Remediation of heavy metal contaminated soils by organic acid extraction and electrochemical adsorption ☆

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A B S T R A C T

Remediation of heavy metal contaminated soils remains a global challenge. Here, low-molecular-weight organic acids were used to extract Cu and Zn from polluted soils, and the extracted heavy metals were subsequently adsorbed by activated carbon electrodes. The electrochemical adsorption mechanism as well as the influence of pH, organic acid type and voltage were investigated, and the soil remediation effect was further evaluated by the cultivation of rape. After extraction by citrate at initial pH 8.3 and electrochemical adsorption at 0.9 V for 7 d, the concentrations of total and bioavailable Cu in soils decreased from 1090 to 281 to 391 and 52 mg kg^{-1}, and those of Zn decreased from 262 to 39 to 208 and 30 mg kg^{-1}, respectively. Cu and Zn ions were mainly electrochemically adsorbed on the carbon cathode and anode, respectively, resulting in decreases of their concentrations to below 1 mg L^{-1} in the leachate. The presence of organic acids improved the remediation performance in the order of citrate > oxalate > acetate. The decrease in the initial pH of citrate solution enhanced the removal rate of Zn, while seemed to have no effect on that of Cu. The removal capacity for heavy metals decreased with decreasing cell voltage from 0.9 to 0.3 V. In the rape cultivation experiment, the Cu and Zn contents in shoot and root were decreased by more than 50%, validating the soil remediation effect. The present work proposes a facile method for heavy metal removal from contaminated soils.

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1. Introduction

Heavy metal contamination of soil is still a severe challenge around the world. The intensifying anthropogenic activities including mining, pesticide abuse and metallurgy are the major sources of heavy metal enrichment in soils (Yuan et al., 2016). As reported in China, there are 16.1% sampling sites exceeding the environmental quality standards, and about 82% of the contamination results from inorganic pollutants including cadmium, copper and zinc according to the investigation by the Ministry of Environmental Protection in 2014 (Zhao et al., 2015; Jing et al., 2018). About 37.3% of the total contaminated soil (involves several million hectares) can be attributed to heavy metal pollution in Europe (Liao et al., 2016). Heavy metal pollution threatens ecological environment and human health through food chains due to their high toxicity, environmental persistence and mobility in soils (Chen et al., 2015). Therefore, it is highly urgent to remediate heavy metal-contaminated soils to decrease their environment threats. Currently, the most widely applied remediation techniques include surface capping, encapsulation, vitrification, solidification and landfilling (Liu et al., 2018; Rui et al., 2019). Despite of their high efficiency, these methods are at the expense of loss of land cropping functions (Liu et al., 2018). Therefore, it is of great significance to develop some "green" and sustainable soil remediation technologies.

Heavy metal ions usually exist as complexes and are adsorbed on the surface of soil particles (Xu et al., 2019). The heavy metals can be trapped or immobilized by using adsorbents with large surface area and high surface activity to reduce their mobility and bioavailability (Komárek et al., 2013). However, the trapped contaminants might be reactivated by natural weathering and

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uncontrolled mechanical disturbance (Liu et al., 2018). Heavy metals can also be removed from soils through some methods including phytoremediation and bioremediation (Ruta et al., 2017; Sarwar et al., 2017). However, these methods are usually of high metal selectivity, and their application is very often limited by the high time consumption and low efficiency (Sarwar et al., 2017; Liu et al., 2018).

Electrochemical remediation, particularly electrokinetic remediation, has emerged as a promising technique, and great progress has been made in the treatment of contaminated soils by this technique in the latest two decades (Yeung and Gu, 2011). In a typical electrokinetic remediation system, heavy metals in the soil are migrated to the oppositely charged electrodes by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis under a direct-current electric field (Peng et al., 2018; Wang et al., 2019). However, electrokinetic remediation is usually used to treat fine-grained soils with low hydraulic conductivity (Peng et al., 2018). In some cases, the metal extraction efficiency of electrochemical remediation is rather limited (Yeung and Gu, 2011). Therefore, it is generally improved by combining with other technologies including bioremediation and desorption of heavy metals from soil particles by the introduction of chemical agents (Fan et al., 2007; Zulfiqar et al., 2017). However, these single or combined processes require strong electric fields ($1-1.5$ V cm^{-1}) to drive the migration of heavy metal ions, resulting in the electrolytic decomposition of water and electrode wear (Mena et al., 2016). The undesirable side reactions will greatly increase energy consumption, and auxiliary equipments are also needed to maintain the pH of the electrolytes (Yeung and Gu, 2011). Therefore, decreasing the applied voltage can effectively reduce the energy consumption and cost in electrochemical soil remediation processes.

Compared with the electrokinetic remediation of soils, the electromigration of heavy metal ions requires lower voltages in aqueous solutions. An interesting remediation approach composed of soil washing and electrochemical heavy metal removal has been proposed in many studies (Pociecha et al., 2011; Voglar and Lestan, 2012). Owing to the high extraction efficiency for heavy metals of synthetic chelating agents including EDTA, DTPA, NTA, and EDDS, heavy metals can be mobilized from soils due to the formation of water-soluble metal-chelate complexes, and subsequently be electrochemically removed from the waters (Ferraro et al., 2015). However, these chelating agents have some disadvantages including hard degradation (particularly EDTA), high toxicity (particularly NTA), and high cost (particularly EDDS) (Zou et al., 2009; Oustan et al., 2011). In addition, the removal process of heavy metals from these stable metal-chelate compounds still requires high applied voltages for the oxidation of chelators or electrocoagulation of heavy metals when an inert or Al/Fe anode is used, respectively (Pociecha et al., 2011; Voglar; Lestan, 2012; Xu et al., 2019).

Low-molecular-weight organic acids including citric acid, oxalic acid, and acetic acid are widely present as natural products of root exudates, microbial secretions, and plant or animal residue decomposition in soils (Gao et al., 2003). These organic acids are easily biodegraded and can be environment-friendly and promising candidates for soil remediation. Many studies have demonstrated that citric acid has a high extraction efficiency for heavy metals in soils (Furukawa and Tokunaga, 2004; Jean et al., 2012). In addition, these organic acids are easily oxidized at relatively low potentials, facilitating the decomposition of metal-chelate compounds and subsequent adsorption of heavy metal ions on the electrode (Trettenhahn and Köberl, 2007).

In this work, a technique combining the re-circulating extraction with low-molecular-weight organic acids and electrochemical

adsorption of heavy metals at low voltages (≤ 0.9 V) was proposed for the remediation of Cu- and Zn-contaminated soils. The contents of heavy metals in soil and leachate and the chemical composition of the electrode were further analyzed to clarify the possible removal mechanism for Cu and Zn, and the soil remediation effect was further evaluated by pot cultivation of rape.

2. Materials and methods

2.1. Soil samples

The soil sample was collected from 10 to 40 cm surface layer of a farmland (E 114°55′47″, N 30°10′18″) close to a metal smelter located in Daye city, Hubei province, China. This region has been chronically exposed to active mining and smelting over sixty years, and the soils are mainly polluted by Cu and Zn. The soil sample was air-dried and crushed to pass 2 mm sieve. Table S1 shows the basic physical and chemical properties of the collected soil sample. The concentrations of total Cu and Zn were respectively 1090 and 262 mg kg^{-1}, which were significantly above the soil environmental quality standards (150 mg kg^{-1} for Cu and 200 mg kg^{-1} for Zn at $6.5 <$ pH ≤ 7.5) of the China National Standard System (GB15618-2018). The concentrations of other heavy metals including Cd, Pb, Ni, Hg, Cr(III,VI) and As(III,V) were lower than the quality standards, and thus were not considered in this experiment.

