In situ electrokinetic (EK) remediation of the total and plant available cadmium (Cd) in paddy agricultural soil using low voltage gradients at pilot and full scales

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HIGHLIGHTS

- EK remediation of Cd was successful in paddy agricultural soil with 20 V.
- Removal efficiency was higher in the 0–10 cm layer and higher in the pilot test.
- Removal efficiency was higher for the total Cd than plant available Cd.
- Reduction (%) of the total Cd and EC was higher near the anode than the cathode.
- Soil pH increased near the cathode but was kept below pH 6 by lactic acid.

GRAPHICAL ABSTRACT
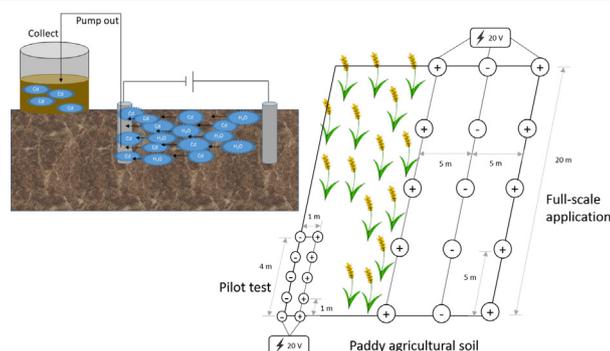
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ABSTRACT

Electrokinetic (EK) remediation has been widely studied at laboratory scales. However, field-scale research is far less. In this study, a 14-day EK remediation was carried out, in a field pilot (4 m^2) test and a full-scale (200 m^2) application for the first time, in a cadmium (Cd) contaminated paddy agricultural field near a mining area. A low voltage of 20 V was applied at both scales; voltage gradient was 20 V m^{-1} and 4 V m^{-1} at the pilot and full scales, respectively. Samples were taken from near the anode and cathode, and in the middle of the electric field, in the soil layers 0–10 cm, 10–20 cm, and 40–50 cm. After the EK remediation, a significant portion of the total Cd was removed in all the layers at the pilot scale, by 87%, 72%, and 54% from the top down, but only in the 0–10 cm layer at the full scale by 74%. As for the plant available (exchangeable and soluble) Cd, significant removal (64%) was only observed in the 0–10 cm layer at the pilot scale. The percentage reduction of the electrical conductivity and removal efficiency of the total Cd was higher near the anode than the cathode. The soil pH was elevated near the cathode but stayed below pH 6 due to the sufficient supply of lactic acid. After the EK remediation, the concentration of the total Cd dropped below the hazard threshold, i.e. 0.4 mg (kg dry wt soil)$^{-1}$ for agricultural

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Heavy metal
Cadmium

paddy fields in China. A total energy of 2 kW·h and 0.6 kW·h was consumed at the pilot and full scales, respectively. This study showed a successful *in situ* EK remediation of Cd contaminated paddy agricultural soil, especially in the surface layer, with low voltage and energy demand.

1. Introduction

Soil heavy metal contamination, especially in agricultural soils, is one of the biggest challenges the world faces (Bhuiyan et al., 2010; Su et al., 2014; Tóth et al., 2016; Kong et al., 2018; Huang et al., 2019; Kumar et al., 2019). In China, agricultural soils have been severely contaminated by heavy metals from mine tailings, metal industries, fertilizers, pesticides, etc. (Niu et al., 2013; Hou et al., 2018; Shifaw, 2018; Huang et al., 2019; Li et al., 2019). High awareness has been raised in terms of metal pollution in agricultural soils around mining areas in China (Wang et al., 2010; Liang et al., 2011). According to a review (Li et al., 2014), the average concentrations of heavy metals Cd, Cr, Pb, Zn, Cu, Ag, Ni, and Hg in the examined soils surrounding mines all violated the Level II standard set for agricultural soils in China (GB15618-1995). Especially for Cd, 86% of the cases did not meet the standard.

Heavy metal contamination in acidic agricultural soils is of special concern due to the high bioavailability of heavy metals at a low pH (Adamczyk-Szabela et al., 2015; Kim et al., 2015; Rieuwerts et al., 2015; Yu et al., 2016). A great number of studies have shown the adverse effects of heavy metals on living organisms (Singh et al., 2011, 2017); there is no lack of severe health damage cases caused by heavy metal intake (Järup, 2003; Jaishankar et al., 2014). Cadmium (Cd) is one of the common heavy metal pollutants that have been widely studied in terms of bioavailability, health effects and remediation (Christensen, 1984; Jaishankar et al., 2014; Yu et al., 2016; Liu et al., 2018).

Common remediation strategies include soil excavation and replacement, chemical precipitation, physicochemical adsorption, biosorption, phytoremediation etc. (Wang et al., 2008; Su et al., 2014; Li et al., 2019). The main principle of these methods is to immobilize and reduce the bioavailability of heavy metals to crops except for phytoremediation that can both immobilize heavy metals mainly in the plant rhizosphere and uptake heavy metals aboveground (Ali et al., 2013). *In situ* application of these methods has shown great results (Su et al., 2014; Li et al., 2019; Wang et al., 2019). However, immobilized heavy metals in the soil remain risky in case of environmental disturbance and uptake by phytoremediation is time-wise inefficient.

