Journal of Hazardous Materials 161 (2009) 565–569

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Short communication

Electrokinetic remediation of fluorine-contaminated soil: Conditioning of anolyte

Do-Hyung Kim [a], Chil-Sung Jeon [a], Kitae Baek [a,*], Sung-Hwan Ko [b], Jung-Seok Yang [c]

[a] Department of Environmental Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730-701, Republic of Korea
[b] Ecophile Inc., Youngin, Kyunggi, Republic of Korea
[c] Korea Institute of Science and Technology (KIST), Gangneung Institute, Gangwon-do 210-340, Republic of Korea

ARTICLE INFO

Article history:
Received 7 September 2007
Received in revised form 19 March 2008
Accepted 19 March 2008
Available online 26 March 2008

Keywords:
pH control
Circulation
Enhanced electrokinetic remediation
Fluorine removal
Anolyte conditioning

ABSTRACT

The feasibility of anolyte conditioning on electrokinetic remediation of fluorine-contaminated soil was investigated with a field soil. The initial concentration of fluorine, pH and water content in the soil were 414 mg/kg, 8.91 and 15%, respectively. Because the extraction of fluorine generally increased with the soil pH, the pH of the anode compartment was controlled by circulating strong alkaline solution to enhance the extraction of fluorine during electrokinetic remediation. The removal of fluorine increased with the concentration of the alkaline solution and applied current density and fluorine removed up to 75.6% within 14 days. Additionally, anolyte conditioning sharply increased the electro-osmotic flow, which enhanced the removal of fluorine in this study. In many respects, anolyte conditioning in electrokinetic remediation of fluorine-contaminated soil will be a promising technology.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Fluoride exists fairly abundantly in the earth's crust and can enter groundwater by natural processes: *weathering* and *leaching*. Chronic intake of excessive fluoride can lead to severe permanent bone and joint deformations of skeletal fluorosis, which is irreversible and has no treatment [1].

Fluorine could be leached from fluorine-containing soil. The Korean government regulated the fluorine level in soil to 400 mg/kg, because the only remedy for fluorosis is prevention. In Korea, fluorine has been used in the steel-making industry as a form of fluorite and in the electronic industry as a form of hydrofluoric acid for cleaning and washing. Generally a fluoride ion, which comes from the solubilization of fluorine mineral, is stable.

The electrokinetic process is one of the most promising remediation technologies for the removal of pollutants from soil. It has been applied to extract various pollutants including heavy metals, polyaromatic hydrocarbon, chlorinated compounds, and radionuclides from soil, sediment or sludge [2–8].

Electro-migration and electro-osmosis are major mechanisms to remove inorganic pollutants in the electrokinetic remediation [9]. The electrolysis reaction of water near electrodes enhanced the extraction or desorption of pollutants from soil surfaces. In the removal of cationic metal ions, the first step is hydrogen ions produced in anodes move toward the cathode. Secondly, metal ions are desorbed or extracted from the soil surface, as a result of the ion exchange reaction between the metal and hydrogen ions, moves toward the cathode. Finally, soil is acidified and metals are removed. Solubility of cationic metals decreases with pH of medium, that is, desorption or extraction of metals from soil decreases with the pH of the aqueous stream. To control the pH of a soil system in electrokinetic remediation, various enhancement methods have been applied including conditioning the electrolyte pH [10,11], adding enhancing chemical reagents to improve metal solubility [12,13] and using ion selective membranes to exclude hydroxide ion migration from the cathode chamber into the soil [14–16]. However, anionic pollutants such as arsenic and fluoride could be desorbed or dissolved in alkaline conditions from soil mineral more than in acidic or a neutral condition [9]. In electrokinetic removal of anionic pollutants, alkaline conditioning of soil could enhance the removal of fluorine from soil [17–20].

In this study, the feasibility of anolyte conditioning to control soil pH in electrokinetic remediation of fluorine was investigated. Anolyte conditioning was carried out by circulating an anolyte solution with a strong base solution.

* Corresponding author. Tel.: +82 54 478 7635; fax: +82 54 478 7629.
E-mail address: kbaek@kumoh.ac.kr (K. Baek).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.03.084

2. Materials and methods

2.1. Fluorine-contaminated soils

The soil used in this study was sampled from the Heohyun-dong, Seoul, Korea. The soil was silty loam with an organic content of 0.12%. The soil was air-dried and passed through a # 10-mesh sieve (<2.0 mm). The initial concentration of fluorine in the soil was 414 ± 32 mg/kg. The initial pH and water content of the soil were 8.91 and 15%, respectively.

