
Restoration of Cadmium Contaminated Soil Using Approaching Anode Method of Polygonal Electrode

Yushan Wan ^{1*}, Anwei Wang ¹, Meng Shen ¹

¹ School of Environmental & Safety Engineering, Changzhou University, Changzhou 213164, CHINA

* Corresponding author: wanyushan@126.com

Abstract

In order to explore the effect of moving anode polygonal electrodes in restoring cadmium contaminated soil, the cadmium contaminated soil was prepared at laboratory and a regular hexagon electrode electric restoration experimental device was set up in this study. The repair effect of fixed anode method and approaching anode method was compared and analyzed under the condition of constantly shortening the distance between anode and cathode and the electric field strength being $2 \text{ V}\cdot\text{cm}^{-1}$. The results showed that the current variation trend of the fixed anode method was similar to that of the approaching anode method. The variation of pH value of both was basically the same, and the decrease trend of pH value of approaching anode method was significant at the later stage of restoration. After 120 h of electric restoration, for both cases, the content of Cd residue near the anode and in the middle of the soil chamber changed slightly, while that near the cathode increased; the weak acid extraction state and reducible state of Cd near the anode and in the middle of the soil chamber decreased significantly than that before the restoration. The removal rate of Cd at type A2 sampling points by fixed anode method was 68%, and the removal rate of Cd at these points was 95% by approaching anode method. The energy consumption of the approaching anode method was reduced by 65% compared with that of the fixed anode method. The approaching anode method is more effective.

Keywords: electrokinetic restoration, cadmium pollution, soil, approaching anode method, energy consumption

Wan Y, Wang A, Shen M (2019) Restoration of Cadmium Contaminated Soil Using Approaching Anode Method of Polygonal Electrode. Ekoloji 28(107): 1041-1047.

INTRODUCTION

At present, heavy metal pollution has been one of the important environmental problems in the world. Among them, the cadmium pollution is the most serious problem, with increasing pollution area, increasing pollution degree, which is mainly caused by the use of chemical fertilizers and pesticides in mining, metallurgy and agricultural fields (Selvi and Aruliah 2018, Habibul et al. 2016). Cadmium pollution, on the one hand, causes serious environmental and economic losses due to its long-term and irreversible nature, and on the other, poses a threat to human life and health due to its toxic, mutagenic, carcinogenic characteristics (Xu et al. 2016). The problem of restoration of cadmium contaminated soil has attracted extensive attention from domestic and foreign scholars, and a series of related technologies have been produced, which can be divided into physical method, chemical method and biological method (Liu et al. 2018). Among them, electrodynamic restoration method has been a hot spot in the field of soil remediation due to its advantages of wide application range, application to low

permeability soil and in-situ remediation (Chang et al. 2018, Zhou et al. 2018). As early as the 1990s, the Netherlands launched five large-scale electric remediation projects for heavy metal pollution sites, dealing with copper, lead, cadmium and nickel in the soil (Lageman 1993). Electrodynamic restoration is increasingly accepted by researchers, but there are some problems with the technique: (1) the polarization phenomenon in the restoration process leads to the increase of energy consumption and slow repair rate; (2) the site restoration uniformity is poor, and the heavy metal content in each part of the soil does not decrease uniformly at the same time; (3) severe corrosion of the electrode by anodic acidity must be overcome; (4) the ability of heavy metals to migrate in soil should be enhanced. Therefore, it is an urgent problem for electrodynamic remediation technologies to find an effective method to reduce the energy consumption and accelerate the repair rate. Kim et al. (2012) studied the removal of salt in saline and alkaline land by using regular hexagon two-dimensional electric system.

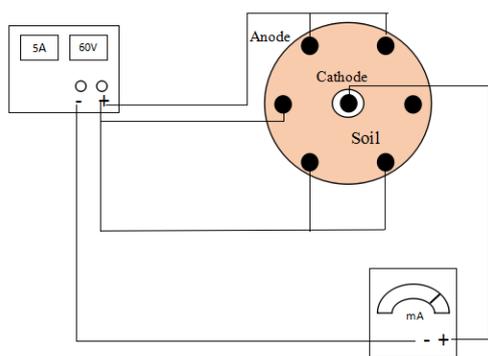


Fig. 1. Schematic diagram of electric restoration device

Zheng Shenshen et al. (2018) used approaching anode technology to reduce energy consumption.