Over the past few decades, electrokinetic (EK) remediation of soil heavy metals has been increasingly investigated, as both a remediation and resource recovery method (Acar and Alshawabkeh, 1993; Acar et al., 1995; US Army Environmental Center, 2000; Kim et al., 2011; Ottosen, 2014). Joint use of EK remediation and other methods have also been investigated (Lee et al., 2009; Selvi et al., 2019; He et al., 2021). Electrokinetic migration, another name for EK remediation, self-explains the main principles of this technology. In EK remediation, two opposite electrodes, i.e. anode and cathode are applied; charged pollutants in the electric field migrate to the electrodes with the opposite charge. The migrated pollutants accumulate close to or at the relevant electrodes and can be removed and/or further recycled. The migration of species is determined by the forces of electromigration (electric attraction), electroosmosis, electrophoresis, and hydraulic potential gradient. The naturally present and electrolyzed hydrogen cations at the anode migrate to the cathode, dragging the water flux along to the cathode (i.e. electroosmosis) and desorbing some heavy metals from soil particles through cation exchange. Opposite to hydrogen cations, the naturally present and electrolyzed hydroxide anions at the cathode migrate to the anode driven by electric attraction but suffocated by the flux of water towards the cathode. For soil heavy metal remediation, metal or metal containing species are usually positively charged and therefore migrate to the cathode, through electroosmosis and electromigration (electric attraction).

During the migration, precipitation of metal hydroxides often happens in an alkaline condition, especially near the cathode where hydroxide anions are electrolyzed. These metal precipitates are not necessarily removed from the soil in EK remediation. However, they are relatively more stable compared to free metal ions and are consequently less bioavailable or harmful to e.g. crops. Risk remains, however, in case of pH drop. For most heavy metals including Cd, when pH is too high, metal hydroxide complexes that are negatively charged and more soluble are formed and can migrate to the anode (Christensen, 1984; Acar et al., 1995; Rieuwerts et al., 2015). Formation of metal hydroxides or hydroxide complexes can cause removal inefficiency. Accordingly, acetic acid and lactic acid electrolytes have been commonly added for soil pH adjustment, which can meanwhile increase electroosmosis and soil heavy metal desorption through cation exchange (Acar et al., 1995; Alshawabkeh et al., 2004; Zhou et al., 2005). Alkaline electrolytes have also been used and preferred by some heavy metals, such as As (Yang et al., 2009). Chelating agents, such as EDTA are also often used to improve soil heavy metal desorption in EK remediation (Amrate et al., 2005; Alcántara et al., 2012; Dong et al., 2013).

A great number of EK remediation studies have shown success in removing soil heavy metals. Various performance enhancing strategies have also been investigated, such as applying approaching anodes, polarity exchange and pulse current (Chen et al., 2006; Shen et al., 2007; Ryu et al., 2010; Lu et al., 2012; Sun and Ottosen, 2012; Yao et al., 2020). Despite the high performance of EK remediation confirmed at bench scales (Reddy and Chinthamreddy, 1999; US Army Environmental Center, 2000; Reddy and Ala, 2005; Alcántara et al., 2012; Lu et al., 2012; Dong et al., 2013), field-scale research has been mainly limited to pilot scales, and full-scale applications are difficult to find (Wieczorek et al., 2005; Kim et al., 2011, 2012, 2013).

For Cd contaminated soils, studies on EK remediation have only been done in the laboratory, some of which are listed in table S1. The studied soils included agricultural, industrial, and commercial soils, with artificial or real site contamination. In most cases of these studies, the removal efficiency of Cd was higher in the spiked soils (Beyrami, n.d.; Kim et al., 2005; Chen et al., 2006; Chung and Lee, 2007) than the soils with real site contamination (Kim and Kim, 2001; Lee et al., 2009; Ryu et al., 2009, 2010), probably due to the loose adsorption to the soils by spiking although settlement was allowed for up to 3 months in those cases. However, high removal efficiencies were also achieved in real contaminated soils by adopting advanced EK remediation strategies such as polarity exchange and approaching anode (Chen et al., 2006; Lu et al., 2012).

A voltage gradient of 100 V m^{-1} was most frequently used in these laboratory studies. However, it is not practical to apply that high voltage gradients in a paddy field in China, since the recommended maximum voltage for outdoor use in wet environments in China is 35 V (GB/T 3805-2008). If 100 V m^{-1} was adopted in *in situ* EK remediation, the voltage can easily go up to a thousand. Therefore, more relevant voltage gradients according to the local regulations should be studied in the laboratory and field.

The aim of this study was to investigate *in situ* EK remediation of Cd contaminated paddy agricultural soil with a relevant voltage (20 V) for outdoor use in China. As far as we are concerned, this research is the first to demonstrate pilot and full-scale EK remediation of Cd contaminated

agricultural soil. More specifically, the removal efficiency of Cd was compared among different soil layers, between the total and plant available Cd, and between two different voltage gradients by adopting the same voltage at both scales. Additionally, the relation between the sampling position (near the anode, near the cathode, and in the middle of the electric field) and the change of soil pH and electrical conductivity, and the removal efficiency of the total and plant available Cd by EK remediation was illustrated.

