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Enhanced electrokinetic remediation of fluorine-contaminated soil by applying an ammonia continuous circulation system

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Abstract−The objective of this research was to investigate the effects of ammonia continuous circulation enhanced electrokinetic remediation of fluorine contaminated soil and to analyze its influence on soil pH after remediation. An experimental study was carried out in self-made electrokinetic apparatus. The voltage gradient was set at 1.0 V/cm and ammonia water with different concentrations was used as electrolyte which circulated in series. Comparative studies were made by using deionized water as electrolyte which circulated separately in one experiment and continuously in another. According to the experiment the continuous circulation of ammonia water increased the current value during the remediation process and maintained current through the soil cell stabler, which not only increased fluorine migration but also reduced energy consumption. Among the given ammonia concentrations (0, 0.01, 0.1 and 0.2 mol/L) the removal rate increased with ammonia concentration. 0.2 mol/L had the highest current (26.8 mA), and the removal rate amounted up to 57.3%. By using ammonia circulation enhanced electrokinetic technology, the difference between pH values of cathode soil and anode soil became smaller. Ammonia continuous circulation enhanced electrokinetics can effectively remediate fluorine contaminated soil and the residual ammonia in the soil can also improve soil fertility.

Keywords: Ammonia Water, Electrokinetic Remediation, Fluorine, Circulation Method

INTRODUCTION

Fluorine is an important soil inorganic pollutant in China. In recent years, a large amount of fluorine has been sent into the environment through steel smelting, production of aluminum, phosphate fertilizer, glasses, ceramics, bricks, extraction of phosphate rocks, processing of fluoride industrials, as well as coal burning. Fluorine enters the soil directly or indirectly through precipitation, infiltration, and eluviation; as a result fluorine pollution in soil has become increasingly serious. Many fluorides can be leached from fluorine contaminated soil. Besides polluting surface water and groundwater, it is also possible for fluorine to enter the human body through drinking water, plant roots and food chain. Chronic intake of excessive fluorine can cause severe permanent bone and joint deformations, such as dental fluorosis and skeletal fluorosis. At present there are 34.174 million people with dental fluorosis and 3.199 million with skeletal fluorosis in China by excess intake of fluoride [1]. This regional endemic fluorosis is irreversible and has no treatment, which endangers human health [2-6]. So it is of great practical significance to study how to remove excess fluorine from fluorine polluted soil.

Electrokinetic technology is an emerging technology for soil remediation and has shown good prospects for remediating soils polluted by heavy metals and organic substances [7-13]. Some published literatures have shown that such a method can also be applied for the remediation of fluorine-contaminated soil [14-18], but the research results suggest that the removal efficiency of fluorine by electrokinetics is lower and unsatisfactory. To improve the removal efficiency of fluorine during the remediation process, different enhanced methods have been taken, such as, saturating the fluorine contaminated soil in sodium hydroxide solution to induce electrolysis reactions in the electrodes, increasing electric conductivity of the medium by adding Na^+ and OH^- ions into soil [14], or using strong alkaline solution as anolyte to enhance the desorption of fluoride and electroosmotic flow, etc [15,16]. Our group also used pulsed electric fields with ion exchange membrane to control concentration polarization and to exclude ions migration from the electrode well into the soil, so as to increase the electrical current and electroosmotic flow [18]. The above enhanced methods increased the removal efficiency, but after electrokinetic experiment, the soil pH increased obviously, ranging from 11.0 to 12.3 compared to the initial pH 8.91 [15]. In another research the pH of the whole soil reached to a point more than 12 with an original soil pH 4.96 [17]. In addition, the difference of the pH values between anode soil and cathode soil was very obvious; the pH value near anode reduced to about 3, and that near cathode increased to about 11, while the initial soil pH was 8.17 or 7.862 [16,18]. As a result, the soil property was changed significantly, which affected soil fertility as well as plant growth. In view of this, we used ammonia water, a fertilizer for agriculture, as electrolyte which circulated in series between anode and cathode to remove fluorine from soil. To make a comparison, deionized water was used as electrolyte which circulated separately in anode or cathode in one group of experiments and circulated in series between anode and cathode in another. This ammonia continuous circulation enhanced electrokinetics was used to investigate the effects of fluorine removal and its influence on

