



Electrokinetic extraction of Cr(VI) from contaminated kaolin numerical and experimental studies

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This paper presents the solution technique which has been developed by applying finite difference method in order to solve one dimensional advection diffusion equation model of contaminant transport under chemical and electrical gradient. The factors such as adsorption and soil pH affecting the phenomena of contaminant transport have been included in the solution technique. For verification of the results of the numerical solution, laboratory electrokinetic tests were conducted and experimental results obtained were compared with numerical solution. The experimental and the numerical solution results showed good concurrence.

Keywords: Electrokinetic extraction, Cr(VI), numerical solution, finite difference method.

Introduction

Heavy metal chromium is commonly used in industries such as leather tanning, textile industries, electroplating, metal finishing, and dye manufacturing, paint and petroleum refining processes¹. Once introduced to the environment and left in an unprocessed state, chromium can trickle through soils and reach the underlying groundwater table thereby polluting groundwater. Thus there is a vital requirement to remediate the contaminated soil. Due to its bioavailability and mobility, Cr(VI) acts as mutagens and carcinogens in biological systems². Electrokinetic extraction, an *in situ* removal of pollutants from both unsaturated and saturated less permeable soils is a broad section of interest for the scientists and researchers for its versatility in the field of application³. Electrokinetic remediation is a process in which a low direct current is applied (mA cm^{-2} of the electrodes' cross-sectional area) or a lower potential gradient is applied to electrodes (V cm^{-1} of the distance between the electrodes) that are placed into the ground. The contaminants are transported by electromigration and electroosmosis due to application of current or low potential gradient⁴ to either the anode or cathode and are then removed from the electrodes.

Based on a well-known Fickian advection dispersion

equation (ADE)^{5,6} the mathematical modeling of 1D contaminant transport has been prepared. The model is basically a set of partial differential equations (PDEs) with some coefficients acting non-linearly. Using a finite difference method an algorithm for numerical solution of the PDEs has been developed. The chemical species concentration during electrokinetic remediation as a function of time and space has been obtained from the analysis. To facilitate computation simple assumptions are made by researchers wherein, pH buffering capacity of soil is neglected⁷. The main objectives of this study were; (1) to simulate transport of Cr(VI) in soils under electrical fields using a set of one-dimensional diffusion-advection equation (ADE) and using finite difference method for its solution, (2) to validate the proposed numerical solution by comparing with the experimental results.

Materials and methods

(a) Soil:

Kaolin, the most commercially available soil was used for this research work since it is purely cohesive in nature and less permeable. According to the literatures^{8,9} the effectiveness of electrokinetic treatment method is more on silty clays with moderate plasticity such as kaolinite. The soil prop-

erties obtained through laboratory studies are presented in Table 1.

Parameters	Value
Specific gravity of solids	2.60
Maximum dry density (kN/m^3)	15.00
Optimum moisture content (%)	22.50
Moulding moisture content (%)	27.00
Liquid limit (%)	45.00
Plastic limit (%)	25.00
Silt size particle (%)	44.00
Clay size particle (%)	49.00

(b) *Experimental method and setup:*

The experimental programme included series of 1D tests with the reactor in horizontal position. Cylindrical test cells made of PVC, total length 25 cm, inside diameter 7.5 cm was provided to accommodate the compacted contaminated soil sample. Kaolin was spiked with Cr(VI) as contaminant obtained from potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Tap water was used as both catholyte and anolyte. Two sets graphite rod electrodes and circular porous graphite electrodes were inserted at anode and at cathode. During the experiments, for applying a constant voltage to the electrodes a DC power supply system was connected to the electrodes and for monitoring the voltage and for measuring the current flow through the soil sample a multimeter was used. The experimental setup is illustrated in Fig. 1.

pH of soil after the tests were determined using pH meter which was immersed in the beaker containing soil water sus-