2.2. Soil remediation experiment

The soil remediation experiment was conducted in an apparatus comprising a circulating heavy metal extraction system and an electrochemical adsorption system (Fig. 1). In the extraction system, 150 g of contaminated soils was put into an acrylic sample tube with length and inner diameter of 70 and 50 mm, respectively. 500 mL of 0.1 M eluent was continuously circulated through the soil sample by a pump at a flow rate of 40 mL min^{-1}. The electrochemical adsorption system mainly included five connected electrolytic cells, with each containing a pair of carbon electrodes with a distance of 5 mm. The voltage between the two oppositely
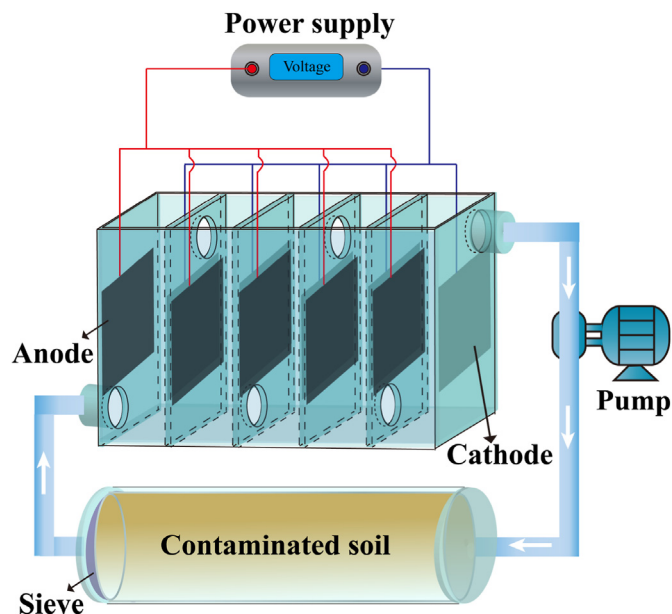

Fig. 1. Schematic of organic acid extraction and electrochemical adsorption apparatus.

charged electrodes was controlled using a battery testing system (CT-4008-5V1A, Shenzhen Neware Electronic Ltd., China). The carbon electrode was prepared by coating a graphite paper (10×12 cm^2) with a mixture of commercial active carbon and polyvinylidene fluoride. The XRD pattern, Fourier transform infrared (FTIR) spectrum and field emission scanning electron microscopy (FESEM) image of the active carbon are shown in Fig. S1.

The influence of operating conditions on the remediation efficiency was investigated with different initial pH values (2.0, 5.0, and 8.3), applied voltages (0.3, 0.6, and 0.9 V), and organic acids (sodium citrate, sodium oxalate and sodium acetate). The description of the experimental conditions was simplified and summarized in Table S2. To simply study the removal rate of heavy metals, the experiments under each condition were conducted for 1−7 d. The pot cultivation of rape was conducted to evaluate the potential applicability of this method (Supporting Information, SI).

2.3. Analytical methods

The total concentrations of heavy metals in soils were measured by acid digestion and detected using an atomic absorption spectrometer (AAS, Varina AAS240FS). The total concentration of heavy metals in soils cannot well indicate their environmental impacts (Tessier et al., 1979). Instead, the bioavailable concentration and fractions of heavy metals in soils are important indicators of the ecotoxicity of heavy metals, which were analyzed by DTPA (Guo et al., 2018) and Tessier sequential extraction method (Tessier et al., 1979), respectively (Supporting Information, SII). The concentration of citrate was detected by a high-performance liquid chromatograph (HPLC, Agilent 1200) with a C18 column.

The crystal structure, functional group, micromorphology and chemical composition of the samples were characterized using XRD (Bruker D8 Advance diffractometer with Cu Kα), FTIR (Nicolet 8700), FESEM (Hitachi SU8000) and X-ray photoelectron spectroscopy (XPS, VG Multilb 2000, Thermo Electron Corporation). The possible electrochemical reaction mechanisms of heavy metals on the carbon electrode during the removal processes were investigated by cyclic voltammetry tests on an electrochemical workstation (CHI660E) (Supporting Information, SIII).

3. Results

3.1. Content of heavy metals in remediated soils

The extraction and electrochemical adsorption of heavy metals were conducted using sodium citrate with initial pH 8.3 at 0.9 V (Cit-8-0.9) to investigate the soil remediation process. Fig. 2a and b shows the concentrations of total and bioavailable Cu and Zn at different time. The total concentrations of Cu and Zn rapidly decreased within the first 2 d, followed by slow decreases thereafter. When the removal reaction reached equilibrium at 4 d, the total concentrations of Cu and Zn decreased from 1090 to 262 mg kg^{-1} to 391 and 208 mg kg^{-1}, respectively. The bioavailable concentration of Cu significantly decreased from 281 to 52 mg kg^{-1} at 2 d, and that of Zn gradually decreased with time from 39 to 30 mg kg^{-1} at 7 d. The soil columns after 7 d of remediation were evenly divided into 12 fractions according to the spatial distribution (Fig. S2a). There was no obvious difference in the concentrations of total and bioavailable Cu and Zn in each fraction (Figs. S2b and c), indicating that heavy metals in the soil can be uniformly removed at the same time. When the adsorption was conducted with open circuit without the application of voltage (Cit-8), the concentrations of total and bioavailable Cu were determined to be 623 and 117 mg kg^{-1}, and those of Zn were 232 and 42 mg kg^{-1}, respectively (Fig. 2a and b). These results indicated

that heavy metal ions in soils could be extracted by sodium citrate, and the removal efficiency could be further improved by electrochemical adsorption.

Extraction efficiency of heavy metals is significantly affected by pH (Zou et al., 2009). In this work, the extraction efficiency was compared by a simple soil washing experiment using sodium citrate solution at different initial pHs (Fig. S3). With the initial pH increasing from 2.0 to 5.0 and 8.0, the concentration of extracted Cu increased from 70 to 101 and 84 mg L^{-1}, while that of Zn decreased from 20 to 17 and 5 mg L^{-1}, respectively. High solution pH facilitates the electrochemical adsorption of cations on carbon electrode (Huang and He, 2013). The pH of the eluent affects the extraction and electrochemical removal process. To investigate the effect of initial pH on the soil remediation efficiency, sodium citrate solutions with different pH values were used as the eluent accompanied by electrochemical adsorption at 0.9 V. As shown in Fig. 2c and d, after 7 d of removal at initial pH 8.3, 5.0 and 2.0, the total concentration of Cu in the three reaction systems decreased to 416, 415 and 405 mg kg^{-1}, and that of Zn decreased to 208, 191 and 155 mg kg^{-1}, respectively. The bioavailable concentration of Cu was 65, 54 and 42 mg kg^{-1}, and that of Zn was 30, 26 and 19 mg kg^{-1}, respectively.

