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Restoration of Saline Soil in Cultivated Land Using Electrokinetic Process

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Abstract: Many agricultural areas have suffered from salinization due to the use of fertilizer and inadequate water management. This study utilized an electrokinetic (EK) process to investigate the movement and removal of salts in greenhouse soil. Each experiment was operated with a constant voltage gradient of 1 V/cm between 6 to 48 h and used tap water as an electrolyte. A significant amount of anions was removed through electroosmotic flow and electromigration. Nitrates showed the highest removal efficiency (81.86%) after 48 h. However, the removal of cations by EK process was negligible; in fact, the exchangeable concentration of potassium after EK treatment actually increased compared to the initial value. In this experiment, the electrical conductivity of the soil was lowered to 60% of the initial value, signifying that salts were removed by EK. Based on the results of this study, EK can be a very effective technique to control the concentration of salts in saline soil.

Keywords: Electrical conductivity, electrokinetic remediation, ionic mobility, saline soil

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INTRODUCTION

The United Nations Environment Program reported that approximately 20% of the world's agricultural land and 50% of its cropland suffers from salinity (1). The salinization is caused by the use of fertilizer to achieve improvements in crop yield and inadequate irrigation (2). Korea has many greenhouses, and salinity has become a serious problem in crop cultivation. Greenhouses intercept rainfall and provide an environment with high temperature, weak light, and high levels of carbon dioxide (3). Fertilizer spread on the cropland cannot be removed from the soil by rainfall, and salts are transferred from the subsoil to the top soil due to water evaporation. Consequently, the surface soil in greenhouses contains a high concentration of salts, and low tolerance of the crops to salinization causes bad harvests. There are many salt types—sodium, nitrate, chloride, calcium, magnesium, potassium, sulfate, etc. Nitrate salts are one of the more toxic species and bring about human health problems such as methemoglobinemia (blue baby syndrome) in infants and epidemiological gastric cancers in adults (4,5), for whom calcium and potassium are essential nutrients. A common way to control salinity is by utilizing excessive irrigation (1,2).

Recently, the electrokinetic (EK) technique has been used to control or remediate contaminated soils (6–10). For this method, electrodes are installed in a soil field and an electrical gradient is applied across the electrodes. Electrolysis reactions are generated at the electrodes under electrical input, producing H^+ and OH^- (8–10). The soil pH decreases to below 3 near the anode and increases to 8–12 near the cathode (7). The main removal mechanisms of contaminants in the EK process are electromigration and electroosmosis (6). Electromigration is the transport of charged ions in pore water under an electrical gradient; positive and negative ions move toward the cathode and anode respectively (10). Electroosmosis is the migration of pore water from anode to cathode and is induced by the zeta potential of soil (11). Therefore, the EK process is suitable for the removal of salts from the soil since the salts exist as charged ions in the soil (4,5,8,12). In addition, current flow is very efficient because saline soil has very high electrical conductivity (EC).

This study evaluated the effect of an electrical gradient and the possibility for the removal and movement of salts. A constant voltage but different durations of time—6, 12, 24, and 48 h—were applied for each EK treatment in the lab-scale experiment.

MATERIALS AND METHODS

Saline Soils

The saline soil used in this study was obtained from greenhouses in Korea that were cultivating pumpkins and peppers. The soil was air-dried, passed through a 2 mm sieve, and mixed uniformly before the experiment. Table 1 shows the soil properties and salt concentrations. The major contaminants were nitrate and potassium salts. The soil was prepared by mixing the samples with tap water in order to adjust the water contents to approximately 30%.

Electrokinetic Apparatus

An acrylic EK apparatus consists of a soil compartment, electrode compartment, and electrolyte reservoir. Figure 1 shows a schematic diagram of the EK experimental system. Anolyte and catholyte reservoirs (4 cm × 4 cm × 4 cm) were located at both sides of the soil compartment (4 cm × 4 cm × 20 cm), and an electrode was placed at each end of the

Table 1. Physico-chemical properties of soil

Characteristic	Value
pH	5.98
EC (dS/m)	4.5
Organic content (%)	5.18
CEC (meq/100 g)	35.72
Particle size distribution (%)	
Sand	35.72
Silt	56.18
Clay	8.1
Initial concentration (mg/kg)	
Cl^-	189.72
NO_3^-	2455.83
SO_4^{2-}	603.35
Ca^{2+}	1934.53
K^+	3085.33
Na^+	840.53

