Electro-migration of nitrate in sandy soil

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Abstract

Migration of nitrate to groundwater has become a serious threat in many agricultural areas. This paper presents the results of experimental laboratory tests studying the nitrate gradient developed in response to an electrical potential. Two systems were tested; the first had no flow (closed system) and the second had flow opposite to the direction of the electrical current. A solution of sodium nitrate in sandy soil was used in both systems. The tests showed that the electro-kinetic process effectively concentrated and retained nitrate close to the anode. The movement of NO_3^- through the soil column was significantly influenced by the development of a pH gradient. Statistical analysis was performed to determine best-fit equations relating the nitrate gradient to the electrical input and pH gradient. A simple one-dimensional finite difference model was used to predict the pH gradient developed during the electro-kinetic process. The experimental measurements closely agreed with the predicted spatial and temporal distribution of the nitrate gradient for both closed and open system configurations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electro-kinetics; Electro-migration; Nitrate migration; pH gradient

1. Introduction

Electro-kinetic process utilizes an electrical potential to control the movement of water and chemicals in soil, a process which involves electro-migration, electro-osmosis

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and/or electrophoreses processes. Electro-migration is the transport of charged ions in solution under electrical potential, while electro-osmosis is the transport of solution in porous media, and electrophoresis is the transport of charged particles through a stationary liquid [1].
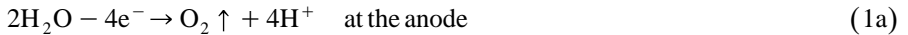
The transport and control of different species under the influence of electric fields have been employed in many fields. Alshawabkeh and Acar [2] had listed many of these applications such as: remediating soils from inorganic and organic species, injection of electron acceptors and nutrients in in-situ bioremediation, injection of grouts in soil stabilization and waste containment, injection of surfactants in solubilization of nonpolar species, soil pore fluid characterization and species extraction in penetrating probes, diversion systems for contaminant plumes, precipitation of migrating plumes, and leak detection systems in containment barriers [3–8].

The previous studies and applications were mostly used in conjunction with clayey soils. Among the few studies conducted on sandy soils is the study made by Wahli [9] that investigated the movement of copper sulfate between carbon-rod electrodes under low DC current. Haran et al. [10] presented a mathematical model predicting the pH gradient and chromate migration in the presence of a constant partial gradient across the soil and using a graphite cathode and iron anode. More comprehensive studies on sandy soils can be of great interest to the application of electrochemical techniques in arid areas. This interest is related to the conservation of irrigation water, avoiding the salt accumulation in soils, and to the protection of groundwater resources from salt contamination. The prevailing environmental conditions in arid areas such as temperature, humidity, type of natural soil, and common irrigation practices are all contributing to the salt accumulation rates in the root zones and groundwater contamination as well. The scarcity of natural water resources in such conditions usually results in the depletion of aquifer storage due to intensive loading on the groundwater resources. In addition, given the high leachability of the natural soil in the region, over-application of irrigation water to assure the crop demands of fertilizers, increases the potential of groundwater contamination. This will be more apparent when irrigating with treated sewage, which usually has high levels of nitrogeneous compounds. The use of electro-kinetic process in agricultural application has been investigated since the early 1950s [11] where it resulted in improving the salt removal efficiency of the subsurface drains and some improvement in plant growth. Typical tests utilized a 20-V DC electrical potential and 3 m of electrode spacing. Electro-osmotic soil desalination research in Russia and Egypt was reported to yield similar results [12,13]. Over the past 30 years, many projects were conducted in different places around the world, but the documented results have been isolated by site and time, and electro-osmosis has been largely unadopted in agriculture application. In a field lysimeter experiment, Cairo et al. [14] have shown that an electrical field was effective in moving nitrates over distances for up to 3 m in a soil that varied from saturated to partially saturated.

This paper reports the results of laboratory experiments conducted to control the migration of sodium nitrates in sandy soil under the application of constant electrical current. Also, the paper reports the numerical simulation results to estimate the nitrates gradient using theoretical and statistical means.

