

Mechanisms of electrokinetic technology to remediate different soils contaminated by cadmium

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Abstract. Five typical soils were selected as Cd-contaminated media in an electrokinetic remediation experiment, to reveal comprehensive relationships between soil physicochemical properties and electrokinetic remediation. Results showed that after 20 days of remediation, removal efficiencies of Cd from red soil, black soil, yellow brown soil, fluvo-aquic soil, and paddy soil were 80.8%, 79.3%, 78.2%, 62.7%, and 74.1%, respectively. Levels of soil pH, conductivity, cation exchange capacity in fluvo-aquic soil and paddy soil treatments were generally higher than the other three types of soils, which indicated some connections between Cd removal efficiencies and the above soil characteristics. Pearson correlation analysis showed that soil H⁺ concentration was significantly correlated with Cd concentration and soil cation exchange capacity, and the correlation coefficients were -0.462 and -0.457, respectively. It is confirmed that H⁺ concentration is one of the important factors affecting the electrokinetic remediation of soil polluted by Cd.

1 Introduction

Due to rapid urbanization and industrialization in China, a great deal of industrial sites have been relocated, leaving thousands of polluted sites [1], which may bring about threats to land utilization, groundwater safety and residents' health. Investigations showed that heavy metals and some organic compounds are the main pollutants detected in industrial sites, among which Cd is a major health hazard and has been found in most abandoned industrial sites [2-3]. According to a survey by Li et al., the mean concentrations of As, Cd, and Hg in soils were about 6.5, 36.5, 7.6 times higher than the Grade II environmental quality standard for soils in China [4]. About 86.4% of the soil samples surpassed the Grade II value of Cd [4]. Accumulated Cd in soil may pose treats to human health by contaminating crops and groundwater, and it can cause respiratory irritation, osteoporosis and significant damage to kidneys [5-6]. Therefore, it is urgent to find an effective way to remediate Cd-contaminated soils.

Electrokinetic remediation (EKR) is a promising soil remediation method and has drawn much concern at present. This technique features simple equipment, low cost, high efficiency in heavily polluted area, especially suitable for in-situ soil restoration. Geokinetics Company applied the EKR to remove 70-80% of Pb and Cu from in-situ soil, and energy consumption of the project was only 65 kW·h/m³ [7]. Shu et al. [8] utilized a pulsed

electric field to further diminish the energy consumption in EKR. Results showed that 94.7% of manganese and 88.2% of ammonia nitrogen were removed from an electrolytic manganese residue site. Selvi and Aruliah [9] developed an integrated approach of bioleaching enhanced EKR in zinc spiked soil and removed 93.08% of zinc in 72 h.

Although EKR has been successful even in low permeability soil or in some in-situ remediation processes [7-8, 10-13], the generation of OH⁻ ions at the cathode may lead to the precipitation of heavy metals, which is called "focusing effect" and this effect is the main shortcoming of wide range of EKR application. Different strategies have been developed to eliminate OH⁻ ions or to make convenient pH conditions favorable for heavy metal elimination in EKR treatment. Zhou et al. [13] studied the EKR performance of Cu contaminated red soil with or without catholyte conditioning. Cu was found accumulated of large quantities in the vicinity of the cathode without catholyte conditioning, due to the formation of precipitation compounds of Cu with OH⁻ ions. Several research groups have reported that heavy metal ions migrated faster in acidic pH environment, that may be related to the significant influence of pH on electromigration or electroosmotic flow [14-15], which are the two main mechanisms determining heavy metal ions migration in EKR [7, 16]. Furthermore, Gidaracos and Giannnis[16] used citric acid or CH₃COOH as catholyte and observed that when catholyte pH value was

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controlled below 4, significant amounts of H^+ ions distributed throughout the soil specimen, resulting in the desorption of Cd from soil particle surfaces and a higher extraction efficiency. Other improved EKR systems have also been conducted to control the soil pH and enhance the metals removals, such as by reversing polarity of the power or circulation of the electrolyte solution in EKR [11, 18]. Adding zero-valent iron into EKR system can help to promote the release of Cr (VI) from the clay and enhance the removal of Cr (VI) [19]. These novel techniques have greatly improved the removal rate of heavy metals in EKR system.