2.2. Analytical methods

The total soil fluoride was obtained using the Korean Standard Test Method. 1.0 g of soil with particle size being less than 0.075 mm and 5.0 g of CaO was put into a 50-ml Ni crucible, then the crucible was placed in a muffle furnace for 5 h at 500 °C, slowly raising the temperature to 800 °C. The samples were fused at 800 °C for 2 h, and were cooled at room temperature. 25 ml of deionized water and 50 ml of 70 wt% $HClO_4$ were added into the samples. The mixture was distilled in a distillation unit for fluorine analysis. 50 ml of distillate was mixed with zirconyl-SPADNS of 10 ml and then the absorbance of the solution was measured at 570 nm using UV–vis spectrophotometer (HS 3300, Humas, Korea).

The soil pH was measured according to the Korean Standard Test Method. 5.0 g of soil was mixed with 25 ml of deionized water in 500 ml beaker. The mixture was agitated vigorously with a glass rod, then left for 1 h, and then the pH of supernatant solution was measured using a pH meter (Istek, Korea). The whole analysis was carried out in triplicate, and the average values were used.

2.3. Experimental apparatus

The electrokinetic apparatus consisted of four major compartments; a soil compartment (4 cm × 4 cm × 20 cm), electrode compartments (4 cm × 4 cm × 1 cm), electrolyte solution reservoirs (4 cm × 4 cm × 4 cm), and a regulated dc power supply (0–300 V, 0–1 A). The anolyte in electrolyte solution reservoirs was circulated with 0.1 M NaOH solution. Both ends of the soil compartment and filter papers were inserted to prevent soil leakage from the soil column to electrolyte solution reservoirs. A graphite sheet electrode was used in this reaction as an inert electrode (4 cm × 4 cm × 1 cm). Fig. 1 shows a schematic diagram of experimental apparatus.

2.4. Extraction experiment

Fundamental extraction experiments were carried out to investigate the effect of pH on the extraction of fluorine from soil. A soil sample of 3 g was mixed in 30 ml of NaOH solution with various concentrations (0.001–1.0 M). The mixtures were agitated by an over-head shaker for 24 h, centrifuged, and the fluoride concentration of the supernatant was analyzed using ion chromatography (Futecs, Korea).

2.5. EK experiment

Soil of 800 g and 200 ml of distilled water were mixed and then the mixture was installed into an electrokinetic cell with water content of 19.0 ± 0.5%. To control the anolyte pH during electrokinetic remediation, the anolyte was circulated with 0.1N NaOH in anode solution reservoirs using peristaltic pumps (Masterflex, Cole-Parmer, USA), with an electrical current density of 2–5 mA cm^{-2}. Experimental conditions were summarized in Table 1. The experiments, Exp. 1 and Exp. 2 were carried out to evaluate the effect of current density on the removal of fluorine. The experiments of Exp. 1 and Exp. 3 were executed to investigate the effect of anolyte concentration on removal of fluorine. After the operation lasting 14 days, the soil samples were sliced into 10 sections.

