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ORIGINAL PAPER

# Stepwise addition of chemical reagents for enhancing electrokinetic removal of Cu from real site contaminated soils

Jih-Hsing Chang · Yan-Hsong Shi ·  
Cheng-Hung Tung

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**Abstract** In this study, a circulation-enhanced electrokinetics (CEEK) system integrated with the stepwise addition of chemical reagents was used to remediate copper-contaminated soils collected from a real site. At first, an optimal extraction process of different chemical reagents was found to obtain the highest copper removal efficiency by conducting batch extraction experiments. The chemical reagents served as extracts including EDTA, NaOH, and sodium dithionite + sodium citrate. Then, CEEK integrated this optimal extraction, that is, the treatment of 6-day EDTA, NaOH, EDTA, sodium dithionite + sodium citrate, and EDTA in a series. According to experimental results, the NaOH and sodium dithionite + sodium citrate could effectively facilitate the copper removal during the extraction and electrokinetics (EK) processes. The optimal extraction process for this real contaminated soil (94% copper removal efficiency) was the alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate. The copper removal efficiency of the real contaminated soil could reach around 55% after 30-day CEEK treatment. The continuous decline of soil copper concentration of this integrated EK technique could be achieved as the remediation time was extended sufficiently.

**Keywords** Electrokinetics · Copper · EDTA · Soil remediation

## 1 Introduction

Soil contamination has been considered as one of the most important environmental issues in the world. In Taiwan, the contaminated-soil problem of heavy metals has been paid attention for a period of time and undertaken many remediation activities. Many techniques of soil remediation have been used such as phytoremediation, acid washing, soil replacement, and electrokinetics (EK) [1]. For the phytoremediation, plants are utilized to uptake heavy metals from the contaminated soil, which will not disturb the natural environment. However, the removal efficiency and the length of treatment time are difficult to estimate for the effective remediation. The consideration of the acid washing process, the constitution of soils will be decomposed, lose the fertilizer and even results in other environmental problems (i.e., the acid wastewater). In contrast, the EK process possesses many advantages including: (1) producing the electro-osmotic (EO) flow as the flushing liquid in the heterogeneous soils (2) controlling the stream direction of EO flow associated with groundwater (3) possessing high removal efficiency for various pollutants (4) exerting competitive economical effectiveness [2]. Although EK presents many advantages, some drawbacks of EK have also been mentioned. One major disadvantage is the soil acidification during EK operation (even the soil acidification may be beneficial to the release of heavy metals from the soil), which may dramatically destroy the soil constituents and cause the failure of the EK system owing to zero charge of the soils [3]. As using in agricultural lands, the fertile soils may not be cultivated after EK

J.-H. Chang (✉) · Y.-H. Shi  
Department of Environmental Engineering and Management,  
Chaoyang University of Technology, 168 GiFong East Road,  
WuFong Hsiang, Taichung County 41349, Taiwan  
e-mail: changjh@cyut.edu.tw

C.-H. Tung  
Department of Environmental Engineering, National Chung  
Hsing University, 250, Kuo Kuang Road,  
Taichung 40277, Taiwan

treatment due to the loss of organic nutrients and the low pH condition. In Taiwan, most sites contaminated by heavy metals are agricultural lands, it is expected that the contaminated soils can be recovered for the agricultural usage. A specific circulation-enhanced EK process was developed for preventing treated soils from the acidification [4], which was used in this study.

For the EK application to remediate heavy-metal contaminated soils, some researches have achieved certain satisfactory results. Li et al. demonstrated that Pb, Cd, and Cr in the sand soil could be successfully removed up to 90% by EK process [5]. Hansen et al. utilized EK to clean up the soil contaminated by several different heavy metals obtained effective results as well. Sah and Chen focused on the remediation of Cd and Pb contaminated soil and reported some useful data including metals stability in the cathode zone and metal species variation during EK treatment [6, 7]. Even the EK system presents the promising application for soil remediation but sometimes fails under certain conditions. As a result, some advanced EK processes have been developed and was used to many applications [8, 9]. Among these advanced EK systems, the chelating agents combined with EK was one of the most popular methods. Since chelating agents were considered to complex with heavy metals and avoid the precipitates of heavy metals in the soil, the use of chelating agents could enhance the removal efficiency of heavy metals. Wong et al. employed the EK integrated with Ethylene diamine tetraacetic acid (EDTA) to treat Pb and Zn contaminated soils under a constant voltage gradient (150 V/m) for 6 days. They found that the addition of EDTA ( $5 \times 10^{-2}$  M– $2 \times 10^{-1}$  M) in the cathodic reservoir could remove around 100% Pb and Zn [10]. Some researchers demonstrated the relative low toxicity of EDTA [11]. Other researchers reported that three different chelating agents including HEDPA, EDTA, and citric acid showed different degrees of achievements [12]. However, the EK integrated single chelating can not completely clean up heavy-metal contaminated soils with complicated situations [13].

