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Hydrodechlorination of TCE in a circulated electrolytic column at high flow rate

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Abstract

Palladium-catalytic hydrodechlorination of trichloroethylene (TCE) by cathodic H₂ produced from water electrolysis has been tested. For a field in-well application, the flow rate is generally high. In this study, the performance of Pd-catalytic hydrodechlorination of TCE using cathodic H₂ is evaluated under high flow rate (1 L min⁻¹) in a circulated column system, as expected to occur in practice. An iron anode supports reduction conditions and it is used to enhance TCE hydrodechlorination. However, the precipitation occurs and high flow rate was evaluated to minimize its adverse effects on the process (electrode coverage, clogging, etc.). Under the conditions of 1 L min⁻¹ flow, 500 mA current, and 5 mg L⁻¹ initial TCE concentration, removal efficacy using iron anodes (96%) is significantly higher than by mixed metal oxide (MMO) anodes (66%). Two types of cathodes (MMO and copper foam) in the presence of Pd/Al₂O₃ catalyst under various currents (250, 125, and 62 mA) were used to evaluate the effect of cathode materials on TCE removal efficacy. The similar removal efficiencies were achieved for both cathodes, but more precipitation generated with copper foam cathode (based on the experiments done by authors). In addition to the well-known parameters such as current density, electrode materials, and initial TCE concentration, the high velocities of groundwater flow can have important implications, practically in relation to the flush out of precipitates. For potential field application, a cost-effective and sustainable *in situ* electrochemical process using a solar panel as power supply is being evaluated.

Keywords

Pd; Electrolytic hydrodechlorination; TCE; High flow; Electrochemical

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1. Introduction

Chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene, and trichloroethane have been reported at 40% of Superfund sites in the United States (Wu et al., 2008). Industrial use of TCE, mainly for degreasing, and consequent improper release of the residue to the environment result in public health problems (Bakke et al., 2007; Chen et al., 2001; Mao et al., 2012a; Xie et al., 2013). Most chlorinated compounds can be transformed to non-toxic substances with various reductive biological (Lee and Batchelor, 2002), chemical (Stroo and Ward, 2010), or electrochemical processes (Chen et al., 2003; Mao et al., 2012a; Mao et al., 2011).

Since groundwater is electrochemically conductive and contains low-concentration of chlorinated compounds, in situ electrochemical remediation of TCE has attracted considerable interest. Both oxidation at the anode and reduction at the cathode have been reported for TCE transformation (Xie et al., 2013). The reductive conditions in the environment exert the main influence on the destruction process (Vodyanitskii, 2014). In other words, reduction is more preferable for TCE transformation. Cathodic reduction of chlorinated compounds has been investigated, as it is faster and more efficient than that by anodic oxidation (Mao et al., 2012a). In an electrolytic system, anode and cathode could play a key role by donating or accepting electrons, respectively. The main degradation mechanism at the cathode is hydrochlorination, which involves the interaction between atomic hydrogen formed at the cathode and the reducible chemical species (e.g. TCE) (Zheng et al., 2012). During hydrodechlorination, chlorine atoms are removed and carbon-hydrogen bonds are formed, as given by:

Atomic hydrogen formation depends on hydrogen-metal bond energy. The good hydrodechlorination catalyst should have strong bond with H to allow proton-electron transfer process but weak enough to ensure the bond breaking and the product release (e.g. Ag, Pt, Pd, Ni, Cu) (Brewster, 1954; Zheng et al., 2015). A variety of carbon materials (Al-Abed and Fang, 2006; Saez et al., 2010), elemental metal materials (Liu et al., 1999) have been investigated as cathodes for reduction of chlorinated compounds. It should be noted that the electrocatalytic activity of a cathode for hydrodechlorination, depends on cathode material. As an instance, Pd has shown superior capacity for adsorption and storage of H over other metals due to its relatively lower binding energy with H (Xie et al., 2013).

