International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Comparison of the influence of EDTA, nitrilotriacetic acid, diethylenetriamine pentaacetic acid, chitosan, fulvic acid and pine needle extract on the removal of multiple heavy metal by electrokinetic remediation

Xiaoyan Ge<sup>1</sup>, Xinshan Song<sup>1,\*</sup>, Jing Xie<sup>1</sup>, Wei Huang<sup>1</sup>, Yuhui, Wang<sup>1</sup>, Zhongshuo Xu<sup>1</sup>, Yifei Wang<sup>1</sup>, Xiaoxiao Hou<sup>1</sup>, Xin Cao<sup>12,\*</sup>

<sup>1</sup> College of Environmental Science and Engineering, Textile Pollution Controlling Engineering Center of Ministry of Environmental Protection, Donghua University, Shanghai 201620, China
<sup>2</sup> Shanghai Institute of Pollution Control and Ecological Security, Shanghai, 200092, China
\*E-mail: <a href="mailto:caoxin@dhu.edu.cn">caoxin@dhu.edu.cn</a>, <a href="mailto:newmountain@dhu.edu.cn">newmountain@dhu.edu.cn</a>

Received: 5 June 2022 / Accepted: 28 July 2022 / Published: 10 September 2022

Eliminating multiple heavy metal pollution from contaminated soil is challenging and expensive during remediation. In this study, pine needle extract (PNE) coupled with electrokinetic remediation (EKR) was first time implemented to enhance the Cd, Cu and Ni removal from contaminated soil. The PNE enhanced EKR and improved the processing compared to chemical enhancing agents, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA) as well as organic enhancing agents, such as chitosan (CTS) and fulvic acid (FA). The Cd, Cu and Ni removal efficiencies (average of five sections) reached  $62\pm1.3\%$ ,  $37\pm0.6\%$  and  $55\pm0.9\%$ , respectively. The observations indicated that the exchangeable and reducible fractions of Cd, Cu and Ni decreased close to the anode. Meanwhile, the oxidizable fraction decreased for part of the enhancing agents after the EKR treatments. Possible molecular mechanisms of metal extraction from soils in the PNE treatment are discussed according to the Fourier transform infrared (FTIR) analysis outcome. The metal accumulation did not occur during PNE treatment. Compared to the other five enhancing agents, the removal efficiency of PNE was determined to be identical. However, PNE will be advantageous with respect to its economic cost and natural fertilizing benefits.

**Keywords:** Electrokinetic remediation; Pine needle extract; Heavy metals; Compound pollution; Speciation analysis

# **1. INTRODUCTION**

The soil contaminated with Cd, Cu, Ni and other toxic metals is a common environmental issue. Excessive heavy metals have been discharged into the environment and subsequently accumulated in food chains. This poses a significant threat to ecosystems [1]. As heavy metals cannot be degraded, removing them from polluted soils is a challenge. Therefore, there is an urgent need for effective remediation and separation methods that can ensure the removal of heavy metals with the least damage to soil ecosystems. In order to remediate heavy metal contaminated soil, treatment techniques such as phytoremediation [2], chemical washing [3], application of biomass [4], microbial remediation [5] and electrokinetic remediation (EKR) [6,7] have been extensively implemented.

Among the above technologies, electrokinetic remediation (EKR) is an effective and reliable method for removing heavy metals due to its evident advantages and excellent performance, even for soil with low permeability [8]. During the application of low direct-current to the electrodes inserted into the soil matrix, dissolved metals ions present in the soil's porous medium can migrate towards the anode and cathode due to the electric field [9]. During the EKR process, water molecules are electrolyzed to H<sup>+</sup> at the anode and OH<sup>-</sup> at the cathode under the electric field. A series of electric effects occur, including electromigration, electroosmosis and electrophoresis [10]. In most cases, the transport mechanism for heavy metal ions typically relies on electromigration. Under an electric field, the charged metals cations in the soil's pore solutions migrate towards the oppositely charged electrodes. Subsequently, the distribution of heavy metals takes place, followed by their accumulation near the cathode and in the middle of the soil cell [11]. Electroosmosis is known as the directed transport of liquid under an external electric field [12]. The motion of charged particles under the effect of an electric field is defined as electrophoresis [13]. As the influence of electrophoresis is very minimum, it can be disregarded during during an EKR process [14].

In the EKR process, the extremely high pH produced during water electrolysis at the cathode results in the precipitation of heavy metal cations, which is called the "focusing effect". To avoid the focusing effect, enhancing agents are adopted widely that interact with heavy metals to form stable and soluble complexes. Enhancing agents can be divided into the following categories: inorganic acids (e.g. HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>), organic acids (e.g. acetic acid, oxalic acid, citric acid, fulvic acid) or complexing agents (e.g. EDTA, NTA, DTPA). Xu et al. reported that 93%, 92% and 40% Cd removal was possible by nitric acid, acetic acid and ethylenediaminetetraacetic acid (EDTA), respectively [15]. Chang et al. used 0.1 M EDTA as an enhancing agent and achieved 79% Pb removal [16].

However, ethylenediaminetetraacetic acid (EDTA) is refractory to biodegradation and hence, can cause secondary pollution. Nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA) are biodegradable and have an excellent enhancing capacity for various heavy metals. As they consist of  $R_2N$ –CH(R)-COOH molecular fragment (Figure 1 A-C), they are commonly used as enhancing agents. The metal accumulation has been observed to occur in the middle of soil chambers while using EDTA and NTA as chelates to enhance EKR [17]. Up to now, there hasn't been a unified understanding of this issue. As the metal accumulation mechanism is unclear, it is difficult to predict the place of accumulation after EKR. Therefore, it is necessary to search for an eco-friendly, low-accumulating and cost-effective alternative.

