



Electrically induced reduction of trichloroethene in clay

Song Jin^{a,b,*}, Paul H. Fallgren^c

^a School of Resources and Environment, Hefei University of Technology, Hefei, PR China

^b Department of Civil and Architectural Engineering, University of Wyoming, 1000 University Avenue, Laramie, WY 82071, USA

^c Western Research Institute, 365 North 9th Street, Laramie, WY 82072, USA

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ABSTRACT

Chlorinated compounds such as trichloroethene (TCE) are recalcitrant contaminants commonly detected in soil and groundwater. Contemporary remedies such as electron donor amendment tend to be less or ineffective in treating chlorinated compounds in matrix of lower permeability, such as clay. In this study, electrically induced reduction (EIR) was tested by inserting electrodes in saturated clay containing 122.49–125.43 mg TCE kg⁻¹. Weak electric potentials (E) of 6, 9, and 12 V m⁻¹ were applied, and up to 97% of TCE were depleted during the study period. Corresponding increases in chloride concentrations was observed during TCE depletion, indicating a reductive dechlorination pathway. No migration of TCE was observed between the two electrodes, neither were intermediate compounds such as dichloroethene (DCE) or vinyl chloride (VC). Results were also tested against a mathematical equation we previously established for field applications. Electrically induced reduction may offer a novel method for in situ degradation of chlorinated contaminants, especially in low-permeable media such as clay.

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1. Introduction

In situ remediation of non-aqueous phase liquid (NAPL), especially dense NAPL (DNAPL)-contaminated low-permeable media (LPM), such as clay soils, is one of the major challenges to the industry. Low media permeability (<10⁻⁸ cm²) reduces the effectiveness of most in situ treatments, including air sparging/soil vapor extraction, chemical oxidation, and enhanced bioremediation. Techniques based on electrical current technologies such as electrical resistance heating and electrokinetic remediation are emerging technologies that have been tested and used for treating NAPL-contaminated LPM [1–4]. These technologies involve the placement of two electrodes at each end of a saturated soil matrix to initiate heating or ionic migration and reactions at the electrodes. Depending on the electrical potential applied to the electrodes, electrokinetic processes (up to 46 V m⁻¹) or electrical resistance heating (67 V m⁻¹) can occur in the soils [1,5,6].

Chlorinated solvents such as trichloroethene (TCE) are a common group of DNAPL contaminants that tend to accumulate in subsurface soils, groundwater, and sediments. Due to the elevated oxidizing status, reductive reactions are usually applied in treating chlorinated solvents. Reductive dechlorination mediated by electron donor amendments and microbial enhancements

or zero-valent iron have been applied in situ for porous (i.e., high permeability) media; however, these treatments are less effective in LPM. Electrokinetic remediation of chlorinated solvent-contaminated LPM have been studied in both laboratory bench- and field-scale tests where electric fields induced migration of contaminants through the treatment zones or to the electrodes where direct “electroreduction” occurs [1,3,5]. Electrokinetic treatments were demonstrated to be effective in reducing chlorinated solvent in soil; however, electrokinetic treatment tends to be energy intensive, and the deployment of elevated electrical potential may expose safety hazard and heat loss [7].

Electrochemically induced oxidation–reduction (redox) reactions (i.e., electrically induced reduction or “EIR”) are another electrical method used in remediation. It involves feeding an electrical current through electrodes, creating favorable conditions for redox reactions to occur in the medium between the electrodes. Van Cauwenberghe [8] performed a field test to immobilize inorganic contaminants and reduce organic contaminant concentrations in soils. Unlike electrokinetic processes, EIR does not rely on the migration of contaminants toward the electrodes. In addition, the applied electric potential (E) is substantially lower than those used in electrokinetic process. For example, $E < 35$ V m⁻¹ was used in studies by Ho et al., Rahner et al., and Rohrs et al. [1,9,10]; and $E < 12$ V m⁻¹ was applied in Jin et al. [11]. The EIR occurs when a low voltage and amperage field is imposed in a conductive matrix between the two electrodes. The induced electric field is created with soil particles acting as capacitors and discharging and recharging electricity. Fig. 1 illustrates the capacitor structure of a soil particle, where redox reaction zones are created and interface on

* Corresponding author at: Department of Civil and Architectural Engineering, University of Wyoming, 1000 University Avenue, Laramie, WY 82071, USA. Tel.: +1 970 212 2766; fax: +1 970 377 9406.

