Experimental study on electrokinetic remediation of Pb-contaminated kaolinite

Gang Li¹, Jia Liu² and Jinli Zhang³,⁴

¹ Shaanxi Key Laboratory of Safety and Durability of Concrete Structures, Xijing University, Xi’an, Shaanxi 710123, China;  
² School of Geological Engineering and Geomatics, Chang’ an University, Xi’an, Shaanxi 710054, China;  
³ State Key Laboratory of Coastal and Offshore Engineering, Dalian University of Technology, Dalian, Liaoning 116024, China  
⁴ Email: jlzhang@dlut.edu.cn

Abstract. The treatment of heavy metal pollution by electrokinetic remediation has the characteristics of low cost, easy operation and less secondary pollution and has broad application prospects. Electrokinetic remediation tests, and some combined with a permeable adsorbing layer were conducted to analyze the distribution patterns of conductivity, Pb(II), pH and moisture content in lead (Pb)-contaminated kaolinite. The influences of factors such as remediation time, type of fillers and location of a permeable adsorbing layer on the remediation effects of Pb-contaminated kaolinite were explored. The results reveal that the soil water content decreases with increasing energization time and that the water content near an anode chamber was highest, whereas that near a cathode chamber was lowest. When the test was conducted for 7 days, the conductivity near the cathode side was relatively high, whereas the Pb near the anode side was largely removed. Prolonged energization time was conducive to the removal of Pb. In an electrokinetic test, no alkaline region was detected in kaolinite. When a permeable adsorbing layer was placed in the middle of a soil sample, the removal effect was the best. Compared with bone char, a permeable adsorbing layer of calcareous sand significantly improved the Pb removal rate and effectively reduced energy consumption.

1. Introduction
With the rapid development of industrial technology in China, heavy metal pollution has become increasingly severe. According to the "National Survey Bulletin on Soil Pollution", published by the Ministry of Environmental Protection and the Ministry of Land and Resources of the People’s Republic of China in 2014, 16.1% of the total land area in China had above-standard heavy metal contents, 19.4% of arable land had above-standard heavy metal contents, 36.3% of the land surrounding enterprises that produce or use heavy metal shad above-standard heavy metal contents, and 21.3% of solid waste disposal site shad above-standard heavy metal contents[1]. Thus, the deterioration of soil quality in China is an alarming issue and environmental pollution problems are prominent, posing a serious threat to human life and property. As a common heavy metal element, lead (Pb) has long been used in industrial products such as batteries, dyes, construction materials and gasoline. It is widely distributed in soil, water and the atmosphere and can enter animal and human bodies through the food chain and drinking water, thus affecting human health and ecological safety.
Electrokinetic remediation is a new technology that has gradually emerged in recent years. An electric field is formed by placing a direct current (DC) at both ends of a soil sample. Contaminants in the soil migrate to the electrode sides by electro dialysis, electro migration and electrophoresis under the action of the electric field, thereby achieving remediation of the contaminated soil[2-3]. Ren et al. prepared Pb-contaminated soil samples and tested them under an electric field of 1 V/cm to study the effect of a citric acid-sodium citrate solution at different pH values on the electrokinetic remediation of the soil. They found that the lower the pH value, the better the removal efficiency of Pb[4]. Tan et al. remediated Pb-contaminated soil at an industrial contaminated site using electrokinetic and flushing jointed remediation. The results revealed that the concentration of Pb in the soil decreased from 410 ± 16 mg/kg to 252 ± 10 mg/kg, which was lower than the soil health risk assessment threshold of Chongqing[5]. Ammami et al. used citric acid as an electrolyte solution and 4.94 g/L TW20 as a flushing agent to improve the remediation efficiency of contaminated soil; the removal rates of cadmium (Cd), Pb and zinc (Zn) after 22 days of treatment were 38.6%, 33.4% and 51.6%, respectively[6]. Oh et al. used sonification (200 kHz)-electrokineic remediation to treat contaminated soil for 30 min, and the removal rates of arsenic (As), Cd, and Pb reached 25.55%, 8.01% and 34.90%, respectively[7]. Alcantara et al. found that the most effective flushing agents were 1% TW80 and 0.1 mol/L EDTA after comparing the effects of various agents on the remediation of Pb- and phenanthrene-polluted soils; the removal rates were 95.1% and 93.3%, respectively, which after 30 days of treatment[8]. Cang et al. compared the oxidation effects of flushing agents added to a cathode in pyrene and Pb co-contaminated soil and found that the best removal effect was achieved when an anode and cathode were supplemented with 10% HPCD and 0.5 mol/LNa$_2$S$_2$O$_8$; the removal rates of pyrene and Pb were 50% and 94%, respectively, which after 335 h treatment with pH controlled at 3.5[9]. Dong et al. achieved total removal rates of 72.8% and 81.7% for petroleum hydrocarbons and Pb respectively, which after 30 days of treatment using an electrokinetic remediation method and 0.1 mol/L EDTA added to the cathode, with pH controlled at 5.6[10].