The electrochemical adsorption efficiency of heavy metals is also affected by the cell voltage. As shown in Fig. 2e and f, when the remediation was conducted at 0.9, 0.6 and 0.3 V for 7 d, the total concentration of Cu decreased to 416, 433 and 536 mg kg^{-1}, respectively. Higher voltage promoted the removal of Zn within the first 3 d, but the total concentration of Zn was about 210 mg kg^{-1} at 7 d for all the three tests. The removal rate of bioavailable Cu and Zn both increased with increasing voltage.

Sodium oxalate or sodium acetate was then used as the extractant instead of sodium citrate to compare their soil remediation efficiency (Fig. 2g and h). After 7 d of reaction using sodium citrate, sodium oxalate, and sodium acetate, the total concentrations of Cu in soils were 416, 750 and 1060 mg kg^{-1}, and those of Zn were 208, 242 and 256 mg kg^{-1}, respectively. The bioavailable concentrations of Cu in these reaction systems respectively decreased to 65, 102 and 280 mg kg^{-1}, while those of Zn all decreased to about 30 mg kg^{-1}. The presence of organic acids improved the remediation performance following the order of citrate > oxalate > acetate, which was in agreement with their extraction ability for heavy metals (Fig. S4).

The fractions of Cu and Zn were analyzed through the Tessier sequential extraction method to well evaluate the soil remediation efficiency (Fig. 3). In the original soil, the contents of various Cu fractions, including exchangeable, carbonate-bound, Fe/Mn oxide-bound, organic matter-bound, and residual fractions, were 9, 123, 257, 342, and 357 mg kg^{-1}, and those of Zn were 15, 24, 31, 58 and 135 mg kg^{-1}, respectively. After a single extraction removal for 7 d (Cit-8), the contents of the five Cu fractions were decreased by 55.6%, 65.3%, 40.8%, 25.8% and 39.6%, and those of Zn fractions by 49.5%, 15.6%, 13.5%, 8.3% and 5.9%, respectively. In the reaction system of Cit-8-0.9, the contents of the five Cu fractions were reduced by 59.2%, 88.6%, 79.6%, 60.2% and 42.4%, and those of Zn fractions by 61.4%, 24.4%, 28.4%, 4.2% and 19.4%, respectively. These results indicated that the heavy metals of different fractions can be effectively removed by the extraction of citrate and electrochemical adsorption.

The changes in different fractions of Cu and Zn in the reaction system of Cit-5-0.9 were similar to those in Cit-8-0.9 (Fig. 3). However, in Cit-2-0.9, the exchangeable fraction of Cu and Zn increased by 68.2% and 24.7%, respectively, indicating that some other fractions of heavy metals were converted into exchangeable fraction. With decreasing voltage, the removal rate of each fraction of Cu decreased, while that of Zn showed no obvious changes.
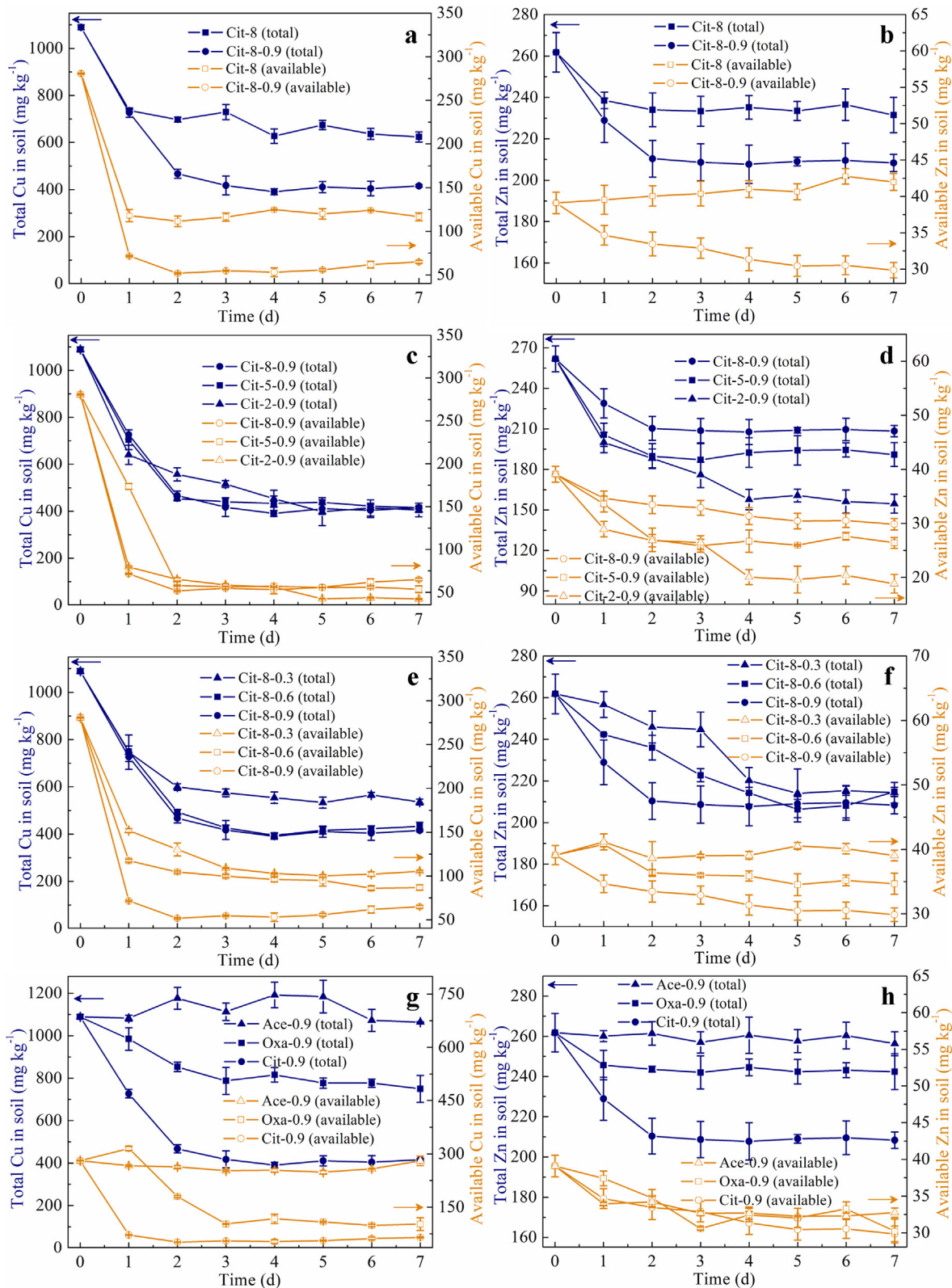
Fig. 2. Concentrations of total and available Cu and Zn in the soil at different time for the reaction systems of Cit-8-0.9 and Cit-8 (a, b), Cit-8-0.9, Cit-5-0.9 and Cit-2-0.9 (c, d), Cit-8-0.3, Cit-8-0.6 and Cit-8-0.9 (e, f), and Cit-8-0.9, Oxa-0.9 and Ace-0.9 (g, h).

When oxalate or acetate was used instead, the removal rate of each fraction of both Cu and Zn was relatively low.

