



Influence of polarity exchange frequency on electrokinetic remediation of Cr-contaminated soil using DC and solar energy



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ABSTRACT

Electrokinetic remediation (EKR) is a remediation method that can effectively remove heavy metals from soil. Traditional EKR uses an external power source to consume electrical energy, in the present study, through the experiment of different electrode exchange frequency to remediate Cr contaminated soil, the effect of polarity exchange electric remediation and the influencing factors of Cr(VI) to Cr(III) conversion are discussed. Five experiments were conducted using DC power supply with conventional EKR (T1), DC power supply with polarity exchange EKR (T2, T3) and solar energy with EKR (T4, T5). The results showed that the T1 experiment had the maximum removal rate of total Cr (42.03 %) and Cr(VI) (85.50 %) but had an adverse effect on soil pH. T2, which exchanged polarity every 24 h, and T3, which exchanged polarity after 84 h, had smaller adverse effects on soil pH, but the removal efficiency was reduced due to repeated migration. The reduction of Cr(VI) to Cr(III) occurred during the EKR processes, the content of Cr(III) increased greatly. Furthermore, few differences were observed between DC power and solar power on the EKR experiments. Therefore, the combination of electrokinetics and solar energy is a feasible method for Cr-contaminated soil.

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1. Introduction

Soil is fundamental to human survival and development. Soil pollution caused by industrialization, urbanization, agricultural intensification and economic development was a serious threat to human health and environmental safety (Kim et al., 2012; Lee and Kim, 2010; Ma et al., 2018). Chromium is a toxic element that negatively affects animals and plants metabolic activities, Cr(VI) is oxidizability and high permeability to skin, and teratogenic and carcinogenic effects (Kaviyarasi et al., 2021; Shiv et al., 2021). Currently, soil heavy metal pollution was becoming more and more serious, which showed that the total exceeding standard rate was 16.1 %. Among these results, 19.4 % of the arable land sites exceeded the environmental quality standard (Zhou et al., 2018).

Electrokinetic remediation (EKR) was a relatively cheap, effective and environmentally friendly technology, it could effectively remediate heavy metals contaminated soil, even the soil with low permeability (Vocciante et al., 2017; Wang et al., 2019). In typical

EKR applications, electrodes were inserted on both sides of the soil, and low direct current was applied, so pollutants could reach the anode or cathode region through electromigration, electroosmosis and electrophoresis (Kim et al., 2015; Masi et al., 2017; Rezaee et al., 2019). The above process was accompanied by electrolysis reactions and geochemical reactions. The oxidation reaction occurs in the anode compartment ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$) to generate hydrogen ions (H^+), and the reduction reaction takes place in the cathode compartment ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) to generate hydroxide ions (OH^-) (Hassan et al., 2015; López-Vizcaíno et al., 2017; Villen-Guzman et al., 2015). H^+ and OH^- during EKR process divide the whole soil area into acidic and alkaline areas. Chemical precipitation and adsorption of heavy metals usually occurred under basic pH conditions, which could block the pore of soil and simultaneously result in the generation of focusing phenomenon (Li et al., 2020), thus preventing the migration of heavy metals and reducing the efficiency of remediation. Through polarity exchange, the decrease of pollutant removal efficiency caused by focusing effect and soil acidification can be effectively reduced, which reverses the polarity of the electric field and neutralizing the H^+ and OH^- generated (Cai et al., 2015; Lu et al., 2012; Zhou et al., 2018).

Polarity exchange electrokinetic remediation can effectively reduce the accumulation phenomenon in the cathode region of soil,

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Table 1
The soil physical and chemical properties.

Parameters	Contents
Soil type	loam
pH	6.56
Water content (%)	30.00
Total organic carbon (mg/g)	0.5898
Cr^{6+} (mg/kg)	905.13
Cr^{3+} (mg/kg)	235.19
Total Cr (mg/kg)	1140.32

enhance the current, and improve the removal efficiency of Cr in the soil, especially the removal rate of Cr(III). Zhou et al. (2018) used traditional electrokinetic remediation and polarity exchange electrokinetic remediation to test Cr-contaminated soil. Electrokinetic parameters such as current value, electroosmosis, soil pH value, and removal efficiency of three valence states of Cr were studied. The removal efficiency of Cr in different valence states was improved by using polarity exchange electrokinetic remediation instead of traditional electrokinetic remediation technology, and the removal rates of total Cr was 43.65 %, Cr(VI) was 91.88 % and Cr(III) was 19.32 %.

The problem of polarity exchange electrokinetic remediation was the reduced remediation efficiency due to the repeated migration of pollutants. Lu et al. (2012) found that the removal of chromium 88 % and cadmium 94 % under the polarity exchange electrokinetic every 48 h, and the concentration of pollutants in the middle part significantly higher than that at both ends. This meant that the technology could reduce the focusing effect of pollutants, but it brought about the problem of reciprocating migration of pollutants.

Many studies had been conducted on the EKR of heavy metals, but only paid little attention to Cr-contaminated soil and polarity exchange electrokinetic remediation. In addition, the conversion between Cr(VI) and Cr(III) during the polarity exchange electrokinetic remediation process has rarely been discussed, and few studies have been conducted on the evolution of current with the concentration of Cr in electrolytes and the factors affecting pH during the process. In this study, the feasibility of using direct current and solar exchange electrodes for remediation of chromium-contaminated soil was investigated in comparison. The results would help to understand the effect of different valence chromium forms on the removal of chromium in soil.

2. Methods and materials

2.1. Experimental soil

Chromium-free soil was from Huaqiao University, Fujian Province, China, with a depth of 20 cm. The grain size analysis showed that the texture was loam. The samples were dried at room temperature without rocks, weeds and plant roots, and then crushed to remove large particles through a 10-mesh (2 mm) sieve.

The contaminated soil was prepared by adding $\text{K}_2\text{Cr}_2\text{O}_7$ solution to the soil, and the content of chromium in the prepared soil reached 1200 mg/kg. After the soil was stabilized for a period of time, the total concentration of Cr and Cr^{6+} was 1140.32 mg/kg and 905.13 mg/kg, which indicated that there was a certain chemical reduction process in the process of soil stabilization, soil properties are shown in Table 1.

2.2. Materials

All chemicals were analytical grade or higher (Xilong Scientific Co., Ltd, China, and Sinopharm Chemical Reagent Co., Ltd,

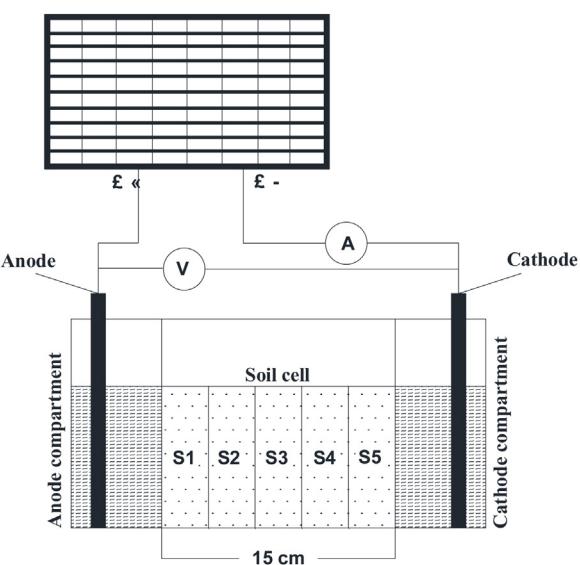


Fig. 1. Schematic diagram of the experimental reactor for EK remediation using solar energy.

China.) and used as purchased without further purification. Ultra-pure water was used to this research work.