On the basis of the preliminary experiment, this study focuses on improvement of restoration effect using hexagonal electrode configuration and approaching anode method, by fixing the cathode and gradually pushing the anode to the cathode (i.e. gradually shorten the distance between the anode and the cathode). The method of further reducing energy consumption and improving restoration efficiency is explored to provide relevant data and basis for actual restoration process.

MATERIAL AND METHOD

Experimental Equipment and Soil

As shown in **Fig. 1**, the disc-shaped electric reaction chamber is made of plexiglass, with a radius of 17 cm and a depth of 14 cm. In the center of the device is the cathode chamber with a radius of 3 cm. The anode made of steel electrode is arranged according to the regular hexagon, and the cathode is made of high-purity columnar graphite electrode (diameter of 1cm). In addition, the other components of include DC power supply, separator, copper wire and non-woven screen, etc.

The experimental soil was collected from farmland near Changzhou University in Jiangsu province. The soil was dried and finely ground before being screen by a 100-mesh sieve. A certain amount of cadmium chloride was weighed and dissolved in deionized water. Then the cadmium chloride was added to the soil samples, stirred for fully mixing, and then cultured at room temperature for 20 days. Through measurement, the main properties of soil are shown in **Table 1**. 3 kg of prepared cadmium contaminated soil was weighed and put into the soil chamber, and a certain amount of deionized water was added, before being pressed with appropriate pressure. Subsequently, 500 mL of citric

Table 1. The main physical and chemical properties of soil

physicochemical properties	contaminated soil
pH	6.78
moisture content /%	4.42
Total Cd content/ $\text{mg}\cdot\text{kg}^{-1}$	47.58
Content of Cd in weak acid extraction state / $\text{mg}\cdot\text{kg}^{-1}$	20.31
Content of Cd in reducible state/ $\text{mg}\cdot\text{kg}^{-1}$	25.77
Content of Cd in oxidizable state/ $\text{mg}\cdot\text{kg}^{-1}$	0.31
Content of residual Cd / $\text{mg}\cdot\text{kg}^{-1}$	1.19

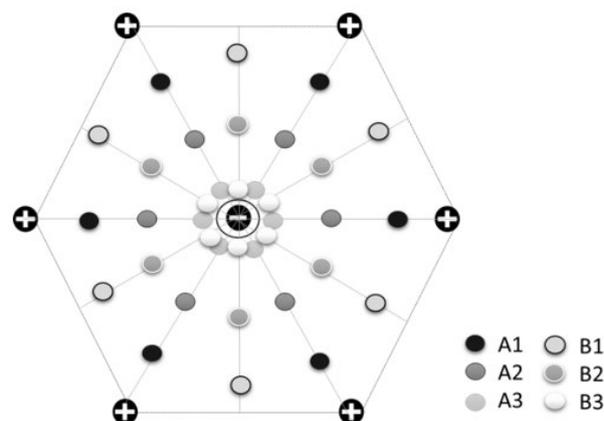


Fig. 2. Layout of the sampling points

acid was added to the cathode chamber, connected to the power supply, with a constant voltage being applied.

Fig. 2 shows the layout of the sampling points. A type sampling pointing are located on a line segment with anode and cathode as two ends, B type sampling points are located on the perpendicular bisector of the line segment with the center of the adjacent anode as the end. A1 and B2 type sampling points are on the same concentric circle, so as A2 and B2 type sampling points and A3 and B3 type sampling points. The distance between the A1, A2, A3 type sampling point and the anode was 4 cm, 8 cm and 12 cm, respectively.

Experimental Scheme

Fixed anode method: the electric field strength of the device is controlled at $2 \text{ V}\cdot\text{cm}^{-1}$, the pH of cathode electrolyte is controlled to be acidic condition by peristaltic pump, the current is measured every 2 hours. After 120 hours of operation, the soil chamber shall be dried and equally divided into 16 patches, and then the soil pH, total cadmium content and contents of cadmium in various state are measured.

