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Remediation of copper contaminated kaolin by electrokinetics coupled with permeable reactive barrier

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Abstract

Electrokinetics is an in situ soil remediation technique by which the flow direction of the pollutants can be controlled and the soil with low permeability can be treated. In this study, the remediation of copper contaminated kaolin by electrokinetic process coupled with activated carbon permeable reactive barrier (PRB) was investigated. The experimental results showed that the integration of PRB with electrokinetics successfully removed copper from kaolin with pH control of the catholyte. The average removal rate reached the highest of 96.60% when the initial Cu^{2+} concentration was 2000 mg/kg. Compared to the electrokinetic process without PRB, the application of the coupled system could reduce the pollution of the electrolyte.

Keywords: Electrokinetics; Permeable reactive barrier; Soil remediation; Heavy metal

1. Introduction

Soil is the basic environmental elements constituting ecosystem, and the important material basis of human being surviving and developing. However, soil contamination with heavy metals and organic pollutants has become one of the major environmental and human health concerns worldwide[1]. Currently, various technologies for soil remediation have been developed, including solidification/stabilization[2], phytoremediation[3], soil washing[4], bioremediation[5] and electrokinetics (EK)[6].

EK is a promising technology to remediate fine-grained soils contaminated with inorganic, organic, and mixed contaminants, which is particularly suitable for low-permeability clay and silt soils. The EK process involves a direct-current electric field imposed on the contaminated soil, and the pollutants migrate towards the side of the system by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis[7]. Therefore, the

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flow direction of the contaminants can be controlled, and the remediation seldom brings secondary pollution. It has become an important development direction of soil remediation.

Studies on the electrokinetic remediation of contaminated soils indicate that many factors can affect the process and the removal efficiency. Many researches focused on the way how to improve the efficiency, reduce costs and facilitate the applicability, and some prove to be effective, such as: (1) controlling the pH of the electrolyte[7]; (2) adding surfactants, complexing agents (chelating agents) or high molecular polymer[8,9]; (3) application of an combined system, such as EK-bioremediation[10], EK-oxidation/reduction[11,12] and EK-PRB[13,14,15]. The integration of PRB with EK provides the capability for enrichment or detoxification of the contaminants with different kinds of PRB materials during the remediation, which makes it possible to treat soil contamination with complex pollutants[16]. The remediation using Pd/Fe PRB coupled with EK was studied to remove pentachlorophenol[13] and hexachlorobenzene[15] from the soil, and the dechlorination of the pollutants was proved. Some adsorbents were used as PRB such as carbonized foods waste[17], acalcined hydrotalcite[18], and activated bamboo charcoal[16], which facilitated the removal of heavy metals (Cu^{2+}, Cr^{6+}, Cd) from the soil during the EK remediation.

In this study, a combined system of EK-PRB with activated carbon was used to remediate copper contaminated kaolin. The activated carbon serves as an adsorbent of the contaminant during the electroosmosis and electromigration process, reducing the pollution of the electrolyte. This study aims to investigate the effects of operating conditions on the remediation, the removal rates of the contaminant and the change of the soil characteristics for this EK-PRB system.

2. Materials and methods

The schematic diagram of the lab-scale reactor is shown in Fig. 1. The reactor consists of three compartments: the anolyte cell (80 mm × 100 mm × 80 mm), the soil cell (250 mm × 100 mm × 80 mm), and the catholyte cell (80 mm × 100 mm × 80 mm). The filter paper was placed between the soil and the electrode compartments to prevent soil particles from penetrating into the electrolyte cells.
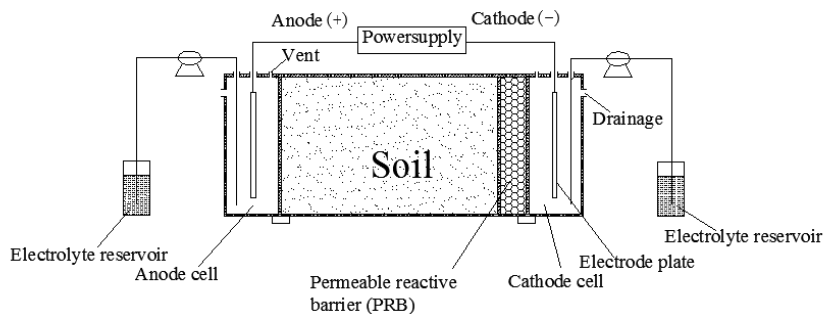

