Korean J. Chem. Eng., **31**(11), 2008-2013 (2014)
DOI: 10.1007/s11814-014-0137-9

pISSN: 0256-1115
eISSN: 1975-7220

Pulse-enhanced electrokinetic remediation of fluorine-contaminated soil

Ming Zhou[†]**, Shufa Zhu, Fang Liu, and Dongfang Zhou**

Chemical Engineering and Pharmaceutics School, Henan University of Science and Technology, Luoyang, P. R. China

(*Received 25 September 2013 • accepted 9 May 2014*)

Abstract−The presence of abundant fluorides in soil can pose potential threats to environment and human health. We investigated the effects of pulsed electric field on electrokinetic remediation of fluorine-contaminated soil by varying the pulse interval. Although the remediation time was increased, experimental results indicated pulse-enhanced electrokinetic remediation could improve the removal efficiency of fluorine better than the conventional electrokinetic remediation in the same intensity of electric field. The fluorine removal efficiency of the former (30 min, pulse interval) was 80.93% and that of normal electrokinetic remediation was 72.40%, because pulsed electric field could reduce the concentration polarization and increase the electrical current, electroosmotic flow and the electrical voltage part in soil cell. Therefore, in the later phase of electrokinetic remediation, when electrical current and the fluorine removal efficiency decreased obviously, at this time the pulse-enhanced method would be a considerable choice to eliminate fluorine in contaminated soils.

Keywords: Electrokinetic Remediation, Fluorine, Soil, Pulse, Ion Exchange Membrane

INTRODUCTION

China is facing a grave situation in soil pollution, and a large number of pollutants caused by human activities have entered into the soil with the rapid urbanization, and industrial and agricultural development. These soil contaminants include heavy metal pollutants such as cadmium, lead, chromium and nickel, organic pollutants such as benzene, toluene and trichloroethylene, and other pollutants, such as fluoride. Soil contamination with fluorides is usually ignored compared to soil pollution by heavy metals and organic pollutants. One important reason is that fluorine is considered by some people as one of the beneficial elements to human beings that do no harm to the body. Sure, small amounts of fluorides may be beneficial for bone strength and reduce tooth decay. But high concentration of fluorine and its compounds are also dangerous for humans, plants and animals [1,2]. For sodium fluoride, the lethal dose for a 70 kg adult is 5-10 g (32 to 64 mg elemental fluorine/kg body weight) [3]. Chronic excess fluoride consumption can lead to skeletal fluorosis, a disease of the bones that affects millions in China. Besides being toxic, high concentration of fluorine ions leads to the inhibition of some enzyme reactions, to the linking of biogenous elements and the disturbance of their balance in the organism [4]. In addition, soil pollution by fluorides has an unfavorable effect on the surrounding environment. Considerable amounts of fluorides can be leached from contaminated soil and cause groundwater contamination, and high concentration of fluorides can be absorbed by plants, which affects the growth and development of plants. Therefore, decontamination of the fluorine-contaminated soil is one of the most important challenges.

Electrokinetic remediation is an effective and green technology that was introduced for the remediation of soil, sludge and sediment contaminated with inorganic and organic pollutants. The basis of electrokinetic remediation lies in the application of a low intensity direct electric current to the contaminated environment [5]. On direct current electrical field, contaminants can be transported by electroosmosis, electromigration and other processes to either the cathode or anode, and the accumulative contaminants are extracted by the following methods: adsorption/electroplating onto the electrode, precipitation at the electrode, complexing with ion exchange resins or pumping water near the electrode [6]. Its advantages include applicability to a wide range of contaminants, applicability in low permeability soil and better removal efficiency [7]. Thus, electrokinetic remediation has been successfully applied to remove a wide range of contaminants, such as a variety of heavy meals, organic pollutants, and other pollutants such as uranium from contaminated soil, sludge and sediment [8-16].