In this study, the removal of Pb from Pb-polluted kaolinite was investigated using electrokinetic remediation tests. The distribution characteristics of conductivity, Pb(II), pH and water content in soil were the focus of analysis. The effect of energization time, type of filler material and position of the adsorbing layer on the remediation effect of Pb-contaminated kaolinite and the energy consumption during remediation were investigated. The research results may be used to promote the use of electrokinetic remediation in engineering applications.

2. Materials and methods

2.1. Test materials and equipment

The test used kaolinite produced from a kaolin mine in Jiahe, Xuzhou, China, where the liquid and plastic limits were 40% and 21%, respectively. The specific gravity was 2.57, the cohesion was 22.04 kPa, the internal friction angle was 16.25° and the coefficient of permeability was 4×10$^{-6}$ cm/s (The coefficient of permeability was measured by variable head method).

The test equipment mainly consists of a reaction chamber, a DC stabilized power supply, a voltage module, a current module, a solution-replenishing device, an overflow-collecting device, and a data collection system (Figure 1). The tests were performed using either a titanium electrode or a graphite electrode. The area of the electrode was 100×70 mm$^2$. The reaction chamber was constructed of polyvinyl chloride (PVC) plates, with a size of 310×90×120 mm$^3$. The effective size of the soil sample chamber was 100×70×100 mm$^3$, and divided into the zone of T1, T2, T3, T4 and T5, respectively. The effective size of the electrolysis chamber was 70×70×100 mm$^3$. The soil chamber and the electrolysis chamber were separated by filter paper, a glass fiber membrane filter, and a porous PVC plate to prevent soil particles from entering the electrolysis chamber. A solution-replenishing hole was placed at the bottom of the cathode chamber and an overflow hole was placed on the sidewall. The electrolyte was pumped into the electrolysis chamber at a constant rate by a peristaltic pump. The excess
The electrolyte was discharged from the overflow hole to eliminate the influence of the hydraulic pressure difference on the test results.

![Electrokinetic remediation device.](image)

**Figure 1.** Electrokinetic remediation device.

### 2.2. Experiment method

The prepared PbNO₃ solution was added to 600 g of kaolin soil. The mixture was stirred for 30 min with a -0.1 MPa vacuum mixer. The gas in the soil was extracted to saturate the sample to prepare a contaminated soil sample with a water content of 45% and an initial pollutant concentration of 1000 mg/kg. During sample loading, the sensors, separator, and the glass fiber membrane filter were first installed in the test device, and then the sand sample was loaded into the reaction chamber in 5 lots. The sand sample was compacted during loading to prevent the generation of air bubbles. The electrolyte was then filled into the anode and cathode chambers and aged for 24 h before the test started. The electrolyte used in the combined remediation test was a mixture of 0.1 mol/L KNO₃ solution and citric acid solution (pH=4.8). During the experiment, the hydraulic head of the electrolyte in the anode chamber was kept constant using a Marriotte bottle. The electrolyte solution from the replenishing reservoir was pumped to the cathode chamber at a constant rate by the peristaltic pump. The pumping rate was 0.8 mL/min. The test scheme is summarized in Table 1.

