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Electrochemically enhanced reduction of trichloroethene by passivated zero-valent iron

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ABSTRACT

Zero-valent iron (ZVI) is commonly used for the *in situ* remediation of groundwater aquifers contaminated with trichloroethylene (TCE); however, ZVI is susceptible to passivation over time, which can significantly reduce its treatment efficiency. Recent studies have suggested that electrically-induced reduction (EIR) or "E-Redox" technology, which applies a low-level direct current (DC), can restore the reactivity of passivated ZVI *in situ*. In this study, a continuous-flow column reactor was used to assess the effects of low-voltage DC on the abiotic reduction of TCE in groundwater and on the performance of passivated ZVI. In experiments with partially passivated ZVI, the application of DC increased the rate and the extent of TCE reduction; both were correlated with the level of applied voltage (0–12 V). The results provide evidence that EIR may partially recover the reduction potential of passivated ZVI and shows promise as a technique to extend the longevity of zero-valent iron. Several mechanisms, including the reduction of ferric iron minerals to ferrous iron at the ZVI surface, likely results in the enhanced TCE reduction.

1. Introduction

Permeable reactive barriers (PRBs) are commonly used to remove contaminants from groundwater by intercepting a plume as it flows through a trench or wall containing reactive materials, resulting in contaminant immobilization, degradation, and/or transformation [1–4]. Zero-valent iron (Fe^0 or ZVI) is the most common reactive medium used in PRBs to treat groundwaters contaminated with halogenated aliphatic hydrocarbons such as trichloroethene (TCE) [1,5,6]. The predominant mechanism by which TCE is abiotically reduced to ethane by ZVI is the ß-elimination pathway [7] as shown in Eq. (1). Unlike microbially catalyzed reductive dechlorination, toxic daughter products like dichloroethenes and vinyl chloride are not generated during β-elimination.

$$4Fe^0 + C_2HCl_3 + 5H^+ \rightarrow 4Fe^{2+} + C_2H_6 + 3Cl^- \quad (1)$$

Despite the successful use of ZVI for remediation of TCE-contaminated groundwater, several factors may negatively impact the performance of ZVI, including high dissolved oxygen levels [2,8], pH [9], the presence of nitrate [3,10,11], the accumulation of metabolic daughter products like cis-1,2-dichloroethene and vinyl chloride [12,13] through non- ß-elimination reactions, and the formation of biofilms [14,15]. These factors may support reactions that produce various iron oxides and carbonate mineral deposits on the ZVI surface [9,16–20], impeding electron transfer to TCE thereby impeding TCE reduction, resulting in ZVI passivation [8,21]. Passivation of ZVI decreases the longevity of ZVI-based remediation technologies, which can substantially increase the cost of remediation, especially in cases where PRBs are used. The prevention and restoration of passivated ZVI continues to be critical challenges for improving the longevity and sustainability of PRBs [22–25].

Different electrochemical remediation technologies (*e.g.*, electrical thermal and electrokinetic remediation) that utilize different ranges of electrical potentials or current have been developed for use in *in situ* remediation [26–28]. Recent development applies a low potential gradient electric field between at least two sets of electrodes through an environmental matrix to induce redox reactions without electromigration or electroosmosis. Within an electric field, soil or sediment particles may act as “micro-conductors”, where soil redox reactions and their triggered contaminant destruction occur at interfaces between soil particles

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and pore water [29]. So named "electrically-induced reduction (EIR)" technology has been reported to be successfully applicable for inducing TCE reduction in soil and groundwater [30,31]. Another application of EIR is the reversal of ZVI passivation [32,33]. Chen et al. [33] first demonstrated that TCE reduction was partially restored for passivated ZVI; however, their experiments were conducted in static column reactors, without recharge of TCE as would be expected in the field environment where there is groundwater flow. The present study was conducted to determine the effects of EIR on restoring TCE-reducing performance of passivated ZVI under constant water flow and continuous and constant input of TCE to better resemble natural conditions.

2. Materials and methods

2.1. TCE-contaminated artificial groundwater preparation

Chloride-free artificial groundwater composed of 59.0 mg $NaHCO_3$/L and 6.90 mg K_2CO_3/L (Sigma–Aldrich, St. Louis, MO, USA) was prepared using deionized, water. The artificial groundwater [33] was degassed by vacuum until there were no air bubbles released from solution, and then transferred to a 5-L Tedlar gas sampling bag (SKC Inc., Eighty Four, PA, USA). To achieve consistent aqueous concentrations of TCE in all experiments, a TCE stock solution was prepared by adding 100 mL TCE to 3.7 L degassed deionized water. After stirring at room temperature for three months, it was assumed that the solution at the top of the reservoir was saturated with TCE ($\sim$1.070 g/L). Appropriate aliquots of the TCE stock solution were removed and transferred via syringe to the 5 L Tedlar bag that contained a known volume of degassed artificial groundwater. Replicate samples were collected from the Tedlar bag at the start of each experiment to determine the influent concentration of TCE. The artificial groundwater conductivity was measured at 75 μS/cm.