However, few studies have been proposed to focus on variation of the soil circumstances, and these changes may in turn influence the effectiveness of EKR. When an electric current was applied to soils, it may result in fundamental soil physical-chemical changes, such as soil pH and/or conductivity, soil zeta potential, as well as electrolyte concentration, which might impact the performance of EKR through distributing of chemical speciation and transporting of soil constituents, including metals [20]. In our previous study, it was found that morphology and distribution of Cd by EKR in several types of soils was quite different [21]. The mechanisms of Cd migration, adsorption and transformation are relatively complicated that need to be revealed to overcome the restriction of soil characteristics in EKR.

Therefore, it is necessary to investigate the changes in physicochemical properties of natural soils, electric conditions variation, as well as Cd distribution in the remediation field. In this work, conventional EKR experiment was conducted as a preliminary process to determine the feasibility of electrokinetic technique to remediate cadmium pollution from different soils, and to investigate the relationship between soil characteristics and Cd distribution in soil specimen after treatment. The results may contribute to the feedback mechanisms of different soil types and broaden EKR application in Cd-polluted industrial sites.

2 Materials and methods

2.1 Soil sample

Red soil, black soil, yellow-brown soil, fluvo-aquic soil, and paddy soil were sampled from Hubei and Heilongjiang provinces in China. After natural air-dried, stones and grass roots removed, soils were grinded through 100 mesh sieve. Physicochemical properties of different soils are summarized in Table 1.

Cadmium nitrate solution was added in the soils to yield $500 \text{ mg}\cdot\text{kg}^{-1}$ of Cd polluted soils.

Table 1. Soil physicochemical properties in different treatments

Treat.	Soil type	Soil pH	Soil conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	Soil CEC ($\text{c mol}\cdot\text{kg}^{-1}$)	Organic matter content (%)
1	red soil	5.56	106	21.1	1.83
2	black soil	6.88	53	24.6	3.85
3	yellow-brown soil	5.71	88	22.0	1.66
4	fluvo-aquic soil	6.13	344	21.6	2.58
5	paddy soil	5.25	303	33.9	2.19

2.2 Electrokinetic experiments

Five treatments of different soil types were set as experiment treatments (Table 1). Each soil sample was compacted within the soil chambers for 30 days until stabilized. 0.1 M of citric acid was added in the electrolyte chambers on both sides as electrolyte solution, and a proper amount of distilled water was added to control soil moisture content by 35%.

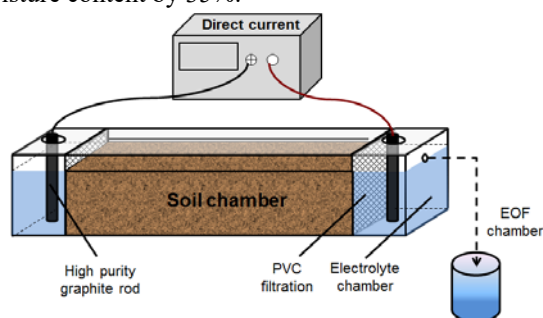


Fig.1. Scheme of electrokinetic experimental apparatus

Experimental device (Fig. 1) were a series of PVC electrolytic chambers with a soil chamber of 20 cm (length) \times 10 cm (width) \times 10 cm (height), and two graphite

electrodes chambers were set on both sides (10 cm \times 10 cm \times 5 cm). Direct current was used as power supply, and potential gradient was set to 1 V cm^{-1} , with high purity graphite rod as positive and negative electrode materials. During 20 days of experiments, electrical current and electroosmotic flow (EOF) were monitored.

2.3 Analytical methods

After experiment, each soil sample was divided into five portions, from cathode to anode at equal intervals and labeled as S1~S5, respectively. After dried in air, and sieved with a 2 mm mesh, soil physicochemical properties and Cd content were measured.

Soil physicochemical properties were detected using the analytical method of agrochemical properties of soil as follows [22]: A mass of 5g of the soil (dry weight) was mixed with 12.5g of distilled water (soil-to-liquid ratio of 1 to 2.5), and then soil pH was detected by a pH meter. Soil electrical conductivity (soil-to-liquid ratio of 1 to 5) was also detected by a conductivity meter. Soil organic matter was measured by the oil bath-potassium dichromate thermal oxidation method [22]. Soil cation exchange capacity (CEC) was measured by barium chloride-sulfuric acid exchange method [23].

