RESEARCH ARTICLE

Removal behavior and mechanisms of cadmium and lead by coupled ethylenediaminetetraacetic acid washing and electrochemical reduction: influence of current conditions

Song Gao[1] · Yun Wang[1] · Zhuoqun Wang[1] · Xinyuan Tong[2] · Ruilian Sun[1]

Abstract

Ethylenediaminetetraacetic acid (EDTA) washing has been used extensively to remediate heavy metal-contaminated soils. Electrochemical reduction treatment of spent washing solution is an effective method of EDTA regeneration. However, at present, these two technologies are usually regarded as two independent treatment processes. This research raised a new heavy metal-contaminated soil treatment strategy—a combination technique of coupled EDTA washing and electrochemical reduction. We speculated that the combination of EDTA washing and electroreduction treatment could improve the efficiency of Cd and Pb removal from contaminated soil. In this study, the removal performance and mechanisms of Cd and Pb under different current conditions were investigated based on a coupling of EDTA washing and electrochemical reduction. The combination technique can increase Cd and Pb removal efficiencies by 13.37–15.24% and 14.91–27.05%, respectively, compared with EDTA washing alone. Sequential extraction analysis showed that the reducible fraction improved metal removal efficiency. The percentage of metal removed increased with an increased current value and EDTA concentration. In addition, pulse current mode removed more Cd and Pb than continuous current, although the difference was not significant ($p > 0.05$). However, pulse current could effectively eliminate the cathodic hydrogen evolution reaction, resulting in a further heavy metal deposition at the cathode. The combination technique exhibited enhanced removal efficiency due to EDTA regeneration in the suspension and the cathodic reduction reaction. The most cost-effective treatment in 48 h was a pulse current mode of 32 min on/16 min off-32 mA-EDTA-10 mM, where 47.56% of Cd and 77.00% of Pb were removed from the soil with an electric energy consumption of 8.24 Wh.

Introduction

Over the past two centuries, contamination caused by mining various heavy metals (such as Cd and Pb) has been severe and widespread (Hansen and Rojo 2007). Several remediation strategies have been developed and proposed for cleaning soils contaminated with heavy metals (Dermont et al.

2008; Yang et al. 2009; Jiang et al. 2010; Kołodyńska 2013; Zhou et al. 2014; Jelusic et al. 2014; Zhou et al. 2014; Pedersen et al. 2015; Pańczuk-Figura and Kołodyńska 2016; He et al. 2019; Kaurin et al. 2020; Liu et al. 2020).

Soil washing, which involves the separation of contaminants from the soil by solubilizing them in a washing solution, is one of the most frequently used techniques (Im et al. 2015; Wang et al. 2016; Pourfadakari et al. 2019; Kaurin et al. 2020). As a widely used washing solution, ethylenediaminetetraacetic acid (EDTA) can combine with several types of toxic metal ions in soil to form stable (Me-EDTA)$^{(4-n)-}$ complexes, as illustrated in Eq. (1) (Jelusic et al. 2014; Song et al. 2016, 2019a, b; Kaurin et al. 2020). Moreover, some previous studies (Im et al. 2015; Pourfadakari et al. 2019; Song et al., 2022) have demonstrated the cost-effectiveness of using EDTA. After

✉ Ruilian Sun
  ruiliansun@sdu.edu.cn

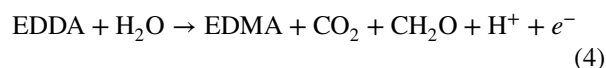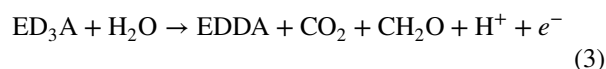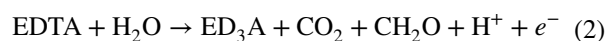[1] Environment Research Institute, Shandong University, Qingdao 266237, China

[2] School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

EDTA washing, most of the available forms of metals are extracted—removed from the soil matrix and transferred to the washing solution.

$$Me^{n+} + EDTA^{4-} \rightarrow (Me - EDTA)^{(4-n)-} \qquad (1)$$

Numerous strategies have been developed to remove heavy metals from the spent washing solution. Electrochemical reduction (electrodeposition) is one of the most recent technologies applied for heavy metal removal (recovery) based on the chelating effect. In addition, Nepel has confirmed that electrochemical reduction can reuse the washing solution (de Morais Nepel et al. 2020). Many studies have confirmed that the cathodic removal of heavy metals has several benefits in terms of costs, safety, and versatility (Paul Chen and Lim 2005; Peng et al. 2011). The migration of metal-chelate complexes is based on the application of a low electric field generated by an anode and a cathode, and the process potentially uses a cation exchange membrane (CEM) to separate the anode and cathode compartment (Xu et al. 2020), as follows:

a) The $(Me-EDTA)^{(4-n)-}$ electromigrated toward the anode can be anodically degraded. As illustrated in Eqs. (2–4) (Song et al. 2019a, b), leading to the release of metals and loss of chelating materials:

$$EDTA + H_2O \rightarrow ED_3A + CO_2 + CH_2O + H^+ + e^- \qquad (2)$$

$$ED_3A + H_2O \rightarrow EDDA + CO_2 + CH_2O + H^+ + e^- \qquad (3)$$

$$EDDA + H_2O \rightarrow EDMA + CO_2 + CH_2O + H^+ + e^- \qquad (4)$$

b) The complexes in the cathode compartment, on the contrary, can be electrodeposited on the cathode, which can carry out metal recovery and provide a chelating agent regenerated simultaneously, as illustrated in Eq. (5) (Song et al. 2019a, b):

$$(Me - EDTA)^{(4-n)-} + (4 - n)e^- \rightarrow Me + EDTA \qquad (5)$$
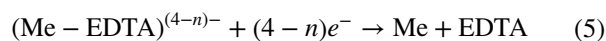
The application of continuous current (CC) is the most applied current mode in the electrochemical reduction processes. Several studies have reported that Cu can be removed from alkaline synthetic wastewater baths using CC (Dudek and Fedkiw 1999; Souto et al. 2011). However, there are various competing reactions at the cathode that affect the mass transport process of heavy metals. The most common competing reaction is when the H^+ ions are reduced to hydrogen gas (H_2), as illustrated in Eq. (6) (Paul Chen and Lim 2005; Peng et al. 2011).