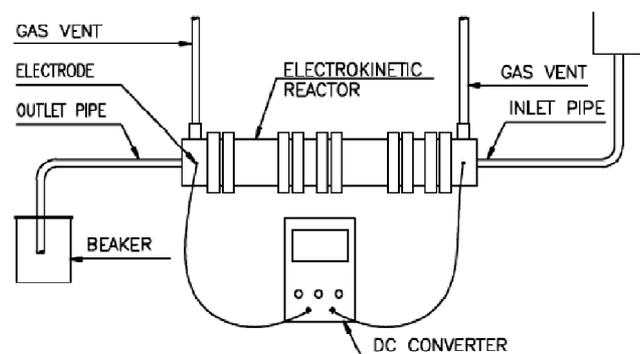


Fig. 1. Schematic diagram of experimental setup.

Table 2. Experimental condition for Cr(VI) removal

Sl. No.	Initial conc. (mg/kg)	Initial water content (%)	Treatment period (h)	Voltage gradient (V/cm)
1.	100	40	50	0.8
2.	100	40	70	0.8
3.	100	40	100	0.8
4.	100	40	120	0.8

pension, and pH value was displayed on the pH meter. Two standard calibration curves were prepared for measuring the effluent concentration and residual Cr(VI) concentration in soil by the spectrophotometric method using diphenylcarbazide (DPC) as described in Article No. 3500-Cr D. Colourimetric method APHA 1987, 15th edition. On adding the DPC reagent to the solution it combines with Cr(VI) to form a complex giving a violet pinkish colour in acidic medium and the absorbance was read at 540 nm in UV-Vis spectrophotometer. Concentration of Cr(VI) was determined directly for effluent and in case of soil sample, it was digested using (0.2 M) H_2SO_4 . Digestion was carried out to lessen the interference of organic matters and to convert metal linked with particulates to a form (the free metal) required to determine its concentration by spectrophotometer. Analysis of Cr(VI) in the samples was done with Double Beam Spectrophotometer 2203 at a wave length of 540 nm.

(c) *Mathematical model for decontamination of chromium(VI) by electrokinetic process:*

The mathematical model is basically a set of partial differential equations (PDEs) with some coefficients acting non-linearly. This section presents the solution technique developed by applying finite difference method (FDM) to solve one dimensional ADE model of contaminant transport. The concentration of chemical species during electrokinetic remediation as a function of time and space has been obtained from the analysis. The unknown quantity of the contaminant transport is the concentration, c_i , which represents the mass of pollutant. The followings are the assumptions made for the transport model:

- (1) Since there was no water level difference of the electrode reservoirs the flux due to hydraulic gradient was not considered;
- (2) The electrical field ($\partial E/\partial x$) is assumed to be constant across the sample;

(3) The soil porosity and hydraulic conductivity are constant in time and space.

These conditions simplified the governing transport model of the contaminant. Diffusion - advection PDEs and algebraic equations describe transport of target chemical species Cr(VI). Application of an electric gradient results in fluid flux. To describe electroosmosis, the fluid flux due to electrical gradient, through fine grained soils the Helmholtz-Smoluchowski theory is usually used. The electroosmotic permeability coefficient k_{eo} ($m^2 V^{-1} s^{-1}$), and hydraulic conductivity in Darcy's law are similar. The electroosmotic flow rate, J_w ($m s^{-1}$), as expressed by^{10,11} is as follows:

$$J_w = -k_{eo} \nabla \phi \tag{1}$$

The value of electroosmotic permeability coefficient k_{eo} is a function of zeta potential, viscosity of fluid, porosity and electrical permeability of soil and given by Mitchell¹⁰ and Eykholt and Daniel¹². Hydraulic conductivity is influenced by the distribution of pore and porosity but electroosmotic permeability coefficient is not dependent on porosity. The value of k_{eo} has been considered to be constant in numerous electrokinetic models¹³⁻¹⁶.

(d) *Solution of contaminant transport model by finite difference method:*

The following steps have been followed while solving ADE using FDM:

- (1) Equations solved numerically using an explicit forward time and centered space (FTCS) scheme.
- (2) Boundary conditions have been selected considering the effect of adsorption.
- (3) Formation of the concentration matrix using computer programming through EXCEL.

