in the following cycles (Polettini et al. 2007). Also, it prevented desorbed metals from reabsorbing on soil residuals (Strawn and Sparks 2000). As the washing cycles increase, the removal of total Pb approached a plateau in the second extraction and then remained almost constant. In contrast, the removal of total As and Cs were steadily increased from the first to the
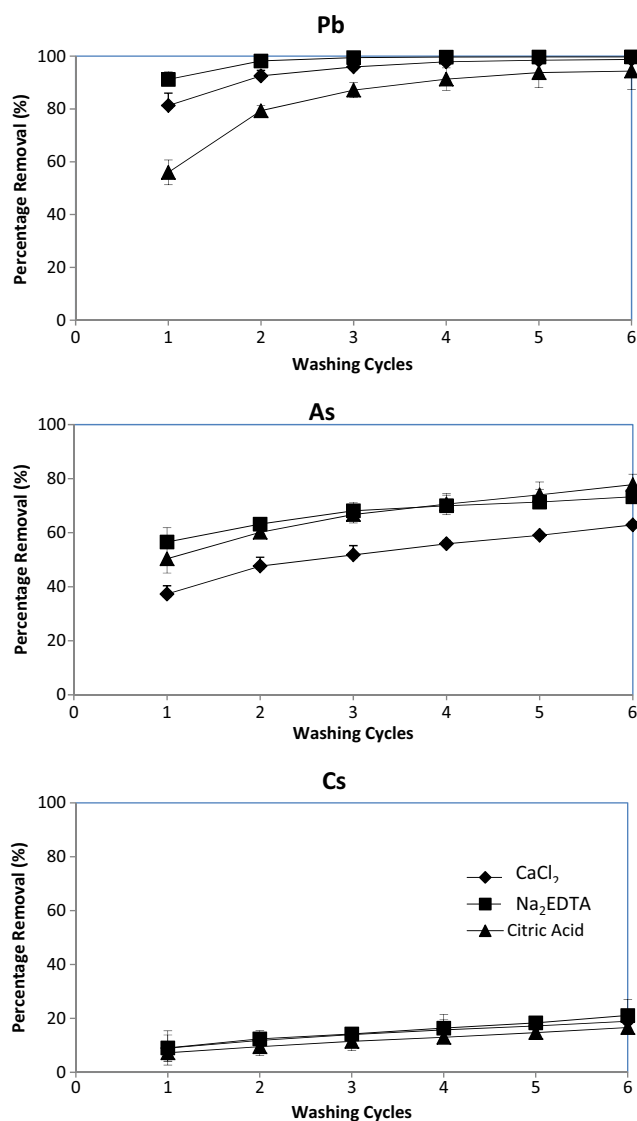
Fig. 2 Cumulative extraction of Pb, As, and Cs from contaminated soils over six consecutive extraction cycles (2 h/cycle) with 0.01 M $CaCl_2$, citric acid, and Na_2EDTA (L/S ratio = 20 mL g^{-1}, pH = 2). Soil was polluted with 1000 mg kg^{-1} Pb, 40 mg kg^{-1} As, and 40 mg kg^{-1} Cs. Samples were collected in the anode area of soils under 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area

sixth extraction. The results are in agreement with our previous finding that the majority of Pb was easy to transform to labile forms such as soluble and exchangeable fractions in acidic environment, especially in the anode region which is extracted in the first two washing cycles (Mao et al. 2016). In contrast, As and Cs were mainly in more stable fractions which were gradually transformed to labile forms and removed by consecutive washing (Polettini et al. 2007; Mao et al. 2016).
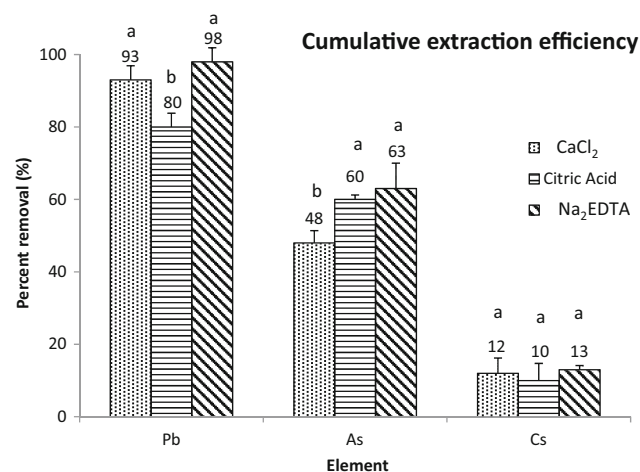
The treated soils were collected in the anode area of soils under 4 V cm^{-1} EKF and 0.4 M citric acid applied in the cathode areas. The pHs of extractant solutions were adjusted

to 2.0. The solution pH adjustment ensured the adequate metal ions for determining the optimal washing time and cycles. Based on the current results, a washing process of 2 h duration with double cycles was efficient for Pb washing with extractants at 0.01 M and L/S ratios of 20 mL g^{-1}. The optimal washing variables for As and Cs need to be investigated further.