Our group used electrokinetic remediation technology to remove fluorides from contaminated soil. Experiments proved that the method is feasible, but the removal percent of fluorides is lower in general if no enhancing treatment is applied, especially the later phase of remediation experiment [17]. Now it was reported that electrokinetic remediation method can also use ion exchange membrane for separation of contaminated soil and the electrolyte in the electrode compartment. The main purpose for using an ion exchange membrane is that ions are hindered in entering contaminated soil from the electrode compartment. Therefore, no electric current is wasted for carrying ions from one electrode compartment to another, which can enhance the remediation efficiency [18,19]. But the coming problem is concentration polarization. Concentration polarization refers to the emergence of concentration gradients at a membrane/solution interface resulting from selective transfer of some species through the membrane under the effect of transmembrane driving forces [20]. Concentration polarization can affect the performance of the remediation process. When an electric current is passed through an

---

[†] To whom correspondence should be addressed.
E-mail: axore@163.com

ion exchange membrane, the ionic concentration on the surface of membrane is decreased due to concentration polarization. There are no more ionic species available to carry the current. Thus, the voltage drop across the boundary layer increases, resulting in a higher energy consumption [21]. Recently, it was reported that pulsed electrokinetics could improve the removal efficiency of heavy metals and decrease the effect of concentration polarization. The reason is that using a pulsed electric field, during the period with current "OFF", the diffusion gradients (produced during the period with current "ON") can be diminished [22-25]. Therefore, we tried to use electrokinetic method by applying pulsed electric field to remove fluorides from contaminated soil at different pulse interval. Feasibility of pulse-enhanced electrokinetic remediation with ion exchange membrane on fluorine-contaminated soil was investigated.

MATERIALS AND METHODS

1. Site-specific Soil

The site-specific soil samples used in this study were collected from fluorine-contaminated farmland near an aluminum smelting plant in Luoyang City, China's Henan province. They were sampled from the surface layer (0-20 cm) using a plastic spade and were silty loam. The collected soil samples were air-dried and analyzed for the characteristics [26]. The fluorine concentration, organic matter content and pH of soil samples were 1,437 mg/kg, 1.764% and 7.862, respectively. Five binding fractions (Ws: water soluble fraction; Ex: exchangeable fraction; Fe/Mn: fraction associated with Fe and Mn oxides; Or: fraction associated with organic matter; Res: residual fraction) of fluorine were analyzed by sequential extraction. In this study, fluorine, mainly bound to the water soluble fraction (69.92%) and the residual fraction (20.95%) in fluorine-contaminated soil samples. Ex-F, Fe/Mn-F and Or-F in the soil were 1.918%, 3.497%, 3.715%, respectively. Under ambient conditions, the soil samples were air-dried and sieved through the 2-mm nylon sieve prior to their use.

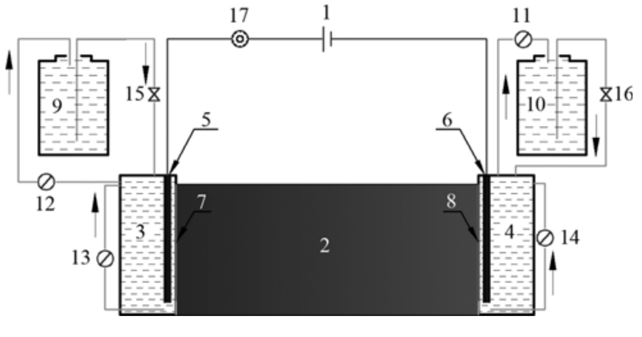

Fig. 1. A schematic diagram of the experimental apparatus (not to scale).

1. The DC power supply (GPC6030D, Gw instek, China); 2. The soil cell (10 [L] cm×6 [W] cm×8 [H] cm); 3, 4. The electrode compartment (4 [L] cm×6 [W] cm×8 [H] cm); 5, 6. Working electrode (graphite sheet, 1 [L] cm×6 [W] cm×8 [H] cm); 7. Anion exchange membrane (3361BW, Shanghai Shanghua Water Treatment Material Co., Ltd.); 8. Cation exchange membrane (3362BW, Shanghai Shanghua Water Treatment Material Co., Ltd.); 9, 10. The electrolyte reservoir; 11-14. 4-Channel peristaltic pump (BT00-300T/DG-4, longerpump, China); 15, 16. Simple flow regulator; 17. Timer

2. Electrokinetic Experiments

Electrokinetic experiments were performed in a self-made experimental apparatus (see Fig. 1 for the schematic of the apparatus).