Generally speaking, the adsorbed heavy metals in soils can be divided into five species: exchangeable, carbonate salts, organic matter, iron-manganese oxides and residuals [14, 15]. The exchangeable species mainly are adsorbed on the soil clay and the binding strength is relatively low; the carbonate salts are mostly in the presence of carbonate precipitates and easily varied by the pH circumstance; the organic matter species are accumulated in the bio-environment such as bacteria and plant fragments and in the presence of complex compounds; the iron-manganese oxides possess strong covalent bonds in the soil and can be reduced under low pH or reduction potential conditions; the residuals are the most difficult to be released from the soil, which might be dissolved in the very strong acid. Most

remediation techniques can only remove parts heavy metals of the above five species from soils even the usage of chelating agents such as EDTA. Therefore, a target-oriented remediation technique is quite necessary, that is, one specific chemical agent serves to remove the heavy metals in turns of their species. Accordingly, the total amount of heavy metals in the soil based on the above extraction process is theoretically possible to be removed.

Regarding the above five metal species, EDTA may extract the exchangeable and carbonate salts [16]. Thus, an effective removal could be reached when heavy metals were in presence of these two species in contaminated soils. Stevenson reported that around 80% organic matter in the soil could be dissolved in the NaOH solution [17]. Based on this concept, the heavy metal species of organic matter may be removed by the NaOH solution. Likewise, the usage of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and sodium citrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ ) could dissolve the iron-manganese oxides [18], which may aid the release of this part of heavy metals from the soil. As a consequence, the extraction process of EDTA, NaOH, sodium dithionite, and sodium citrate were examined in this study in order to comprehensively enhance the removal efficiency of heavy metals from contaminated soils. When an optimal extraction process was found, these chemical reagents were applied to CEEK remediation to treat the real-site contaminated soil. The target metal of this research was copper that has been the most frequent pollutant in contaminated lands of Taiwan. In summary, this work tried to find out an innovative CEEK technique to effectively remove the heavy metals in the contaminated soil.

## 2 Experimental

Soil samples were collected by many plastic tubes (ca. 500 g soil in each tube) from a specific contaminated waste site in Taiwan. This site was an abandoned plant of chemical productions and contaminated by Cu and Cd. The Cu concentration was higher than the soil-control limitation regulated by Taiwan EPA, therefore, Cu was chosen as the target pollutant in this study. The soil characteristics including soil texture, pH, soil moisture, organic matter, specific surface area, and ECEC were analyzed. Table 1 lists the soil properties and the analytical methods used. It should be noticed that soil pH was relatively low (4.3) and the organic matter was relatively high (5.6%). The original copper content in soil sample was extracted by the strong acids (nitric acid and hydrochloric acid with 3:1 volume ratio). Then, the copper concentration of the soil sample was determined using by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Co. model iCAP-600), which could obtain the metal content of

**Table 1** The soil properties of the copper contaminated sites

Item	Result	Analytical method
Soil texture	Sandy loam	ASTM D 422 ~ 463
Soil pH	4.3	NIEA S410.62C
Soil moisture (%)	11.0	NIEA S280.61C
Soil organic matter (%)	5.6	Head, 1980 [19]
Specific surface area (m <sup>2</sup> /g)	35.6	BET-201 AEL
ECEC (meq/100 g)	10.1	NIEA S202.60A

the soil sample based on proper calculation. The soil samples were collected by different collecting tubes from the real contaminated site. In order to gain the practical data, the soil sample of each tube was put into the EK reactor without mixing process. Hence, there were different copper concentration of different soil samples. In general, the copper concentration of the soil ranged ca. 1,000–3,000 mg/kg. The chemicals were purchased from Riedel-de-Haën Co. The purity of EDTA was 85% and all other chemical reagents were ca. 99.0%.

