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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.

Keywords

humic substances; trichloroethylene; electrochemical; treatment; groundwater

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

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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 $5 \mu\text{g L}^{-1}$. 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 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 IrO₂ and Ta₂O₅ 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 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 1M 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 PdCl₂ solution (to ensure 10 mg Pd coating) and 0.1 M HCl, and rotated at 300 rpm until the dark orange PdCl₂ 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 PdCl₂ 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 **Figure 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 (**Figure 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 μ S cm⁻¹. HS stock solution was prepared by dissolving 40 mg of humic acids in 50 mL of DI water (200 mgTOC L⁻¹). The feedstock solution was prepared to concentrations of 1, 2, 5 or 10 mgTOC L⁻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 groundwater was 8 ± 0.3 and the initial oxidation-reduction potential (ORP) value was $210 \pm 5 \text{ mV}$. The temperature was kept constant at 20°C . Flow Darcy's velocity of 0.25 cm min^{-1} (2.8 mL min^{-1}) was maintained by a peristaltic pump (Cole Parmer, Masterflex C/L). A constant current (60 mA) was applied by an Agilent E3612A DC power supply.

The TCE final removal rate (FDR) was calculated by:

$$FDR(\%) = \frac{C_0 - C_t}{C_0} * 100 \quad \text{Equation 1}$$

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}).

2.3 Chemical analyses methods

TCE and cis-DCE concentrations were measured by a 1200 Infinity Series HPLC (Agilent) equipped with a 1260 DAD detector and a Thermo ODS Hypersil C18 column ($4.6 \times 50 \text{ mm}$). 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. pH and ORP of the electrolyte were measured by pH meter and ORP meter with corresponding microprobes (Microelectro, USA). The microprobes allow the measurement on these parameters using a small amount of liquid ($\approx 0.2 \text{ mL}$).

Total organic carbon (TOC, mg L^{-1}) and dissolved organic carbon (DOC, mg L^{-1}) originating from HS were measured at each sampling port (**Figure 1**) to evaluate the changes of HS during the treatment. TOC and DOC were analyzed by total organic carbon analyzer TOC-L CPH-CPN (Shimadzu, Japan) after samples acidification (pH 2) with concentrated HCl. DOC was measured after sample filtration through $0.45 \mu\text{m}$ filters (Millipore).

The absorbance values at the selected wavelengths (436 nm (A_{436}), 365 nm (A_{365}), and 254 nm (UV_{254})) were measured to evaluate the influence of electrochemical treatment on HS characteristics [40, 41]. UV-VIS spectrophotometric measurements of the samples were performed on UV Shimadzu (UV-1800) double beam spectrophotometer using 1 cm quartz cells. UV absorption at 254 nm (UV_{254}) was measured to calculate specific UV absorbance ($SUVA_{254}$, $\text{L mg}^{-1} \text{ m}^{-1}$), which presents aromatic content in DOC. $SUVA_{254}$ was calculated by **Equation 2** (USEPA 2003). In addition, we calculated $SUVA_{365}$ ($\text{L mg}^{-1} \text{ m}^{-1}$) (**Equation 3**). Specific color absorbance (SCA_{436} , $\text{L mg}^{-1} \text{ m}^{-1}$) was calculated by **Equation 4** to signify organic carbon normalized color forming moieties [41]. The disappearance of HS color during the treatment indicates transformation of the organic matter [40, 41].

$$SUV A_{254} = \frac{UV_{254}}{DOC} \times 100 \left(Lmg^{-1}m^{-1} \right) \quad \text{Equation 2}$$

$$SUV A_{365} = \frac{A_{365}}{DOC} \times 100 \left(Lmg^{-1}m^{-1} \right) \quad \text{Equation 3}$$

$$SCA_{436} = \frac{A_{436}}{DOC} \times 100 \left(Lmg^{-1}m^{-1} \right) \quad \text{Equation 4}$$

Scanning electron microscope (Hitachi S-4800 FESEM) was used to identify the changes in the palladized iron foam cathode surface due to the presence of HS in the stock solution. The cathode surface was characterized before and after electrochemical treatment in the absence of TCE.

3. Results and discussion

Figure 2a shows the influence of HS content (given as TOC) on TCE electrochemical removal. The experiments were conducted in the electrochemical cell shown in the Figure 1 without presence of porous material (glass beads or limestone gravel). For an initial TCE concentration of 5.3 mg L⁻¹, the FDR decreased from 82.9% in the absence of HS to 70.9%, 61.4%, 51.8% and 19.5% in the presence of 1 mgTOC L⁻¹, 2 mgTOC L⁻¹, 5 mgTOC L⁻¹, and 10 mgTOC L⁻¹, respectively. Presence of HS in groundwater negatively affects TCE removal by electrochemical reduction. The inverse correlation between HS content and TCE removal rate is linear (**Figure 2b**). No significant interactions were observed between TCE and HS in the control experiments.

