An Investigation on the Efficiency of Electro kinetic Coupled with Carbon Active Barrier to Remediate Nickel Contaminated Clay

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ABSTRACT: There have been increasing interests in finding new and innovative solution for removal of contaminants from soils recently. In the present investigation, electro kinetic (EK) process coupled with activated carbon barrier to remove Nickel from kaolinite clayey soil is investigated. Laboratory tests were performed by applying a constant voltage to nominal electric field strength of 1 and 1.25 V/cm with initial Ni concentration (500 mg/kg) for 3 and 7 days. Results revealed that, the coupled technology of EK with barrier when filled with activated carbon could effectively prevent the reverse electro osmotic flow which has adverse effect on the Ni removal from soil. In addition, 20-50% of Nickel migration towards the cathode during the tests was achieved.

Key words: Activated carbon, Barriers, Electro kinetic, Nickel, Soil remediation, Kaolinite

INTRODUCTION

Every year, huge amounts of hazardous wastes are generated in the world. Due to inefficient waste handling techniques and hazardous waste leakage, thousands of sites are contaminated by heavy metals, organic compounds and other hazardous materials, which made an enormous impact on the quality of groundwater, soil and associated ecosystems (Virkutyt *et al.,* 2002). One of the emerging technologies to clean up heavy metals contaminated soils is electro kinetic (EK) remediation technique, which has been proven to be a very effective tool to clean up contaminated low hydraulic permeability fine grained soils (Virkutyt and Sillanpaa, 2007; Chung and Lee, 2007; Reddy and Saichek, 2003). Basically, the technique is based upon the action of an electric

field generated between inserted electrodes in the soil, sludge and sediments, either by applying a direct current or a constant voltage (Virkutyt *et al.,* 2002; Amrate and Akretche, 2005; Akretche, 2002). The application exploits two main transport processes of ions in solution: electro osmosis and electro-migration (Lynch *et al.,* 2007; Alshawabkeh and Acar, 1992). Electro-osmotic (EO) contribution to contaminant transport is linked to a wide range of parameters such as pH condition, zeta potential and ionic concentration (Lynch *et al.,* 2007). The surface charge of water-saturated clays is typically negative which resulted in the direction of EO flow from the anode to cathode (Virkutyt *et al.,* 2002; Vane and Zang, 1997). The dominant and most important electron transfer reactions, which the electro kinetic process is greatly affected by, is the electrolysis of water (Virkutyt *et al.,* 2002; Amrate

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and Akretche, 2005) with the following chemical reactions:

$$\text{Anode}: H_2O \rightarrow 2H^+ + 1/2\,O_2\,(g) + 2e^-$$

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow 2OH^- + H_2\,(g)$$
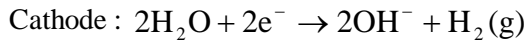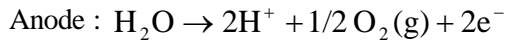
The generated hydrogen and hydroxyl ions are transported through specimen in opposite directions by electrical migration, diffusion and advection. The advance of base front is slower than the advance of the acid front because of the counteracting electro-osmotic flow and also because the ionic mobility of H^+ is about 1.76 times that of OH^-. Consequently, the acid front dominates the chemistry across the specimen except for small sections close to the cathode (Alshawabkeh and Acar, 1992; Acar *et al.,* 1990; Probstein and Hicks, 1993). The electro kinetic can be used in combination with other cleanup techniques (Chung and Lee, 2007; Lynch *et al.,* 2007). Ground water remediation using permeable reactive barriers (PRB) also is an innovative technology developed in the early 1990s (Simon and Meggyes, 2000). Treatment walls- so called PRB, first reported by Mc Murthy and Elton (1985), involve construction of permanent, semi-permanent or replaceable units across the flow path of a dissolved phase contaminant plume (Turlough *et al.,* 2002). The material used in the barrier may vary depending on the type of contaminants being treated.

There are some studies on nickel (Ni) removal from contaminated soil which had not high removal and migration efficiency in a basic EK (Hamdan and Reddy, 2008; Reddy and Chinthamreddy, 1999; Kim *et al.,* 2008; Maturi and Reddy, 2006). Some researchers reported reverse EO in heavy metals removal during EK process which has negative effect on migration efficiency (Kim et al, 2008; Genc *et al.,* 2008; Weng *et al.,* 2007). However, not any particular method has been proposed to avoid reverse EO. The aim of this research was to investigate the applicability of the activated carbon as a material of barrier coupled with EK to remediate Ni contaminated kaolinite clayey soil avoiding reverse EO occurrence.

