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Evaluation of EK System by DC and AC on Removal of Nitrate Complex

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Abstract: DC (Direct current) is used in electrokinetic (EK) technology to extract hazardous materials from soils. Besides, AC (alternating current) electric field is also used to induce particle and fluid motion in electrokinetics. The influence of AC and DC on electrokinetic phenomena was studied for the removal of nitrate complex in soil environment. The experiments were performed by employing three systems – DC, AC, and AC overlapped DC. The removal of cations was higher at the anodic spot while applying DC. Involvement of AC on cation removal was very poor and nitrate removal was about 50%. AC and DC can be used for the removal of nitrate complex in agricultural soils.

Keywords: Alternating current, direct current, electrokinetics, nitrate, removal

INTRODUCTION

The Korean farmers have a tendency to apply large quantity of fertilizers in the green house soil for increasing the production of food products in a short period. The addition of excess fertilizers makes the soil with

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saturated ions such as nitrate, phosphate, chloride, sodium, calcium, potassium etc. which imposes a serious issue for the Korean agricultural industry. The accumulation of these ions affects the quality of the plants leading to decline of crop yield. In order to remove the hazardous particles, electrokinetic (EK) has become a chosen remediation technology (1,2). Generally, direct current (DC) is used in EK technology to extract hazardous materials from the soils or slurries by electroosmosis, electromigration, and electrophoresis as well as through electrolysis (3). The electrokinetic process encourages the migration of cations at cathode while anions move toward anode and deposit at anodic area. Alternating current (AC) is also used in EK, a technique which was used for the controlled manipulation of particles and separation of mixtures (4,5). AC power has a property on changing polarity of electrodes at some frequency, which causes some different moving mechanisms of aqueous ions and water in the soil. Electroosmotic flow and electrophoresis are linear in the applied voltage and thus can not produce any net flow under alternating current conditions (6). The interaction effects on particle shape, orientation, porosity, and relative disparity between electrical parameters (conductivity and di-electric constant) of soil particles and pore fluid on electrical response of bulk soil at very low and very high frequency of excitation by an alternating current were studied by Thevanayagam (7). The ratio of conductivities (and permittivities) of the solid particle to pore fluid had a significant influence on the electrical response of soils. Pangram and Wong (8) developed a way to measure rock permeability by using low frequency AC electrokinetics. The application of AC electric currents as power source with DC for electrokinetic remediation in a soil environment was investigated by Lageman group (9,10). They have been concentrating many projects on electro-bioreclamation of organic contaminants such as volatile organics, semi-volatile organics, dense non-aqueous phase liquids, heavy fuel oils, creosote, and polycyclic aromatic hydrocarbons by employing AC electrokinetics. They noticed distinct and positive effect on biodegradation in the soil.

It is known that nitrogen behavior in soil is very complex. More than 98% is relatively unavailable because it is tied up in soil organic matter (11). Hence, it was expected that AC (alternating current) can enhance the biodegradation and DC (direct current) can remove the nitrate and free cations by an electromigration process. In the present study, an attempt was made to remove the nitrate complex salts by the application of AC and DC.

MATERIALS AND METHODS

Soil samples contaminated with nitrate were collected from JinJu, Korea for the evaluation of DC and AC in electrokinetics. Before the

Table 1. Original characteristics of soil used in the present study collected from Jinju

Soil characteristics	Value
pH	5.6
EC (dS/m)	5.4
Organic (g/kg)	25
P_2O_5 (mg/kg)	1,384
Calcium (g/kg)	1.8
Potassium (g/kg)	0.9
Magnesium (g/kg)	0.25
Sodium (g/kg)	0.04
Nitrate (mg/kg)	1,878
Ammonium (mg/kg)	12

EK process, the soil was dried at room temperature for 24 hrs and sieved with a #10 mesh sieve (<2.00 mm). The initial pH value of this soil was 5.6 and electrical conductivity was 5.4 dS/m. The total organic content was 25 g/kg. The concentrations of phosphate, calcium, potassium and magnesium were 1,384 mg/kg, 1.8 g/kg, 0.9 g/kg, and 0.25 g/kg, respectively. The initial concentration of nitrate was 1,878 mg/kg (Table. 1).