3.3 Extraction efficiencies of various extractants

The extraction efficiencies of Pb, As, and Cs with Na_2EDTA, $CaCl_2$, and citric acid solutions were investigated. The washing process of 2 h with double cycles was conducted for the extraction. Results of the removal as percentages were shown in Fig. 3.

Obviously, complete removal of Pb, As, and Cs was not achieved after the washing procedure. Not all extractants targeted at metals/metalloids in soil—they also interacted with other soil components such as Fe oxides (Nowack et al. 2006a). The removal percentages of Pb (80–98 %) were significantly higher than those of As (48–63 %) and Cs (10–13 %). This discrepancy is probably due to the metal(loid) speciation and distribution among solid-phase components in treated soils. The majority of Pb was in the labile fractions upon acidification which could easily form soluble complexes with extractants (Mao et al. 2016). Nevertheless, As and Cs were mainly in the OM-bounded, Fe/Mn-bounded, and residual fractions which made them to have less access to the extractant (Kirpichtchikova et al. 2006; Mao et al. 2016). Furthermore, As and Cs might not form the stable complexes which was easy to reabsorb with the extractants (Tokunaga and Hakuta 2002).

Fig. 3 Removal efficiency of Pb, As, and Cs over two consecutive extractions (2 h/cycle) with 0.01 M $CaCl_2$, citric acid, and Na_2EDTA (L/S ratio = 20 mL g^{-1}, pH = 2). Soil was contaminated with 1000 mg kg^{-1} Pb, 40 mg kg^{-1} As, and 40 mg kg^{-1} Cs. Samples were collected in the anode area of soils under 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area

The cumulative extraction efficiencies of Pb with these three extractants were in the following order: Na_2EDTA (98 %) > $CaCl_2$ (93 %) > citric acid (80 %). This indicated that $CaCl_2$ and citric acid were both suitable alternatives to Na_2EDTA for extracting soil Pb. In addition, the total removal of Pb with $CaCl_2$ was 13 % larger than that with citric acid implying that Pb tends to form the stronger complex with Cl^- than with citric acid. Therefore, $CaCl_2$ was an excellent extractant for removing Pb in soils.

3.4 Washing efficiency enhanced by EKF

The enhancement of EKF on extraction efficiency was investigated in Pb-contaminated soils. The washing procedure of 2 h duration with double cycles was conducted on Pb-contaminated soils after the first stage and reversed EKF processes, respectively. The $CaCl_2$ solution was 0.01 M with L/S ratios of 20 mL g^{-1} without pH adjustment. The results of extraction efficiencies were shown in Fig. 4.