2. Materials and methods

2.1. Research site

This research was conducted in a paddy agricultural field in Gaolian village (25°04′ N, 113°40′ E), Dongtang town, Renhua district, Shaoguan city, Guangdong province, China. The field is near the Fankou lead-zinc mining area. According to the study by Ye et al. (2018), Cd contamination level was found very high in the Fankou lead-zinc mining area, with the average concentration of 3.68 mg (kg dry wt soil)$^{-1}$, while the national soil background level is 0.097 mg (kg dry wt soil)$^{-1}$ and the crust level is 0.18 mg (kg dry wt soil)$^{-1}$ (Ye et al., 2018). The soil was classified as clay. More soil properties are listed in Table S2.

2.2. Experimental design and setup

Before the setup, agricultural residuals and big gravels in the soil surface layer (0–5 cm) were removed, followed by ploughing the soil within the depth of 50 cm. For the assembly of electrodes in the soil, 50 cm deep and 11 cm wide holes were firstly dug in the soil at the two parallel edges of the treated area. Perforated PVC pipes (60 × 6.3 cm^2, length×diameter) that were sealed at the bottom and wrapped by a piece of microporous fabric were then inserted into the holes. The fabric prevented soil or sand particles from entering the pipes but allowed liquid and ions in the soil to permeate. A length of 10 cm of the PVC pipes was exposed above the ground to isolate the holes from the surrounding soil. The electrodes were then placed into the PVC pipes. Two thinner pipes (d = 2.5 cm) were inserted into both PVC pipes for pumping electrolyte in and out. The schematic diagram is displayed (Fig. 1).

Two tests were carried out in the field: 4 m^2 pilot test (2 m^3, 4 × 1 × 0.5 m^3, length×width×depth) and 200 m^2 full-scale application (100 m^3, 20 × 10 × 0.5 m^3, length×width×depth). At both scales, direct current with 20 V was used, so the voltage gradient was 20 V m^{-1} and 4 V m^{-1} for the pilot test and full-scale application, respectively. Cylindrical graphite electrodes with 0.5 m length and 4 cm diameter were used. In the pilot test, five series-wound pairs of electrodes were applied in parallel (Fig. 1b), with 1 m interval distance. One line of electrodes acted as cathodes, and the other as anodes. The distance between the opposite electrodes was also 1 m. The total covered area was 4 m^2 in the pilot test. In the full-scale application, both series-wound electrodes and shunt-wound electrodes were applied (Fig. 1c). Two sets of five series-wound electrodes with 5 m interval distance were placed in parallel on the two edges of the field. The distance between the two edges was 10 m. These two lines of electrodes on the edges acted as anodes. Another five series-wound electrodes with 5 m interval distance were placed in the middle of the edges and acted as the shared cathodes. The distance between the cathodes and anodes was also 5 m. The total covered area in the full-scale application was 200 m^2.

During the EK treatment, an electrolyte containing 0.5 mol L^{-1} lactic acid was added to both electrode PVC pipes every 24 h for the first 72 h, followed by a 68 h break. After that, lactic acid was added again every 48 h. The electrolyte was added to both anode and cathode PVC pipes so that the water levels in the PVC pipes were around the soil surface level. In total, 5000 mL lactic acid was added.

One soil sample was taken before and after the EK remediation at the positions near the anode, near the cathode, and in the middle of the electric field in the soil layers 0–10 cm, 10–20 cm, and 40–50 cm.

Sampling positions in the pilot test (Fig. 1b) and in the full-scale application (Fig. 1c) are shown by red stars. Soil total Cd, plant available (exchangeable and soluble) Cd, pH and soil electrical conductivity were measured. Electric current was recorded in the field throughout the EK remediation.

2.3. Soil Cd analysis

Bioresidues and stones were first removed from the soil samples. Oven-dried soil samples were then ground and filtered through a 0.149 mm nylon sieve before further processing. The total and plant available Cd were both measured using graphite furnace atomic absorption spectrophotometer (Hitachi Z-2000).

2.3.1. Total Cd extraction

The total Cd was extracted through complete soil digestion (GB/T 17141-1997, 1997). Soil samples were weighed accurately between 0.1 g to 0.3 g in 50 mL Teflon crucibles. The weighed soil samples were then soaked with water in the crucibles, followed by the addition of 5 mL HCl (1.19 g mL^{-1}) and heated at 110 °C in the fume hood until there was 2–3 mL liquid left. After the samples cooled down, 5 mL HNO$_3$ (1.42 g mL^{-1}), 4 mL HF (1.49 g mL^{-1}), and 2 mL HClO$_4$ (1.68 g mL^{-1}) were added, and the samples were heated again with lids on at 180 °C for 1 h. After that, samples continued being heated but without the lids and with constant shaking. When white smoke (HClO$_4$) arose, the lids were put back on the crucibles, and the samples kept being heated until the black organic matter was fully digested. Then the lids were removed again and heating continued until the samples tuned viscous. After the samples cooled down a bit but were still warm, 1 mL HNO$_3$ (0.24 g mL^{-1}) was added to dissolve the samples. The dissolved samples were then moved to 25 mL volumetric flasks, followed by the addition of 3 mL (NH$_4$)$_2$HPO$_4$ (5% w/w). After the samples totally cooled down, the flasks were filled with 0.2% v/v HNO$_3$ solution until the 25 mL line. The solution was ready for measurement. Standard solutions were prepared in 25 mL volumetric flasks containing 3 mL (NH$_4$)$_2$HPO$_4$ (5% w/w) and Cd(NO$_3$)$_4$ with a final concentration series of 0, 1, 2, 4, 6, and 10 μg L^{-1}, filled with 0.2% v/v HNO$_3$ solution.