E-mail address: sjin@uwyo.edu (S. Jin).

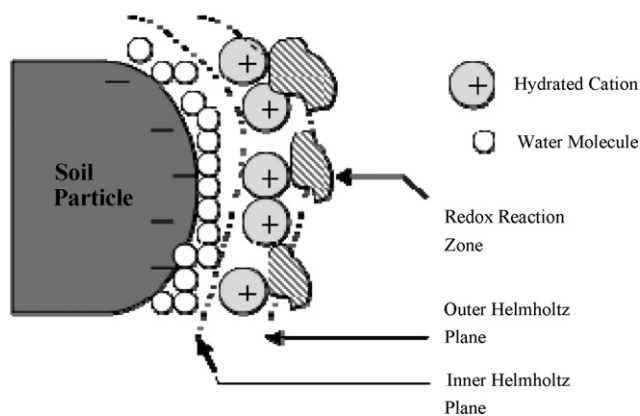


Fig. 1. Capacitor structure of a soil particle within a low voltage and low amperage DC field (modified from Doering et al. [18]).

the outer Helmholtz plane. The hygroscopic water in the inner Helmholtz plane serves as a dielectric and the hydrated cations interface with the redox reaction zones. The redox reactions are possibly due to electrolysis of water where



reaction (1) occurs at the anode and reaction (2) occurs at the cathode. Both reactions can also occur at the soil particle–water interface where the induced redox reaction results in the transformation of contaminants.

To date, the few studies of EIR in treating chlorinated organic contaminants were all performed in water or other porous media such as saturated sand [10–12]. In this study, we investigated EIR in degrading TCE in low-permeability clay. We hypothesized that higher surface area in clay can create more redox reaction zones (see Fig. 1), therefore favor the reductive dechlorination of TCE. Additionally, saturated clay soils typically consist of iron, magnesium, titanium, and other constituents in aqueous phase that may catalyze and enhance the redox reactions such as EIR [2,9,12]. Based on preceded results, DC is the preferred source than AC power for EIR. We used graphite electrodes and weak DC voltage ($E < 12 \text{ V m}^{-1}$) to create an induced reductive zone throughout the saturated clay matrix for TCE degradation. Parameters that are key for field applications of EIR, such as electrode spacing, were also investigated.

2. Materials and methods

2.1. Clay characterization

A clay (fat clay) soil provided by Durham Geo (Stone Mountain, Georgia, USA) was used for this study. Clay specific conductance and pH were measured from a saturated paste extract using EC and pH electrodes and meters, respectively [13,14]. Soluble components of the saturated paste extract were measured by inductively coupled plasma-mass spectrometry for cations and metals, and ion chromatography (Dionex DX-100 ion chromatograph equipped with a 4 mm × 250 mm IonPac AS14 anion exchange column; Sunnyvale, California, USA) for anions. A 1:1.25 soil weight to water volume ratio was used to extract available phosphorus from the soil, and the extract was analyzed by using an ion chromatography [15]. Particle size analysis was conducted to confirm the clay soil texture by following the hydrometer procedure as described by Gee and Bauder [16].

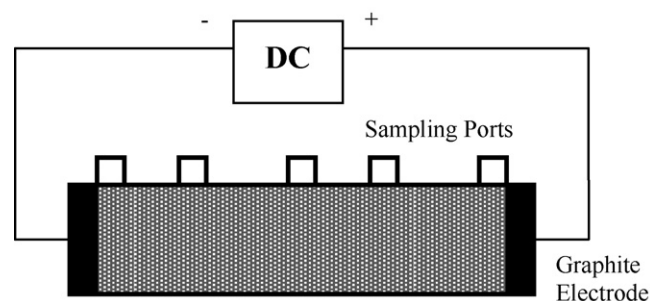


Fig. 2. Column test diagram for the EIR of TCE in saturated clay.