Changes in TOC and DOC concentrations (**Figure 3**) and absorbance values at the selected wavelengths were measured at each sampling port (**Figure 1**) to assess the influence of HS on TCE removal. Control experiments did not show any significant sorption of HS on the acrylic reactor. The electrochemical treatment was conducted in the same flow through setup with a Fe/Pd cathode followed by an anode reactor in the presence of 5 mgTOC L⁻¹ from HS. After 120 minutes of treatment, TOC concentration decreased by 44.6% after the cathode (Port 2) followed by no significant change after anode (Port 3). DOC decreased by 21.0% after the cathode at Port 2 and 29.9% after the anode at Port 3. DOC values decrease over time (**Figure 3**) after flow through both the cathode and anode. However, the decrease in DOC values after 80 min is less than the decrease in DOC in the first 80 minutes of treatment. This reflects changes in HS characteristics and degradation of complex HS molecules into the smaller, dissolved forms. A decrease in TOC and DOC values was measured in the flow-through experiments without electric current application. Both TOC and DOC decreased at Port 2: 11.9% and 19.9%, respectively, but without any significant change at Port 3: 11.8% of TOC and 21.1% of DOC. The results reflect the effect of sorption on the cathode material. The different behavior of DOC with and without electric current application proves that the electrochemical processes influence HS and consequently TCE removal.

The TOC and DOC behavior indicate that there is significant interaction between HS and the cathode material. HS affects the cathode performance causing a decrease in TCE hydrodechlorination and removal. It was reported that NOM can serve as an H₂ acceptor; the H₂ produced from ZVI corrosion is transferred to NOM in the presence of Pd [40]. There are a few possible mechanisms that HS could affect TCE reduction via hydrodechlorination [35, 37, 39, 40, 42, 43]: a) HS could act as an acceptor of H₂ formed at the cathode surface, resulting in HS catalytic hydrogenation; b) with the presence of a Pd site, the HS could serve as a competitive electron acceptor to H⁺, inhibiting H₂ formation (**Reaction 1**), and c) the large HS molecules adsorbed to the surface could cause steric congestion and form physical barrier to diffusion of the contaminant molecules to the reactive sites (Pd) and inhibit H₂ formation.

It is evident (**Figure 3**) that the processes at the anode cause a lesser impact on HS characteristics than those at the cathode. MMO anodes are capable of producing hydroxyl radicals but they have a strong interaction with the hydroxyl radicals (active type of electrodes). This causes low oxygen overpotential and, therefore, low efficiency for removal of organics [44]. Under the applied current and due to the type of the anode (active electrodes), it is not expected that HS or TCE concentrations will significantly change via oxidation at the MMO anode.

To confirm the changes in HS characteristics during treatment and that their interaction with the cathode surface inhibit TCE reduction, we investigated changes in HS absorption properties. Electrochemical treatment of a solution containing 5 mgTOC L⁻¹ from HS were conducted and SUVA₂₅₄, SUVA₃₆₅ and SCA₄₃₆ values were measured before and after the treatments with and without electric current application (**Table 3**.) Changes in SUVA₂₅₄ provide a quantitative measure of aromatic content per unit concentration of carbon [45]. However, SUVA₂₅₄ should not be used as a single measure to prove the reduction of aromaticity [46]. Yet, changes in its value indicate changes in the HS structure since there are no other substances present (e.g. nitrates) that could interfere with UV absorption. The SUVA₃₆₅ was also calculated to address changes in aromaticity while SCA₄₃₆ was defined to signify organic carbon normalized color forming moieties.

The SUVA₂₅₄, SUVA₃₆₅ and SCA₄₃₆ values decreased after treatment, compared to no significant change in experiments without electric current application (with exception to SCA₄₃₆) (**Table 3**). The electrochemical processes affect HS characteristics, mostly after reaction with the cathode surface (as measured in Port 2). SUVA₂₅₄, SUVA₃₆₅, and SCA₄₃₆ values did not change after the anode which is in correlation with TOC and DOC changes. This further confirms that the HS reacts with either electrons or H₂ that is formed at the cathode surface. SEM images (**Figure 4**) show the palladized cathode foam surface after electrochemical treatment. **Figure 4a** shows black spots on the Pd sites at the cathode, which originate from carbon (C) from the HS. This is proved by an elevated carbon (C) peak corresponding to Pd sites at the cathode (**Figure 4a**) compared to the sites with lower Pd

load (**Figure 4b**). SEM images indicate that HS interacts with reactive Pd sites, which lowers TCE dechlorination rate.

Additional experiments were conducted to understand the impact of interactions between TCE and porous media such as limestone gravel or glass beads (**Figure 5**). The HS behavior in the presence of limestone but without TCE (**Figure 6**) and the simultaneous influence of HS and limestone gravel on TCE concentration decay (**Figure 5**) were also evaluated.

Glass beads were used in the reactor to provide a non-reactive equivalent and uniform porous volume in the absence of limestone gravel to facilitate comparison of TCE removal rates. No TCE losses were measured in the control experiments due to presence of glass beads or limestone gravel. In the absence of HS, TCE degradation occurred more rapidly in the presence of limestone than glass beads (**Figure 5**). This may be related to the entrapment of hydrogen and oxygen gas bubbles between glass beads in the electrodes' vicinity. As previously reported, the entrapment of the gas bubbles decreases the electrode's active surface area thus adversely affects the TCE removal [47]. There was no entrapment of the bubbles within the limestone gravel and electrode vicinities; the limestone gravel fill was porous enough to allow gas bubbles movement from the immediate area surrounding the electrodes.

