



Influence of humic substances on electrochemical degradation of trichloroethylene in limestone aquifers



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ABSTRACT

In this study we investigate the influence of humic substances (HS) on electrochemical transformation of trichloroethylene (TCE) in groundwater from limestone aquifers. A laboratory flow-through column with an electrochemical reactor that consists of a palladized iron foam cathode followed by a MMO anode was used to induce TCE electro-reduction in groundwater. Up to 82.9% TCE removal was achieved in the absence of HS. Presence of 1, 2, 5, and 10 mgTOC L⁻¹ reduced TCE removal to 70.9%, 61.4%, 51.8% and 19.5%, respectively. The inverse correlation between HS content and TCE removal was linear. Total organic carbon (TOC), dissolved organic carbon (DOC) and absorption properties (A_{254} , A_{365} and A_{436}) normalized to DOC, were monitored during treatment to understand the behavior and impacts of HS under electrochemical processes. Changes in all parameters occurred mainly after contact with the cathode, which implies that the HS are reacting either directly with electrons from the cathode or with H₂ formed at the cathode surface. Since hydrodechlorination is the primary TCE reduction mechanism in this setup, reactions of the HS with the cathode limit transformation of TCE. The presence of limestone gravel reduced the impact of HS on TCE removal. The study concludes that presence of humic substances adversely affects TCE removal from contaminated groundwater by electrochemical reduction using palladized cathodes.

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1. Introduction

Karst aquifers tend to produce high yield due to highly transmissive zones formed by the interconnected fractures and conduits. Karst aquifers are valuable water resource systems; about 40% of the groundwater used for drinking in the U.S. comes from karst aquifers [1]. However, the same characteristics, including presence of fissures, sinkholes and underground streams, make karst aquifers highly vulnerable to contamination [2–6]. The high capacity to store and transport contaminants coupled with lack of filtration make karst aquifers significant pathways for humans and wildlife exposure to contaminants [7]. Other parts of the world with large areas of karst include China, Europe, the Caribbean, and Australia. There is a significant lack of understanding of contaminant transport in karst and a need for development of remediation strategies for such complex and potentially deleterious systems.

Trichloroethylene (TCE) is a chlorinated solvent that was widely used in industrial cleaning solutions and as a degreasing agent due

to its unique chemical and physical characteristics and solvent effects. Improper disposal of TCE coupled with its low solubility and limited degradation led to persistent TCE contamination at many hazardous waste sites in the U.S., many of which are in karst regions. Because of its potential carcinogenic and mutagenic effects, the USEPA has set the Maximum Contaminant Levels (MCLs) for TCE in drinking water at a low concentration of 5 µg L⁻¹. Methods that have been used to remove or degrade TCE in groundwater include microbial transformation [8–12] and chemical oxidation or reduction [13–16]. Electrochemical methods are also widely investigated, due to the advantage of *in situ* formation and control of oxidizing and/or reducing conditions [17–24].

Because of its chemical nature, attention was focused on cathodic reduction and dehalogenation of TCE [24]. TCE electro-reduction was evaluated in divided electrochemical cells, with anolyte and catholyte separated by the membrane [25,26], as well as in undivided, mixed electrolyte cells [18–20,27,28]. Using mixed electrolyte cells provides advantages over divided cells for *in situ* implementation of electrochemical groundwater treatment. These advantages include avoiding the use of membranes between the electrodes (which require maintenance and cleaning) and less energy expenditure. The main limitation of mixed electrolyte cells is the competition between oxygen produced at the anode and the

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target contaminants for the reduction at the cathode. However, adverse oxygen influence can be minimized by the use of proper electrode materials and electrode arrangements [17–20,25]. Our recent work proves that using a cathode followed by an anode electrode in an open electrolyte system (no ion exchange or membrane between electrodes) induces reduction of TCE via hydrodechlorination (HDC) in groundwater [17,25]. Furthermore, utilization of palladized cathodes enhances HDC mechanism and TCE degradation in electrochemical reduction systems [26,29–34].

In limestone groundwater systems, aquifer recharge from surface water will carry natural organic matter (NOM), as a direct result of the hydrological connectivity and limited filtration between the surface and subsurface [35]. Therefore, it is important to evaluate the impact of NOM when optimizing groundwater treatment. NOM can inhibit reduction of chlorinated aliphatic compounds in groundwater via zero valent iron due to competition between TCE and NOM for adsorption on Fe^0 surface sites [36]. However, other studies reported positive effect of NOM on reduction of contaminants [37–39]. When sorbed on Fe^0 surface sites, certain structures within humic acids serve as the electron shuttles to effectively transfer electrons and accelerate the dechlorination efficiency and rate. The influence of presence of NOM, which can be significant in karst aquifers, on the electrochemical reduction of TCE in groundwater was not investigated.