3.2. Concentrations of heavy metals in leachate

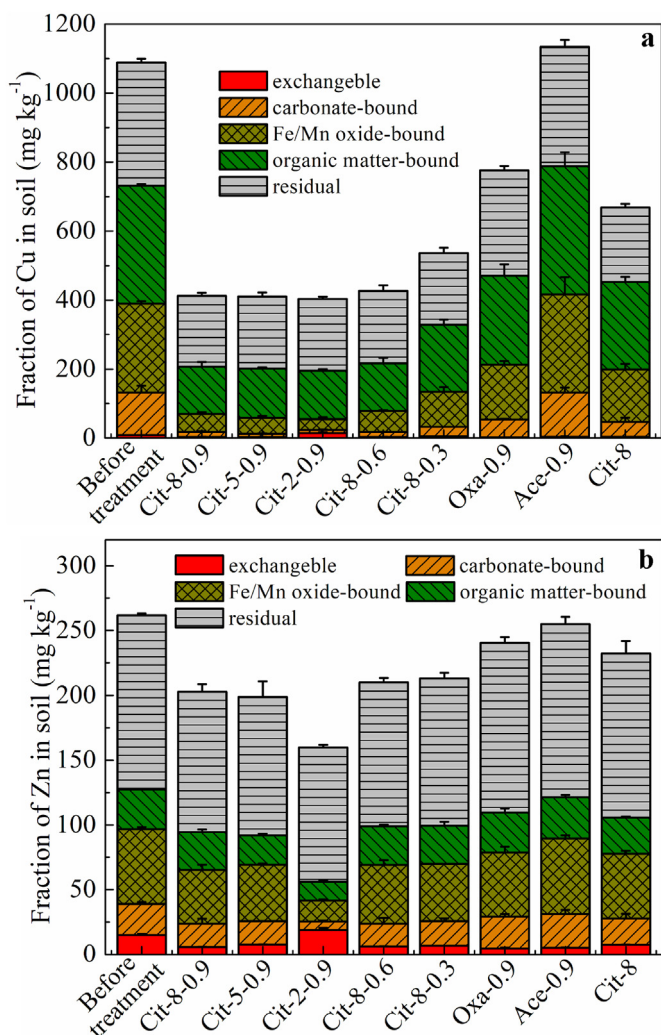Fig. 4 shows the electrochemical adsorption rate of the carbon

Fig. 3. Distribution of Cu (a) and Zn (b) fractions in the soil before and after treatment under different conditions.

Fig. 4. Concentrations of Cu (a) and Zn (b) in the leachate at different time under different conditions.

electrodes for heavy metals from leachates. In the reaction system of Cit-8, the concentration of Cu and Zn rapidly increased to 83.3 and 4.6 mg L^{-1} after 2 d, respectively, and then tended to equilibrium. In the reaction system of Cit-8-0.9, the concentrations of Cu and Zn respectively decreased to 6.3 and 2.9 mg L^{-1} after 1 d, and both decreased to about 1 mg L^{-1} after 7 d. No precipitate was observed on the electrode surface or in the solution, suggesting that the extracted heavy metal ions could be efficiently removed by electrochemical adsorption without the occurrence of heavy metal precipitation.

After 7 d of reaction for the systems of Cit-8-0.9, Cit-5-0.9, and Cit-2-0.9, the concentrations of Cu were 1.0, 2.0 and 0.9 mg L^{-1}, and those of Zn were 1.0, 3.6 and 17.1 mg L^{-1}, respectively (Fig. 4), suggesting that low pH did not facilitate the electrochemical adsorption of Zn, but Cu could be electrochemically removed within a wide pH range. Therefore, the optimal pH value for the remediation was controlled at 8.3. The pHs of the leachates increased to 8.7, 8.2 and 2.9 at 7 d when the initial pHs were 8.3, 5.0 and 2.0, respectively (Fig. S5).

After 7 d of electrochemical reaction, the concentrations of Cu and Zn reached 1.9 and 1.4 mg L^{-1} at 0.6 V, and increased to 32.4 and 2.1 mg L^{-1}, respectively, at 0.3 V, indicating that the electrochemical adsorption of heavy metals becomes slower at a lower
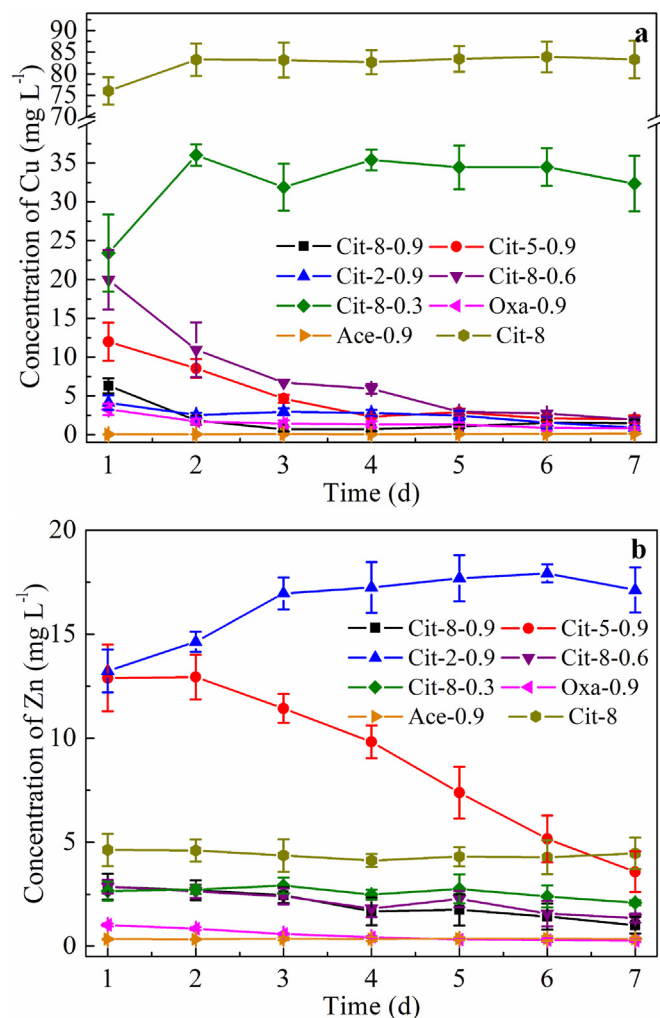
voltage. When sodium oxalate was used instead, the concentrations of Cu and Zn decreased from 3.3 to 1.0 mg L^{-1} at 1 d to 0.8 and 0.3 mg L^{-1} at 7 d, respectively. When sodium acetate was used as the eluent, the concentrations of heavy metals were lower than 0.4 mg L^{-1} in the whole removal process, which was in line with the low extraction ability of sodium acetate for heavy metals.