Experimental approaches were divided into two phases: 1. the extraction experiment of different chemical reagents to find an optimal extraction procedure; 2. the addition of the optimal chemical reagents to serve as the working solution of CEEK to understand the removal efficiency and to evaluate the CEEK feasibility.

### 2.1 Extraction experiment

Batch extraction experiments were conducted with different chemical reagents at the soil to solution ratio (by weight) of 1:10. To a series of glass tubes (tube volume is 12 mL), a desired amount of copper contaminated soil and solution of chemical reagent were added. The tubes were placed in a shaker and shaken constantly for 2 h to reach the equilibrium condition. To separate the soil from the solution, the mixtures were then centrifuged at 2,500 rpm (1,000g) for 10 min using a centrifuge (Prescison Scientific Co. model K-9). The copper concentration of the centrate was analyzed by the ICP-AES. Table 2 lists five different extraction tests including: 1. A five-times continuous extraction of EDTA, the extract would be replaced by the fresh EDTA solution of  $1 \times 10^{-2}$  M for each extraction. 2. The alternative extraction of EDTA and acid, the

$1 \times 10^{-2}$  M EDTA,  $5 \times 10^{-3}$  M hydrochloric acid + citric acid, and  $5 \times 10^{-3}$  M nitric acid + citric acid were served as an extract respectively. 3. The temperature effect of EDTA extraction,  $1 \times 10^{-2}$  M EDTA solution was used under 40, 50, and 60 °C, respectively. 4. The alternative extraction of EDTA and NaOH, the  $1 \times 10^{-2}$  M EDTA and  $2.5 \times 10^{-1}$  M NaOH were served as an extract respectively. 5. The alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate, that is, the  $1 \times 10^{-2}$  M EDTA,  $2.5 \times 10^{-1}$  M NaOH, and  $8.5 \times 10^{-2}$  M sodium dithionite + sodium citrate were served as an extract respectively. The pH of the EDTA, NaOH, and sodium salts was ca. 10, 12, and 8, respectively.

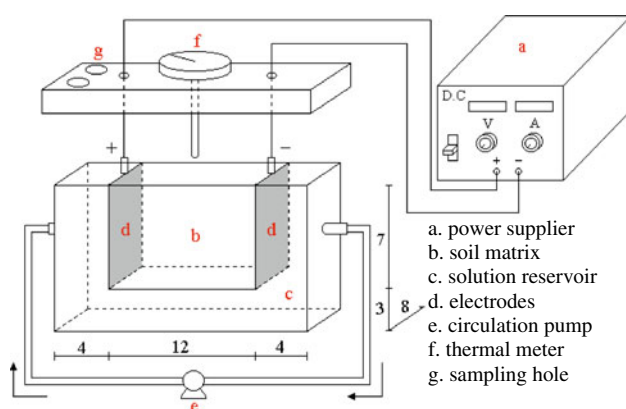
### 2.2 CEEK experiment

Figure 1 shows the sketch of the laboratory CEEK reactor. The CEEK cell was made of PVC with the dimension of 20.0 cm in length, 8.0 cm in width and 10.0 cm in height. It was divided into two compartments; the central one was for storing around 600 g of the soil sample (packed by two different tubes of the site soil detonated by A and B, respectively) and the other was for working solution (ca. 900 mL). To avoid the soil leakage, a pair of nylon meshes (Spectrum model PP, mesh opening 149 μm) and a filter paper (Whatman No. 1) was placed between the soil sample and electrodes. A DC power supplier (IP 200-21 DS) was applied to the CEEK system at a constant voltage gradient 1.0 V/cm. Graphite plates were served as the electrodes and placed at each electrolytic compartment right behind the membranes. A circulation pump was used to carry the working solution from the cathode to anode for neutralizing pH of working solution. During the run, the temperature was around 25 °C since the voltage strength of 1.0 V/cm in this study was quite low.