Approaching anode method: the restoration experiment based on approaching anode method is similar to that based on fixed anode method. The difference is that for approaching anode method, the anode moves 3 cm towards the cathode every 24 h,

Table 2. Procedure of approaching anode method

Time/h	0-24	24-48	48-72	72-120
Distance from cathode/cm	15	12	9	6
Voltage/V	30	24	18	12

while adjusting the voltage to control the electric field strength at $2 \text{ V}\cdot\text{cm}^{-1}$. The concrete procedure of approaching anode method is shown in **Table 2**.

Analysis Method

The analysis and determination methods of soil pH value and moisture content are listed in the literature (Lu 2000).

Total cadmium content and contents of all forms of cadmium were determined by flame atomic absorption spectrophotometry. (1) Standard curve plotting: since the flame atomic absorption spectrophotometry (Agilent 240FSAA) employed in this experiment has the automatic dilution function, only $0.50 \text{ mg}\cdot\text{L}^{-1}$ Cd standard solution was prepared. (2) Total cadmium was determined after nitric acid-hydrofluoric acid-trichloric acid digestion. (3) The cadmium in soil was determined by BCR continuous extraction (Liu et al. 2015a).

RESULTS AND DISCUSSION

Fixed Anode Electrodynamic Restoration

The change of current during the fixed anode process is shown in **Fig. 3**. The current showed a rapid upward trend during the first 12 h, then increased slowly from 12 h to 32 h and reached the maximum value at 32 h, after that it started to decrease and then tended to be stable. The reason for the current increase in the early stage is that H^+ produced by anode electrolysis converted heavy metal ions in soil into free state. Studies have shown (Wang et al. 2008) that the concentration of mobile ions in the soil directly affects the current size during the electrodynamic restoration process, so the current increased quickly. In contrast, the cathode electrolysis produced OH^- , and as the reaction proceeded, the cation and OH^- formed hydroxide precipitation, and only a small fraction of H^+ converted heavy metal ions in the soil into free state, so the current increased slowly. The reason for the current decrease in late stage are: (1) Positive ions in soil, H^+ produced by anode and OH^- produced by cathode were neutralized preferentially, which reduced the mobile free ions in the soil solution on one hand, and caused soil interstitial obstruction on the other hand (Liu et al. 2016); (2) During the experiment, bubbles such as O_2 and H_2 were generated from cathode and anode, which increased the resistance of the electrode surface, thus resulting in a reduced current. (3) The H^+ produced by

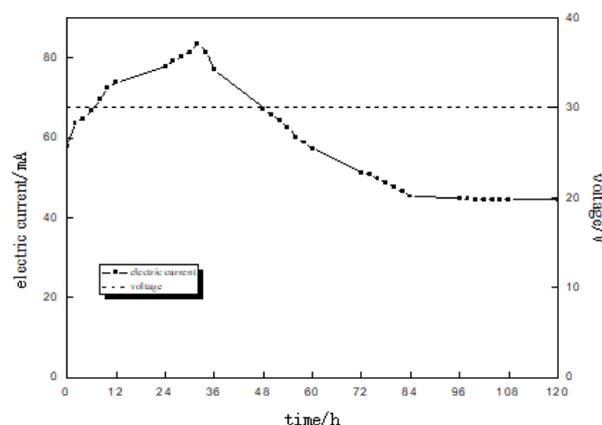


Fig. 3. The time-dependent variation of current and voltage during restoration with fixed anode method

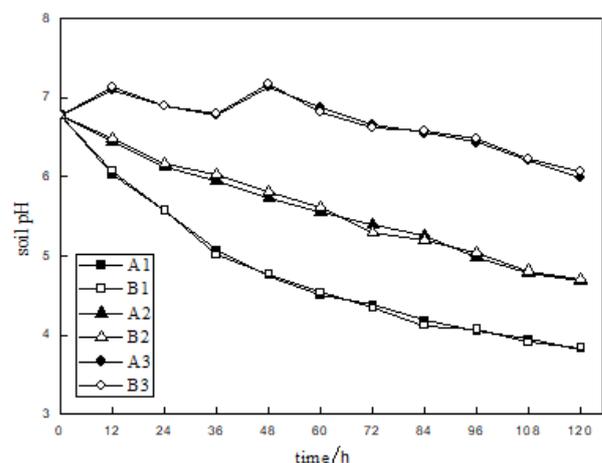


Fig. 4. The time-dependent variation of soil pH value at different sites during restoration with fixed anode method

the anode and OH^- produced by the cathode migrated to the cathode and anode respectively under the electric field, so the acid and base could not be neutralized in time, resulting in decrease of current (Xu et al. 2017).