2.2. Direct current column reactors study

Two sets of columns (internal diameter 9 cm) with lengths of 20, 50, 100, and 150 cm were constructed and positioned horizontally. Electrodes were installed at each end (Fig. 2) of the columns. The electrodes were made from graphite and connected to an AC–DC transformer with adjustable DC voltage outputs of 6, 9, and 12 V. Graphite electrodes were used due to its high efficiency in reduction of TCE in water [11]. Also, graphite electrodes do not corrode like stainless steel as observed by Rohrs et al. [10]. The clay soil was saturated with RO water containing TCE to reach a target concentration of approximately 100–120 mg kg⁻¹. Each column was filled with the saturated clay and sealed. One set of columns were connected to the DC source set at 6 V, and the other set of columns were not connected to serve as the control. The columns were sampled by using syringes from each sampling port. Trichloroethene samples were extracted by using *n*-hexane and analyzed by using an Agilent 6890 gas chromatograph with an electron capture detector (GC-ECD; Santa Clara, California). Helium was used as carrier gas, the detector, injector, and final oven temperatures were 250, 250, and 100 °C, respectively. Samples were analyzed individually to rule out potential migration or degradative gradient through the column. Detected value from a composite sample was reported. Electrical potential and current across the column were measured by a multimeter. Chloride and pH were monitored throughout the experiments. Sampling/monitoring events were performed at 0, 1, 3, and 7 d. Experimental runs using the DC source set at 9 and 12 V were performed by using the same procedure described above.

3. Results and discussion

3.1. Clay characterization

Particle size analysis confirmed the clay in texture of the soil used for this study (Table 1). Permeability of the clay was low ($6.6 \times 10^{-12} \text{ cm}^2$) but within range (10^{-9} to 10^{-15} cm^2) of typical clays [17]. An elevated concentration of iron (14.175 mg/kg) was observed, indicating that redox reactions in the clay may occur at a relatively high rate. The mean resistance of the clay saturated with water was measured to be 1.41 kΩ.

3.2. Clay column tests

Reductive dechlorination was reported as the primary pathway in electrically mediated remediation of chlorinated compounds [1,5,10,11]. Reductive dechlorination of TCE in an electrical field tends to go through the beta elimination pathway, in which TCE is reduced by the electrons and chloride is released. No intermediates accumulate during the reaction, though acetylene was detected and later degraded [1,5,10]. Therefore, anodic conditions as given by Eq. (1) may favor reductive dechlorination. In our column tests, sampling across the column length showed no migration of TCE

Table 1
Baseline parameters of clay soil.

Parameter	Measured value	Unit
pH	6.80	
Specific conductance	1.19	mS/cm
Bulk density	1.32	g/cm
Permeability	6.6×10^{-12}	cm
% Sand	0.0	
% Silt	0.0	
% Clay	100.0	
USDA textural classification	Clay	
Chemical oxygen demand	38.325	mg/kg
Total organic carbon	3.916	mg/kg
Chloride	31.2	mg/kg
Fluoride	<0.095	mg/kg
Nitrate	6.15	mg/kg
Phosphate	<0.095	mg/kg
Sulfate	30.0	mg/kg
Sodium	153.7	mg/kg
Magnesium	43.1	mg/kg
Potassium	1.163	mg/kg
Calcium	5.001	mg/kg
Iron	14.157	mg/kg
Manganese	488	mg/kg
Aluminum	7.631	mg/kg
Cadmium	<0.005	mg/kg
Chromium	11.40	mg/kg
Cobalt	6.10	mg/kg
Copper	12.3	mg/kg
Nickel	12.3	mg/kg
Zinc	36.9	mg/kg

between the electrodes; suggesting that EIR may be the dominant mechanism for TCE degradation when voltages were applied at 6–12 V.