2. Background

Application of an electrical potential across a chemical solution commonly yields the following result. At one electrode, electrons are lost from the ions in solution (oxidation) while electrons are released to the ions in solution at the other electrode (reduction). The negatively charged electrode, called the cathode, attracts positive-charge ions (cations) while the positively charged electrode, the anode, attracts negatively charged ions (anions). Different ions are typically competing to give up electrons at the anode and take electrons at the cathode. If there are no other easily oxidizable anions near the anode, water will react and hydrogen ions will be produced. Similarly, hydroxyl ions will be produced at the cathode. As a result, a pH gradient will develop between the electrodes [6]. The general trend for a soil column filled with solute is that the pore fluid gets acidic (pH = 1–4) near the anode and basic near the cathode (pH = 10–13) [15,16]. The primary electrode reactions are:

$$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \quad \text{at the anode} \tag{1a}$$

$$4H_2O + 4e^- \rightarrow 2H_2 \uparrow + 4OH \quad \text{at the cathode.} \tag{1b}$$

The ionic species in the pore fluid, including ions generated by electrolysis, carry a portion of the current that depends on ion concentration and types [17]. The portion of the current carried by a specific ion in a solution decreases as the number of species in the solution increase. pH of the solution also affects the response of ions to an electrical field. The ionic mobilities of H^+ and OH^- are an order of magnitude higher than other ions [9], implying that a high or low pH will reduce the electrical response of other ions.

Theoretical models for multi-component species transport under electric fields have lagged behind the advancing theoretical formulation of the multi-dimensional hydro-chemical transport of groundwater due to chemical and hydraulic potential [2]. Theoretical background and fundamental relations governing the migration of ions in porous media have been summarized in several earlier studies [3,10,17,18]. Most of the presented theories are based on convective diffusion equations with chemical reactions and on the Nernst–Planck equations. One-dimensional finite element model has been frequently used in many of these studies to evaluate the acid/base distribution and flow patterns in electrochemical flow. Many assumptions were considered in the developed models such as completely diluted solutions, rapid and/or instantaneous dissociation–association of chemical reactions, and small double-layer thickness. The incomplete solubility of modeled solutes, the complex determination of soil zeta potential required for electro-osmotic flow calculations, and the long time associated with the adsorption equilibrium are all factors that contribute to the inaccurate results obtained from the current developed models.

3. Laboratory experiments

Two types of experiments utilizing closed and open systems were conducted to evaluate the applicability of using an electro-kinetic process to concentrate and retain

nitrate close to the anode for further removal. The soil used in both types of experiments was pure silica sand free of silt and/or minerals with bulk and particle densities estimated at 1.52 and 2.65 gm/cm^3, respectively. Particle sizes of the sand ranged between 0.2 and 0.6 mm. A solution of sodium nitrate was used as the interstitial solution in the two sets of experiments. The effect of selected design parameters on the performance of the process was studied. A brief description of each set of experiments and the main findings are presented in the following section. More details and elaboration on the results for both systems can be found elsewhere [19,20].

3.1. Closed system

The closed system experiments were conducted with clear plastic columns oriented horizontally and containing uniform and homogeneous compacted soil. All column tubes were 25-cm long with 6.5 cm internal diameters. One end of the tube was capped, while the other had a removable cap inserted after the column was filled with soil and solution. Three types of electrode materials were tested; carbon, copper, and stainless steel. Plates of the two electrodes had dimensions of 4 cm in diameter and 0.2 mm in thickness. The column was filled with the sodium nitrate solution and its open end was then capped and sealed using silicon cement. Fig. 1 shows a sketch of the experimental setup.

A constant electrical current was input to the soil column by means of a DC power supply. Constant current was maintained in all tests to keep the net rates of the electrolysis reaction constant and to minimize complicated current-boundary conditions. A voltmeter and ammeter were used to monitor input voltage and circuit amperage. The
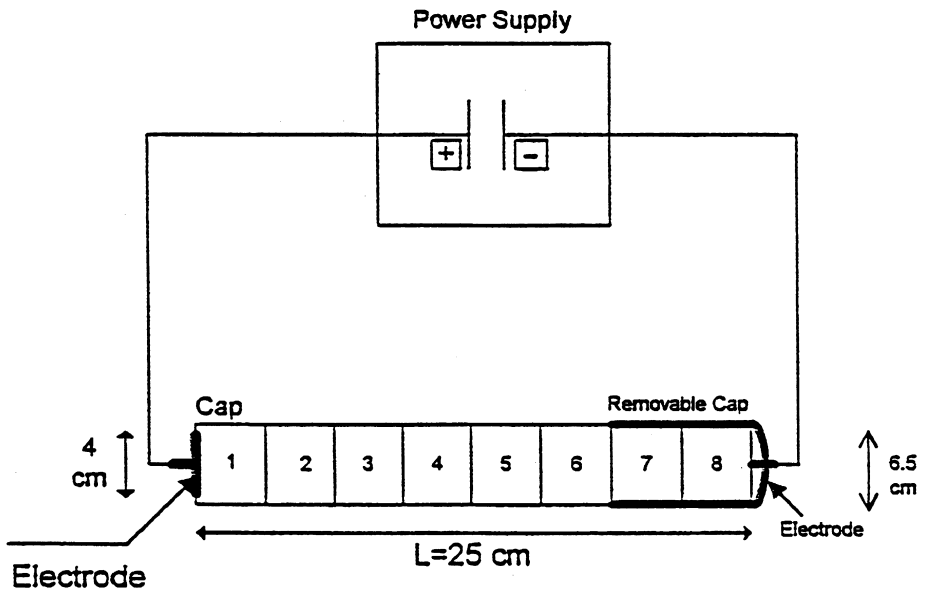