Fig. 4 shows the time-dependent variation of soil pH value at different sites during restoration with fixed anode method. At A1 and B1 type sampling points that are 4 cm away from the anode, the soil pH value presented a downward trend. After 120 h of electrodynamic restoration, soil pH dropped to about 4.0, which indicates that the H^+ produced by the electrolytic water reaction migrated to the soil to form an acidic migration zone. At A3 and B4 type sampling points that are 12 cm away from the anode, at the first 60 h, the soil pH value fluctuated periodically within a

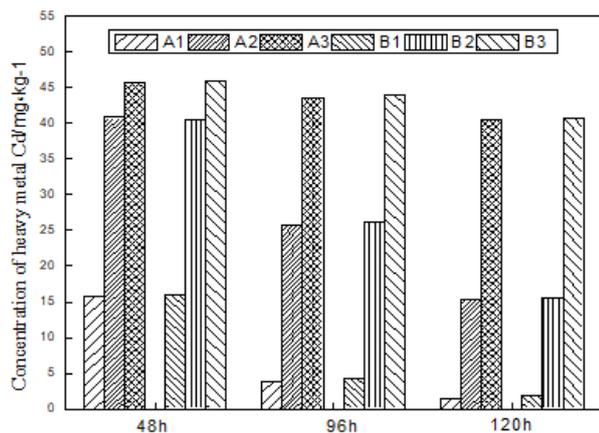


Fig. 5. The time-dependent variation of residual Cd concentration at different sites during restoration with fixed anode method

range of 6-7.2. With the increase of restoration time and the regulation of cathode liquid, the soil pH value kept decreasing. From the perspective of the whole restoration process, the soil pH at the A2 and B2 type sampling points that are 8cm from the anode, the soil pH presented a slow downward trend. After the restoration, the soil pH value of the entire electrodynamic reaction chamber was between 4.0 and 6.1. This indicates that acidic migration zone gradually formed in the whole soil without anode soil pH control, which facilitated the dissolution and removal of heavy metals. However, a excessive low soil pH will change the polarity of Zeta potential, which will affect the removal of heavy metal ions. Therefore, an optimal soil pH value can not only keep heavy metal ions in the dissolved state but also maintain the negative Zeta potential of the soil (Liu et al. 2015b).

Fig. 5 The time-dependent variation of Cd concentration at different sites. With the extension of restoration time, the concentration of Cd at the A type and B type sampling points gradually decreased due to the migration of Cd ions. The more it was close to the anode, the lower the Cd concentration was. During the first 48 h, the removal rate of Cd at A1 and B1 type sampling points that are 4 cm away from the anode reached about 65%, while the removal rate of Cd at A3 and B3 type sampling points that are near the cathode was relatively lower. This is due to that H^+ was produced in the anode and migrated, and the closer it was to the anode, the lower the soil pH was. A low pH can ensure good Zeta potential, which is conducive to the release of heavy metals from soil particles and accelerating the electrodynamic restoration process (Cao et al. 2001). However, there is no significant difference in Cd content between the A type sample

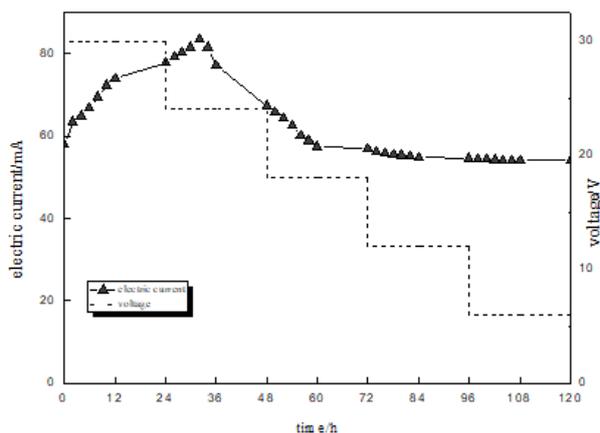


Fig. 6. The time-dependent variation of current and voltage during restoration with approaching anode method

points and B type sampling points, which is consistent with the variation of soil pH value at A and B type sampling points. This indicates that the removal of heavy metal Cd in soil is largely affected by soil pH.