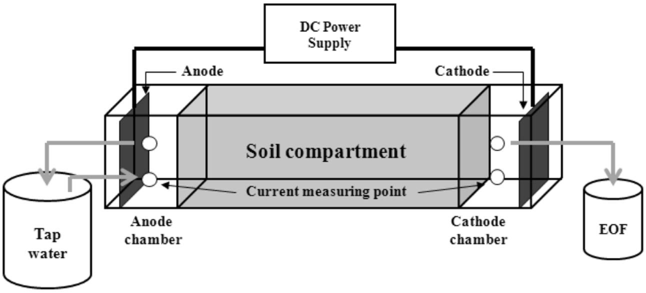


Figure 1. The schematic diagram of EK experimental system.

electrolyte chamber. A platinum-coated titanium electrode and a graphite electrode were used for the anode and cathode respectively. Filter paper was inserted between the electrolyte reservoir and the soil compartment to prevent soil loss. The anolyte was circulated using a peristaltic pump, and an electroosmosis flow (EOF) bottle was connected to the cathode chamber.

Electrokinetic Experiment

Four EK experiments were conducted with different time durations in order to evaluate the removal efficiency and the salt movement. For each experiment, a prepared soil sample was installed into the soil compartment. Tap water was used to fill the cathode chamber below the overflowing level and circulated into the anode reservoir. A constant voltage of 1 V/cm was applied to all experiments. The current was measured with an ampere meter in solution chambers located on both sides of the soil compartment. EOF which overflowed the cathode chamber was collected. Experiments were carried out over 6, 12, 24, and 48 h time intervals. After each experiment, the soil compartment was separated from the equipment and sliced into 10 equal sections for further analysis.

Analytical Method

Soil samples collected from the reactors after EK treatment were dried in an oven at 105° C for 5 h and crushed. A 10 g mass of dried soil was mixed with 50 ml of de-ionized water for 1 h and filtered out. The filtrate was used for measurements of the pH, EC, and anion concentrations (NO_3^-, SO_4^{2-}, and Cl^-). Cations (Ca^{2+}, K^+, and Na^+) were extracted with 1.0 N NH_4OAc (CH_3COONH_4) adjusted to pH 7 using CH_3COOH and

NH_4OH. 50 ml of NH_4OAc solution and 5 g of dried soil were mixed thoroughly for 30 min, and the filtrate was analyzed to measure cation concentrations. Salts were also analyzed for samples originating from the EOF and anolyte in order to verifying the amount of removal and movement over time. A pH/ISE meter (Istek 735P, Korea) and a conductivity meter (Istek 455C, Korea) were used to measure pH and EC respectively. Ion chromatography (Futecs, Korea) was used for the analysis of anions, and cations were measured with an atomic absorption spectrometer (AA 6300, Shimadzu, Japan).

RESULTS AND DISCUSSION

Soil pH and Current

The pH distribution for the soil sections after the EK experiments is shown in Fig. 2. The electrolysis of water is induced through electricity; therefore, hydrogen and hydroxide ions were produced at the anode and cathode respectively. Consequently, pH increased around the cathode and acidification occurred around the anode region. There was a big variation in pH with operation time due to the different periods of electricity being applied. The current was measured during the experiments and is shown in Fig. 3. The electric current flowing into the soil compartment was highly dependent upon the electrical conductivity

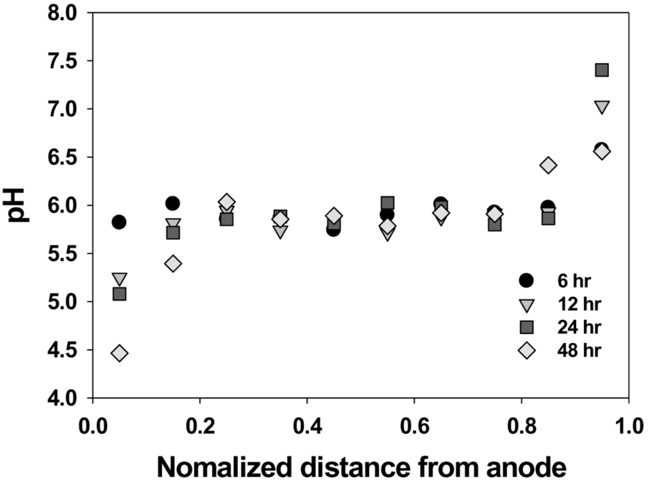


Figure 2. The pH distribution of soil section after EK treatment.

