

Electrokinetic Remediation of Cadmium (Cd), Copper (Cu) and Nickel (Ni) Co-contaminated Soil with Oxalic Acid, Acetic Acid or Citric Acid as the Catholyte

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Electrokinetic remediation (EKR) of Cd, Cu, and Ni co-contaminated soil was investigated using three organic acids (oxalic acid, acetic acid, or citric acid) as promising catholytes. Four experiments were performed to explore the effects of the three organic acids on pH and TDS (total dissolved solids) values, removal performance, content, distribution, and changes in speciation of heavy metal ions (exchangeable, reducible, oxidizable and residual fractions). Application of organic acids (oxalic acid, acetic acid, or citric acid) as catholyte coupled with EKR alleviated significant pH jumps and improved the efficiency of heavy metal removal. The application of the three organic acids and CK improved the remediation performance for Cd, Cu, and Ni, with citric acid being the most effective, followed by acetic acid, oxalic acid, and finally, CK. The Cd, Cu, and Ni removal efficiencies (average of five sections) for the citric acid treatment reached 61±1.6% (from 300 mg/kg to 182 mg/kg), 41±0.5% (from 845 mg/kg to 345 mg/kg), and 52±1.3% (from 436 mg/kg to 225 mg/kg), respectively. Heavy metal speciation analysis showed that the contents of the exchangeable and reducible fractions decreased near the cathode for all three organic acid treatments compared with the CK treatment only.

Keywords: Electrokinetic remediation, cadmium, copper, nickel, organic acid.

1. INTRODUCTION

Soil contaminated with heavy metals is currently considered one of the most serious environmental problems. Excessive disposal of heavy metals in the environment causes accumulation and introduction into food chains. This may cause serious harm to plants and animals, including humans [1]. Unlike organic contaminants, heavy metals cannot be degraded. Therefore, it is necessary to develop effective separation technologies to permanently remove heavy metals from contaminated soil. So far,

various treatment techniques have been developed and applied, such as phytoremediation [2-4], chemical washing [5-6], bioleaching [7], and electrokinetic remediation (EKR) [8-12].

Comparing the above remediation technologies, electrokinetic remediation (EKR) has obvious advantages and excellent performance owing to its low cost, even for low-permeability soils [13]. EKR technology involves inserting electrodes into the soil and applying low voltage direct current [14]. EKR has been explored for several decades and the main mechanism of EKR technologies has been elucidated in previous studies [15]. Coupled with the electrolysis of water at the anode and cathode, a series of electric effects are produced, such as electromigration, electroosmosis, and electrophoresis. Among them, electromigration is the dominant transport mechanism for heavy metal ions in most cases. In an electric field with a low, direct current voltage gradient (0-2 V/cm) or a low current (0-1 A), positively charged heavy metal cations present in soil pore solutions migrate toward the cathode, while negatively charged ions migrate to the anode. Heavy metal ions that accumulate near the cathode can be removed through electroplating, adsorption onto the electrode, precipitation or coprecipitation at the electrode, pumping water near the electrode, or trapping with filter materials [16]. Electroosmosis refers to the movement of an ionic liquid in a charged soil micropore under the influence of an electrical double layer (EDL) and electric field [17]. Electrophoresis is the movement of charged particles or colloids in an electric field, which is always opposite to the direction of electroosmotic water flow [18]. Hence, in contrast with electromigration and electroosmosis, the effect of electrophoresis should be ignored in a low-permeability soil during the EKR process [19].

In the EKR process, the extreme pH value generated by the electrolysis of water at the cathode can lead to the precipitation of heavy metal cations that are migrating toward the cathode. This phenomenon is called the “focusing effect” and causes a reduction in removal efficiency [20]. Among many methods of avoiding the focusing effect, the addition of enhancing agents is an effective method to improve the dissolution of heavy metals through forming soluble heavy metal complexes. Enhancing agents usually include inorganic acids [20], organic acids [22], and/or complexing agents [23]. Due to their high removal efficiency for heavy metals, synthetic chelating agents, such as EDTA, DTPA, NTA, EDDS, and EGTA, are frequently applied to improve the EKR of Cd, Cu, Pb, and Ni [24]. However, these chemical chelating agents have some drawbacks, including poor biodegradability (particularly EDTA), potential toxicity (particularly NTA), and relatively high cost (particularly EDDS) [25]. Therefore, it is imperative to search for environmentally friendly and economically viable alternatives.

Oxalic acid, acetic acid, and citric acid are commonly present in nature in the form of root exudates, microbial secretions, and decomposition residues of plants or animals in soils. These low-molecular-weight organic acids have been used to improve the removal efficiency of heavy metals from soil, because they are easily biodegraded, environmentally benign, and commercially available for soil remediation. Many studies have demonstrated that the above-mentioned acids have improved effects on soil pH conditioning and excellent extraction efficiencies for heavy metals [26-27].

The main objective of the present study, therefore, was to investigate the influence of these three catholytes (oxalic acid, acetic acid, or citric acid) on pH and TDS (total dissolved solids) values, and the content and removal rates of Cd, Cu, and Ni under a voltage gradient of 1 V/cm and a duration of 7 days. In addition, the migration mechanism and speciation variation of Cd, Cu, and Ni during the electrokinetic

remediation process was analysed. The results form a foundation for the optimisation and selection of catholytes for enhancing the EKR of heavy metal-contaminated soil.

2. MATERIALS AND METHODS

2.1. Soil properties

The soil was obtained from depths of 0~20cm in Songjiang District, Shanghai, China. The physicochemical properties of the soil are displayed in Table 1. The soil was air-dried naturally, ground to pass through a 10-mesh sieve, and stored in a sealed container. To simulate a farmland soil seriously polluted by heavy metals, the target contents of Cd^{2+} 、 Ni^{2+} 、 Cu^{2+} for contaminated soil were set at 300mg/kg、400mg/kg and 800mg/kg. These values exceed the environmental quality soil standards of China (GB15618-2018). Simulated contaminated soil samples were spiked with $\text{Cd}(\text{NO}_3)_2$ 、 $\text{Ni}(\text{NO}_3)_2$ and CuSO_4 solution. The soil samples were stirred thoroughly each day and stored in a sealed container for subsequent use.

The reagents (HCl, HNO_3 , HClO_4 and HF) for soil sample digestion were all of pure grade. $\text{Cd}(\text{NO}_3)_2$ 、 $\text{Ni}(\text{NO}_3)_2$ and CuSO_4 and other reagents were analytically pure. The reagents were purchased from Sinopharm Chemical Reagents Co. Ltd., China.