Soil samples were digested with HF-HNO₃-HClO₄ and Cd content were measured following the method of National Standard of the PR China [24].

2.4 Relevance analysis

SPSS 19.0 software was used, and Pearson correlation analysis was carried out to understand the relationship between soil physicochemical properties and Cd content.

3 Results and discussion

3.1 Electrical current

Electrical current of the five types of soil during EKR was monitored. Due to desorption of ions on the surface of soil particles and directional migration of these ions in the electric field [25], a higher current intensity on the early stage of the experiment was observed (Fig. 2). The rapid increase of current intensity in paddy soil and fluvo-aquic soil may be related to their higher conductivity [26-27], as shown in Table 1. After reached a maximum value, the current intensity decreased gradually as the ions migrated from the soil chamber and/or OH⁻ combined with H⁺ ions to yield H₂O. At the end of EKR process, the current intensity in paddy soil, fluvo-aquic soil and yellow-brown soil treatments decreased close to zero, which may be ascribed to the migration of most anions or cations into the cathode or anode electrolyte, or the formation of hydroxide precipitation in the soil, thereby weakening of the current intensity. It was found that electromigration played a leading role in the removal of anions and cations in EKR [20]. The current intensity in red soil and black soil treatments maintained a relatively high level (>10mA) on the later stage of EKR, that may be beneficial to the removal of Cd.

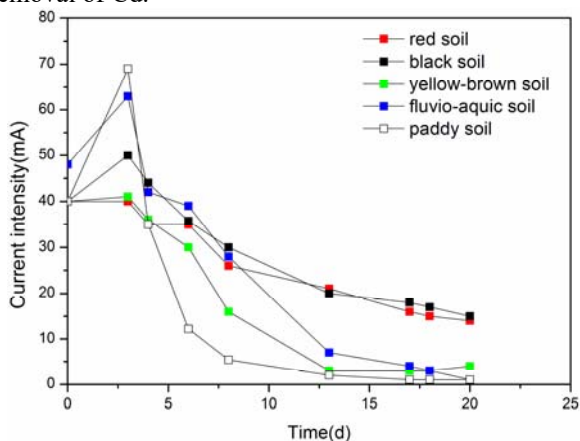


Fig.2. Current intensity of five soil treatments

3.2 Electroosmotic flow

EOF is the movement process of pore liquid from anode to cathode, and it is another important mechanism of heavy metal migration in EKR [16]. During the first 5 days, large amount of EOF was collected in all treatments (Fig. 3), among which the EOF volume in red soil

treatment was slightly higher than the others. The EOF in paddy soil and fluvo-aquic soil kept a sustained and stable growth throughout the later stage of remediation. Yang et al. [20] suggested that electroosmosis just played a major role in the first two weeks, and then electromigration continued to play its part in the movement of metal ions. That is to say, the effect of EOF on Cd ions migration in the system is not so obvious on the later stage of the process.