2.3. Experimental setup

Fig. 1 showed a schematic diagram of the experimental reactor for the EK remediation using solar energy. The EKR experimental system was composed of one Plexiglas reactor used as a soil cell (inner length of 15 cm, width of 10 cm, and height of 10 cm), two electrode compartments (inner length of 5 cm, width of 10 cm, and height of 10 cm), one DC power supply (UTP3315TFL, UNI-T Group Co., Ltd, China) or solar cell, and two multimeters (UT890D, UNI-T Group Co., Ltd, China). Graphite sheet electrodes were used as the working electrodes in the experimental system (inner length of 1 cm, width of 10 cm, and height of 10 cm). Two pieces of filter paper were placed in the soil cell between the two electrode compartments to separate the treated soil and working fluids. One multimeter was connected in series to monitor the real-time electric current. Another multimeter was connected in parallel to monitor the voltage regularly.

Solar panels were made of polysilicon 35 cm long, 25 cm wide and 2.5 cm thick. The rated voltage was 18 V, the rated peak power was 10 W, and the photoelectric conversion efficiency was 190.24 %.

2.4. Electrokinetic remediation

The experimental conditions were shown in Table 2. For Tests 1–3, EKR was carried out with a DC power supply, while for Test 4 and Test 5, EKR was performed with a solar cell. The solar panels were installed on the balcony (the fourth floor, about 12 m high). The longitude of the test site was E 118.0892 and the latitude was N 24.6126. The polysilicon was placed 45 degrees above the ground, facing south to make sure there was enough sunlight on the panel. Test 4 and Test 5 run 10 h a day (8 a.m. to 6 p.m.) (168 h in 17 March 2019 days). The 17-day EKR experiment included 5 sunny, 12 cloudy and rainy days, and the daily temperature fluctuated between 9 °C and 26 °C.

For each EKR experiment, each chamber was filled with about 1.5 kg of contaminated soil. 0.5 L electrolyte solution was added to the device. Before the start of the EKR experiment, the contami-

Table 2
Experimental conditions of electrokinetic remediation.

Test	Electrolyte	Energy	Voltage (V/cm)	Remediation duration (h)	Polarity exchange frequency (h)
1	ultrapure water	DC power	1	168	0
2	ultrapure water	DC power	1	168	24
3	ultrapure water	DC power	1	168	84
4	ultrapure water	Solar cell	–	168	0
5	ultrapure water	Solar cell	–	168	84

nated soil was soaked in electrolyte solution for 12 h in advance to make the electrolyte in the tested soil completely saturated.

In the course of the experiment, the electrolyte was supplemented once a day, the height difference between cathode and anode electrolyte was measured, the direction of EOF was determined, and the volume of electromagnetic field was calculated. The concentrations of Cr⁶⁺ and total Cr in anode solution and cathode solution were determined periodically. The pH value of the electrolyte in the electrode chamber was monitored every day, and the reading values of current and voltage intensity were measured regularly by a general meter. At the end of each experiment, the samples were taken out and divided into five parts from anode to cathode (S1–S5). Secondly, the average chromium content of the five parts was calculated, and the chromium content in the soil was given. The contents of pH, Cr⁶⁺ and total Cr in soil samples from different sections were analyzed. The Cr removal efficiency was calculated according to the average content of Cr.

2.5. Analytical methods

During the experiment, the pH value in the electrode chamber was measured by pH meter, which was sampled from the electrode chamber (about 15 mL at a time). In order to reduce the adverse effects on EKR, the samples were sent back to the original electrode chamber immediately after determination. The concentration of Cr (VI) in electrolyte was determined by UV-vis spectrophotometer (Jinghua UV-2102C, China) at 540 nm by diphenylcarbazide colorimetry. After Cr(III) was oxidized to Cr(VI) with excess potassium permanganate, the total Cr concentration in the electrolyte was determined by diphenylcarbazide colorimetry.

The soil pH values of 5 different profiles were measured by pH meter in 1RU 2.5 (soil: water) suspension. 1 g of soil was extracted with 15 mL KCl 0.4 M, and the extract was filtered with 0.45 μm filter membrane. The soil was analyzed by visible spectrophotometer at 540 nm. The concentration of total chromium in soil was determined by wet digestion. Soil samples were oxidized to Cr(VI) by excess potassium permanganate, then digested with HNO₃:H₂SO₄:H₃PO₄ mixed solution and determined by diphenylcarbazide colorimetric method. The concentration of Cr(III) was obtained by the difference between total Cr and Cr(VI).

In addition, all of the analyses were performed in duplicate, and the data represent the average values.

2.6. Calculations of Cr removal efficiency and energy consumption

The Cr removal efficiency, η , was calculated as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (2.6-1)$$

where C is the Cr concentration (mg·kg⁻¹) at the end of EKR and C₀ is the initial Cr concentration (mg·kg⁻¹).

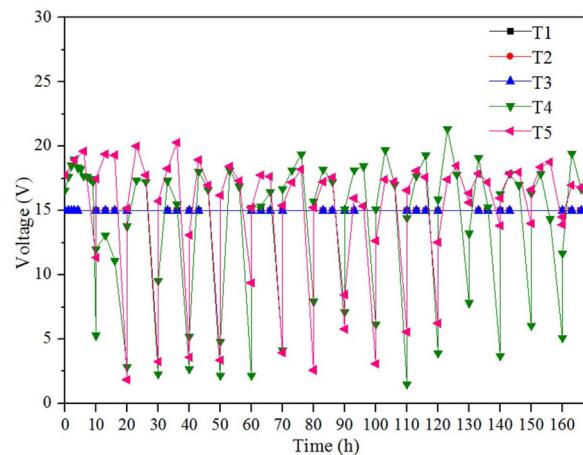


Fig. 2. Changes in electric voltage during the experiment.

The accumulated energy consumption (W) in EKR was calculated as follows:

$$W = \frac{\int_0^t UIdt}{V} \quad (2.6-2)$$

where U is the voltage in the circuit (V), I is the electric current (A), t is the remediation time (h), and V is the soil volume (m³).

3. Results and discussion

3.1. Changes in electric current and voltage

3.1.1. Changes in electric voltage

Electric voltage is one of the key factors in the EKR of contaminated soil (Rojo et al., 2012). In general, the higher the voltage gradient is, the better the remediation efficiency. The variation trends in electrical voltage during EKR were given in Fig. 2. Fig. 2 shows that the changes in electrical voltage in Tests 1, 2, and 3 were different from those in Tests 4 and 5. In Tests 1, 2 and 3, the electrical voltage remained constant because of the constant DC power supply, so there was overlap among T1, T2 and T3. In contrast to the DC power supply, the voltages of T4 and T5, provided by solar panels, were greatly influenced by weather. During the experiment, The voltage fluctuates greatly with time and was periodic. On a working day (8 a.m. to 6 p.m.), the voltage rises to its maximum (11:00 to 2 p.m.) and then drops until it reaches its lowest level (6 p.m.). Except for the electrical voltage at 6 pm, the voltage value at other times was essentially above 10 V. The voltage peaks reached 22.80 V at midday on the thirteenth day. Nevertheless, in bad weather conditions, the highest voltage during the day was only 13.77 V. Because of heavy rain weather conditions on the second day, the seventh day and the tenth day, the electrical voltage in these periods was lower during the EKR experiment.