Fig. 1. The schematic diagram of the lab-scale electrokinetic reactor

The kaolin used in this study was produced by Sinopharm Chemical Reagent Co., Ltd in China. Before being packed in the cell, the kaolin was added with $Cu(NO_3)_2 \cdot 3H_2O$ at a certain Cu^{2+} initial concentration (mg Cu^{2+}/kg kaolin) and a moisture content of 40%. After being packed in the cell, the kaolin was balanced with $NaNO_3$ solution (0.1 M) in both sides of the electrode compartments for 24 hours.

A series of experiments were performed under different operation conditions (Table 1). Activated carbon was used in some experiments (EK1~EK3) to develop the PRB system. The soil cell was loaded with 1500 g kaolin for EK0 and 1200 g kaolin for EK1~EK3. The Electrolyte solutions for the anode and the cathode were prepared with $NaNO_3$ (0.1 M), and refreshed with $NaNO_3$ (0.1 M) and citric acid-sodium citrate buffer solution (pH = 5) respectively by two peristaltic pumps at a flow rate of 1.67 mL/min during the remediation process. Two graphite plates (90 mm × 80 mm × 5 mm) were used as the anode and the cathode. The experiments were run at a constant voltage gradient of 1.0 V/cm for 4 days.

Upon the completion of the remediation process, the kaolin was separated equally into four (EK1~EK3) or five (EK0) sections, and a fraction of each section was taken to determine the soil pH, water content, electrical

conductivity and the residual Cu concentration. The soil samples were dried at 50 ºC, ground with an agate mortar and digested with HNO_3-HF-$HClO_4$ for determination of Cu concentration by ICP (iCAP6300, Thermo Scientific, USA). The pH of the electrolyte and the soil were measured using a pH meter (PB-10, Sartorius, Germany). The electrical conductivity of the soil was measured using a conductivity meter (FE30, Mettler-Toledo, China). The electric current data during the remediation processes were measured by a digital multimeter.

Table 1. Summary of the experimental conditions applied.

Experiments	Cu^{2+} (mg/kg)	Activated carbon (g)	Duration (d)	Voltage gradient (V/cm)
EK0	1000	None	4	1
EK1	1000	82	4	1
EK2	1500	82	4	1
EK3	2000	82	4	1

3. Results and discussion

3.1. Soil pH

The distribution of soil pH after the remediation experiments is shown in Fig. 2. The soil pH value decreased during the treatments compared to the initial value of 5.6, and the soil pH of most sections was between 3 and 4. In general, the pH of soil close to the anode was lower than that close to the cathode due to the generation of proton ions via water electrolysis at the surface of the anode ($2H_2O \rightarrow 4e^- + 4H^+ + O_2$). The proton ions generated at the anode were transported towards the cathode and the soil pH gradually decreased from the anode side. The catholyte pH increased from 6.4 at first and then decreased to a steady value of around 5.5 after 2 h during the tests since the hydroxide ions were generated via water electrolysis at the cathode ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$) and neutralized by the citric acid-sodium citrate buffer solution. Compared to the EK process without PRB, the tests of EK-PRB exhibited a little higher soil pH, probably because the activated carbon in PRB could adsorb some of the hydroxide ions generated at the cathode that migrated towards the anode. Our previous study showed that the removal rate of Cu could be affected since the copper hydroxide formed due to the migration of the hydroxide ions through the soil without pH control at the cathode. It has been reported that a low pH environment can be generated in soil of low acid/base buffer capacity and extraction of metals can be achieved with a reasonable degree of success[7]. Therefore, controlling soil pH is very important for the success of EK remediation.
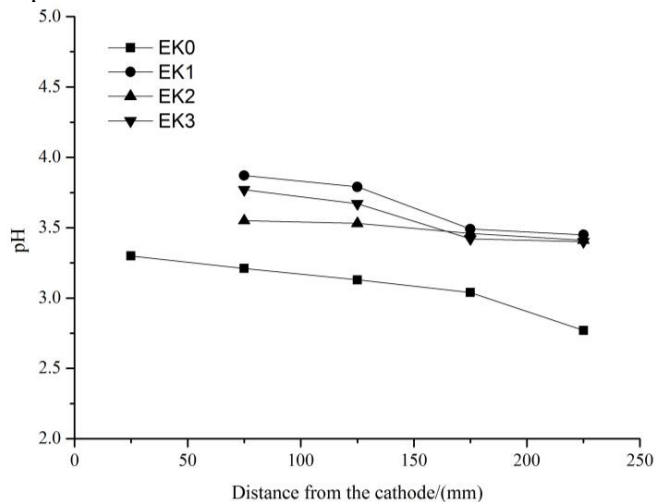