The procedure of conductivity measured as follows, 5.000 g of dried sample was placed in a 50 ml centrifuge tube, and 25 ml distilled water was added. The centrifuge tube was put into a rotary mixer with constant speed, and rotated evenly for 2 hours until the soil and water were fully mixed. Subsequently, the centrifuge tube was centrifuged at a rate of 5000 r/min for 10 min, and the supernatant was extract for conductivity measured by a conductivity meter.

**Table 1.** Electrokinetic remediation schemes for kaolinite.

| Test | Time/d | Permeable adsorbing layer | Location |
|------|--------|---------------------------|----------|
| EK1  | 3      | ——                        | ——       |
| EK2  | 5      | ——                        | ——       |
| EK3  | 7      | ——                        | ——       |
| EK4  | 7      | Bone char                 | Cathode  |
| EK5  | 7      | Bone char                 | Center   |
| EK6  | 7      | Calcareous sand           | Center   |
The procedure of Pb(II) content measured as follows, 5.000 g of dried sample was placed in a 50 ml centrifuge tube, and 20 ml of nitric acid was added. The centrifuge tube was put into the ultrasonic oscillator with 30 min, and then placed in a thermostatic oscillator oscillation for 2 hours to fully digest. Subsequently, the centrifuge tube was centrifuged at a rate of 5000 r/min for 10 min. The supernatant was extract for Pb(II) concentration measured by atomic absorption spectrophotometer.

2.3. Calculation of removal rate and energy consumption
The Pb(II) removal rate in the electrokinetic remediation test was calculated as follows:

\[ E_r = \left( \frac{m_0 - m_e}{m_0} \right) \times 100\% \]  

where \( E_r \) is the removal rate, %; \( m_0 \) is the initial mass of pollutant, mg; and \( m_e \) is the mass of the residual pollutant, mg.

The energy consumption in the electrokinetic remediation test was calculated as follows:

\[ E_c = \frac{1}{M_c} \int U I dt \]  

where \( E_c \) is the energy consumption to remove a unit mass of pollutant, Wꞏh/mg; \( M_c \) is the total removal of pollutant, \( M_c = M_0 - M_e \), mg; \( E_T \) is the total energy consumption, Wꞏh; \( U \) is the applied potential at time \( t \), V; \( I \) is the current at time \( t \), A; and \( t \) is the treatment time, h.

3. Results and discussion
3.1. Distribution of electric conductivity in kaolinite treated by electrokinetic remediation
During the electrokinetic remediation tests of Pb-contaminated kaolinite (with a Pb content of 1,000 mg/kg), the DC voltage of 20 V was applied to two ends of a soil sample. The electrodes were coated with titanium alloy, with a mixture of 0.1 mol/L KNO₃ and 0.035 mol/L citric acid as the electrolyte solution. In the tests, catholyte was supplemented at a rate of 0.8 mL/min using a peristaltic pump. The energization time was set at 3, 5 and 7 days. Figure 2 shows the soil electric conductivity distribution after electrokinetic remediation. The figure shows that the conductivity of the soil sample is related to the distance to the anode and the electrolysis time. At 3 d of the tests, the conductivity near the anode was high, whereas the conductivity near the cathode was very low. The high-conductivity zone moved toward the middle of the soil sample over time, whereas the conductivity was low in the vicinity of the electrodes. At 7 d of the tests, the high-conductivity zone appeared near the cathode. During the electrokinetic remediation, the chemical reactions occurred at the electrodes

\[ 2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \text{ (Anode)} \]  

\[ 2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \text{ (Cathode)} \]  

\[ M + H_2O \rightarrow MO + 2H^+ + 2e^- \]  

where M is the metal.