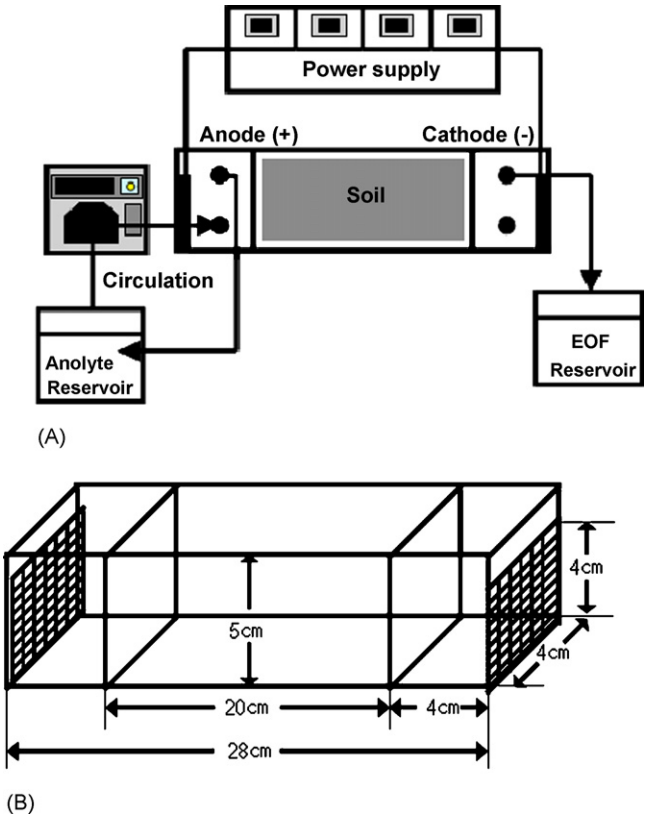

Fig. 1. Schematic and dimensions of experimental apparatus: (A) anolyte circulation system and (B) dimension of experimental apparatus.

3. Results and discussion

3.1. Extraction experiment

Fig. 2 shows the extraction efficiency of fluorine from soil. As the concentration of NaOH, that is, an extraction reagent, increased from 0.1 M to 0.5 M, the extraction of fluorine increased slightly from 1.3% to 4.9%. The concentration of extracting solution increased from 0.5 M to 1.0 M, the removal of fluorine from soil increased sharply from 4.9% to 22.8%. These results show that the extraction of fluorine from soil increases with the concentration of the reagent, NaOH. Even though NaOH was very effective in extracting fluorine, the removal was less than 22% even at the concentration of 1.0 M. This means that simple extraction with NaOH is not effective in removing fluorine from contaminated soil.

3.2. Voltage gradient

Fig. 3 shows the time course of the voltage gradient. Generally, the voltage gradient increased with the operation time

Table 1
Experimental condition of electrokinetic process

Exp. no.	Anolyte electrolyte (M)	Current density (mA cm^{-2})	Duration (day)
Exp. 1	NaOH (0.1)	2	14
Exp. 2	NaOH (0.1)	5	14
Exp. 3	NaOH (0.5)	2	14
Exp. 4	NaOH (0.5)	3	14

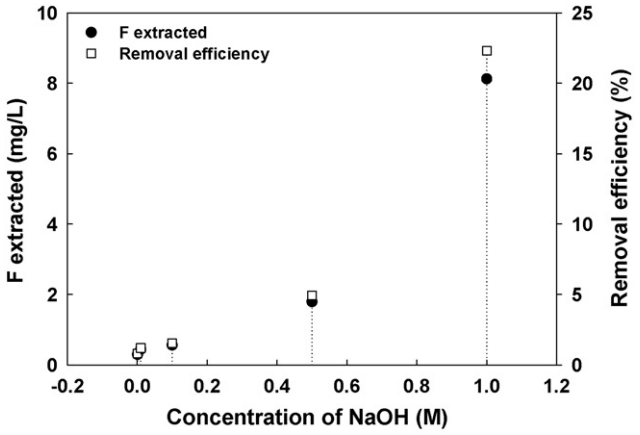

Fig. 2. Extraction efficiency of fluorine as a function of NaOH concentration.

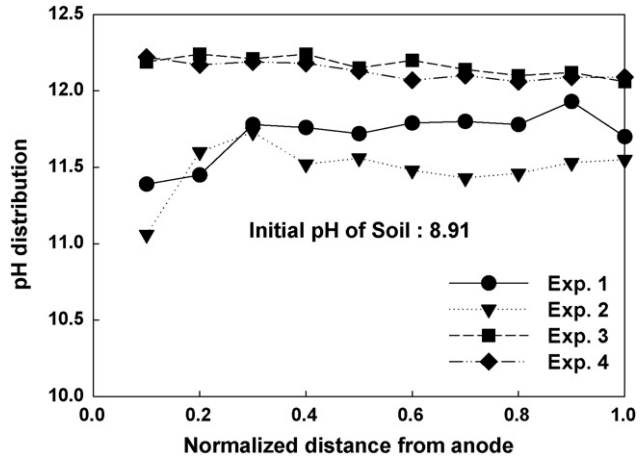

Fig. 4. pH distribution in soil section after electrokinetic treatment.

in electrokinetic remediation with a constant current, because conductivity of soil decreased due to the electromigration of electrolyte. In this system, the voltage gradient decreased sharply with operation time and reached a plateau as shown in Fig. 3. The reason for this was the circulation system. The fresh cation, that is, sodium, was supplied to the electrokinetic system periodically and the supplied cation increased electrical conductivity of the system and decreased the voltage gradient. In all experiments, the voltage gradient reached a plateau after 100 h operation.