To understand HS behavior in presence of limestone, we measured the TOC and DOC changes during treatment under 60 mA and without current application (**Figure 6**). In absence of electricity, TOC and DOC values decreased by 11.9% and 19.9%, respectively, in the presence of glass beads due to the adsorption on the cathode material. Changes in TOC and DOC were more significant in the presence of limestone (55.8% of TOC and 49.6% of DOC) indicating significant interaction between limestone and HS, which has been reported in the literature [48]. Both TOC and DOC changed significantly in the presence of limestone after electrochemical treatment (41.7% of TOC and 29.9% of DOC). This is in contrast with presence of glass beads, which resulted in smaller changes (less than 20% for both TOC and DOC). This result implies that the limited adsorption and transformation of HS in the system is most likely due to a reduction in the active cathode area due to bubbles entrapment. The different behavior patterns of DOC with and without current application in the presence of limestone gravel indicate changes in the complex structure of HS.

Finally, the effect of HS on TCE removal was negligible (<5%) when glass beads were used as porous media, while the impact of HS was greater (45%) when the reactor was filled with limestone. These data demonstrate that lack of HS and TCE interaction with the cathode situated with glass beads is due to bubbles entrapment, thus limiting the cathode active area.

4. Conclusions

The influence of humic substances on electrochemical reduction of TCE in groundwater from limestone aquifers is evaluated using palladized iron foam cathode and an MMO anode in a flow-through column. HS adversely affects electrochemical removal of TCE. The TCE removal decreased from 82.9% in the absence of HS to 19.5% in the presence of 10 mgTOC

L^{-1} . The inverse correlation between HS content and TCE removal was linear, which will facilitate prediction of HS influence on TCE removal in field implementation. Electrochemical treatment using a palladized iron foam cathode followed by an anode influences HS characteristics. TOC, DOC and absorption properties of HS ($SUVA_{254}$, $SUVA_{365}$ and SCA_{436}) significantly change during treatment, mainly after interaction with the cathode surface. HS reacts with the cathode via sorption and with electrons or H_2 that is formed at the cathode surface. This adversely affects TCE hydrodechlorination and overall TCE removal. The impact of HS on TCE removal was reduced in the presence of limestone gravel as a granular porous media.

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Highlights

- Humic substances (HS) adversely affect TCE electrochemical reduction.
- The inverse correlation between HS content and TCE removal is linear.
- HS interfere with the hydrodechlorination of TCE at the cathode.
- The impact of HS on TCE removal was reduced in the presence of limestone gravel.

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

Fig. 2.

The effect of HS content on TCE removal by electrochemical treatment: a) TCE concentration decay in the presence of HS and b) correlation between HS content and TCE removal (experimental conditions: 5.3 mg L⁻¹ TCE, 60 mA current, 2.8 mL min⁻¹ flow velocity, Fe/Pd cathode followed by anode set up).

Fig. 3.

TOC and DOC changes as normalized concentrations (C/C_0) at each port during treatment (experimental conditions: 5 mgTOC L⁻¹, 60 mA, 2.8 mL min⁻¹, Fe/Pd cathode followed by anode set up).

Fig. 4. SEM images of the cathode surface after the electrochemical treatment: a) Pd sites and b) Fe areas within the palladized cathode after the treatment and corresponding spectra (experimental conditions: 5 mgTOC L⁻¹, 60 mA, 2.8 mL min⁻¹, Fe/Pd cathode followed by anode set up).

Fig. 5. TCE decay in the presence and absence of limestone gravel and HS (experimental conditions: 5.3 mg L^{-1} TCE, 5 mgTOC L^{-1} , 60 mA , 2.8 mL min^{-1} , Fe/Pd cathode followed by anode set up).

Fig. 6. TOC and DOC change in the reactor with limestone gravel (experimental conditions: 5 mgTOC L⁻¹, 60 mA, 2.8 mL min⁻¹, Fe/Pd cathode followed by anode set up).

Table 1

The experimental conditions for treatments in the absence of limestone gravel

Experiments No.	Current (mA)	mgTOC L ⁻¹	TCE (mg L ⁻¹)
Control	-	-	5.3
1	60	-	
2	60	1	
3	60	2	
4	60	5	
5	60	10	
6	-	5	
7	60	5	-

Table 2

The experimental conditions for treatments in the presence of limestone gravel

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

Table 3

SUVA₂₅₄, SUVA₃₆₅ and SCA₄₃₆ decrease after the treatment without and with current application

Parameter	Removal % at Port 2		Removal % at Port 3	
	Without current	With current	Without current	With current
SUVA ₂₅₄	<1	81.9	<1	81.9
SUVA ₃₆₅	7.8	78.4	8.4	76.1
SCA ₄₃₆	26.5	74.2	27.4	72.1