Electrokinetic Cell Configuration

The EK cell is made up of acrylic sheet with a dimension of $24 \times 4 \times 6\,cm^3$. It is divided into three compartments. The central one is for storing the soil sample and the other two for working the reservoir solution consisting of catholyte and anolyte. The air-dried soil sample was mixed with an electrolyte solution (about 20% to 30% water content), then carefully stored in the central compartment. The length of the central compartment is 10 cm. Titanium and graphite electrodes were placed at each electrolytic compartment and served as anode and cathode respectively. To avoid the soil leakage to the water reservoirs, a pair of nylon meshes (mesh opening 149 μm) (12) and a filter paper (Whatman 2) were placed between the soil sample and the electrodes. The used soil for EK remediation was a kind of silty loam. DC power supply (3 A–30 V, ED Laboratory, ED-245B) was used for impressing 2 V/cm in EK system. AC power (constant 60 Hz) was impressed at different voltages and overlapped with DC power which was connected in series.

Electrokinetic Experiment

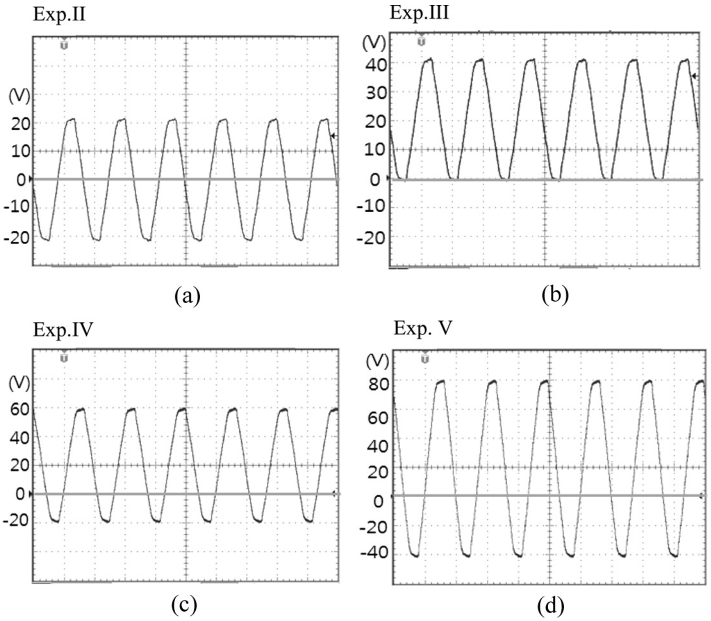
Before starting the experiment, the collected soil 400 g was dried at room temperature for 24 hrs and 120 ml of distilled water was mixed. The mixture of the soil was packed in the section of soil compartment in the electrokinetic cell. The catholyte was used as 0.16 M acetic acid and distilled water circulated as anolyte. In Exp. I, DC power voltage was used about 20 V. AC power 20 V of peak voltage was used in Exp. II. Besides, AC power 20, 40, and 60 V was overlapped with DC power (20 V) and employed for other experiments III, IV, and V, respectively. On the basis of voltage profile, it can be assumed that the polarity of electrodes was changed periodically (13) in the Exp. III, IV, and V. The frequency of AC power was 60 Hz. The experimental condition of the study in the electrokinetic process is shown in Table 2. Figure 1 shows the wave form of voltage profile with time for variable AC peak voltages. Each experiment was carried out for about 7 days. After finishing the experiment, the soil samples were divided into 5 parts and used for chemical analysis.