In every electrokinetic experiment, 200 ml distilled water and 600 g dry soil sample were mixed and packed into the soil cell of apparatus. Distilled water was also used as the anolyte and catholyte. At a 15 ml/min flow rate, a four-channel peristaltic pump was used to circulate the electrolyte in the electrode compartment and electrolyte reservoir. The electrolyte of the electrode compartment and electrolyte reservoir was refreshed every 24 hours and the cumulative fluorides in anolyte and catholyte were measured. After electrokinetic experiment, the fluorides in the membranes were leachinged by TISAB (total ionic strength adjusting buffer, 85 g $NaNO_3$ and 58.80 g $C_6H_5Na_3O_7 \cdot 2H_2O$/trisodium citrate dihydrate in one liter) and added into the corresponding electrolyte (anion exchange membrane corresponded to anolyte and cation exchange membrane corresponded to catholyte). Then the treated soil was taken out and segmented to ten equal slices, dried and crushed lightly in a mortar by hand before the measurement of fluorine concentration and soil pH.

The cyclic process of pulsed electric fields consisted of a period with electric current in "ON" (application of an electric field) followed by a period with electric current in "OFF" (no application of an electric field). The specific experimental conditions are in Table 1.

3. Analytical Methods

An alkali fusion-selective ion electrode technique was used to measure total fluoride in soil (fluoride ion selective electrode, SPSIC, China) [27]. Before the measurement, TISAB was added to liberate fluorine ion, and adjust the pH of the solution to 5.5. Soil pH was determined in the ratio 1 : 2.5 of soil : distilled water suspension by the pH meter (pHS3C, SPSIC, China). The organic matter content of soil was measured by the PE-2400 elemental analyzer (PerkinElmer, USA). Electrical current through the soil cell and voltage in the different parts of electrokinetic apparatus were measured using the multimeter (F15B, Fluke, USA) during the remediation process. The sequential extraction procedure to fractionate different forms of fluorine in soil is listed in Table 2 [28]. To ensure data quality, all chemical analyses were performed in duplicate.

RESULTS AND ANALYSIS

1. Electrical Voltage in the Different Parts of Experimental Apparatus

Electrical voltage is one of the key factors in the electrokinetic remediation of contaminated soil. During electrokinetic remediation

Table 1. Electrokinetic experimental conditions

Run	Anolyte/ Catholyte	Voltage (V)	Treatment time (h)	Power on/ Off interval (min)
A	Distilled water	40	120	Normal
B	Distilled water	40	120	30
C	Distilled water	40	120	60
D	Distilled water	40	120	90
E	Distilled water	40	120	120

Table 2. The sequential extraction procedure to fractionate different forms of fluorine in soil

Fluorine species	Extract	Condition
Ws-F	Distilled water	Shake 0.5 h at 60 ºC
Ex-F	1.0 mol/L $MgCl_2$	Shake 1 h at 25 ºC
Fe/Mn-F	0.04 mol/L NHOH·HCl	Shake 1 h at 60 ºC
Or-F	0.02 mol/L HNO_3+30% H_2O_2+3.2 mol/L NH_4Ac	Shake 0.5 h at 25 ºC
Res-F	The total fluorine content minus other forms of fluorine in soil	

Note: Ws (water soluble fraction); Ex (exchangeable fraction); Fe/Mn (fraction associated with Fe and Mn oxides); Or (fraction associated with organic matter); Res (residual fraction)

using ion exchange membrane, the removal process is briefly divided into two steps: transport in the contaminated soil and transport across the ion exchange membrane to electrode compartment [23]. In the presence of ion exchange membrane, variations of electrical voltage between both ends of soil cell, contaminated soil and electrode (across the ion exchange membrane) can indicate the running state of electrokinetic remediation. Electrical voltage in the different parts of electrokinetic apparatus is shown in Fig. 2. In the figure, V_1 is the electrical voltage across anion exchange membrane between the anode and the left contaminated soil; V_2 is the electrical voltage part between both ends of soil cell, and V_3 is the electrical voltage across cation exchange membrane between the cathode and the right contaminated soil.

From Fig. 2, V_1 and V_3 exhibited the same trend. Because total voltage remained the same (40 V) in this experiment, therefore the changing trend of V_2 was exactly opposite to V_1 and V_3. Meanwhile, from Fig. 2(a) and Fig. 2(b), the highest voltage drop occurred in the parts across the anion exchange membrane (V_1) and through the contaminated soil (V_2), and the two parts were the main contributor of energy consumption.