MATERIALS & METHODS

Kaolinite which used in the tests was obtained from Marand clay company, Tabriz, Iran. It contained 63-64% of SiO_2, 22–23% of Al_2O_3, and trace amount of Fe_2O_3 and MgO. Approximately 98% of the kaolin particles had size smaller than 20µm, and 40% of the kaolin particle had size smaller than 2 µm. laboratory tests were carried out on the soil to determine its physical, chemical and mineralogical properties. Soil and activated carbon characteristics are reported in Tables 1 and 2. The pH of the kaolin slurry, prepared from kaolin mixed with distilled water in the ratio of 1:1 (w/w), was 8.2. To achieve 500 mg kg^{-1} Nickel concentration, 1.2388 g of $Ni(NO_3)_2$ was dissolved in de-ionized water and 1.8 Kg of kaolin was then artificially contaminated by solution. The contaminated kaolin was left at room temperature, 25 ºC, for 12 h before it was packed into the reactor cell to attain equilibrium. The activated carbon, which was used in the present study, is produced by MERCK Company.

Table 1. Chemical composition of Marand kaolinite

| Parameter	Content (%)
SiO_2	63-64
Al_2O_3	22-23
Fe_2O_3	0.5-0.65
TiO_2	0.04
CaO	1.4-1.6
MgO	0.35
Na_2O	0.4
K_2O	0.25
SO_4	0.0
L.O.I	9

Laboratory scale EK tests were conducted in a rectangular 30cm $\times$ 12 cm 10 cm Plexiglas container, length of the soil was 15 Cm and the thickness of barrier wall was 0.5 cm. Carbon Active barrier layouts and EK cell schematic are shown in (Fig. 1). 0.05 M KNO was chosen as a conductive solution due to its higher conductivity

Table 2. Physico-chemical properties of Marand kaolinite and Activated carbon

Parameter	Marand kaolinite clayey soil	Activated Carbon
pH	8.2	----
Percent finer than 32μ	100%	----
Percent finer than 20μ	98%	----
Percent finer than 2μ	40%	----
pH_{zpc}	4.6	----
surface area ($m^2\ g^{-1}$)	----	891
Single point surface area ($m^2\ g^{-1}$)	----	942
Bulk density ($g\ cm^{-3}$)	----	2.1060

than distilled water for higher current to pass through soil to facilitate the ions migration (Virkutyt and Sillanpaa, 2007). The barrier containing activated carbon was placed in the soil beside the cathode. Description of different tests conducted in the present study is given in Table 3.

A direct current (DC) power supply was used to generate constant electric gradient of 1 and 1.25 V/cm for 3 and 7 d. The electrode pates used in this study was perforated stainless steel electrodes (A316). The current fluctuations were monitored during the tests. Electrode plates were placed directly into the soil. New electrodes were used for each test to avoid any cross-contamination between the tests. The EK testing box and valves
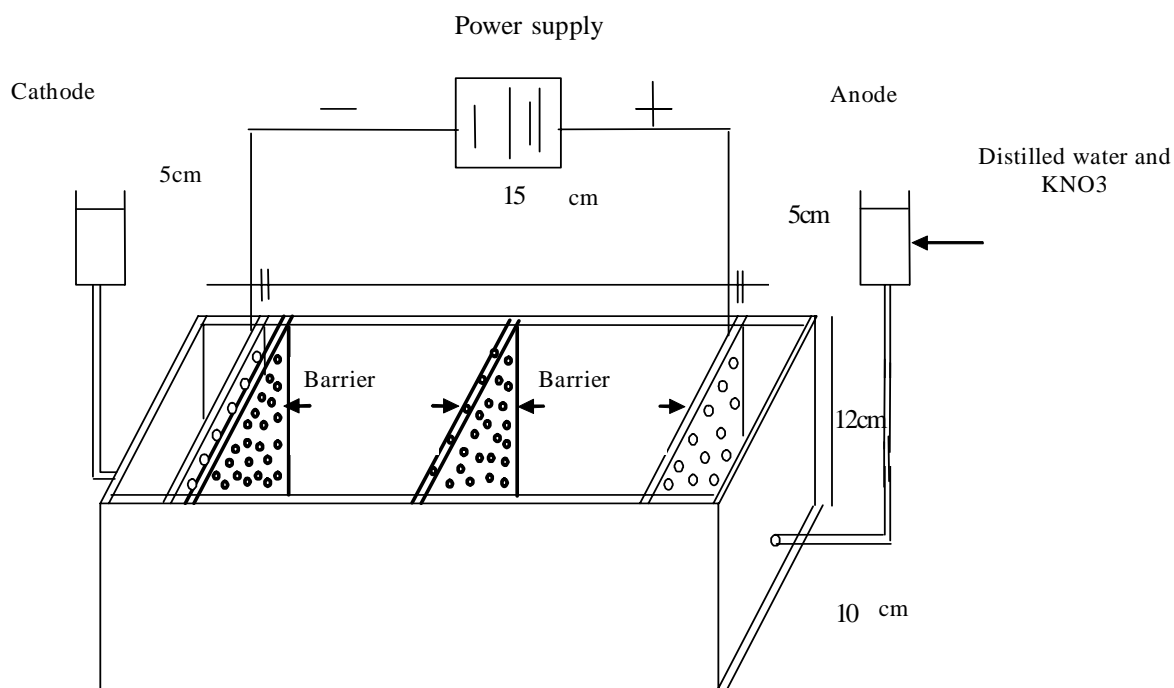
Fig. 1. Schematic representation of electro kinetic cell, walls thicknesses are 0.5 cm