3.3. Electrode characterization

The mechanism for the electrochemical reaction of heavy metals on the carbon electrode was analyzed by cyclic voltammetry (CV). No redox peak was observed in the CV curve of the carbon electrode in KNO$_3$ solution, while a pair of redox peaks near 0 V (vs. SCE) appeared in the presence of Cu^{2+} and Zn^{2+} (Fig. S6a), suggesting the electrochemical redox reaction of Cu^{2+}/Cu according to the higher standard reduction potential of Cu^{2+} than Zn^{2+} (Yang et al., 2018). When sodium citrate was further added to the above mixed solution, the intensity of the redox peak of Cu^{2+}/Cu decreased with a shift to lower potentials (Fig. S6b), likely due to the formation of Cu-citrate complexes, which suppressed the electrochemical reduction of Cu^{2+} (Shin et al., 2016). In addition, a broad anodic peak appeared from 0.4 V (vs. SCE) in Cu- and Zn-containing leachate extracted by sodium citrate (Fig. S6c), indicating the

electrochemical oxidation of citrate (Trettenhahn and Köberl, 2007). According to the potentials of the electrodes in the process of electrochemical removal, electrochemical reduction of Cu^{2+} and oxidation of citrate might occur on the cathode and anode, respectively, when the voltage was controlled to be above 0.6 V (Fig. S7).

The chemical composition of the carbon electrodes was detected after the remediation. No obvious change was observed in the XRD patterns and FTIR spectra (Fig. S8), likely due to the shielding effect of the strong diffraction peaks of carbon electrodes. Some reddish-brown deposition was observed on the cathode at 0.9 and 0.6 V due to the reduction product of Cu^{2+} in the electrochemical adsorption process (Yang et al., 2018), which was in accordance with the results of CV tests (Fig. S6). The micromorphology of the electrodes was examined by SEM after electrochemical reaction (Fig. S9). Some micron-sized particles were formed on the cathode in the reaction system of Cit-8-0.9 due to the formation of Cu. The anode was covered by a layer of organic matter, which might be attributed to the electrochemical oxidation of citrate or carbon.

The chemical composition of the electrodes was further characterized by XPS after electrochemical reaction in the reaction system of Cit-8-0.9. The XPS broad scans including Cu 2p spectra and Zn 2p spectra suggested that Cu was adsorbed on the cathode, and Zn was predominantly adsorbed on the anode with little adsorption on the cathode (Fig. S10). The Cu $2p_{3/2}$ peak could be fitted by two peaks corresponding to $Cu(OH)_2$ (about 934.7 eV) and Cu(0) (about 932.4 eV) (Biesinger et al., 2010; Xu et al., 2019), and the percentages of $Cu(OH)_2$ and Cu(0) were detected to be 68.4% and 31.6%, respectively (Fig. S10 b). As shown in Fig. S10 d, the C 1s peak could be deconvoluted into three peaks at 284.3, 285.5 and 288.3 eV, respectively, which could be assigned to C−C/C=C in the aromatic rings, C−OH (hydroxyl) and O−C=O (carboxyl) groups (Zheng et al., 2017). The peak at 291.4 eV in the spectrum of pristine electrode was ascribed to the C−Fx from the binder (PVDF) (Park et al., 2014). After electrochemical adsorption, the increase in the percentage of O−C=O on the cathode and anode might be due to the adsorption of citrate and the electrochemical oxidation of carbon or citrate, respectively.

3.4. Pot cultivation of rape

The pot cultivation of rape was conducted using the untreated (the control) and remediated soils to evaluate the effect of soil remediation. Compared with the control, the remediated soil from the reaction system of Cit-8-0.9 resulted in larger shoots and leaves of the rape seedlings (Figs. 5 and S11a), and enhanced the average mass of the seedlings from 78 to 120 mg (Fig. S11b). The bioaccumulation of Cu and Zn in different parts of the rape seedlings was further determined (Fig. 5). As a result, the soil remediation decreased the content of Cu in the root and shoot from 248 to 101 mg kg^{-1} to 106 and 52 mg kg^{-1}, and that of Zn from 526 to 231 mg kg^{-1} to 215 and 113 mg kg^{-1}, respectively.

The nutrient metal ions (such as Na^+, Mg^{2+}, and Ca^{2+}) would also be washed out by sodium citrate solution during the remediation. The concentration of Mg in the soils was measured and used as an indicator for the contents of nutrient metal ions (Xu et al., 2019). When sodium citrate solutions with different pH values were used as the eluent accompanied by electrochemical adsorption at 0.9 V, the loss amount of Mg decreased with increasing pH (Fig. S12). After 7 d of reaction in the system of Cit-8-0.9, the concentration of Mg slightly decreased from 502 to 442 mg kg^{-1}, which would not affect the plant growth.
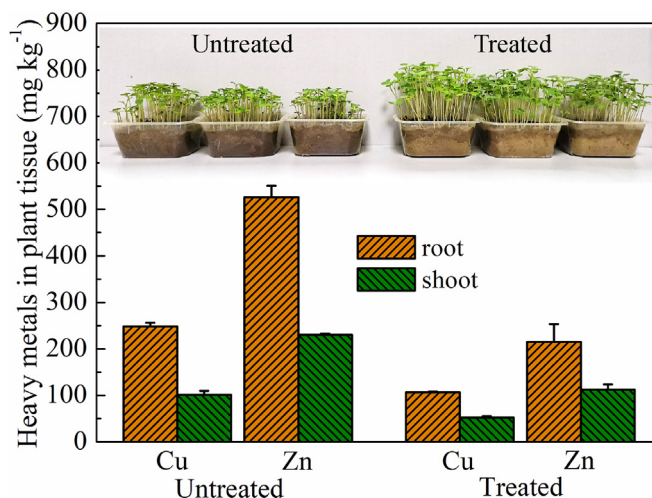

Fig. 5. Photos of the rape seedlings cultivated in the untreated and remediated (Cit-8-0.9) soils and the corresponding contents of Cu and Zn in the root and shoot of the rape seedlings.

4. Discussion

4.1. Extraction of heavy metals from soils

The heavy metals in the soil could be washed out by using sodium citrate solution for soil remediation (Fig. 2a and b). Organic acids can complex with heavy metals, thermodynamically facilitating the desorption of heavy metals from soils in the forms of surface complexes and precipitates (Hahladakis et al., 2014). As a ternary acid, citrate has a higher extraction ability than acetate (unary acid) and oxalate (binary acid) for heavy metals (Fig. S4), due to more hydroxyl and carboxyl groups for complexing (An et al., 2011). In addition, citrate can reduce the oxidizing substances including manganese oxides in soils, leading to the release of adsorbed heavy metals (Abumaizar and Smith, 1999; Wang and Stone, 2006). Therefore, the heavy metals in the soil could be mobilized by sodium citrate solution and flushed away with the leachate.

After extraction by sodium citrate, the total concentration of Cu in soil was decreased by 42.8%, while that of Zn was only decreased by 11.6% (Fig. 2a and b). As reported, 39% and 57% of Pb could be washed out using citric acid from mine and farmland soils, respectively. The difference in the removal rate is due to that the mine soil contains a higher fraction of residual Pb (Wang et al., 2014). The non-detrital fractions of heavy metals in soil including exchangeable, carbonate-bound, Fe/Mn oxide-bound and organic matter-bound fractions are easy to be extracted. The residual fraction of heavy metals comprises the metals that are tightly bound to soil particles and hard to be mobilized (Wang et al., 2014). Therefore, a high percentage of residual fraction is not conducive to the removal of heavy metals from soils (Wuana et al., 2010). In this work, the percentages of residual fraction of Zn and Cu were respectively 51.4% and 32.8% in the soil samples (Fig. 3), suggesting that Cu is more easily extracted by sodium citrate than Zn. In a soil washing test using artificially prepared soil containing heavy metals, the extraction efficiency of Cu was still higher than that of Zn, which was mainly attributed to the higher stability constant of Cu-citrate complex (Wuana et al., 2010). Therefore, a higher removal efficiency can be achieved for Cu than for Zn.