2.3.2. Plant available Cd extraction

The plant available Cd was extracted through leaching (HJ 804-, 2016). About 10 g soil samples were weighed accurately in 100 mL conical flasks. 20 mL extraction solution (0.1 mol L^{-1} TEA + 0.01 mol L^{-1} CaCl$_2$ + 0.005 mol L^{-1} DTPA; pH 7.3 adjusted by HCl) was added to the flasks. At room temperature, the samples were shaken at 200 rpm for 2 h, followed by centrifugation at 5000 rpm for 10 min. The liquid supernatant was filtered through a 30 μm filter paper. The filtrate was ready for measurement. Standard solutions were prepared in 100 mL volumetric flasks containing CdCl$_2$ with a final concentration series of 0, 0.01, 0.02, 0.04, 0.08 and 0.12 mg L^{-1}, filled with extraction solution.

2.4. Statistical analysis

IBM SPSS Statistics 25 was used for statistical analysis. Repeated Measures ANOVA with simple main effects test was used. Values before and after the EK remediation were the within-subject variables and depth and scale (voltage gradient) were the between-subject factors. Natural logarithmic transformation was made to the soil electrical conductivity and concentrations of the total and plant available Cd for the normal distribution of values.

3. Results and discussion

3.1. Soil electrical conductivity, electric current, and pH

After the EK remediation, the soil electrical conductivity dropped from 140–330 μS cm^{-1} to 70–190 μS cm^{-1} (F = 29.2,
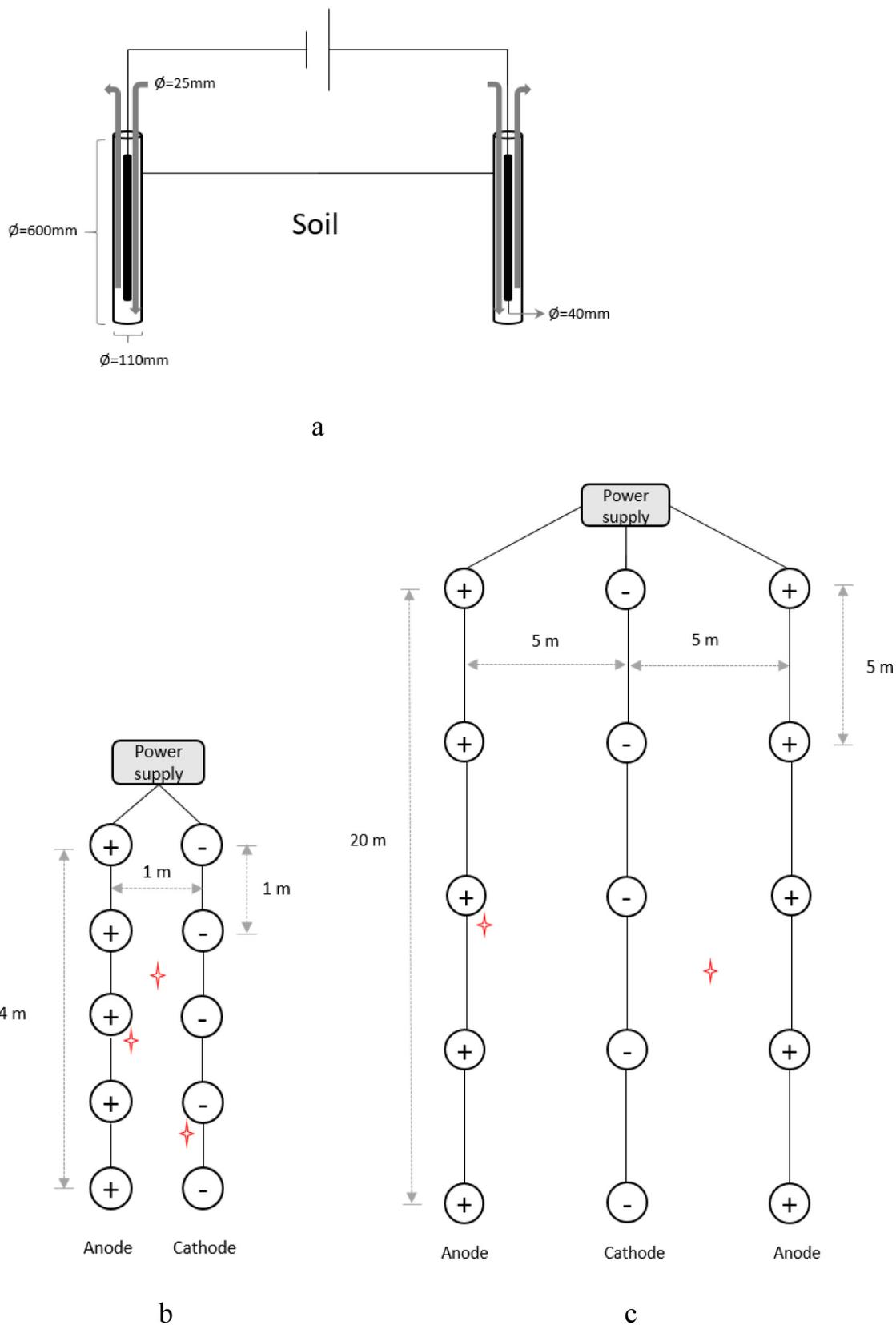
Fig. 1. Schematic diagram of the experimental setup: a) electrode installation in the soil; b) electrode assembly in the pilot test; c) electrode assembly in the full-scale application. Red star marks show the sampling positions.