3.3. pH distribution of soil after EK experiments

Fig. 4 shows the pH distribution of soil sections after electrokinetic treatment. The aspects were different from the general pH distribution of the soil section in conventional electrokinetic remediation. The pH of the soil sample ranged from 11.0 to 12.3 compared to initial pH of 8.9. As the concentration of NaOH for anolyte conditioning increased from 0.1 M to 0.5 M, the average pH of the soil increased from 11.7 (Exp. 1) to 12.2 (Exp. 3). At the same concentration of NaOH (Exp. 1 and Exp. 2), the soil pH for Exp. 1 was slightly higher than Exp. 2 because the current density increased from 2 mA cm^{-2} to 5 mA cm^{-2}. The production of H^+ increased at the higher current density. As a result, a greater fraction of hydroxide ions in conditioning solution were used for neutralizing the hydrogen ion produced by electrolysis reactions at anode. It is well known that the extraction of fluorine from soil is enhanced by an alkaline condition because hydroxide (OH^-) can be interchanged with fluoride (F^-) [17,20]. Based on this pH distribution, higher fluorine extraction could be expected.

3.4. Accumulated electro-osmotic flow

Fig. 5 shows accumulated electro-osmotic flow during electrokinetic remediation. As current density increased from 2 mA cm^{-2} (Exp. 1) to 5 mA cm^{-2} (Exp. 2), the accumulated electro-osmotic flow increased dramatically from 980 ml to 2750 ml at the concentration of 0.1 M NaOH for anolyte conditioning. As the concentration of NaOH increased from 0.1 M (Exp. 1) to 0.5 M (Exp. 3), the flow increased sharply from 980 ml to 3820 ml. The electro-osmotic flow increased with soil pH and current density applied in electrokinetic process. Shapiro and Probstein [4] reported that the electro-osmotic flow rate of alkaline conditioning was significantly enhanced compared with that in the case of acidic conditioning. The reason for enhancement in electro-osmotic flow rate is that all soil particles become more negatively charged with an increasing pH. As similar with reports of several groups [4,9] the anolyte conditioning with alkaline solution dramatically enhanced the electro-osmotic flow.

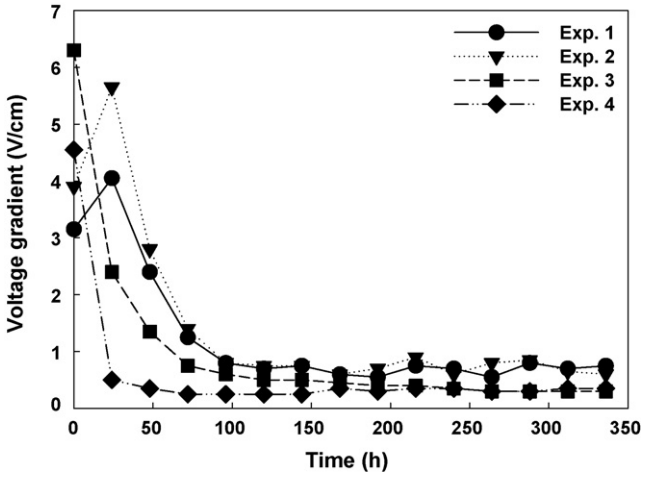

Fig. 3. Voltage gradient during electrokinetic extraction of fluorine.

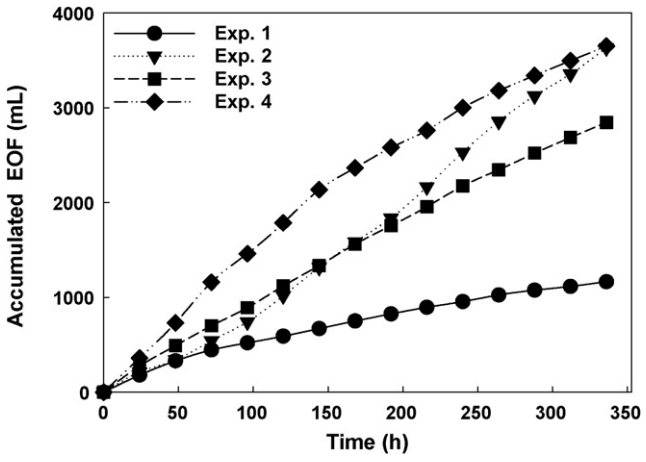

Fig. 5. Accumulated electro-osmotic flow during electrokinetic remediation.