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \qquad (6)$$

In some cases, the H_2 can cause loose or spongy deposits, and therefore, interference from the H_2 evolution reaction should be minimized (Paul Chen and Lim 2005). Recently, some studies have highlighted that pulse current (PC) could obtain the coating with smoothness and homogeneity composition (Baskaran et al. 2006; Yang et al. 2016). It illustrated that the variation in the current mode enables the removal of Cu with the formation from crystalline oxides to crystalline Cu in its metallic form (de Morais Nepel et al. 2020). These studies indicated that the current conditions during the electrodeposition process could influence both the heavy metal removal behavior and the mass transport process of the electroreduction.

Many studies have focused on EDTA washing and its subsequent electrochemical reduction treatments but have considered the two technologies as two independent processing steps. Few studies have attempted to combine the two treatments. In this study, we propose a treatment involving the coupling of EDTA washing and electrochemical reduction. Heavy metal-contaminated soil (target metals were Cd and Pb) collected from a mining area was used as the test soil. Laboratory experiments to treat soil suspensions were performed based on both coupling strategies under different current conditions (current value and current mode) and two individual strategies. The primary objectives of this study were to compare the target metal removal ability using a combination technique and the two processes independently to clarify the target metal transformation and migration mechanisms under different current conditions and provide essential data and reference for further development of the combination technique.

Materials and method

Chemicals, electrodes, and membrane materials

All chemicals used in this study were analytical reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A graphite electrode sheet with dimensions of 100 mm [L] × 50 mm [W] × 1 mm [H] and an ASTM 304 stainless steel sheet with the same dimensions were used as the anode and the cathode respectively. Neosepta CMB® (Astom, Japan) was selected as the cation exchange membrane material.

Experimental soil

The contaminated soil used for remediation experiments was collected from an actual mining area in Huludao City, Liaoning Provence, China. Table 1 lists the main characteristics

Table 1 Characteristics of the experimental soil

| Items	Values
Clay (< 2 μm)	17.76%
Silt (2–20 μm)	67.16%
Sand (20 μm–2 mm)	15.08%
Organic matter (g kg^{-1})	5.7
Conductivity (mS cm^{-1})	1.7
pH	6.94
Cd (mg kg^{-1})	20.58
Pb (mg kg^{-1})	570.55

of the soil. The collected soil was oven-dried at 40 °C. Then, the material was pulverized and sieved with a 100-mesh sieve until a homogeneous sample was obtained. The soils were then sealed and stored at 20 °C for subsequent experiments.

Experimental setup design

A schematic of the remediation setup and the conceptual diagram of current variation with time for different current modes are illustrated in Fig. 1. The experimental setup was a cuboid composed of plexiglass, with dimensions of 180 mm [L] × 60 mm [W] × 60 mm [H]. The device was separated into two parts using a CEM. One part was 120-mm-long and was used as a washing suspension compartment, and the other part, a 60-mm-long compartment, was used as the anode reservoir. The two electrodes were vertically immersed in the two compartments. The power supply (ITech, IT6322A, China) was connected to the electrode

Fig. 1 A schematic of the remediation setup (**a**), and the conceptual diagram of current variation with time for different current modes (**b**). CC continuous current, PC pulse current
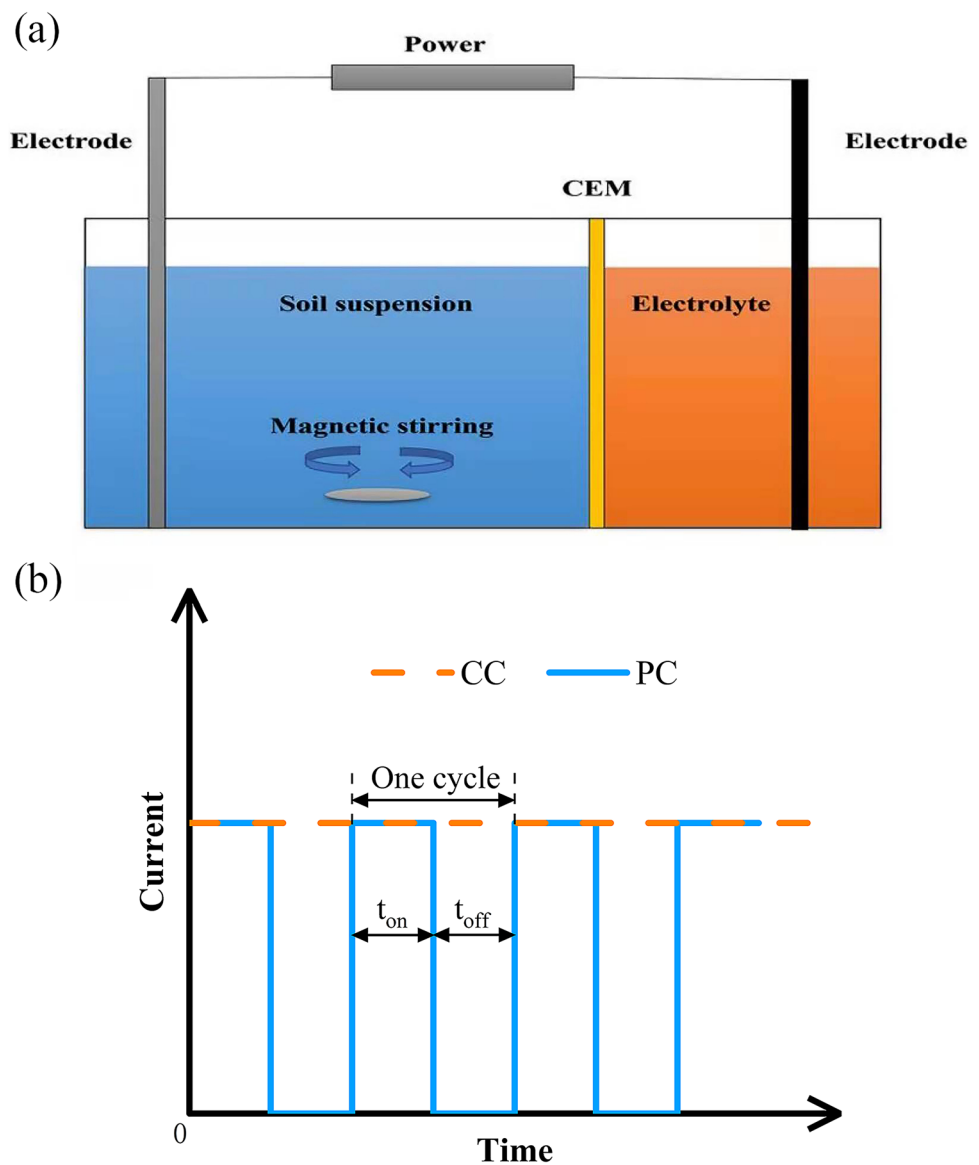
wires to provide CC and PC. Under PC, a cyclic process was obtained comprising a period with the current "ON" (i.e., application of an electric field) followed by a period with the current "OFF" (i.e., no application of an electric field) (de Morais Nepel et al. 2020). The electrical energy consumption was recorded using a host computer (ITech-IT9000).