Table 3. Tests conducted in the present study

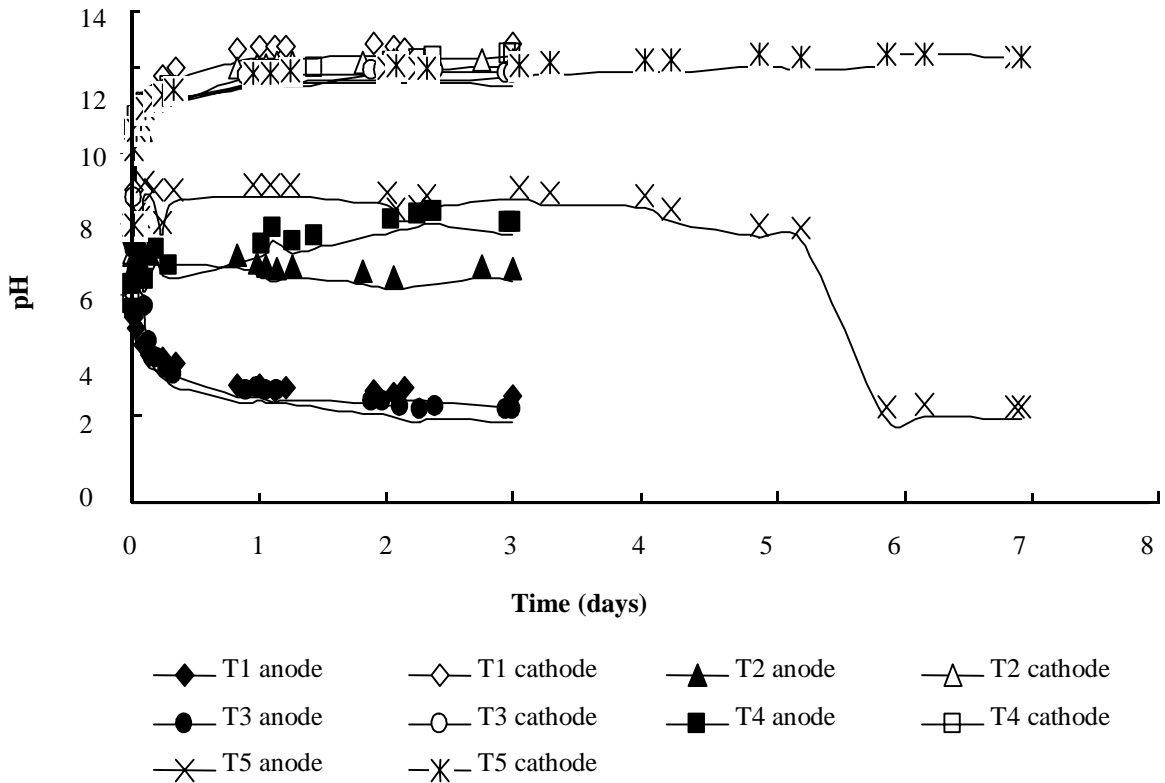| Test	Voltage applied (V/cm)	Test duration (days)	Description
T1	1	3	No barrier used
T2	1	3	into the soil beside the cathode
T3	1.25	3	No barrier used
T4	1.25	3	into the soil beside the cathode
T5	1	7	into the soil beside the cathode