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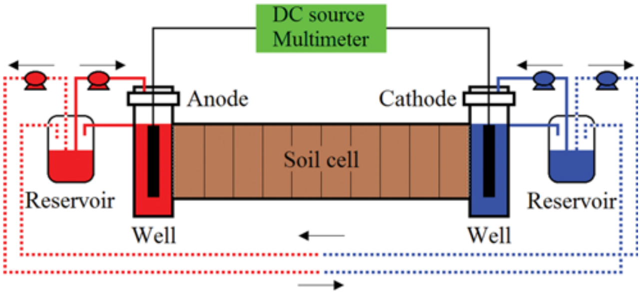

Fig. 1. A schematic diagram of the electrokinetic apparatus.

soil pH values.

MATERIALS AND METHODS

1. The Experimental Soil and Apparatus

The experimental soil was sampled from a farm field near an aluminum plant in Xin'an County, Henan province. The soil was 0-20 cm surface soil, being air dried under ambient conditions and ground to pass through a 2 mm sieve. The soil was silty loam with an organic matter content of 20.51 g/kg. The initial pH value of the soil was 8.17, electrical conductivity 405 μs/cm, and total fluorine content 1058 mg/kg.

The experiment was carried out in a self-made electrokinetic apparatus, the schematic diagram of which is shown in Fig. 1. The major components of the apparatus include a direct current power supply (GPC-6030D, Good Will Instrument Co., China), a soil cell (6×8×10 cm, organic glass material), two nylon meshes, filter papers, and two high purity graphite sheet electrodes, two electrode wells, two electrolyte reservoirs, a four channel peristaltic pump (BT00-300T+DG-4, Baoding Longer Precision Pump Co., Ltd. China), a digital multimeter (F-15B, Fluke, USA).

2. Experimental Methodology

200 mL deionized water and 600.0 g soil sample were mixed evenly and then installed in the soil cell. Deionized water or ammonia water solution was continuously supplied to the electrode well to maintain the constant external hydraulic gradient in the electrode well. Each electrolyte solution was refreshed every 24 hours. When the electrolyte circulated separately (Fig. 1, red and blue real line), the electrolyte in the anode well and anode reservoir circulated in one channel of the peristaltic pump, and that in the cathode well and cathode reservoir circulated in another channel of the peristaltic pump. The liquid level of the electrode wells was controlled automatically by the overflow. When the electrolyte circulated in series (Fig. 1, red and blue real line and broken line), the electrolyte circulated in the other two channels of the peristaltic pump.

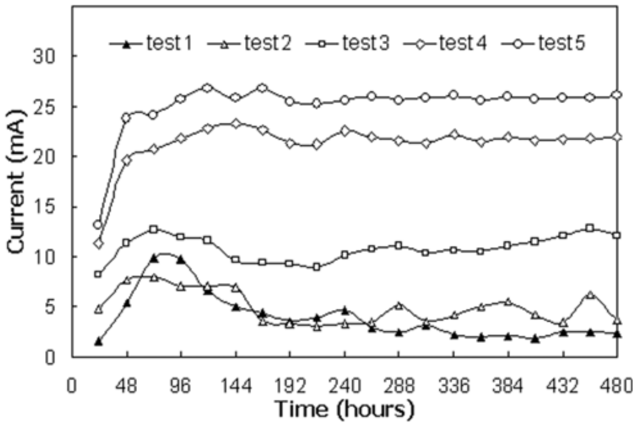

Fig. 2. Variation of electric current through the cell with time.

An electric field 1.0 V/cm was applied to the soil column for 20 days in all tests. The current was measured at fixed time each day with a multimeter. The electrolyte in the reservoir was circulated with a peristaltic pump at the flow rate of 10 ml/min. After 20 days of experimentation, the soil column was divided into ten equal-length sections from anode to cathode. After the soil samples were air-dried, the soil pH, conductivity, and fluorine contents of each section were measured, as well as the pH of the electrolyte and the fluorine concentration in the electrolyte. In total there were five groups of experiments, the design of which is shown in Table 1.