pH, Conductivity, and Electroosmosis Measurements

After finishing the EK experiments, pH and electrical conductivity (EC) of the soil were estimated. The soil pH was measured according to the standard method for the soil examination (ministry of environment, Korea). The soil was dried in air and 5.0 g was mixed with 25 ml of distilled water in 50 ml vial. The mixture of soil and water was agitated with a magnetic stirrer for 1 hr at 300 rpm. After calibration with pH standard solution, the pH of soil was measured by pH meter (Istek Inc, Model 76P). Electrical conductivity (EC) was measured for the same ratio of the mixture by employing EC meter (Istek Inc, Model 47 C). The average value of triplicate samples is presented. Electroosmotic flow was

Table 2. Experimental condition of variable power sources

Experimental number	DC (V)	AC (peak voltage)	Catholyte	Anolyte
Exp. I	20	–	0.16 M Acetic acid	Distilled water
Exp. II	–	20		
Exp. III	20	20		
Exp. IV	20	40		
Exp. V	20	60		



(a) (b)

(c) (d)

Figure 1. Waveform of voltage with time for variable power sources: (a) Exp. II, (b) Exp. III, (c) Exp. IV, (d) Exp. V.

measured in electrokinetics with time by a collection of excess of electrolyte from the cathode chamber.

Chemical Analysis

Air-dried soil 5 g mixed with 50 ml of 1 N ammonium acetate in a 100 ml flask and agitated for 30 minutes. The mixture of the soil was filtered with filter paper (Whatman 2) and the concentration of cations such as calcium, potassium, sodium, and magnesium in the soil were analyzed with ICP (Inductively Coupled Plasma, GBC, and Australia).

Concentration of nitrate in the soil was obtained by the following analytical way. The air-dried soil 10 g was put in 100 ml flask and 50 ml of 2 M KCl was added in the flask with the soil. The mixture of the soil in the flask was agitated for 30 minutes and the filtered solution was obtained with filter paper (Whatman 2). The solution was used for the estimation of nitrate in the soil by using QuAAtro auto analyzer (BRAN + LUEBBE, Germany).

RESULTS AND DISCUSSION

During the formation of soil organic matter, nutrients such as nitrogen (N), phosphorus (P), and sulphur (S) are incorporated into the soil structure, allowing the soil to act as a reservoir of these and other nutrients. Soil organic matter can bind nutrients through the process of cation exchange. Ammonium, calcium, magnesium, and potassium are nutrient cations that are held on cation exchange sites on organic matter. While a non-uniform AC electric field can move suspended particles using dielectrophoretic forces, it also moves the fluid through the electrothermal effect or AC electroosmosis (14–16). Apart from the physical/chemical effects of electrical heating by AC, the temperature increase has a pronounced and positive effect on bioremediation (8). In the present study, AC was selected to induce the electrical field on individual soil particles and to find the influence on nitrate complex. DC current was used to remove cations at cathode and anions at anode.

Electrical Conductivity (EC)

Figure 2 shows electrical conductivity of soil sections after completing the electrokinetic process. In DC influenced systems, the conductivity was higher at anode and cathode when compared to the middle portion of

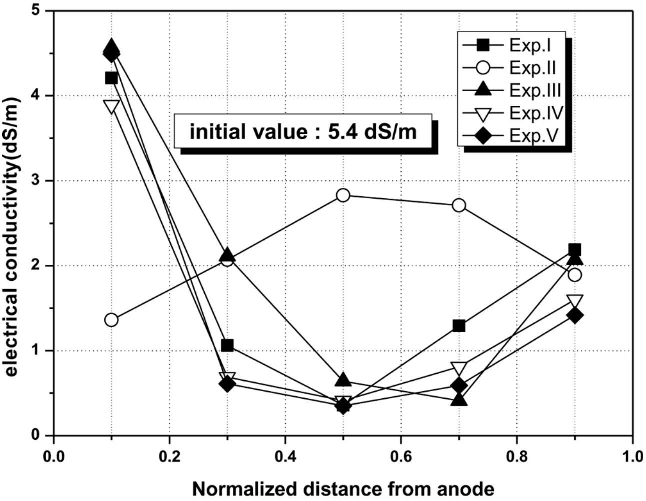


Figure 2. Changing of soil electrical conductivity in various experimental conditions.