Furthermore, both anode and cathode materials influence the dechlorination rate (Mao et al., 2012b). An inert anode generates O_2 , which competes with contaminants for reactive hydrogen and limits the dechlorination rate. Iron anodes generate ferrous ions rather than

O₂, which support the reduction process (Eq. 4 and 5). Additionally, cathode materials that have longer service life and higher hydrogen evolution overpotential will improve the remediation efficiency (Mao et al., 2011). On the other hand, oxidation processes constitute efficient methods to remove organic pollutants from water and groundwater (Oturán and Aaron, 2014). They are mostly based on in situ production of strong oxidizing agents such as hydroxyl radicals ([•]OH) by means of electrochemical reactions to effectively decontaminate groundwater. [•]OH radicals could be generated directly by oxidation of water on a high O₂ evolution overvoltage anode (Panizza and Cerisola, 2009). Therefore, we investigate these variables using a combination of electrolytic reduction and Pd-catalytic hydrodechlorination. In the presence of Pd catalyst, the following reactions are expected (Gilbert et al., 2010; Yuan et al., 2013):

Although presence of ferrous ions leads to formation of a reducing environment, it also results in precipitates, which may gradually cover the surface of electrodes and decrease the removal rate of contaminants. Besides electrode materials, operation conditions such as flow rate, current, pH, and initial concentration of TCE will affect the transformation rate.

In field applications, the pumps that are used in wells generate flow rates higher than a gallon per minute (USEPA, 2005). Therefore, investigating the influence of high flow rates (on the order of liters per minute) on the efficiency of the transformation process is needed. In systems using the iron anode, the inevitable limitation of the iron performance is provided by the corrosion of zero-valent iron and deposition of minerals, which decrease the reductive capacity and clog the system (Vodyanitskii, 2014). It is assumed that the high flow rate would favor the transformation of contaminants since it would flush out precipitations and prevent clogging.

The main objective of this paper is to evaluate the effect of a high flow rate of 1 L min⁻¹ on the removal rate of TCE and precipitate formation. A circulated electrolytic system with various electrode materials (iron, copper, MMO) is used for degradation of aqueous TCE under the high flow rate.

2. Experimental Methods

2.1. Chemicals and Materials

Trichloroethylene (99.5%) was purchased from Sigma-Aldrich. Excess amounts of TCE were dissolved in deionized water (18 MΩ) produced by Millipore. This solution was used to prepare aqueous TCE solution during experiments. Palladium on alumina powder (1% wt. Pd, Sigma-Aldrich) with an average size of 3.2 mm was used as catalyst in flow-through

experiments. The electrodes were cast iron (Macmaster-Carr, USA), mixed metal oxide (MMO, mesh type, 3N International, USA), and copper foam (99.99%, 40 PPI, ERG, USA); all were 2 mm in thickness. Randomly distributed holes (4 mm in diameter) were drilled through the iron plate electrode for fluid flow.

2.2. Reactor

A vertical acrylic column (3.175 cm inner diameter 30 cm length)(Fig. SM-1) was used to simulate a continuously circulated system. The total volume of the column was 245 mL.

The following electrode arrangements were tested: a) two MMO electrodes as an anode and a cathode, b) a cast-iron anode and a MMO cathode, and c) a cast-iron anode and a copper foam cathode. The column was prefilled with 4-mm glass beads with a porosity of 0.65. There were no glass beads between the electrodes to facilitate mixing of the electrolytes and limit development of high resistance zone. 10 g of Pd/Al₂O₃ pellets were placed on the cathode surface to investigate the role of palladium pellets on the transformation rate. Experiments were also conducted using iron anode and copper foam cathode without Pd catalyst for comparison.

Simulated groundwater was prepared by mixing 142 mg Na₂SO₄ in a 2 L of deionized water (3 mM Na₂SO₄) along with addition of 2 mL of the saturated TCE stock solution to prepare a solution with 5 mg L⁻¹ initial concentration of TCE. The solution was pumped up through the column with a flow rate of 1 L min⁻¹ using a peristaltic pump (Masterflex, model 7720066). To minimize TCE losses due to adsorption, a glass tube and Viton pump tubing (Cole Parmer, USA) were used to connect all parts of the reactor. Effluent was returned to the source bottle to be re-circulated through the column. At specific time intervals, 1 mL of aqueous solution was collected from two sampling ports. Various currents; 500, 250, 125, and 62 mA were tested under the conditions of 1 L min⁻¹ flow rate and 5 mg L⁻¹ initial concentration of TCE. Prior to set up assembly, the iron anode was polished by sand paper while the cathode was immersed in diluted HCL solution (10 wt %) and rinsed with distilled water. All experiments were conducted at room temperature. Each set of experiments was repeated in triplicate to ensure reliability of the results.