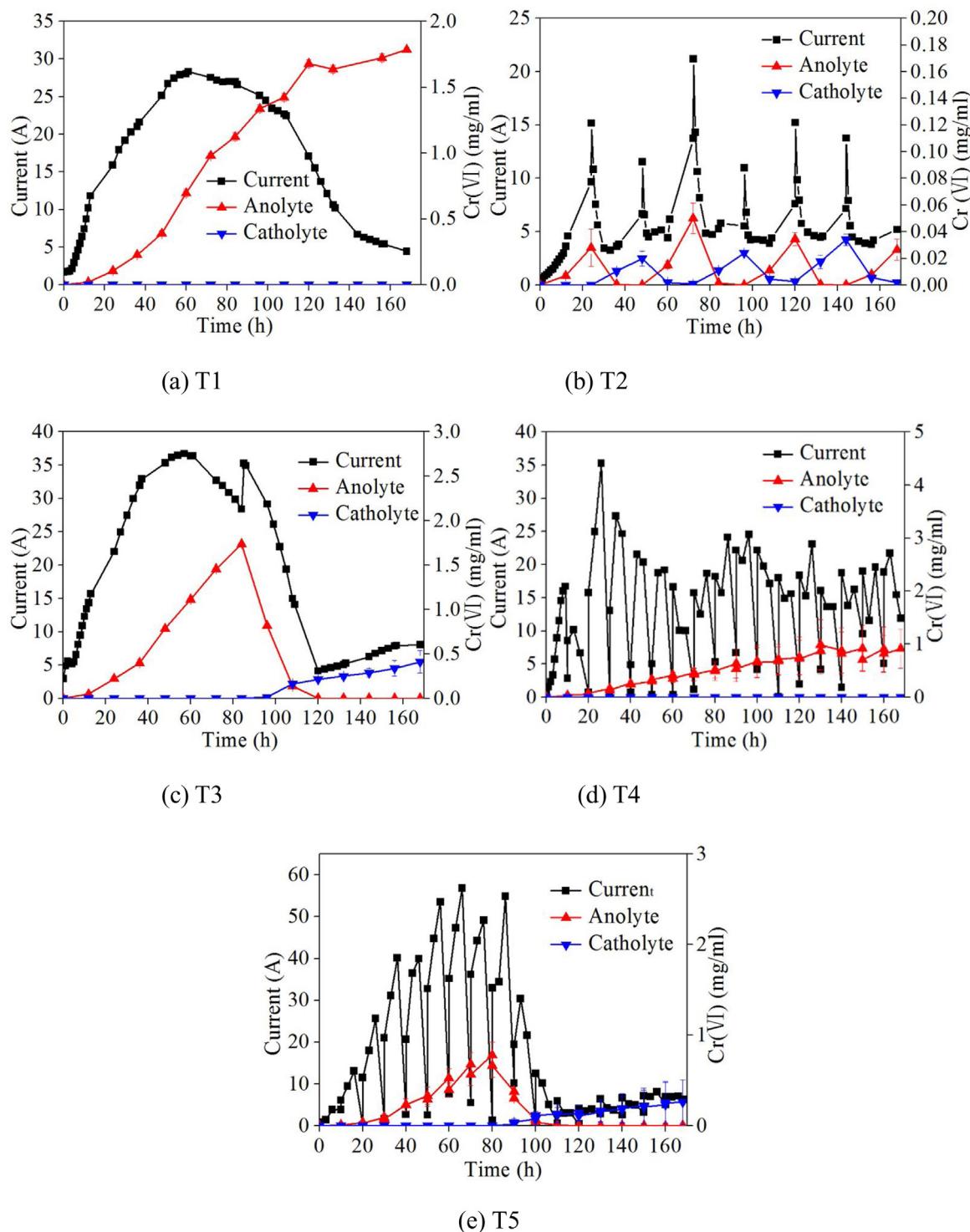


Fig. 3. Changes in electric current and Cr(VI) concentration in the electrode compartments during the experiment.

3.1.2. Changes in electric current

Fig. 3 shows the changes in the electrical current with time for each test. From the figure, the current of the four tests of experiments shows different trends. In the first 84 h of T1 and T3, the current increased first, reached the peak within 60 h (28.33 mA and 36.72 mA), and then decreased slowly to 26.98 mA and 28.40 mA, respectively. Because of the full saturation of the electrolytes in the tested soils before beginning the EKR experiments, the current at the beginning was not 0 mA. As electrokinetic remediation proceeded, more and more exchangeable metal ions were desorbed

from the soil into the soil pore fluid, which promoted the increase in current. After 60 h, under the action of electromotive force, the mobility of Cr to the electrode and the concentration of Cr(VI) in soil pore fluid increased, resulting in a peak current. It can be seen Fig. 3a and c that the migration of hexavalent chromium to the anode had almost the same change rate as the increase of current in the first 60 h. The electric current in the EKR experiments was strongly related to the concentration of mobile metal ions in the soil compartment. There were three main reasons why the current started to decline after 60 h. First, the concentration of mobile

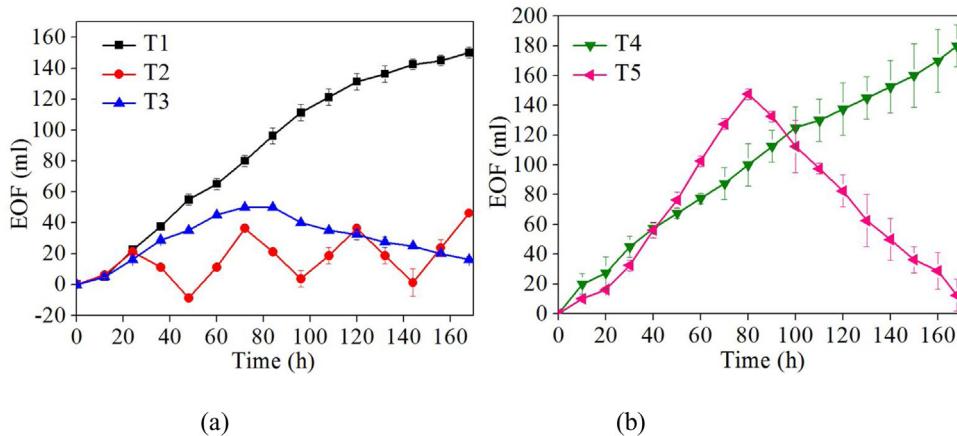


Fig. 4. Changes in electroosmotic flow during the experiment.

metal ions in the soil decreased due to the migration of soluble ions to the opposite electrode (Al-Hamdan and Reddy, 2008; Fu et al., 2017; Shin et al., 2017; Xu et al., 2016). Second, the resistance increased as a result of Cr(OH)_3 precipitation in the area near the cathode due to the high pH conditions (Suzuki et al., 2014). Third, electrode polarization and concentration polarization occurred in the electrode chamber at the later stage of the EKR experiments, which increased the resistance, decreased the electrical conductivity, and thus reduced the electrical current (Jeon et al., 2015; Zhang et al., 2010).

After 84 h, the electrical current of T1 continued to decline slowly and stabilized at a constant value. However, the electrical current of T3 showed a different trend because the cathode was exchanged with the anode at the 84th hour. In contrast to T1, an obvious increase and decrease in electrical current was present after 84 h. The current increased rapidly when the power was switched on, reached a peak value of 35.28 mA within one hour, and then decreased immediately and at a faster rate than in T1. Finally, after the electrical current decreased to 4.13 mA, there was a slight increase, and the current stayed at a constant value. The reasons for this phenomenon were as follows. From Fig. 3c, the concentration of Cr(VI) in the anode chamber decreased rapidly, and Cr(OH)_3 precipitation was observed in the anode chamber during the EKR experiment. This is because part of the original Cr(VI) in the anode chamber followed to migrate back to the soil with the conversion of current flow due to the exchange of anode and cathode, and the other part was reduced to Cr(III) in the anode chamber with the increase of pH. In addition, the H^+ and OH^- produced in the electrolysis reaction will be neutralized to form water during the electromigration process, thus reducing the ion concentration in the whole system, resulting in a reduction in the transfer of Cr(VI), OH^- , and H^+ in the pore fluid, resulting in a decrease in current. Finally, the formed Cr(OH)_3 precipitate was dissolved in the anode region (the original cathode region) by H^+ , and the current increased slightly (Zhou et al., 2018).

In the T2 experiment, the change in electrical current in the first 24 h was the same as that in T1 and T3. Since the anode and cathode exchanged every 24 h, the current changed periodically. After each electrode exchange, the current immediately increased, reached a peak, then dropped to approximately 5 mA, remained stable for approximately 5 h, and finally increased slowly. Fig. 3b shows that the Cr(VI) concentrations in the anode chamber and cathode chamber changed periodically with the current, while the Cr(VI) concentrations in the electrode compartments were always very low. At the 72nd hour, when the electrical current peaked, the highest concentration of Cr(VI) was only 0.58 mg/mL. The current also first increased, reached a peak, and then declined due to

the same reason as in T3. It can be inferred that the reciprocating migration of Cr(VI) is easily caused by the exchange of electrodes every 24 h.