As a naturally occurring and common humic substance (HS), fulvic acid (FA) has no potential toxicity. Because of its peculiarity polyfunctionality, it can interact with heavy metals in soil. It has a significant influence on the mobility of As [18] (Figure 1 E-F). There have been few studies on FA as a reinforcing agent coupled with EKR to remove heavy metals [19,20]. Chitosan (CTS) has demonstrated

good complexing ability with heavy metals as it consists of -NH<sub>2</sub> and -OH. Moreover, due to its nontoxicity and cost-effectiveness, it has been widely used for water purification and soil remediation (Figure 1 D). However, using chitosan as an enhancing agent coupled with EKR to enhance Cd, Cu and Ni removal from contaminated soils has not been thoroughly studied. Pine needle extract (PNE) contains various organic acids (e.g. amino acids, shikimic acid), which have outstanding alkali buffering abilities and can supplement soil fertilizers [21]. To the best of our knowledge, pine needle extract has not been implemented as an enhancing agent for heavy metal removal from contaminated soil. Thus, we hypothesized that applying PNE as an electrolyte coupled with EKR could alleviate the pH jump and reduce heavy metal accumulation. This innovative attempt provides a new perspective for developing a green and low-cost electrolyte for EKR.



**Figure 1.** Common chelator structures and a typical metal complex, A: EDTA; B: DTPA; C: NTA; D: CTS; E: FA; F: a typical metal complex

In this work, the PNE was coupled with EKR to improve the removal efficiency of Cd, Cu and Ni from contaminated soil. Simultaneously, EDTA, NTA, DTPA, CTS, and FA coupled with EKR were implemented as enhancing agents to investigate their performance in heavy metal removal. In addition, the migration mechanism, distribution and speciation variation of heavy metals after the EKR was analyzed. A cost estimate per unit of heavy metal removal was also conducted for six enhancing agents.

## 2. MATERIALS AND METHODS

#### 2.1. Soil characteristic and material preparation

The reagents used to digest soil samples in this study were of reagent grade and the other chemicals were of analytical grade. Three different solid-liquid ratios (mass/volume: g/mL, 1:15, 1:5, 1:1) of PNE (pine needle extract) were applied to obtain optimal parameters. Pine needles were harvested from fresh, tender snow pines on the campus. A series of operation, such as washing, naturally air-drying in the dark, crushing (to fine segments of 1cm), addition of deionized water, soaking overnight in a water bath (temperature at  $60^{\circ}$ C for 8 h) were conducted for preparation of the extract. Finally, the above solution was pressed through filtration unit with a yarn mesh (180 mesh) to produce a pine needle extraction solution. This solution was then preserved at 4-5°C.

The original soil was collected at a depth of 20cm from a garden located in Donghua University, Songjiang Campus, Shanghai, China. The soil samples were spread and air-dried naturally, sieved using a 10-mesh, and then stored in containers. To prepare the contaminated soil with target contents of about  $300 \text{mg/kg Cd}^{2+}$ ,  $800 \text{mg/kg Cu}^{2+}$  and  $400 \text{mg/kg Ni}^{2+}$ , the aqueous solution of  $Cd(NO_3)_2$ ,  $CuSO_4$  and  $Ni(NO_3)_2$  were added to the above soil in a proportion of soil: solution =1kg: 3L. The polluted soil was mixed thoroughly to achieve a homogenized state, cultivated and aged in opaque boxes at room temperature for half a month, while air-drying. The main physicochemical characteristics of the soil were tested. The pH, total organic matter, cation exchange capacity and water content of the soil were 7.58, 18.74g/kg, 23.56cmol/kg and 19.25%, respectively. The initial contents of Cd, Cu and Ni in spiked soils were  $300\pm3.0$ ,  $845\pm6.4$  and  $436\pm3.6$  mg/kg, respectively. These values are by far higher than the soil environmental quality standards of the China National Standard System (GB15618-2018) to simulate a farmland soil severely contaminated by Cd, Cu and Ni.

#### 2.2 Experimental apparatus and EKR setup

The EKR apparatus is shown in Figure 2. The EKR apparatus is made of plexiglass (L 20cm/W 7.5cm/H 8cm). The reactor is composed of a soil chamber (L/W/H=15cm/7.5cm/8cm), two electrode chambers (L/W/H= 3cm/7.5cm/8cm), two filter chambers (L/W/H=0.5cm/7.5cm/8cm), one DC power supply, two micro peristaltic pumps, and two electrolyte reservoirs. There are 25 holes (Ø 1cm) evenly distributed over the plexiglass. The seven enhancing agents (CK, EDTA, NTA, DTPA, CTS, FA and PNE) were pumped into the soil chambers by the micro peristaltic pumps. Two identical pieces of carbon felts (width: 7cm, height: 10cm, thickness: 2mm) are used as the working electrodes connected to a DC power supply (SPA3005D, Nanjing, China). A multimeter (VC86E) is connected to monitor the electric current. In filter chambers filter papers were used to block impurities. The soil chamber is composed mainly of five equal sections, namely S1~S5 from cathode to anode. In each experiment 600g of contaminated soil sample and 1L of the prepared enhancing agent were used.



**Figure 2.** Schematic view of a single EKR apparatus; Pump: peristaltic pump; DC: direct current; Cathode and anode: carbon felt; Enhancing agents: EDTA, NTA, DTPA, CTS, FA and PNE; S1~S5: five soil sections (from cathode to anode)

Table 1. Electrokinetic remediation experimental design with different solid-liquid ratio of PNE

NO.	Catholyte	Solid-liquid ratio (g/ml)	Anolyte	Content <sup>b</sup> C H N (%)	Voltage gradient (V/cm)	Duration (d)	Electrode
СК	Tap water	/		/			
EK-1	<b>PNE</b> <sup>a</sup>	1:1	Тар	3.91 11.09 0.48	1	7	Carbon felt
EK-2	PNE	1:5	water	1.94 10.82 0.35	1	1	(Thickness 2mm)
EK-3	PNE	1:15		0.07 10.74 0.30			<b>_</b> )

<sup>a</sup> PNE: pine needle extract. <sup>b</sup> means the contents of C, H and N in the PNEs.