2.3. Chemical analysis

Aqueous TCE concentration was measured by HPLC (1200 Infinity Series) equipped with a 1260 DAD detector. 1 mL samples were diluted immediately after filtration (0.2 µm filter, Milipore) with 1 mL of acetonitrile in a 2 mL vial for HPLC analysis. Oxidation-reduction potential (ORP) and pH probes recorded the effluent pH and ORP through the connection with the computer via the USB port. ORP and pH were measured by microprobes and recorded every 30 seconds. Final removal efficiency (FRE) of the aqueous TCE was determined using the following equation:

$$FRE = \frac{C_{aq(0)} - C_{aq(t)}}{C_{aq(0)}} \times 100 \%$$

Where $C_{aq(0)}$ and $C_{aq(t)}$ are the TCE concentration (mg L⁻¹) in the influent and effluent.

3. Results and Discussion

3.1. Effect of anode on dechlorination

MMO electrodes, in comparison with other types of electrodes such as iron, nickel, and copper, are more likely to retain their structure for a long-term operation; which is a key aspect of a successful remediation in the field (Peterson et al., 2007). However, using an inert anode generates oxygen gas, which competes with target contaminant for reaction with hydrogen. The reduction potential of O_2 (1.229 mV vs. SHE) (Bard and Faulkner, 2001) is higher than that of TCE (Wiedemeier et al., 1999) (0.42 V vs. SHE from TCE to cis-DCE). The performance of two types of anode, MMO and cast iron, under the same operation conditions (500 mA current and 1 L min^{-1} flow rate) is presented in Fig.1.

The overall removal efficiency by MMO and iron electrodes was 66% and 96%, respectively. Lower removal efficacy was achieved with the MMO anode due to the inevitable generation of O_2 , which limits the reductive transformation process. Higher ORP values (60 and 110 mV) appear in the electrolyte when MMO anode is used. These electrodes readily evolve oxygen and have low chemical activity for organics oxidation (Bagastyo et al., 2011). Using a cast iron anode improved the removal efficiency by 50% due to the development of a very reducing environment (-800 mV). However, ferrous ions generated from the iron anode precipitate in presence of hydroxyl.

3.2. TCE reduction on cathode

Copper and MMO cathodes were compared for electrochemical reduction of TCE with an iron anode. Table 1 summarizes the final removal efficiency of TCE hydrochlorination and the amount of precipitation for different electrode configurations and electric currents.

MMO cathodes with palladium pellets slightly improved the removal efficiency compared to the copper cathode. Under the lower currents (125 and 62 mA), the copper cathode produced more precipitates compared to the MMO cathodes. Based on the results, current can be reduced to 62 mA to decrease the amount of precipitation and avoid further problems in aquifer while maintaining satisfactory removal efficiency, and lowering the cost of energy applied.

Based on experimental results for a low flow rate system (1 mL min^{-1}), which is one order of magnitude slower under the same conditions which have been reported by the authors simultaneously to compare the lower flow rate system with the higher one, the removal efficiency is the same for both high and low flow rate (about 88%), while the amount of precipitation is nearly doubled under the lower flow rate (1265 mg under 1 mL min^{-1} flow rate compared to 756 mg under 1 L min^{-1} rate). Therefore, the influence of both current, which determines the supply of H_2 and the generation of Fe^{2+} , and flow rate, which flushes out the precipitates, should be optimized. Fig. 2a–c shows how various strategies affect the TCE removal rate under the different currents applied.

Higher current increases removal rates but causes production of more precipitation and (Table 1) requires higher energy consumption. Optimum conditions are required to obtain high removal efficiency with minimal impact on the aquifer. These experiments imply that

by dividing the current applied by half, the amount of precipitation decreased (Table 1). This means that it is viable to apply lower current to control the production of precipitates with the same removal efficiency.

Pd has a high hydrogen adsorption-dissociation capacity; it acts as a collector of hydrogen gas produced by cathodic hydrolysis of water. The active atomic H formed by dissociating H_2 effectively dechlorinates TCE. When MMO anode and MMO cathode were used and the amount of Pd pellets was doubled, the removal rate only improved by 10%. This small improvement compared with the added cost of Pd pellets could be addressed because of the MMO is a higher overpotential material, which produces hydrogen very slowly. On the other hand, the role of Pd as a hydrogen collector completely depends on the hydrogen release rate. It suggests that in larger scale application in the field, using an optimum amount of Pd with other operation conditions is necessary for efficient implementation. To sum up, as the precipitates could cover the surface of Pd over time, there needs to be more consistent and global effort to identify site characterization and groundwater physiochemical properties which could affect long-term reactivity of Pd pellets. Additionally, development of simple and cost-effective methods to recover Pd-pellets reactivity could be a significant challenge and further research will be required to improve the functionality of Pd-pellets as catalyst in electrochemical remediation systems.