Fig. 1. Sketch of the experiment setup of the closed system.

current levels utilized in this set of experiments were 1.5 ± 0.05, 3.0 ± 0.05, 5.0 ± 0.05 and 10.0 ± 0.05 mA. The monitored voltages ranged from 30 to 90 V.

To preserve the chemical gradient developed by the electrical gradient, the soil column was frozen at the end of each test before turning off the power supply using a freezing technique utilized by Wahli [9]. After the experiment had run for the desired duration, the soil column was horizontally laid in a large styrofoam box and liquid nitrogen was poured into the space between the soil column and the box for a few minutes until the soil column was completely immersed. The power supply was turned off and the soil column was removed from the box. The soil column was then cut with electrical saw into 6–8 separate 2.5- to 3.5-cm-long sections at the marks indicated on the column's outer surface. The segments were stored in sealed beakers in a freezer until analysis. Each segment was allowed to thaw for one day, after which its solution was extracted using a vacuum pump connected to a 0.45-μm filter funnel. The nitrate in the solution was then measured using Ion Chromatography (DIONEX 2320i IC).

Analysis of the results indicates that the electro-kinetic process effectively concentrated and retained nitrate close to the anode. The migration of NO_3^- towards the anode was directly dependent on the electrical input applied (current intensity * duration). Fig. 3 shows that the 60% nitrate removal is achieved at the cathode after 5 h, while only 20% removal is achieved within the middle potion ($X/L = 0.3$ to 0.8). Significant clean up of Na^+ was observed after application of an electrical current for a long duration (12 h) in 70% of the soil sample close to the cathode. Under the same experimental conditions, substantial, but nearly equal migration of NO_3^- was produced using either carbon or copper electrodes. Less movement of NO_3^- was reported using stainless steel electrodes. Drop in the sodium concentrations near the cathode indicates its precipitation due to the elevated pH and alkaline environments. The results also showed that the nitrate migration rate was higher with closer electrode spacing and with a lower initial nitrate concentration.

3.2. Open system

The effectiveness of an electrical potential in retaining or concentrating nitrates under flowing conditions was evaluated using a set of horizontal cylindrical test columns. Sodium nitrate solution was introduced into the column test with a specified concentration for each experiment and at a predetermined constant rate from the anode compartment to the cathode compartment. Constant electrical current through the soil column was maintained. Fig. 2 shows a sketch of the open system setup. Results were evaluated to determine the hydraulic velocity below which the electrical effect was significant. The results revealed that the electro-migration can be an effective means for concentrating and retaining nitrate close to the anode in saturated sandy soil even under a hydraulic gradient [20]. For example with a 3-mA electrical input, nitrate was concentrated near the anode for hydraulic flow velocities less than 100 cm/h.

The results of the closed and open system experiments showed that the movement of NO_3^- through a soil column was influenced by pH. Initially, the nitrates advanced towards the anode rapidly, and with time, the pH gradient between electrodes increased and the nitrate movement was reduced. This reduction is likely attributed to the variation
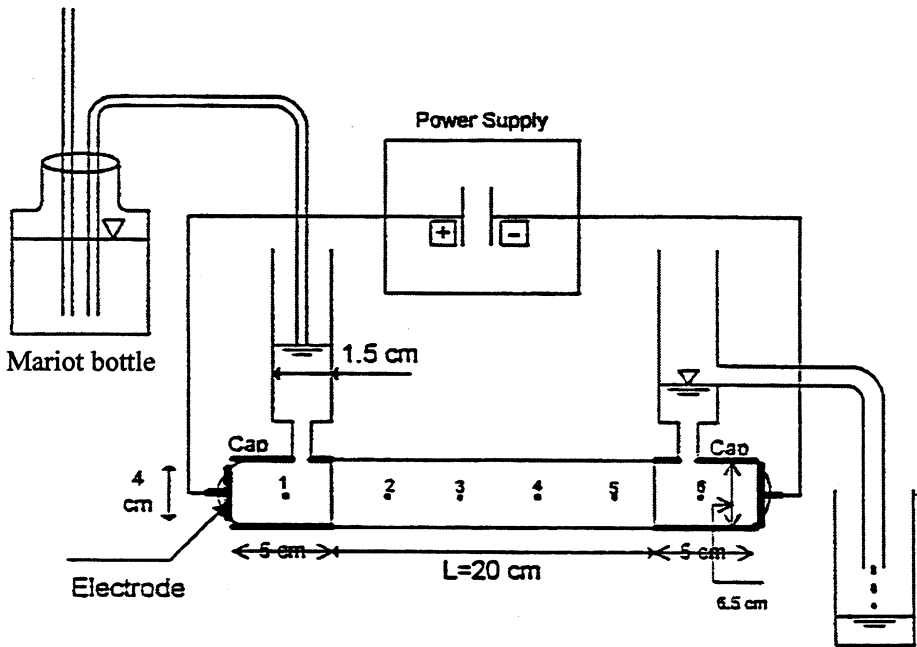
Fig. 2. Sketch of the experiment setup of the open system.