df = 1, p < 0.0005; Fig. 2), indicating the migration and removal of soil salts (Acar et al., 1995). The percentage reduction of the soil electrical conductivity was higher near the anode, using the data from all

the soil layers and both scales (Fig. 3). Electrical conductivity is directly associated with the number of free ions and electric charge. The lower percentage reduction in the middle of the electric field
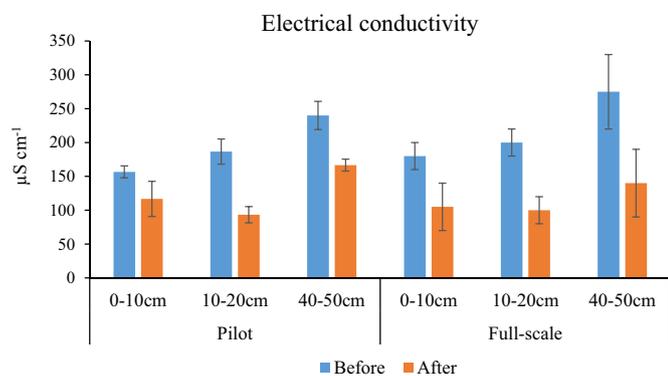
Fig. 2. Soil electrical conductivity before and after the EK remediation. Mean ± SE.

and near the cathode was most likely due to the migrated-in free ions from the anode side.

The electric current fluctuated corresponding to the addition of lactic acid (Fig. S1). Electric current is also affected by the number of free ions and charge. Every time the electrolyte was added, the electric current rose simply due to the added free ions and dissolution of acid soluble fraction in the soil, followed by a decrease periodically and after 140 h while the ions reached the oppositely charged electrodes or migrated out of the soil matrix. The electric current was higher in the pilot test than the full-scale application because the voltage was the same but the scale was bigger and therefore the electric resistance was bigger in the full-scale application.

Due to the production of hydroxide anions at the cathode, soil pH is usually elevated especially near the cathode (Acar et al., 1995). In this case, although the soil pH also increased a bit near the cathode, it (combined data from all the soil layers and both scales) stayed acidic or weakly acidic (below pH 6) with the addition of lactic acid electrolyte (Fig. S2). Low-pH induced high bioavailability of heavy metals in agricultural soils (Adamczyk-Szabela et al., 2015; Kim et al., 2015; Rieuwerts et al., 2015; Yu et al., 2016) is a common problem but an advantage over alkaline soils in the application of EK remediation. Relatively low soil pH is suitable for the migration and removal of soil Cd, since hydroxide precipitation happens significantly when the pH is higher than 7; hydroxide complexes start to form when the pH is around 10 and start to move to the anode (Christensen, 1984; Acar et al., 1995; Rieuwerts et al., 2015).
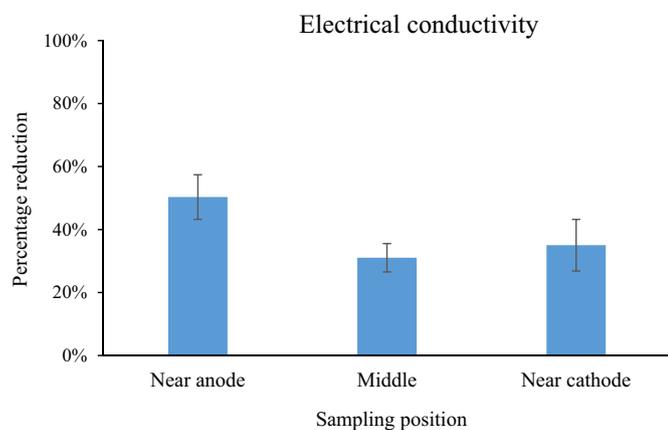

Fig. 3. Percentage reduction of soil electrical conductivity after the EK remediation near the anode, near the cathode, and in the middle of the electric field using combined data from all the soil layers and both scales. Mean ± SE.
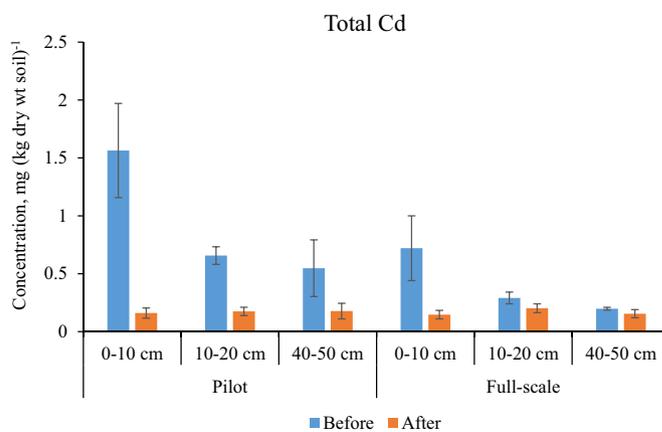

Fig. 4. Concentrations of the total Cd in the soil layers 0–10 cm, 10–20 cm, and 40–50 cm before and after the EK remediation in the pilot test and full-scale application. Mean ± SE.