Table 2. Experimental design for electrokinetic remediation experiments with different enhancing agents

NO.	Enhancing agent	Concentration/ Solid-liquid ratio	Molecular formula/ Content	Solvent	Molecular Weight	Voltage gradient (V/cm)	Duration (d)	Electrode
CK	Tap water	/	H <sub>2</sub> O		18			
<b>EK-4</b>	EDTA	0.1mol/L	$C_{10}H_{16}N_2O_8$	NaOH	292.24			
EK-5	NTA	0.1mol/L	N(CH <sub>2</sub> COOH) <sub>3</sub>	NaOH	191.14			
EK-6	DTPA	0.1mol/L	$C_{14}H_{23}N_3O_{10}$	NaOH	393.35			Carbon
EK-7	CTS	1g/L	(C <sub>6</sub> H <sub>11</sub> NO <sub>4</sub> )n	HAC	161.2/unit	1	7	felt
EK-8	FA	1g/L	$C_{14}H_{12}O_8$	Deionized water	308.24			(Thickness 2mm)
EK-9	PNE	1:1(g/mL)	C (49.9%) <sup>a</sup> H (6.4%) N (1.1%)	Deionized water	/			

EDTA: ethylenediaminetetraacetic acid; NTA: nitrilotriacetic acid;

DTPA: diethylenetriamine pentaacetic acid; CTS: chitosan: FA: fulvic acid;

PNE: pine needle extract. <sup>a</sup> means the contents of C, H and N in solid pine needle.

To investigate the performance of different solid-liquid ratios of PNE, three different ratios (1:15, 1:5 and 1:1) were used as catholyte. Table 1 shows the experimental design scheme for different solid-liquid ratios of PNE. 1V/cm (voltage gradient) and 7days (remediation time) were applied as operation parameters, according to our previous experimental results. Tap water is used as the control group (CK). After the EKR experiment soil samples were collected in the middle line of S1~S5 parts, air-dried and ground evenly. After the above experiments, the optimal solid-liquid ratio was obtained. The seven experiments with seven different enhancing agents were conducted to investigate their performance on removal rate, residue rate, distribution and speciation of Cd, Cu and Ni. The data are illustrated in Table 2.

#### 2.3 Analytical methods

In this study, the electrical conductivity (EC) of a soil sample is reflected through the values of TDS (total dissolved solids). The soil pH and TDS (total dissolved solids) were measured by conventional methods (soil: water=1mL: 2.5g). To explore the influence of functional groups of PNE on heavy metal removal, the Fourier-transformed infrared (FTIR) spectra of the pine needle powder were obtained using the KBr wafer technique (Nicolet 6700 FT-IR, USA).

Soil samples were digested in a digestive equipment and the contents of heavy metals were analyzed by atomic absorption spectrophotometry (TAS-986, Beijing, China). Improved BCR methods were conducted to determine the binding forms of heavy metals with soil compounds [22].

## 2.4 Energy consumption and removal efficiency

The accumulated energy consumption (W) in the EKR experiments was calculated as: W= $\int_{0}^{t} UId_{t}$ 

where U is the voltage between the cathode and anode (V), I is the electric current (A), and t is the remediation time (h).

Removal efficiencies of heavy metals were calculated as following equations:

$$R_e = \frac{C_{0-}C}{C_0} \times 100\%$$
  
$$\overline{R_e} = \frac{1}{5}(R_{e1} + R_{e2} + R_{e3} + R_{e4} + R_{e5})$$

where  $C_0$  is the initial metal content (mg/kg) and C is the final metal content after EKR (mg/kg);

R<sub>e</sub> is the removal rate of each section;  $\overline{R_e}$  are the average removal rates of S1~S5.

#### 2.5 Quality control of the data

According to the technical specification for Soil Environmental Monitoring (HJ/T 166-2004), soils samples were collected and analyzed. All experiments with the soil samples were performed in triplicate, including digestion and measurement. Additionally, reagent blanks were used in each batch

of samples. Results are expressed as mean  $\pm$  standard deviation (n=3). The accuracy of the experiments was checked by applying the recovery studies using the standard addition method. The ANOVA test was used to compare the heavy metal removal with different enhancing agents. P<0.05 was regarded as level of significance.

# **3. RESULTS AND DISCUSSION**

## 3.1 Electrical current density and energy consumption variations of PNE

Figure 3 presents the variation of electrical current density and accumulated energy consumption versus duration for different PNE solid-liquid ratios (g/mL, 1:1, 1:5 and 1:15) under a voltage gradient of 1V/cm.



**Figure 3.** Variations of current density (A) and accumulated energy consumption (B) in EKR experiments with pine needle extract. CK: Tap water; PNE: pine needle extract. 1:1, 1:5 and 1:15 mean solid: liquid ratio (mass/volume: g/mL) under the voltage gradient of 1V/cm.

As shown in Figure 3A, the electrical current density of the CK and the other three experiments gradually increased with the increase in remediation time. The current densities were stabilized in the range of 0.3~0.4 mA/cm<sup>2</sup>. The highest solid-liquid ratio has the shortest time and reaches the maximum current density. The current density for different PNE solid-liquid ratios 1:1, 1:5, 1:15 and CK reached their peak values at 44h, 70h, 100h and 130h, respectively. Figure 3B shows the total energy consumed by EKR experiments. The values constantly increased with the increase in remediation duration, which

was consistent with previous studies [23]. The maximum cumulative energy consumption of the CK experiment at the end of 149 hours was 0.065KWh, 0.081KWh, 0.079KWh and 0.064KWh for the 1:1, 1:5 and 1:15 ratios, respectively. The cumulative energy consumption (p=0.446) for the CK and solid-liquid ratio of 1:15 was not significantly different. The cumulative energy consumptions of 1:1 and 1:5 were significantly higher than those of the CK (1:15 ratio), which were consistent with the previously obtained high current densities.