the soil. It indicates that negative and positive charges of ions are highly accumulated at anode and cathode respectively. It is due to the domination of DC effect on electromigration. In Exp. II, the conductivity of soil at the anode area was 1.4 dS/m which increased toward cathode. In the present study, AC reduced conductivity value from 5.4 dS/m (initial value) to 2.9 dS/m at the middle portion of the soil. The significant reduction of conductivity at the anode and cathode portion of the soil from the initial value may be due to the AC-thermal effect on biodeterioration of nitrate complex in the soil by the influence of AC on individual soil particles. While applying AC, the soil temperature was 30°C. The temperature was 26°C when applying DC alone, which is the same as the room temperature. At the middle portion of the soil, AC (Exp. II) does not work well on the reduction of EC when compared to other systems. It may be due to the distance of the electrodes and non-uniform temperature effect on the soil particle. Schlegel (17) suggested that the bio-degradation rate was double with every 10°C increase in temperature which was confirmed by Lageman and Pool (18). Green et al. (19) conducted measurements of particle motion under the influence of non-uniform AC electric fields. The non-uniform AC electric fields produced spatially varying power densities in the fluid resulting in non-uniform temperature fields in the fluid, leading to local changes in conductivity and permittivity. Hence, the authors feel that a detailed study is needed to find the impact of temperature on nitrate complex.

Electroosmotic Flow

Figure 3 shows cumulative electroosmotic flow with time in different conditions. In the AC applied system (Exp. II), there was no significant electroosmotic flow. It reveals that changing polarity with the same magnitude of opposite power phase makes the pore fluid not move toward the cathode significantly. In the other systems, the electroosmotic flow increased with time linearly where the electroosmotic flow moved from anode to cathode. The electroosmotic flow in Exp. I and Exp. III sharply increased with time when compared to Exp. IV and Exp. V. The highest electroosmotic flow was noticed in Exp. III. Although high AC was used in Exp. IV and Exp. V, the overall electroosmotic flow was lower when compared to Exp. I and III. The lower electroosmotic flow in Exp. IV and V is due to the polarity changes of the electrode in AC with DC. It can be concluded that the effect of polarity changes in Exp. III may be lower when compared to other systems. It is also known that the electroosmotic flow is influenced by many factors in the soil like zeta potential, pH, buffer capacity, and ionic strength and so on (20).

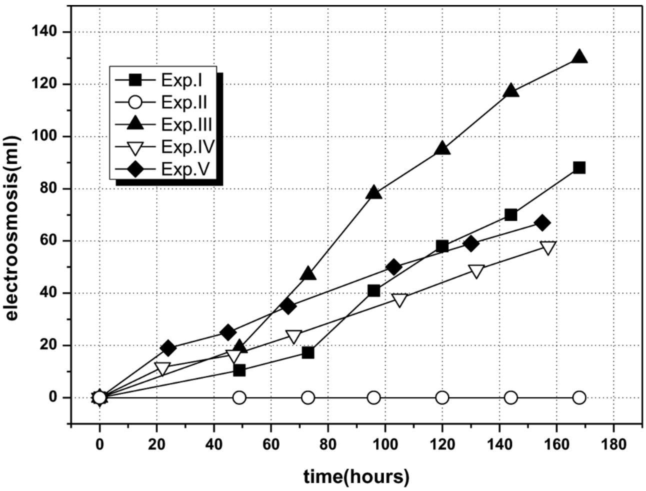


Figure 3. The volume of accumulated electroosmotic flow for various experimental systems.

pH of Soil and Electrolyte

The pH distribution of soil mixtures at variable positions from anode and the pH value of anolyte and catholyte for all systems are presented in Figures 4 and 5. There was no fluctuation of pH in Exp. II from anode to cathode. The pH distribution of soil for other experiments was almost the same as the general pH profiles in the conventional EK remediation (21). It indicates that the influence of DC on pH of soil is higher when compared to AC. The anolyte pH was in the range of 7 and catholyte was in acidic side about 3 in Exp. II. In other systems (Exp. I, Exp. III–V), the pH of catholyte was about 12 and anolyte was around 2. Since acetic acid was added as catholyte, the pH shifted to the acidic side in the catholyte of Exp. II. It indicates that the AC current does not influence the pH of anolyte and catholyte in EK process. The influence of DC on the pH of the electrolyte was considerable which is useful in the separation of anions and cations.