Table 1. Physicochemical properties of the tested soil

Property	Value
pH	7.58
Moisture content (%)	19.25
Temperature of tested soil (°C)	27
Cation exchange capacity (cmol/kg)	23.56
Total carbon content (g/kg)	18.74
Gravel content (%)	27.52
Silt content (%)	41.7
Clay content (%)	30.78
Cd concentration (mg/kg)	300±3.0
Cu concentration (mg/kg)	845±6.4
Ni concentration (mg/kg)	436±3.6

2.2 EKR apparatus and experimental design

Fig.1 shows a schematic diagram of the EKR apparatus. The experimental apparatus is made of plexiglass with the dimensions 20cm×7.5cm×8cm (L×B×H). It consists of five principle parts: a soil chamber (length 15cm, width 7.5cm and height 8cm), two symmetrical electrode chambers (length 3cm, width 7.5cm and height 8cm), two filter chambers (length 0.5cm, width 7.5cm and height 8cm), power supply and electrolyte storage and delivery system. 25 holes with a diameter of 1cm are drilled through the plexiglass on the four sides of the filter chamber. To connect with the micro peristaltic pump through a silicone tube (outer diameter 3mm, and inner diameter 1mm), holes with a diameter of 2.8mm are drilled on the left and right outer walls of the electrolysis chamber at 1cm and 5cm from the bottom, respectively. Meanwhile, the peristaltic pump circulates the electrolyte at a pump speed of 1.0 mL/min. A pair of carbon felt electrodes (width 7cm, height 10cm, thickness 2mm) is placed in each electrode chamber to apply the electric field by a DC regulated power supply (SPA3005D, Nanjing, China). The electric current is monitored by a multimeter (VC86E, Shenzhen Victor Hitech, China). To separate the soil particles and other impurities, filter papers were inserted in each of the two filter chambers. The soil chamber is divided into five virtual sections, which are numbered S1, S2, S3, S4 and S5 from cathode to anode.

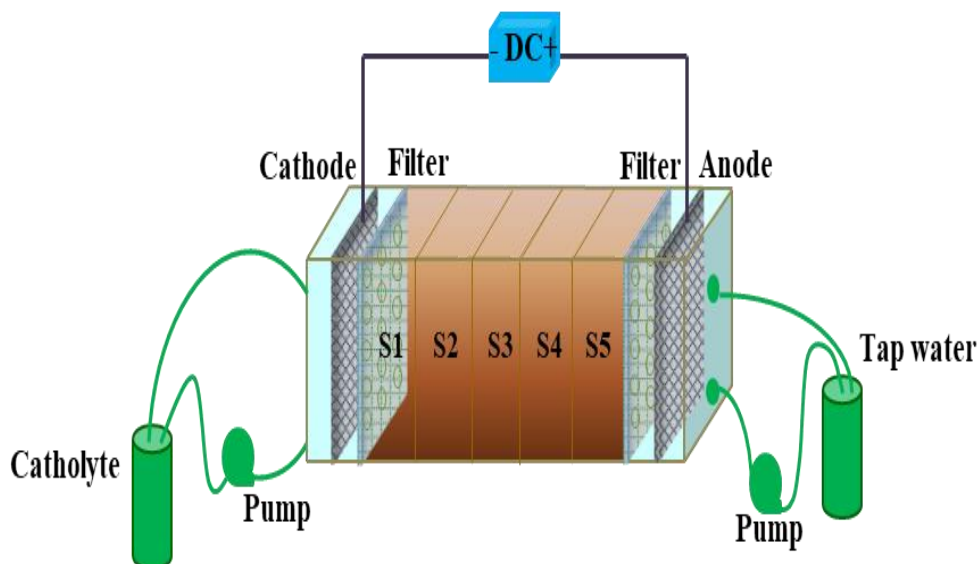


Figure 1. Schematic representation of a single EKR apparatus

The experimental design scheme is shown in Table 2. To investigate the effect of the three organic acids on pH conditioning at the cathode and heavy metal removal, oxalic acid, acetic acid, or citric acid were used as the catholyte and tap water was used as the anolyte. Four groups of apparatus (CK, oxalic acid, acetic acid or citric acid) of the same size were run with a voltage gradient of 1 V/cm over a duration of 7 days. Samples were taken on the 7th day of operation. At the end of the experiment, three soil samples were collected at equal intervals at the midline of the five sections of the soil, then air-dried, mixed, and ground evenly.

Table 2. Experimental conditions of the four electrokinetic experiments

NO.	Catholyte	Concentration (mol/L)	Anolyte	Voltage Gradient (V/cm)	Duration (d)	Electrode
CK	Tap water	/				
EK-1	Oxalic acid	0.1	Tap water	1	7	Carbon felt (Thickness 2mm)
EK-2	Acetic acid	0.1				
EK-3	Citric acid	0.1				

2.3 Analytical methods

TDS (total dissolved solids) refers to the total amount of inorganic salts and organic matter dissolved in water. In this study, TDS is used to indirectly reflect the electrical conductivity (EC). Soil samples pH was determined in a 2.5:1 (liquid/solid, the distilled water is measured in mL and soil is measured in grams) suspension using a pH meter (HQ40d, HACH, USA). The TDS was measured in a 5:1 (liquid/solid) with the meter (TDS-5, Guangdong, China).

The concentrations of the metals Cd, Cu and Ni in the sludge sample were analyzed by electric hot plate digestion and atomic absorption spectrophotometry (TAS-986, Beijing, China).

The binding forms of Cd, Cu and Ni with soil compounds were determined using modified BCR (Community Bureau of Reference) method [28-29]. The metal speciation in soil are sorted into four forms: (1) the exchangeable fraction (F1, metal ion and associated carbonates), (2) the reducible fraction (F2, bound with iron and manganese oxides), (3) the oxidizable fraction (F3, bound with organic substance), (4) residual fraction (F4, bound with crystalline mineral structures).

2.4 Calculations of removal efficiency

The Cd, Cu and Ni removal efficiencies are calculated as follows:

$$R_e = \frac{C_0 - C}{C_0} \times 100\%$$

$$\overline{R_e} = \frac{1}{5} (R_{e1} + R_{e2} + R_{e3} + R_{e4} + R_{e5})$$

where C is the heavy metal concentration after remediation (mg/kg) and C_0 is the initial heavy metal concentration (mg/kg); R_e is the removal efficiency of the section i; $\overline{R_e}$ are the average removal efficiencies of sections 1 to 5.

2.5 Statistical analysis

All statistical analyses were conducted using Excel and Origin 9.1. The results are expressed with mean values \pm standard deviation from three independent samples. All the experiments were done at room temperature ($27\pm 2^\circ\text{C}$).