3.2. Removal of soil Cd

The original concentration of the total and plant available Cd ranged from 0.19 to 2.26 mg (kg dry wt soil)$^{-1}$ and 0.08 to 0.92 mg (kg dry wt soil)$^{-1}$, respectively, including data from all sampling points and layers. After only 14 days' EK remediation, the concentration of the total and plant available Cd dropped to 0.08–0.31 mg (kg dry wt soil)$^{-1}$ and 0.03–0.11 mg (kg dry wt soil)$^{-1}$, respectively. The concentration of the total Cd after the EK remediation was lower than the hazard threshold, i.e. 0.4 mg (kg dry wt soil)$^{-1}$ for agricultural paddy fields set corresponding to the soil pollution management in China (GB 15618-2018).

3.2.1. Removal efficiency by scale (voltage gradient), soil layer, and Cd fraction

In general, the removal efficiency of soil Cd was the highest in the top 0–10 cm layer and the remediation performance was higher in the pilot test than the full-scale application (Table 1; Figs. 4 and 5). In addition, removal efficiency was higher for the total Cd than the plant available Cd (Table 1). In the pilot test, 87%, 72%, and 54% of the total Cd was removed by EK remediation, respectively from the top to the bottom layer (Table 1). In the full-scale application, significant removal of the total Cd (74%; Table 1) was only observed in the top soil layer. As for the plant available Cd, significant removal only occurred in the top soil layer in the pilot test (64%; Table 1). Although in all the soil Cd × scale × layer combination cases, there was a trend of reduction of soil Cd concentrations, the simple main effects test did not give a significant p value
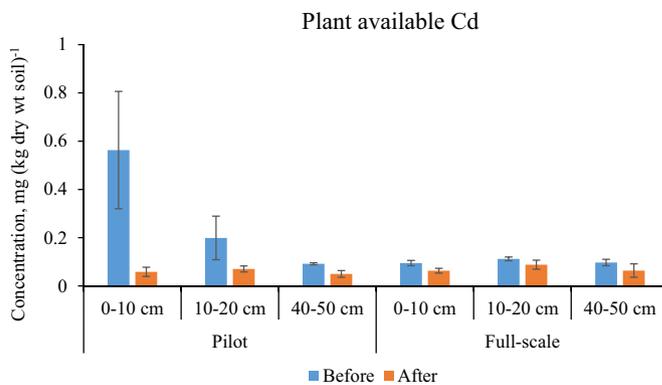

Fig. 5. Concentrations of the plant available Cd in the soil layers 0–10 cm, 10–20 cm, and 40–50 cm before and after the EK remediation in the pilot test and full-scale application. Mean ± SE.

Table 1
Removal efficiency of soil Cd and statistical difference between the natural logarithmic values of soil Cd concentrations before and after the EK remediation using Repeated Measures ANOVA with simple main effects test.

Soil Cd	Scale	Soil layer, cm	Removal efficiency, %	Statistical results		
				F	df	p
Total	Pilot test	0–10	87	26.70	1	0.001
		10–20	72	9.44	1	0.013
		40–50	54	5.53	1	0.043
	Full-scale	0–10	74	8.14	1	0.019
		10–20	26	0.48	1	0.505
		40–50	23	0.27	1	0.619
Plant available	Pilot test	0–10	64	11.27	1	0.008
		10–20	47	2.5	1	0.148
		40–50	45	1.42	1	0.265
	Full-scale	0–10	31	0.40	1	0.545
		10–20	22	0.09	1	0.769
		40–50	47	1.08	1	0.326

for all the cases (Table 1; Figs. 4 and 5). This might be because the simple main effects test tends to lose power.

The voltage gradient in the pilot test ($20\,\mathrm{V\,m^{-1}}$) was five times that in the full-scale application ($4\,\mathrm{V\,m^{-1}}$), which resulted in the lower removal efficiency of soil Cd in the full-scale application, especially in the deeper soil layers. In EK remediation, the main driving forces, i.e. electroosmosis, electromigration, and electrophoresis, are all affected by the intensity of power supply and the distance between the opposite electrodes, i.e. voltage gradient. Studies have been conducted on the effect of voltage gradient on the removal efficiency of heavy metals including Cd and higher voltage gradients are generally favored for higher removal efficiencies (Beyrami, n.d.; Essa et al., 2013; Mena et al., 2016).