Fig. 2. Fluctuations of pH in anode and cathode chamber during the tests
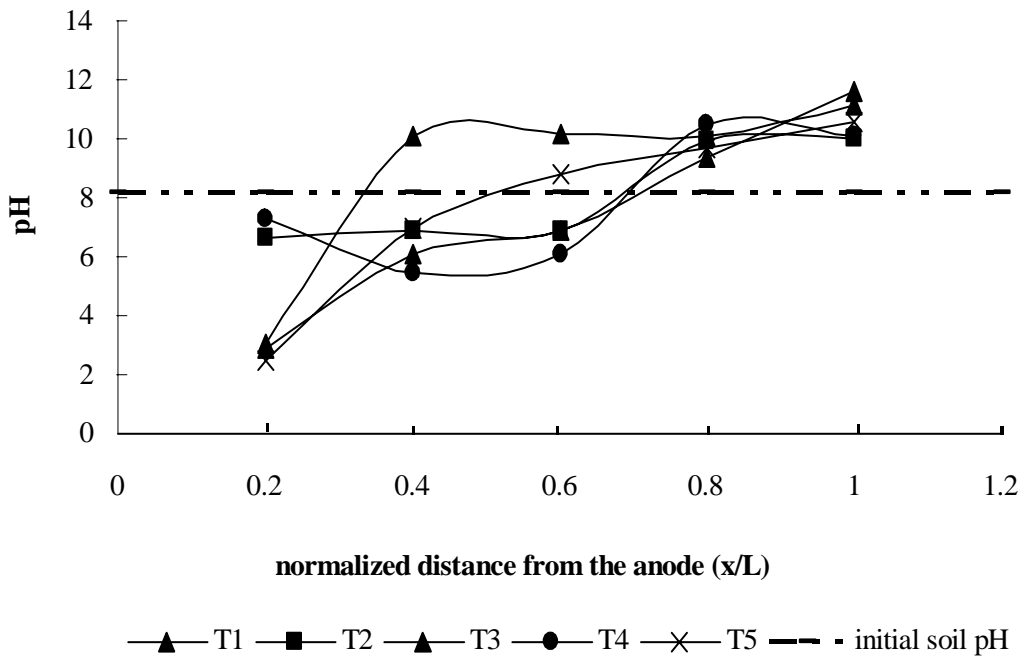

Fig. 3. Distribution of pH during the electro kinetic treatment, where x is a distance from anode and *L* is a length of soil at the end of tests

were soaked in a dilute acid solution for 24 h, and then rinsed with distilled water before each test.

The soil sample was sectioned into five after the completion of each test and the different soil sections were acid digested. The total metal concentration in the homogenized samples after EK treatment was determined after drying for 24 h at 42 °C. The digestion procedure was carried out according to U.S.EPA 3050B method (USEPA, 1992). The Nickel concentration was measured using an atomic absorption spectrometry (Buck Scientific 210VP). The pH of the soil sample was measured at the end of the tests, using a Cyber Scan PC 510 pH-meter.

RESULTS & DISCUSSION

The pH variation in anode and cathode chamber is shown in (Fig. 2). Compared to the initial pH values, pH changed significantly in the anode and cathode chamber in the tests no. T1, T3 and T5. In the tests T2 and T4 the anode pH profile is not as same as other tests. Anode chamber pH did not change significantly and it did not decrease. However, the cathode pH became basic in all tests (Fig. 2). pH changing in

the tests was related to the production of H^+ and OH^-, respectively in the anode and cathode due to the electrolysis of water. Not pH changing in the anode compartment in test T2 and T4, which activated carbon was used into the soil beside the cathode is not well understood yet and should be further investigated.The pH profile along the cell at the end of each test is shown in (Fig. 3). In the tests with no barrier (T1 and T3), pH profile became acidic near the anode sections and became highly basic near the cathode sections.

In all tests, soil pH changing was accordant to the anode and cathode compartment pH changing. It means that the development of acid and base front into the soil had significant influence on soil pH. The soil section pH near the cathode became basic in all tests and the soil section pH near the anode in tests no. T1, T3 and T5 decreased. In the tests T2 and T4, which activated carbon was used, the soil section pH near the anode did not change significantly due to not changing in anode pH in tests no. T2 and T4.