3. RESULTS AND DISCUSSION

3.1 Changes in soil pH

Fig.2 shows the changes in pH with different catholytes in the five soil sections collected from the cathode to the anode (S1-S5) on the 3rd, 5th, and 7th day of the EKR process. The initial soil pH was 7.6. According to Fig.2, the addition of the three organic acids maintained a weakly acidic state in the soil and inhibited a pH jump at the cathode, while CK alone was not conducive to inhibiting a pH jump. As remediation time lengthened, the CK group began to show an obvious pH jump at the cathode. For CK, the pH ranged between 7.1–7.7 on the 3rd day, 4.1–9.2 on the 5th day, and 3.3–11.7 on the 7th day. The three organic acids maintained the pH in the acidic range with increasing remediation time; pH ranges for the oxalic acid, acetic acid, and citric acid treatments on the 7th day in the 5 sections were between 3.4–6.4, 3.4–6.5, and 3.7–5.1, respectively. Hence, the three organic acids effectively inhibited the pH jump at the cathode, with the citric acid showing the best performance. This is consistent with the removal efficiencies for Cd, Cu, and Ni in the citric acid as shown in Fig. 5.

Previous studies have investigated whether an acid treatment at the cathode section could control soil pH or alleviate the focusing effect. Wu *et al.* used 0.1 M acetic acid as the electrolyte under a voltage gradient of 1.25 V/cm and a duration of 7 days to determine the soil pH and Cr removal efficiency in five sections of the EKR apparatus. In the above treatment, the soil pH varied from an initial value of 8.7 up to nearly 10 [30]. This may be ascribed to the high buffering capacity of the tested soil, which prevented the transport of the acid through the soil and increased the pH throughout the soil system during the EKR process.

3.2 Changes in soil TDS

Fig.3 presents the changes in soil TDS (total dissolved solids) values for different soil sections from the cathode to the anode (S1-S5) after EKR using CK, oxalic acid, acetic acid, or citric acid. The changes in soil TDS reflect the dissolution and migration of ions in the pore fluid [30]. TDS values in the assays with the three organic acids increased with increasing remediation time from 3 to 5 days near S5 and decreased on the 7th day. In terms of the influence of different organic acids on TDS, it was found that the TDS values for the CK and oxalic acid treatments remained at a low level on the 3rd and 5th days, while TDS was relatively high for the acetic acid and citric acid treatments. The maximum values for TDS reached 1470 ppm for the citric acid treatment on the 5th day in S5, which may be related to the influence of acidification due to the low pH of 3. The variations in TDS values among the various sections during each experiment were caused by ion transport as a result of the applied DC potential.

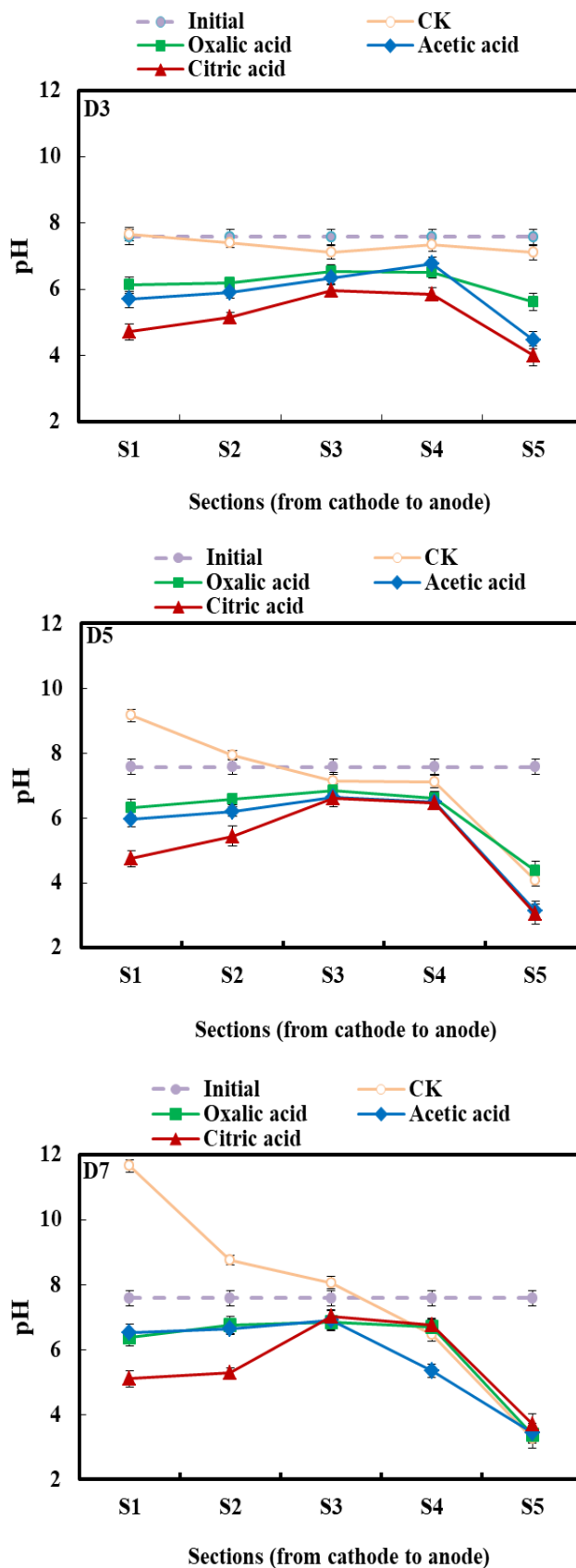


Figure 2. Changes in pH for the 5 sections of the EKR apparatus D3: on the 3rd day; D5: on the 5th day; D7: on the 7th day.