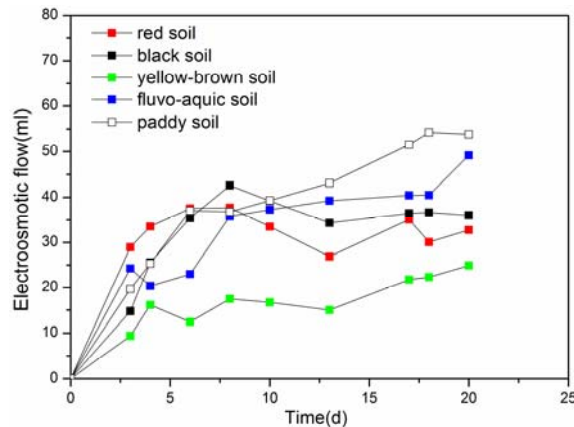


Fig.3. EOF volume of five soil treatments

Furthermore, for there is a quantitative relationship between EOF and system voltage [28], the difference of EOF under the same electric field is mainly affected by soil coefficient of electroosmotic permeability, which may bring about different ability of transporting soluble heavy metal ions. In order to compare electroosmotic abilities affected by soil types, the electroosmotic permeability (K_e) value was calculated based on the method offered by Weng et al. [29]. As shown in Table 2, the electroosmotic permeability varies between 1.05×10^{-6} and $5.82 \times 10^{-6} \text{ cm}^2/(\text{s}\cdot\text{V})$. A relatively high K_e value was found in paddy soil, and a low K_e value was observed in yellow-brown soil. K_e value as is known to be related to the soil types, soil mineral compositions, pore size and distribution of its particles, as well as the interaction of soil-water-electrolyte system [30]. Weng, et al. [31] reported that the formation of SDS micelle was capable of enhancing K_e value in the EKR system, by increasing the zeta potential of the soil particles, which determines the velocity of fluid flow between soils [32] and subsequently affects the removal rate of heavy metals.

Table 2. K_e values in different treatments

Treat.	1	2	3	4	5
$K_e \times 10^{-6} \text{ cm}^2/(\text{s}\cdot\text{V})$	2.18	1.91	1.05	3.49	5.82

3.3 Soil pH

Soil pH is one of the most important factors influencing EKR of heavy metal contaminants. In the experiment, citric acid was added to control the pH value of soil and also to combine with Cd to form soluble citrate [33-34], thereby accelerating the migration of Cd ions in the electrical field and enhancing the EOF [9]. Fig. 4 shows that the pH values in red soil, black soil and

yellow-brown soil in the same section are generally lower than those in other soils. From section S2 to section S5, the pH values in paddy soil and fluvo-aquic soil greatly increased and remained in alkaline condition of pH 7.0-9.0. This pH condition might make it difficult to drive Cd ions to migrate freely or desorb from soil particles to some extent.

However, pH values in red soil, black soil and yellow-brown soil were different from the other two treatments, that is, the soil pH was acidic (pH 4.0) at S1-S4 and suddenly changed to weak alkaline (pH 8.5) near cathode. pH value in these treatment soils maintained a lower acidic environment under electrical condition may be beneficial to the removal of Cd.

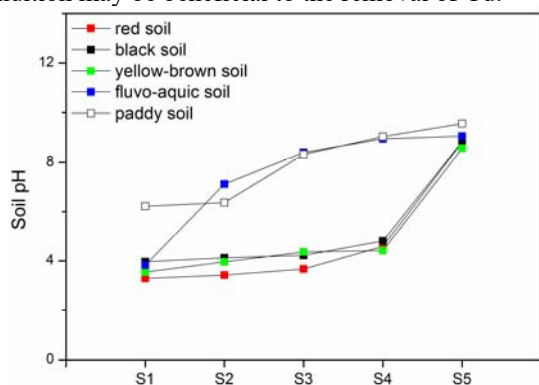


Fig.4. Soil pH in each section (S1~S5 means from anode to cathode, the same as below)

3.4 Soil CEC

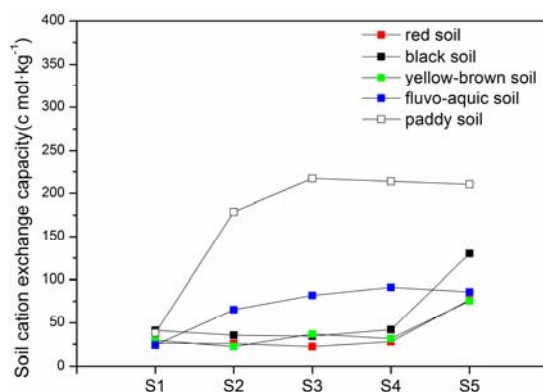


Fig.5. Soil cation exchange capacity in each section

Soil CEC is the total amount of cations adsorbed by soil colloids, which may reflect the buffer capacity of soil. Compared with other soils, CEC contents in paddy soil and fluvo-aquic soil were higher than the other three treatments, and it increased gradually from anode to cathode (Fig.5). That was somewhat similar to the trend of pH (Fig.4). CEC may be another important factor affecting the efficiency of EKR of heavy metals. With the increase of soil CEC, the ability of cation adsorption and distribution will be enhanced, and the amount of Cd adsorbed by soil will be improved, thus inhibiting the migration of Cd [35]. However, few researchers focused on this index.