Approaching Anode Restoration Method

According to above conclusion, it can be known that the more it is close to the anode, the better the soil remediation effect is, due to the effects of soil pH and Zeta potential at different locations in the soil. On this basis, the approaching anode method was applied to further experiment. After the experiment started, the anode moved a certain distance towards the cathode at regular intervals, and the repair voltage was adjusted to control the electric field strength at $2 V \cdot cm^{-1}$. The curve of voltage and current variation with restoration time during this process is shown in **Fig. 6**. The voltage between the anode and the cathode decreased continuously as the distance between them decreased. The current variation is similar to that in fixed anode restoration. When the current is stable, the current value is greater than that in the fixed anode method.

In the above fixed anode experiment, the soil pH values at A and B type sampling points that are equally distanced from the anode were observed to be similar, so it can be concluded that the pH value at sampling points on the same concentric circle differ slightly. Only A type sampling points were selected for analysis in the approaching anode experiment.

As shown in **Fig. 7**, the pH value change under approaching anode method was basically the same as that under the fixed anode method. In the late stage, the soil pH value at different points in approaching anode method decreased significantly compared with that in fixed anode method. This is due to that the distance

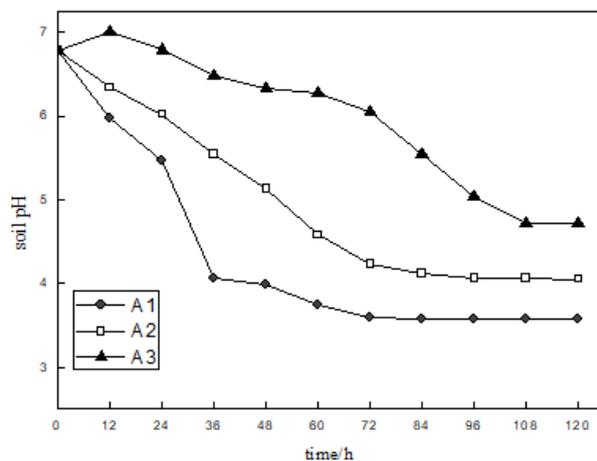


Fig. 7. The time-dependent variation of soil pH value during restoration with approaching anode method

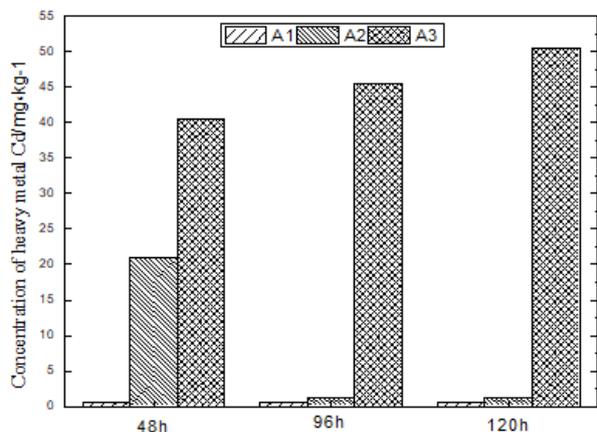


Fig. 8. The time-dependent variation of Cd concentration at different sites during restoration with approaching anode method

between the anode and the cathode decreased continuously, so the H^+ produced by the anode flowed faster to the cathode.

Fig. 8 shows the time-dependent variation of Cd concentration at different sites during restoration with approaching anode method. At 48 h, the concentration of Cd at A1 type sampling points that are 4 cm away from the anode has reached a low value. After 96 h, it can be seen that some cadmium in the soil are concentrated at the A3 type sampling points that are near the cathode, and Cd concentration at other points has been reduced to about $2 \text{ mg}\cdot\text{kg}^{-1}$.