In T4 and T5, similar to the change of voltage, the change of current was affected by weather conditions and had a certain rule. At the same frequency of electrode exchange, T4 and T5, which used solar energy as the working power source, occasionally had an electrical current much higher than that of T1 and T3, which used DC power. However, the concentration of Cr(VI) in the T4 and T5 electrode cells was significantly lower than that in T1 and T3. In a working day (8: 00 a.m. to 6: 00 p.m.), the current increases first and then decreases. Unlike T3, the current of T5 did not increase or decrease significantly after 84 h, and its current was affected by overcast and rainy weather.

In one working day (8:00 am to 6:00 pm), the electric current first increased, reached a maximum and then declined. Unlike T3, an obvious increase and decrease in electrical current was not observed after 84 h because the electric current of T5 was significantly influenced by the weather conditions.

The electrical current experimental results suggest that more Cr(VI) ions migrated to the electrode chambers during the EKR process in T1 and T4, especially T1, which partially explains the probable reason for the higher Cr removal in T1. In conclusion, the electrical current through the soil was strongly correlated with the concentration of mobile ions in the EKR process. Therefore, the electrical current was an important index to measure the amount of ion electromigration.

3.2. Changes in electroosmotic flow

Electroosmotic flow (EOF) is the motion of liquid induced by applying an electric voltage across a porous soil (Cameselle and Pena, 2016). As shown in Fig. 4, in all experiments, the electroosmotic flow moves towards the cathode, as in the majority of EKR experiments. This is because most soil particles have a negative surface charge. The positively charged ions farther from the surface of the soil particles move by electrostatic forces towards the cathode when an external electric field was applied (Zhou et al., 2018). As these ions move, they bring along all adjacent water molecules. Electroosmosis can effectively remove some soluble chromium compounds in contaminated soil. During the EKR experiments, the electroosmotic flow was calculated by measuring the volume change in the catholyte.

From Fig. 4a, the electroosmotic flow in T1 was higher than that in T2 and T3. In the T2 and T3 experiments, repeated changes in electroosmotic flow direction occurred due to electrode exchange,

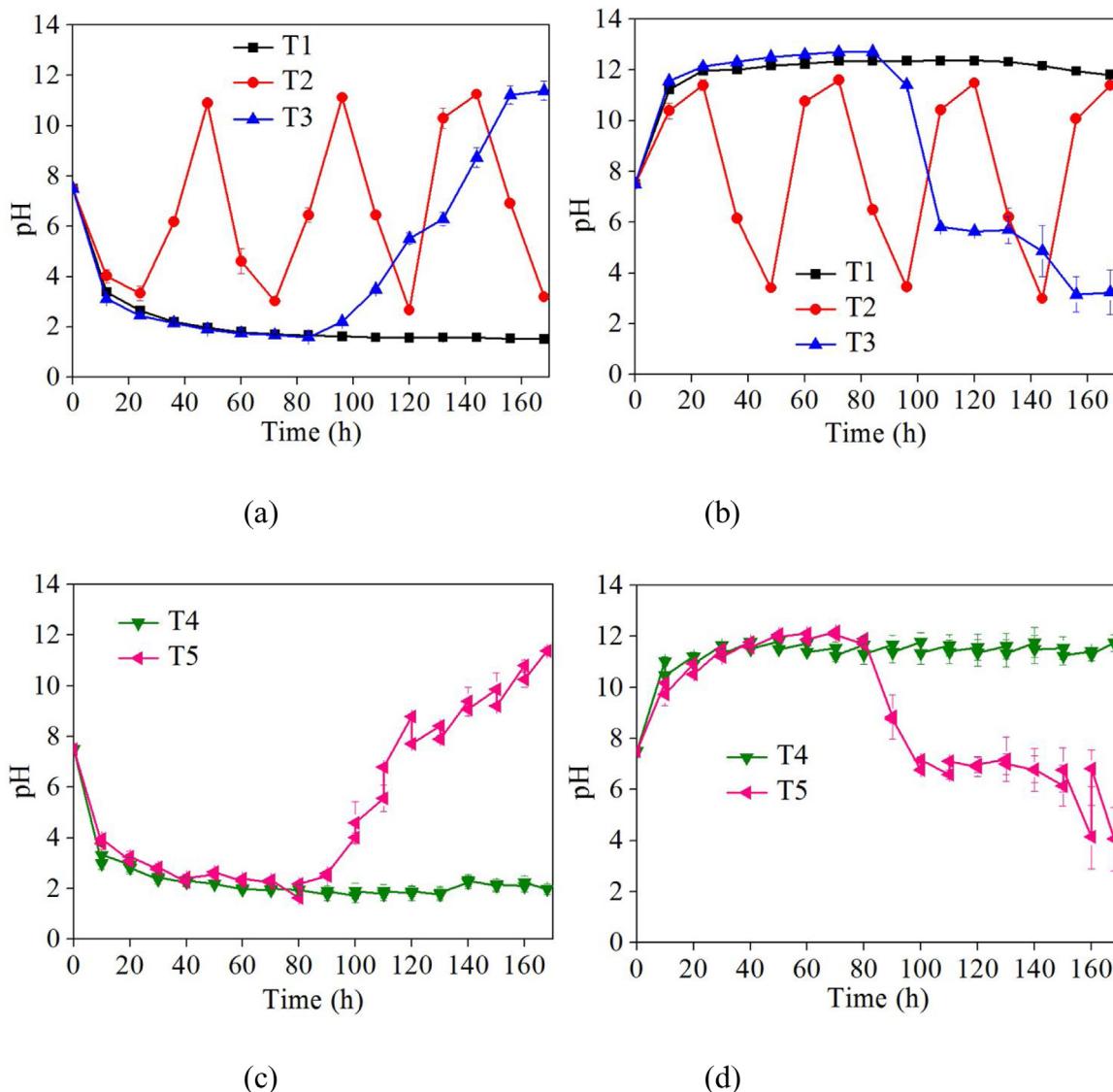


Fig. 5. Changes in pH in the electrode compartments with time during the experiments: (a) and (c) anode chamber; (b) and (d) cathode chamber.

which was also one of the main problems leading to the accumulation of Cr in T2 and T3 in the middle of the soil compartment.

Fig. 4b shows the cumulative amount of electroosmotic flow during the solar energy experiment. The magnitude of the electroosmotic flow was greatly affected by the electric current. T4 and T5, which used solar cells as the working power source, had higher electroosmosis flow because the highest current was larger than that of T1, T2 and T3, which used DC power as the working source.

3.3. Changes in pH during the electrokinetic experiment

3.3.1. Electrolyte pH

Due to the importance of pH in system behavior, it is necessary to monitor the pH of the electrode chambers during EKR experiments. The changes in electrolyte pH with time during the EKR processes were shown in Fig. 5. For T1 and T4, the pH of the anolyte decreased rapidly at first and finally stabilized at approximately 2. The pH of the catholyte increased rapidly with time and then tended to be stable, eventually remaining above 10. However, compared with T1, T4, which used solar energy, only needed 10 h of EKR every day. Therefore, when the experiment began on the second day, the pH of the anode electrolyte was higher than that on the previous day,

and the pH of the cathode electrolyte was lower than that on the previous day. In addition to the factors not considered in previous studies, this may also be due to the loss of H^+ and OH^- in the anodic solution due to the fact that some H^+ and OH^- ions remain in the filter paper and enter the soil through the filter paper. After a period of EKR, the pH of the cathode solution decreased gradually at T1, which may be due to the production of a large amount of EOF, H^+ on the cathode side to neutralize the OH^- in the cathode chamber, resulting in a decrease in pH.

In the T2 experiment, the pH of the anolyte and catholyte fluctuated between 3 and 11 due to the exchanged polarity every 24 h. In general, no pH control measures were adopted in the EKR experiment; after one day's energizing, the pH of the anolyte and catholyte was approximately 2 and 12, respectively.