Transport of heavy metal under chemical and electrical gradients ignoring the chemical reaction during electrokinetic extraction is described by the following equations (assumed voltage gradient constant throughout the entire test):

$$J_i = -D_i^* \frac{\delta c_i}{\delta x} - c_i (u_i^* + k_{eo}) \frac{\delta \phi}{\delta x}$$

Material balance equation for each species

$$\frac{\delta c_i}{\delta t} = -\nabla J_i + Ri$$

Considering no chemical reactions are implicated in the trans-

port model is expressed as follows¹⁷:

$$\frac{\delta c_i}{\delta t} = D_i^* \frac{\delta^2 c_i}{\delta x^2} - v_i \frac{\delta c_i}{\delta x} \tag{2}$$

where, $v_i = -(\mu_i^* + k_{eo}) \frac{\delta \phi}{\delta x}$

The type of model is single degree and second order equation of parabolic nature. The analytical solution technique to solve this model being more complex, simple FDM has been used in this study. In the present study, Fig. 2 presents a two-dimensional domain discretized as time t and distance x as length of polluted site increasing in the longitudinal direction. Explicit method has been used for formulation. The field is split into regular rectangular grids with k as time step and h as the spatial size in the x -direction longitudinally from the source of the remediation¹⁸.

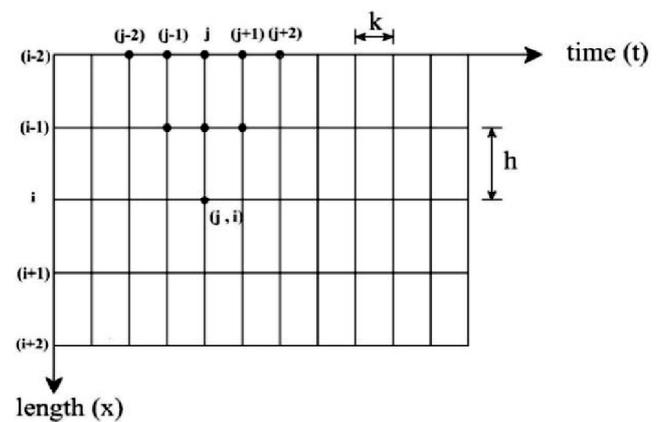


Fig. 2. Discretization of finite difference mesh in 1D decontamination problem.

Here, $x = ih$; and $t = jk$;

where, each of $i, j = 0, 1, 2, 3, \dots$

In the present study, solution of the partial differential equation has been done by using a forward difference scheme for single order derivative of concentration with respect to time, and central difference scheme both for single order derivative of concentration with respect to space and second order derivative of concentration with respect to space for better computation from the point of view of accuracy and stability¹⁹.

Forward approximation

$$\frac{\delta c_i}{\delta t} = \frac{c_i[j+1][i] - c_i[j][i]}{k}$$

Central difference approximation

$$D_i^* \frac{\delta^2 c_i}{\delta x^2} = D_i^* \left\{ \frac{c_i[j][i-1] - 2c_i[j][i] + c_i[j][i+1]}{h^2} \right\}$$

$$v_i \frac{\delta c_i}{\delta x} = v_i \left\{ \frac{c_i[j][i+1] - c_i[j][i-1]}{2h} \right\}$$

$$\frac{c_i[j+1][i] - c_i[j][i]}{k} = D_i^* \left\{ \frac{c_i[j][i-1] - 2c_i[j][i] + c_i[j][i+1]}{h^2} \right\} - v_i \left\{ \frac{c_i[j][i+1] - c_i[j][i-1]}{2h} \right\}$$

$$\begin{aligned} \frac{1}{k} c_i[j+1][i] - \left(\frac{1}{k} - 2 \frac{D_i^*}{h^2} \right) c_i[j][i] \\ - \left(\frac{D_i^*}{h^2} + \frac{v_i}{2h} \right) c_i[j][i-1] \\ - \left(\frac{D_i^*}{h^2} + \frac{v_i}{2h} \right) c_i[j][i+1] = 0 \end{aligned}$$