Experimental plan

The experimental plan (three independent experiments and seven coupling experiments with a remediation time of 48 h) was conducted under the conditions listed in Table 2. The duration was designed to maintain an identical total charge transfer between CC and PC experiments under the same current (Sun et al. 2013a, b). Among them, W1 and W2 were prepared by single EDTA washing for 48 h, during which the contaminated soil suspension was prepared with 40 g contaminated soil and 200 mL extracting solution. EDTA concentrations were 10 mM and 50 mM, respectively, following a series of extraction experiments with different concentrations of leaching materials on the experimental soil (Fig. A1 details the results). T0 was a control test under experimental conditions similar to T1 but with the soil washed with deionized water (DW). Soil suspensions for T1–T7 were prepared using EDTA solution (10 mM) with a liquid/soil ratio of 5:1, which is the same as that of EDTA washing. T1 and T2 were prepared with different EDTA concentrations (10 mM and 50 mM), and the coupled electrochemical reduction process was carried out using a CC of 32 mA. T3 and T4 were carried out using different current values and similar EDTA concentrations based on CC conditions (16 mA–10 mM and 64 mA–10 mM, respectively). T5, T6, and T7 were carried out under similar current value and EDTA concentration conditions (32 mA–10 mM), with PC ratios (t_{on}/t_{off}) of 16 min/16 min, 32 min/16 min, and 48 min/16 min, respectively. The soil suspension and a sodium nitrate supporting electrolyte (0.1 mM, 100 mL) were added to the corresponding compartments. At 6, 12, 24, 36, and 48 h (actual power

"ON" time), 5 mL of the soil suspension was taken-out of the soil washing compartment and centrifuged at 8000 rpm (RCF = 6793 g×) for 5 min to achieve liquid–soil separation. The supernatant was filtered through a 0.45-μm membrane and stored in a 10-mL plastic colorimetric tube. The solid phase was collected by rinsing twice with purified water, completely air-dried, and preserved for later determination and analysis.

Analysis and calculation

Soil pH

Soil pH was measured by suspending 5.0 g dry soil in 25 mL distilled water. After agitation, pH was measured using a pH analyzer (Orion Star A211, Thermo Fisher Scientific, Waltham, MA, USA).

Soil heavy metal concentrations

Total Cd and Pb in the soil were digested using the HNO_3-HF-$HClO_4$ digestion method (Gao et al. 2013b, a; Tang et al. 2017) and then measured with atomic absorption spectrometry (AAS-Thermo, Ice3000 series). AAS also measured the concentration of Cd and Pb in the liquid phase. Analysis was conducted in triplicate in both cases, and mean values were used.

Removal efficiency and mass balance

The removal efficiency was calculated using Eq. (7):

$$\text{Removal efficiency} = (m_0 - m_1)/m_0 \qquad (7)$$

where m_0 refers to the mass of heavy metal in the initial soil and m_1 refers to the mass of heavy metals remaining in the soil after treatment. The mass balance was defined based on the relationship between the sum of mass found in

Table 2 Experimental design of treatments

Exp	Extractant	Current value (mA)	Concentration(mmol/L)	Current mode	Pulse ratios (min on/min off)
W1	EDTA	/	10	/	/
W2	EDTA	/	50	/	/
T0	DW	32	/	CC	/
T1	EDTA	32	10	CC	/
T2	EDTA	32	50	CC	/
T3	EDTA	16	10	CC	/
T4	EDTA	64	10	CC	/
T5	EDTA	32	10	PC	16 min on/16 min off
T6	EDTA	32	10	PC	32 min on/16 min off
T7	EDTA	32	10	PC	48 min on/16 min off

different cell parts at the end of the experiment. The initial mass was calculated based on the mean initial concentration (Sun and Ottosen 2012).

BCR sequential extraction

Modified BCR (European Community Bureau of Reference) sequential extraction was performed to monitor changes in heavy metal fractions (Yang et al. 2009). The metal fractions were classified as F1 exchangeable (EXC), F2 reducible (RED), F3 oxidizable (OXI), and F4 residual (RES).