Fig. 4. show the accumulation of EO flow collected during these tests. In the tests with no carbon barrier (T1 and T3), the EO flow was
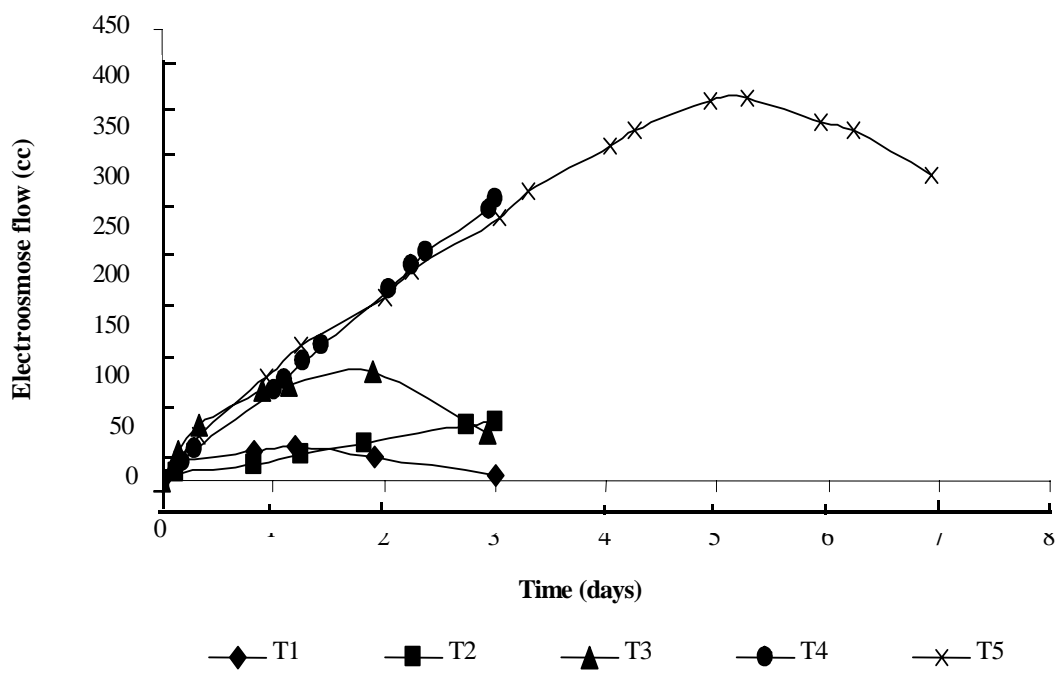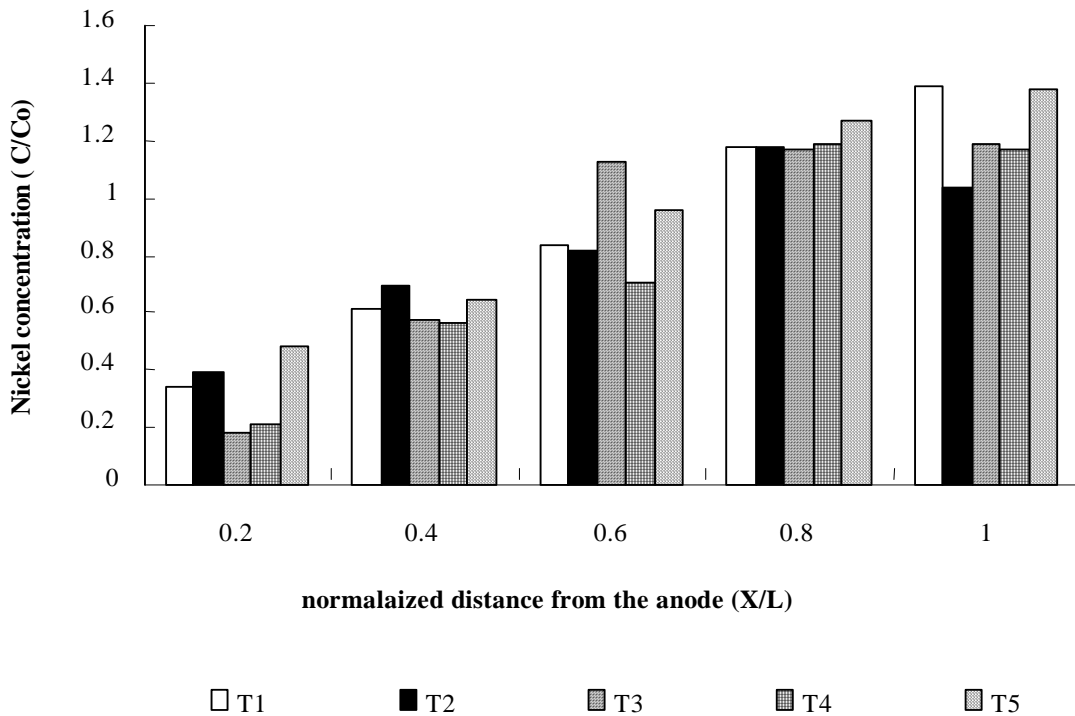