Concentration polarization occurred in the ion exchange membrane, because V_1 and V_3 increased gradually with time. Meanwhile, V_1 and V_3 in the pulse current system (run B-E) were obviously lower than that in the normal direct current system (run A), and V_1 and V_3 decreased gradually with the decrease of power on/off interval. It proved that the pulse current could decrease the voltage drop of this part effectively and control the concentration polarization; therefore these saved voltages can be distributed to the soil cell (V_2) to drive the transfer of fluorides from the contaminated soil, which can partly explain the probable reason for higher fluorine removal in pulse-enhanced electrokinetic remediation with shorter power

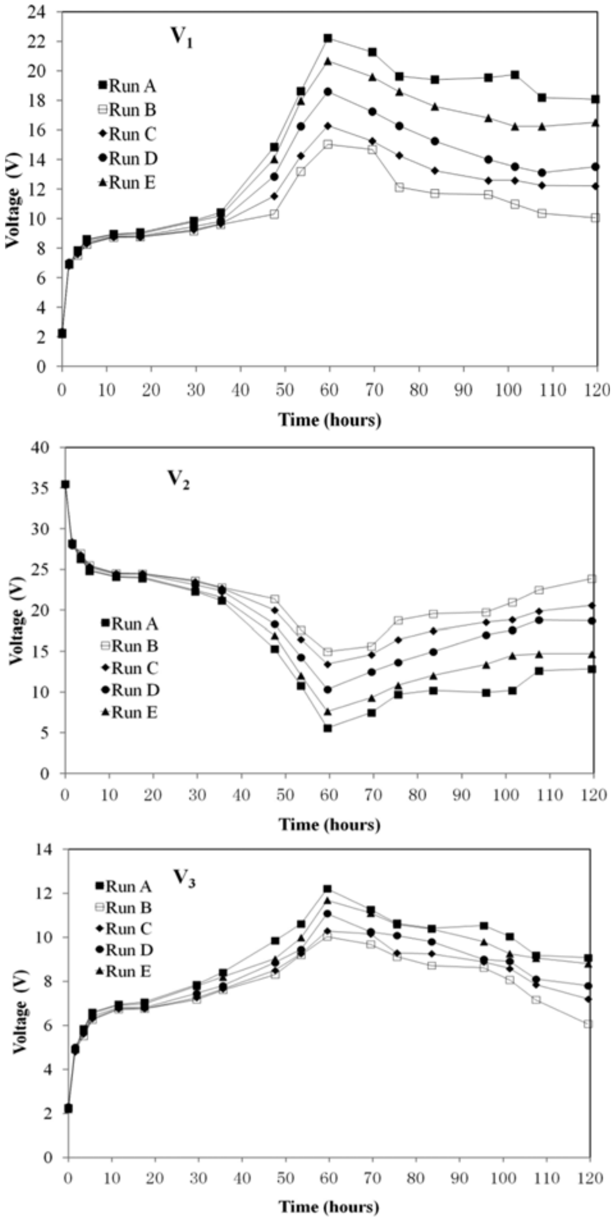

Fig. 2. Electrical voltage in the different parts of the experimental apparatus.

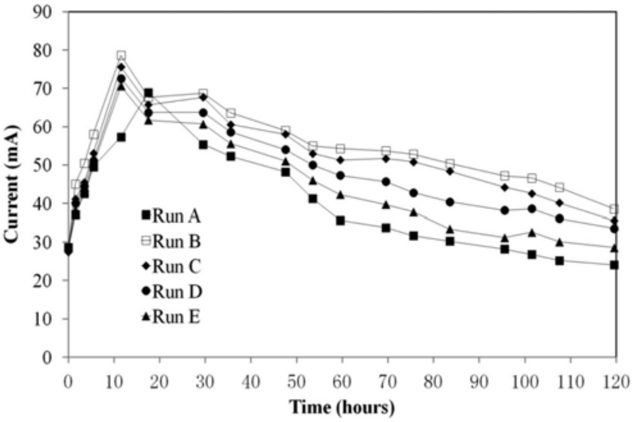

Fig. 3. Changes of current across soil cell during electrokinetic remediation.

on/off interval (Run B).