This may be because active components such as amino acids, which carry hydroxyl, carboxyl and other oxygen-containing groups can provide  $H^+$  to the soil under a high solid-liquid ratio. These  $H^+$  can replace the heavy metal ions adsorbed on the surface of soil particles and maintain the soil pH in an acidic range, allowing heavy metal ions to move freely. On the other hand, a large amount of free  $H^+$  can neutralize the OH<sup>-</sup> produced at the cathode by electrolysis and prevent the binding with metal ions to form precipitates. The metal ions can migrate more freely between soil pores [23].

#### 3.2 Soil pH and TDS (Total dissolved substance) variations

Figure 4 shows the variation in pH and TDS in S1~S5 (from cathode to anode) at the end of the EKR of PNE. According to Figure 4A~C, the pine needle extract with a high solid-liquid ratio (1:1) was beneficial for maintaining weakly acidic soil and inhibited the pH jump at the cathode. In contrast, the pine needle extract with a low solid-liquid ratio (1:15) and CK failed to inhibit a pH jump. With the increase in remediation time, the CK and the pine needle extract with a low solid-liquid ratio (1:15) started to demonstrate a noticeable pH jump at the cathode. The soil pH of the CK and the pine needle extract with low a solid-liquid ratio (1:15) were in the range of 4.1~9.2 and 3.1~8.6 on the fifth day, followed by 3.3~11.6 and 3.0~11.4 on the seventh day. The soil in the pine needle extracts having a high solid-liquid ratio (1:1) remained in the acidic range with the increase in remediation time. The pH was in the range of 3.1~6.0 on the fifth day and 3.1~6.4 on the seventh day of the five sections. In comparison to assays with low PNE concentration, the pine needle extract with a high solid-liquid ratio contains more natural organic acids, which can provide more H<sup>+</sup> to the soil. It can be inferred that the solid-liquid ratio for inhibiting a pH jump at the cathode is (1:1).

Figure 4 shows the variation of soil TDS values for each soil section (S1~S5) from the cathode to the anode at the end of the EKR with PNE. Based on the effect of three different solid-liquid ratios on TDS, the TDS values of the CK and pine needle extract with a low solid-liquid ratio (1:15) were always at a low level with the increase in remediation time. In contrast, the pine needle extract with a high solid-liquid ratio (1:1) had a relatively high value. TDS values increased with the increase in solid-liquid ratios on the 3rd and 5th day near S5. The maximum TDS value reached 1640ppm for the PNE with a solid-liquid ratio of (1:1) on the fifth day in S5, which was associated with the effect of acidification reaching a pH near 3. The variation of TDS values in each section during the EKR experiment was caused by ion migration the application of DC potential.



**Figure 4.** Variations in pH and TDS in different soil sections of PNEs and CK. pH on 3rd day (A); pH on 5th day (B); pH on 7th day (C); TDS on 3rd day(D); TDS on 5th day (E); TDS on 7th day (F); S1~S5: five soil sections (from cathode to anode)

#### 3.3 Heavy metal removal efficiency and residual content distribution after EKR

Six enhancing agents, three amino carboxylic acids (EDTA, NTA, DTPA) and three organic compounds (CTS, FA, PNE) were applied as electrolytes. Their performance in Cd, Cu and Ni removal was investigated. The removal and residual content distribution after the EKR are illustrated in Table 3

and Figure 5. In contrast to the CK, the average removal of Cd, Cu, and Ni was considerably enhanced for different levels of the agents. These results were found to be similar to the previous study [24].

For the three chemical chelating compounds, the highest Cd  $(53\pm0.8\%)$ , Cu  $(59\pm1.1\%)$  and Ni  $(47\pm1.0\%)$  removal values were obtained for DTPA, followed by EDTA and NTA. In contrast to the CK, the removal of Cd with DTPA, EDTA and NTA was improved by 29%, 25% and 0.7%, respectively. The removal of Cu with DTPA, EDTA and NTA improved by 46%, 34% and 10%, respectively. The removal of Ni with DTPA, EDTA and NTA improved by 30%, 21% and 10%, respectively. Based on the above data, DTPA demonstrated the best enhancement for removing Cd, Cu and Ni. Its because DTPA is an elongated version of EDTA having a stronger enhancing agent for soil metal extraction [25].

For the three organic chelating compounds, the highest Cd ( $78 \pm 1.3\%$ ), Cu ( $46 \pm 1.2\%$ ) and Ni ( $72 \pm 2.5\%$ ) removal were obtained with CTS, followed by PNE and FA. The CTS, PNE and NTA demonstrated an improved Cd removal by 54%, 38% and 14%, respectively, as compared to the CK. The CTS, PNE and NTA demonstrated an improved Cu removal by 33%, 24% and 14%, respectively, as compared to the CK. The removal rate of Ni by CTS, PNE and NTA was improved by 54%, 38% and 12%, respectively. Identical removal rates for Cd, Cu and Ni were achieved by CTS and the other two organic enhancing agents. This result could be attributed to the presents of functional groups (-NH<sub>2</sub> and -OH), which form complexes with heavy metals [26]. CTS is regarded as an electroactive biomaterial with high electrical conductivity [27]. In addition to the heavy metal removal capacity, CTS is regarded as a biodegradable enhancing agent.