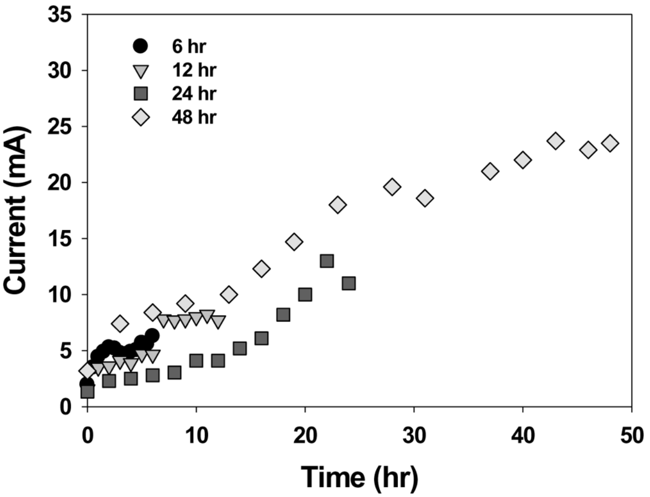


Figure 3. The electrical current change during experiment.

(EC), which changed with the ionic concentration in the pore water. The current increases in proportion to the number of existing ions; the current increased gradually because the EOF passed through the soil compartment and enhanced the dissolution of salts into the pore water.

Salts in the Soil Section After the EK Process

The charged ions were transported in the soil under electrified conditions and removed through electromigration and electroosmotic flow. The effective ionic mobility (u_j^*) in electromigration can be predicted by the following equation (10,13):

$$u_j = \frac{D_j z_j F}{RT}, \quad u_j^* = u_j \tau n$$

where D_j is the diffusion coefficient, u_j is the theoretical ionic mobility, z_j is valence, F is Faraday's constant (96,847 C/mol), R is the universal gas constant (8.3144 J/K · mol), and T is the absolute temperature. The effective diffusion coefficient is affected by the tortuousity factor (τ) and the porosity (n) of the soil (13). Generally, the range of tortuousity factor is 0.2–0.5 and porosity is 0.1–0.7 (10). According to this equation, the effective ionic mobility is proportional to the diffusion coefficient.

Ionic diffusion coefficients and the mobility of targeted ions are presented in Table 2. Salt concentrations in the soil compartment after

Table 2. Diffusion coefficient (D_j), ionic mobility (u_j), and effective ionic mobility (u_j^*) of some salts in soil

Species	$D_j \times 10^6$ cm^2/s	$u_j \times 10^6$ cm^2/Vs	$u_j^* \times 10^6$ cm^2/Vs
Cl^-	20.3	791.7	166.3
NO_3^-	19.0	741	155.6
SO_4^{2-}	10.6	826.8	173.6
Ca^{2+}	7.92	617.8	129.7
K^+	19.6	764.4	160.5
Na^+	13.3	518.7	108.9

EK treatment is shown in Fig. 4. As the operation time increased, anions such as chlorides, nitrates, and sulfates moved towards the anode and the concentrations decreased near the cathode (14). The chloride and nitrate ions showed similar trends. The removal of nitrates was higher than for chlorides and occurred very rapidly, even though nitrates have low ionic mobility. The nitrate ions were eluted from the soil surface and transferred under an electrical gradient because of the high solubility of nitrates in water. Some research groups have tried to control nitrate under hydraulic gradient flow toward cathode (5,8,15–17). They showed that nitrate can be moved and accumulated near the anode against hydraulic potential, therefore, the major transport mechanism is electromigration probably. Eid et al. had also developed that nitrate was influenced by pH gradient (16). And nitrate can be converted to N_2 gas at a low pH near the anode as the results of Manokararajah and Sri Ranjan (5). These lead to higher removal efficiency than the others. Sulfate ions accumulated near the anode and in the middle of the soil compartment. The concentration of sulfates in the soil decreased during the first 12 h, but increased a little near the cathode after 24 h; more variation was observed after 48 h. There were two different transport mechanisms for anions. One was electromigration towards the anode, and the other was electroosmotic flow toward cathode. According to the results, electromigration was superior to electroosmosis for the transport of nitrates, while the variation in sulfates for the soil sections was large due to it having the highest ionic mobility of the salts being analyzed. Also, the effect that sulfate was accumulated at point about 0.6 (normalized distance from anode) caused by two different transport mechanisms generated opposite direction each other and slightly increase appeared in 24 h duration, too.

