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Electrochemical dechlorination of trichloroethylene in the presence of natural organic matter, metal ions and nitrates in a simulated karst media

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Abstract

A small-scale flow-through limestone column was used to evaluate the effect of common coexisting organic and inorganic compounds on the electrochemical dechlorination of trichloroethylene (TCE) in karst media. Iron anode was used to produce ferrous ions and promote reducing conditions in the column. The reduction of TCE under 90 mA current, 1 mL min⁻¹ flow rate, and 1 mg L⁻¹ initial TCE concentration, was inhibited in the presence of humic acids due to competition for direct electron transfer and/or reaction with atomic hydrogen produced at the cathode surface by water electrolysis. Similarly, presence of 10 mg L⁻¹ chromate decreased TCE reduction rate to 53%. The hexavalent chromium was completely reduced to trivalent chromium due to the ferrous species produced from iron anode. Presence of 5 mg L⁻¹ selenate decreased the removal of TCE by 10%. Chromium and selenate complexation with dissolved iron results in formation of aggregates, which cover the electrodes surface and reduce TCE dechlorination rate. Presence of 40 mg L⁻¹ nitrates caused reductive transformation of TCE up to 80%. Therefore, TCE removal is influenced by the presence of other contaminants that are present as a mixture in groundwater in the following order: humic acid, chromate, selenate, and nitrate.

Keywords

simulated karst aquifer; TCE; humic acid; metal ions; nitrate; mixture of contaminants

1. Introduction

Chlorinated solvents, hexavalent chromium, selenates, and nitrates are priority groundwater pollutants that pose public health risks [1]. Electrochemical methods are of interest for

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treating such contaminants in groundwater because of the capability to adjust redox conditions to changes in the influent composition and flow rate [2–4]. Electrochemical processes are effective for removal of chlorinated solvents such as trichloroethylene (TCE), regulated metals, and nitrates [5] via electrochemically induced oxidation or reduction mechanisms [6–10]. Indirect electrochemical reduction of TCE via hydrochlorination involves the reaction of chlorinated compounds with atomic hydrogen produced at the cathode due to water electrolysis [11]. For materials with higher hydrogen evolution overpotential, such as silver, copper and lead, the kinetics of hydrogen evolution may be relatively slow, which implies that any other reducible species such as TCE molecules can acquire the atomic hydrogen from the cathode [6, 28]. Another process for trichloroethylene removal is dechlorination in the presence of iron, however, presence of co-oxidants, such as chromate, selenite, or nitrate limit this process [6, 12–14].

Groundwater from karst aquifers is an important source of drinking water, accounting for 25% of the world and 40% of the US groundwater resources [15]. Karst aquifer, formed from the dissolution of soluble rocks such as limestone and dolomite, are significant routes of contaminant exposure for human and wildlife [16]. They are complex systems not only because the dissolution process creates complex networks of preferential flow pathways but also because it is hard to evaluate the manner in which groundwater flow is transmitted through the system [17]. Surface runoff that often contains hydrocarbons, metal species, nitrate, and other organic contaminants may enter karst groundwater systems through infiltration. Thus, studying the fate and transport process of groundwater in a simulated limestone block is of significant scientific and engineering importance.

Natural organic matter (NOM) is present in the groundwater due to hydrological connectivity and limited filtration between the surface and subsurface in karst aquifers [18]. The presence of NOM can influence the remediation processes due to possible competition for transformation mechanisms of target contaminants. NOM is ubiquitous in karst aquifers with a high tendency to be adsorbed on mineral surfaces such as Fe oxides [19]. Presence of NOM in groundwater negatively impacts the removal of contaminants by Fe but there is still a limited knowledge on the effect of coexisting NOM and other contaminants on remediation, especially in karst aquifers [20]. NOM may suppress the remediation of target contaminants not only by direct electron transfer at the surface of the cathode or reaction with atomic hydrogen produced at the cathode surface [11], but also by complex production and aggregation in solution. Humic acids aggregate with iron species and form precipitates, especially, with calcium and magnesium naturally presented in groundwater [20]. In systems using the iron anode, the inevitable limitation of the iron reduction is driven by the corrosion of zero-valent iron and deposition of minerals, which decrease the reductive capacity and clog the system [21]. The deposition of aggregates may impact the long-term activity of the remedial system due to precipitation on the iron surface which would causes clogging the pores, decreasing the permeability, and developing preferential flow path [20].