Comparison of Two Restoration Methods

Fig. 9 shows the distribution of various forms of cadmium in soil after 120 h electrokinetic restoration between using fixed anode method and approaching anode method. It can be seen that the content of Cd residue near anode and in the middle soil varied little,

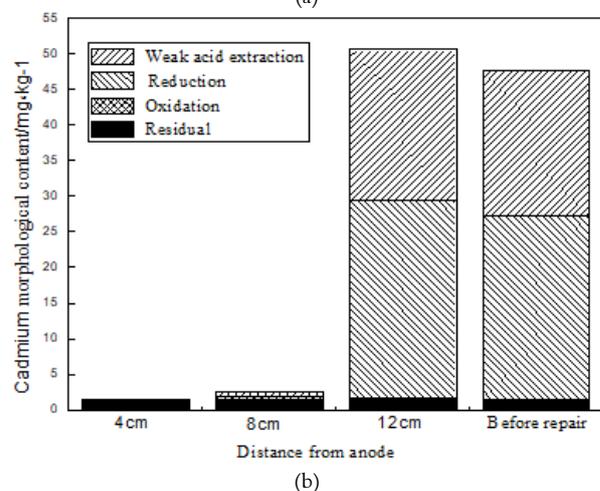
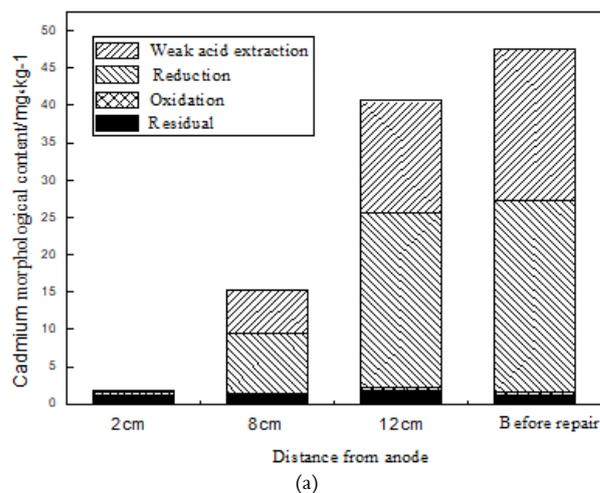


Fig. 9. Distributions of total Cd and various forms of Cd in soil after electrokinetic restoration

which may be due to the fact that the Cd in residue state is difficult to be transferred by the force of the electric field. However, the content of residual Cd near the cathode increased. This may be due to that Cd deposited in the soil near the cathode during the migration from the anode to the cathode, and became the residue state. The Cd in weak acid extraction state and reducible state near the anode and in the middle soil layer decreased significantly compared with that before restoration. This shows that the electrokinetic restoration had a good migration effect on Cd in weak acid extraction state and reducible state. After 120 h treatment, the cadmium concentration in most areas of the soil decreased significantly.

The Cd concentration at A2 type the sampling points was analyzed by combining **Fig. 5**, **Fig. 8** and **Fig. 9**. It can be seen that the removal rate of cadmium after 48 h restoration with fixed anode method was only 13%, while the removal rate of cadmium restoration with approaching anode method was about 60%. At the

end of the experiment, the removal rate of Cd at A2 type sampling points with fixed anode method was 68%, while the removal rate of Cd with approaching anode method was 95%.

The energy consumption of soil restoration was calculated according to formula (1)

$$E = U \int I dt \quad (1)$$

where E is the power consumption required by electrokinetic restoration, kWh; U is voltage, V; I is current, A; t is operation time, h.

Comparing the energy consumption of the two electrokinetic restoration methods, it can be known that the energy consumption of the approaching anode method was reduced by 65% compared with that of the fixed anode method after operating for 120 h. This is due to that the distance between the anode and cathode gradually decreases, the voltage between them decreases, and the part of the soil over which the anode moves no longer consumes energy. So the approaching anode restoration has great advantages.

CONCLUSIONS

(1) In the fixed anode restoration process, the current during the first 12 h showed an upward trend, and then increased slowly from 12 h to 32 h and reached the maximum value at 32 h. After 32 h, the current began to decrease and then tended to be stable. During the whole restoration process, the soil pH value showed a slow downward trend. After the restoration, the soil pH value of the entire electrokinetic reaction chamber was between 4.0 and 6.1, which is conducive to the removal of heavy metals.

