



Electrochemical degradation of trichloroethylene in aqueous solution by bipolar graphite electrodes



Ljiljana Rajic, Roya Nazari, Noushin Fallahpour, Akram N. Alshwabkeh*

Civil and Environmental Engineering Department, Northeastern University, Boston, MA 02115, USA

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ABSTRACT

In this study, we tested the use of the bipolar electrodes to enhance electrochemical degradation of trichloroethylene (TCE) in an undivided, flow-through electrochemical reactor. The bipolar electrode forms when an electrically conductive material polarizes between feeder electrodes that are connected to a direct current source and, therefore, creates an additional anode/cathode pair in the system. We hypothesize that bipolar electrodes will generate additional oxidation/reduction zones to enhance TCE degradation. The graphite cathode followed by graphite anode sequence was operated without a bipolar electrode as well as with one and two bipolar graphite electrodes. The system without bipolar electrodes degraded 29% of TCE while the system with one and two bipolar electrodes degraded 38% and 66% of TCE, respectively. It was found that the removal mechanism for TCE in bipolar mode includes hydrodechlorination at the feeder cathode, and oxidation induced by peroxide. The results show that the bipolar electrodes presence enhance TCE removal efficiency and rate and imply that they can be used to improve electrochemical treatment of contaminated groundwater.

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1. Introduction

Trichloroethylene (TCE) was first detected in groundwater in 1977 and has been one of the most frequently detected priority contaminants in groundwater at hazardous waste sites in the United States [1]. The primary sources that release TCE into the environment are metal cleaning and degreasing operations. At many TCE spill sites, residual amounts of TCE persist in a pure liquid phase (commonly referred to as dense, non-aqueous-phase liquids, DNAPLs) within pore spaces or fractures. The dissolution of residual TCE results in a contaminated plume of groundwater (USEPA 2007). Because of potential carcinogenic and mutagenic effects [2], the Maximum Contaminant Levels (MCLs) for TCE in drinking water is set to $5 \mu\text{g L}^{-1}$. In addition, vapor intrusion into building has been a growing concern in recent years at sites with TCE contamination in soil or groundwater.

Methods to remove TCE and other chlorinated organic chemicals (COCs) from groundwater include microbial degradation [3–5], photochemical oxidation [6,7], sonochemical processes [8,9], chemical reduction via zero-valent iron [10–13] and palladium-based materials [14–16], and a combination of UV with

ozone, hydrogen peroxide, Fenton's reagent, or oxalate-complexes [17–21].

Electrochemical treatment has a significant advantage over other treatments since the electrochemical processes can be controlled in order to generate reducing and/or oxidizing conditions to transform contaminants [16,22–31]. Reduction via hydrodechlorination (HDC) is favorable degradation path for TCE from groundwater [23,25,26,32–34]. HDC occurs via a reaction of chlorinate substance with atomic hydrogen that forms at the cathodes and is the main reduction mechanism at hydrogen formation potentials. Additionally, electrochemical oxidation of COCs can be achieved directly at the anode (e.g., boron doped diamond electrodes) [35] or via electrochemically formed hydroxyl radicals and other reactive oxygen species in bulk [29,30,36,37].

The sequential oxidation and reduction processes can be utilized for the transformation of COCs and lead to the creation of less toxic by-products [27,34,38]. Authors previously reported that shifts between oxidation and reduction, via electrode polarity reversal, improve TCE removal [39]. However, due to the highly oxidized nature of TCE, inducing HDC as a primary mechanism is valuable and can be supported by placing the cathode upstream of the anode [40].

Multiple reaction zones in the undivided electrochemical cells can be also achieved by the bipolar electrode mode [41]. Bipolar electrolysis is an efficient approach for electrolytes of low electrical conductivity such as groundwater, and it is extensively used for the

* Corresponding author.

E-mail address: aalsha@coe.neu.edu (A.N. Alshwabkeh).

electrocoagulation/flotation applications. The bipolar mode consists of two feed electrodes at both ends that are connected to a power source and other electrodes without connections that are placed between. Due to the potential difference between the electrolyte and the electrode, one side of bipolar electrodes becomes anodic, and cathodic polarity generates on the other. Besides iron or aluminum plates, which produce reducing conditions, bipolar electrodes can consist of zero-valent iron (as packed between feed electrodes) [41,42]. Also, granular graphite packed-bed bipolar electrodes can be used in order to generate oxidizing conditions [43,44]. These packed-bed flow-through reactors are efficient due to high active area but corrosion and clogging cause the need for continuous reactor maintenance.

Graphite bipolar electrodes would be the best choice for groundwater treatment since they are not costly and are environmentally friendly (made of non-hazardous materials). However, graphite electrodes are moderately efficient towards both reduction [45] and oxidation [46] when used in monopolar mode. The slow HDC on graphite cathodes is caused by the slow evolution of atomic hydrogen that reacts with the chlorinated chemical. The graphite anodes have limited activity and are defined as modified active anodes; the oxygen atom to be transferred to an oxidizable substrate first becomes bonded to the previously functionalized anode surface.

Here, we evaluated the use of bipolar plate graphite electrodes to remove TCE from synthetic groundwater. We used a cathode followed by an anode arrangement in an undivided electrochemical cell as novel approach of utilizing graphite material to generate reaction zones for TCE degradation in aqueous solution. We tested the influence of the number of the bipolar electrodes, current intensity and initial TCE concentration on degradation rate.