The working solution included the  $1 \times 10^{-2}$  M EDTA,  $2.5 \times 10^{-1}$  M NaOH, and  $8.5 \times 10^{-2}$  M sodium dithionite + sodium citrate, respectively. Each working solution was added into the reservoir for 6 days; the sequence followed the order of EDTA, NaOH, EDTA, sodium dithionite + sodium citrate, and EDTA. For the change of each working solution, the original solution was discharged and the reservoir was rinsed by DI water. Then, the fresh solution was poured into the reservoir and retained 2 h for

**Table 2** The stepwise soil extraction tests with different chemical reagents

Test No	1st extract	2nd extract	3rd extract	4th extract	5th extract
1	EDTA	EDTA	EDTA	EDTA	EDTA
2	EDTA	Acid	Acid	EDTA	
3	EDTA (40 °C)	EDTA (50 °C)	EDTA (60 °C)		
4	EDTA	NaOH	EDTA	NaOH	EDTA
5	EDTA	NaOH	EDTA	Sodium salts	EDTA



**Fig. 1** The sketch of the laboratory CEEK reactor

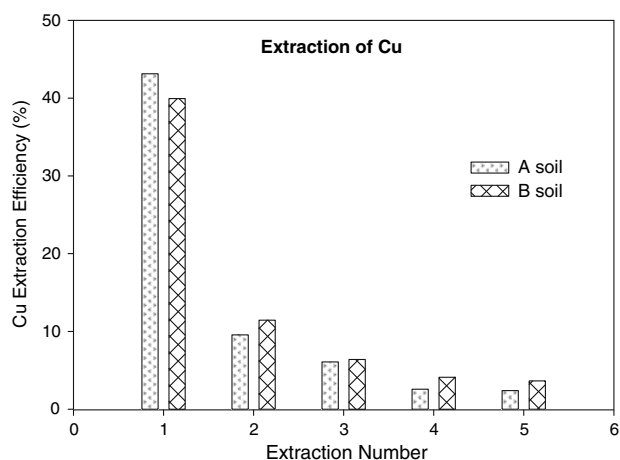
next run. The total treatment time was 30 days. For a period of selected time, 3.0 g soil sample was collected in the region at anode, middle, and cathode, respectively. The pH of working solution and soils, conductivity of working solution, system current, and Cu concentration in the soil were determined.

### 3 Results and discussion

#### 3.1 Extraction remediation

##### 3.1.1 The continuous extraction of EDTA

Figure 2 shows the copper removal efficiency versus EDTA extraction times. The original copper concentration for two different contaminated soil samples (A and B) was 1,237 and 3,249 mg/kg, respectively. In Fig. 2, the copper removal efficiency of soil A and B after the first extraction was around 43 and 40%, respectively. After the second, third, fourth, and fifth extraction, the copper removal



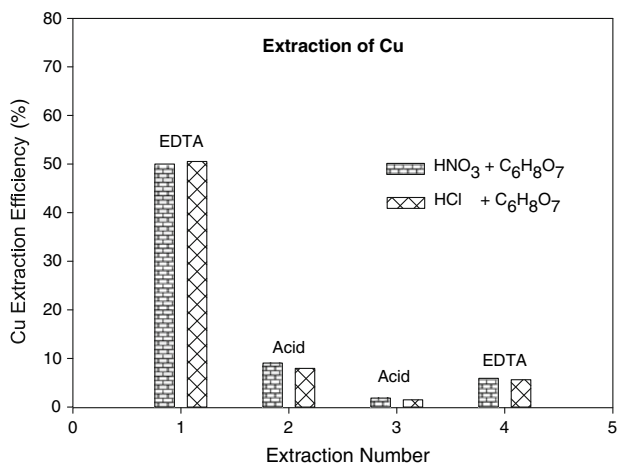
**Fig. 2** Copper removal efficiency versus EDTA extraction times

efficiency of soil A was around 9.6, 6.1, 2.5 and 2.4%, respectively. For soil B, the copper removal efficiency was around 11.5, 6.4, 4.1 and 3.6%, respectively, after second, third, fourth, and fifth extraction. The copper removal efficiency declined with the extraction times and the total copper removal efficiency of soil A and B was pertaining to 64%. The above phenomena indicate that certain copper species were unable to be extracted by EDTA and still bound with soils. Some lab-scale studies reported that the copper removal efficiency could achieve to 90% by EDTA extraction [16, 20], which was inconsistent with our extraction results. The difference might be attributed to different soil characteristics and the period of contaminated time, i.e., contaminated soils of real sites were difficult to be remediated completely.