2. Electrical Current Across Soil Cell

During the electrokinetic remediation process, the variations of electrical current across soil cell are shown in Fig. 3. Electrical current in five runs showed the same trend. The electrical current first increased, reached a maximum, and then gradually decreased. The reason is that when the voltage gradient was established, electrical current was first low because it took some time for electrolyte to enter the contaminated soil and for soil contaminants and minerals to dissolve and desorb from the soil surface. After 24 hours, the electrical current reached a maximum because of electromigration of pollutants to electrode and high ion concentrations in pore fluid. Then thte electrical current began to decrease due to the decrease in the migration of anions and cations in pore fluid. Furthermore, hydroxide ions moving towards the anode can be neutralized by hydrogen ions moving towards the cathode, hence forming water and decreasing the ion concentration in the system.

Obviously, the electrical current in the pulse current system (run B-E) was higher than that in the normal direct current system (run A). Meanwhile, with the decrease of power on/off interval, electrical current through soil cell increased gradually, especially between run C (60 min interval) and run D (90 min interval), and run D (90 min interval) and run E (120 min interval). Run B exhibited the highest electrical current value in five runs. The reason is that more high transient current occurred in the pulse current system with the shorter power on/off interval, and pulse current could control the concentration polarization and lower the resistances of ion exchange membrane effectively. But between run B and run C, the dominance diminished.

3. Electroosmotic Flow During Electrokinetic Experiment

Electroosmotic flow is the motion of liquid induced by an applied potential across a porous soil. Some soluble fluorides and fluorine complexes in the contaminated soil could be removed by electroosmotic flow. At a basic pH, the surface charge of soil particles is negative and electroosmotic flow is toward the cathode [29]. During the electrokinetic experiment, electroosmotic flow was calculated by measuring the volume change in the catholyte; the cumulative amount of electroosmotic flow is shown in Fig. 4. Except for run E, electroosmotic flow in the pulse current system was also higher than that in the normal direct current system, and increased gradually with the decrease of power on/off interval.

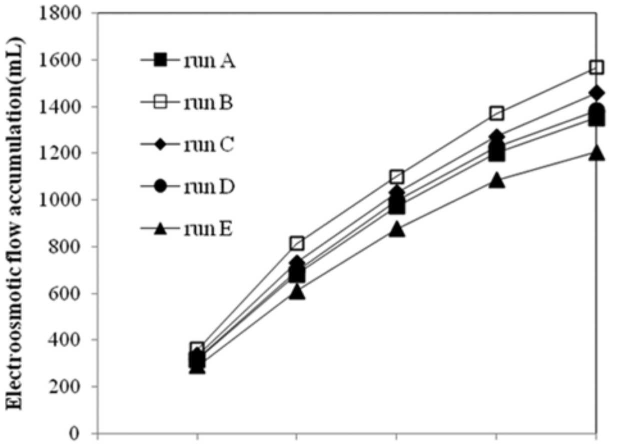

Fig. 4. Electroosmotic flow during electrokinetic remediation.

Electroosmotic flow of electrokinetic remediation can be calculated [30]:

$$Q_e = K_{eo}PA \qquad (1)$$

where Q_e (cm^3/s) is the electroosmotic flow, K_{eo} (cm^2/Vs) is the coefficient of electroosmotic permeability, P is the electrical potential gradient (V/cm), and A (cm^2) is the cross-sectional area of the soil. According to the equation, electroosmotic flow is directly proportional to the electrical potential gradient under the assumptions of constant porosity and a constant coefficient of electroosmotic permeability. From Fig. 2(b), run B exhibited the maximum electrical potential gradient in both ends of the soil cell; therefore, run B had the largest Q_e compared to other experimental runs. Meanwhile, though run E had higher electrical potential gradient than run A, the longer “OFF” time affected significantly the motion of liquid, so run E had the minimum Q_e.

4. Soil pH After Electrokinetic Experiment

Variations of soil pH are shown in Fig. 5. Electrokinetic remediation using ion exchange membrane can also change soil pH. When the applied current density reaches the limiting current density of the membrane, water splitting will happen at the interface between membrane and solution as a consequence of concentration polarization. Thus, though H^+ and OH^- are hindered in entering contaminated soil from the electrode compartment by ion exchange membrane, H^+ generated by water splitting at the anion exchange membrane transported toward the cathode by electromigration and resulted in a decreased soil pH in the anode region [23]. Water splitting can also take place at the cation exchange membrane, and OH^- produced by electrolysis reaction migrated from cathode to anode and resulted in an increased soil pH in the cathode region. Therefore, after the electrokinetic experiment, soil pH gradually increased from anode to cathode.