of pH gradient with time. The relationship between pH and NO_3^- gradients, observed in both the closed and open system tests, suggested the use of pH gradient in the prediction of the nitrate gradient developed in response to an electrical potential. This required to first obtain the pH gradient using numerical simulation, then the outputs were introduced in the developed pH-nitrate relationships for the prediction of nitrates.

4. The pH model

A one-dimensional finite difference model was developed to predict the pH gradient developed during an electro-kinetic process using the current analytical theories. Constant electrical current and hydraulic potential are considered with a saturated and homogeneous sandy soil. The soil matrix is assumed to have ideal electrolyte solution properties and the mass transfer chemistry is assumed to be dominated by the concentration profiles of acid and base. In this study, the chemical reactions of existing species in the bulk are neglected and only attributed to the water hydrolysis. The closed system experiments showed that a lower pH was developed at the anode in case of carbon electrode than in case of copper and steel electrodes. This can be explained by the competitive copper and iron ions released from their respective electrodes in the aqueous solution and leading to less generated hydrogen ions from the hydrolysis reaction. For simplification purposes, this type of reaction was not considered in the following model

and therefore, the results were only compared to the experimental ones associated with the carbon electrodes.

The initial condition was defined by the initial pH of the pore fluid and boundary conditions are defined by the measured pH values. Since the species generated at the boundaries are different, the simulation was performed for H^+ and OH^- simultaneously on a separate basis. The electrical neutralization at the location where H^+ and OH^- meet was maintained through imposing the following constraint:

$$H^+ + OH \rightarrow H_2O. \tag{2}$$

Nernst–Planck equation can be used to express the total mass transfer due to electrical and material gradients in electrochemical system as follows:

$$q_{tc} = \left[-D_x \left(\frac{\partial C}{\partial X} \right) + V_x C - \frac{zF}{RT} D_x C \left(\frac{\partial \phi}{\partial X} \right) \right] n dA \tag{3}$$

where q_{tc} is the total material flux into a porous media comprised of three components; the influx due to chemical gradients, the influx due to the hydraulic gradient, and influx due to electrical gradients. C is the solute concentration in the pore solution, D_x is the longitudinal dispersion coefficient in saturated medium, V_x is the average seepage velocity, z is the charge on ion, F is the Faraday's constant, R is the universal gas constant, T is the temperature (°K), ϕ is the electrical potential, and n is the medium porosity (0.43 in this study).

D_x is composed of two components as:

$$D_x = \alpha_x V_x + D^* \tag{4}$$

where $\alpha_x V_x$ represents the dispersion of the species caused by the average linear seepage velocity, α_x is the longitudinal dispersivity which depends on the size and frequency of the pores in the medium and D^* is the molecular diffusion coefficient and represents the diffusion of the chemical in the pores [21]. A value of $\alpha_x = 0.01$ was chosen [22]. The molecular diffusion coefficient D^* in the pore fluid is related to the diffusion coefficient in the free solution by:

$$D^* = \rho D_0 \tag{5}$$

where ρ is a coefficient depending on porosity and tortuosity of the medium . Rowe [23] reported that ρ values vary between 0.13 and 0.49.

The diffusion coefficients in the free solution for both H^+ and OH^- and their effective diffusion coefficient, D_{eff}, with respect to a counter ion species available in the original pore fluid were estimated [24] as suggested using:

$$D_{eff} = \frac{D_+ D_- (Z_+ - Z_-)}{Z_+ D_+ - Z_- D_-} \tag{6}$$

where Z is ionic charge. The effective diffusion coefficient for H^+ was calculated with respect to NO_3 while OH^- was calculated with respect to Na. In this study, diffusion coefficients (D^*) of $5.8e - 5$, $4.2e - 5$ cm^2 s^{-1} were calculated for H^+ and OH^-, respectively.