3. Analytical Method

The organic matter content in the soil samples was analyzed by combustion in an Elemental Analyzer (PE2400, Perkin Elmer, USA). Soil pH was measured with pH meter (pHS-3C, E-201-C pH compound electrode, Shanghai Precision and Scientific Instrument Co., Ltd. China) and soil electrical conductivity (EC) with a conductometer (DDSJ-308A, Shanghai Precision and Scientific Instrument Co., Ltd. China) in a 1 : 2.5 soil to water suspension [19]. The fluorine content in soil was determined by way of alkaline fusion in conjunction with a fluoride ion selective electrode and that in electrolyte by fluoride ion selective electrode method (pF-1 fluoride ion selective electrode and a calomel reference electrode, Shanghai Precision and Scientific Instrument Co., Ltd. China) [20,21]. Electrical current through the soil cell was measured by a multimeter during the remediation process.

RESULTS AND DISCUSSION

1. Variation of Current during Remediation Process

The electric current across soil cell was an important factor influencing the migrant of pollutants during the remediation process.

Table 1. Electrokinetic testing program

Test no.	Electrolyte	Circulation manner	Voltage gradient (V/cm)	Operation duration (days)
Test 1	Deionized water	Separate circulation	1.0	20
Test 2	Deionized water	Continuous circulation	1.0	20
Test 3	0.01 mol/L Ammonia water	Continuous circulation	1.0	20
Test 4	0.1 mol/L Ammonia water	Continuous circulation	1.0	20
Test 5	0.2 mol/L Ammonia water	Continuous circulation	1.0	20

Variation of electric current through soil cell during the experimental process is shown in Fig. 2. As shown, the current increased continuously since the start of the experiment; after reaching a certain point, the current reduced slowly and fluctuated greatly when deionized water was used as electrolyte (test 1, test 2). When ammonia water was used as electrolyte the current increased obviously with the rise of the ammonia concentration, and the current reached the highest value 26.8 mA (test 5) and fluctuated slightly.

The electric current was highly related to the concentration of mobile ions in the soil solution during the remediation process [22]. At the beginning of the experiment the fluid in the anode well flowed towards cathode through soil and formed electroosmosis under the function of electric field. Meanwhile, the ions in the soil pore water transferred to the opposite electrode; therefore, the current augmented gradually due to their mutual reaction. As time went on, the concentration of the transferable ions in the soil pore water reduced gradually when deionized water was used as electrolyte. At the same time, H^+ and OH^- generated from the electrolysis reaction in anode and cathode made soil minerals dissolve or precipitate; therefore, the concentration of transferable ions in soil solution became continuously higher or lower, which led to an obvious fluctuation in the current [23,24]. However, when ammonia was used as electrolyte, with the rise of the ammonia concentration, the concentration of the transferable ions NH_4^+ and OH^- in the soil solution also increased, and as a result the current value increased obviously and varied slightly. A stable current can reduce energy consumption during the remediation process [22].

2. Variation of Electrolyte pH with Operation Time

Fig. 3 shows the variation of electrolyte pH with operation time during the remediation process. When deionized water was used as electrolyte which circulated separately (test 1), the pH value of the cathode electrolyte increased significantly, while that of the anode electrolyte decreased obviously. Under the manner of circulation in series, when deionized water was added into electrolyte, the pH value stabilized at about 7.5 (test 2). However, when ammonia with different concentrations was added into electrolyte, the variation of the pH was between 9.35-10.24 (test 3), 9.75-10.79 (test 4) and 10.09-10.91 (test 5), respectively.

The electrolyte was refreshed at fixed time every day, and the electrolysis reaction of water existed all the time during the remediation process, so that OH^- was generated at cathode and H^+ at anode. The initial pH of the deionized water for the experiment was 7.0. When deionized water was used as electrolyte under separate circulation manner, the pH of the cathode electrolyte rose to 12.16 obviously, while that of the anode decreased to 2.72. However, when deionized water was used as electrolyte under continuous circulation manner, OH^- and H^+ generated by electrolysis at cathode and anode formed water again so that the pH stabilized at about 7.5. The initial pH value of the ammonia 0.01, 0.1, 0.2 mol/L was 10.63, 11.13 and 11.28, respectively. When ammonia was used as electrolyte under continuous circulation manner, because of the alkaline nature of ammonia, the anodic reaction was as follows:

$$4\ OH^- - 4e^- \rightarrow O_2 + 2\ H_2O \tag{1}$$

The reaction led to a lower concentration of OH^- in ammonia; in the meantime the buffering function of ammonia also reduced the pH value of the electrolyte.