3.5 Soil organic matter

Fig. 6 shows organic matter content of soil specimen in five treatments. Among them, the content of organic matter in black soil, fluvo-aquic soil, and paddy soil is generally higher than that of in red soil and yellow-brown soil. It was similar to the changes of organic bound Cd measured by Tessier extraction method in our previous experiments [21]. It may be due to the Cd complexes with oxygen-containing functional groups (carboxyl, phenol, hydroxyl, etc.) in soil organic matter [36], which promotes the transformation of Cd from water-soluble and exchangeable state to organic bound state [37]. Another possible reason is that Cd adsorbed on soil particles leads to a decrease in mobility [38]. The content of organic matter, carbonate and mineral components in soil will have a certain impact on EKR [37]. Whereas heavy metals also have a feedback regulation mechanism on soil, and their accumulation in the soil will weaken the mineralization rate of organic matter, resulting in an increase in its content [39].

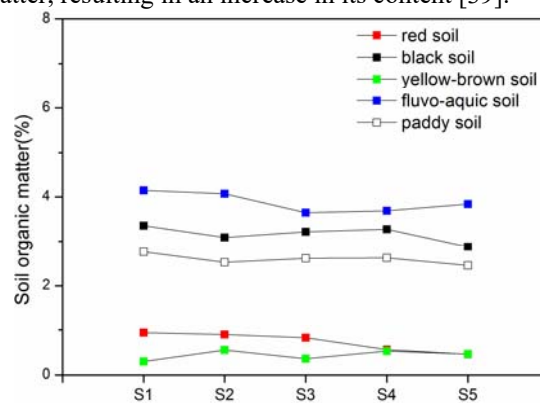


Fig.6. Soil organic matter in each section

3.6 Soil conductivity

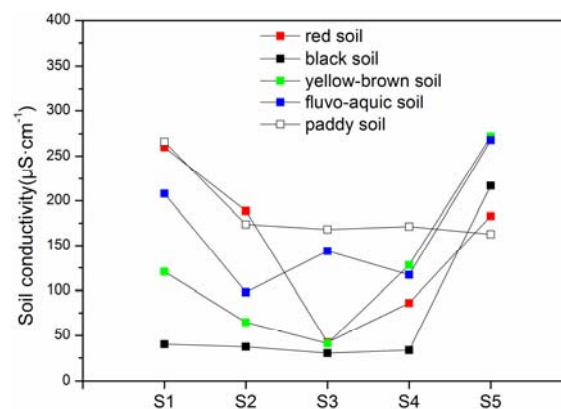


Fig.7. Soil conductivity in each section

Fig. 7 presents soil conductivity of the five treatments. As seen in the figure, the conductivity value was higher in soil section S1 and S5, compared with that in section S2-S4. This distribution may be ascribed to the H⁺ near cathode (S5) and OH⁻ near anode (S1) brought about by water electrolysis. After citric acid was added and EKR process finished, the conductivity value in red soil, black soil and yellow-brown soil all increased, this was consistent with observation by Iannelli et al. [40], probably because these soils were rich in Fe, Al or

mineral components. When the soil environment is acidic (pH 3.3), Fe and Al ions will migrate to the cathode in large quantities, thus forming obvious alkaline cation migration zones and acid anion migration zones [35]. Zhou et al. [14] found that by adding 10 mM CaCl₂ would enhance Cu removal from EKR system. It may be ascribed to the reason that ions in soil specimen would enhance the electrical intensity for migration of heavy metals. In contrast, the electrical conductivity value in paddy soil and fluvo-aquic soil did not increase significantly, which indicated that the velocity of ion migration was slow and it might be related to its weak alkaline pH condition. Variation of conductivity in black soil is similar to the distribution of pH value showed in Fig. 4: in the alkaline condition of anode region, the conductivity level is low; in the acidic condition of anode region, the conductivity level is high. This could be explained that most cations in black soil might have migrated out of the soil and into the cathode electrolyte chamber, while anions moved slowly, that were mainly concentrated near the anode.