Fig. 2. The soil pH of different section after the operations.

3.2. Electrical conductivity of the soil

After 4 days of operation, the electrical conductivity of kaolin of different section presented increasing trend from the cathode to the anode (Fig. 3). The results illustrated that the content of free ions in kaolin close to the anode was higher than that near the cathode. It was because that the acid condition facilitated the dissolution of ions in the soil. Furthermore, the anolyte was refreshed with $NaNO_3$, and the protons (H^+, Na^+) were transported towards the cathode. The electrical conductivity was higher with EK than that with EK-PRB, probably because of the lower soil pH in EK test.
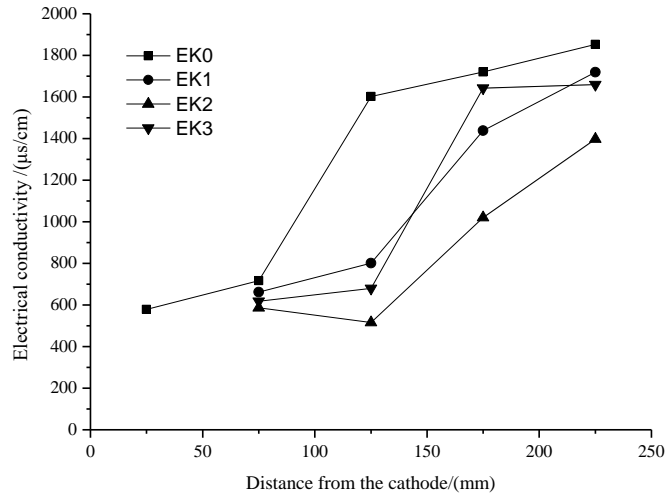

Fig. 3. The electrical conductivity of soil after the operations.

3.3. Water content of the soil

Fig. 4 shows the water content of the soil at different section after the experiments. Compared to the initial soil water content of 40%, after the operations of 4 days, soil water contents of most sections dropped slightly after the tests, probably because the heat generated during the electrokinetic process evaporated water. The water contents of the soil adjacent to the electrolyte cells were higher than those of the middle soil. Soil water content is an important factor that alters the electroosmotic flow rate and hence decontamination of the soil by EK process[16]. In this study, water of the soil could be supplemented through the refreshment of the electrolyte. Considering the contamination of the electrolyte can be reduced by using EK-PRB process (shown in 3.4), the recirculation of water is considered to be adopted in the future study.
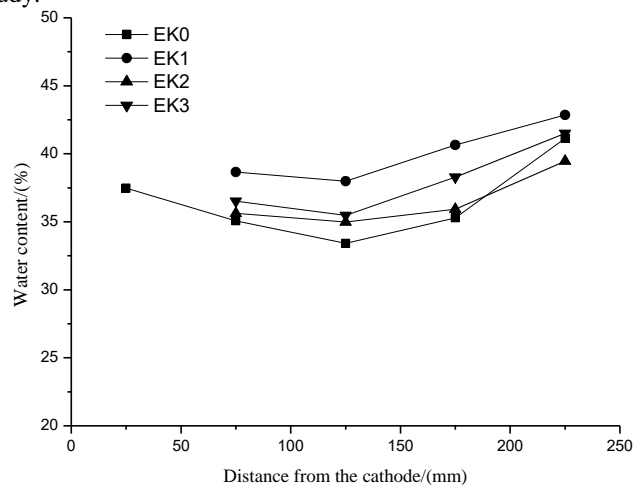

Fig. 4. The water content of soil at different section after the operations.