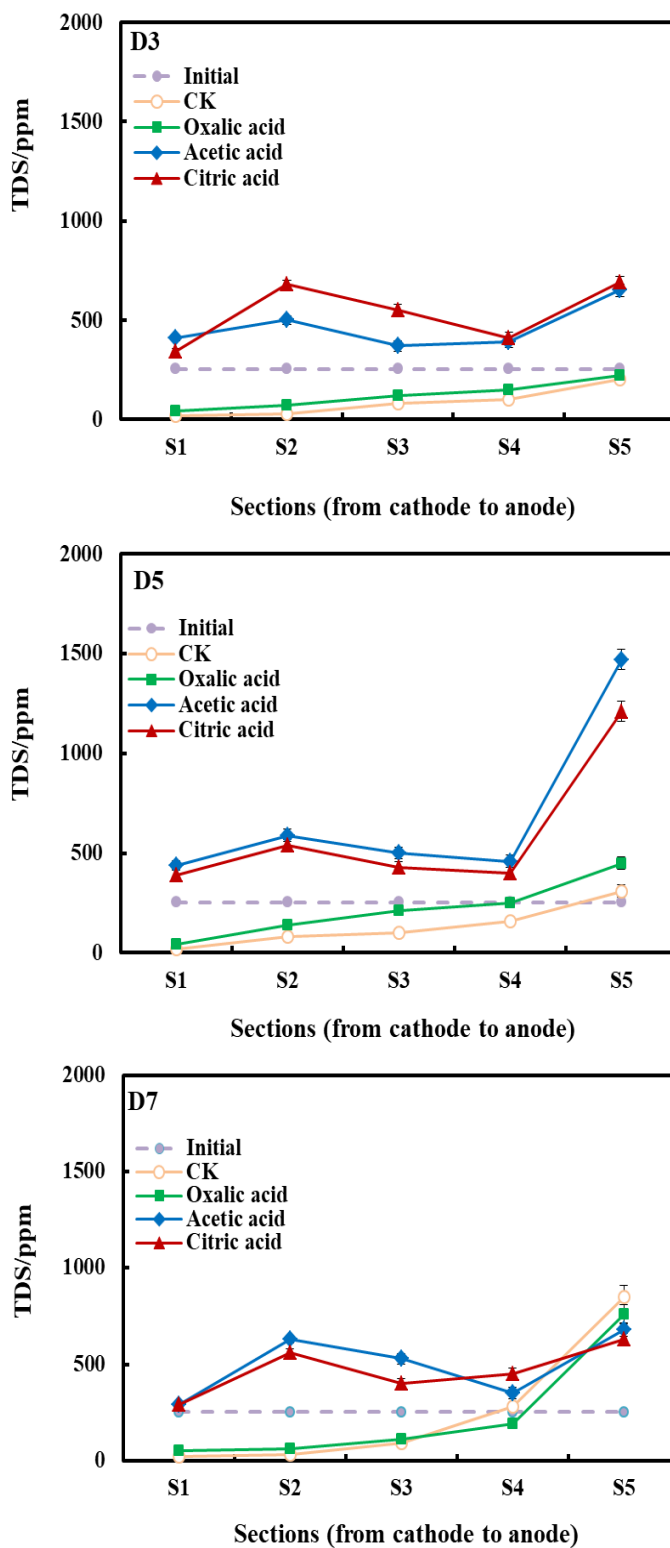


Figure 3. Changes in TDS for the 5 sections of the EKR apparatus D3: on the 3rd day; D5: on the 5th day; D7: on the 7th day.

3.3 Distribution of the residues of Cd, Cu and Ni for the different catholyte experiments

The performances of the three organic acids as catholytes were investigated for the removal of Cd, Cu, and Ni. The removal efficiencies and distribution of the residual contents after EKR are

illustrated in Fig. 4 and Fig. 5. Compared with CK, the average removals for Cd, Cu, and Ni by the organic acids were all considerably enhanced, each to a different degree.

Out of the three organic acids, the highest Cd, Cu, and Ni removals (average of five sections) were obtained in the citric acid treatment at $61 \pm 1.6\%$ (from 300 mg/kg to 182 mg/kg), $41 \pm 0.5\%$ (from 845 mg/kg to 345 mg/kg) and $52 \pm 1.3\%$ (from 436 mg/kg to 225 mg/kg), respectively, followed by acetic acid and oxalic acid. Compared with CK, the removal rate of Cd in the citric acid, acetic acid, and oxalic acid treatments improved by 39.2%, 38.2%, and 25.1%, respectively, while the removal rate of Cu improved by 31.1%, 25.6%, and 15.8%, respectively, and the removal rate of Ni improved by 38.0%, 32.0%, and 15.1%, respectively. The removal of Cd, Cu, and Ni in the five sections of the EKR was closely related to the electrolyte pH. According to the above data, citric acid produced the best enhancement of the removal of Cd, Cu, and Ni. This is consistent with a study by Yang *et al.*, where three organic acids (citrate, oxalate, and acetate) were used to extract Cu and Zn from polluted soils, and the relative performances of the three organic acids were in the same order as in the present study, which was in line with their extraction abilities for heavy metals [31]. As a ternary acid, citric acid possesses a greater number of hydroxyl and carboxyl groups for complexation, accounting for its higher extraction capacity for heavy metals compared to acetic acid (monoacid) and oxalic acid (dibasic acid). In addition, citric acid can also reduce oxidising substances such as manganese oxides in soil, resulting in the release of adsorbed heavy metals [32-33]. Benamar *et al.* used 1 M citric acid as catholyte and pure water as anolyte to treat multi-contaminated sediments under a voltage gradient of 1 V/cm for a duration of 21 days. The removal efficiencies of Cd and Cu were 24.3% and 36.4%, respectively, and hence the remediation efficiency occurred in different ranges for different experimental studies [34].

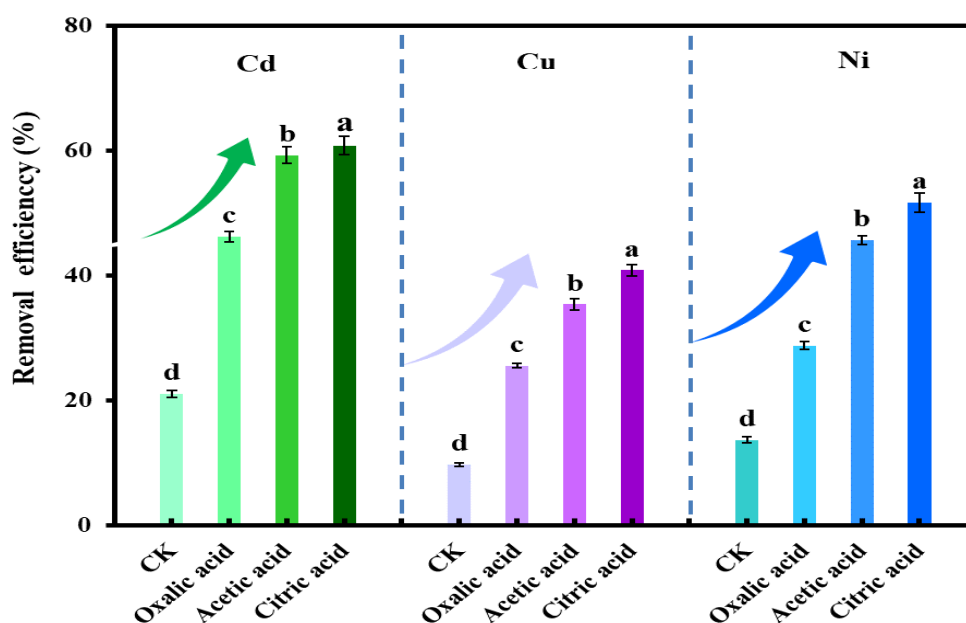


Figure 4. The average removal efficiencies of Cd, Cu, and Ni for the three organic acids. CK: Tap water. The lowercase letters (a, b, c, and d) represent statistically significant differences (P -value < 0.05).