Energy consumption

Based on voltage and current, energy consumption was calculated using Eq. (8):

$$E = \int VIdt \tag{8}$$

where E is the energy consumption (Wh), V is the voltage between the working electrodes (V), I is the current (A), and t is the duration (h).

Electrodeposition morphology analysis

The electrodeposition coatings deposited on the cathode were further analyzed using a scanning electron microscope (SEM) (Quanta 250 FEG, USA).

Results and discussion

Variation of soil pH

Figure 2 shows the variation in soil pH. The initial soil pH was 6.9, and it decreased after EDTA washing. Similar drops in pH have also been observed in a previous study (Kaurin et al. 2020). Soil pH increased after the combination technique compared to initial values because of the OH$^-$ generated at the cathode (Yeung and Gu 2011). Due to OH$^-$ neutralization, soil pH reached about 7.0 and remained constant until the T1, T2, T3, T5, T6, and T7 experiments were finished. Since the pH variation in the T5–T7 experiments was similar to that in T1 under the same current value (32 mA), current modes had minimal effect on soil pH in the coupling condition. The high current value applied in the T4 treatment resulted in the soil pH increased to approximately 9.4. Some researchers (Zhou et al. 2014) have reported that when the applied current value reaches the limiting current density of an ion exchange membrane, water splitting occurs at the interface between CEM and the suspension. Therefore, CEM hinders the migration of H$^+$ and OH$^-$ in the electric field,
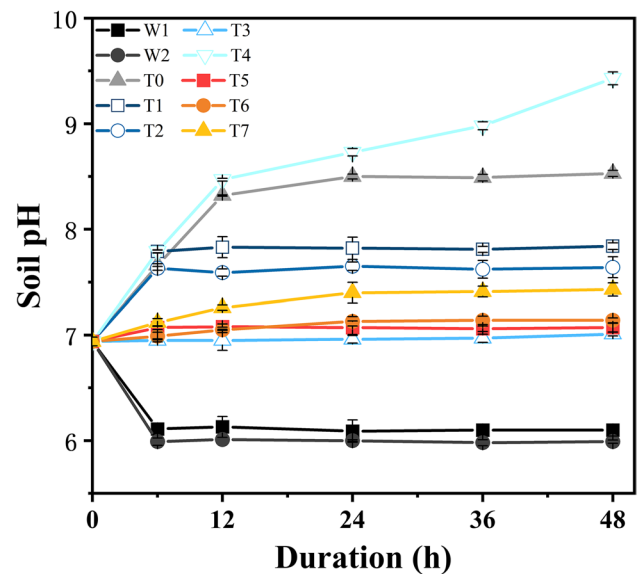
Fig. 2 Evolution of soil pH as a function of experimental duration during experiments

increasing soil pH. The magnitude of the current applied played a significant role in controlling soil pH during the combination process.

Target metal removal

Figure 3 shows the variation in target metal removal efficiency under separate processes and coupled processes during the remediation. It illustrates that target metals were further removed from the soil suspension due to the combination technique, although with varying removal efficiencies. Cd was removed from the soil matrix in the following order of efficiency: T2 (CC–32 mA–50 mM): 54.71% > T4 (CC–64 mA): 52.12% > T6 (PC–32 min/16 min–32 mA): 47.56% > T5 (PC–16 min/16 min–32 mA): 47.25% > T1 (CC–32 mA–10 mM): 46.60% > T7 (PC–48 min/16 min–32 mA): 46.01% > W2 (EDTA–50 mM): 41.43% > T3 (CC–16 mA): 37.75% > W1 (EDTA–10 mM): 31.36% > T0 (DW): 5.98%. Conversely, Pb was removed from the soil matrix in the following order of efficiency: T2 (CC–32 mA–50 mM): 80.93% > T4 (CC–64 mA): 80.50% > T6 (PC–32 min/16 min–32 mA): 77.00% > T1(CC–32 mA–10 mM): 76.93% = T7 (PC–48 min/16 min–32 mA): 76.93% > T5 (CC–16 min/16 min–32 mA): 75.60% > T3 (CC–16 mA): 66.23% > W2 (EDTA–50 mM): 66.02% > W1 (EDTA–10 mM): 49.88% > T0 (DW): 6.47%. Furthermore, Fig. 4 depicts the changes in the distributions of target metal contents in soil suspension (in the soil or liquid phases) of all experiments. The mass of the target metals in the soil phase of the soil suspension decreased obviously after treatment

compared to their initial values. Figure 5 illustrates BCR fractionation before and after all experiments. The target metal recoveries of BCR ranged from 98 to 108%.

## Metal removal: comparison of combination technique and separate processes

Figure 3 illustrates that the target metals were not significantly removed from the soil phase through a single electrochemical reduction process in the T0 (control) treatment. The reason was that deionized water was used as the washing solution, and the hydroxide ions generated by electrolysis precipitated heavy metals, decreasing metal removal efficiency (Jensen et al. 2006). According to the results, EDTA played a key mediating role between metal desorption from soil particle surfaces and electrodeposition. In addition, EDTA can inhibit cathodic electrolysis reactions and makes electrochemical reduction reactions more efficient.