3.4. Removal of Cu from the soil

After 4 days of remediation, Cu concentrations in the soil were much lower than the initial ones. Both EK and EK-PRB operations prove to be successful in removing Cu from the soil (Fig. 5). The removal efficiency can be calculated by the following Eq. (1):

$$\eta = \frac{c_0 - c_t}{c_0} \times 100\% \tag{1}$$

where η is the removal efficiency, c_0 (mg/kg) the initial Cu concentration of the sampling point, and c_t (mg/kg) the final Cu concentration of the sampling point after EK remediation. The average removal rate for EK3 test reached the highest of 96.60%. As for EK1~EK3, the removal rates increased with the rise of the initial concentration of Cu^{2+}. Fig. 6 shows the cumulative mass ratio of Cu in the catholyte for EK0 and EK1, calculated according to Eq.(2):

$$\text{The cumulative mass ratio} = \frac{\text{The cumulative mass of Cu in the catholyte (mg)}}{\text{The initial total mass of Cu (mg)}} \tag{2}$$

The cumulative mass ratio of Cu in the catholyte increased with the reaction time and reached 0.49 at the end of the test for EK0. Compared to the removal rate of Cu from the soil for EK0 (an average of 86.92%), the cumulative mass ratio of Cu in the catholyte was lower than the theoretical value due to the precipitation of Cu on the graphite electrode. The comparison of the results for EK0 and EK1 indicate that PRB filled with activated carbon has high adsorption capacity for Cu, reducing the pollution of the electrolyte and its further treatment. PRB is widely used in the groundwater treatment[19,20,21], and it is reported to be effective for the enrichment or detoxification of contaminants applied with EK remediation[13,14,18].
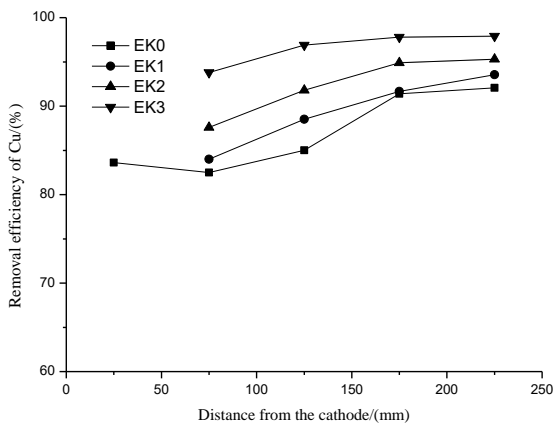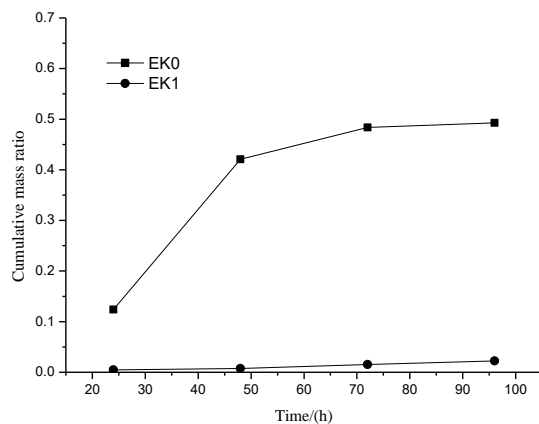

Fig. 5. The removal efficiency of Cu from kaolin

Fig. 6. The cumulative mass ratio of Cu in the catholyte

4. Conclusions

This study investigated the remediation of Cu contaminated kaolin with the integrated EK-PRB treatment. The removal efficiency of Cu increased with the rise of the initial concentration, and the average removal rate reached the highest of 96.60% after 4 days of operation with an initial Cu^{2+} concentration of 2000 mg/kg. The control of the catholyte pH using citric acid-sodium citrate buffer solution facilitated the removal of Cu from kaolin by preventing Cu^{2+} from precipitating. Furthermore, the use of PRB filled with activated carbon reduced the contamination of the electrolyte.

Therefore, the present study provided laboratory demonstration of the feasibility of removing copper from kaolin through the application of EK-PRB. Further experiments might be undertaken to treat the real contaminated soil and

analyze the economic feasibility.

Acknowledgement

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