Among heavy metals, chromium (Cr) and selenium (Se) are common contaminants in surface water and in numerous industrial activities such as preservation of wood, electroplating and metal finishing [22]. Zero-valent iron is capable of treating dissolved metal ions such as selenium and chromium [23]. The removal of the reduced chromium

species Cr(III) occurs through precipitation of the sparingly soluble $\text{Cr}(\text{OH})_3$ or precipitation of mixed iron(III)-chromium(III) oxyhydroxide solids [24–26]. Nitrate is one of the main co-contaminants found at sites contaminated with chlorinated solvents and metals and is easily combined with various organic and inorganic substances [27]. Nitrate is also found in groundwater naturally at a very low concentration level. Since nitrate and TCE reduce at the cathode via reaction with atomic hydrogen, a process leading to a competition between target contaminant (TCE) and nitrate, it is important to evaluate its influence on the remediation process even in concentration lower than maximum contaminant level (MCL). Although presence of ferrous due to iron anode electrolysis leads to formation of a reducing environment, it also results in precipitates, which may act as an insulator that gradually cover the surface of electrodes and decrease the removal rate of contaminants by terminating the further redox reactions [28].

There is a limited literature on the treatability of mixtures of organic and inorganic groundwater pollutants, especially in limestone karst aquifers. In this study, a detailed investigation of the TCE removal efficacy in the presence of other groundwater contaminants (e.g. Chromate, Selenate, Nitrates) was performed and information is provided for assessing the application of designed system in karst environment rich in NOM. Besides the fact that these contaminants are often found in mixtures and are most commonly found in groundwater, we chose them to represent the combination of chemical species with different characteristics that can interfere with the transformation mechanisms. This is an important aspect of the optimization of remediation technologies for the treatment of real groundwater with complex geochemistry. A limestone column was specially designed to simulate the channel flow in the karst aquifer. The application of an electrochemical reactor in a limestone system with an iron anode to remediate TCE in the presence of dichromate, selenate, nitrate, and humic acids is evaluated in this study.

2. Experimental Methods

Chemicals and Materials

The chemicals used in this study include trichloroethylene (99.5 %, Sigma Aldrich), potassium dichromate (reagent grade, JT Baker), sodium selenate (99.8%, Alfa Aesar), sodium nitrate (reagent grade, JT Baker), sodium bicarbonate (reagent grade, Fisher Chemical), humic acid (Alfa Aesar), and calcium sulfate (99.9%, JT Baker). Excess amount of TCE was dissolved in 18.2 MΩ.cm deionized water. This saturated solution was used to prepare aqueous TCE solution during experiments. Electrodes were cast iron (MacMaster-Carr, USA) and copper foam (99.99%, 40 PPI, ERG, USA). The cast iron electrode used in this study was a cylinder rod with outer diameter of 0.95 cm. Before starting the experiment, iron anode was polished by coarse paper and the cathode was immersed by diluted HCl solution (10 wt%) and rinsed with distilled water prior to assembly.

Reactor

A flow-through column reactor that consists of limestone block with a flow channel of 2.5-inch inner diameter and 13-inch length was used (Figure 1). The limestone column was selected to simulate a karstic aquifer media. Oxidation-reduction potential (ORP) and pH