Transport of Salt Ions

Figures 6–9 show the concentration of calcium, potassium, magnesium, and sodium cations in the soil sections after the completion of EK experiments. Initially, calcium ion concentration was 1.8 g/kg in the soil. The

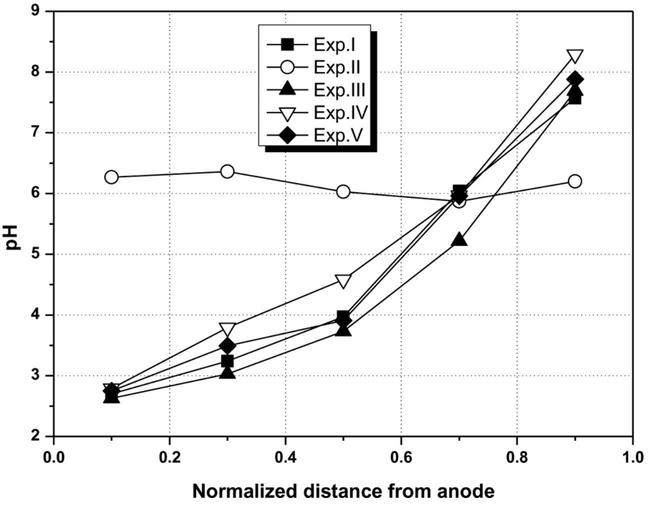


Figure 4. The pH distribution of soil after EK experiments.

concentration of other cations were in the following order: K > Mg > Na. The removal of cations in EK system was higher at anodic spot due to the movement of positive charges towards cathode. The electroosmotic flow from anode to cathode also caused the cations to transport towards the cathode area while applying DC power. The availability of cations is

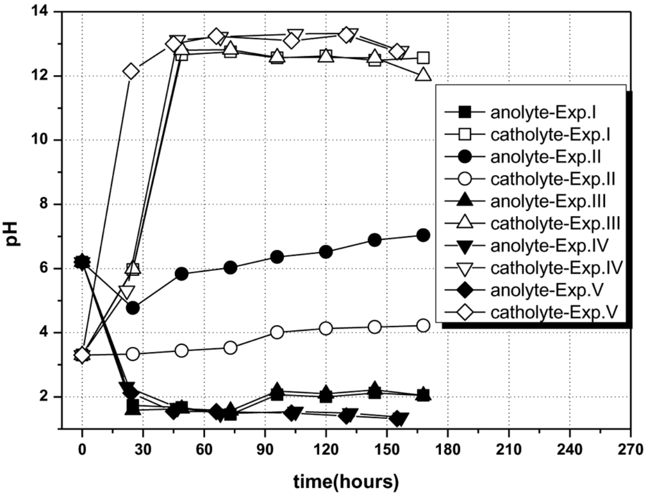


Figure 5. pH profile of electrolyte during EK process.

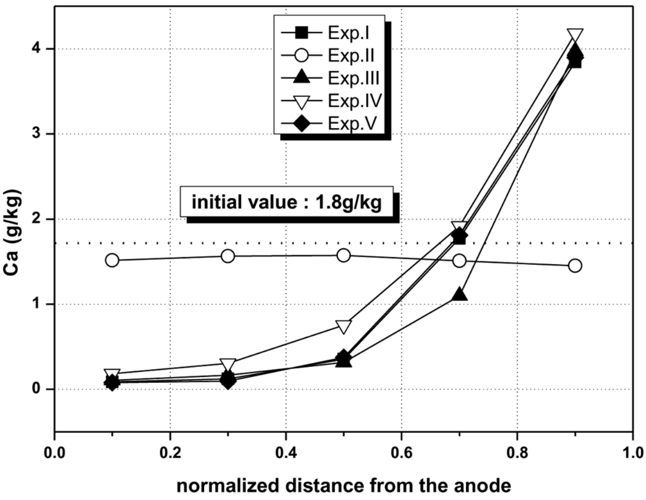


Figure 6. Calcium concentration in soil after EK process.