Fig. 3 Variations in target metal removal efficiencies from soil phase of the suspension during the treatments: a for Cd; b for Pb
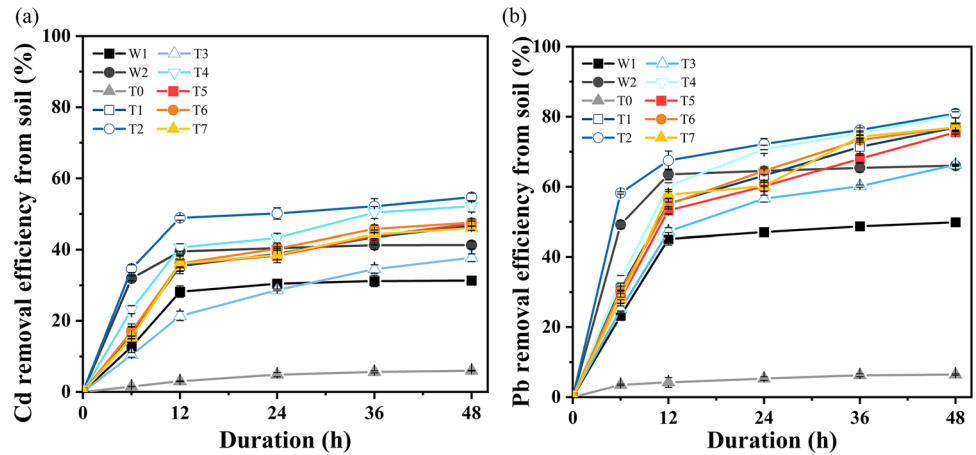
Fig. 4 Distribution of the target metals in the soil suspension before and after treatments: a for Cd; b for Pb
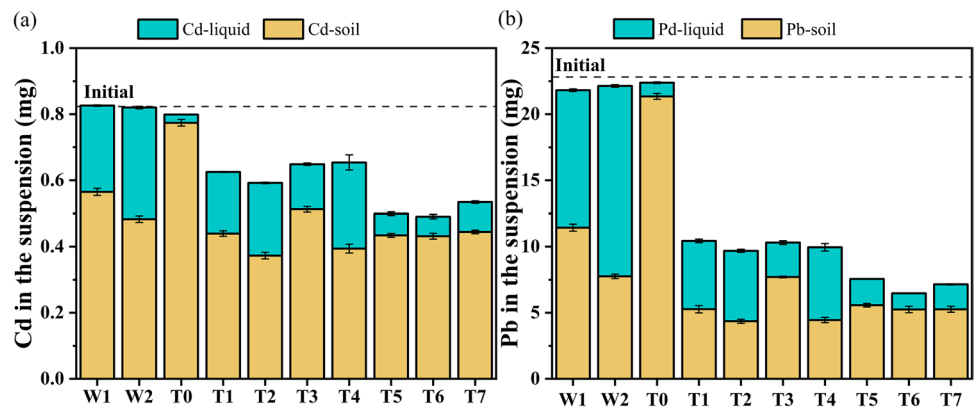
Fig. 5 BCR fractionation changes in Cd (a) and Pb (b) in soil before and after all treatments. EXC exchangeable fraction, RED reducible fraction, OXI oxidizable fraction, RES residual fraction
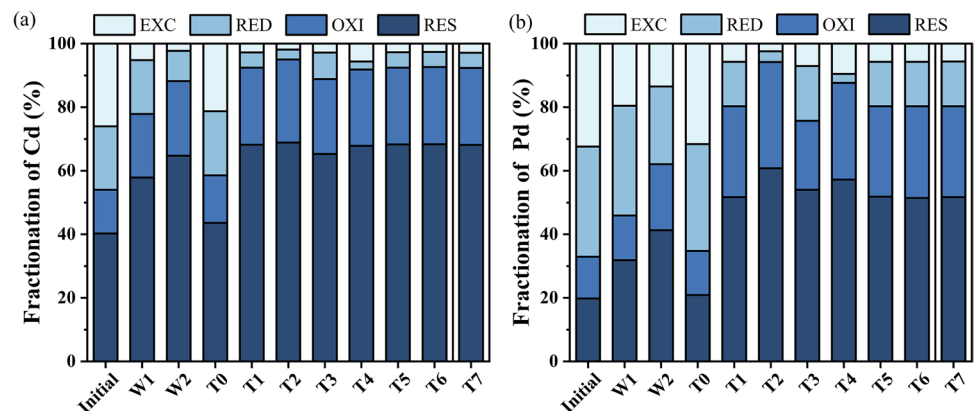
Concerning the effect of the electrochemical reduction process, under similar EDTA concentrations, the combination technique yielded higher metal removal efficiencies than single EDTA washing. Figure 3 illustrates that removal efficiency under coupling increases with increased current values (T1 vs. T3, T4), implying that a higher current facilitates heavy metal removal from the soil matrix. In addition, the current mode (CC and PC) at the same value (32 mA) achieved almost the same effect of improving heavy metal removal efficiency during the remediation experiments (T1 vs. T5, T6, T7). Compared with separate processes, the efficiency of target metal removal from the soil phase under the combination technique increased in the cases of Cd and Pb by 6.39–20.76% and 16.35–30.62%, respectively. However, Cd removal from the soil phase was lower than Pb. The main reason was that the stability constant (K) of the PbEDTA^{2-} complex is more considerable than that of CdEDTA^{2-} (Begum et al. 2013). Compared with the original soil, the exchangeable and reducible Pb decreased more than Cd. In addition, Cd mainly exists in the form of residue, which is more closely bound to soil particles and is more difficult to remove from the soil.

It has been confirmed that the extraction efficiency of EDTA decreases and then increases with the increase of pH (Begum et al. 2012). In this study, the extraction efficiency of W2 was more remarkable than W1, which may be caused by the superposition of two factors, the increase of EDTA concentration and the decrease of pH of the soil suspension. A similar study (Begum et al. 2013) also found the difference in extraction efficiency caused by different concentrations of EDTA. After W1 and W2 achieved the optimal extraction effect, the target metal removal efficiencies under the coupled process increased continuously during the remediation, confirming the combination technique's synergistic enhancement effect.