probes recorded the effluent pH and ORP through the connection with the computer via the USB port. Simulated ground water was prepared by dissolving 2 mL of saturated TCE solution in a 2 L aqueous solution containing $0.413 \text{ g L}^{-1} \text{ NaHCO}_3$ and $0.172 \text{ g L}^{-1} \text{ CaSO}_4$ (1 mg L^{-1} initial concentration of TCE). Chromate, selenate, and nitrate solutions were prepared by dissolving K_2CrO_4 (JT Baker), Na_2SeO_4 (Alfa Aesar), and NaNO_3 (JT Baker) into deionized water, respectively. The specific concentrations have been chosen in relation to Maximum Contaminant Levels (MCL) of the contaminants. The aqueous stock solution of humic acids was prepared by dissolving 20 mg humic acids in 50 mL DI water. The humic acids stock solution was used to prepare solutions containing 1, 2, and 5 mg L^{-1} total organic carbon (TOC) originating from humic acids. Simulated groundwater was pumped through the column with a flow rate of 1 mL min^{-1} . The constant flow rate was maintained by using a peristaltic pump (Masterflex, model 7720066). To minimize the TCE loss by absorption, glass tube and Viton pump tubing (Cole Parmer, USA) was used as a connection between all parts of the reactor. At specific time intervals, 1 mL samples were taken from sampling port 3. Various current intensities (30, 60, and 90 mA) were applied using an Agilent E3612A DC power supply under the conditions of 1 mL min^{-1} flow rate and 1 mg L^{-1} initial concentration of TCE according to the optimized system's operation described in Mao et al., 2012 [6]. The most efficient current density (90 mA) was selected for conducting the experiments for this study. Control experiments were conducted without electricity under the same concentrations of contaminants suggested that the adsorption of contaminants on limestone block was limited (2.5%). All experiments were conducted at room temperature. Each set of experiments was repeated in triplicate to ensure reliability of the results.

Chemical analysis

Aqueous TCE concentration was measured by HPLC (1200 Infinity Series) equipped with a 1260 DAD detector. 1 mL of sample was diluted immediately after filtration ($0.2 \mu\text{m}$ filter, Milipore) with 1 mL acetonitrile in a 2 mL vial for HPLC analysis. Oxidation-reduction-potential (ORP) and pH were recorded by microprobes. Selenate and nitrate ions were analyzed 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 . To measure the selenate and nitrate in a mixture, 1 mL of sample was taken for each and filtered ($0.2 \mu\text{m}$ filter, Milipore). Dichromate ion was measured by diphenylcarbazide method using Hach Chroma Ver 3 reagent at 540 nm wavelength (UVmini-1240 spectrophotometer- Shimadzu). TOC was measured by total organic carbon analyzer (Shimadzu TOC-VWS). We calculated the amount of iron released during the experiments based on the Faraday's law.

3. Results and Discussion

3.1. Effect of humic acids on TCE reduction

The effluent TCE concentration decay versus influent by iron anode and copper cathode in the presence of various concentration of humic acids is presented in Fig. 2 (1, 2, and 5 mgTOC L^{-1}).

Several studies have shown the negative effect of NOM on Fe activity for chlorinated hydrocarbon degradation, which is attributed to strong competition for reactive sites [29,30] and changing reduction potential of surface sites [20]. As observed, in the absence of humic acids, more than 90% of the TCE was transformed after 240 minutes of operation. Increasing the amount of humic acids resulted in a decrease in dechlorination rate but the final remediation efficacy is the same (around 79%). NOM surpasses contaminant reduction via reacting either directly with electrons or with H_2 produced at the cathode surface [11] and alteration of surface electrostatic and reductive potentials [31–34]. In this way, humic acids play a negative role as they may compete with target contaminant at the cathode surface and result in a decline in remediation rate of TCE. In addition, NOM could react with ferrous ions to produce Fe-humate precipitates which could contribute to the coverage of iron anode surface and surpass further production of ferrous species. Decrease in the formation of ferrous species affects the system ability to create reducing conditions that are necessary to support TCE degradation.

3.2. Role of selenate, dichromate, and nitrate reduction on TCE remediation

Table 1 summarizes the removal of TCE in the presence of nitrates, chromates and selenates as well as removal efficiencies for each contaminant. All electrolysis experiments were conducted under an optimized condition (90 mA current, 1 mL min^{-1} flow rate, and 1 mg L^{-1} TCE) in the limestone column.

It is clear that chromium influences the TCE reduction rate more strongly than selenate and nitrate. This system is able to reduce different amounts of chromate added to the solution (Table 1). Significant reduction in Se (VI) was achieved (around 100 and 83 % for 1 and 5 mg L^{-1} initial concentration added, respectively). In addition, the removal rate for nitrate is around 70% for all initial concentrations added. The concentration profile for TCE and contaminants during the treatment is shown in Fig. 3.