Enhancing	Average removal (%)				
agent	Cd	Cu	Ni		
СК	$24 \pm 0.6^{f}$	$14 \pm 0.6^{\rm f}$	$17 \pm 0.9^{f}$		
EDTA	$49 \pm 1.0^{d}$	$48 \pm 0.7^{b}$	$39 \pm 0.7^{d}$		
NTA	$25 \pm 0.7^{\rm f}$	$24 \pm 0.8^{e}$	$28 \pm 0.8^{e}$		
DTPA	$53 \pm 0.8^{\circ}$	$59 \pm 1.1^{a}$	$48 \pm 1.0^{\circ}$		
CTS	$78 \pm 1.3^{a}$	$46 \pm 1.2^{b}$	$72 \pm 2.5^{a}$		
FA	$38 \pm 0.9^{e}$	$28 \pm 0.7^{d}$	$29 \pm 0.5^{e}$		
PNE (1:1)	$62 \pm 1.3^{b}$	$37 \pm 0.6^{\circ}$	$55 \pm 0.9^{b}$		

Table 3 Average removal values for Cd, Cu and Ni by different enhancing agents

CK: Tap water; DTA: ethylenediaminetetraacetic acid; NTA: nitrilotriacetic acid; DTPA: diethylenetriamine pentaacetic acid; FA: fulvic acid; PNE (1:1): pine needle extract

(mass/volume: g/mL 1:1).

The values shown in the table are means  $\pm$  SD (n=3).

The lower-case letters (a, b, c, d, e and f) represent statistical significant differences (P-value < 0.05).

The residue and distribution of heavy metals after the EKR experiment are illustrated in Figure 5. For the three chemical agents the residual values for Cd, Cu and Ni in other sections were found to be lower than in S2~3. For DTPA treatment, the residue of each section is generally low. Nevertheless, the

residual values for Cd in S2 with EDTA and S2~3 with NTA were significantly higher than 1. The maximum residue for Cd (1.53) was obtained for S3 under NTA treatment, followed by 1.36 for S2. The maximum Cu residue (1.50) was obtained for S3 under EDTA treatment, followed by 1.19 for S1 under CK treatment. The peak value (1.57) for the Ni residue was obtained for S3 under the EDTA treatment, followed by 1.15 for S1 under the CK treatment. The DTPA demonstrated a better enhancing capacity than EDTA and NTA for the three heavy metals.

For the three organic agents, the amounts of Cd, Cu and Ni residues in most sections were significantly lower than in S1~2. With the exception of S1 for Cu, the residues in all five sections were considerably reduced after CTS treatment. For the residue of Cd, S1 with FA reached a value of 1.51. Meanwhile, S2 of FA and S1 of PNA were both close to 1. Unlike Cd, S1 of CTS, FA and PNE exceeded 1 for Cu. The maximum residue of Cu was observed in S2 for the FA treatment while reaching the value of 1.64. From S1 to S2, the residue of Ni in the FA treatments exceeded 1.



**Figure 5.** Distribution of Cd (A), Cu (B) and Ni (C) residual contents after EKR; CK: Tap water; EDTA: ethylenediaminetetraacetic acid; NTA: nitrilotriacetic acid; DTPA: diethylenetriamine pentaacetic acid; CTS: chitosan; FA: fulvic acid; PNE: pine needle extract.S1~S5: five soil sections (from cathode to anode)

#### 3.4 Variation of the Cd fractions before and after EKR

Residue Cd speciation was analyzed using an improved BCR sequential extraction procedure. Figure 6A shows the Cd fraction variation after EKR. The mobility, bioavailability and removal efficiency can be affected by heavy metal speciation. According to Figure 6A, the vast majority of Cd speciation was in the exchangeable (225 mg/kg) and reducible (69.9 mg/kg) fraction in the original soil before electrokinetic remediation. In comparison, it contained little oxidizable (2.93 mg/kg) and residual (2.32 mg/kg) speciation. The tested soil in this study was less complex than natural soil because it was spiked artificially.

As shown in Figure 6A, heavy metals mobility and dissolution in the CK assay were improved [28]. The exchangeable Cd amounts in five sections of the DTPA treatment were all lower than the starting values and the CK values for the three chemical enhancing agents. During the DTPA treatment, the Cd in the exchangeable fraction from S1 to S5 was determined to be 123, 164, 138, 41.4 and 8.90 mg/kg, respectively. The Cd in the reducible fraction from S1 to S5 was 47.7, 49.2, 57.0, 22.6 and 6.01mg/kg, respectively. The contents of exchangeable and reducible Cd reduced remarkably after the enhanced EKR experiments. The NTA treatment raised the proportion of exchangeable Cd in S3 and S4. The identical phenomena occurred in S2 under the EDTA treatment. This indicated that the application of EDTA and NTA moved the "focus belt" towards the middle sections.

For the three organic enhancing agents, the exchangeable Cd significantly increased in S1 under the FA treatment. In the other four sections of the FA treatment, the exchangeable Cd decreased. Therefore, each section of the CTS treatment eradicated the exchangeable and the reducible Cd. Except for S1 of the PNE treatment, the exchangeable Cd in the other four sections decreased at different levels. The proportion of exchangeable Cd increased from the anode to the cathode. In addition to the total Cd distribution, Cd migrated mainly from the anode to the cathode during the addition of CK, CTS, FA and PNE, which was significantly different for EDTA, NTA and DTPA. After EKR, the change in the concentration of oxidizable and residual Cd was visible.

The CTS treatment produced the best results. The contents of exchangeable Cd for the CTS treatment from S1 to S5 were determined to be 83.2, 64.5, 47.4, 9.60 and 5.49 mg/kg, respectively. From S1 to S5, the content of reducible Cd in the CTS treatment was 31.0, 26.6, 17.9, 6.11 and 3.76mg/kg, respectively. That outcome could be attributed to the acetic acid which existed as a solvent of CTS and provided acidity to soils. The H<sup>+</sup> provided by the acetic acid neutralized the OH<sup>-</sup> ions produced at the cathode, which subsequently slowed down the "focus effect". Meanwhile, the anode-produced H<sup>+</sup> migrated towards the cathode chamber. The exchangeable Cd was exchanged against H<sup>+</sup> in the migration process and entered the liquid phase. Apart from this effect, CTS' high performance may be attributed to its -NH<sub>2</sub> and -OH functional groups, which can form complexes with heavy metals.