3. Changes of Fluoride Concentration in Electrolyte during Remediation Process

Fig. 4 displays the fluoride concentration in the electrolyte during remediation process. At the initial stage of the experiment, the fluoride concentration in the electrolyte increased gradually, and reached a peak when experimenting for approximately 96 h, then reduced gradually and fluctuated slightly. When deionized water was used as electrolyte which circulated separately, the highest fluoride concentration in the anolyte was 77.9 mg/L, while that in the catholyte was 19.5 mg/L. During the process of electrolyte circulating in series, with the rise of the ammonia concentration, the fluoride concentration in the electrolyte also increased.

During electrokinetic remediation of fluorine contaminated soil, on the one hand, fluorine ions with negative charge in pore fluid were transferred to positively charged anode, that is, fluorine was driven into electrolyte by electromigration. The ion velocity μ_{em} is governed by electric field strength and ionic charge number.

$$\mu_{em} = vzFE \tag{2}$$

where v is the ion mobility [$cm^2/(V\cdot s)$], z is the ionic charge number, F is Faraday's constant (C/mol), and E is the electric field strength (V/cm) [11].

On the other hand, it is very easy for ions with negative charges on the soil particle surface and the cation in the soil pore fluid to

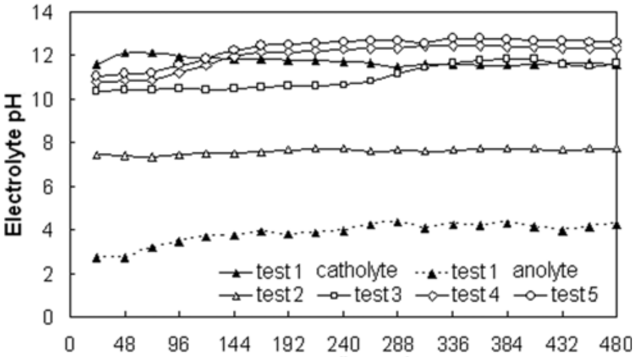

Fig. 3. Variation of electrolyte pH with time.

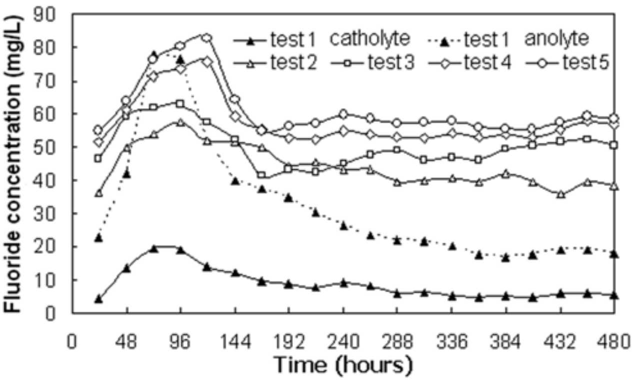

Fig. 4. Change of fluoride concentration in electrolyte with time.

form diffuse double layer, which induces the soil pore solution to move from anode to cathode and therefore forms electroosmotic flow. Fluorine moved to cathode by electroosmotic flow was in the form of fluoride or other soluble ions, such as fluoride complexes $(AlF)^{2+}$ and AlF_2^+ [14,25]. The electroosmotic permeability can be calculated using the following equation:

$$Q=k_eEA \quad (3)$$

where Q is the electroosmosis volumetric flow rate (cm^3/s), k_e is the coefficient of electroosmotic permeability [$cm^2/(V\cdot s)$], E is the electric field strength (V/cm), A is the cross-sectional area (cm^2) [26].