Though soil pH for five runs exhibited the same trend, there was some minor difference in soil pH between runs A, B, C, D and E. From Fig. 5, in the run A, pH value was higher near the anode and was lower near the cathode than that at the runs B, C, E and D, which was ascribed to the fewer electrode reactions and the lower produce rate of H^+ and OH^- in run A.

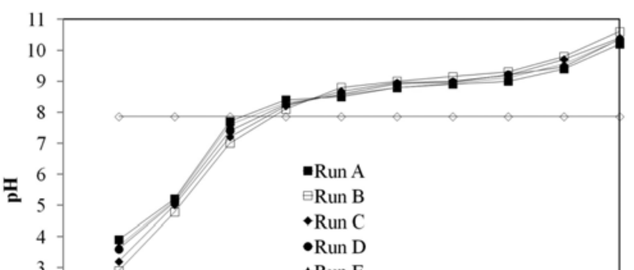

Fig. 5. Soil pH in soil sections after electrokinetic remediation.

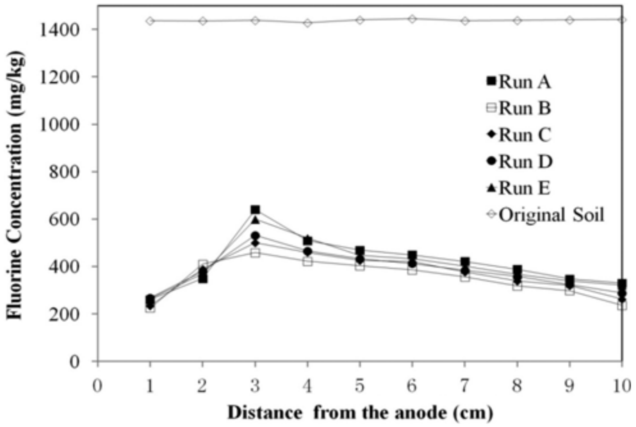

Fig. 6. Residual fluorine concentration in soil sections after electrokinetic remediation.

5. Fluorine Removal from Contaminated Soil

Fig. 6 shows the concentration of residual fluorine in ten soil sections after electrokinetic remediation. The cumulative amount of fluorine of five runs in the anolyte and catholyte is shown in Fig. 7, during the electrokinetic remediation process.

From Fig. 6, compared to the initial total fluorine concentration (1,437 mg/kg), the concentration of fluorine in treated soil obviously decreased (all experimental runs). As fluorine has a negative charge, fluorides desorbed from contaminated soil were moved across the anion exchange membrane to the anode by electromigration. Meanwhile, fluorine could also be removed as soluble fluorides and fluorine complexes by electroosmosis flow. This combination of electromigration and electroosmosis flow eliminated fluorine in the contaminated soil; therefore the concentration of fluorine in treated soil decreased.