It could be seen that most copper was removed from the soil under the first extraction from Fig. 2. The minor copper was removed under the subsequent extractions. This indicated that 2-h extraction period of time for EDTA was quite sufficient. Because the exchangeable and carbonate copper species could be chelated by EDTA, the remaining species of copper in the soil were the ion-manganese oxide and residuals of copper. In other words, the 64% copper species in this real-site soil was in the presence of the exchangeable and carbonate.

##### 3.1.2 The alternative extraction of EDTA and acid

Since the EDTA extraction experiments were conducted under pH 8 condition, this relatively high pH circumstance might result in copper precipitates, which was possible to hinder the copper removal. As a consequence, the alternative process of EDTA and acid extraction was induced to clarify the pH concern. Two different acid solutions were used as the extracts:  $5 \times 10^{-3}$  M nitric acid + citric acid (pH = 2.58) and  $5 \times 10^{-3}$  M hydrochloric acid + citric acid (pH = 2.60). Figure 3 shows the copper removal efficiency versus alternative extraction of EDTA and acid. The copper removal efficiency of first EDTA extraction was averagely around 50%. The removal efficiency of subsequent nitric acid + citric acid and hydrochloric acid + citric acid extraction was 9 and 8%, respectively. Then, the copper removal efficiency of repeated acid + citric acid and hydrochloric acid + citric acid extraction was 1.8 and 1.5%, respectively. After the final EDTA extraction, the copper could be separated from soil ca. 6%. The total copper removal efficiency of this alternative extraction process was around 66%, which was close to the results of continuous extraction of EDTA. That means both acid solutions could not enhance the copper removal efficiency in this case. According to the previous study [22], the above acid solutions can obtain effective removal efficiency of heavy metals in the presence of exchangeable,

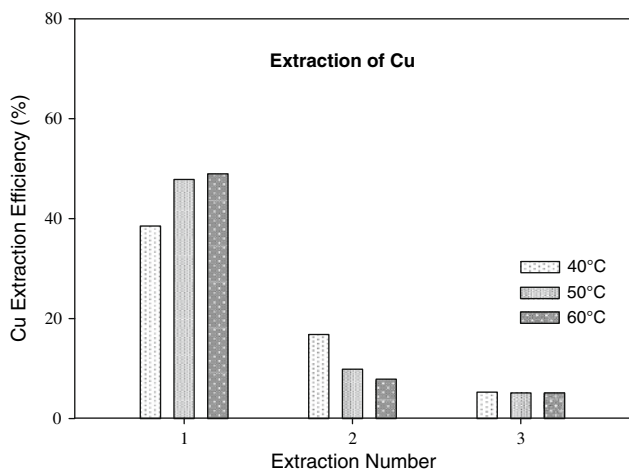


**Fig. 3** Copper removal efficiency versus alternative extraction of EDTA and acid

carbonate, organic, and iron-manganese species. This effective removal did not occur in this study, which might be attributed to the specific soils in the real contaminated site.

3.1.3 The temperature effect of EDTA extraction

Figure 4 shows the copper removal efficiency versus EDTA extraction times under different temperatures at 40, 50, and 60 °C. During the first extraction, the copper removal efficiency of 40, 50, and 60 °C treatment was 38, 48, and 49%, respectively. It seemed that the higher temperature could increase the higher removal efficiency of the EDTA extraction. The removal of second EDTA extraction at 40, 50, and 60 °C was 17, 10, and 8%, respectively, which presented reverse phenomenon compared with the first extraction. The removal of third EDTA extraction at



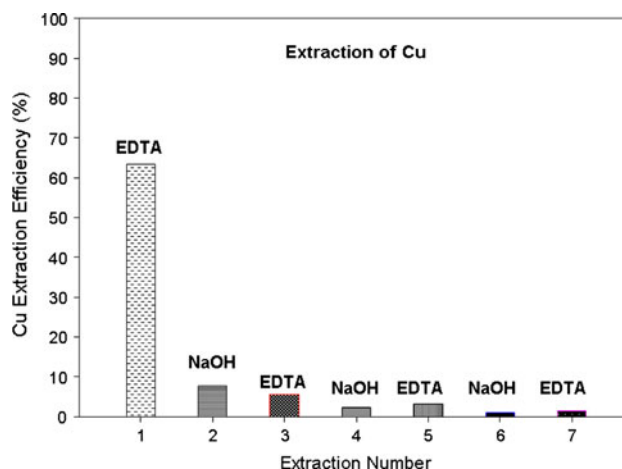
**Fig. 4** Copper removal efficiency versus EDTA extraction times under different temperatures