When the cell voltage was controlled at 0.9 V, the removal rates

of total Cu and Zn were respectively increased by 21.3% and 9.4% compared with those at open circuit (Fig. 2a and b). The concentrations of heavy metals in the soil consistently decreased within the first days of remediation (Fig. 2), suggesting that the heavy metals are strongly attached on soil particles and it is necessary to wash the soils for many cycles to sufficiently extract the heavy metals. Therefore, it is important to improve the extraction efficiency by enhancing the mass transfer process of heavy metals in soils (Leštan et al., 2008). In a single soil washing process without electrochemical adsorption, the concentration of heavy metals in the leachate rapidly increased and reached equilibrium, which hindered the transfer process of heavy metals from the soil to the eluent (Fig. 4). However, the removal efficiency of heavy metals could be further improved by replacing the leachate with fresh extractant in each washing cycle (Xu et al., 2019). In this work, electrochemical adsorption of heavy metals can be considered as a renewal of the sodium citrate solution to further facilitate the extraction of heavy metals from soils.

After the remediation, the total concentrations of Cu and Zn in soils were higher than the limit values recommended by the Soil Environment Quality Standard (GB15618-2018) (Fig. 2a and b). The extraction efficiency of heavy metals from the clay soil containing more than 30% of clay is relatively low (Rui et al., 2019), which is due to the strong adsorption of heavy metals on clay with large specific surface area and low permeability (Semer and Reddy, 1996; Kuhlman and Greenfield, 1999). In this work, the extraction of heavy metals would be suppressed by the high percentage of clay (40%) in the soil sample (Table S1). However, the total concentration of heavy metals is not a direct and dependable indicator for the potential effects on ecological environments, and the toxicity of heavy metals is highly dependent on their existence forms (Tessier et al., 1979; Lanno et al., 2004). The dissolved and exchangeable fractions of heavy metals show higher mobility and bioavailability than the deposited ones (Kim et al., 2015). In this work, the bioavailable concentrations of Cu and Zn could be decreased by 81.6% and 23.5%, respectively (Fig. 2a and b). The efficiency of a soil remediation process can be well evaluated by bioassay testing because it reflects the changes in the ecotoxicity of heavy metals instead of evaluating the risk of heavy metals based on their chemical concentrations (Sayles et al., 1999). Heavy metals in soil are toxic to plant growth (Sheng et al., 2008). The development of rape seedlings could be significantly improved by the remediation (Fig. 5), suggesting a rapid decrease in the toxicity of heavy metals in soils. Therefore, this remediation approach could be potentially used for agricultural land remediation.

With increasing initial pH of sodium citrate solution, the extraction efficiency of Cu increased first and then decreased with time, and that of Zn continuously decreased (Fig. S3), which is in agreement with previous results (Furukawa and Tokunaga, 2004). The extraction process of heavy metals is significantly affected by the relative strength of binding energy between heavy metals and soil or citrate. Heavy metals are easily washed out from soils under low pH because H^+ can release the heavy metals bound to the hydrous oxides and desorb the heavy metals electrostatically adsorbed on soil particles (Zou et al., 2009). Increasing pH facilitates the adsorption of heavy metals on negatively charged soil colloid particles (Zou et al., 2009). The complexing ability of citrate for heavy metals increases firstly and then decreases with increasing pH due to the formation of different heavy metal-citrate complexes under different pHs (Furukawa and Tokunaga, 2004; Kim and Duquette, 2006). The relative strength of binding energy between heavy metals and soil or citrate varies under different pHs, leading to variations of the corresponding extraction efficiency of Cu and Zn. After extraction using sodium citrate at initial pH of 2.0, 5.0 and 8.3 accompanied by electrochemical adsorption for 7 d, the total concentrations of Cu in the soil decreased to similar values in all the three systems (Fig. 2c and d), possibly because the continuous washing reduced the differences in the extraction efficiency of Cu under different pHs.

4.2. Electrochemical removal of heavy metals from leachates

The concentrations of Cu and Zn in the leachate could be rapidly decreased by electrochemical adsorption at 0.9 V (Fig. 4). As an excellent electrode material for the electric double layer capacitor, active carbon could be used for the electrosorption of heavy metal ions. The cations will be electrochemically migrated to the cathode and stored in the diffuse layer during the electrosorption process (Tang et al., 2019). However, the Cu and Zn ions in the leachate would bind with citrate to form soluble complexes including $(Cu_2Cit_2(OH))^{3-}$ (Furukawa and Tokunaga, 2004; Kim and Duquette, 2006; Shin et al., 2016). The electrosorption process of complexing heavy metals might differ from that of free heavy metals in aqueous solutions (Xu et al., 2019). The formation of complex between EDTA and heavy metals suppresses the adsorption of heavy metals (Voglar and Lestan, 2012). The complex reaction between citrate and heavy metals might also inhibit the electrosorption of heavy metals on carbon electrodes. The removal rate and capacity of Cu^{2+} and Zn^{2+} decreased in the presence of citrate during the electrochemical adsorption in Cu and Zn-containing solution (Fig. S13). The electrochemical removal of heavy metals from the metal-EDTA complexes involves the electrochemical oxidization of EDTA coupled with electrochemical adsorption or deposition of heavy metal ions (Voglar and Lestan, 2012). The oxidation of citrate might also occur on the anode due to the high potential of the anode during the electrochemical removal as suggested by the CV tests (Figs. S6 and S7a). The concentration of citrate in the leachate was detected to gradually decrease with reaction time (Fig. S14). Therefore, the negatively charged heavy metal-citrate complexes would be electrostatically adsorbed and electrochemically oxidized on the anode, and the heavy metal ions could be subsequently removed by the carbon electrode. Although the complexation ability of organic acids for heavy metal cations is lower than that of synthetic chelating agents (Jean et al., 2012), the heavy metals extracted by organic acids could be more easily electrochemically removed at a lower voltage. Therefore, the undesirable side reactions could be avoided with a higher electrical energy efficiency. The relatively lower complexation ability of low-molecular-weight organic acids could be compensated by recirculating soil washing after electrochemical adsorption of heavy metals.

The Cu and Zn were mainly adsorbed on the cathode and anode, respectively (Fig. S10). Active carbon contains many hydroxyl and carboxyl groups, providing strong adsorption sites for heavy metal ions (Zheng et al., 2017). The content of carboxyl groups on the anode could be further increased due to the electrochemical oxidation reaction (Figs. S9b and S10d). When the negatively charged heavy metal-citrate complexes were accumulated on the anode, the dissociated Cu^{2+} and Zn^{2+} could be adsorbed by the carbon anode after the oxidation of citrate. Compared with Zn^{2+}, Cu^{2+} is easier to be electrochemically reduced due to its higher standard reduction potential (0.1 V vs. SCE) (Shin et al., 2016; Yang et al., 2018). According to the reduction peak in the CV curve of carbon electrode in the leachate (Fig. S6c), the electrodeposition of Cu^{2+} would occur on the cathode with the potentials lower than −0.5 V (vs. SCE) when the voltage was controlled at 0.9 V (Fig. S7b). Therefore, besides the complexing adsorption and electrostatic adsorption, electrochemical deposition also facilitates the removal of Cu.