Fitting parameters X_1, X_2, X_3, X_4

$$\begin{aligned} X_1 c_i[j+1][i] + X_2 c_i[j][i-1] + X_3 c_i[j][i] + \\ X_4 c_i[j][i+1] = 0 \\ c_i[j+1][i] = - \frac{1}{X_1} \{ X_2 c_i[j][i-1] + X_3 c_i[j][i] + \\ X_4 c_i[j][i+1] \} \end{aligned} \quad (3)$$

$$\begin{aligned} c_i[j][i] = - \frac{1}{X_1} \{ X_2 c_i[j-1][i-1] + X_3 c_i[j-1][i] + \\ X_4 c_i[j-1][i+1] \} \end{aligned} \quad (4)$$

Thus, the above mentioned finite difference scheme eq. (4) has been applied for computer program and it presents the concentration of Cr(vi) at different distance from anode at various time, $c[j][i]$ based on 1D contaminant migration

model. X_1, X_2, X_3 and X_4 are four fitting parameters as follows:

$$X_1 = \frac{1}{k} \quad (5)$$

$$X_2 = - \left(\frac{D_i^*}{h^2} + \frac{v_i}{2h} \right) \quad (6)$$

$$X_3 = - \left(\frac{1}{k} - 2 \frac{D_i^*}{h^2} \right) c_i[j][i+1] = 0 \quad (7)$$

$$X_4 = - \left(\frac{D_i^*}{h^2} - \frac{v_i}{2h} \right) \quad (8)$$

The sum of these four fitting parameters in 1D model is zero indicating consideration of non-decaying type of contaminant solute in this study.

(e) *Boundary condition for the FDM model:*

The migration of cations always tends towards cathode because the movement of the electroosmotic flow and ionic migration is in the same direction. In case of anions electroosmotic flow and ionic migration resist each other. The flow of anions depends upon the resultant of the two movements. Experimental data to date indicate that ionic migration is always greater than electroosmosis so the movement of anion should be towards anode. The boundary condition applied for Cr(vi) contaminated kaolinite soil in electrokinetic extraction are

$$J|_{x=0} = C J_w \quad (9)$$

$$J|_{x=L} = 0 \quad (10)$$

where, J is the mass flux of chemical species, x is the distance from anode and L is the length of the sample. Column tests had been performed for the determination of effective diffusion coefficient which is a major input parameter for the ADE modeling purpose. An analytical model was then used to calculate the effective diffusion coefficient using the C/C_0 results. Migration behaviour of Cr(vi) in kaolinite clay has been simulated in the model. The formulation of discretized partial differential equation was followed by solving with numerical method of finite difference and computer programs for its implementation. The computer programs have been developed in EXCEL VBA. Input soil parameters of finite difference model are presented in Table 3.

Table 3. Input soil parameters of finite difference model

No.	Parameter	Value
1.	Length of soil specimen	0.250 m
2.	Number of nodes	61
3.	Time step (<i>k</i>)	1 s
4.	Porosity	0.43
5.	Electroosmotic permeability coefficient	$1.07 \times 10^{-13} \text{ m}^2/\text{V/s}$
6.	Initial concentration of Cr(VI)	100 mg/kg of soil
7.	Electrical potential (V)	20
8.	Effective diffusion coefficient of Cr(VI) (<i>D</i> [*])	$7.59 \times 10^{-9} \text{ m}^2/\text{s}$
9.	Effective ionic mobility of Cr(VI) (<i>u</i> [*])	$-5.88 \times 10^{-7} \text{ m}^2/\text{V/s}$
10.	Duration	50, 70, 100, 120

Results and discussion

One of the important observations in electrokinetic process is the change of pH with in the soil sample. Due to the DC voltage applied between the electrodes, the pH near the anode region decreases due to formation of H⁺ ions and the pH near the cathode region increases due to formation of OH⁻ ions. Fig. 3 represents the pH-distribution across the specimens upon completion of the tests. The initial soil pH was 7.96. As the process persist the pH of pore fluid close to the anode reduces more rapidly and pH of pore fluid near the cathode compartment is considerably higher than the initial pH values. The increase in the pH from the anode to the cathode is a direct consequence of the acid front generation at the anode flushes across the cell.