A number of challenges are foreseen for the field application of EIR in remediating chlorinated contaminants. For example, optimal electrical potential is associated with electrode spacing, applied voltages, matrix resistance, and other factors. Initiating EIR without causing other electrochemical processes such as electrophoresis, electrokinetic ion migration or resistance heating is important to achieve a cost-effective remedial design. Based on data from the preceded studies [11], we developed the following equation to determine the proper electrical potential:

$$U = \varepsilon R x C t^{-1} \quad (3)$$

where U is the applied potential (V), ε the empirical constant ($\text{mA d kg mg}^{-1} \text{m}^{-1}$), R the resistance of the saturated matrix ($\text{k}\Omega$), x the distance between electrodes (m), C the concentration of TCE (mg kg^{-1}), t is the time for complete dechlorination of TCE (d).

The column tests provided an approach to determine ε using Eq. (3) by controlling U and x , fixing C , and determining t , while the R value was system specific and measurable.

When an electric field (E) of 6 V m^{-1} was applied to saturated clay columns of lengths 20, 50, 100, and 150 cm for 7 d. The concentration fraction of TCE ($[\text{TCE}] / [\text{TCE}]_0$; $[\text{TCE}]_0 = 125.43 \text{ mg kg}^{-1}$) in the 20-cm column decreased to 0.05 (from 125.43 to 6.27 mg kg^{-1}), while a decrease of 0.30 was observed in the 50-cm column (from 125.43 to 87.80 mg kg^{-1}) (Fig. 3a). Slight decrease in TCE concentration was observed in the 100-cm column; however, the concentration fraction decreased by 0.17 more in the 150-cm column than that in the 100-cm column, probably due to adsorption by soil particles when the electrical field applied was negligible. Increased chloride concentrations in the 150-cm columns also confirms that more TCE was being reduced than in the 100-cm (Fig. 3b), while the highest chloride concentration in the 20-cm column corresponded with the highest rate of TCE reduction occurred within that electrode separation. The chloride concentrations in the unconnected columns did not increase (ranging from 9.08 to 10.13 mg L^{-1}). No daughter products, such as dichloroethenes

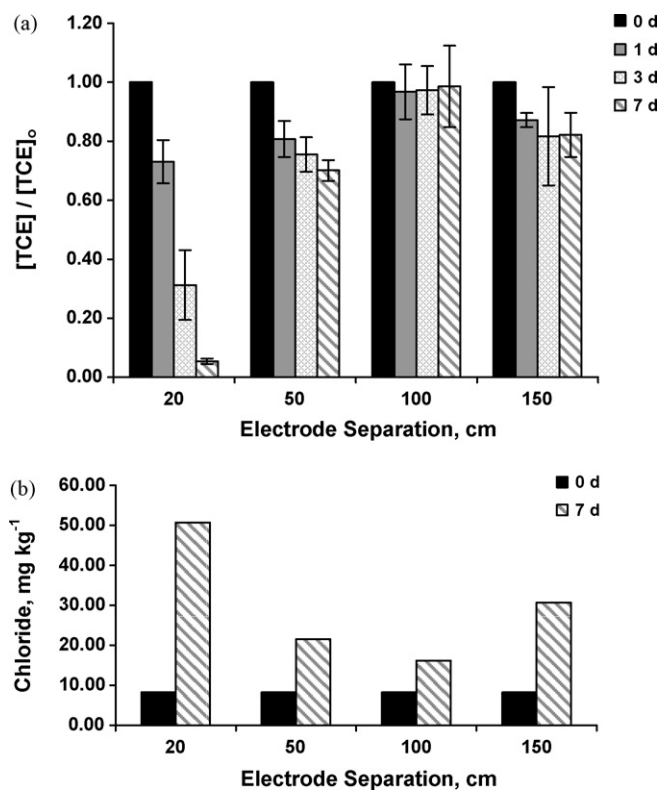


Fig. 3. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 6 V m^{-1} . The initial concentration of TCE ($[\text{TCE}]_0$) was $125.43 \text{ mg kg}^{-1}$. Error bars indicate standard deviation of replicate sampling (3–5 replicates).