40, 50, and 60 °C was almost identical, i.e., 5%. Based on the above experimental results, it can be seen that the increased temperature can solely enhance the copper removal rate but not the total removal capacity (ca. 63% for different temperatures). That is, there is no significant influence of temperature on breaking the binding strength between copper and soils.

3.1.4 The alternative extraction of EDTA and NaOH

According to the above data, the maximal copper removal by EDTA extraction was around 64% for this real contaminated soil. The popular used acid solutions such as nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCL) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) possessed limited extraction capacity. The increased temperature could not enhance the copper desorption in the soil either. Since the above extraction aims at desorbing the copper species of exchangeable and carbonate, the copper species in the organic matter needs other means to remove. Stevenson reported that NaOH could dissolve around 80% organic matter from the soil [17]. Hence, the copper coupled with dissolved organic matter in the soil may be released into the extraction solution and enhance the removal efficiency; even NaOH with high pH may cause the copper precipitates in the soil.

Figure 5 presents copper removal efficiency versus alternative extraction of EDTA and NaOH. The copper removal efficiency of first EDTA extraction was around 63%. Then, around 8% copper was removed by the NaOH extraction. There was roughly 5% copper was removed by the second EDTA extraction. Then, around 2% copper was removed again by the NaOH extraction. This alternative extraction process was conducted till only 1.5% copper removal by EDTA. The totally accumulated copper removal by this extraction process was around 84%.

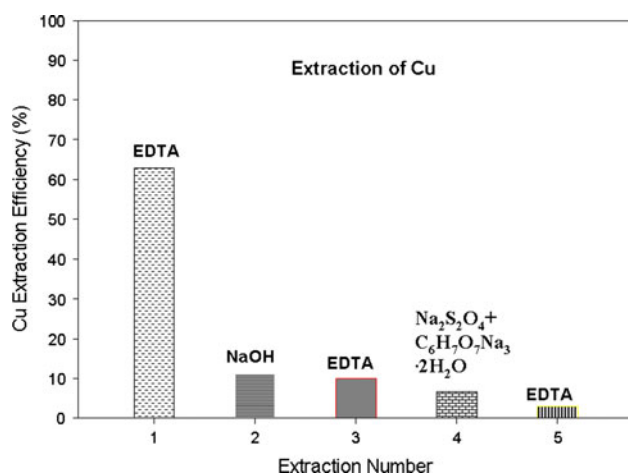


**Fig. 5** Copper removal efficiency versus alternative extraction of EDTA and NaOH

Compared to the copper removal of continuous EDTA extraction (64%), this process could achieve more 20% copper removal from the soil. In addition, the organic matter of the soil was decreased from original 5.6–2.3%. Accordingly, NaOH (pH = 12.88) extraction could aid to remediate this copper contaminated soil by dissolving the organic matter in the soil.

### 3.1.5 The alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate

The copper species in the presence of iron-manganese oxides might be still bound in the soil after the alternative extraction of EDTA and NaOH. Mehra and Jackson reported that sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) + sodium citrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ ) could remove the iron-manganese oxides from the soil [21]. Like the removal concept of NaOH, the copper coupled with iron-manganese oxides in the soil may be released into such extraction solution and enhance the removal efficiency. Figure 6 presents copper removal efficiency versus alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate. The copper removal efficiency of first EDTA extraction was around 63%, which close to the previous experimental result. Then, around 11% copper was removed by the NaOH extraction. There was roughly 10% copper was removed by the second EDTA extraction. Then, around 7% copper was removed by the sodium dithionite + sodium citrate extraction. At the last extraction step, there was around 3% copper removal by EDTA. The totally accumulated copper removal by this extraction process was around 94%. Compared to the copper removal by alternative extraction of EDTA and NaOH extraction (84%), this process could achieve more 10% copper removal from the soil. That is, sodium dithionite + sodium citrate extraction could aid to