Lower removal efficiencies of heavy metals in the deeper soil layers are a very common observation in EK remediation studies, as was in this study, which could be simply the result of vertical migration of heavy metal species along with the soil water flux by gravity (Zhang et al., 2010; Jeon et al., 2015). However, accumulation of heavy metals in the top soil layer was also observed when the voltage gradient was high even though the electrodes were installed with a horizontal electric field (Kim et al., 2012). Kim et al. (2012) found that when the voltage gradient was as high as $100\,\mathrm{V\,m^{-1}}$, soil temperature increased significantly, which might result in the vertical migration of soil water and conveying of some heavy metal species towards the soil surface. It means that although voltage gradient is one of the main driving forces in EK remediation, negative effects can happen in the top soil layers when the voltage gradient is too high. However, since the applied voltage gradients in this study were much lower, i.e. $20\,\mathrm{V\,m^{-1}}$ and $4\,\mathrm{V\,m^{-1}}$ for the pilot test and full-scale application, respectively, no accumulation of heavy metals in the top soil layer was observed. To increase the removal efficiency in the lower soil layers, especially above the 20 cm depth since the top 0–20 cm soil layer is the most relevant in terms of crop contamination in agricultural soils (Zhang et al., 2014), a higher voltage can be applied. Additionally, a vertical electric field can be adopted in the soil to migrate the heavy metals upwards with or without a coupled horizontal electric field application (Zhang et al., 2010).

What is noteworthy is that the removal efficiency was much higher for the total Cd than the plant available Cd in this study, although the plant available metal fraction is the soluble and exchangeable Cd that migrates the most readily (Kim and Kim, 2001; Ryu et al., 2009; Li et al., 2010; Ahmadipour et al., 2014). On the other hand, Cd usually has a high exchangeable and acid soluble fraction in the soil (Ahmadipour et al., 2014) and EK remediation could potentially transfer the strongly bound soil Cd to the weakly bound (exchangeable and soluble) fraction (Ryu et al., 2009). Therefore, it is most likely that the plant available (exchangeable and soluble) Cd was converted/generated through e.g. cation exchange and/or dissolution of the acid soluble fraction with the assistance of the added lactic acid but yet needed to

migrate out of the soil matrix. This could result in the lower removal efficiency of the plant available Cd than the total Cd in this study (Acar et al., 1995). An example can be that the removed plant available Cd equals to the generated, resulting in a zero removal efficiency of the plant available Cd. With a longer treatment period, the removal of the plant available Cd should be more visible.

3.2.2. Removal efficiency in relation to sampling position

Additionally, the relation between the sampling position and the removal efficiency of the total and plant available Cd were illustrated (Figs. 6 and 7), combing the data from all the soil layers and both scales. It was apparent that the removal efficiency of the total Cd was higher near the anode than the cathode, which was consistent with the findings in earlier studies and was often credited to inefficient migration and/or formation of hydroxides close to the cathode (Kim and Kim, 2001; Kim et al., 2005; Hansen and Rojo, 2007; Ryu et al., 2009, 2010). In this study, sufficient lactic acid was supplied in both electrode PCV pipes and the soil pH stayed below pH 6 near the cathode. Therefore, the lower removal efficiency of the total Cd near the cathode was most likely not due to accumulation through hydroxide precipitation but due to the compensation of the migrated-in Cd from the anode side. The removal efficiency of the plant available Cd was similar among the sampling positions with high deviations.

3.3. Comparison with earlier studies

Among the EK remediation studies, field tests only account for a very small portion, not to speak of full-scale applications, and no earlier studies on *in situ* EK remediation of Cd in an agricultural soil were found. However, there are a number of EK remediation studies on the removal of soil Cd at laboratory scales, some of which are listed in Table S1 in the Introduction. In these studies, a voltage gradient of $100\,\mathrm{V\,m^{-1}}$ was frequently used and the remediation time was at most 14 days. The removal efficiency in the soil (maximum depth: 11 cm) with site contamination was below 50% in most of these cases, while it was 87% and 74% in the top 0–10 cm layer for the pilot test and full-scale application, respectively, in this study. The sufficient supply of lactic acid as both catholyte and anolyte could be the main reason why the removal efficiency of Cd in this study was relatively high. Firstly, the added hydrogen cations at the anode could stimulate the migration of water flux from the anode to the cathode through electroosmosis (Acar et al., 1995). Secondly, the exchangeable and acid soluble fraction of Cd that is usually high in the soil (Ahmadipour et al., 2014) could be effectively desorbed through hydrogen cation exchange and dissolution by lactic acid. Lastly, lactic acid is also a good chelating agent (Kakihana et al., 2004) and chelating agents are very important
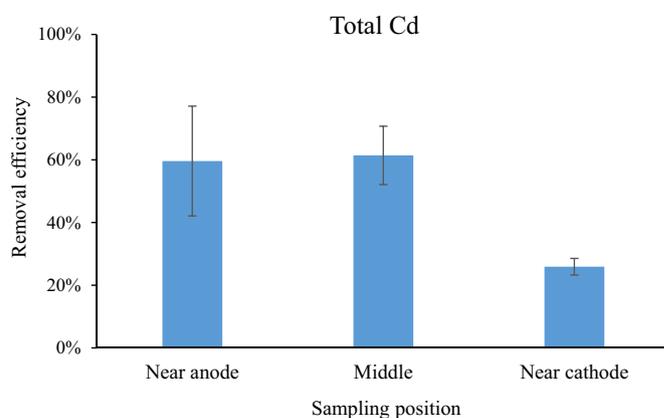