In the first 84 h of the T3 and T5 experiments, the pH change in the electrolytes was similar to that of T1 and T4. The pH of the anolyte and catholyte decreased and increased rapidly at first, then finally stabilized due to the same reason observed for T1 and T4. However, at the 84th hour, the cathode was exchanged with the anode, and the trend in the electrolyte pH for T3 and T5 changed. The anolyte pH in T3 and T5 began to increase slowly and finally reached approximately 11 at 168 h. However, the catholyte pH in

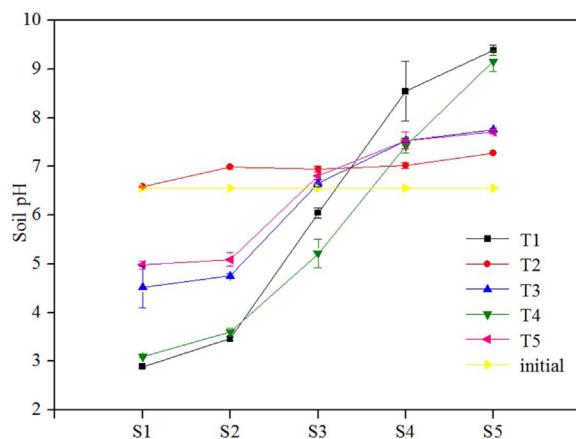


Fig. 6. Changes in soil pH after electrokinetic remediation under different experimental conditions.

T3 and T5 dropped rapidly within 16 h, then stabilized at approximately 6 within 30 h, and finally slowly decreased to 3. The change of pH value of electrolyte was closely related to the change of current. Large current flux will aggravate the effect of water electrolysis, resulting in an increase in the range of pH changes in anodic and cathodic solutions. The pH of the catholytes of T3 and T5 was stable at approximately 120 h because the electrical current of T3 and T5 decreased to the minimum value after 120 h. Finally, the pH of the catholytes decreased slowly because of the slight increase in the electrical current.

The difference between the DC power supply and the solar cell was that the use of the solar cell was greatly affected by weather conditions and intermittent operation, and the pH fluctuation in the electrolytes was more obvious.

3.3.2. Soil pH

The changes in soil pH were presented in Fig. 6. It is well known that EKR experiments can strongly influence soil pH. There was a significant difference in soil pH under three experimental conditions: no electrode exchange (T1 and T4), electrode exchange every 24 h (T2) and electrode exchange after 84 h (T3 and T5). As shown in Fig. 6, with increased electrode exchange frequency, the negative effect on soil pH was smaller. The polarity exchanged EKR had little effect on the pH of the experimental soil, and the anions and cations produced by the electrolytic reaction in the soil were partially neutralized by the newly produced anions after the exchange electrode.

The initial pH of soil was 6.56. After the end of the experiment, the soil pH in T1 and T4 anode decreased to about 3, and the soil pH in cat hode increased to about 9. From the perspective of soil zoning, soil pH decreased in S1–S3 region and increased in S4–S5 region. Because the mobility of H^+ in soil driven by electromotive force was much higher than that of OH^- , the neutralization reaction occurs after the two ions meet between S3 and S4, resulting in an increase in water content in the profile.

In T3 and T5, the pH of the soil near the anode region decreased to approximately 4.5, while that near the cathode region increased to approximately 7.5. Compared with T1 and T4, soil acidification near the anode and alkalization near the cathode were alleviated. The pH in the middle of the soil (S3) remained basically the same as the initial value. Moreover, in the T2 experiment, the pH of all sections of the soil remained at approximately 7. Therefore, EKR with the exchange of polarity can solve to some extent the adverse effects of EKR on soil pH (Cai et al., 2015).

From Figs. 5 and 6, the change trend of pH of cathode and anode electrolyte in the five experimental groups was consistent with

that of soil pH, and the changes of both were closely related to the change of current, which shows that the change of soil pH was affected by the electrolyte pH and the current flux in the whole system.

3.4. Cr removal

3.4.1. The distribution of total Cr

Different electrode exchange frequencies in the experiments resulted in different distribution rules for total Cr (Fig. 7).

In T1 and T4, the accumulation of total Cr gradually increased from the cathode region to the anode region. In the S1 region near the anode, the total reached 1963.97 ± 72.96 mg/kg and 1756.83 ± 99.41 mg/kg, respectively, much higher than the initial concentration. Especially in T, Cr accumulated in S1–S3 region, while Cr in S4 and S5 soil was almost completely removed. This is because Cr in soil mainly exists in the form of Cr(VI) and Cr(III) and the migration capacity of Cr(III) in soil was weaker than that of Cr(VI). Under the action of a unidirectional applied electric field, Cr(VI) moved to the anode by electromigration and accumulated in the anode region (S1). The unidirectional electric field caused changes in soil pH and rapid acidification of the soil in the anode region. The difference of soil pH has a significant effect on the redox reaction between different valence states of Cr. In general, high pH enhances the oxidation ability of Cr, making it transform from Cr(III) to Cr(VI), while low pH enhances the reduction reaction of Cr to transform Cr(VI) into Cr(III). (Wu et al., 2016). Therefore, a large amount of Cr(VI) was reduced to Cr(III), and considerable adsorption of Cr(VI) in the anode region (S1) occurred. Thus, the total Cr concentration in the S1 region was increased. It can also be intuitively seen from Fig. 8 that in T1 and T4, the residual ratio of total Cr in the S1 region was higher than that in T2, T3 and T5.

In T2, the total Cr concentration at the middle of the soil was higher than that at both sides after electrokinetic remediation, but the concentrations in all sections were lower than the initial value. According to the changes in soil pH, the soil pH of all sections in T2 remained at approximately 7, thus weakening the transformation between Cr(III) and Cr(VI).

In T3 and T5, the total Cr concentration in S1–S3 after remediation was higher than the initial value. Cr accumulation was highest in anode region and middle region due to the combined effect of the reciprocating electromigration of Cr(VI) and the reduction of Cr(VI) to Cr(III).

The recoveries of Cr in Tests 1–5 were 93.47 %, 72.40 %, 96.13 %, 83.70 % and 99.85 %, respectively (Fig. 9).

For T1, after the experiment, 35.5 % and 0.00 % of heavy metal chromium were collected in anode electrolyte and cathode electrolyte respectively, with 6.53 % experimental loss and 57.97 % residual in soil. From the mass balance diagram, it can be seen that the main experimental reasons for Cr loss are the loss of Cr caused by soil sampling and the determination of electrolyte pH and Cr^{6+} concentration, and other reasons were that a certain amount of Cr will remain in the reactor and filter paper at the end of the experiment, the suspension and precipitation formed in the cathode chamber can not be completely extracted, and the sampling will be uneven, and the graphite electrode has a certain adsorption capacity to Cr.

For T2, 0.49 % Cr was detected in the anode electrolyte and 0.04 % in the cathode electrolyte, 27.6 % Cr was not detected, and 71.87 % remained in the soil. For the same reason as T1, the uncalculated part of the total mass of chromium at the end of the experiment. The suspended matter and sediment formed in the two electrode chambers may also be the reason for the high proportion of the lost part. As shown in Fig. 9, the content of Cr in the anolyte and catholyte was small. This may be due to the reciprocating migration of Cr caused by changing electrodes every 24 h. Compared with T1