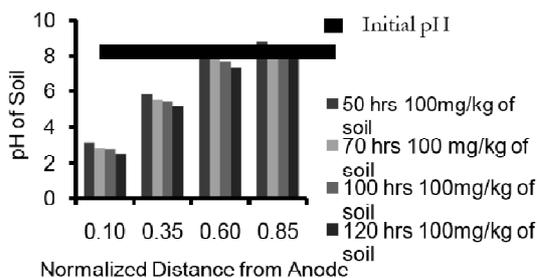


Fig. 3. Variation of pH of soil along the length of sample.

This phenomenon was reported by Acar and Alshawabkeh²⁰ under similar conditions. At lower pH values or acidic environments, Cr(VI) exists as the HCrO₄⁻ ion, while at higher pH values or neutral to alkaline conditions, Cr(VI) exists as the CrO₄²⁻ ion. Griffin *et al.*²¹ reported the distribution of these two Cr(VI) species for different pH and Cr(VI)

concentrations. They also studied the adsorption behaviour of these Cr(VI) species onto soils and reported that the adsorption of HCrO₄⁻ onto soils is significant but the adsorption of CrO₄²⁻ onto soils is negligible. This pH dependence on chromium speciation and the differences in adsorption characteristics of different chromium species explain the different chromium removal rates obtained from the electrokinetic experiments in this study.

From this experimental study it is seen that pH of soil varies with time and normalized distance as well. From the very beginning of the experiment some amount of chromium had been adsorbed, which doesn't take part in the electrokinetic process. Adsorption percentage should be balanced for the sake of accuracy. From previous experimental studies it has been observed that adsorption effect varies with pH of the soil sample²². The variation of adsorption with time has been considered in the boundary values. In the experiment 100 mg/kg concentration of Cr(VI) has been used. For simplification of the mathematical model the variation of pH and adsorption percentage is taken as linear. The variation of pH at anode and cathode as obtained from experiments with time is given in Fig. 4 and the variation of adsorption with time corresponding to the pH value is given in Fig. 5.

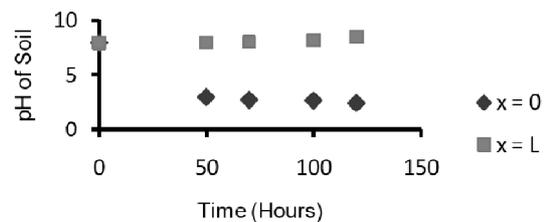


Fig. 4. Variation of pH with time after electrokinetic remediation process (at anode and cathode).

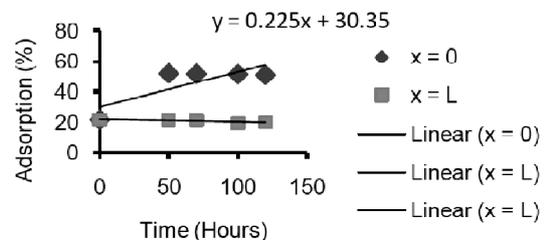


Fig. 5. Variation of adsorption with time after electrokinetic remediation process (at anode and cathode).