The concentration of Cu in the leachate was similar at different

initial pHs, but that of Zn increased with decreasing pH (Fig. 4). The inorganic adsorption capacity of heavy metals on carbon decreases with decreasing pH, likely due to the competitive adsorption in the hydroxyl and carboxyl sites between protons and heavy metals (Bediako et al., 2015). The process of electrostatic adsorption of carbon electrode for heavy metals and the electrochemical deposition of Cu^{2+} are less affected by pH (Liu et al., 2017). The change of solution pH showed slight impacts on the electrochemical removal of Cu.

The removal efficiency of heavy metals from the leachate decreased with decreasing voltage (Fig. 4). At a lower voltage, the anode potential became lower (Fig. S7a), resulting in the decrease of oxidative decomposition of heavy metal-citrate complexes and the subsequent electrochemical adsorption of heavy metals (Liu et al., 2017). In addition, the increase in the cathode potential at lower voltages would inhibit the electrodeposition of Cu^{2+} (Fig. S7b). To balance the mass transfer between the leachate and soil, the reduced electrochemical removal of heavy metals at a low voltage would further lead to decreases in the extraction of heavy metals from soils (Fig. 2e and f).

5. Conclusions

In this work, Cu and Zn could be efficiently removed from contaminated soils by combining extraction with organic acids and subsequent electrochemical adsorption. The species and initial pH of the eluent and the applied voltage affect the soil remediation efficiency. The extraction using sodium citrate at pH 8.3 accompanied by electrochemical adsorption at 0.9 V could decrease the total concentrations of Cu and Zn in the soil by 64.1% and 20.8%, and the bioavailable concentrations by 81.6% and 23.5%, respectively. The extracted Cu and Zn in the leachate can be subsequently removed by electrochemical deposition and adsorption. The pot cultivation of rape demonstrated that the ecotoxicity of heavy metals can be significantly reduced by the remediation. The present work provides an effective and environment-friendly approach for the remediation of heavy metal contaminated soils.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Xiong Yang: Formal analysis, Writing - original draft, Investigation. **Lihu Liu:** Formal analysis, Writing - review & editing. **Wenfeng Tan:** Supervision. **Chengshuai Liu:** Supervision. **Zhi Dang:** Supervision. **Guohong Qiu:** Supervision, Project administration, Conceptualization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114745.

References

Abumaizar, R.J., Smith, E.H., 1999. Heavy metal contaminants removal by soil washing. J. Hazard Mater. 70, 71—86.

An, C.J., Huang, G.H., Wei, J., Yu, H., 2011. Effect of short-chain organic acids on the enhanced desorption of phenanthrene by rhamnolipid biosurfactant in soil-water environment. Water Res. 45, 5501—5510.

Bediako, J.K., Wei, W., Kim, S., Yun, Y.S., 2015. Removal of heavy metals from aqueous phases using chemically modified waste Lyocell fiber. J. Hazard Mater. 299, 550—561.

Biesinger, M.C., Lau, L.W.M., Gerson, A.R., Smart, R.S.C., 2010. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. Appl. Surf. Sci. 257, 887—898.

Chen, H.Y., Teng, Y.G., Lu, S.J., Wang, Y.Y., Wang, J.S., 2015. Contamination features and health risk of soil heavy metals in China. Sci. Total Environ. 512—513, 143—153.

Fan, X.Y., Hui, W., Luo, Q.S., Ma, J.W., Zhang, X.H., 2007. The use of 2D non-uniform electric field to enhance in situ bioremediation of 2,4-dichlorophenol-contaminated soil. J. Hazard Mater. 148, 29—37.

Ferraro, A., van Hullebusch, E.D., Huguenot, D., Fabbricino, M., Esposito, G., 2015. Application of an electrochemical treatment for EDDS soil washing solution regeneration and reuse in a multi-step soil washing process: case of a Cu contaminated soil. J. Environ. Manag. 163, 62—69.

Furukawa, M., Tokunaga, S., 2004. Extraction of heavy metals from a contaminated soil using citrate-enhancing extraction by pH control and ultrasound application. J. Environ. Sci. Health A 39, 627—638.

Gao, Y.Z., He, J.Z., Ling, W.T., Hu, H.Q., Liu, F., 2003. Effects of organic acids on copper and cadmium desorption from contaminated soils. Environ. Int. 29, 613—618.

Guo, T., Lou, C.L., Zhai, W.W., Tang, X.J., Hashmi, M.Z., Murtaza, R., Li, Y., Liu, X.M., Xu, J.M., 2018. Increased occurrence of heavy metals, antibiotics and resistance genes in surface soil after long-term application of manure. Sci. Total Environ. 635, 995—1003.

Hahladakis, J.N., Lekkas, N., Smponias, A., Gidarakos, E., 2014. Sequential application of chelating agents and innovative surfactants for the enhanced electro-remediation of real sediments from toxic metals and PAHs. Chemosphere 105, 44—52.

Huang, C.C., He, J.C., 2013. Electrosorptive removal of copper ions from wastewater by using ordered mesoporous carbon electrodes. Chem. Eng. J. 221, 469—475.

Jean, L., Bordas, F., Bollinger, J.C., 2012. Column leaching of chromium and nickel from a contaminated soil using EDTA and citric acid. Environ. Pollut. 164, 175—181.

Jing, F., Chen, X.M., Yang, Z.J., Guo, B.L., 2018. Heavy metals status, transport mechanisms, sources, and factors affecting their mobility in Chinese agricultural soils. Environ. Earth Sci. 77, 104.

Kim, R.Y., Yoon, J.K., Kim, T.S., Yang, J.E., Owens, G., Kim, K.R., 2015. Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. Environ. Geochem. Health 37, 1041—1061.

Kim, S., Duquette, D.J., 2006. Effect of chemical composition on adhesion of directly electrodeposited copper film on TiN. J. Electrochem. Soc. 153, C417—C421.

Komárek, M., Vaněk, A., Ettler, V., 2013. Chemical stabilization of metals and arsenic in contaminated soils using oxides — a review. Environ. Pollut. 172, 9—22.

Kuhlman, M.I., Greenfield, T.M., 1999. Simplified soil washing processes for a variety of soils. J. Hazard Mater. 66, 31—45.

Lanno, R., Wells, J., Conder, J., Bradham, K., Basta, N., 2004. The bioavailability of chemicals in soil for earthworms. Ecotoxicol. Environ. Saf. 57, 39—47.

Leštan, D., Luo, C.L., Li, X.D., 2008. The use of chelating agents in the remediation of metal-contaminated soils: a review. Environ. Pollut. 153, 3—13.

Liao, X.Y., Li, Y., Yan, X.L., 2016. Removal of heavy metals and arsenic from a co-contaminated soil by sieving combined with washing process. J. Environ. Sci. 41, 202—210.

Liu, L.W., Li, W., Song, W.P., Guo, M.X., 2018. Remediation techniques for heavy metal-contaminated soils: principles and applicability. Sci. Total Environ. 633, 206—219.