During the reduction process, hexavalent chromium is being reduced to trivalent chromium, which further reacts with ferrous hydroxide present in simulated ground water due to iron anode reaction [1]. The removal of Cr(VI) from wastewater is mostly due to chemical reduction by electrogenerated ferrous, instead of direct electrochemical reduction on the cathode [6]. Chromium hydroxide and probably other mineral precipitations result in the loss of reactivity for TCE removal in our column because of the action of covering the reactive surface of electrodes. These ions can be easily absorbed on the positively charged surface of iron (II) hydroxide where they are subsequently reduced by Fe^{2+} , which results in poorly soluble products. The removal efficacy of TCE decreased intensely when the solution contains Cr (VI). In this study, the decay profiles under various initial concentrations (1, 5, and 10 mg L^{-1} chromate) depicted that TCE removal rate decreased by 1.5 times in the presence of Cr (VI). The decrease in the removal efficiency can be attributed to the accumulation of Fe-Cr precipitates, which may result in a positive shift in corrosion potential, a declining rate of electron transfer, or the decrease of iron active surface area [36].

By increasing the initial concentration of selenate, the capability of the system for removing both selenate and TCE reduction decreased. Although the removal efficacy of TCE is higher

when the same amount of selenate added (Table 1) comparing to chromium (Table 1), it is still lower than control experiment with no other contaminants (only TCE). This procedure suggests that the formation of chromium and selenate precipitates inhibit the iron anode system performance. Precipitation of minerals throughout the column, gradually decrease the reactivity of electrodes and permeability of the system and further limit the removal of contaminants [36,37]. The validity of the system for removal of TCE co-contaminated with selenate presented in Fig. 3-b. Reduction of selenate ions primarily relates to the reducing environment containing ferrous species. Ferrous hydroxide can reduce Se (VI) and co-precipitate the produced elemental selenium [6]. The remediation rate of TCE decreased by 15% when 5 mg L⁻¹ of selenate was added. It can be concluded that the accumulation of precipitates not only can affect the access of contaminants to the electrode surface but also, decrease porosity and hydraulic conductivity, which in turn restricts simulated groundwater flow [35].

The results demonstrate that nitrate exerts a lesser influence on TCE remediation efficacy compared to selenate and chromate, which was also found by Vodyanitskii and Mineev (2013). It has been reported that TCE and nitrate are removed through the electrode-based electrochemical processes at cathode surface, therefore their removal efficiencies are subject to the factors that are related to the mass transfer effect of contaminants on electrode/liquid interface, such as hydraulic residence time and surface area of the electrode [6]. According to previous studies, a flow-through cell with the cathode placed in front of the anode with respect to the flow direction, nitrate presence adversely affects TCE hydrodechlorination by using a cathode followed by an anode sequence [9]. Further study by Lu et al. (2010) on TCE degradation in the presence of nitrate indicated that higher nitrate concentration directed to an increased amount of precipitates that acted as a physical barrier and slowed degradation rate of TCE. In our study, adding nitrate to the synthetic ground water solution has the least significant influence on TCE removal efficiency. The electro-reduction of nitrate at the cathode is a very complex process which starts with nitrate ion adsorption at the cathode and involves the simultaneous transfer of the electrons that leads to a series of reactions representing competition between nitrate and TCE for active cathode surface. As Fig. 3-c shows that the remediation rate for TCE was negligibly influenced by nitrate presence, TCE removal efficiency decreased by approximately 5%. It is possible that nitrates are mostly removed via electrocoagulation process [38], which minimized their competition with TCE for the atomic hydrogen at the cathode.

3.3. Removal of TCE and a mixer of contaminants

Preliminary experiments have been conducted by the authors simultaneously to compare the removal rate of TCE in acrylic and limestone set-up. Based on primary experimental results (no data presented), the removal efficiency is higher using limestone rather than acrylic column under the same conditions. There could be some possible mechanisms due to limestone specific characteristics that may provide a well-made media for particles to accumulate and make a bigger mass which further sink down to the reactor, instead of being proposed either at the surface of the electrodes or clogging the effluent. Here, in Fig. 4, we present the system's ability to remove TCE, chromate, selenate, and nitrate simultaneously. We performed the cleanup of a mixture of contaminants under optimized operational

conditions (90 mA current, 1 mL min⁻¹ flow rate, and 1 mg L⁻¹ initial concentration of TCE) for the highest initial concentration of chromate, selenate, and nitrate (10, 5, and 40 mg L⁻¹) in order to evaluate the potential efficacy of the current system on a mixture of several contaminants. Results indicate that the removal efficiency for contaminants in a mixture is equal to the removal of individual contaminant under same conditions. The influence on TCE removal is in the following order: chromate, selenate, and nitrate.