3.7 Cd removal efficiencies

Removal efficiencies of Cd under different soil conditions are shown in Table 3. After 20 days of EKR, Cd was completely removed from red soil chamber near the anode section and its major part was found near the cathode. However, Cd residues in the paddy soil and fluvo-aquatic soil were higher than that in other treatments, most likely due to the poor pH condition in these soils. In addition, Cd residues in fluvo-aquatic soil sample of section S2 and yellow-brown soil sample of section S4 suggested that “focusing effect” might occur in these sections, where distributed large amount of hydroxide precipitation of Cd.

The overall removal efficiencies of Cd from red soil, black soil, yellow-brown soil, fluvo-aquatic soil and paddy soil were 80.8%, 79.3%, 78.2%, 62.7%, and 74.1%, respectively (Table 3). This indicated that the EKR technique might have enormous potential in different Cd-contaminated soils. However, the difference of removal efficiencies between five treatments may originate from soil pH, soil conductivity, surface charge of soil, etc. Take fluvo-aquic soil for example, the

removal efficiency of Cd within it is slightly lower than that of the other treatments, which may be related to its unique soil properties such as pH and/or organic matter. The variation of soil pH detection can explain the reason why the removal rate of Cd in fluvo-aquic soil and paddy soil is not high, that is, the mobility of Cd in weak alkali state is poor. On the contrary, red soil, black soil and yellow-brown soil sustained a lower acidic condition under electrified, which is very beneficial to the removal of cadmium. As for their internal relationship, this will be discussed later.

Table 3. Soil physicochemical properties in different treatments (S1 ~S5 represent anode to cathode)

Treat.	Cd Removal efficiency (%)					Aver.
	S1	S2	S3	S4	S5	
1	100.0	100.0	99.9	97.0	7.1	80.8
2	99.4	99.6	92.0	53.6	51.7	79.3
3	99.7	99.5	99.4	18.6	73.6	78.2
4	85.7	14.8	57.7	72.9	82.5	62.7
5	74.5	80.3	83.9	68.5	63.3	74.1

3.8 Correlation analysis

Correlation analysis of H⁺ concentration, CEC, conductivity, and organic matter between with Cd concentration at S1~S5 sampling points of five types of soils was carried out by SPSS software. Results are shown in Table 4. The correlation coefficients of H⁺ concentration with soil Cd concentration and CEC were -0.462 and -0.457, respectively. It is further confirmed that the soil pH is an important factor affecting the EKR of Cd polluted soil. It has great influence on the development of different physicochemical processes such as precipitation, dissolution, adsorption, desorption or ion exchange [41]. Moreover, pH value determines chemical forms of the compounds in the system. Therefore, it also determines the transport process of these compounds in EKR.

In addition, there is an intrinsic relationship between H⁺ concentration and CEC distribution in soil. The results also explained the similarity of trends in soil pH and CEC (Fig. 4 and Fig. 5). However, there was no significant correlation between other indexes and Cd concentration.

Table 4. Pearson correlation analysis between soil physicochemical properties and Cd concentration (n=25)

Items	H ⁺ concentration in soil	Soil conductivity	Soil CEC	Soil organic matter	Cd concentration
H ⁺ concentration in soil	1				
Soil conductivity	0.081	1			
Soil CEC	-0.457*	0.293	1		
Soil organic matter	-0.383	0.013	0.267	1	
Cd concentration	-0.462*	0.141	0.214	0.078	1

Note: Significant correlation exists between "*" at 0.05 level in the table.

4 Conclusions

From this experiment about Cd removal by EKR, the conclusions have been summarized as follows:

(1) In the process of EKR, the soil pH value, conductivity and CEC in fluvo-aquic soil and paddy soil were generally higher than those in black soil, yellow-brown soil and red soil, which indicated that the physicochemical properties are related to the effect of EKR.

(2) Removal efficiencies of Cd from red soil, black soil, yellow brown soil, fluvo-aquic soil, and paddy soil were 80.8%, 79.3%, 78.2%, 62.7%, and 74.1%, respectively. It showed that the EKR is an efficient technology for removing Cd from natural soils with different properties.

(3) Among the five types of soils, the correlation analysis confirmed that the concentration of H^+ is negatively correlated with the distribution of Cd in soil, and it also has a significant correlation with the distribution of CEC.

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