The mutual function of electromigration and electroosmosis made fluorine accumulate in anodic electrolyte and cathodic electrolyte. The electromigration quantity of F^- and the electroosmosis quantity of fluorine complexes such as $(AlF)^{2+}$ and AlF_2^+ were in proportion to the electric field strength [27], which was in proportion to current if electrode area kept constant. After the start of the experiment the current through the soil increased gradually and reached a peak (Fig. 2), and the fluoride concentration in the two electrolyte wells increased step by step proportional to current. With the development of the experiment, on the one hand, the current through the soil became weaker, causing a lower electroosmotic flow. On the other hand, the fluorine content in soil also reduced gradually, which resulted in lower fluoride content in electrolyte. So fluoride concentration in electrolyte showed initial increasing and then decreasing trend. The accumulation of fluorine in the electrolyte augmented little by little [16]. The fluorine in soil can be removed by way of refreshing the electrolyte every day to avoid the fluorine in the electrolyte from entering soil again and being adsorbed to soil particle surface; therefore, a higher removal efficiency of fluorine can be guaranteed.

During the electrokinetic remediation process, the removal of pollutants was affected by four mechanisms — electromigration, electroosmosis, electrolysis reaction and electrophoresis, among them electromigration was the major mechanism [22,28,29]. Most researchers believed that the amount of pollutants removed by electromigration was ten times or even more than that by electroosmosis; therefore, the fluorine moved into anode solution by electromigration under separate circulation manner was obviously higher than that moved into cathode solution by electroosmosis. Under continuous circulation manner, with the increase of the ammonia concentration, the pH value also increased little by little, which led to a much higher pH of the soil pore solution than the zero point charge (ZPC) of the soil colloid. The soil particles had negative zeta potential, which made the negative charge on the soil particle surface increase [30]. The cation in the pore fluid interacted with the negatively charged soil particle surface, which led to an increase in the cation adsorption; therefore, the thickness of the diffuse double layer increased and the electroosmotic flow intensified. Shapiro and Probstein reported that the electroosmotic flow rate of alkaline conditioning was significantly enhanced compared to that in the case of acidic conditioning [15]. At the same time anions were repulsed, which facilitated the desorption of fluorine. The desorption of fluorine increased with the rise of the electrolyte pH. During the electromigration process, the migration happened only when fluorine existed in water soluble form in the soil solution [25], and the removal amount of fluorine was also increased by electromigration. The interaction of electroosmosis and electromigration made the fluoride concentration in the electrolyte increase accordingly.

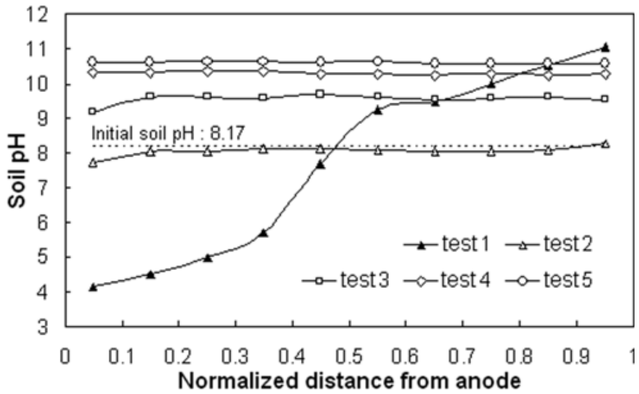

Fig. 5. Soil pH distribution in soil sections after electrokinetic treatments.

4. Changes of Soil pH and Electrical Conductivity after Remediation

Fig. 5 demonstrates the changes of soil pH after remediation. The difference between the soil pH at anode and cathode was most obvious in test 1. But in tests 2-5, the soil pH at anode and cathode changed slightly; especially in test 2 the soil pH almost kept unchanged after electrolysis. With the increase of the ammonia concentration, the soil pH also increased after remediation.