Interestingly, it can be seen from Fig. 2 that the pH of T5–T7 after treatment was less than T2; however, the removal efficiency of T5–T7 for heavy metals was higher than T2. Theoretically, a high pH means a high chelating ability of EDTA, which has been confirmed that the corresponding complexes of the ML systems (M = Cd^{2+}, Pb^{2+}, L = EDTA) have the following log sequences: (a) Cd^{2+}: log K_{ML} (pH = 7) < log K_{ML} (pH = 8), (b) Pb^{2+}: log K_{ML} (pH = 7) < log K_{ML} (pH = 8) (Begum et al. 2013). Such an observation indicated that except for pH, other factors affect the removal efficiency of Cd and Pb in the soil. On the one hand, when the electrochemical reduction occurs at the cathode, thereby facilitating EDTA regeneration, which could further extract the heavy metals on soil particle surfaces; this was proved by a previous study as a synergistic effect of coupling strategy (Song et al. 2022). On the other hand, enhancement of target metal removal efficiency under the coupled condition could be related

to Cd and Pb fractionation, which were weakly bound to the soil.

According to Fig. 5, the exchangeable and residual fractions were the dominant Cd BCR fractions in the contaminated soil in the initial state, accounting for 26% and 40% of the fractions, respectively. Conversely, Pb contained more reducible and exchangeable fractions, which accounted for 32% and 35%, respectively. The target metals in the residual fraction were the major contaminants remaining in the soil phase after remediation. They were strongly bound to the soil and considerably immobile during treatment (Ryu et al. 2009). After EDTA washing (W1 and W2), the mass of various forms of Cd and Pb in the soil decreased, and the exchangeable heavy metals largely dropped. In addition, the reducible Cd and Pb percentages in soil decreased in the T1–T7 treatments and accounted for significant proportions of total metal removals from the soil phase. Numerous researchers have reported similar observations (Gao et al. 2013b, a; Wang et al. 2016). The results indicate that the coupling strategy can effectively remove the reducible heavy metals from the soil.

Metal removal: comparison of CC and PC modes in the combination technique

Figure 4 shows barely any difference in the mass of target metal remaining in the soil based on different current modes under similar current conditions (T1 vs. T5, T6, T7). A similar study observed no significant improvement under PC in Cu-contaminated soil (Sun et al. 2012). Figure 5 also indicates that the target metals in the exchangeable and reducible fractions decreased. In contrast, the oxidizable and residual fractions increased following a coupling strategy based on both CC and PC. However, according to the mass balance (Table 3), Cd in the supernatant decreased from 0.186 mg to 0.059–0.090 mg, whereas Pb content dropped from 5.163 mg to 1.226–1.991 mg. Considering the almost similar speciation fractions and different electrodeposition mass following the coupling strategy, PC did not influence soil fractionation and may have only influenced the mass transport process between the suspension and the cathode.

Figures 6 and 7 show the surface morphologies of the target metal deposits obtained under CC and PC. From Fig. 6, it was evident that there were many apparent pits on the deposit surfaces based under CC. In addition, higher current values increased the number and size of pits on the surface. Loose and spongy deposits have been attributed to the existence or formation of some interfacial inhibitors, which influence the surface morphology of electrodepositions, such as H$_2$ generation during the deposition process (Paul Chen and Lim 2005). However, the deposit surfaces under PC (Fig. 7) were smooth, excluding T7, which contained some minor pits. Compared to the process

Table 3 Metal mass balance, removal efficiency, and consumption of electric energy: (a) for Cd; (b) for Pb (KWh g⁻¹ of Me means the electricity required to remove 1 g of heavy metal from the soil)

(a) Cd Tests	Metals in the anolyte (mg)	Metals in the soil (mg)	Metals in the supernatant (mg)	Metals on the cathode (mg)	Removed mass of Cd (mg)	Mass balance (%)	Removal efficiency (%)	Energy consumption (Wh)	Energy consumption (KWh g⁻¹ of metal)
W1	-	0.565	0.261	-	0.258	100	314	-	-
W2	-	0.483	0.337	-	0.340	100	41.3	-	-
T0	-	0.774	0.025	0.052	0.049	103	5.98	26.8	546
T1	-	0.440	0.186	0.249	0.384	106	46.7	9.87	25.7
T2	-	0.373	0.219	0.242	0.450	101	54.7	8.64	19.2
T3	-	0.512	0.136	0.220	0.311	106	37.8	7.01	22.5
T4	-	0.394	0.260	0.231	0.429	108	52.1	18.4	42.9
T5	-	0.434	0.065	0.353	0.389	104	47.3	8.54	22.0
T6	-	0.432	0.059	0.366	0.392	104	47.6	8.24	21.0
T7	-	0.444	0.090	0.354	0.379	108	46.0	9.17	24.2

(b) Pb Tests	Metals in the anolyte (mg)	Metals in the soil (mg)	Metals in the supernatant (mg)	Metals on the cathode (mg)	Removed mass of Cd (mg)	Mass balance (%)	Removal efficiency (%)	Energy consumption (Wh)	Energy consumption (KWh g⁻¹ of metal)
W1	-	11.44	10.38	-	11.384	95.6	49.9	-	-
W2	-	7.756	14.38	-	15.067	97.0	66.0	-	-
T0	-	21.35	1.036	1.331	1.477	104	6.47	26.8	18.1
T1	-	5.266	5.163	12.58	17.557	101	76.9	9.87	0.56
T2	-	4.352	5.333	12.82	18.470	98.6	80.9	8.64	0.47
T3	-	7.708	2.595	11.64	15.114	96.2	66.2	7.01	0.46
T4	-	4.450	5.497	11.48	18.372	93.9	80.5	18.4	1.00
T5	-	5.568	1.991	17.16	17.254	108	75.6	8.54	0.49
T6	-	5.248	1.226	17.98	17.574	107	77.0	8.24	0.47
T7	-	5.264	1.878	16.63	17.558	104	76.9	9.17	0.52