2. Materials and methods

All chemicals used in this study were analytical grade. TCE (99.5%) and *cis*-dichloroethylene (*cis*-DCE, 97%) were purchased from Sigma–Aldrich. H_2O_2 (30%) was purchased from Fisher Sci. Calcium sulfate was purchased from JT Baker, oxalic acid (anhydrous, 98%) from Acros Organics, sodium chloride, sodium acetate and sodium bicarbonate from Fisher Scientific. Graphite electrodes with dimensions of 3.6 cm diameter by 5 mm thickness were used as electrode materials in all experiments. Deionized water (18.2 M Ω cm) obtained from a Millipore Milli-Q system was used in all the experiments.

TCE concentration was measured by a 1200 Infinity Series HPLC (Agilent) equipped with a 1260 DAD detector and a Thermo ODS Hypersil C18 column (4.6 \times 50 mm). The mobile phase was a mixture of acetonitrile and water (60:40, v/v) at 1 mL min⁻¹. 2 mL samples were collected from the sampling ports for analysis.

Analyses of chloride ions were performed using an ion chromatography (IC) instrument (Dionex 5000) equipped with an AS20 analytical column. A KOH solution (35 mM) was used as a mobile phase at a flow rate of 1.0 mL min⁻¹. pH and oxidation–reduction potential (ORP) of the electrolyte were measured by pH meter and ORP meter with corresponding microprobes (Micro-electro, USA). The microprobes allow the measurement on these parameters using a small amount of liquid (\approx 0.2 mL). The amount of H_2O_2 produced during the treatment with bipolar electrodes was analyzed at 405 nm after coloration with $TiSO_4$. The measurement was performed at UV–vis Spectrophotometer (Shimadzu UV1800). The electrochemical reactor with electrode and sampling port locations are shown in Fig. 1.

Synthetic groundwater was prepared by dissolving 413 mg L⁻¹ sodium bicarbonate and 172 mg L⁻¹ calcium sulfate in deionized water. The concentrations of bicarbonate ions and calcium ions are representative of groundwater from limestone aquifers, resulting

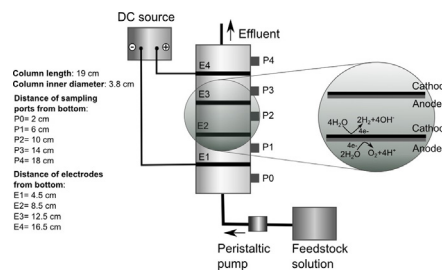


Fig. 1. A schematic of the electrochemical flow-through reactor, the polarization of the bipolar electrodes and example of the reactions occurring at the electrodes. E1 and E4 are feeder electrodes; E2 and E3 are bipolar electrodes (if used); P0, P1, P2, P3 and P4 are sampling ports.

in electrical conductivity of 800–920 μ S cm⁻¹. Excess TCE was dissolved into 18.2 M Ω cm high-purity water to form a TCE saturated solution (1.07 mg mL⁻¹ at 20 °C), which was used as stock solution for preparing aqueous TCE solutions. The feedstock solution was stored in a common Tedlar[®] bag. The headspace in the bag was minimized to limit TCE losses to the gas phase. The initial pH of the contaminated synthetic groundwater was 8 ± 0.3 , and the initial ORP value was 210 ± 5 mV. The temperature was kept constant at 20 °C. Darcy's velocities were selected as 0.25 cm min⁻¹ (3 mL min⁻¹). A constant flow velocity was maintained by a peristaltic pump (Cole Parmer, Masterflex C/L). A constant current intensity during treatments was applied by an Agilent E3612A DC power supply. The experiments conditions are given in Table 1. All experiments were conducted for 180 min, and electrolysis steady state conditions were assumed when change in concentration was less 0.5% per minute which accounts for other TCE losses, such as adsorption or volatilization.

TCE removal was calculated by the following equation:

$$\% \text{removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial TCE concentration (mg L⁻¹) and C_t is TCE concentration at a defined time during treatment (mg L⁻¹). The current efficiency (CE) was calculated according to Faraday's law.

It is important to be able to predict the rate at which contaminants are removed in order to design the full scale application of the technology. The removal kinetic with bipolar mode found to be pseudo-second order (PSO), which is described by Eq. (2) [47,48]:

$$\frac{t}{c_t} = \frac{1}{c_s} t + \frac{1}{k c_s^2} \quad (2)$$

where t is time (min), c_s is the concentration at steady state (mg L⁻¹) and k is PSO coefficient (L min⁻¹ mg⁻¹). Plot of t/c_t against t should give a linear relationship; to confirm the suggested kinetic model, the PSO yields were compared with pseudo-first order (PFO) coefficients.

3. Results and discussion

The influence of the number of bipolar electrodes on TCE removal rate is shown in Fig. 2a. The overall TCE removal achieved by monopolar mode was 29% while by bipolar mode with one and two electrodes removal was 38% and 66%, respectively. Results indicate that TCE concentration decay during treatment is affected by the presence of bipolar electrodes. Fig. 2b shows the removal kinetics described by the PSO. The correlation coefficients for the PFO kinetic model are low ($R^2 < 0.90$) while there is a good correlation coefficient for the PSO kinetic ($R^2 > 0.98$). PSO coefficients achieved by monopolar mode, bipolar mode with

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