3.3. pH and ORP changes

Fig. 3 shows ORP and pH changes under various electrode configurations while other parameters remain constant under a flow rate of 1 L min^{-1} and 250 mA.

The effluent ORP values continuously decrease to a very reducing environment when an iron anode is used. Anodic reaction under these conditions generates ferrous ions, which further react with hydroxyl to form $Fe(OH)_2$ and then uptake O_2 to produce $Fe(OH)_3$, thus providing a reducing condition. The most reducing environment (ORP close to -800 mV) took place with MMO cathode and Pd pellets were applied with an iron anode. In comparison, when copper cathode is used with palladium pellets, the similar ORP conditions appear but the rate differs. This is probably due to the difference between the hydrogen evolution potential of MMO and that of copper cathode. For materials with higher hydrogen evolution overpotential, such as silver, copper and lead (Halmann, 1993), the kinetics of hydrogen evolution (Eq. 3) may be relatively slow. Thus, TCE molecules have a better chance to acquire the atomic hydrogen from the cathode (Mao et al., 2012b).

The effect of current on pH and ORP is presented on Fig. 4. This figure shows changes resulting from the most effective electrode configuration, which is coupled of iron anode and MMO cathode plus palladium particles under different currents.

The higher current can accelerate the reaction rate within the reactor; therefore, an increase in current results in an imminent rise in pH and drop of ORP. Increasing the current provides more Fe , OH^- , and H^+ evolution and both anodic and cathodic reactions occur quickly. Moreover, as the electrical current is responsible for H_2 production, an increase in current generates more H_2 , resulting in more active H on the Pd surface and higher dechlorination rate.

4. Conclusions

This study demonstrates that a two-electrode system containing iron anode can effectively remove TCE in groundwater under a flow rate of 1 L min⁻¹. However, the amount of precipitation might be a limiting factor and should be controlled. The effects of electrode materials and current, on precipitation, pH and ORP are presented in the study. The best design for Pd-catalytic dechlorination of TCE includes iron anode, MMO cathode, and palladium due to the high removal efficacy attained with their combined use (96%, 92%, 90% and 84% when the current is 500, 250, 125 and 62 mA, respectively). Additionally, under low current (62 mA), fewer precipitates are produced. Implementing this system in the field requires considering other aspects. Proper evaluation of influent flow rate is required for equipment design. The groundwater flow rate is used for estimating the pump and treat operation conditions and contaminant loading. High flow rate systems utilize more supplies, which consume more energy and would be costly. However, there are always changes in parameters, especially, groundwater flow rate due to seasonal rainfall and the system should be sufficiently flexible to endure all these conditions. Although, this system is effective even under 62 mA, further research is required to identify possible strategies to address other potential barriers to dechlorination within aquifers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- Hydrodechlorination is an effective process to transform TCE in groundwater.
- The best design for Pd-catalytic dechlorination of TCE is iron anode, MMO cathode.
- High flow rate would favor the process since it would flush out precipitations.

Fig. 1. Effect of anode type on TCE degradation under the conditions of 500 mA current and 1 L min⁻¹ flow rate. This is a two-electrode design which both include MMO cathode and palladium pellets.

Fig. 2. Decay of the aqueous TCE concentration in the effluent under different electrode configurations. Curves refer to (a) iron anode-MMO cathode with Pd pellets, (b) iron anode, copper cathode including Pd pellets, and (c) iron anode, copper cathode without Pd pellets.

Fig. 3. Effluent pH and ORP changes under different electrode configurations. Experiments were conducted with 250 mA current and 1 L min⁻¹ flow rate.

Fig. 4.
Time profiles of electrolyte pH and ORP at different electrolysis currents.

Table 1

Effect of current on remediation efficiency and the amount of precipitation (1.5 Column)

Flow rate: 1 L min ⁻¹ - TCE initial Conc.: 5 mg L ⁻¹ -Running Time: 3 h			
	Current (mA)	Precipitation (mg)	Removal Rate (%)
Anode: Iron Cathode: MMO Catalyst: Pd	500	2390	96
	250	1264	92
	125	700	90
	62	381	84
Anode: Iron Cathode: Copper Catalyst: Pd	250	1101	96
	125	756	83
	62	419	82
Anode: Iron Cathode: Copper Catalyst: No Pd	250	945	43
	125	830	40
	62	419.5	41