Fig. 4. Variations of the electro osmotic flow during EK tests

Fig. 5. Normalized Ni concentration at the end of electro kinetic tests

reversed at the end of second day. In tests with carbon active barrier which was taken 3 days (T2 and T4) reverse EO flow did not occur and the direction of EO flow was toward the cathode during the tests. However, in the 7 days test with carbon active barrier (T5), the reverse EO flow happened at the end of fifth day (Fig. 4). In other words, applying the carbon active barrier could prevent the reverse EO flow and maintain the system working for 5 days which seems a considerable enhancement in comparison with occurrence of reverse EO in second day in the basic conventional EK process. Occurrence of reverse EO in fifth day of the test (T5) may be related to the exhausting of the activated carbon barrier used in the test.

As a result of existence of negative zeta potential in clayey soils, the EO flow is usually from the anode toward the cathode. Other experiments have determined the dependence of the zeta potential of most charged particle on solution pH, ionic strength, types of ionic species, ion concentration, sorption capacity of the soil, temperature and type of clay minerals (Virkutyt *et al.,* 2002; Alshawabkeh and Acar, 1992; Vane

and Zang, 1997; Acar *et al.,* 1990). Because of the complexity of soil chemistry and occurrence sophisticated phenomenon in EK process, researchers did not mention exact and precise reasons of reverse EO occurrence. However, it is speculated that in the present study, high Ni (500 mg kg^{-1}) concentration in the tests without barrier may have influence on zeta potential of the soil. The surface charge of clays is a function of the pH and ionic strength. The change in net surface charge caused a change in the direction of EO. The higher Ni concentration (500 mg/kg) made higher ionic strength, which affect the surface charge and zeta potential. Moreover, it is also possible that the nitrate interacted with the clay surface due to its higher concentration. Hence, the reverse EO flow was found at the end of the second day. In other tests when carbon active barrier was used, due to its high sorption capacity part of the Ni^{2+} was absorbed by activated carbon. Therefore, the ionic strength decreased and reverse EO did not happened. In the test T5, may be due to the saturation of carbon active sorption, again the reverse EO flow happened.

Fig. 5. shows the Ni concentration, normalized with respect to starting values in the soil (500 mg kg), in each of the five sections of the soil sample at the end of tests at 1 and 1.25 V/cm. As shown, the Ni migrated from the anode and accumulated in the sections near the cathode. The Ni migration from the 60% of soil length toward the cathode in tests no. T1, T2, T3, T4 and T5 were about 40.3%, 37.06%, 37.3%, 50.6% and 20.4% respectively. Moreover, when an electrical gradient of 1.25 V/cm was applied, the Ni migration from the anode toward the cathode was more than the one with 1 V/cm.

Changes in the pH profiles in the soil had a great influence on contaminant migration. Indeed, tests conducted in the present study showed that pH has a significant impact on Ni migration in the soil. Due to the low pH at the anode, there was insignificant concentration of Ni found close to the anode. However, when the normalized distance from the anode reached 0.5, Ni concentration significantly increased (Fig. 5). For example, about 80% of Nickel migrated from the first section toward the other sections in tests T3 and T4. The high pH indicated that some OH^- ions were reaching the soil and possibly interfering with the mobility of nickel ions. The high pH environment was favorable to make $Ni(OH)_2$ which precipitate near the cathode sections and decrease the soil conductivity. According to this fact, the higher Ni concentrations were found near the cathode sections.

CONCLUSION

In this study, application of activated carbon barrier to hinder reverse EO flow during EK process to remove Ni from contaminated kaolinite was investigated. Laboratory scale tests demonstrated that reverse EO flow, which has negative effect on Ni migration during EK process, could be hindered efficiently by utilization of activated carbon as a barrier material coupled with EK. Moreover, barrier location may be an important factor in Nickel migration. Therefore, further investigations should be conducted to find the effect of carbon active barrier location on EK processes during Ni and other heavy metals removal from fine grained soils.

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