Liu, P.Y., Yan, T.T., Zhang, J.P., Shi, L.Y., Zhang, D.S., 2017. Separation and recovery of heavy metal ions and salty ions from wastewater by 3D graphene-based asymmetric electrodes via capacitive deionization. J. Mater. Chem. 5, 14748—14757.

Mena, E., Villaseñor, J., Rodrigo, M.A., Cañizares, P., 2016. Electrokinetic remediation of soil polluted with insoluble organics using biological permeable reactive barriers: effect of periodic polarity reversal and voltage gradient. Chem. Eng. J. 299, 30—36.

Oustan, S., Heidari, S., Neyshabouri, M.R., Reyhanitabar, A., Bybordi, A., 2011. Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelating agents. In: International Conference on Environment Science and Engineering. IPCBEE, pp. 152—155.

Park, Y., Shin, S.H., Hwang, H., Lee, S.M., Kim, S.P., Choi, H.C., Jung, Y.M., 2014. Investigation of solid electrolyte interface (SEI) film on LiCoO₂ cathode in fluoroethylene carbonate (FEC)-containing electrolyte by 2D correlation X-ray

photoelectron spectroscopy (XPS). J. Mol. Struct. 1069, 157–163.

Peng, W.H., Li, X.M., Xiao, S.T., Fan, W.H., 2018. Review of remediation technologies for sediments contaminated by heavy metals. J. Soils Sediments 18, 1701–1719.

Pociecha, M., Kastelec, D., Lestan, D., 2011. Electrochemical EDTA recycling after soil washing of Pb, Zn and Cd contaminated soil. J. Hazard Mater. 192, 714–721.

Rui, D.H., Wu, Z.P., Ji, M.C., Liu, J.F., Wang, S.R., Ito, Y., 2019. Remediation of Cd- and Pb-contaminated clay soils through combined freeze-thaw and soil washing. J. Hazard Mater. 369, 87–95.

Ruta, L.L., Kissen, R., Nicolau, I., Neagoe, A.D., Petrescu, A.J., Bones, A.M., Farcasanu, I.C., 2017. Heavy metal accumulation by Saccharomyces cerevisiae cells armed with metal binding hexapeptides targeted to the inner face of the plasma membrane. Appl. Microbiol. Biotechnol. 101, 5749–5765.

Sarwar, N., Imran, M., Shaheen, M.R., Ishaque, W., Kamran, M.A., Matloob, A., Rehim, A., Hussain, S., 2017. Phytoremediation strategies for soils contaminated with heavy metals: modifications and future perspectives. Chemosphere 171, 710–721.

Sayles, G.D., Acheson, C.M., Kupferle, M.J., Shan, Y.G., Zhou, Q., Meier, J.R., Chang, L., Brenner, R.C., 1999. Land treatment of PAH-contaminated soil: performance measured by chemical and toxicity assays. Environ. Sci. Technol. 33, 4310–4317.

Semer, R., Reddy, K.R., 1996. Evaluation of soil washing process to remove mixed contaminants from a sandy loam. J. Hazard Mater. 45, 45–57.

Sheng, X.F., Xia, J.J., Jiang, C.Y., He, L.Y., Qian, M., 2008. Characterization of heavy metal-resistant endophytic bacteria from rape (Brassica napus) roots and their potential in promoting the growth and lead accumulation of rape. Environ. Pollut. 156, 1164–1170.

Shin, S., Park, C., Kim, C., Kim, Y., Park, S., Lee, J.H., 2016. Cyclic voltammetry studies of copper, tin and zinc electrodeposition in a citrate complex system for CZTS solar cell application. Curr. Appl. Phys. 16, 207–210.

Tang, W.W., Wang, X.X., Zeng, G.M., Liang, J., Li, X.D., Xing, W.L., He, D., Tang, L., Liu, Z.F., 2019. Electro-assisted adsorption of Zn (II) on activated carbon cloth in batch-flow mode: experimental and theoretical investigations. Environ. Sci. Technol. 53, 2670–2678.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.

Trettenhahn, G., Köberl, A., 2007. Anodic decomposition of citric acid on gold and stainless steel electrodes: an in situ-FTIR-spectroscopic investigation. Electrochim. Acta 52, 2716–2722.

Voglar, D., Lestan, D., 2012. Electrochemical treatment of spent solution after EDTA-based soil washing. Water Res. 46, 1999–2008.

Wang, G.Y., Zhang, S.R., Xu, X.X., Li, T., Li, Y., Deng, O.P., Gong, G.S., 2014. Efficiency of nanoscale zero-valent iron on the enhanced low molecular weight organic acid removal Pb from contaminated soil. Chemosphere 117, 617–624.

Wang, Y., Stone, A.T., 2006. The citric acid–$Mn^{III,IV}O_2$ (birnessite) reaction. Electron transfer, complex formation, and autocatalytic feedback. Geochem. Cosmochim. Acta 70, 4463–4476.

Wang, Y.X., Huang, L.H., Wang, Z.X., Wang, L.S., Han, Y.F., Liu, X.W., Ma, T., 2019. Application of Polypyrrole flexible electrode for electrokinetic remediation of Cr(VI)-contaminated soil in a main-auxiliary electrode system. Chem. Eng. J. 373, 131–139.

Wuana, R.A., Okieimen, F.E., Imborvungu, J.A., 2010. Removal of heavy metals from a contaminated soil using organic chelating acids. Int. J. Environ. Sci. Tech. 7, 485–496.

Xu, J.W., Liu, C., Hsu, P.C., Zhao, J., Wu, T., Tang, J., Liu, K., Cui, Y., 2019. Remediation of heavy metal contaminated soil by asymmetrical alternating current electro-chemistry. Nat. Commun. 10, 2440.

Yang, X., Liu, L.H., Tan, W.F., Qiu, G.H., Liu, F., 2018. High-performance Cu^{2+} adsorption of birnessite using electrochemically controlled redox reactions. J. Hazard Mater. 354, 107–115.

Yeung, A.T., Gu, Y.Y., 2011. A review on techniques to enhance electrochemical remediation of contaminated soils. J. Hazard Mater. 195, 11–29.

Yuan, L.Z., Xu, X.J., Li, H.Y., Wang, N.N., Guo, N., Yu, H.W., 2016. Development of novel assisting agents for the electrokinetic remediation of heavy metal-contaminated kaolin. Electrochim. Acta 218, 140–148.

Zhao, F.J., Ma, Y.B., Zhu, Y.G., Tang, Z., McGrath, S.P., 2015. Soil contamination in China: current status and mitigation strategies. Environ. Sci. Technol. 49, 750–759.

Zheng, J., Xia, L., Song, S.X., 2017. Electrosorption of Pb(II) in water using graphene oxide-bearing nickel foam as the electrodes. RSC Adv. 7, 23543–23549.

Zou, Z.L., Qiu, R.L., Zhang, W.H., Dong, H.Y., Zhao, Z.H., Zhang, T., Wei, X.G., Cai, X.D., 2009. The study of operating variables in soil washing with EDTA. Environ. Pollut. 157, 229–236.

Zulfiqar, W., Iqbal, M.A., Butt, M.K., 2017. Pb^{2+} ions mobility perturbation by iron particles during electrokinetic remediation of contaminated soil. Chemosphere 169, 257–261.