The assumption of constant electrical gradient in time across the specimen is realized to be not valid due to the dependence of electrical field upon the specific conductance of the pore fluid in time and space. However, earlier studies have considered this assumption to provide a first order approximation for an analytical solution [17]. The same assumption was utilized here which eventually simplifies Eq. (3) to:

$$q_{tc} = \left[kc - D_x \frac{\partial c}{\partial x} \right] n dA \tag{7}$$

and the parameter k is defined by:

$$k = -\frac{zF}{RT} D_x \frac{\partial \varphi}{\partial x} + k_x \frac{\partial h}{\partial x} = -k_m + k_h. \tag{8}$$

It has to be noted that the portion of k due to electro-osmotic potential was omitted because of the low surface charge and zeta potential in case of sandy soil. The mass balance equation across the soil column in one-dimensional condition is:

$$\frac{\partial q_{tc}}{\partial x} = -\text{Rd} \frac{\partial c}{\partial t} \tag{9}$$

where Rd is the retardation coefficient calculated using dry bulk density of the sand, r_b, the partition coefficient, k_p, and the porosity of the soil, n (0.43 in this study) as:

$$\text{Rd} = 1 + r_b k_p / n. \tag{10}$$

Retardation coefficients of 5 and 1 were calculated for H^+ and OH^-, respectively. It is been reported that no heterogeneous chemical reactions occur on the sand [25]. Therefore, the sorption process can be reasonably approximated by the retardation coefficients.

Substituting Eq. (7) into Eq. (9), the following equation results:

$$D_x \frac{\partial^2 c}{\partial x^2} - K \frac{\partial c}{\partial x} = \text{Rd} \frac{\partial c}{\partial t}. \tag{11}$$

Eq. (11) can be represented in normalized dimension as:

$$\frac{\partial^2 C^*}{\partial X^2} - P \frac{\partial C^*}{\partial X} = \frac{\partial C^*}{\partial T} \tag{12}$$

where C^* represents either the H^+ or OH^- normalized concentration, P is the Peclet number, X is normalized distance and T is normalized time. C^*, P, X, and T are further defined as:

$$C^* = 1 - \frac{C}{C_0} \tag{13a}$$

$$P = \frac{KL}{D_x} \tag{13b}$$

$$X = \frac{x}{L} \tag{13c}$$

$$T = \frac{D_x t}{\text{Rd } L^2} \tag{13d}$$

where C_0 is the initial concentration of either H^+ or OH^-; L is the length of the column; and t is the time.

The finite difference form of Eq. (12), using a central difference implicit solution scheme in X and the Crank–Nickolson scheme in T, is:

$$\left[C_{i-1}^* - 2C_i^* + C_{i+1}^*\right]^{k+1} - 0.5\Delta XP\left[C_{i+1}^* - C_{i-1}^*\right]^{k+1} - \frac{2\Delta X^2}{\Delta T}\left[C_i^*\right]^{k+1}$$

$$+ \left[C_{i-1}^* - 2C_i^* + C_{i+1}^*\right]^k + - 0.5\Delta XP\left[C_{i+1}^* - + C_{i-1}^*\right]^k$$

$$+ \frac{2\Delta X^2}{\Delta T}\left[C_i^*\right]^k = 0 \tag{14}$$

where ΔX is the length increment in the normalized X direction; i is the index of length increments, ΔT is the time increment; and k is the index of time increments.

The initial concentration was defined from the initial pH value, obtained experimentally. The boundary condition concentrations were defined from the pH values obtained experimentally at the boundary sections at termination of the electro-kinetic tests. The

Table 1
Closed system, no flow, experimental conditions

Test no.	Initial C_0 (ppm)	Electrode material	Current (mA)	Duration (h)	Length (cm)
1	850	carbon	5	24	25
2	850	copper	5	24	25
3	85	steel	5	5	25
4	85	copper	10	5	25
5	85	copper	5	5	25
6	85	carbon	5	5	25
7	85	copper	3	5	25
8	85	steel	3	5	25
9	85	copper	5	5	25
10	85	copper	5	5	12.5
11	85	carbon	5	3.5	25
12	85	carbon	5	1.5	25
13	85	carbon	5	6.5	25
14	85	carbon	5	24	25
15	85	carbon	5	5	25
16	85	carbon	5	12	25
17	85	carbon	3	12	25
18	85	carbon	1.5	12	25
19	600	carbon	1.5	12	25
20	85	carbon	1.5	12	25

electrical gradient $(\partial\phi/\partial x)$ required to determine k at different time increments was approximated via dividing the voltage difference between the end electrodes by the column length. Eq. (5) was solved numerically using the Newton–Raphson method of numerical integration to define the pH gradient developed under an electro-kinetic process.