Fig. 6. The relation between the sampling position (near the anode, near the cathode, and in the middle of the electric field) and the removal efficiency of the total Cd in the soil using combined data from all the soil layers and both scales. Mean ± SE.
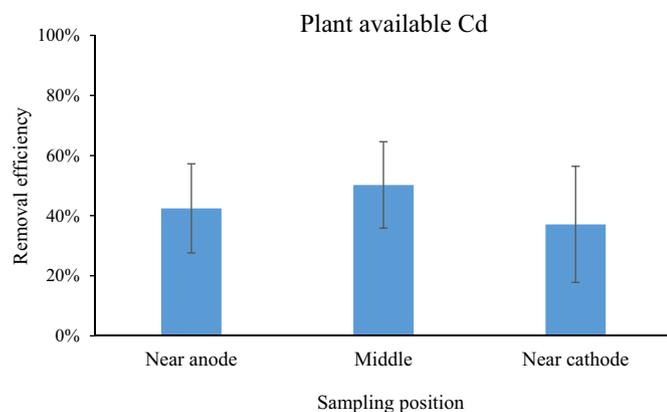
Fig. 7. The relation between the sampling position (near the anode, near the cathode, and in the middle of the electric field) and the removal efficiency of the plant available Cd in the soil using combined data from all the soil layers and both scales. Mean ± SE.

additives in EK remediation to enhance the desorption and solubility of heavy metals and consequently the enhanced removal (Acar et al., 1995). Hence, in this study, lactic acid might have significantly enhanced the solubility of Cd, after which Cd easily migrated out of the soil matrix by the forces of electromigration and enhanced electroosmosis. However, in the earlier laboratory studies (Table S1), the added electrolytes or additives were not as multifunctional as lactic acid.

Additionally, some studies in South Korea demonstrated field applications of EK remediation in the removal of other heavy metals, i.e. Pb, As, and Cu in agricultural soils (Kim et al., 2012, 2013; Jeon et al., 2015). In these cases, at least 4 weeks and 50 V m^{-1} were applied (Kim et al., 2012, 2013; Jeon et al., 2015). In the soil layer 0–50 cm, the best removal efficiency found among these South Korean cases was around 65% on average for the total Pb in the 0–40 cm soil layer in 4 weeks (Kim et al., 2013), while it was 71% for the total Cd in the 0–50 cm soil layer in 14 days in this study. However, since high pH is favored by As to form hydroxide complexes for higher solubility (Yang et al., 2009), alkaline electrolyte (NaOH) was used in these studies, which could have compromised the removal efficiency of other heavy metals, including Pb. In addition, Cd generally has higher mobility and exchangeable and acid soluble fraction compared to Pb, which could account for a higher removal efficiency for Cd than Pb by EK remediation (Kim and Kim, 2001; Kim et al., 2001, 2005; Ahmadipour et al., 2014).

Considering the far lower voltage gradients used in this study, i.e. 20 V m^{-1} and 4 V m^{-1} in the pilot test and full-scale application, respectively, the removal of the total Cd was quite successful compared to the earlier laboratory and field studies. This study is the first to show a significant *in situ* EK remediation of soil heavy metal Cd with relatively low voltage gradients. The requirement of low voltages is particularly relevant and important for the application of *in situ* EK remediation of heavy metals in soils in China due to the restriction of outdoor voltage use (maximum 35 V recommended for wet environments).

3.4. Energy consumption

The energy consumption was low, i.e. 2 kW·h and 0.6 kW·h in the pilot test and full-scale application, respectively. The energy consumption was higher in the pilot test because the electric current was higher and voltage was the same.

4. Conclusions

In only 14 days, *in situ* EK remediation of soil heavy metal Cd was successfully run in a 4 m^2 pilot test and a 200 m^2 full-scale application in a paddy agricultural field near a mining area with a low voltage of 20 V and low energy consumption of 2 kW·h and 0.6 kW·h, respectively. In general, EK remediation was better performed in the pilot

test due to the higher voltage gradient. Remediation was especially efficient in the surface soil layer (0–10 cm), with 87% and 74% removal efficiency of the total Cd in the pilot test and full-scale application, respectively. However, the plant available Cd was only significantly removed in the surface layer in the pilot test (64%). The reason why the plant available Cd had a lower removal efficiency than the total Cd was probably due to the desorption of the plant available Cd which compensated for the removal. The percentage reduction of the soil electrical conductivity and the removal efficiency of the total Cd was higher near the anode than the cathode. The soil pH was kept below 6 by lactic acid although it increased a bit near the cathode. The results showed a high potential of *in situ* EK remediation in the removal of Cd in agricultural soils with low voltage and energy demand.

CRediT authorship contribution statement

Zongping Cai: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Data curation, Visualization, Funding acquisition, Project administration, Resources. **Yan Sun:** Validation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization, Data curation, Funding acquisition. **Yanghong Deng:** Investigation. **Xiaojie Zheng:** Investigation. **Shuiyu Sun:** Funding acquisition, Project administration, Writing – review & editing, Supervision, Resources. **Martin Romantschuk:** Writing – review & editing, Supervision. **Aki Sinkkonen:** Writing – review & editing, Supervision.

Declaration of competing interest

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

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147277.

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