Fig.5 illustrates the residue ratio and distribution of Cd, Cu, and Ni after electrokinetic remediation for 7 days at a voltage gradient of 1 V/cm. For the three organic acids, the residue ratios of Cd, Cu, and Ni in S2 were significantly higher than in other sections. The residue ratios of Cd for the three organic acids in five sections were lower overall; however, the residue ratio of Cd in S3 in the CK treatment was close to 1. The maximum residue ratio of Cd (0.93) occurred in S3 in the CK group, followed by 0.87 in S1 for the same treatment. For Cu, the maximum residue ratio (1.01) occurred in S3 in the citric acid treatment, followed by 0.94 in S4 of the same treatment. The peak value for the residue ratio of Ni (0.94) occurred in S1 in the CK treatment, followed by 0.93 in S3 of the same treatment. According to the above data, acetic acid has a stronger enhancing capacity than oxalic acid and citric acid for Cd, Cu, and Ni. It is therefore clear that the three organic acids coupled with EKR technology exhibited excellent removal performances compared to CK. The tested soils used in this study were artificially spiked, and most of the heavy metal contaminants were weakly bound fractions. Therefore, they could be effectively removed in the process of combining organic acids with EKR technology.

3.4 Changes in Cd distribution and speciation

The total concentration of heavy metals in soil cannot fully reflect their environmental impact. Heavy metal speciation affects mobility, bioavailability, and removal efficiency. Thus, an improved BCR sequential extraction procedure was used to analyse residual Cd speciation in the soil samples. Fig.6 shows the variation in Cd distribution and speciation after electrokinetic remediation. The original soil contained mostly Cd in exchangeable (225 ± 2.7 mg/kg) and reducible (70 ± 1.6 mg/kg) fractions, while only little oxidizable (2.9 ± 0.1 mg/kg) and residual (2.3 ± 0.1 mg/kg) Cd was present. This may be because the soil was artificially configured, causing it to be less complex than actual soil.

According to data in Fig.4 and Fig.5, the CK treatment was able to improve heavy metal mobility and dissolution. In the presence of the three organic acids, the exchangeable Cd concentration in five sections was consistently below the initial and CK values. The content of exchangeable Cd in the samples collected from the oxalic acid treatment from S1 to S5 was 105 ± 2.5 , 140 ± 2.8 , 115 ± 1.9 , 73 ± 1.6 , and 45 ± 1.5 mg/kg, respectively. The exchangeable Cd in the oxalic acid treatment significantly decreased after EKR. The content of reducible Cd in the oxalic acid treatment from S1 to S5 amounted to 80 ± 2.9 , 73 ± 2.2 , 63 ± 2.8 , 51 ± 1.9 , and 29 ± 0.9 mg/kg, respectively. Reducible Cd in S1 and S2 obviously increased, while it decreased in S3 to S5. Unlike the exchangeable and reducible Cd, the oxidizable and residual Cd were generally not significantly altered by the oxalic acid treatment, except for the residual Cd in S5 which increased from 2.3 ± 0.1 mg/kg to 8.4 ± 0.3 mg/kg. This may have been a result of the ability of the exchangeable Cd to easily migrate, then desorb from soil particles under the influence of the electric field and be removed.

Similar to oxalic acid, acetic acid and citric acid treatments also resulted in decreased proportions of exchangeable Cd in S1 to S5. The content of exchangeable Cd for the acetic acid treatment from S1 to S5 was 99 ± 2.6 , 154 ± 2.8 , 134 ± 2.1 , 51 ± 2.3 , and 16 ± 0.6 mg/kg, respectively. The content of reducible Cd for the citric acid treatment from S1 to S5 was 59 ± 1.7 , 158 ± 2.3 , 99 ± 2.1 , 98 ± 1.9 , and 8.5 ± 0.2 mg/kg, respectively. Similar results occurred for reducible Cd in the acetic acid and citric acid treatments.

Reducible Cd for the acetic acid treatment decreased from 70 ± 1.6 mg/kg to 35 ± 1.3 , 47 ± 1.2 , 40 ± 1.1 , 14 ± 0.7 , and 4.2 ± 0.3 mg/kg in S1 to S5, respectively, and reducible Cd in the citric treatment decreased to 38 ± 1.5 , 53 ± 1.2 , 32 ± 1.8 , 29 ± 0.9 , and 3.0 ± 0.1 , respectively.