5. Results for NO_3^- prediction

The statistical program Table Curve [26] was used to find the regression equation "best" relating the nitrate gradient developed under an electro-kinetic process to the corresponding pH gradient.

The regression equation developed to predict NO_3^- for closed system conditions that best fit closed system test results was:

$$C/C_0 = a + b\,\frac{\ln(\mathrm{pH})}{\mathrm{pH}} \tag{15}$$

where C/C_0 is the relative concentration of NO_3^- and a and b are the regression coefficients.

The regression analysis was performed on each individual experiment to determine the corresponding a and b coefficients. The experimental conditions are summarized in Table 1; regression analysis coefficients for the closed system experiments are summa-

Table 2
Summary of the regression analysis results for prediction of nitrate concentration in closed system experiments

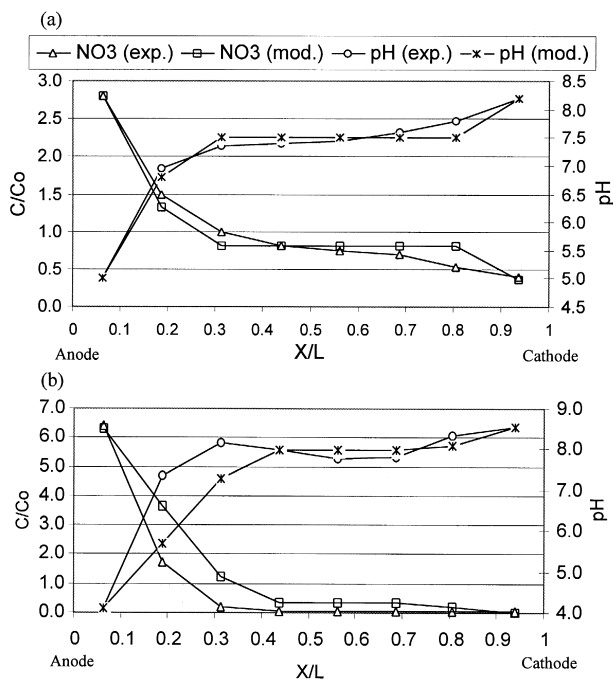| Test no.	b	a	R^2
1	14.66	−3.0	0.74
2	18.0	−3.9	0.9
3	33.79	−8.0	0.8
4	43.00	−10.6	0.89
5	53.3	−13.65	0.94
6	37.5	−9.26	0.97
7	31.15	−7.07	0.88
8	24.23	−5.3	0.9
9	77.83	−19.67	0.93
10	128.9	−33.1	0.98
11	56.2	−13.66	0.78
12	43.7	−10.16	0.64
13	56.6	−13.8	0.67
14	56.9	−13.5	0.71
15	23.7	−5.29	0.78
16	72.8	−18.6	0.97
17	33.49	−8.0	0.63
18	47.93	−11.4	0.94
19	11.39	−1.95	0.54
20	46.5	10.89	0.78

Fig. 3. Model and experimental results for NO_3^- and pH gradients for 5 mA electrical input with no solute flow, carbon electrodes and initial sodium nitrate concentration of 85 ppm, (a) after 5 h, and (b) after 12 h.

rized in Table 2. The computed pH and NO_3^- values for Experiments 6 and 16 are shown in Fig. 3.

There was overall agreement between the estimated and measured values. The numerical model simulated pH through the soil column quite adequately at the early times. Some deviation between the modeled and measured values can be observed with longer periods of time. This can be attributed to the selected input values for D_H, D_{OH}, Rd_H, and Rd_{OH}, values chosen from the literature. Some of the difference may also be due to inaccuracies in the measurement of pH. There also was consistency between the experimental and computed NO_3^- gradients. Results shown in Fig. 3 support the validity

Table 3
Open system experiment parameter values

Test no.	Current (mA)	Fluid velocity (cm/h)	Test duration (h)	Solute concentration (ppm)
1	3	9.5	12	85
2	3	17.3	12	85
3	3	32.3	12	85
4	3	70.3	12	85
5	6	17.3	12	85
6	3	17.3	12	170

Table 4
Summary of the regression equation results for prediction of nitrate concentration in open system experiments