#### 3.5 Variation of the Cu fractions before and after EKR

Figure 6B depicts the variation of the Cu fractions before and after EKR. The predominant Cu fractions in the initial soil were exchangeable (356 mg/kg) and reducible (236 mg/kg) Cu, followed by oxidizable (217 mg/kg) and residual (36.6 mg/kg) Cu. Similar to the Cd fractions, the proportion of residual Cu was the lowest of the four fractions.

There was an apparent removal of the reducible and oxidizable Cu for the three chemical agents and CK in each section. As shown in Figure 6, the result suggested that most of the Cu was converted

into the exchangeable form. The application of EKR caused a significant change in heavy metal speciation. In the case of DTPA, the exchangeable Cu in the S1, S4 and S5 fractions was less than the initial values. There were obvious accumulations in the S2 fraction (590 mg/kg) and the S3 fraction (554 mg/kg) of the DTPA assays. Under the DTPA treatment, the reducible Cu fraction from S1 to S5 was determined to be 15.1, 60.8, 26.2, 3.26 and 6.42mg/kg, respectively. Meanwhile, S1 to S5 had an oxidizable Cu fraction of 13.4, 17.3, 17.8, 5.59 and 0.99mg/kg, respectively. The residual Cu fraction in S1 to S5 was 5.56, 4.96, 6.08, 4.49 and 2.05mg/kg, respectively. The reducible and oxidizable fractions of Cu under the DTPA treatment decreased significantly after EKR. The above data indicated that introducing DTPA could induce clear variations in Cu speciation. Moreover, the proportion of exchangeable Cu in S2 and S3 with NTA treatment increased. The exchangeable Cu fraction in S3 of the EDTA treatment increased significantly. The accumulations occurred in the above sections. This phenomenon may be caused by the electric field that forced the Cu-EDTA<sup>2-</sup> and Cu-NTA<sup>-</sup> chelates to migrate and accumulate in the middle of the soil chamber.

The exchangeable Cu increased significantly with the addition of organic enhancing agents in S1~2 for the CTS treatment and S1~3 for the FA and PNE treatments. Similarly, the three organic enhancing agents significantly reduced the oxidizable fraction of Cu in each section. However, for the three organic agents, the reducible Cu fraction decreased from S1 to S3. Due to their proximity to the anode similar to CK, the four fractions in S4 and S5 remained in the soil after EKR.

# 3.6 Variation of the Ni fractions before and after EKR

Figure 6C represents the Ni fraction variations before and after the EKR experiments. The primary speciation in the initial soil the was exchangeable (242mg/kg) and reducible Ni (109mg/kg), followed by oxidizable (52.6 mg/kg) and residual (32.4 mg/kg) Ni speciation. The Ni in oxidizable and residual fractions constitutes only a small proportion of the total Ni content in the initial soil.

During the EDTA treatment, the exchangeable and reducible Ni fractions were variously decreased with a maximum removal of up to 80% and 99% for S1 after the EKR. The exchangeable Ni obviously accumulated in S3. Under the NTA treatment, the exchangeable and reducible Ni in S5 were removed effectively while demonstrating maximum removal of 53% and 97%, respectively. Under the DTPA treatment, the exchangeable Ni in four sections except for S2 was removed efficiently. In S5, the exchangeable and reducible Ni was removed to a maximum removal of 91% and 99%, respectively.

The reducible and oxidizable Ni was removed during the CTS and PNE treatments. Under the CTS treatment, the apparent removal of both exchangeable and oxidizable Ni was 90% and 91% for S3. While there were significant reductions in the exchangeable and reducible Ni from the S3 to S5 fractions following the FA treatment, there was an apparent increase in the exchangeable Ni in S1 and S2. Interestingly, the residual Ni increased in the assays with FA from S3 to S5. Similar to the FA assay, the residual Ni increased from S1 to S3 with the addition of PNE. Previous study has reported that heavy metal binding types in soil can be transformed from a difficult removal type (residual speciation) to an easily removal type (exchangeable, adsorbed, or reducible speciation) during the electrokinetic remediation process [29].



**Figure 6.** Variations of the Cd (A)、 Cu (B) and Ni (C) fractions after EKR; CK: Tap water; EDTA: ethylenediaminetetraacetic acid; NTA: nitrilotriacetic acid; DTPA: diethylenetriamine pentaacetic acid; CTS: chitosan; FA: fulvic acid; PNE: pine needle extract; S1~S5: five soil sections (from cathode to anode).

# 3.7 Characteristics of PNE

The EDTA, NTA and DTPA have been found to combine with various heavy metals while forming highly soluble metal-chelate complexes, such as Cu-EDTA<sup>2-</sup>, Cu-NTA<sup>-</sup> and Cu-DTPA<sup>3-</sup> [30].

The de-complexed metal cations can reenter the soil matrix due to anodic oxidation and accumulate in different sections. A similar phenomenon possibly occurred in the experiments with EDTA, NTA and DTPA treatments.

The FTIR spectrum of PNE is shown in Figure 7. The intensity of the bands at 3600-3100cm<sup>-1</sup> and 3000-2800cm<sup>-1</sup> were assigned to the O-H stretching vibration and C-H stretching vibration, respectively [31]. The intensity of the bands at 1800-1000 cm<sup>-1</sup> was attributed to the oxygen functional group [32]. Thus, the intensity of the bands at 3415 cm<sup>-1</sup>, 1733 cm<sup>-1</sup>, 1622 cm<sup>-1</sup> and 1515 cm<sup>-1</sup> were attributed to O-H and C=O stretching, N-H bending and C-N stretching vibrations, respectively. The PNE contains -OH, -COOH and other oxygen-functional groups. Similarly, it contains other functional groups, such as -COOH, -OH and -NH<sub>2</sub> in CTS according to the FTIR of CTS and FA [33]. The divalent heavy metals can be desorbed from the soil by interacting with -COOH and -NH<sub>2</sub> groups of these enhancing agents while resulting in the formation of complexes. According to previous studies, heavy metals and their complexes such as metal-CTS, heavy metal-EDTA complexes can migrate out of the soil by electromigration and electroosmosis to form precipitates in electrode chambers, which could explain the removal mechanisms of complexing agents [34,35].