The acid and base generated by the electrolysis of water are the major sources for the change of soil pH during electrokinetic treatment. During the process of electrokinetic remediation, electrolysis reaction of water happened at cathode and anode. H^+ and OH^- were generated and entered the soil, which led to a variation of soil pH near anode and cathode [22,31], that is, the soil pH at anode reduced and that at cathode increased; as a result the difference between the pH values increased. However, under continuous circulation manner, OH^- and H^+ generated from electrolysis reaction at anode and cathode interacted with each other and formed water again. The difference between pH values of cathode soil and anode soil became smaller. After the remediation the soil pH was determined by initial soil pH and electrolyte pH. With the rise of the

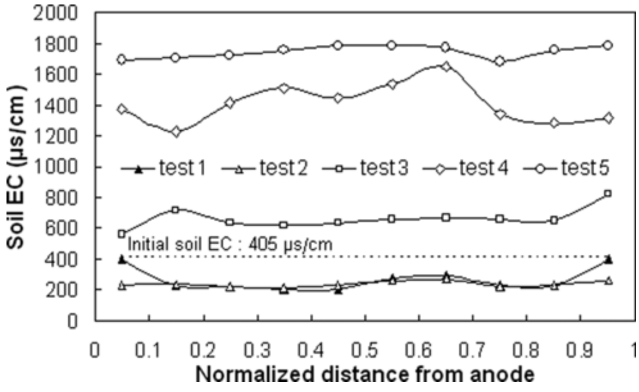

Fig. 6. Soil EC in soil sections after electrokinetic treatments.

ammonia concentration, the soil pH increased after remediation.

Fig. 6 shows the variation of soil electrical conductivity after remediation. When deionized water was used as electrolyte, the soil electrical conductivity after remediation was lower than that of the initial soil (405 μs/cm). When ammonia water was used as electrolyte, the soil electrical conductivity after remediation increased with the rise of the ammonia concentration.

The soil electrical conductivity indicates the conductive ability of the soil solution, and the transmission of the soluble ions in the soil can increase the electrical conductivity of the soil pore water [8]. The soluble ions include NH_4^+ and OH^- generated by ammonia ionization, H^+ and OH^- generated by water electrolysis, the natural ions in the soil as well as the ions of the pollutants. In test 1 and test 2 which used deionized water as electrolyte, the soluble ions in the soil entered electrolyte through electromigration and electroosmosis; as a result, the soil electrical conductivity was lower than that of the initial soil. But when ammonia water was used as electrolyte, NH_4^+ and OH^- with different concentrations moved into soil through electromigration and electroosmosis, so that the soil electrical conductivity increased with the concentration of the electrolyte after remediation.

5. Residual Fluorine Content in Soil after Remediation

Fig. 7 shows the fluorine content, expressed in a ratio between the residual and initial content, in ten different slices of the soil after remediation treatment. Compared with the total fluorine content 1,058 mg/kg in the initial soil, the fluorine content in soil after remediation was generally lower. When deionized water was used as electrolyte, the removal rate of soil fluorine under separate and continuous circulation manners was 20.3% (test 1) and 41.4% (test 2), respectively, and the residual fluorine in the soil focused in the middle of soil cell after remediation. When ammonia was used as electrolyte and circulated continuously, the removal rate of soil fluorine was 52.3% (test 3), 55.8% (test 4) and 57.3% (test 5), respectively, that is, the removal rate increased with ammonia concentration.

The soil pH can influence the forms of fluorine in soil and is a determinant factor for fluorine solubility in soil solution. Fluorine solubility shows a minimum at pH 6.0-6.5 and is increasing at $pH<6$ as well as at $pH>6.5$. In acid soil when $pH<6$, Al-F-complexes, such as $(AlF_3)^0$, $(AlF_4)^-$, $(AlF)^{2+}$ and AlF_2^+, are the main forms of fluorine in soil solution. The higher solubility of fluorine in acid soils should be closely related to the formation of Al-F-complexes, which shifted the equilibrium towards fluorine in solution. With the increase of pH, the stability of Al-F-complexes decreases; therefore, total fluorine solubility decreases too. In alkaline soils with $pH>6.5$, the solubility of free fluoride (F^-) increases with pH value because favorable electrostatic potential of variable charged materials diminishes, raising the negative surface charge and resulting in a repulsion of negatively charged fluoride [32,33]. F^- is the major form of fluorine in soil solution.