Concentration profiles and removal efficacies at steady state condition (100% chromate, 90% selenate, and 80% nitrate) suggest that these contaminants can be removed simultaneously. In the contrary, the remediation rate of TCE decreased by 50% in the mixture of contaminants. As a mixture, the amount of precipitations and complexes produced might be more than that they were applied individually. Lower removal rate of TCE could be presumably due to production of insoluble precipitates with ferrous species and also the competition for the reduction at the cathode surface.

4. Conclusion

Limestone block column experiments showed that the efficiency of iron anode and copper cathode system for TCE removal is influenced by the presence of humic acid and strong oxidants such as chromate, selenate, and nitrate. The influence on TCE removal is in the following order: humic acid, chromate, selenate, and nitrate. Dichromate, selenate are reduced to the insoluble ions, which presumably forms precipitates result in covering iron anode surface. The layer of sediments on iron anode prevents electron transfer reaction and lessen dechlorination rate. Humic acids also form aggregates in solution via cathodic reactions, which eventually out-compete with TCE for reduction and decrease or cease the degradation process. Thus, in humic acid-rich environments, the concentration of humic acid is a factor that requires monitoring in order to avoid any adverse impact in long-term in situ applications. It was also found that this system is capable of removing these contaminants as a mixture, while the remediation rate of TCE is significantly low (around 40%) compared to the control experiment (only TCE). In the mixture of contaminants, the removal efficiency of TCE declined due to competition for the same transformation mechanisms and based on the result, the removal efficiency for contaminants in a mixture is equal to their individual as they may react with a specific mechanisms and produce different precipitates with various structure and particle size which definitely affect the system in a different way. Since humic acid, metal ions, and nitrate are the most often co-existing compounds with TCE in groundwater, results obtained in this study can provide a better understanding of remediation process. Furthermore, notwithstanding the fact that current system is convenient to be applied for remediation of a mixture of contaminants, for field implementation, more series of technical and engineering challenges should be considered in order to achieve the process, which is applicable for long-term performance. Although the limestone block is a simulation of a karst aquifer, it should be pointed out that the results mentioned here need to be tested in field conditions as different factors may impact the system significantly. Broad research is still needed to identify and address these issues.

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Fig. 1.
Schematic of the flow-through system with iron anode followed by copper cathode.

Fig. 2. Effect of humic acid content (1, 2, and 5 mgTOC L⁻¹) on TCE (1 mg L⁻¹ initial concentration) degradation under the condition of 90 mA current intensity and 1 mL min⁻¹ flow rate.

Fig. 3.

Normalized TCE concentration profiles co-contaminated with (a) chromium (1, 5, and 10 mg L^{-1}), (b) selenate (1 and 5 mg L^{-1}), and (c) nitrate (2, 10, and 40 mg L^{-1}). All experiments were conducted under the same operational conditions (90 mA current, 1 mL min^{-1} flowrate, and 1 mg/L initial concentration of TCE).

Fig. 4. Normalized concentration profiles for TCE, nitrate, selenite, and chromium as a mixture. The experiment was conducted under the same operational conditions (90 mA current, 1 mL min⁻¹ flow rate, and 1 mg L⁻¹ initial concentration of TCE).

Table 1

The removal rate of target contaminants.

Limestone Block- 90 mA- 1 mL/min			
	Initial Concentration (mg/L)	Contaminant removal efficacy (%)	TCE removal efficacy (%)
Dichromate	1	>99	70
	5	>99	57
	10	>99	53
Selenate	1	>99	89
	5	83	76
Nitrate	2	73	91
	10	71	86
	40	72	81

The amount of iron added based on Farady's Law is 0.375 gr (0.35 mg L^{-1}) for each set of experiment (90 mA current and 240 min of experiment).