**Fig. 6** Copper removal efficiency versus alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate

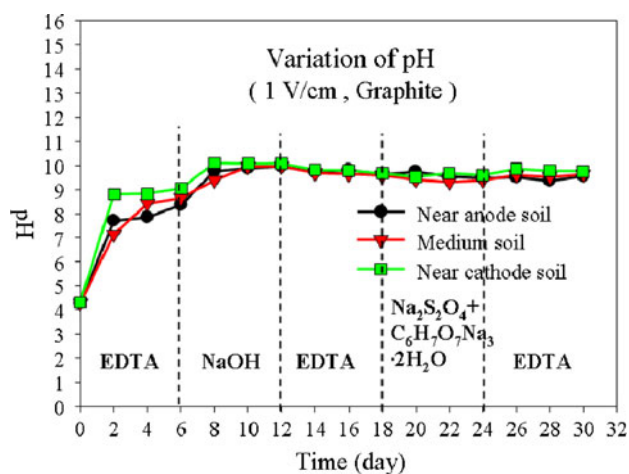
remediate this copper contaminated soil by the removal of iron-manganese oxides in the soil.

### 3.2 Electrokinetics remediation

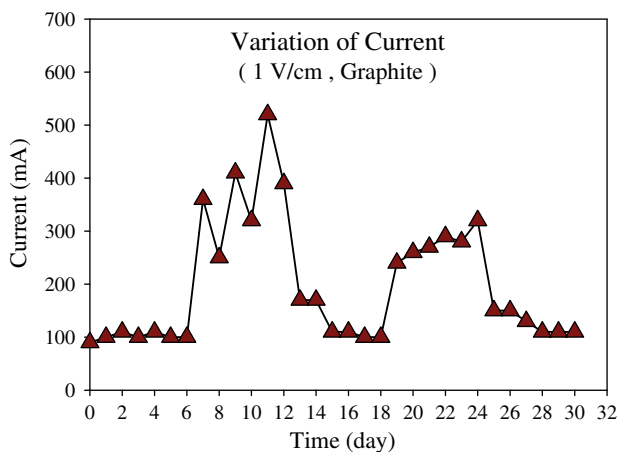
Based on the above experimental results, the optimal extraction process was the alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate. This means those chemical reagents could remove each specific species of copper form the soil. Inducing those extraction solutions into EK system can potentially achieve high copper removal efficiency.

#### 3.2.1 Soil pH and current variation in the electrokinetics

In our previous studies, the pH of working solution in this specific CEEK system could be controlled at roughly neutral pH range [22]. Due to the neutral pH solution, the soil pH would be maintained at the neutral range as well. In this case, some high pH extracts were used such as EDTA (pH around 11) and NaOH (pH around 13). These high pH solutions just increased the pH temporarily; the pH of solution always could be maintained at 9 because the pH control by the water-electrolysis (acid and base yield at the anode and cathode, respectively) and the circulation system in the CEEK. Figure 7 shows the soil pH variation versus treatment time. The soil pH increased from the original low pH (4.3) to relatively high pH (9.5) and maintained stably. It could be seen that the soil pH at different positions possessed almost the same pH value. In contrast, the EK systems without the circulation system usually resulted in the low soil pH at the anode and the high soil pH at the cathode. The relatively high pH has two advantages for EK remediation. The first, the electro-osmotic flow rate can be maintained to stably clean up the contaminated soil [23]. The second, the EDTA possesses the extensive chelating



**Fig. 7** Soil pH variation versus treatment time



**Fig. 8** The current variation versus treatment time under the voltage gradient of 1.0 V/cm

ability to remove the heavy metals from the contaminated soil.