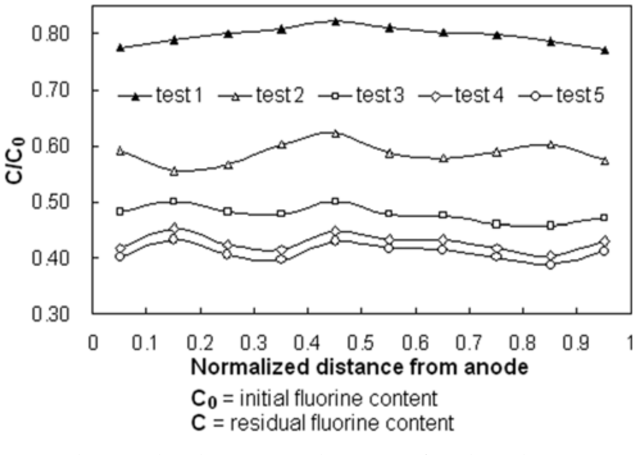

Fig. 7. Fluorine distribution in soil sections after electrokinetic treatments.

When deionized water was used as electrolyte and circulated separately (test 1), the electrolysis reaction of water generated OH^- at cathode and H^+ at anode, respectively, which made the soil solution pH near the cathode area increase and that near the anode area decrease. The ionic mobility of OH^- was only half of the ionic mobility of H^+, so the soil with low pH was of a large amount in the soil cell. In acidic conditions, it is difficult for soil fluorine to desorb and become water soluble form. At the same time, the current through the soil cell was weaker (Fig. 2), and the total amount of fluorine removed from soil through electromigration and electroosmotic was less, so the removal rate of soil fluorine was comparatively lower. When deionized water was used as electrolyte and circulated in series (test 2), OH^- and H^+ generated at cathode and anode interacted with each other, so that the pH of the electrolyte stabilized at about 7.5, and the removal rate of soil fluorine increased.

During the process of removing fluorine from soil by electrokinetics, because electromigration and electroosmosis had opposite direction, fluorine in soil had many forms (F^-, fluoride, fluorine complexes such as $(AlF)^{2+}$, AlF_2^+ and so on) and opposite charges, and fluorine moved out of soil in opposite direction under the function of electric field; therefore, the residual fluorine after remediation was focused in the middle of the soil cell. By using ammonia enhanced electrokinetic remediation method, ammonia circulated in series and NH_4^+ and OH^- in ammonia entered soil under the function of electric field. The concentration of the transferable ions in soil solution was intensified, which increased remediation current and electroosmotic flow as well as soil pH. When soil $pH>6.5$, it was significantly in positive correlation to the desorption quantity of soil fluorine. With the increase of pH value of the soil solution, the solubility of free fluoride (F^-) increases. In addition, a large amount of OH^- precipitated with Ca^{2+}, Fe^{3+} and Al^{3+} in soil, therefore reducing their chances to coordinate with F^-. Moreover, a large amount of OH^- exchanged with F^- which were adsorbed to clay mineral and Humus soil colloid. What's more, the ionic radius of OH^- ($r=1.32$-1.40 Å) was very close to that of F^- ($r=1.33$ Å); they had equal charges and similar polarizability, so that OH^- could substitute F^- in mineral lattice. As a result, the amount of F^- ions, the main form of fluorine was increased; therefore, a large amount of water-soluble fluorine entered electrolyte from soil under electrokinetic functions and were removed successfully [15,24].

When ammonia was used as electrolyte and circulated continuously, with the rise of ammonia concentration, the amount of soil fluorine moved to cathode by electroosmotic flow and to anode by electromigration became greater at the same time, that is, the removal efficiency of fluorine by electrokinetics increased with the concentration of ammonia water.

CONCLUSION

(1) Ammonia circulation enhanced electrokinetics can effectively remove fluorine from soil. Under electric field function, in the form of fluoride, F^-, $(AlF)^{2+}$, AlF_2^+ and so on, fluorine entered electrolyte from soil under the interaction of electromigration and electroosmosis; therefore, the contaminated soil can be remediated.

(2) Among the five groups of experiments, when 0.2 mol/L ammonia was used as electrolyte and circulated in series, the current for remediation was high up to 26.8 mA and varied slightly; as a result the optimal remediation result was achieved while reducing energy consumption. Under such experimental conditions, the removal rate of fluorine reached 57.3%.

(3) After remediation by ammonia circulation enhanced electrokinetics, the difference of soil pH at anode and cathode becomes smaller, and the residual ammonia in soil can also be used as fertilizer to improve the soil fertility.

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