(DCEs) and vinyl chloride (VC) were detected throughout the tests. Due to possible movement of the highly mobile chloride ions in the electrical field formed during the EIR, a stoichiometric balance of chloride versus TCE reduction is difficult to establish. However, the relative amount of chloride remaining in the clay qualitatively correlates to the level of TCE reduction in different columns, as shown in Fig. 3.

The concentration fraction of TCE ($[\text{TCE}]_0 = 122.77 \text{ mg kg}^{-1}$) in the 20-cm column decreased to 0.03 (from 122.77 to 3.68 mg kg^{-1}) within 7 d when an E of 9 V m^{-1} was applied to the saturated clay (Fig. 4a). The concentration fraction of TCE in the 50-cm columns decreased to 0.16, which is substantially less than what was observed when an E of 6 V m^{-1} was applied to the saturated clay. The increase in TCE dechlorination correlated with increases in chloride concentration (Fig. 4b). The $[\text{TCE}] / [\text{TCE}]_0$ for the 100 and 150-cm columns decreased by less than 0.30, indicating such electrode spacing lowers reactivity at an E of 9 V m^{-1} . Chloride concentrations in the unconnected columns were between 8.91 and 9.38 mg L^{-1} , indicating little, if any, reductive dechlorination without an E applied to the clay. The concentration fraction of TCE ($[\text{TCE}]_0 = 122.49 \text{ mg kg}^{-1}$) in the 20-cm and 50-cm columns decreased to 0.05 and 0.32, respectively, within 7 d when an E of 12 V m^{-1} was applied to the saturated clay (Fig. 5a). The concentration fraction of TCE in the 100-cm columns decreased to 0.49, but this E appeared to have little effect on TCE in the 150-cm column. The increase in TCE dechlorination in the 100-cm column correlated with increases in chloride concentration, as shown in Fig. 5b. The results demonstrate a proportional relationship between the effective electrode spacing and the E applied. We presumed that increasing E may expand the reaction zones. This was supported by the decreased pH (see Table 2) in the column, which reflects the release of H^+ resulting from the reductive dechlorination. The

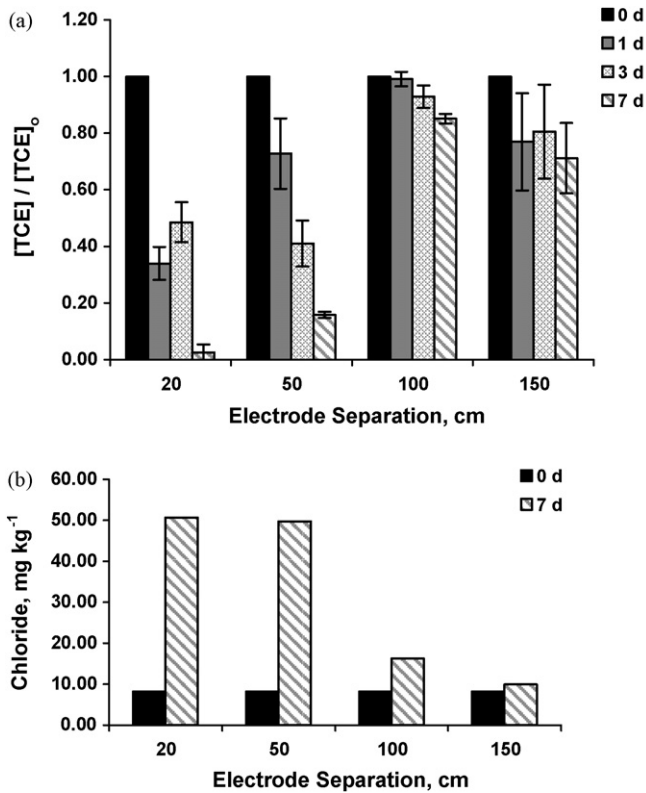


Fig. 4. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 9 V m^{-1} . The initial concentration of TCE ($[\text{TCE}]_0$) was 122.77 mg kg^{-1} . Error bars indicate standard deviation of replicate sampling (3–5 replicates).