From Fig. 7, under the chosen experimental conditions, it was

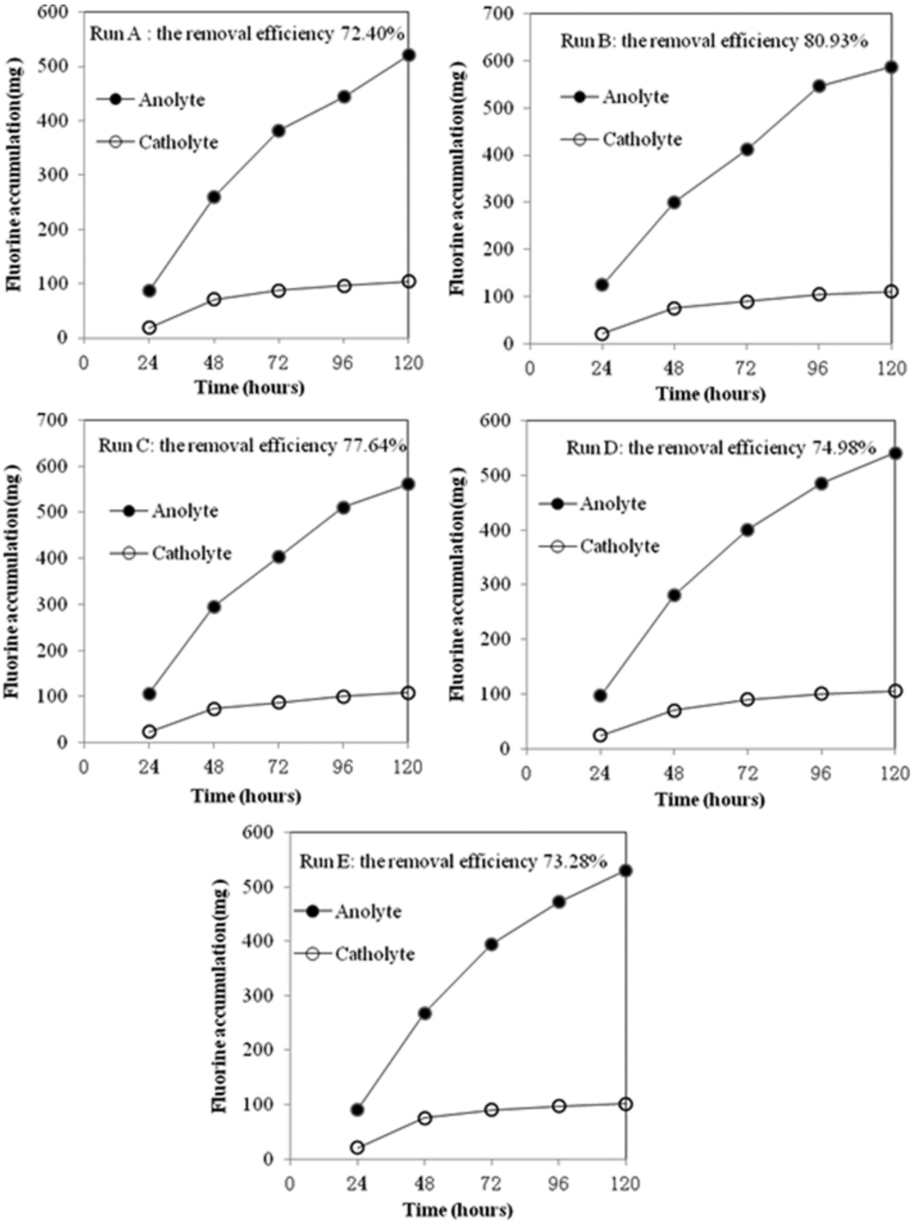

Fig. 7. Cumulative mass of fluorine in the electrolyte during electrokinetic remediation.

apparent that run B had the highest removal efficiency of fluorine in five experimental runs (80.93%, which was calculated according to the cumulative amount of fluorine in anolyte (587.6 mg) and catholyte (110.2 mg)/total fluoride content in 600 g contaminated soil (1437*0.6=862.2 mg)). Experimental results showed that pulse-enhanced electrokinetic remediation was a more effective method to remove fluorine pollutants from contaminated soils, because of higher electric current and V_2 quickly to migrate fluorine to the electrode.

Meanwhile, in Fig. 7, cumulative fluorine in anolyte is much more than that in catholyte in all experiments. This indicates that electromigration was the predominant removal mechanism for electrokinetic remediation of fluorine-contaminated soils. After electrokinetic experiments, 60.35%, 68.15%, 65.12%, 62.76% and 61.51% of fluorine in Run A-E were attracted to thte anode and removed by electromigration.

CONCLUSION

This paper provides a preliminary characterization of fluoride removal from contaminated soil using pulsed electric fields applied to the electroremediation cell. Although it increased the amount of remediation time, experimental results showed that pulse-enhanced electrokinetic remediation could improve the removal efficiency of fluorine better than conventional electrokinetic remediation at the same intensity. The main reason was that the pulse-enhanced method could control the concentration polarization and increase the electrical voltage part in the soil cell, electrical current and electroosmotic flow, which favored the removal of fluorine from the soil. Therefore, in the later phase of the electrokinetic experiment, when electrical current and the fluorine removal efficiency obviously decreased, at this time the pulse-enhanced method was a considerable choice to eliminate fluorine in contaminated soils.

ACKNOWLEDGEMENT

The authors acknowledge the financial support for this study by Youth Scientific Funds of Henan University of Science and Technology (2012QN036).