Figure 2. Conductivity distribution treated by electrokinetic remediation.
3.2. Distribution of Pb(II) in kaolinite treated by electrokinetic remediation
After each set of tests, the soil samples were sliced, and the residual Pb content of kaolinite was measured. The test results are shown in Figure 3. For the Pb-contaminated kaolinite remediated using the electrokinetic method, when the energization time was 3d, the Pb-enrichment zone appeared in the middle of the soil samples, whereas the Pb content was low near the electrodes. When the energization time increased, the Pb-enrichment zone moved in the direction of the cathode, which indicating that under the joint action of electroosmotic flow and electrophoresis, Pb(II) migrated from the anode to the cathode and entered the cathode chamber, and eventually depositing as a precipitate. When the energization time reached 7 d, Pb near the anode side had been largely removed and Pb had migrated in the direction of the cathode.

![Figure 3. Pb(II) distribution treated by electrokinetic remediation.](image)

3.3. Distribution of pH and water content in kaolinite treated by electrokinetic remediation
Figure 4 (a) shows the pH distribution in the kaolinite sample after the electrokinetic remediation test. The initial pH of the kaolinite used in the experiment was 7.69. After the test, the pH was less than 7, which is an acidic environment, and there was no alkaline region. With increasing energization time, the pH of the entire soil sample tended to be the same, primarily due to the presence of citric acid in the electrolyte. The water content distribution in the kaolinite sample after electrokinetic remediation is presented in Figure 4 (b). The soil samples had an initial water content of 45%. After 3, 5 and 7 d of electrokinetic remediation, the water content exhibited a decreasing trend. The water content near the anode chamber was highest, whereas that near the cathode chamber was lowest. The decrease in soil water content was primarily due to the evaporation caused by electroosmotic flow and heat generated during electrolysis.

![Figure 4. Distribution of pH and water content treated by electrokinetic remediation.](image)
3.4. Distribution of Pb(II) in kaolinite treated by combined electrokinetic remediation

To improve the efficiency of electrokinetic remediation, the permeable material with a high adsorption capacity for Pb(II) was added to the kaolinite samples. The permeable adsorbing materials used in the test included bone char and calcareous sand. Bone char was used in two groups of tests, placed near the cathode (EK4) and in the middle of soil sample (EK5). Bone char placed along the cross section of a soil sample was 30 g after compaction. Calcareous sand placed in the middle of the soil sample along its cross section (EK6) was 20 g after compaction. The experimental time was set to 7 d. A DC of 20 V was applied in the test. The electrolyte was a mixture of 0.1 mol/L KNO₃ and 0.035 mol/L citric acid.

Figure 5 shows the Pb distribution in kaolinite treated by combined electrokinetic remediation. As shown in the figure, when the permeable adsorbing layer is located in the middle of the soil sample, the Pb content in the soil sample is low in the area that is approximately 6 cm from the anode side, whereas the Pb content in the soil sample exceeds the initial Pb content in the area that is approximately 4 cm from the cathode side, which indicating that Pb(II) migrated from the anode to the cathode in the combined electrokinetic remediation tests. By comparison, Pb(II) removal was significantly improved when the permeable adsorbing layer was placed in the middle of the soil sample. When the bone char layer was placed near the cathode, the Pb(II) content was low along the entire length of the soil sample, but the overall removal rate did not significantly increase.

3.5. Distribution of pH and water content in kaolinite treated by combined electrokinetic remediation

Figure 6 shows the distribution of pH and water content in kaolinite treated by combined electrokinetic remediation. To prevent the forming of an alkaline region in the soil samples, citric acid was used as a buffer in the tests. Figure 6 shows that in the EK4 and EK5 tests, an alkaline region of a specific length appeared in the soil samples, whereas no alkaline region appeared in the EK3 and EK6 tests. The primary reason for the alkaline region was the consumption of H⁺ by complexation reaction and bone char decomposition. After adding calcareous sand to the middle of the soil samples, the pH of the soil samples gradually increased, but all soil samples remained in the acidic to neutral range. Upon completion of the tests, the water content in each group of soil samples significantly decreased. In comparison, the water contents of EK4, EK5 and EK6 were higher than that of EK3, because the currents of the former tests are all smaller than the latter, which leading to weaker electroosmotic effect and thus higher water contents in the EK4, EK5 and EK6 tests.