(2) The current variation of the approaching anode method was similar to that of the fixed anode method. When the current was stable at the later stage, the current value was greater than that of the fixed anode method. The pH value variation during the first 24 h by approaching anode method was basically the same as that of the fixed anode method, while in the later period of restoration, the pH value under approaching anode method decreased more significantly.

(3) For both restoration method, after 120 h of electrokinetic restoration, the content of Cd residue near the anode and in the middle soil layer changed little, while the content of Cd residue near the cathode increased. The Cd in weak acid extraction state and reducible state near the anode and in the middle soil layer decreased significantly than that before the restoration. At the end of the experiment, the removal rate of Cd at the A2 type sampling sites with fixed anode method was 68%, and the removal rate of Cd in the same site with approaching anode method was 95%.

(4) As the distance between the anode and cathode decreased, the voltage between them decreased, and part of the soil over which the anode moved no longer consumed electricity. Therefore, during the whole restoration process, the energy consumption of approaching anode method was reduced by 65% compared with the fixed anode method. The approaching anode method is more effective and has a certain application prospect.

ACKNOWLEDGEMENTS

This research was supported by project of the National Natural Science Foundation of China (41641032).

REFERENCES

- Cao X, Chen Y, Wang X, et al. (2001) Effects of redox potential and pH value on the release of rare earth elements from soil. *Chemosphere*, 44: 655- 661.
- Chang J, Wang Y, Shen S (2018) A specific configuration of circulation-enhanced electrokinetics (CEEK) to remediate real-site Cd and Pb contaminated soils. *Journal of Hazardous Materials*, 359: 408-413.
- Habibul N, Hu Y, Sheng G (2016) Microbial fuel cell driving electrokinetic remediation of toxic metal contaminated soils. *Journal of Hazardous Materials*, 318: 9-14.
- Kim D, Jo S, Choi J, et al. (2012) Hexagonal two dimensional electrokinetic systems for restoration of saline agricultural lands: A pilot study. *Chemical Engineering Journal*, 198-199: 110-121.
- Lageman R (1993) Electroreclamation applications in the Netherlands. *Environmental Science & Technology*, 27: 2648-2650.
- Liu D, Liu F, Miao D (2015) Optimization of soil heavy metal sequential extraction procedures. *Geoscience*, 29: 390-396.

- Liu F, Fu R, Xu Z (2015) Optimization of electrode configuration in soil electrokinetic remediation. *Environmental Science*, 36: 678-685.
- Liu H, Cang L, Hao X, Wang Y, Zhou D (2016) Field-scale electrokinetic remediation of heavy metal contaminated sites. *Chinese Journal of Environmental Engineering*, 10: 3877-3883.
- Liu L, Li W, Song W, Guo M (2018) Remediation techniques for heavy metal-contaminated soils: Principles and applicability. *Science of the Total Environment*, 633: 206-219.
- Lu R (2000) *Methods of soil agricultural chemistry analysis*. Peking University press, 228-235.
- Selvi A, Aruliah R (2018) A statistical approach of zinc remediation using acidophilic bacterium via an integrated approach of bioleaching enhanced electrokinetic remediation (BEER) technology. *Chemosphere*, 207: 753-763.
- Wang Q, Zhou D, Cang L, et al. (2008) Application of bioassays to evaluate a copper contaminated soil before and after a pilot-scale electrokinetic remediation. *Environmental Pollution*, 157: 410.
- Xu L, Zhang Y, Dong P, et al. (2017) Effects of cathode electrolyte on electrokinetic remediation of cadmium-contaminated red soil. *Research of Environmental Sciences*, 30: 257-274.
- Xu Y, Xu X, Hou H, et al. (2016) Moisture content-affected electrokinetic remediation of Cr (VI)-contaminated clay by a hydrocalumite barrier. *Environmental Science and Pollution Research*, 23: 6517-6523.
- Zheng S, Shen Z, Chen X, Wang W (2018) Electrokinetic remediation of heavy metal contaminated soils using enhanced with approaching anodes technique. *Journal of Agro-Environment Science*, 26: 240-245.
- Zhou M, Xu J, Zhu S, Wang Y, Gao H (2018) Exchange electrode-electrokinetic remediation of Cr-contaminated soil using solar energy. *Separation and Purification Technology*, 190: 297-306.