In this study we evaluate: a) the influence of humic substances (HS) on electrochemical reduction of TCE and b) the influence of the electrochemical processes on HS in groundwater from limestone aquifers. A reactor consisting of a palladized cathode followed by an anode in an open electrolyte arrangement (no ion exchange membrane) is used to induce TCE reduction in flow-through column experiments.

2. Experimental

2.1. Materials and chemicals

All chemicals used in this study were analytical grade. TCE (99.5%) and cis-dichloroethylene (cis-DCE, 97%) were purchased from Sigma-Aldrich. Calcium sulfate was purchased from JT Baker, sodium chloride, and sodium bicarbonate from Fisher Scientific. Humic acids (HS) were purchased from Alfa Aesar. Hydrochloric acid (HCl) was from Sigma-Aldrich. Deionized (DI) water (18.2 M Ω -cm) obtained from a Millipore Milli-Q system was used in all experiments. Ti/mixed metal oxide (MMO) mesh (3N International) was used as anode. The Ti/MMO electrode consists of IrO_2 and Ta_2O_5 coating on titanium mesh with dimensions of 3.6 cm diameter by 1.8 mm thickness. Iron foam cathode (100 pores per inch, PPI, 90% iron and 10% nickel, Heze

Table 1

The experimental conditions for treatments in the absence of limestone gravel.

Experiments No.	Current (mA)	mgTOCL ⁻¹	TCE (mgL ⁻¹)
Control	–	–	
1	60	–	
2	60	1	
3	60	2	5.3
4	60	5	
5	60	10	
6	–	5	
7	60	5	–

Jiaotong Group Corp., China) was perforated with 0.5 cm diameter holes to avoid hydrogen bubbles accumulation in the cathode vicinity. Prior to palladization, the iron foam electrodes were immersed in 1 M HCl to remove any foreign metal and surface oxide layers. After a thorough rinsing with DI water, the palladization was performed in a closed beaker with a PdCl_2 solution (to ensure 10 mg Pd coating) and 0.1 M HCl, and rotated at 300 rpm until the dark orange PdCl_2 solution turned colorless. The procedure was always performed under the same conditions to ensure the same surface quality. The exact amount of deposited Pd was calculated from the concentrations of the PdCl_2 solution measured spectrophotometrically at 480 nm, before and after plating. After palladization, the foams (Fe/Pd) were rinsed with DI water.

2.2. Electrochemical setup

The electrochemical set up is shown in Fig. 1 and the experimental conditions are summarized in Table 1 and Table 2. A flow through column with an electrochemical reactor is used for testing transformation of TCE in groundwater. The reactor includes a palladized iron foam cathode followed by Ti/MMO anode in an open electrolyte system to induce TCE reduction [17]. When used, limestone gravel (8–15 mm size) was placed to evaluate the influence of aquifer material on TCE removal and the behavior of HS (Fig. 1). The column was set vertically and upward flow conditions were used in all experiments. The electrochemical reactor without limestone gravel had glass beads (diameter 3 mm) below (upstream) the cathode and above the anode (downstream) for comparison.

Synthetic groundwater was prepared by dissolving 413 mg L⁻¹ sodium bicarbonate and 172 mg L⁻¹ calcium sulfate in DI water. The concentrations of bicarbonate ions and calcium ions are representative of groundwater from limestone aquifers, resulting in electrical conductivity of 800 to 920 $\mu\text{S cm}^{-1}$. HS stock solution was prepared by dissolving 40 mg of humic acids in 50 mL of DI water (200 mgTOCL⁻¹). The feedstock solution was prepared to concentrations of 1, 2, 5 or 10 mgTOCL⁻¹. Excess TCE was dissolved in DI water to form a TCE saturated stock solution (1.07 mg mL⁻¹ at 20 °C). The stock 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

Table 2

The experimental conditions for treatments in the presence of limestone gravel.

Experiments No.	Current (mA)	mgTOC L ⁻¹	TCE (mgL ⁻¹)
1	–	–	
2	60	–	
3	60	5	5.3
4	–	5	
5	60	5	–
6	60	–	–

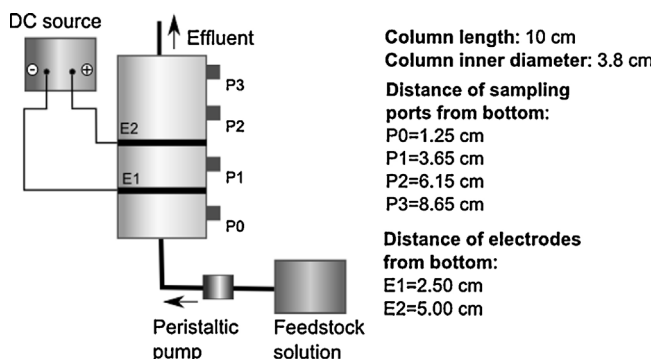


Fig. 1. The flow-through system with a cathode followed by an anode setup.

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