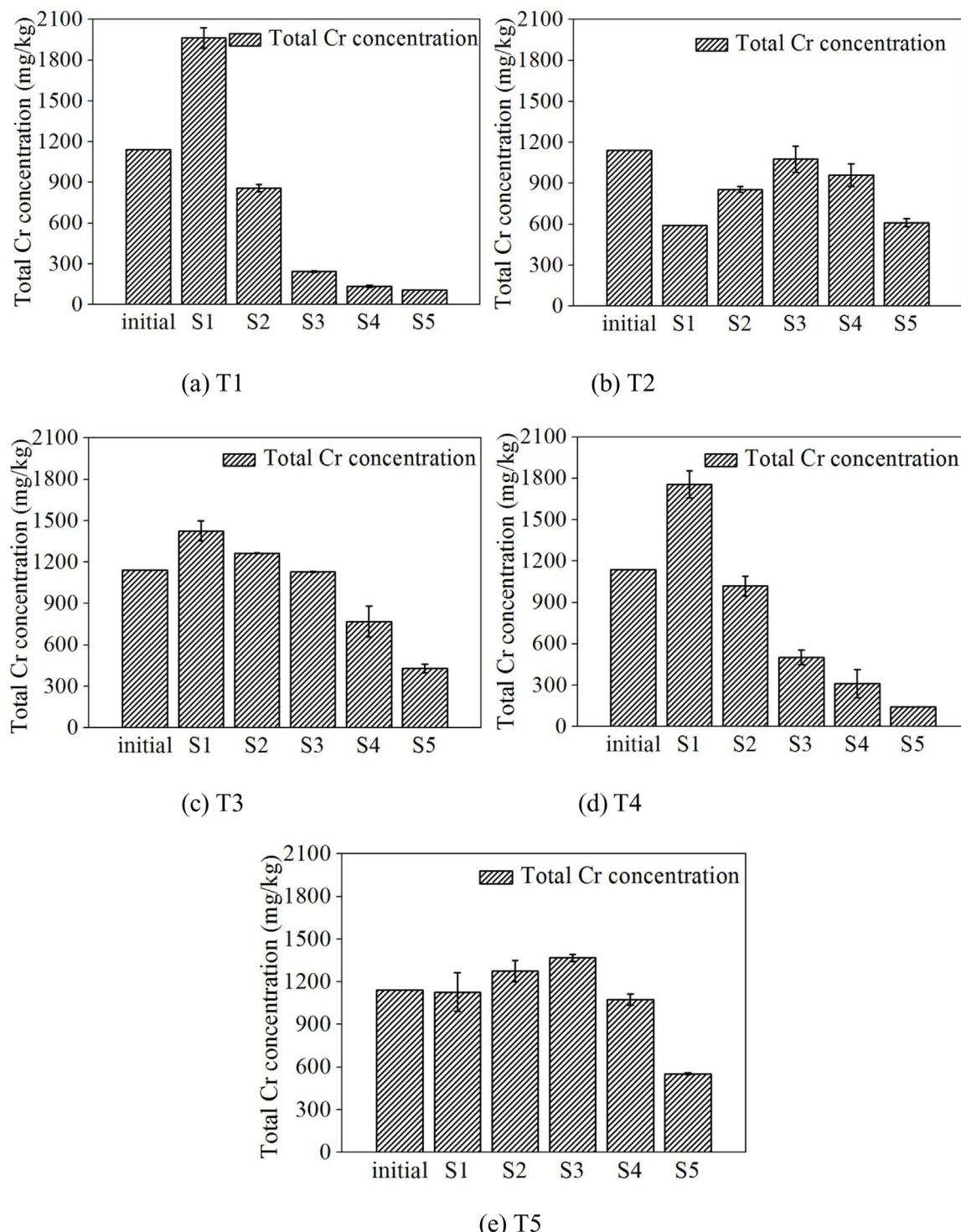


Fig. 7. Total Cr distribution in soil after electrokinetic remediation under different experimental conditions.

and T4, which did not exchange electrodes, more Cr remained in the soil and was not removed.

For T3, 0.01 % and 8.09 % of the initial soil Cr was detected in the anolyte and catholyte, respectively; 3.87 % was unaccounted for, and 88.03 % remained in the soil cell. For T5, 0.00 % and 5.15 % of the initial soil Cr was detected in the anolyte and catholyte, respectively; 0.15 % was unaccounted for, and 94.70 % remained in the soil cell. As shown in the figure, the amount of Cr retained in the soil of T3 and T5 was significantly higher than that in the other experiments. This indicates that the reciprocating migration of Cr

caused by the exchange of electrodes after 84 h was significantly better than that caused by the exchange of electrodes every 24 h. There was also more conversion between Cr(VI) and Cr(III), which will be discussed later. Strong reciprocating migration may also be the reason why the unaccounted portions of T3 and T5 were relatively small.

For T4, 18.19 % and 0.00 % of the initial soil Cr was detected in the anolyte and catholyte, respectively; 16.30 % was unaccounted for, and 65.51 % remained in the soil. The unaccounted portion of the total Cr was due to essentially the same reason as for T1.

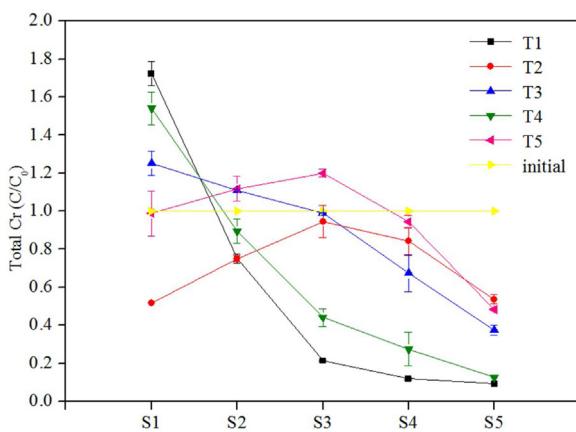


Fig. 8. The ratio of the residual Cr to the initial Cr concentration after electrokinetic remediation.

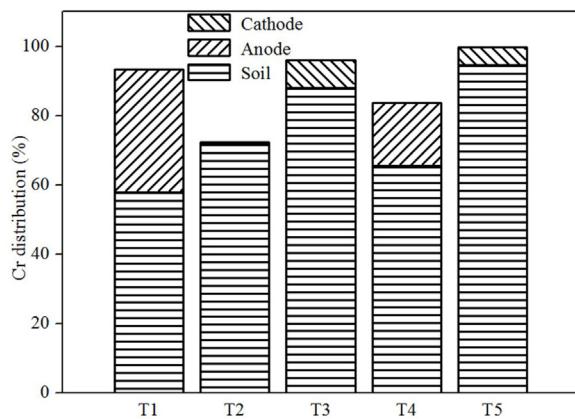


Fig. 9. Mass balance calculations indicating the final distribution of total Cr after electrokinetic remediation under different experimental conditions.

More chromium remained in the soil of the experiment using solar cells compared to the DC power experiment, and this difference was mainly due to weather conditions. When using solar cells, it is difficult to keep the voltage and current stable as the sunlight changes the result is that more chromium remains in the soil, slightly reducing the removal efficiency.

3.4.2. The distribution of Cr(VI) and Cr(III)

Compared with the initial concentration, the total Cr(VI) concentration decreased in all regions after the experiment, especially in T1 and T4 (Fig. 10). Since the Cr(VI) in the soil was mainly in the form of CrO_4^{2-} and HCrO_4^- , the Cr ions desorbed from the soil will migrate to the anode under the action of electromigration (Chirakkara et al., 2015).

In T1 and T4, Cr(VI) accumulated in the S1 region near the anode (Fig. 10(a) and (d)), and the residual content in the soil gradually increased from the cathode to anode. The accumulation of Cr(VI) on the anode side was higher than on the cathode, indicating that Cr(VI) migrated from the cathode to the anode side in the form of oxygen-containing anions driven by electromotive force. Cr(VI) commonly existed as a soluble ion in alkali soil and was adsorbed with pH decreased. After the EKR test, the soil pH increased near the cathode side, and the alkaline soil was more conducive to the oxidation of Cr(III) to Cr(VI) ions, and then the mobility of Cr was also enhanced, which partly explained the high removal rate of Cr(VI) in S4 and S5. However, by comparing T1 and T4, it can be found that stable and continuous electrical input will make the migration of

metal ions more stable, so the EKR removal efficiency of DC power supply was slightly higher than that of solar cells.

However, the distribution trend of Cr(VI) in T2, T3 and T5 experimental groups was completely different from that of T1 and T4, that is, the accumulation of Cr(VI) in the middle of the soil (S3) was the highest, which may be due to the repeated migration of, Cr(VI) in the contaminated soil under the action of electric field force. In addition, through the experiment, it can be found that the direction of EOF was opposite to that of Cr(VI). The effect of electromigration was greater than that of electroosmosis on the migration of Cr(VI). The larger EOF was not conducive to the removal of Cr(VI) by electromigration, but also aggravates the reflux of Cr(VI) from anodic solution to soil.