2.2. Preparation of Ottawa sand and zero-valent iron mixture

For experiments with sand only, dry sand (Ottawa Sand, EMD Millipore, Billerica, MA, USA) was added to the glass column reactor. For passivated ZVI experiments, ZVI filings (HCA 150-100 mesh; Hepure Technologies Inc., Wilmington, DE, USA), which had been passivated with compressed air at room temperature for three months, were mixed with sand at a ZVI:sand mass ratio of 1:5.

2.3. Glass column reactor

A flow-through glass column reactor (35 cm × 5 cm) was fabricated and used in all experiments. The inlet was located at approximately 1 cm from the bottom of the column where the artificial groundwater entered. There were five threaded ports (Ace Glass, Inc., Vineland, NJ, USA); two ports were used for installation of the cathode and anode. The cathode was located 9 cm from the inlet, and the anode was located 31 cm from the inlet. The two electrodes were constructed from stainless steel sheets (3.5 mm thickness) and were connected to insulated copper wire. The other threaded ports served as sampling ports and were installed between the cathode and anode at a distance of about 10 cm from one another. The lowest sampling port was 9.6 cm from the inlet, the middle port was 19.8 cm from the inlet, and the top port, which served as the effluent for TCE measurements, was located 30 cm from the inlet. All ports were sealed with Teflon® septa and nylon bushings (Ace Glass, Inc., Vineland, NJ, USA).

The glass column was closed with a polytetrafluoroethylene (PTFE; aka Teflon®) cap. There was a hole drilled in the top of the cap to accommodate a Luer-Lok™ fitting and a five-foot long stainless steel tube, at the end of which was a piece of Viton™ tubing to facilitate effluent sampling and waste collection.

A peristaltic pump (Cole-Parmer 73160-20, Vernon Hills, IL, USA) was used to transfer the TCE-amended groundwater from the Tedlar bag to the glass column reactor. All tubing used in the experimental setup was composed of Viton or PTFE. In addition, all couplings that linked segments of Viton tubing were made of polyvinylidene fluoride (PVDF), which is chemically compatible with TCE. An alternating current-to-direct current adapter (AC to DC) with multiple-voltage settings (RadioShack, Fort Worth, TX, USA) was used as the external electrical source.

2.4. Sampling protocol and flow rates

In all experiments, the artificial groundwater was amended with approximately 10 mg/L TCE. For quantitative analysis of TCE, triplicate samples were removed from the three sampling ports of the glass column reactor at each sampling interval by a gastight syringe (Hamilton Model 1750, Hamilton Co., Reno, NV, USA). Replicate samples were also collected from the Tedlar bag at the start of each experiment to determine the influent concentration of TCE. The flow rate of the peristaltic pump was set at 0.55 mL/min, which resulted in a hydraulic retention time in the column reactor of about 12 h; replicate chloride tracer tests confirmed this time. The first samples for analysis from each experiment were collected only after the column had been saturated with the TCE-amended artificial groundwater for at least 24 h. Each set of experiments was conducted in the following order: no direct current application (0 V) followed by 3, 6, and12 V.

2.5. Analytical methods

Gas chromatography–mass spectrometry (GC-MSD) was employed to quantify TCE concentrations in all experiments using the method described by Chen et al. [33]. The detection limit for TCE using this procedure is 0.080 mg/L. To determine chloride (Cl^-) and Fe(II) concentrations in the column effluent, samples were collected in glass vials at each sampling time. An ion chromatograph (Dionex, DX-100, Sunnyvale, CA, USA) was used to analyze chloride with a detection limit of 0.05–0.15 mg/L, depending on the sensitivity setting. The ferrozine method was employed to quantify Fe(II) concentrations in the effluent. Ferrozine reacts with Fe(II) in solution to form a stable magenta-colored complex. Quantification of the Fe(II)-ferrozine complex was performed using the FerroZine Method (Hach Co., Loveland, CO, USA) and a spectrophotometer (Hach DR/4000U) set to measure absorbance at 562 nm. The detection limit for Fe(II) using this procedure is 1.400 mg/L. Ferrous iron standards were prepared by dissolving ferrous chloride tetrahydrate in 0.01 M HCl.

3. Results and discussion

3.1. Experiments in sand column (no ZVI) with voltage applied

As illustrated in the upper half of Fig. 1, there was no detectable removal of TCE in the sand-only column reactor when no voltage was applied. When 6 V was applied, TCE concentrations decreased by about 20%. With the application of 12 V DC to the column reactor, TCE reduction increased by an additional 12–13%, with C/C_0 ratios of 0.67 at the anode after 72 h. Removal of TCE with application of 12 V was similar to that achieved by Wang [34], except that he used a groundwater with a much greater conductivity (3202 μS/cm). The conductivity of the groundwater used in this study was 75 μS/cm and contained no chloride.

Chloride concentrations measured in effluent samples were compared with the amount of TCE that was removed in the column