Obviously, the removal of total Pb was significantly enhanced by the EKF. In soil washing after the first stage EKF process, almost no Pb was removed (0.005 %) in CK which was probably due to the distribution of Pb in soils. Our previous data indicated that Pb in soils was mainly presented in the Fe/Mn oxide and OM-bounded fractions under neutral conditions (Mao et al. 2016). The removal of Pb under EKF without citric acid was significantly increased by 6–15 % in the anode areas under EKF. This probably resulted from soil acidification during the EKF process. The soil pH was significantly polarized upon the electricity current. Sub-region soil pHs near the anode and cathode areas were around 0.9–1.5 and 11–12, respectively (Fig. 5). Since H^+ competes the binding sites with Pb^{2+} on soil OM, acidic environment is beneficial for releasing Pb from less mobile fractions. The extraction efficiency increased as the EKF intensity increases which implied that the higher voltage input accelerates the generation of H^+ through water electrolysis (Park et al. 2009; Lu et al. 2012). H^+ and Pb^{2+} may transport from the anode to the cathode through electromigration and electroosmosis (Kim et al. 2010). However, the pH (6.6–7.5) and low Pb extractions (0.03–0.1 %) in the middle region under EKF were similar to those of CK (Figs. 4 and 5). This implies that soil properties such as high clay content and low permeability might limit the movement of cations (Kim et al. 2008). Low extraction efficiencies of Pb (0.008– 0.01 %) were also observed in cathode areas due to alkaline precipitation (Altin and Degirmenci 2005).
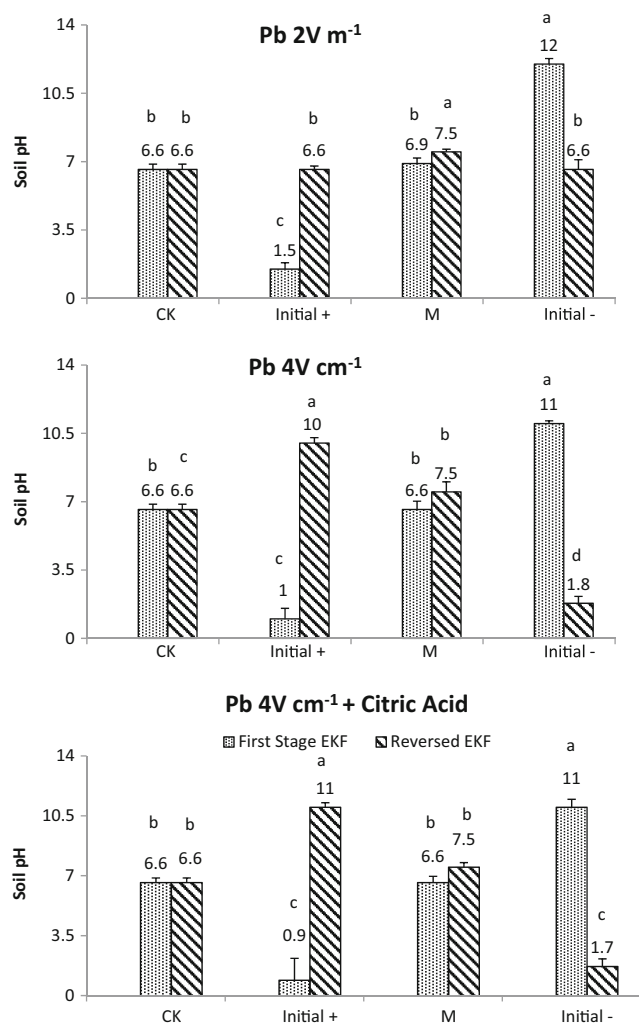
Citric acid at 0.4 M was applied in the cathode areas of soil under 4 V cm^{-1} EKF to alleviate alkaline precipitation of metals. Its effect on lowering pH around the cathode area was limited, and no change was shown compared to that of soil under 4 V cm^{-1} EKF. However, significant increases in Pb
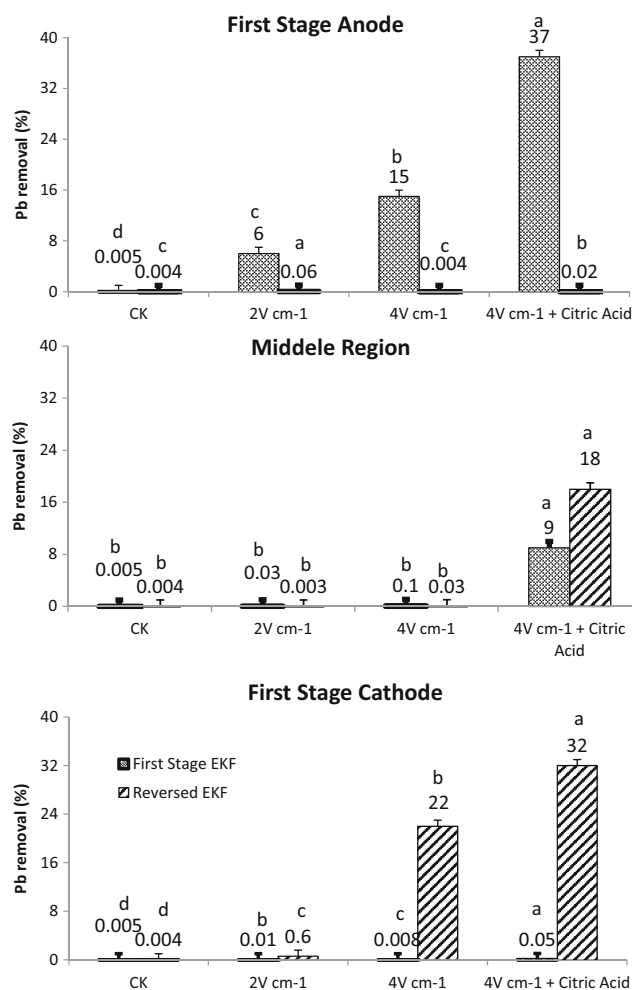
Fig. 4 Washing efficiency of Pb over two consecutive extraction cycles (2 h/cycle) with 0.01 M $CaCl_2$ (L/S ratio = 20 mL g^{-1}, pH = 6) from the first stage anode (+), middle (M), and cathode (−) regions of contaminated soils (1000 mg kg^{-1} Pb). Treatments were implemented under 2 and 4 V cm^{-1} EKF and 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area, respectively. Treatments without EKF were set as the control (CK). The EKF was initially implemented for 48 h (first stage EKF) and then applied for another 48 h with reversed current (reversed EKF). *Means* followed by the *asterisk* (*) were statistically different from the CK at $P < 0.05$