Nevertheless, in the T2 experiment, where the polarity was exchanged every 24 h, the concentration of Cr(VI) in the middle of the soil was more obvious, reaching $732.48 \pm 108.79 \text{ mg/kg}$. This may be because the interval between the exchange of polarity was too short, resulting in the insufficient removal of soil Cr(VI) content. Similar to remediation without electrode exchange, DC power had a slightly higher removal efficiency than solar cells due to its stability regardless of weather conditions.

As shown in the Fig. 11, when EKR remediation was applied, more Cr(VI) was reduced to Cr(III) and then accumulated in the soil. Except for the area near the cathode of T1 and T4, the concentration of Cr(III) after remediation was higher than the initial value. Compared with Cr(VI), Cr(III) was difficult to treat by EKR. This may be due to the alkalinity of the soil environment in the S4-S5 region, resulting in the formation of $\text{Cr}(\text{OH})_3$ precipitation blocking the filter paper and soil pores. The decrease of water level would lead to the reduction of the contact area between graphite plate and water body, which will reduce the electric migration. Which was not only not conducive to the removal of pollutants in soil, but also caused energy consumption (Fu et al., 2017).

Except for T2, the content of Cr(III) in other experiments showed an increasing trend from cathode to anode. Moreover, the residual Cr(III) content in S1 was much higher than the initial value. In general, Cr(III) migrates towards the cathode under the action of electromigration and electromigration. However, this experiment shows that the Cr(III) in the anode area was much higher than that in the cathode section. This may be due to transformation between Cr(VI) and Cr(III).

In T2, the concentration of Cr(III) in all sections of the soil was low, and only a small amount of Cr(VI) was reduced. There were two reasons for this. First, it may be that because of the exchange of polarity every 24 h, the soil pH of all sections remained neutral, reducing the transformation between Cr(VI) and Cr(III). Second, because the exchange time was short, the effect of electromigration on Cr(III) transport was essentially equivalent to that of electroosmosis, so Cr(III) was evenly distributed in the soil.

3.4.3. The transformation between Cr(VI) and Cr(III)

The experimental soil was prepared by adding potassium dichromate solution to the recovered non-polluting soil, so the initial Cr in the experimental soil contained only Cr(VI). After adding chemicals and stabilizing the soil, the content of Cr(VI) in the soil decreased to 79.375 % of the total Cr, indicating that Cr(VI) spontaneously took place in the process of beating, mixing and stabilization of artificially polluted soil. The net reduction of Cr(VI) in soil was 235.19 mg.

After all experiments, the concentration of Cr(III) was higher than the initial value, i.e., the reduction of Cr(VI) to Cr(III) occurred. Cr(VI) commonly existed as a soluble ion in alkali soil and underwent adsorption with a decrease in pH. Cr(III) existed as a soluble ion when the pH was below 4 and undergoes precipitation or adsorption with increased pH (Li et al., 2012).

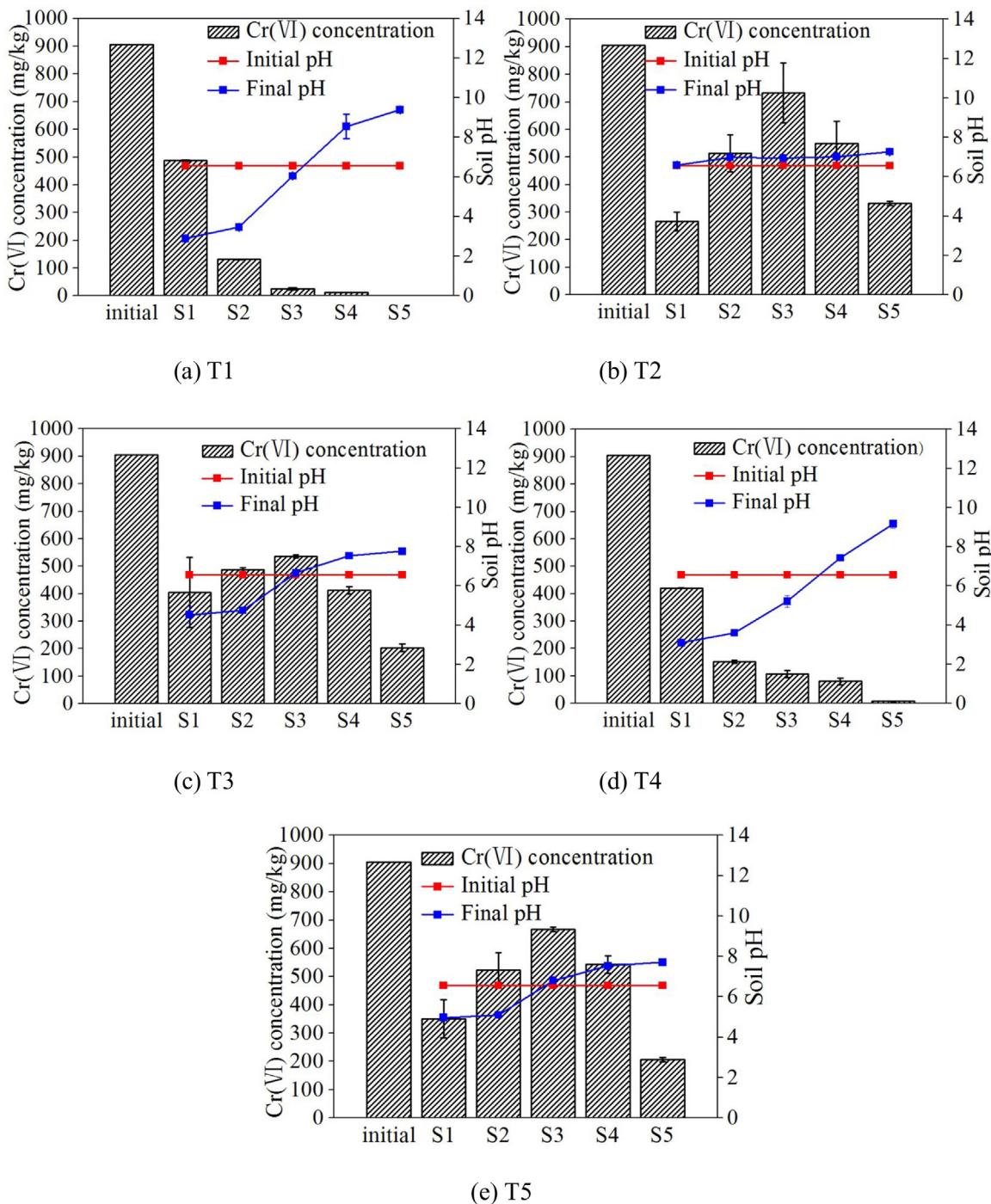


Fig. 10. Cr(VI) distribution (bars) and pH profile (line) in soil after electrokinetic remediation under different experimental conditions.

In T1 and T4, the pH of the soil in areas S1 and S2 near the anode region was less than 4, so most of the Cr(III) in this area existed as soluble ions. With increasing pH, Cr(III) gradually underwent precipitation or adsorption on the soil surface. Especially in the S5 region, most of the Cr(III) was in the form of Cr(OH)_3 as the soil pH reached approximately 10. However, Cr(III) was significantly higher in the S1 and S2 regions than in the S3, S4 and S5 regions. This was due to the reduction of more Cr(VI) to Cr(III) by electromigration to the anode region. It is thus evident that transformation between Cr(VI) and Cr(III) occurred during this process. The conversion between Cr(VI) and Cr(III) in T3 and T5 was similar to that in the T1 and T4 experiments. However, it was unclear from the

data whether transformation between Cr(VI) and Cr(III) occurred in T2 during this process.

In T2, T3 and T5, the reciprocal migration of Cr(VI) caused by the exchange of electrodes resulted in higher Cr(III) concentrations in the S4 and S5 regions than the initial concentration. This was due to the formation of Cr(OH)_3 in S4-S5. These results also indirectly showed that some Cr(VI) in the soil of the cathode region was reduced to Cr(III).