Fig. 6 SEM micrographs of deposits with different continuous current (CC) values: **a** the blank cathode, **b** 16 mA, **c** 32 mA, and **d** 64 mA
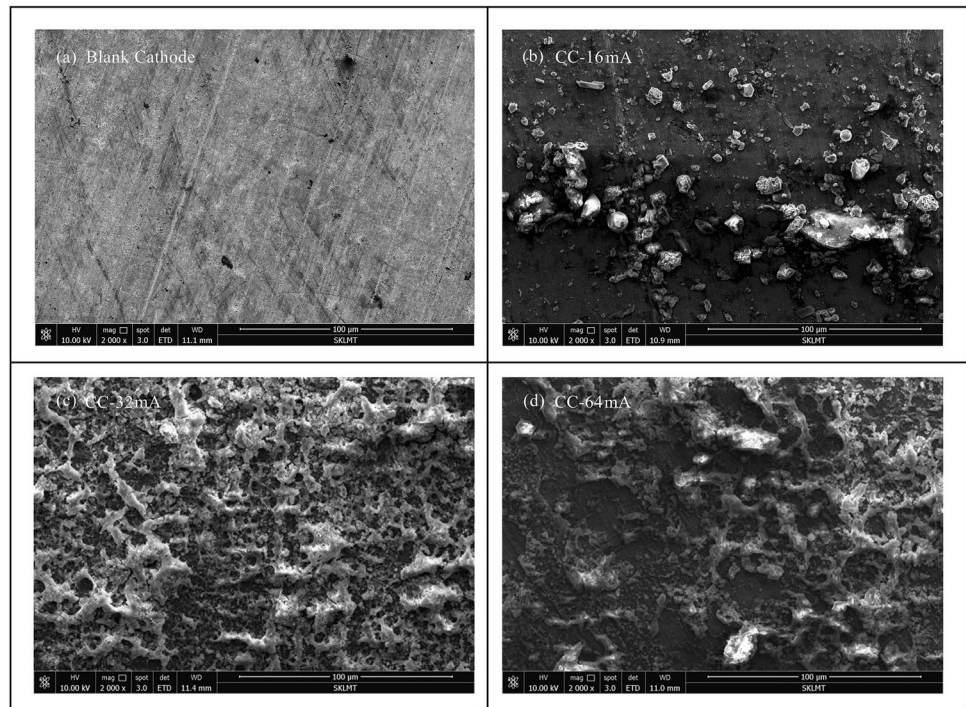
Fig. 7 SEM micrographs of deposits with different pulse current (PC) ratios: **a** the blank cathode, **b** 16 min on/16 min off, **c** 32 min on/16 min off, and **d** 48 min on/16 min off
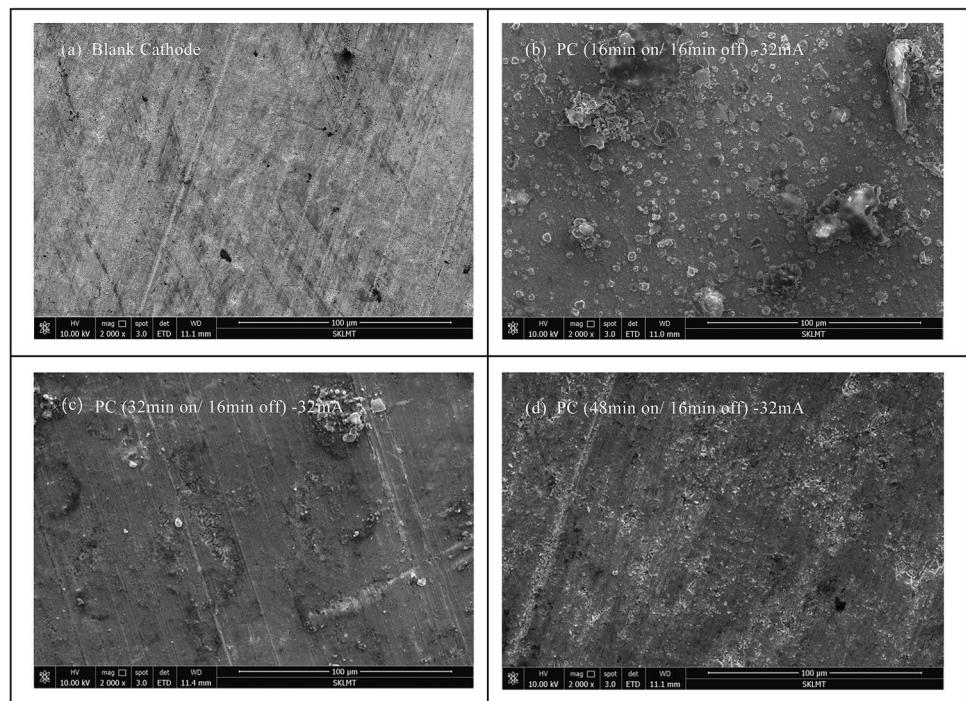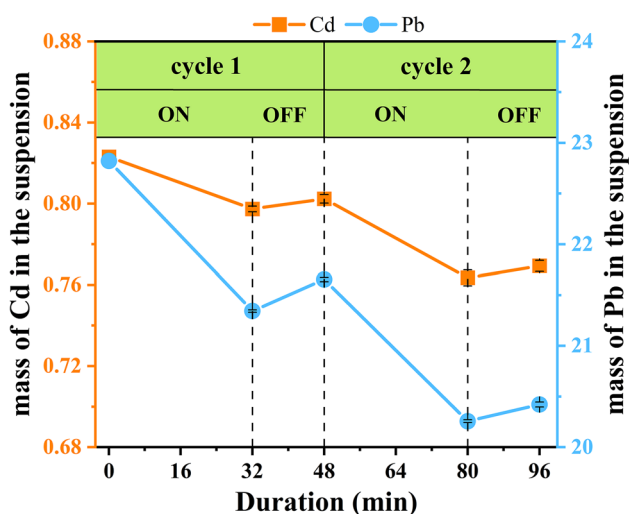