extraction were obtained in both the anode (22 %) and middle (9 %) regions of the soil. This was probably due to the effective solubilization of citric acid as an organic ligand on Pb (Yeung and Gu 2012; Peters 1999). The reverse of the anode and cathode electrodes reduced alkaline precipitation in the first stage cathode region. After the reversed EKF process, soil pHs of the first stage cathode areas were decreased to around 2 under 4 V cm^{-1} EKF and Pb removal efficiencies were increased by 22–32 % compared to CK.

Soil washing in the anode area of soils under 4 V cm^{-1} EKF plus citric acid treatment in the cathode was most favorable after the first stage (37 %) and reversed (32 %) EKF processes, respectively. However, this result was much lower

Fig. 5 Effect of EKF on pH changes of Pb-contaminated (1000 mg kg^{-1}) soils from the anode (+), middle (M), and cathode (−) regions. Treatments were implemented under 2 and 4 V cm^{-1} EKF and 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area, respectively. Treatments without EKF were set as the control (CK). The EKF was initially implemented for 48 h (first stage EKF) and then applied for another 48 h with reversed current (reversed EKF). *Means* followed by the *asterisk* (*) were statistically different to the CK at $P < 0.05$

than the former extraction (98 %) by using the same extractant with lower solution pH (pH = 2) (Table 3). This indicated that lower solution pH was advantageous for the extraction of Pb.

Table 3 Washing efficiency of Pb-contaminated soils

Cycles	Removal of Pb (%)	
	Extraction pH = 2	Extraction pH = 6
1	81 ± 1.2	33 ± 1.6
2	93 ± 4.4	37 ± 2.3

The washing with 0.01 M CaCl$_2$ had two consecutive extraction cycles (2 h/cycle, liquid/solid = 20) at different pHs. Samples were collected in the anode area of treatments after the first stage 4 V cm^{-1} EKF plus 0.4 M citric acid applied in the cathode area

4 Conclusions

This study investigated the feasibility of consecutive soil washing enhanced by EKF. The EKF showed significant influence on polarizing soil pHs upon the electrical current. The acidification near the anode was beneficial for the releasing of Pb, As, and Cs from solid-phase fractions while the alkalization near the cathode caused possible metal precipitation. The effect of citric acid (0.4 M) on neutralizing OH$^-$ was limited. However, the reverse of the anode and cathode electrodes efficiently alleviates the alkaline condition in the first stage cathode areas.

The washing time and cycles were major factors that governed the metal(loid) removal in soil washing process. The most labile species of Pb, As, and Cs were quickly removed by extractant within the first 2 h while the recalcitrant species were slowly removed subsequently. The efficiency of successive washing using low concentration of extractants was higher than that of single extraction with concentrated extractants. The washing process of 2 h duration with double cycles was optimized for the extraction, and CaCl$_2$ and citric acid were both suitable alternatives to Na$_2$EDTA for Pb extraction under EKF. However, the proper extractants for As and Cs need further investigation.

The EKF effectively improved the washing efficiency of Pb in the anode area of soils with CaCl$_2$ by releasing the mobile Pb from the soil solid-phase components. The washing performance increased as the EKF intensities increase while the influence of other electrical parameters such as electrical stimulation period, electrode materials, and electrical configurations needs further studies. Additionally, lower pH of extractant solution was observed to be an important criterion for achieving higher washing efficiency which also requires further investigation.

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