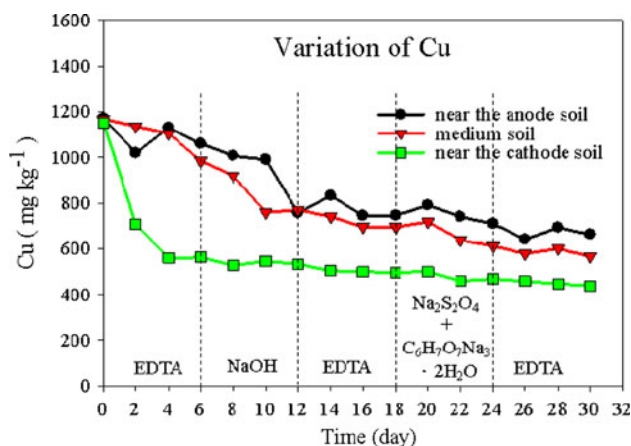
Figure 8 shows the current variation versus treatment time under the voltage gradient of 1.0 V/cm. From the figure, the current increased from 90 to 110 mA after 1-day EDTA process then maintained ca. 100 mA. With the addition of NaOH solution, the current dramatically increased to 360 mA because of the high pH solution with high electrical conductivity. This significant increase of current indicated that most current passed through the solution compartment instead of soil compartment. When the working solution was switched to EDTA subsequently, the current became ca. 100 mA that was the same as the first addition of EDTA. When the sodium salts was served as the working solution, the current roughly varied to 300 mA due to the conductivity of sodium salts. At the final stage of CEEK, the current maintained ca. 100 mA again according to the EDTA addition. Based on experimental results, the CEEK current majorly depends on the electrical conductivity of working solution.

### 3.2.2 Copper removal efficiency of the electrokinetics

Figure 9 shows the variation of copper concentration in the soil versus treatment time. After the first 6-day CEEK + EDTA treatment, the copper removal efficiency was around 15, 20 and 50% for the soil close to anode, medium area, and cathode, respectively. This indicated that EDTA served as the working solution could remove copper as expected. It should be noticed that the relatively high copper removal efficiency at the cathode. This might be attributed to the negative charge of EDTA compound in the high pH CEEK system. When the ions with negative charge will flow from the cathode to the anode due to the electromigration mechanism, the EDTA movement direction will be against the electro-osmotic flow. As a

consequence, the soil close to the cathode might be easily chelated with copper and released into the pore solution. After the 6-day CEEK + NaOH treatment, the copper removal efficiency was around 26, 18 and 3% for the soil close to anode, medium area, and cathode, respectively. The effective removal efficiency at the anode and medium area means NaOH solution could aid to dissolve the organic matter and remove copper from the soil as expected. However, the low removal efficiency at the cathode might be due to the precipitates occurrence. Compared to the batch extraction, the precipitates were more difficult to be removed due to the relatively slow flow velocity of the working solution in the CEEK system (EO flow rate was around 150 mL/day [22]).

In Fig. 9, the copper removal efficiency was pertaining to 1, 6, and 3% for the soil close to anode, medium area, and cathode, respectively, after the second 6-day CEEK + EDTA treatment. After the 6-day CEEK + sodium dithionite + sodium citrate treatment, the copper removal efficiency was around 3, 7 and 2% for the soil close to anode, medium area, and cathode, respectively. These results indicated that the copper coupled with iron-manganese oxides could be removed as expected, even the remediated extent was not significant. The last 6-day CEEK + EDTA treatment could remove the copper of 4, 4 and 3% for the soil close to anode, medium area, and cathode, respectively. The total accumulated copper removal efficiency was 49, 55 and 61% for the soil close to anode, medium area, and cathode, respectively. Even the total copper removal of such CEEK process was less than that of optimal extraction around 30%, the continuous decline of copper removal trend demonstrated that this CEEK integrated with chemical reagents possessed potentially high feasibility. That is, the decrease of copper concentration might be achieved as the remediation time was extended sufficiently.



**Fig. 9** The variation of copper concentration in the soil versus treatment time

#### 4 Conclusions

Based on experimental results of extraction and CEEK, several conclusions can be drawn as follows:

1. The NaOH and sodium dithionite + sodium citrate could effectively facilitate the copper removal of extraction and CEEK in addition to the EDTA remediation.
2. The optimal extraction process for this real contaminated soil (94% copper removal efficiency) was the alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate in this case.
3. The integrated technique of CEEK + the alternative extraction of EDTA, NaOH, and sodium dithionite + sodium citrate could maintain the treated soil at relatively high pH.
4. The copper removal efficiency of the real contaminated soil could reach around 55% after 30-day CEEK treatment.
5. The continuous decline of soil copper concentration of this integrated EK technique might be achieved as the remediation time was extended sufficiently.

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