The reduction of Cr(VI) to Cr(III) can be achieved through a variety of reduction reactions. Cr(VI) oxygen anions can be easily reduced to Cr(III), soil organic matter by electron donors such as organic matter or reduced inorganic matter which were ubiqui-

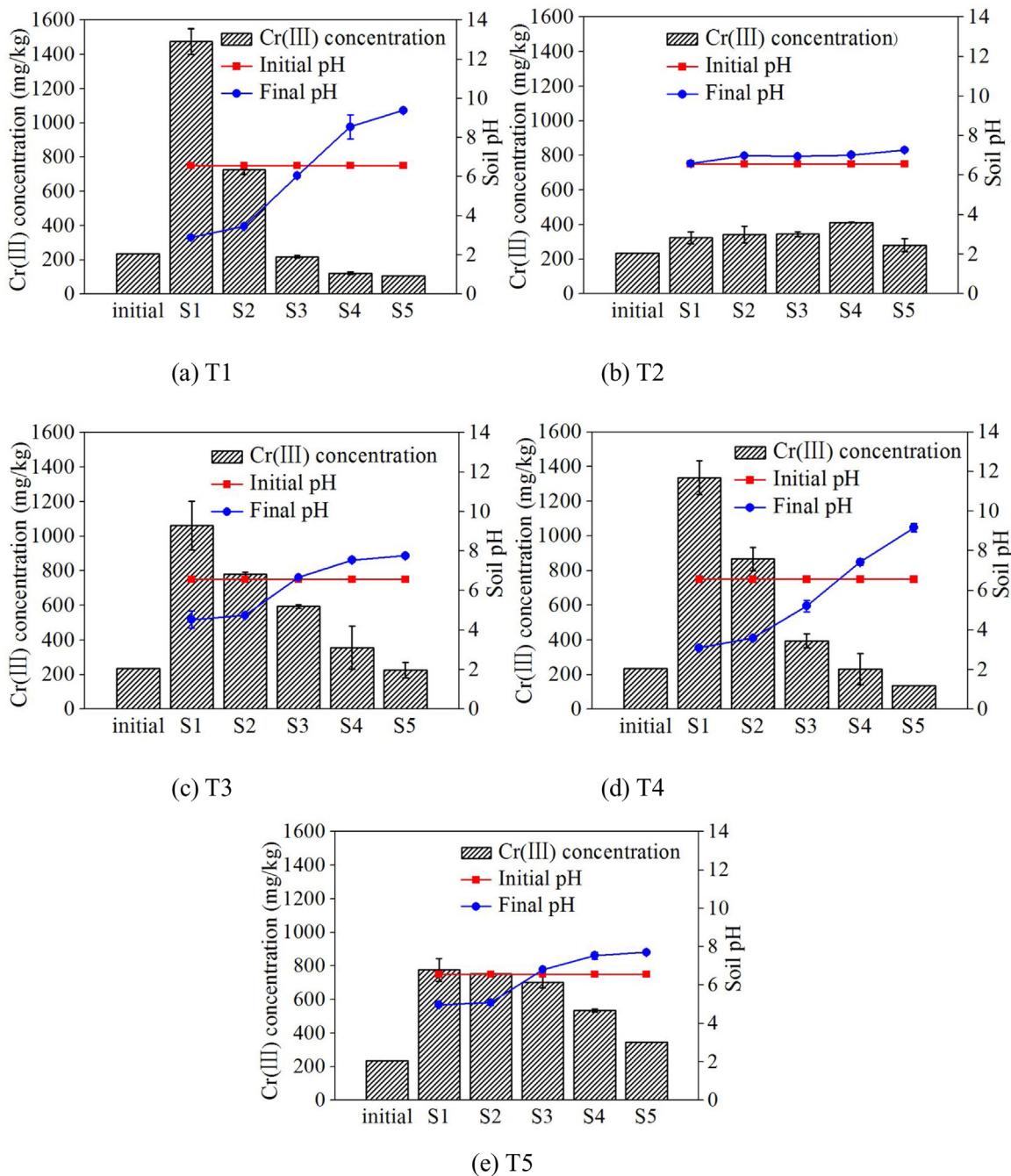


Fig. 11. Cr(III) distribution (bars) and pH profile (line) in soil after electrokinetic remediation under different experimental conditions.

tous in the environment. Soil organic matter will actively induce the spontaneous reduction of Cr(VI) to Cr(III) in the soil (Huang et al., 2015). Although the content of organic carbon in the prepared soil was low (0.5898 mg/g), Cr(VI) was reduced to Cr(III) under alkaline conditions. And the iron content in the soil was high, which may lead to the reduction of Cr(VI) by Fe²⁺.

The oxidation and reduction reactions could occur simultaneously in soil, the soil had the condition from Cr(III) to Cr(VI). During T1-T5, the amount of Cr(VI) reduced to Cr(III) was more than of Cr(III) to Cr(VI).

3.5. Removal efficiency and power consumption

Fig. 12 shows the power consumption and removal efficiency of T1, T2 and T3. The power consumption of T1, T2 and T3

was 42.08, 13.49 and 47.90 kW h/m³ respectively. The electricity demand of T1 and T3 was higher, which may be caused by the loss of ionic substances caused by electrolyte loss during the experiment, which reduces the soil electrical conductivity and increases the soil resistance. In addition, the increase of soil resistance will also have an impact on the change of soil temperature during the experiment, increase energy consumption and make energy loss in the form of heat (Silva et al., 2018). The electricity demand of T2 was lower than that of other groups. For T3, although the energy consumption was the highest, the removal efficiency of total Cr and Cr(VI) was low.

The main cost of EKR using solar energy is the cost of the solar cell. It is difficult to compare the operation cost of DC power with the operation cost of solar energy, but solar energy, as a kind of clean energy, was very promising for EKR.

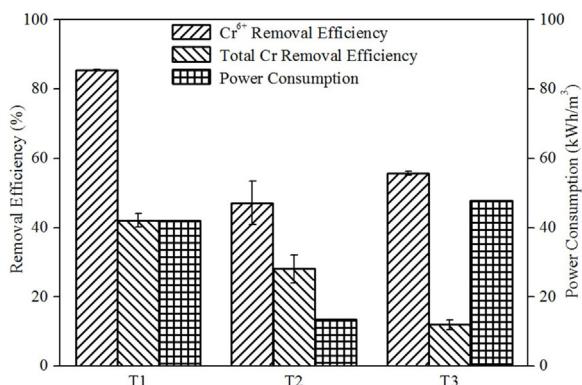


Fig. 12. Energy consumption requirements and Cr removal efficiency after electrokinetic remediation.

4. Conclusions

- (1) Electric voltage was the most important factor affecting the removal efficiency of electrokinetic remediation. When the voltage was constant and stable, the removal efficiency was better. The Cr removal efficiency of DC power was higher than that of solar cells, mainly because solar cells could not provide stable voltage.
- (2) The results showed that the polarity exchange frequency, electrifying time, voltage and current had influence on the pH of electrolyte and soil, the direction and quantity of electroosmotic flow and the supplement amount of electrolyte had influence on the pH of electrolyte, and the buffer capacity and pH of electrolyte have influence on the pH of soil.
- (3) The results showed that polarity exchange could solve the adverse effects of EKR on soil pH. In particular, exchanging the electrodes every 24 h kept the pH of the soil in each section neutral.
- (4) The polarity exchange electrokinetic remediation was a potential technology to eliminate Cr in contaminated soils. This technique reduced focusing phenomena and enhanced electrical current but leaded to the repeating migration phenomenon. Cr in the electrolytes might return to the soil during the EKR process.
- (5) The reduction reaction of Cr(VI) to Cr(III) occurred during the EKR processes. After electrokinetic remediation, the content of Cr(III) in the soil increased greatly, and the toxic effects of Cr(III) to organisms and its influence on human health were greatly reduced.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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