There was no significant transport of cations observed in this study. The concentrations for calcium and sodium decreased after EK treatment, while the concentration variation for potassium was negligible up

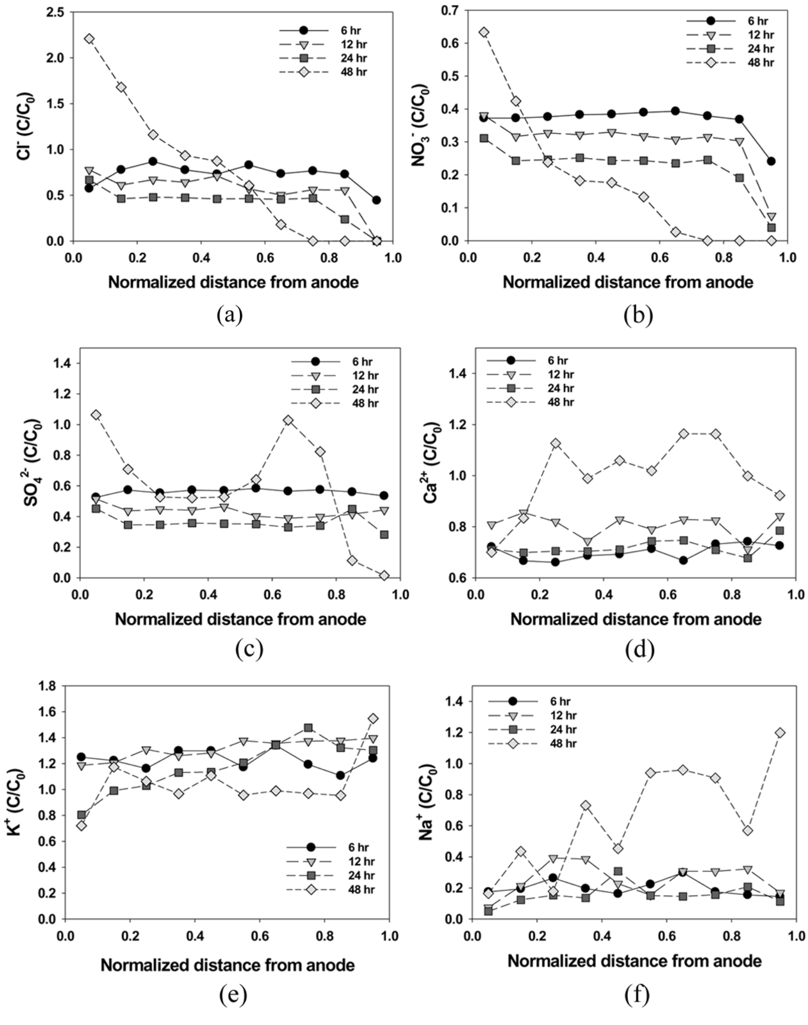


Figure 4. Salts concentration in soil section after EK process: (a) chloride, (b) nitrate, (c) sulfate, (d) calcium, (e) potassium, and (f) sodium.

until the 24 h time interval. On the other hand, an increase in cations was observed in the vicinity of the anode for the 48 h sample due to electroosmotic flow and electromigration. During the experiment, only exchangeable ions by water were desorbed and then removed by electrical flow. However, applying electrical energy changed the physicochemical properties of the soil and affected the transport of the ions. Change in soil pH due to electrolysis lead the increase of exchangeable fraction, therefore, cations can be exchanged with H^+ and extracted cations increased.

Electroosmotic Flow (EOF)

The electroosmotic flow (EOF) is affected by the amount of pore fluid transported under electrical application to soil and is determined by soil type, water content, electrical gradient, electrolyte concentration, and zeta potential (10,11,18). This flow causes ions in pore water to migrate. The electroosmotic flow velocity (v_{eo}) that was estimated by the Helmoholz-Smoluchowski theory is given by the equation (10,11,18):

$$\nu_{eo} = -\frac{D\varepsilon_0\zeta}{\eta}E_\chi$$

where D = dielectric constant, ε_0 = permittivity of vacuum, ζ = zeta potential, η =viscosity, and E_χ = electrical gradient. According to this equation, the electroosmotic flow velocity is proportional to the electrical gradient.