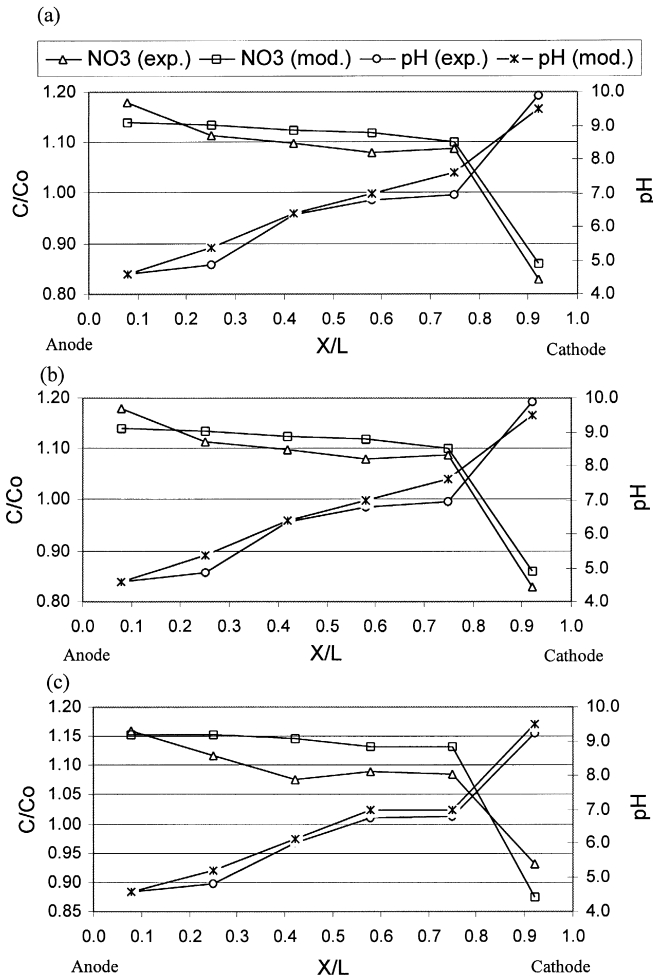| Test no.	B	A	R^2
1	-0.00027	1.07	0.84
2	$-.0011$	1.33	0.79
3	$-.00016$	1.12	0.94
4	$-.00084$	1.1	0.85
5	$-.00146$	1.25	0.85
6	$9.1e-6$	0.96	0.93

Fig. 4. Model and experimental results for NO_3^- and pH gradients for 3 mA electrical input in the presence of V_x of 32 cm/h with carbon electrodes and initial sodium nitrate concentration of 85 ppm, (a) after 4 h, (b) after 8 h, (c) after 12 h.

Table 5
Summary of paired *t*-test comparison of predicted with measured pH values for the six experiments

Test no.	Significance	t_{cal}	SD	Deviation (pH_p-pH_e)	n
1	Ns	0.24	0.66	0.159	18
2	Ns	0.36	0.43	0.154	18
3	Ns	0.31	0.56	0.174	18
4	Ns	0.26	0.39	0.1	12
5	Ns	0.065	0.49	0.03	18
6	Ns	0.23	0.67	0.152	18

of using the developed approach to predict the spatial and temporal distribution of NO_3^- developed under an electro-kinetic process for closed system configurations.

The one-dimensional pH gradient model was also used to simulate changes during an open system electro-kinetic process. The pH gradient results were then used to predict the NO_3^- concentration using the regression equation relating NO_3^- gradient to pH. The regression equation that best fit the open system process was:

$$C/C_0 = a + b\frac{\exp(pH)}{pH} + c\ln(t) \tag{16}$$

where C/C_0 is the relative concentration of NO_3^-, t is the test duration (h) and, a, b, and c are the regression coefficients. Open system test parameters are summarized in Table 3; the regression coefficients obtained from analysis of results of the individual experiments are listed in Table 4.

Results of Experiments 1, 3 and 4 in which the hydraulic flow velocities were 9.5, 32, and 70 cm/h, respectively, then were lumped together to obtain one equation which included a velocity term. The equation that represents the three experiments is:

$$C/C_0 = a + b\frac{\exp(pH)}{pH} + c\ln(t) + dV_x \tag{17}$$

where V_x is the hydraulic velocity in cm/h and d is the regression coefficient. The correlation coefficient for the lumped equation was found to be 0.80. The values of a, b, c, and d parameters are 1.13, -0.00021, 0.032, and -0.00172, respectively.

Table 6
Summary of paired *t*-test comparison of predicted with measured NO_3^- values for the six experiments

Test no.	Significance	t_{cal}	SD	Deviation $(No_{3p}-No_{3e})$	n
1	Ns	0.97	0.059	0.05	18
2	Ns	0.024	0.057	0.001	18
3	Ns	0.08	0.039	0.003	18
4	Ns	0.74	0.056	0.05	12
5	S	1.85	0.06	0.114	18
6	Ns	0.2	0.03	0.006	18

Results of Experiments 2 and 5 were also lumped together (current = 3 and 6 mA, respectively) in one equation after adding a current term. The equation representing Experiments 2 and 5 is:

$$C/C_0 = a + b\frac{\exp(\mathrm{pH})}{\mathrm{pH}} + c\ln(t) + eC_{\mathrm{u}} \tag{18}$$

where C_{u} is the applied electrical current in mA. The correlation coefficient for this equation was found to be 0.82. The coefficients a, b, c, and e are 1.18, -0.00014, -0.024, and 0.02, respectively.