Table 2
Results of electrokinetic experiment

EK exp.	Removal amount (mg)	Average removal efficiency (%)	Energy expenditure (kWh ton^{-1})	Effective removal (mg F Wh^{-1})
Exp. 1	96.7	51.8	564.9	0.38
Exp. 2	125.2	67.1	1,664	0.17
Exp. 3	120.1	64.4	406.2	0.66
Exp. 4	141	75.6	337.9	0.93

3.5. Fluorine removal

Fig. 6 shows fluorine removal by electrokinetic process with anolyte conditioning. As the current density increased from 2 mA cm^{-2} (Exp. 1) to 5 mA cm^{-2} (Exp. 2), the removal efficiency increased from 51.8% to 67.1% at the concentration of 0.1 M NaOH. While the fluorine removal increased from 64.4% to 75.6%, the current density increased from 2 mA cm^{-2} to 3 mA cm^{-2} at the concentration of 0.5 M NaOH. As the concentration of anolyte conditioning solution increased from 0.1 M NaOH to 0.5 M NaOH, the removal of fluorine increased 51.8% to 64.4% at the current density of 2 mA cm^{-2}. Fluoride extracted from contaminated soil was moved toward the anode by electromigration, because fluoride has a negative charge. And fluorine was also moved by electro-osmotic flow as fluoride or other soluble species such as fluorine complexes [19,20]. At a basic pH, the surface charge of the soil particles is negative and electro-osmotic flow is toward cathode. Fluorine was moved toward the anode by electro-migration and moved simultaneously toward the cathode by electro-osmotic flow. Extraction of fluorine increased with the pH of the solution, while the electro-osmotic flow was enhanced by the alkaline pH of the soil. Because the direction of electro-osmotic flow and electro-migration are reversed, fluorine concentration is the highest at the middle section of soil in the electrokinetic cell.

On the basis of voltage (V) and current (I) value, energy expenditure (E) was calculated using the following equation:

$$E = \int VI\,\mathrm{d}t = \int I^2 R\,\mathrm{d}t$$

The energy expenditure has been summarized in Table 2. The energy expenditure decreased with the concentration of the anolyte conditioning solution. To consider the removal efficiency and energy expenditure simultaneously, a new indicator, effective removal (mg F Wh^{-1}) was introduced. This indicator means energy is expended with respect to unit the removal of fluorine by electrokinetic remediation. The value was the highest in Exp. 4, because the energy expenditure was the lowest and the removal efficiency was the highest.

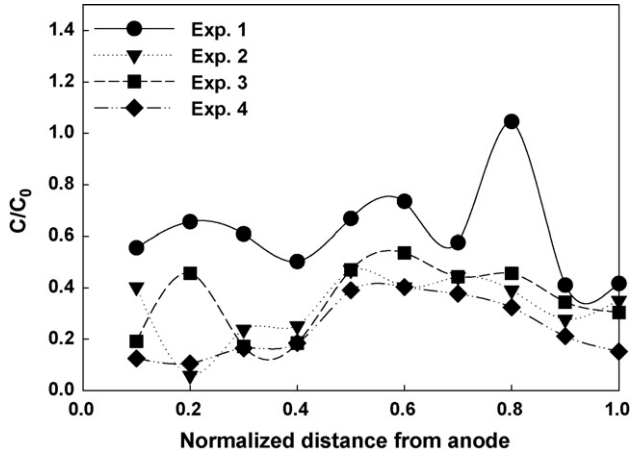

Fig. 6. Fluorine distribution in soil section after application of electrokinetic remediation.