Figure 5 shows the accumulated EOF, with the time and ionic concentrations in the EOF presented in Fig. 6. EOF was not observed at 6 h due to low electric current and because a negligible amount of salts was detected. The highest value in anion concentration was observed at 12 h and then decreased gradually. The effects of electromigration and electroosmosis were compared and removal efficiency of anions by electroosmosis in total removal were presented in Fig. 7. At 6 h duration, anions were not removed by electroosmosis due to no generation of EOF, and as observed in Fig. 6(a), 12 h had the highest removal value

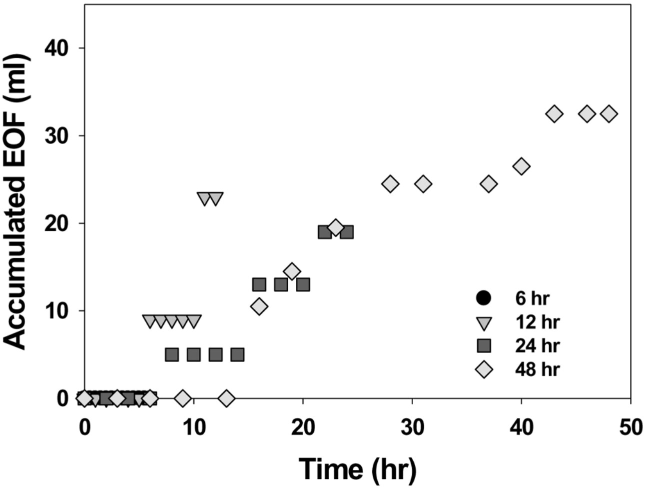
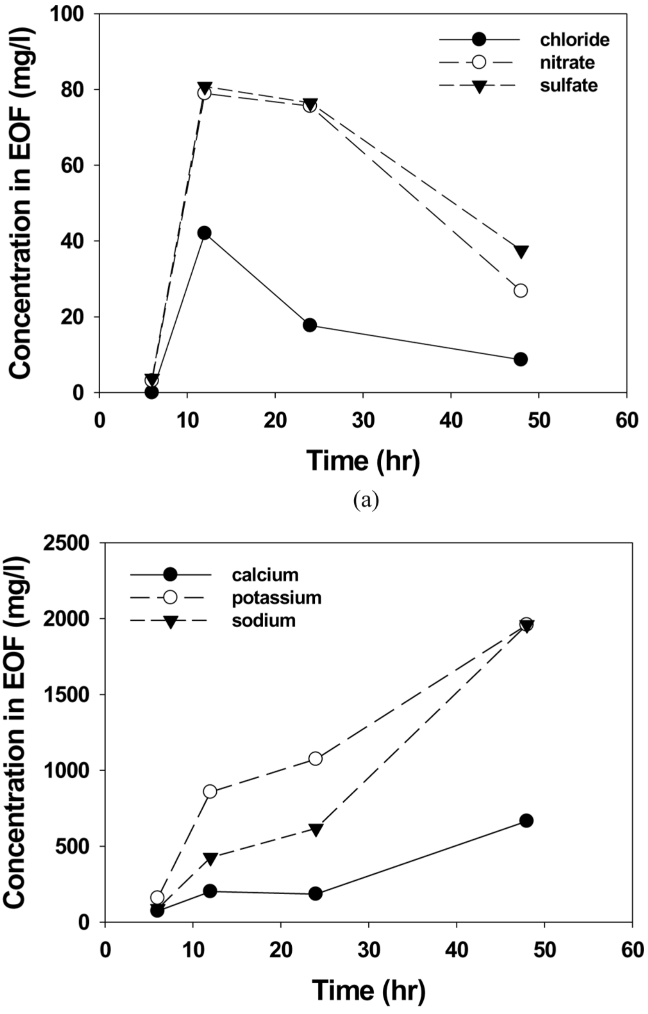


Figure 5. The volume of accumulated electroosmotic flow.



(a)

(b)

Figure 6. Salts concentration in EOF: (a) anion and (b) cation.

in all species. In case of chloride which existed as low concentration, diffusion was generated at soil section to catholyte and electromigration of nitrate dominate the transport in soil, therefore, the removal by electroosmosis of nitrate was very low. Sulfate removal was reached to 4% and decreased slowly with time, since the sulfate was moved by not only electromigration toward the anode but also electroosmosis toward the cathode because of its high ionic mobility.