Experimental and model results for the tests with a hydraulic flow velocity of 32 cm/h (Experiment 3) are presented in Fig. 4. The results show an overall agreement between the estimated and measured values of H^+ and OH^- through the soil column. Paired statistical t-tests showed no significant difference between measured and simulated data at the 5% level for pH and no significant difference between measured and simulated NO_3 values in five of six tests (Tables 5 and 6). Observed differences between model and experimental results are attributed to the assumed values for such inputs as D_{H}, D_{OH}, Rd_{H} and $\mathrm{Rd}_{\mathrm{OH}}$, but pH differences may also have been due to inaccuracies in the measurement of pH.

Fig. 4 shows reasonable agreement between experimental and computed pH and NO_3^- gradient values at different time intervals. The difference between the NO_3^- gradients does not exceed 5% at any point along the column length. Differences between the experimental and regression-derived NO_3^- gradient may be due to inaccurate analysis of NO_3^- concentration and/or differences between the predicted and experimental pH gradients. These results support the use of the finite difference and statistical model to predict the spatial and temporal distribution of NO_3^- developed under an electro-kinetic process in the presence of hydraulic flow.

6. Summary and discussion

Experimental results of both closed and open systems showed that the electro-kinetic process effectively concentrated and retained nitrate close to the anode in saturated sandy soil. The movement of NO_3^- through a soil column was mostly influenced by the developed pH gradient due to electrolysis. The closed systems experiments indicated a precipitation of the sodium salts close to the cathode due to the developed alkaline medium. The open system experiments showed that applying electrical current of 6 mA to a 0.3-m-long column was sufficient to retain significant levels of nitrate against a hydraulic gradient corresponding to a darcian velocity of 0.17 m/h.

On the other hand, a one-dimensional finite difference model effectively predicted the pH gradient developed in the soil column for closed (batch) and open (flowing) systems. It is realized that the boundary conditions along with the electrical gradient can be determined by employing additional relations. However, it is believed that measuring the pH and voltage at the column ends is a feasible and practical task. This eventually simplified the calculations and avoided the errors associated with estimating the

parameters embedded in those additional relations as well. That was reflected in the good agreement between the measured and modeled pH gradients. The developed statistical regression relations then used the estimated pH values to adequately predict the generated NO_3^- gradient for both systems. This approach can be utilized in the evaluation of electro-kinetic systems for controlling nitrate movement in sandy soils. Different operating scenarios can be examined to achieve the best clean-up performance at different times so that optimum remedial settings are configured without the need of conducting expensive pilot-scale tests.

It is important to note that the experimental results along with the developed modeling approach are all based on uncontrolled acidic front generated at the anode. The precipitation of cations in the cathode region leads to a decreased conductivity and eventually large electrical potential. Consequently, the electrical potential difference increases, resulting in an increase of the energy expenditures, especially if the current is constant. Therefore, certain conditioning precautions are usually taken to control the large developed pH for the sake of practical and economical applications. This implies that the statistical relations developed in this study cannot be utilized under such controlled conditions and need to be limited to the conditions under which they were developed. Another phase of experiments with controlled pH gradients is currently underway in which new empirical relations are sought.

Nomenclature

q_{tc}	total species flux (μg s^{-1})
D_x	longitudinal dispersion coefficient (cm^2 s^{-1})
C	species concentration, H^+ or OH^- (ppm)
V_x	average seepage velocity (cm s^{-1})
X	distance (cm)
z	species charge
F	Faraday's constant (96,485 C)
R	universal gas constant (8.3143 J kg^{-1} K^{-1})
T	temperature ($^\circ$K)
Φ	electrical potential
n	medium porosity
α_x	longitudinal dispersivity
D_0	diffusion coefficient in the free solution (cm^2 s^{-1})
D_{eff}	effective diffusion coefficient (cm^2 s^{-1})
K	constant representing the velocity in pore fluid (cm s^{-1})
k_m	k portion due to electro-migration (cm s^{-1})
k_h	k portion due to hydraulic head (cm s^{-1})
h	hydraulic head (cm)
t	time (s)
Rd	retardation coefficient
r_b	soil dry bulk density
k_p	partition coefficient
C^*	normalized species concentration

C_0 initial concentration (ppm or mg/l)
P Peclet number
X normalized distance
L length of soil column (cm)

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