4. Conclusions

In this study, the feasibility of anolyte conditioning with an alkaline solution on electrokinetic remediation of fluorine-contaminated soil was investigated. Soil washing techniques were not effective, even though strong alkaline solution (1.0 M NaOH) were used as a washing reagent. The removal of fluorine increased up to 75.6% by electrokinetic techniques enhanced by anolyte conditioning with a strong alkaline solution. This shows that anolyte conditioning is a very effective enhancement method to remove fluorine from contaminated soil in electrokinetic remediation. This enhancement method can be applied to remove anionic pollutants such as arsenic and chromate from contaminated soil.

Acknowledgement

This research has been supported by a grant from Kumoh National Institute of Technology.

References

[1] J.A. Camargo, Fluoride toxicity to aquatic organisms: a review, Chemosphere 50 (2003) 151–164.
[2] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediations, Environ. Sci. Technol. 27 (1993) 2638–2647.
[3] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, R. Parker, Electrokinetic remediation: basics and technology status, J. Hazard. Mater. 55 (1995) 117–137.
[4] A.P. Shapiro, R.F. Probstein, Removal of contaminants from saturated clay by electroosmosis, Environ. Sci. Technol. 27 (1993) 283–291.
[5] J.H. Chang, Y.C. Liao, The effect of critical operational parameters on the circulation-enhanced electrokinetic, J. Hazard. Mater. 129 (2006) 186–193.
[6] H.-H. Lee, J.-W. Yang, A new method to control electrolytes pH by circulation system in electrokinetic soil remediation, J. Hazard. Mater. 77 (2000) 227–240.
[7] J.Y. Park, S.J. Kim, Y.J. Lee, K.J.W. Baek, EK-Fenton process for removal of phenanthrene in a two-dimensional soil system, Eng. Geol. 77 (2005) 217–224.
[8] J.Y. Wang, D.S. Zhang, O. Stabnikova, J.H. Tay, Evaluation of electrokinetic removal of heavy metals from sewage sludge, J. Hazard. Mater. 124 (2005) 139–146.
[9] S.O. Kim, K.W. Kim, D. Stueben, Evaluation of electrokinetic removal of heavy metals from tailing soils, J. Environ. Eng.-ASCE 128 (2002) 705–715.
[10] D.M. Zhou, C.F. Deng, A.N. Alshawabkeh, L. Cang, Effects of catholyte conditioning on electrokinetic extraction of copper from mine tailings, Environ. Int. 31 (2005) 885–890.
[11] D.M. Zhou, C.F. Deng, L. Cang, A.N. Alshawabkeh, Electrokinetic remediation of a Cu–Zn-contaminated red soil by controlling the voltage and conditioning catholyte pH, Chemosphere 61 (2005) 519–527.
[12] K.R. Reddy, S. Chinthamreddy, Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions, J. Environ. Eng.-ASCE 130 (2004) 442–455.
[13] K.R. Reddy, C.Y. Xu, S. Chinthamreddy, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, J. Hazard. Mater. 84 (2006) 279–296.
[14] A. Rojo, H.K. Hansen, Electrodialytic remediation of copper mine tailings: sulphuric and citric acid addition, Sep. Sci. Technol. 40 (2005) 1947–1956.
[15] L.M. Ottosen, K. Lepkova, M. Kubal, Comparison of electrodialytic removal of Cu from spiked kaolinite, spiked soil and industrially polluted soil, J. Hazard. Mater. 137 (2006) 113–120.

[16] H.K. Hansen, A.B. Ribeiro, E.P. Mateus, L.M. Ottosen, Diagnostic analysis of electrodialysis in mine tailing materials, Electrochim. Acta 52 (2007) 3406–3411.
[17] W.W. Wenzel, W.E.H. Blum, Fluorine speciation and mobility in F-contaminated soils, Soil Sci. 153 (1992) 357–364.
[18] M.A. Elrashidi, W.L. Lindsay, Chemical equilibria of fluorine in soils: a theoretical development, Soil Sci. 141 (1986) 274–280.
[19] V. Pomes, A. Fernandez, N. Costarramone, B. Grano, D. Houi, Fluorine migration in a soil bed submitted to an electric field: influence of electric potential on fluorine removal, Colloid Surf. A: Physicochem. Eng. Aspects 159 (1999) 481–490.
[20] N. Costarramone, S. Tellier, B. Grano, D. Lecomte, M. Astruc, Effect of selected conditions on fluorine recovery from a soil using electrokinetics, Environ. Technol. 21 (2000) 789–798.