3.6. Energy consumption analysis

Figure 7 shows the curves of cumulative energy consumption versus time in the EK3-EK6 tests. As shown in the figure, the cumulative energy consumption rate in the tests gradually increases. The order of energy consumption accumulation is $E_{TEK3}=325.02$ W·h $> E_{TEK6}=298.23$ W·h $> E_{TEK5}=272.24$ W·h $> E_{TEK4}=16.48$ W·h. EK3 has the highest energy consumption and fastest accumulative energy
consumption rate. When EK5 and EK6 were remediated for 120 h, the energy consumption of EK5 was higher than that of EK6. After 5 d, the energy consumption of EK6 exceeded that of EK5, which may be explained by the CaCO₃ component in calcareous sand powder that easily reacts with H⁺ and citric acid to generate more free ions.

![Figure 6. Distribution of pH and water content treated by combined electrokinetic remediation.](image)

Table 2 presents the association between energy consumption and removal rate in the electrokinetic remediation tests. In comparing data related to EK1, EK2 and EK3, energy consumption per unit weight of kaolinite was reduced from 1.12 W·h·mg⁻¹ (EK1) to 0.61 W·h·mg⁻¹ (EK2) and 0.70 W·h·mg⁻¹ (EK3), and the removal rate increased from 13.41% to 34.63% and 46.36%, respectively. Therefore, under identical remediation conditions, the removal rate may be effectively improved by extending the remediation time. The unit energy consumptions of EK4, EK5 and EK6 were 0.04, 0.59 and 0.51 W·h·mg⁻¹, respectively. The removal rates of Pb(II) in EK5 and EK6 were both higher than that of EK3, and the removal rate of EK6 was 11.71% higher than that of EK3. This indicates that the introduction of a permeable adsorbing layer reduces energy consumption, and as an adsorbing layer, calcareous sand has a better remediation effect than bone char does. When calcareous sand adsorbs heavy metal ions, it also reacts with non target ions such as H⁺, thus improving the energy utilization rate.

![Figure 7. Energy consumption in the electroosmotic remediation tests.](image)

**Table 2.** Pb(II) removal rate and energy consumption in the electrokinetic remediation tests.

| Test | $E_r$/% | $E_r$/W·h | $E_r/(W·h/mg)$ |
|------|---------|------------|----------------|
| EK1  | 13.41   | 149.70     | 1.12           |
| EK2  | 34.63   | 212.17     | 0.61           |
| EK3  | 46.36   | 325.02     | 0.70           |
| EK4  | 37.04   | 16.48      | 0.04           |
| EK5  | 46.52   | 272.24     | 0.59           |
| EK6  | 58.06   | 298.23     | 0.51           |
4. Conclusions

(1) The conductivity of the soil sample is related to the distance from an anode and electrolysis time. Extending the energization time is beneficial in the removal of Pb(II). When tests were conducted for 3 d, the conductivity near the anode side was higher than that at the cathode side. When tests were conducted for 7 d, the conductivity near the cathode side was higher and the Pb near the anode side had been largely removed.

(2) After the electrokinetic remediation tests, the pH of kaolinite was less than 7, which indicates an acidic environment, and there is no alkaline region. The water content decreased with increasing energization time, and the soil near the anode chamber had the highest water content, whereas that near the cathode chamber had the lowest water content.

(3) In the combined electrokinetic remediation tests, when the permeable adsorbing layer was placed in the middle of the soil sample, the removal of Pb was significantly improved. As the permeable adsorbing layer, calcareous sand removed Pb more efficiently than bone char. Compared to scenarios without an adsorbing layer, the Pb removal rate by calcareous sand was 11.71% higher, and the energy consumption was effectively reduced.

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