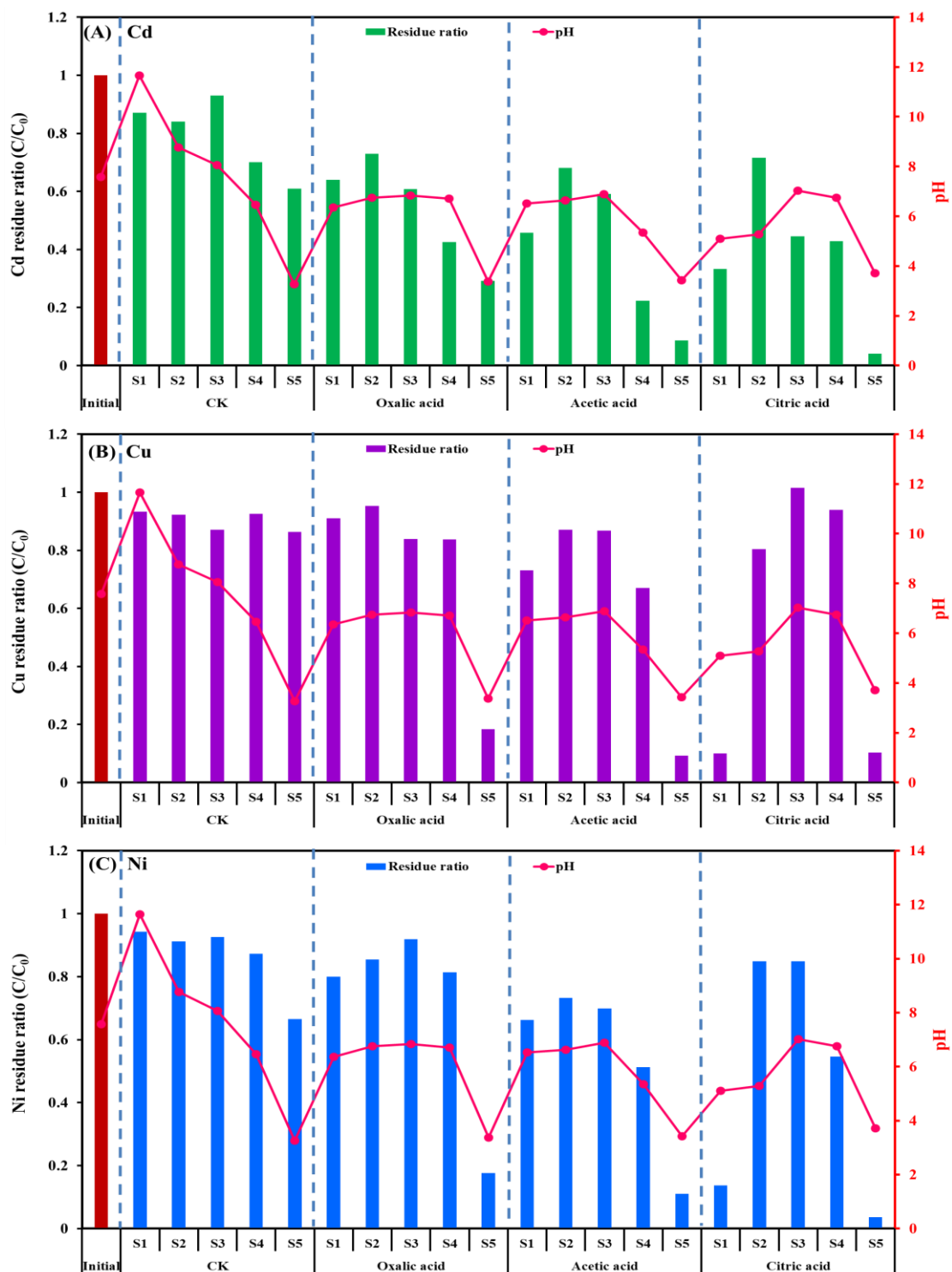


Figure 5. Distribution of the residue ratios of Cd (A), Cu (B), and Ni (C) for different catholyte treatments. CK: Tap water; S1–S5: sampling position (from cathode to anode)

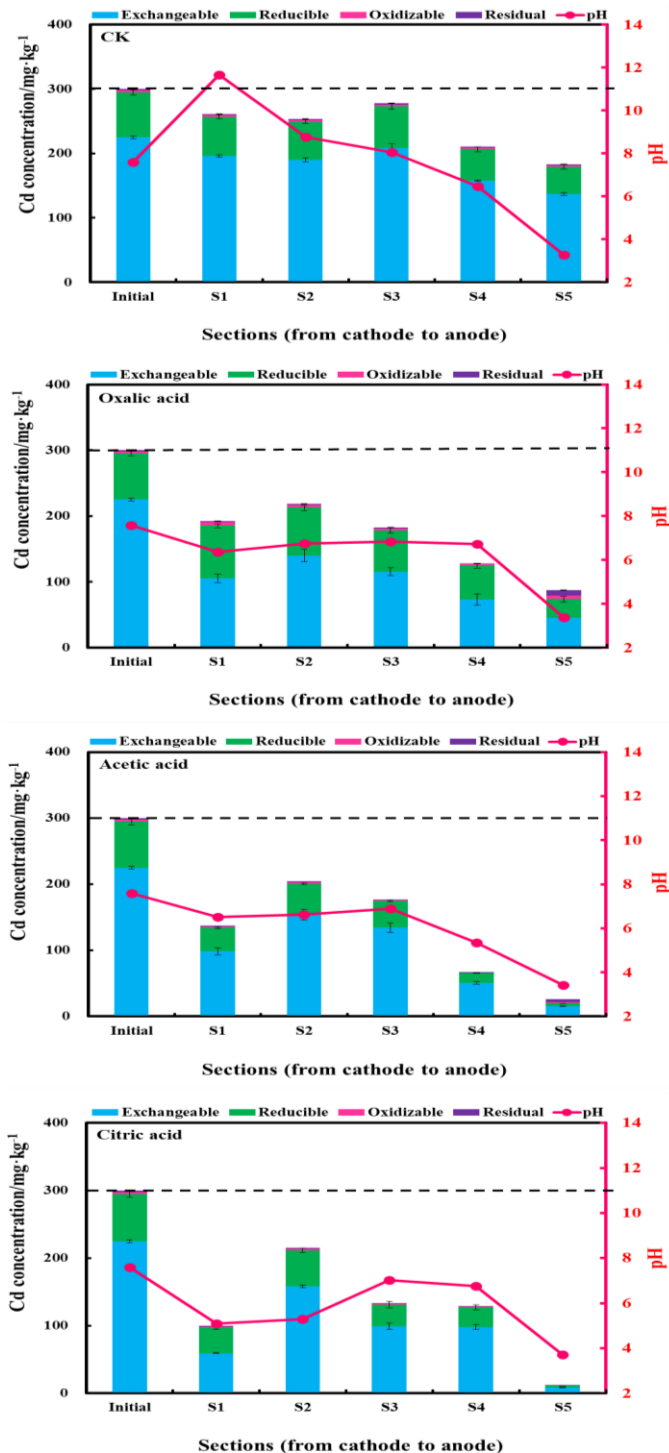


Figure 6. Effects of different catholytes on the distribution and speciation of Cd. CK: Tap water; S1–S5: sampling position (from cathode to anode)

In summary, the contents of exchangeable and reducible Cd decreased markedly, whereas the oxidizable and residual Cd contents remained relatively unchanged. In contrast with the non-detrital fractions of heavy metals, such as the exchangeable, carbonate-bound, and organic matter-bound fractions, the residual fractions are tightly bound to soil particles and difficult to extract [35]. At the same time, lower pH is associated with lower exchangeable contents, which is indicative of the effect of

pH conditioning by the three organic acids. This may result from the fact that the three organic acids are catholytes, which provide protons to soils. These protons neutralize the OH^- which are produced by the cathode. Thus, the “focusing effect” is avoided or at least reduced. In addition, the anode-produced protons migrate toward the cathode, allowing exchangeable Cd to be exchanged against the protons and enter the liquid phase [36].

3.5 Changes in Cu distribution and speciation

Fig.7 shows the variations in Cu distribution and speciation after electrokinetic remediation. Before the electrokinetic remediation experiment, the values for F1 (exchangeable), F2 (reducible), F3 (oxidizable), and F4 (residual) fractions of Cu in the initial soil had contents of 356 ± 4.7 , 236 ± 3.2 , 217 ± 3.9 , and 37 ± 0.9 mg/kg, respectively. Unlike for Cd, the exchangeable, reducible, and oxidizable Cu accounted for most of the total Cu content in the initial soil. Similar to Cd, the content of residual Cu was the lowest.

Oxalic acid treatment resulted in exchangeable and residual Cu contents in S1 to S3 that were higher than the initial values. The exchangeable Cu contents in S1 to S3 amounted to 474 ± 5.5 , 467 ± 6.2 , and 424 ± 5.9 mg/kg, respectively, and the residual contents were 46 ± 0.7 , 47 ± 0.8 , and 46 ± 0.7 mg/kg, respectively. There was obvious accumulation of exchangeable and residual Cu in S1 to S3 in the assays with oxalic acid. Reducible Cu content in the oxalic acid treatment ranged from S1 to S5 at 100 ± 2.1 , 104 ± 2.3 , 83 ± 1.8 , 51 ± 1.9 , and 29 ± 0.8 mg/kg, respectively. The content of oxidizable Cu in the oxalic acid treatment from S1 to S5 was 150 ± 1.4 , 187 ± 2.3 , 156 ± 2.2 , 2.5 ± 0.2 , and 5.3 ± 0.2 mg/kg, respectively. The reducible and oxidizable Cu for the oxalic acid treatment decreased significantly after EKR. The data above show that oxalic acid significantly influenced the speciation of Cu.