From this equation, considering the adsorption effect this can be said that the boundary value at $X = L$ and $X = 0$ (where X is the distance from anode) should change with time. Migration behaviour of Cr(VI) in kaolinite clay has been simulated in the numerical modeling. The experimental and the numerical results have been compared effectively. The results shows good match of experimental and numerical results. It can be seen from the numerical model analysis that efficiency of the electrokinetic extraction is increasing with time although the efficiency for the heavy metal with negative charge is somewhat less with respect to heavy metal with positive charge because of the resultant velocity achieved from the electroosmotic flow and ionic migration. The concentration of Cr(VI) near anode is more than the initial concentration itself, because of the adsorption effect and the pH variation due to electrokinetic extraction method. Certain amount of the contaminant is always present in the soil because the adsorbed percentage of contaminant doesn't take part in the mechanism of the process of removing the contaminant. It is observed that near anode the concentration of Cr(VI) in the soil sample is greater than initial concentration. This phenomenon may be explained from the pH change of the soil sample in different time span. Cr(VI) is present as anion in soil sample and is expected to be accumulated at anode side as observed in all these cases. The final distributions of Cr(VI) concentrations predicted by model simulations are compared with experimental results. Figs. 6-9 show the variation of concentration profile of Cr(VI) in kaolin with distance.

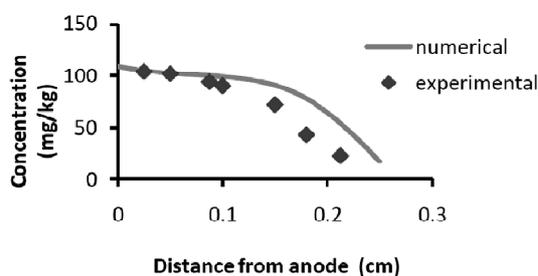


Fig. 6. After 50 h of electrokinetic remediation.

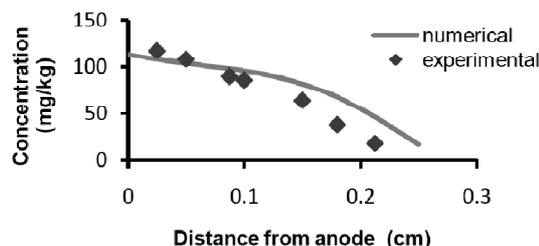


Fig. 7. After 70 h of electrokinetic remediation.

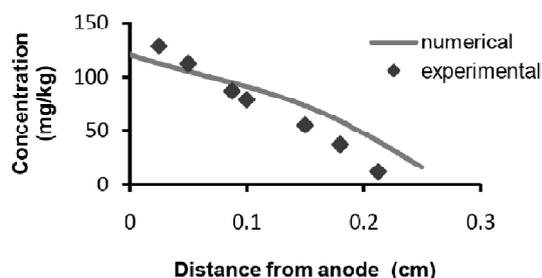


Fig. 8. After 100 h of electrokinetic remediation.

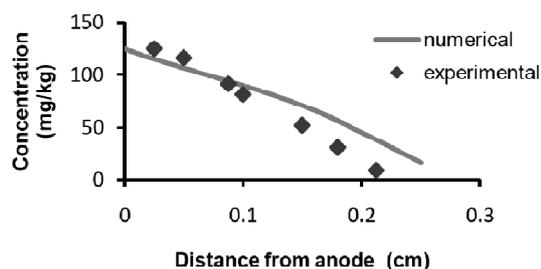


Fig. 9. After 120 h of electrokinetic remediation.

After 50, 70, 100, 120 h processing, both the model predictions and the results obtained from experiments show similar distributions of concentrations of Cr(VI) within the soil mass. A small inconsistency between the model predictions and the experimental results is observed near the cathode. It may be adjusted by proper simulating and fine tuning the soil pH near the cathode in the models.

Conclusion

This paper's focus is to obtain predictive results of concentration of Cr(VI) in soil after electrokinetic remediation, using three variables initial concentration, time of run and

distance from anode. Numerical modeling and experimental study were carried out to simulate Cr(VI) transport in low-permeability kaolinite clay under electrical fields. The model simulations of each test exhibit good forecast of changes in the distribution of concentration of Cr(VI) across the soil bed. The large amount of Cr(VI) was collected and concentrated in the soil portion near the anode. This result means that the unenhanced electrokinetic technology may be considered as the electroaccumulation or electroconcentration process. It can be concluded that the mathematical model has been developed with a simplified solution approach using finite difference method which shows a good conformity with experimental results. The adsorption effect and pH change during the experiment may explain the behaviour of the contaminant concentration near anode and cathode.

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