Figure 7. FTIR spectrum of pine needle powder

## 3.8 Cost analysis of EKR with enhancing agents and electrical energy

The energy consumption and costs for enhancing agents for metal removal are presented in Table 4. The electrical energy consumption of each enhancing agent was determined to be 0.07KWh, as each assay was run with the same voltage gradient and remediation duration (1.0V/cm and seven days). The costs of enhancing agents were also calculated according to the market price. The lowest cost was obtained under CK for total Cd (0.005 yuan/mg metal/kg dry soil, and 24% removal) and Cu (0.003 yuan/mg metal/kg dry soil, 13% removal). For total Ni removal, the lowest cost was obtained in CTS

and FA (72% removal in CTS and 29% removal in FA). When compared to other enhancers, the PNE is relatively less expensive and there are no Cd, Cu and Ni accumulations after the PNE treatment. Even though the PNE does not have the best removal efficiency, its low cost and environmental advantages make it superior (Table 4).

	Test	Initial metals mass (mg/kg dry soil)	Removal metal mass(mg)	Removal efficiency (%)	Consumption of agents/materials (yuan/mg metal/kg dry soil)	Consumption of electric energy (yuan/mg metal/kg dry soil)	Cost for removal of /mg metal (yuan/mg metal/kg dry soil)
Cd	CK		72.2	24.1	/	0.005	0.005
	EDTA		147	49.1	0.032	0.002	0.034
	NTA		74.4	24.8	0.205	0.005	0.210
	DTPA	300±2.98	160	53.4	0.491	0.002	0.493
	CTS		233	77.7	0.021	0.002	0.023
	FA		114	38.0	0.007	0.003	0.010
	PNE		186	62.1	/	0.010	0.010
Cu	CK		114	13.5	/	0.003	0.003
	EDTA		403	47.7	0.012	0.001	0.012
	NTA		201	23.7	0.076	0.002	0.078
	DTPA	845±6.35	500	59.1	0.157	0.001	0.158
	CTS		390	46.2	0.013	0.001	0.014
	FA		237	28.0	0.003	0.001	0.005
	PNE		314	37.2	/	0.004	0.004
Ni	CK		75.6	17.4	/	0.005	0.005
	EDTA		168	38.6	0.076	0.002	0.017
	NTA		120	27.5	0.127	0.003	0.028
	DTPA	436±3.59	206	47.4	0.381	0.002	0.078
	CTS		313	71.8	0.016	0.001	0.004
	FA		127	29.1	0.006	0.003	0.004
	PNE		241	55.4	/	0.05	0.05

Table 4 Consumption of electrical energy and agent costs for metal removal

i. / means the costs of tap water and pine needle were not included. The electric energy consumption of preparation PNE was included.

ii. The agents/materials were according to the Alibaba's official website (20220210). The cost of electric energy was calculated according to 0.6 yuan/KWh.

iii. CK: Tap water; EDTA: ethylenediaminetetraacetic acid; NTA: nitrilotriacetic acid; DTPA: diethylenetriamine pentaacetic acid; FA: fulvic acid; PNE: pine needle extract.

## 4. CONCLUSION

Enhanced electrokinetic remediation experiments have been conducted with EDTA, NTA, DTPA, CTS, FA and PNE. In addition, Cd, Cu and Ni contents, removal efficiencies, distributions and ion speciation were investigated. The high solid-liquid ratio (1g:1mL) of pine needle extract can increase the electric current density and cause variations in pH and TDS values during the EKR process. The results demonstrated that the three chemical and three organic enhancing agents coupled with EKR can improve the Cd, Cu and Ni removal from contaminated soil. The best three removal results for Cd (average of five sections) were determined as  $78\pm1.3\%$  for CTS,  $62\pm1.3\%$  for PNE and  $53\pm0.8\%$  for DTPA, respectively. The best three removal results for Cu (average of five sections) were determined as  $59\pm1.1\%$  for DTPA,  $48\pm0.7\%$  for EDTA and  $46\pm1.2$  for CTS, respectively. The best three removal results for Ni (average of five sections) were determined as  $72\pm2.5\%$  for CTS,  $55\pm0.9\%$  for PNE and

 $48\pm1.0\%$  for DTPA. The speciation analysis for Cd, Cu and Ni showed that the exchangeable and reducible speciation were reduced near the anode and the oxidizable speciation decreased for some enhancing agents after the EKR treatments. The enhancing agents plus electrokinetic remediation can produce various variations of heavy metals distribution and speciation. Moreover, the innovative application of pine needle extract as enhancing agent provided particular insight into the removal of heavy metals from contaminated soil. PNE may not have the best removal efficiency among these six enhancing agents, but it has the best economical cost and environmental benefits.

After enhanced EKR, Cd, Cu and Ni accumulated near the cathode, but the metal accumulation effect was observed in the middle of the soil matrix for some of the enhancing agents. Metal accumulation and the decomplexation effect of metal-chelate complexes need to be explored further.

# CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Xiaoyan Ge: conducted a research, processed the data and did most writing work for this paper. Xinshan Song: designed the experiments and revised the paper. Jing Xie: prepared the experiment testing and data collection. Wei Huang: improved the experiments. Yuhui Wang: improved the experiments. Zhongshuo Xu: helped the experiments. Yifei Wang: helped the experiment testing. Xiaoxiao Hou: helped the data collection. Xin Cao: designed the experiments, prepared and revised the paper.

#### ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (Grant No.52170152 and No.51909034), the National key research and development project (Grant No.2019YFC0408604 and No.2019YFC0408603), the Research Project of Shanghai Science and Technology Commission (Grant No. 21DZ1202402), the Shanghai Sailing Program (Grant No.19YF1401900), and the Fundamental Research Funds for the Central Universities and Graduate Student Innovation Fund of Donghua University (No.CUSF-DH-D-2020074).

#### References

- 1. D. Adriano, W. W. Wenzel, J. Vangronsveld & N. S. Bolan, Geoderma, 122(2004)121.
- X. Y. Zeng, D. S. Zou, A. D. Wang, Y. Y. Zhou, Y. H. Liu, Z. H. Li, F. Liu, H. Wang, Q. R. Zeng, Z. H. Xiao. *Journal of Environmental Management*, 255(2020)109885.
- 3. J. Qiao, Y. Liu, H.Yang, X. Guan, Y. Sun. Frontiers of Environmental Science & Engineering, 15(2021)1.
- 4. Q. G. Zhang, D. S. Zou, X. Y. Zeng, L. C. Li, A. D. Wang., F. Liu, H. Wang, Q. R Zeng, Z. H. Xiao. *Environmental Pollution*, 272(2021)115989.
- 5. A. Bano A, J. Hussain, A. Akbar, K. Mehmood & I. Ali I. Chemosphere, 199(2018)218.
- 6. J. Tang, J. He, T. Liu, X. Xin, H. Hu. Chemosphere, 189(2017) 599.
- 7. F. Chen, Q. Zhang, J. Ma, Q. Zhu, H. Liang. *Frontiers of Environmental Science & Engineering*, 15(2021)113.
- 8. L. Z. Yuan, X. J. Xu, H.Y. Li, N. N. Wang, N. Gu, H. W. Yu. *Electrochimica Acta*, 218(2016)140.
- 9. J. He, C. He, X. Chen, X. Liang, T. Huang, X. Yang, H. Shang(2018). *Environmental Science and Pollution Research*, 25(2018) 17682.
- 10. Y. N. B. Acar & A. N. Alshawabkeh. Environmental Science and Technology, 27(1993) 2638.
- 11. C. Q. He, A. N.Hu, F. F. Wang, P. Zhang, Z. Z. Zhao, Y. P. Zhao, X. Y. Liu. *Chemical Engineering Journal*, 407(2021)126923.
- 12. H. D. Zhou, Z. Y. Liu, X. Li, J. H. Xu. Journal of Hazardous Materials, 408(2020)124885.
- 13. J. G. Sunderland. Journal of Applied Electrochemistry, 17(1987)1048.

- 14. D. Wen, R. Fu, Q. Li. Journal of Hazardous Materials, 401(2021)123345.
- 15. H. Xu, P. Zhao, Q. Ran, W. Li, P. Wang, Y. Luo, C. Huang, X. Yang, J. Yin, R. Zhang. Science of *The Total Environment*,772(2021) 145029.
- 16. J. H. Chang, C. D. Dong, S. H. Huang, S. Y. Shen. Journal of Hazardous Materials, 383(2020)121194.
- 17. A. Giannis, D. Pentari, J. Y. Wang, E. Gidarakos. Journal of Hazardous Materials, 184(2010) 547.
- 18. L. Weng, W. H. Van Riemsdiik, T. Hiemstra. Environmental Science & Technology, 43 (2009)7198.
- 19. M. Bahemmat, M. Farahbakhsh, M. Kianirad. Journal of Hazardous Materials, 312(2016)307.
- 20. A. A. Kamnev, M. Colina, J. Rodriguez. Food Hydrocolloids, 12(1998) 263.
- 21. A. Giannis, E. Gidarakos, A. Skouta. Desalination, 211(2007)249
- 22. N. Dolev, Z. Katz, Z. Ludmer, A. Ullmann, R. Goikhman. *Environmental Research*, 183(2020)109140.
- 23. J. Tang, J. He, Z. Qiu, X. Xin. Journal of soils and sediments, 19(2019)1286.
- 24. Y. Wang, Z. Han, A. Li, C. Cui. Environmental Pollution, 283(2021) 117111.
- 25. R. Fu, D. Wen, X. Xia, W. Zhang, Y. Gu. Chemical Engineering Journal, 316(2017) 601.
- 26. Y. Song, L. Cang, Y. Zuo, J. Yang, D. Zhou, T. Duan, R. Wang. Chemosphere, 243(2020) 125439.
- 27. P. K. A. Hong, C. Li, S. K. Banerji, Y. Wang. Journal of Hazardous Materials, 94(2002) 253.
- 28. A. Giannis, A. Nikolaou, D. Pentari, E. Gidarakos. Environmental Pollution, 157(2009) 3379.
- 29. P. P. Falciglia, D. Malarbì, F. G. A. Vagliasindi. *Electrochimica Acta*, 222(2016) 1569.
- 30. A. Y. Yukselen, K. R. Reddy. *Electrochim Acta*, 86(2012) 164.
- 31. Y. Song, L. Cang, H. Xu, S. Wu, D. Zhou. Journal of Hazardous Materials, 377(2020) 106
- 32. A. A. Kamnev, M. Colina, J. Rodriguez. Food Hydrocolloids, 12(1998):263.
- 33. Y. Y. Chen, B. Y. Wang, J. Xin, P. Sun, D. Wu. Ecotoxicology and Environmental Safety, 164(2018)440.
- 34. S. Annamalai, M Santhanam, M.Sundaram, M. P. Curras. Chemosphere, 117(2014) 673
- 35. Y. Cao, X. Qian, Y. Zhang, G. Qu, T. Xia, X. Guo. Chemical Engineering Journal, 362(2019) 487.

© 2022 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).