the reason for the high EC value at closer to cathode. There was no significant removal of cations where slight reduction of cations can be noticed in Exp. II. The slight reduction of cations may be due to the influence of AC on organic complex in soil particles. The reduction of cations may be due to the mobility of electrolyte at interstitial space in soil by Brownian motion (22).

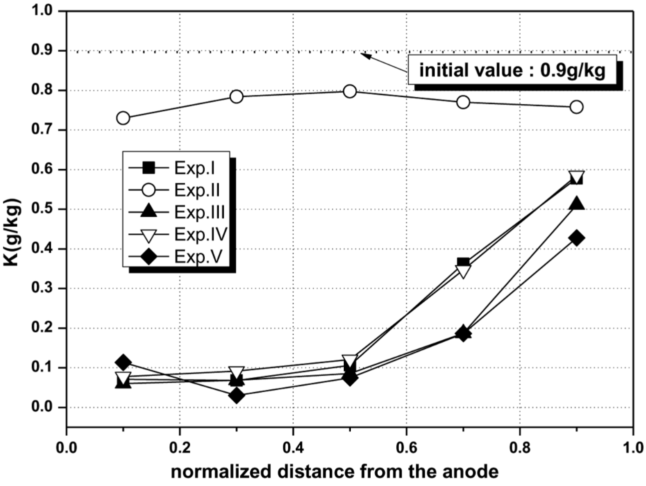


Figure 7. Potassium concentration in soil after EK process.

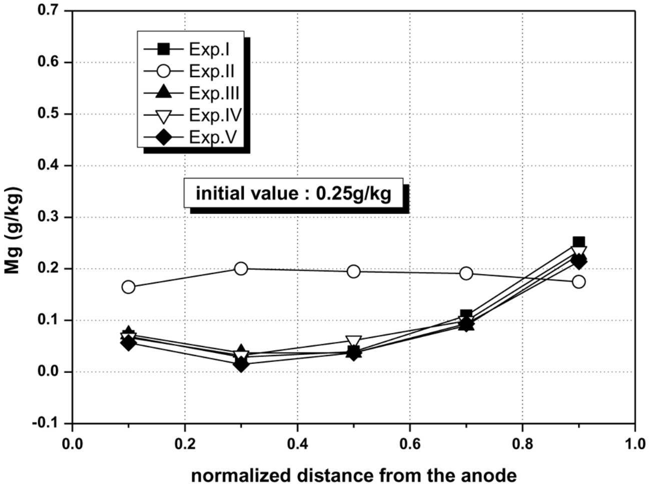


Figure 8. Magnesium concentration in soil after EK process.

Figure 10 shows the concentration profile of NO_3^- in different sections of soils. All experiments show that the concentrations were much lower than the initial value. The initial value of nitrate was 1,878 mg/kg whereas the accumulation of nitrate was in the range between 420 and 810 mg/kg at anodic area in Exp. I and III to V. It shows that DC

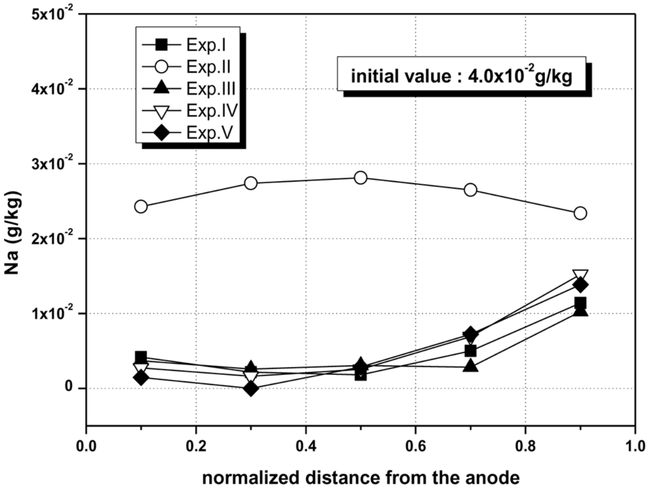


Figure 9. Sodium concentration in soil after EK process.