For the acetic acid treatment, the quantities of exchangeable Cu in S2 to S4 were 395 ± 5.1 , 390 ± 4.9 , and 393 ± 3.7 mg/kg, respectively. Obvious accumulation of exchangeable Cu occurred in S2, S3, and S4. Cu of other speciation in S1 to S5 decreased to different levels. The highest removal efficiency was obtained in S5. The removal efficiencies in S5 were 91.4% (31 ± 0.6 mg/kg), 94.0% (14 ± 0.3 mg/kg), 91.2% (19 ± 0.2 mg/kg), and 61.1% (14 ± 0.5 mg/kg), respectively.

For the citric acid treatment, the content of exchangeable Cu in S3 and S4 was 507 ± 6.7 mg/kg and 421 ± 4.9 mg/kg, respectively, and the content of reducible Cu was 241 ± 4.8 and 267 ± 3.9 mg/kg, respectively. In the above sections, there was obvious accumulation of exchangeable and reducible Cu. This may be due to the binding of dissolved Cu ions with citrate to form soluble complexes in the wide pH range, such as $(\text{Cu}_2\text{Cit}_2(\text{OH}))^{3-}$ and $(\text{Cu}_2\text{Cit}_2(\text{OH}))^{4-}$, which would migrate toward the anode under the electric forces [37-38]. Apart from the above-mentioned sections, Cu of all speciation demonstrated different removal efficiencies among the five sections. The best removal of the exchangeable Cu was obtained in S1 at 95.6% (from 356 mg/kg to 16 mg/kg), while the best removal of the reducible Cu occurred in S5 and S1 at 94.4% (from 236 mg/kg to 13 mg/kg) and 93.3% (from 236 mg/kg to 16 mg/kg), respectively. The oxidizable Cu was removed in S1 and S5 by 81.8% and 88.7% (from 217 mg/kg to 40 mg/kg and 24 mg/kg), respectively. For the residual Cu, the removal in S1 and S5 reached 63.2% and 76.9% (from 37 mg/kg to 13 mg/kg and 8.4 mg/kg), respectively.

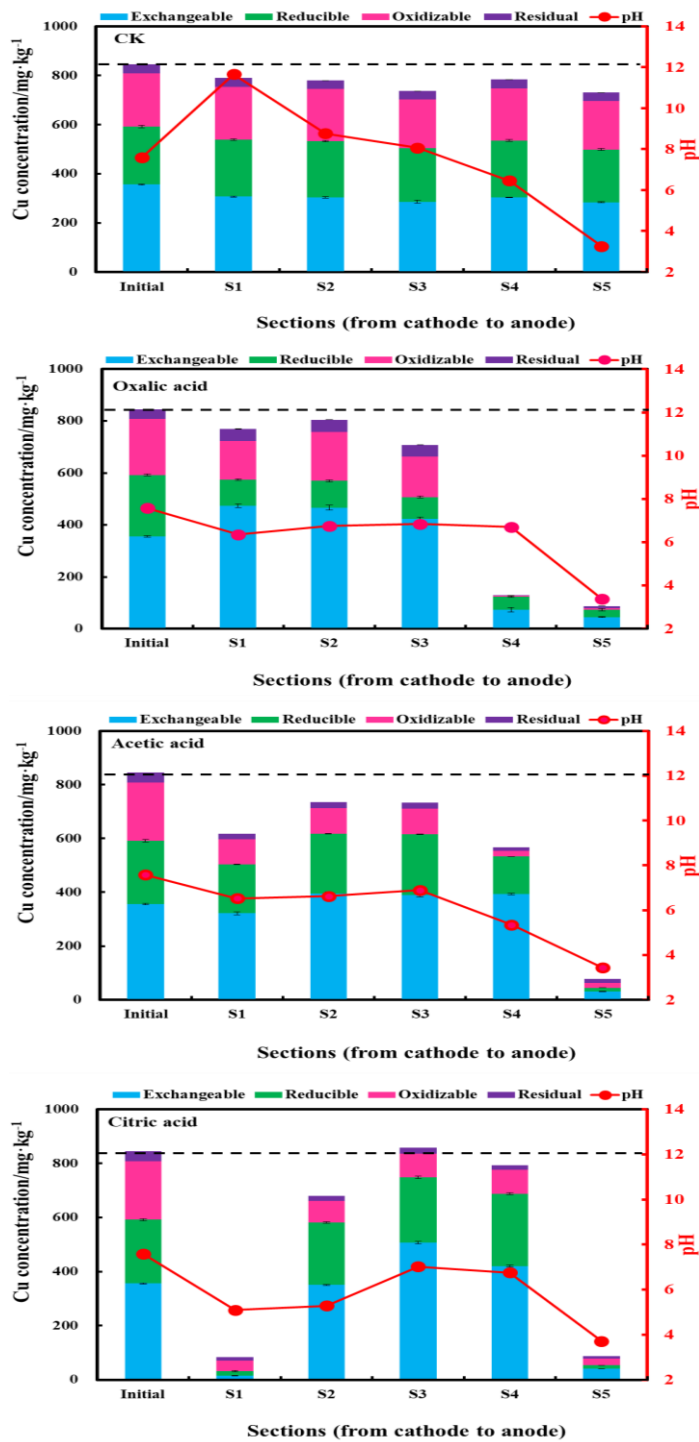


Figure 7. Effects of different catholytes on distribution and speciation of Cu. CK: Tap water; S1–S5: sampling position (from cathode to anode)

Interestingly, citric acid was the particular acid for which a relatively high removal of Cu in S1 and S5 was achieved. This observation was also obtained for Ni speciation. This may be related to the pH of 5.1 in S1 for the citric acid treatment. The pH in S1 for the oxalic acid and acetic acid treatments were 6.4 and 6.5, respectively. The results for accumulation of exchangeable and reducible Cu in S3 and S4 suggest that citric acid may have caused a transformation in speciation under the influence of the electric field.

3.6 Changes in Ni distribution and speciation

Fig.8 presents the variations in Ni distribution and speciation before and after electrokinetic remediation. The main speciation of Ni in the initial soil was in the form of exchangeable (242 ± 5.7 mg/kg) and reducible (109 ± 1.8 mg/kg) Ni, followed by oxidizable (53 ± 0.8 mg/kg) and residual (32 ± 0.7 mg/kg) fractions. Exchangeable and reducible Ni accounted for the majority of the total Ni content of the initial soil.