REFERENCES

1. J. A. Camargo, *Chemosphere*, **50**, 251 (2003).
2. M. Domingos, A. Klumpp, M. C. S. Rinaldi, I. F. Modesto, G. Klumpp and W. B. C. Delitti, *Plant. Soil*, **249**, 297 (2003).
3. R. Liteplo, R. Gomes, P. Howe and H. Malcolm, *World Health Organization, Geneva*, **100** (2002).
4. G. A. Evdokimova, *Chemosphere*, **42**, 35 (2001).
5. A. N. Alshawabkeh, A. T. Yeung and R. M. Bricka, *J. Environ. Eng.*, **125**, 27 (1999).
6. P. Lu, Q. Y. Feng, Q. J. Meng and T. Yuan, *Sep. Purif. Technol.*, **98**, 216 (2012).
7. V. Jurate, S. Mika and L. Petri, *Sci. Total. Environ.*, **289**, 97 (2002).
8. G. Peng, G. Tian, J. Liu, Q. Bao and L. Zang, *Desalination*, **271**, 100 (2011).
9. J. L. Chen, S. F. Yang, C. C. Wu and S. Ton, *Sep. Purif. Technol.*, **79**, 157 (2011).
10. L. Cang, Q. Y. Wang, D. M. Zhou and H. Xu, *Sep. Purif. Technol.*, **79**, 246 (2011).
11. A. Giannis, D. Pentari, J. Y. Wang and E. Gidarakos, *J. Hazard. Mater.*, **184**, 547 (2010).
12. P. Zhang, C. J. Jin, Z. H. Zhao and G. B. Tian, *J. Hazard. Mater.*, **177**, 1126 (2010).
13. V. R. Ouhadi, R. N. Yong, N. Shariatmadari, S. Saeidijama, A. R. Goodarzia and M. Safari-Zanjania, *J. Hazard. Mater.*, **173**, 87 (2010).
14. C. S. Jeon, J. S. Yang, K. J. Kim and K. Baek, *Clean-Soil. Air. Water*, **38**, 189 (2010).
15. J. W. Ma, F. Y. Wang, Z. H. Huang and H. Wang, *J. Hazard. Mater.*, **176**, 715 (2010).
16. G. N. Kim, D. B. Shon, H. M. Park, K. W. Lee and U. S. Chung, *Sep. Purif. Technol.*, **80**, 67 (2011).
17. S. F. Zhu, J. H. Zhang and T. Y. Dong, *Environ. Earth Sci.*, **2**, 379 (2009).
18. L. M. Ottosen, H. K. Hansen, S. Laursen and A. Villumsen, *Environ. Sci. Technol.*, **31**, 1711 (1997).
19. H. K. Hansen, A. Rojo and L. M. Ottosen, *J. Hazard. Mater.*, **117**, 179 (2005).
20. E. M. V. Hoek, M. Guiver, V. Nikonenko, V. V. Tarabara and A. L. Zydney, *Encyclopedia of Membrane Science and Technology*, **3**, 2219 (2013).
21. T. R. Sun, L. M. Ottosen and P. E. Jensen, *J. Hazard. Mater.*, **237-238**, 299 (2012).
22. H. K. Hansen and A. Rojo, *Electrochim. Acta*, **52**, 3399 (2007).
23. T. R. Sun and L. M. Ottosen, *Electrochim. Acta*, **86**, 28 (2012).
24. B. G. Ryu, S. W. Park, K. Baek and J. S.Yang, *Sep. Purif. Technol.*, **44**, 2421 (2009).
25. B. G. Ryu, J. S. Yang, D. H. Kim and K. Baek, *J. Appl. Electrochem.*, **40**, 1039 (2010).
26. Y. Lee and S.-W. Oa, *Environ. Eng. Res.*, **17**, 145 (2012).
27. N. R. Mcquaker and M. Gurney, *Anal. Chem.*, **49**, 53 (1977).
28. W. Chen, *Bioinformatics and Biomedical Engineering (ICBBE 2010)*, 1 (2010).
29. D.-H. Kim, C.-S. Jeon, K. Baek, S.-H. Ko and J.-S. Yang, *J. Hazard. Mater.*, **161**, 565 (2009).
30. J. Hamed, Y. Acar and R. Gale, *J. Geotech. Energy*, **117**, 241 (1991).