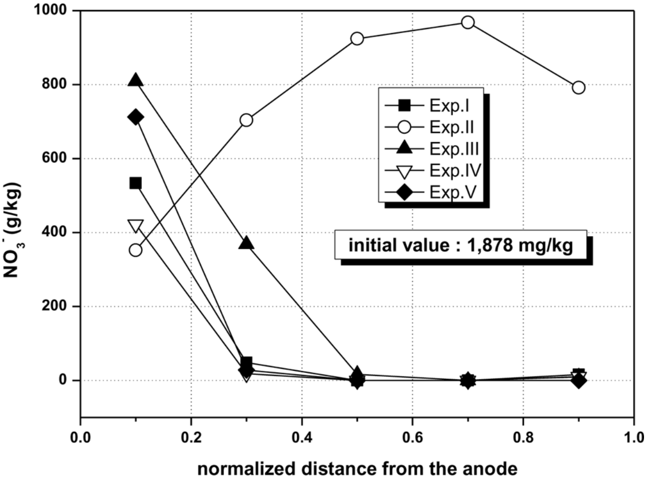


Figure 10. Nitrate concentration in soil after EK experiments.

removes the nitrate significantly in the soil towards anode by electromigration. In Exp. II, the nitrate concentration profile was different from other systems. The highest value was noticed at the center area of the soil sections. The nitrate value was lower at anode (380 mg/kg) when compared to other systems. The removal of nitrate was about 80% at anode and about 48% at cathode while applying AC. It can be assumed that the rising of temperature by AC may enhance the bacterial activity on nitrate reduction. It may be due to the bio-degradation of nitrates in organic complex (18). In a biological degradation process, an electron donor (carbon source), and an electron acceptor are needed. The electron donor provides a source of energy. An additional effect of increased temperatures is that organic compounds, such as humic and fulvic acids that are present in clay, dissolve in the soil and can also act as a carbon source (10). Hence, it is believed that the electron donor may supply electron to nitrate and reduces as nitrogen/ammonia gas. Further study is needed on bacterial multiplication by AC on nitrate removal process. The nitrate profile was similar to the EC profile as in Fig. 2. It can be assumed that the available anions including nitrates influence on the EC of the soil, where Ca and K ion increased EC at cathodic area. Oh and Park (23) suggested that the analysis of real permittivity should be performed at frequencies above 100 kHz. In the present study AC-EK was done at 60 Hz which supports the observation made by Fukue et al., (13) who suggested that ions can not be attracted toward cathode and anode in the AC system even at 1 kHz. This basic study will be useful to conduct further investigations on the combined action of AC and DC in EK on nitrate removal technology.

CONCLUSIONS

In the present study, the influence of AC and DC current, as the power of EK technology on the physicochemical phenomena of the soil was investigated. The electroosmotic flow from anode to cathode was restricted in Exp. II due to the changing polarity of electrodes. In Exp. II, EC values were higher at the middle of the soil and the value was lower near the anodic area. It may be due to the removal of anions at the anodic area by AC. The higher value of EC in the other system is due to the availability of nitrate at the anodic area. EC was increased due to the availability of cations like Ca, K closer to cathode. The pH profile was similar to the case of the conventional EK remediation in all the systems whereas in Exp. II there was no significant change in pH. In summary, EK technology is very effective for removing salt ions from the soil by DC. The reduction of nitrate was about 80% closer to anode and 48% at anodic area while applying AC. It indicates that the reduction may be due to bacterial impact on nitrates. DC also removes nitrate significantly by electromigration. While applying AC overlapped DC, the efficiency was lower when compared to DC alone.

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