Heavy metal accumulation did not occur following treatment with the three organic acids or CK. In the oxalic acid treatment group, the exchangeable and reducible Ni were almost completely removed, at removal rates of 97.0% (from 242 mg/kg to 7.2 mg/kg) and 97.5% (from 109 mg/kg to 2.7 mg/kg), respectively, in S5 after EKR. For the acetic acid treatment, a high removal rate of both exchangeable and reducible Ni was also obtained, at rates of 93.3% (from 242 mg/kg to 16 mg/kg) and 93.6% (from 109 mg/kg to 7.0 mg/kg) in S5, respectively. For the oxalic acid treatment, the exchangeable and reducible Ni reached maximum removal rates of 92.1% (from 242 mg/kg to 19 mg/kg) and 87.9% (from 109 mg/kg to 13 mg/kg), respectively, in S5. Cu speciation in S1 and S5 in the acetic acid treatment and Ni speciation in S1 and S5 in the citric acid treatment both exhibited a relatively higher removal rate than the other sections.

4. CONCLUSION

In this study, the effects of enhanced electrokinetic remediation were studied with oxalic acid, acetic acid, and citric acid as catholytes under laboratory conditions using artificially spiked soil with heavy metals (Cd, Cu and Ni) for a duration of 7 d and a voltage gradient of 1 V/cm. Furthermore, soil pH and TDS values, Cd/Cu/Ni contents, removal efficiency, distribution, and ion speciation were considered. The results showed that:

- All three organic acids effectively inhibited a pH jump during the EKR process. The three organic acids kept the pH in the acidic range with increasing remediation time. The pH profile along the sections of apparatus after electrokinetic remediation was generally consistent with the removal efficiencies for Cd, Cu, and Ni.

- The maximum values for TDS reached 1470 ppm for the citric acid treatment on the 5th day in S5, which is likely related to the influence of acidification due to the low pH of 3. The variations in TDS values among the various sections during each experiment were caused by ion transport due to the applied DC potential.

- The results demonstrate that EKR with the three organic acids can improve the efficiency of heavy metal removal from Cd, Cu, and Ni co-contaminated soil. The extent of improvement was best for citric acid, followed by acetic acid, then oxalic acid, and finally, CK. The Cd, Cu, and Ni removal efficiencies (average of five sections) for the citric acid treatment reached $61\pm 1.6\%$ (from 300 mg/kg to 182 mg/kg), $41\pm 0.5\%$ (from 845 mg/kg to 345 mg/kg), and $52\pm 1.3\%$ (from 436 mg/kg to 225 mg/kg), respectively.

- Heavy metal speciation analysis showed that the contents of the exchangeable and

reducible fractions were obviously decreased near the cathode for the three organic acids treatments, compared with CK. An application of organic acids as catholyte coupled with EKR can cause significant variations in heavy metal distribution and speciation.

● These observations will be helpful for optimising and selecting catholytes for improving the electrokinetic remediation of Cd, Cu, and Ni co-contaminated soils. After organic acid-enhanced EKR, the accumulation of Cd, Cu, and Ni transferred from the cathode to the middle of the soil matrix for the citric acid. This finding needs to be explored further.

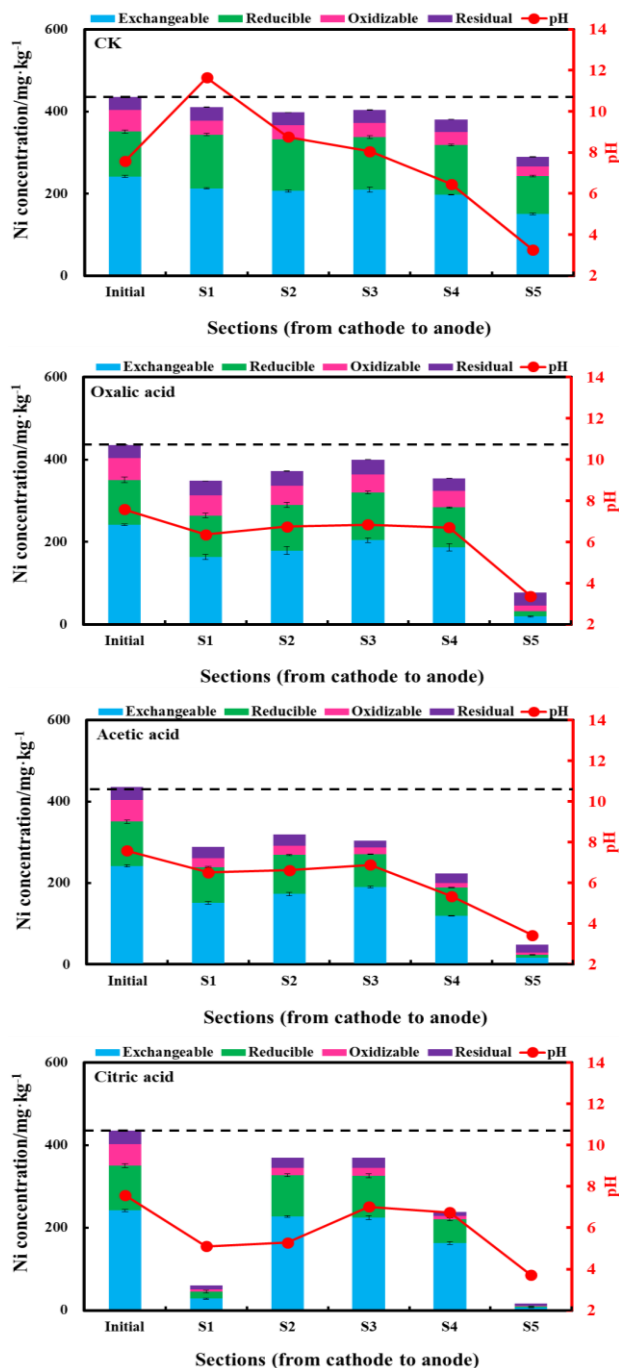


Figure 8. Effects of different catholytes on the distribution and speciation of Ni. CK: Tap water; S1–S5: sampling position (from cathode to anode)

DECLARATIONS:**COMPETING INTERESTS:**

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. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part.

AVAILABILITY OF DATA AND MATERIALS:

All data generated or analyzed during this study are included in this published article and its supplementary information files.

CODE AVAILABILITY:

This paper is not involved in any software application or custom code.

AUTHORS' CONTRIBUTIONS:

Xiaoyan Ge: did the experiments, processed the data and did most writing of this paper. Jing Xie: did the experiments. Xinshan Song: designed the experiments and revised the paper. Xin Cao: designed the experiments. Yuhui Wang: designed the experiments. Zhongshuo Xu: designed the experiments. Yifei Wang: prepared the test soil. Xiaoxiao Hou: prepared the test soil.

ETHICAL APPROVAL:

This paper not report on or involve the use of any animal or human data or tissue.

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