under PC, the limiting factor of the poor deposition effect under CC is mainly due to a cathodic H_2 evolution reaction (El-Sherik et al. 1997; Paul Chen and Lim 2005), which played a significant role in electrodeposition morphology. Such pits resulted from H_2 bubbles that remained attached to cathode surfaces for extended periods. The different rates of the electrode reactions and mass transport processes resulted in significant drops in the concentrations of $(Me-EDTA)^{(4-n)-}$ at the cathode surface diffusion layer, leading to a competing reaction, in this case, H_2 evolution, as illustrated in Eq. (6). Therefore, the H_2 barrier obstructed the mass transport process between the suspension supernatant and cathode surface. A short period in "OFF" for the diffusion phenomenon can be used

during the interval of the off-time so that the diffusion gradients (produced during the "ON" time) can be diminished (Hansen and Rojo 2007) and (Me-EDTA)$^{(4-n)-}$ at the cathode surface replenished adequately. Hence, the H_2 evolution reaction was effectively shielded (Paul Chen and Lim 2005), and the mass transport barrier caused by H_2 was broken. Considering the relatively more uniform deposits obtained from the T5–T7 treatments, it can be concluded that PC can improve the grain structure of the deposited coating with refined crystalline grains and homogeneity (Baskaran et al. 2006; Palacios-Padrós et al. 2010; Caballero-Briones et al. 2011). However, in the PC mode, it is also necessary to avoid setting an unreasonable pulse ratio, which may cause H_2 evolution reactions like in the T7 treatment.

The most intriguing aspect of the results is that the mass of target metal in suspension increased during the power-off period and dropped during the subsequent power-on period (Fig. 8). It implied that the treatment process in the washing suspension could increase the redox potential in the soil suspension through aeration (Sun et al. 2013a, b) and provide a basis for the oxidation of heavy metals that have been deposited on the cathode. The re-oxidized metal ions are pulled back into the soil suspension by a large amount of regenerated EDTA, as illustrated in Eq. (5), resulting in a rise of mass in suspension. An automatic lifting device that matches the pulse frequency could be installed to address such a shortcoming. When the PC is off during the cycle, the automatic lifting device lifts the cathode out of the washing suspension, which protects the metal coating deposited on the cathode from desorption during the power-off period.
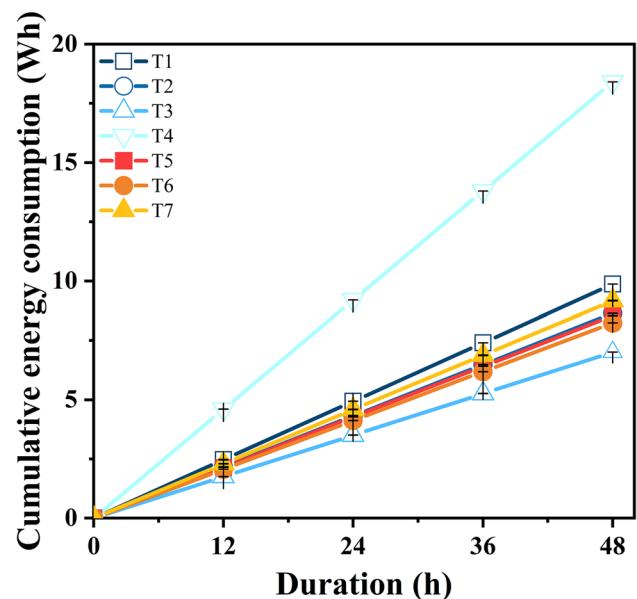
Electrical energy consumption

Energy consumption is one of the most important considerations when considering electrochemical reduction to apply to treat contaminated soils. Figure 9 shows that electric energy consumption increased with processing time. The T4 treatment achieved a maximum total energy consumption of 18.40 Wh, whereas 7.01 Wh (T3) was the minimum value in all the experiments. Under similar current values and EDTA concentrations, the combination technique based under CC required more electric energy than those based on PC (T1 > T7 > T5 > T6), which confirmed that PC effectively alleviated the excess energy losses caused by mass transport obstacles. Table 3 lists the energy consumed to remove 1% of target metals from soil. Under similar removal efficiencies from the soil, the cost increased with the applied current value. The PC consumed lower electrical energy compared with CC. Considering electrical energy consumption and the mass of heavy metals removed, T6 (32 min on/16 min off−32 mA) was the most cost-effective treatment for removing heavy metals, demonstrating the advantages of the PC in reducing energy consumption.

Conclusion

This study investigated the Cd and Pb removal behavior and mechanisms following the coupling of EDTA washing and electrochemical reduction. The removal efficiencies and mechanisms were studied under varying soil pH and current conditions, the target metal removal efficiencies, and

Fig. 8 Summary statistics of the mass of Cd and Pb in soil suspension of T5 (PC-32 min on/16 min off) in the first two cycles

Fig. 9 Electric energy consumption of T1–T7

energy consumption were compared among different treatments. The following conclusions were obtained:

EDTA played a critical mediating role in the mass transfer between metal desorption from soil. The combination technique coupling of EDTA washing and electrochemical reduction improved target metal (Cd and Pb) removal efficiencies under the present experimental conditions. The combination technique can increase the pH of the soil and improves the extraction efficiency of EDTA. The synergistic enhancement could regenerate EDTA in the suspension during remediation to further extract heavy metals from soil and promote further removal of reducible fractions of heavy metals from the soil. Compared with the CC current mode, the PC condition did not improve target metal (Cd and Pb) removal efficiency from the soil based on the coupled approach; furthermore, the PC condition could not alter the speciation fractions of heavy metals. However, the dissolved metals under CC conditions mainly stayed in the liquid phase of the suspension, which required more remediation time or further treatment of the lixiviant using other methods. In contrast, the PC mode could alleviate the mass transport obstacles caused by cathodic H_2 evolution, promote mass transfer between suspension supernatant and the cathode surface, improve the grain structure of the deposited coating, and reduce energy consumption.

In brief, EDTA washing and electrochemical reduction coupling is an innovative remediation strategy for enhanced heavy metal removal from the soil in mining areas.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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