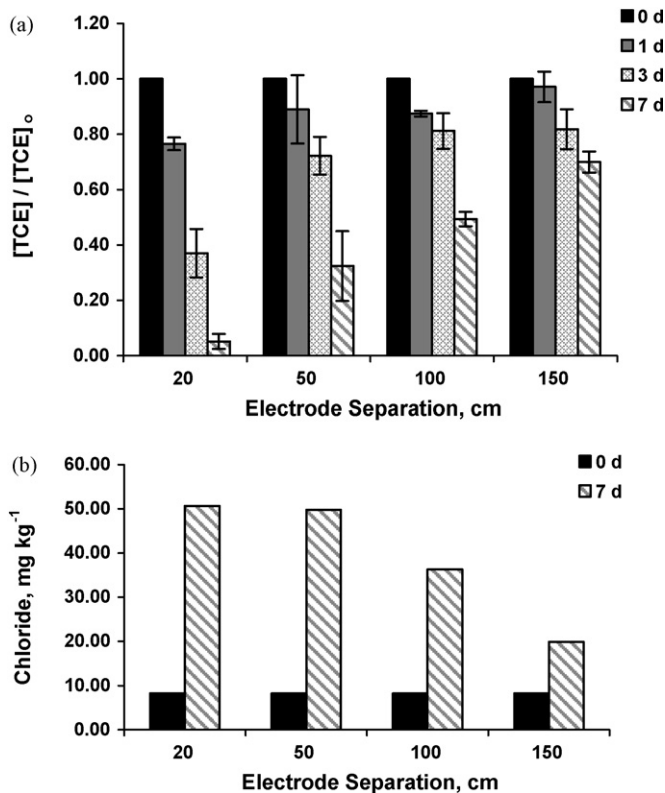


Fig. 5. Normalized TCE concentration fractions (a) and chloride concentrations (b) in saturated clay within an electric field of 12 V m^{-1} . The initial concentration of TCE ($[\text{TCE}]_0$) was 122.49 mg kg^{-1} . Error bars indicate standard deviation of replicate sampling (3–5 replicates).

Table 2

Final pH of saturated clay in electrically connected columns.

Electrode separation, cm	Applied potential, V	pH
20	6.0	7.03
	9.0	6.59
	12.0	6.54
50	6.0	8.09
	9.0	6.62
	12.0	6.31
100	6.0	7.65
	9.0	6.68
	12.0	6.63
150	6.0	7.30
	9.0	7.10
	12.0	6.13

observed un-correlation between TCE depletion and the voltage potentials (e.g., TCE depletion in 20-cm columns under 6, 9 and 12 V m^{-1}) suggests that there might be an optimal voltage that can be applied to achieve the maximal efficiency.

The mean empirical constant ε for Eq. (3) was determined to be $1.43\text{ mA d kg mg}^{-1}\text{ m}^{-1}$ (standard error = 0.19) from the presented results. This empirical constant could be used to determine the maximum electrode spacing x for an array in the field or the U that needs to be applied to the array of electrodes. The amount of energy input for EIR by using a low E ($<12\text{ V m}^{-1}$), as deployed in this study is substantially smaller when compared to other electrically mediated remediation. Conventional or alternative sources of DC power can be used for the field applications of this technique. Sustainable energy sources such as solar or wind can provide a continuous E in the contaminated matrix. Overall, the results from this study indicate that EIR may offer a viable alternative for degrading TCE and other halogenated contaminants in matrices of low-permeability.

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