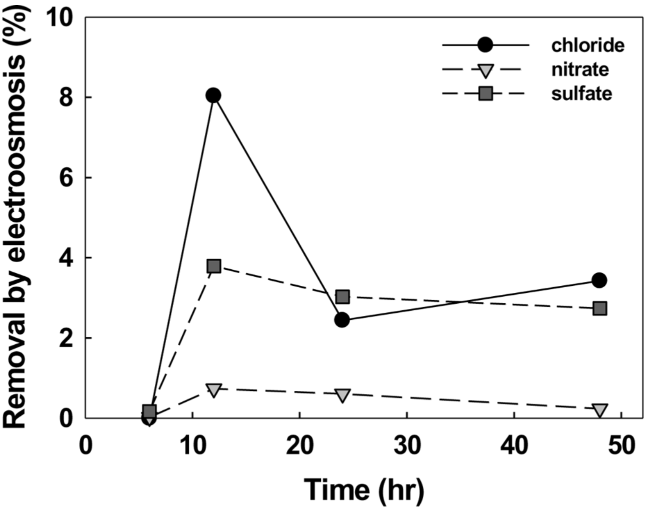


Figure 7. The anionic removal efficiency by electroosmosis in total removal (%).

The direction of both the electromigration and electroosmotic flow of cations was towards the cathode; therefore, the cations were transported by EOF. As shown in Fig. 6, the concentration of cations in EOF increased gradually as the operation time increased.

Electrical Conductivity (EC)

Soil EC is proportional to the existing charged ions at the soil surface; Figure 8 shows the soil EC after EK treatment. Higher EC values were observed nearer to the anode than the cathode, meaning that ions were transported toward the anode and accumulated there (5). This result was in accord with the nitrate concentration in the soil sample after the EK experiment, shown in Fig. 4(b). Nitrate ions were the major cause for the increase in EC of the soil because its initial concentration was higher than the other anions. Table 3 shows the average decrease in

Table 3. EC decrement during EK process

Time (hour)	6	12	24	48
EC (dS/m)	4.26	3.81	3.45	2.68
Decrement (%)	5.25	15.31	23.23	40.47

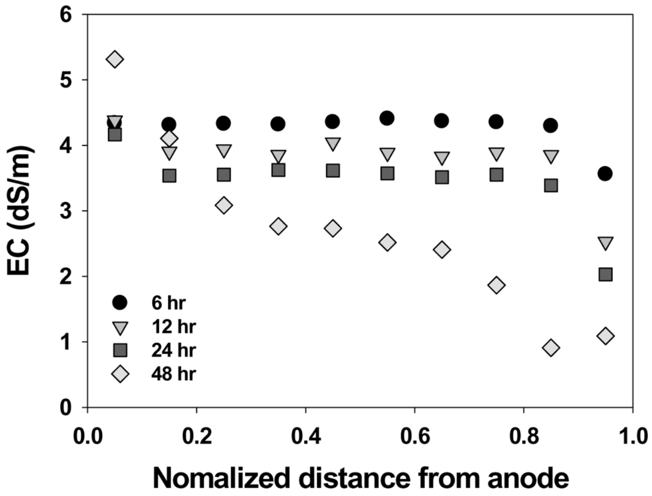


Figure 8. Change of soil EC during EK experiment.

EC after electrokinetic treatment. The decrease in EC after EK treatment means that the saline soil was restored because the salinity of soil is indirectly measured by the EC. In general, the EC value for soil should be lower than 2.5 dS/m for cultivating crops. Even though the whole soil sample in the EK cell did not meet this benchmark, approximately 40% of the saline soil was restored through electrokinetic treatment.

CONCLUSION

The lab-scale EK experiments were conducted to investigate the movement and removal of salts in greenhouse soil. The movement of salts is determined by their ionic mobility and solubility. Anions including chlorides, nitrates, and sulfates were transported through the soil compartment by an electrical field. The removal efficiency for nitrate ions was 63.41% for 6 h, and reached up to 81.86% for 48 h due to their high solubility. Chloride and sulfate ions showed similar rates of removal with both at approximately 50%. Over time, the contribution of EOF to the removal of anions decreased gradually while the contribution of electromigration increased because the direction of the two mechanisms was opposite. Even though the direction of migration and osmotic flow for cations was the same, there were no remarkable changes in characteristics for the cations. EC decreased significantly with increases in operation time, and EC had a high correlation to the nitrate concentration.

Additional research is necessary to achieve higher removal efficiency and to determine the optimum experimental duration on a field scale.

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