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Electrochemical transformation of trichloroethylene in aqueous solution by electrode polarity reversal

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Abstract

Electrode polarity reversal is evaluated for electrochemical transformation of trichloroethylene (TCE) in aqueous solution using flow-through reactors with mixed metal oxide electrodes and Pd catalyst. The study tests the hypothesis that optimizing electrode polarity reversal will generate H₂O₂ in Pd presence in the system. The effect of polarity reversal frequency, duration of the polarity reversal intervals, current intensity and TCE concentration on TCE removal rate and removal mechanism were evaluated. TCE removal efficiencies under 6 cycles h⁻¹ were similar in the presence of Pd catalyst (50.3%) and without Pd catalyst (49.8%), indicating that Pd has limited impact on TCE degradation under these conditions. The overall removal efficacies after 60 min treatment under polarity reversal frequencies of 6, 10, 15, 30 and 90 cycles h⁻¹ were 50.3%, 56.3%, 69.3%, 34.7% and 23.4%, respectively. Increasing the frequency of polarity reversal increases TCE removal as long as sufficient charge is produced during each cycle for the reaction at the electrode. Electrode polarity reversal shifts oxidation/reduction and reduction/oxidation sequences in the system. The optimized polarity reversal frequency (15 cycles h⁻¹ at 60 mA) enables two reaction zones formation where reduction/oxidation occurs at each electrode surface.

Keywords

trichloroethylene; electrochemical; groundwater; polarity reversal

1. Introduction

Trichloroethylene (TCE), a toxic chlorinated solvent, has been widely used as a degreasing agent, dry cleaning solvent and chemical extraction agent. Inappropriate disposal of chlorinated solvents have caused widespread groundwater TCE contamination. TCE is listed by the US Environmental Protection Agency (US EPA) as a priority pollutant and with a

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Maximum Contaminant Limit of $5 \mu\text{g L}^{-1}$. Methods for removal of TCE from contaminated groundwater include biological transformation (e.g., Li et al. 2011, Semkiw and Barcelona 2011, Tiehm and Schmidt 2011), chemical oxidation (e.g., Teel et al. 2001, Yamazaki et al. 2001, Waldemer et al. 2007, Lee and Lee 2010, Tsai et al. 2011, Yue-hua et al. 2011, Yuan et al. 2012a) reduction by zero valent iron (e.g., Li et al. 2003, Liu et al. 2006, Philips et al. 2010, Petersen et al. 2012) and palladium-based materials (e.g., Lowry and Reinhard 2001, Ma et al. 2012, Lin et al. 2009, He et al. 2007, Wu and Richie 2006), photocatalytic degradation using TiO_2 catalyst (e.g., Che et al. 2011, Farooq et al. 2009) and ultrasonically enhanced oxidation (e.g., Rashid and Sato 2012, Ayyilidiz et al. 2007, Destailats et al. 2001). Although these methods have advantages, there are limitations including high operating cost, long reaction time, and incomplete removal or accumulation of toxic byproducts. Electrochemical transformation of dissolved organics has attracted a considerable interest due to the method's ability to control and manipulate groundwater redox conditions (e.g., Alshawabkeh and Sarahney 2005, Petersen et al. 2007, Li and Farrell 2008, Mishra et al. 2008, Alshawabkeh 2009, Gilbert et al. 2010, Scialdone et al. 2010, Mao et al. 2011, Lakshmipathiraj et al. 2012, Mao et al. 2012a, Mao et al. 2012b, Yuan et al. 2012, Yuan et al. 2013). Anode reactions can induce direct electrolytic oxidation of the target compound and water oxidation. Cathode reactions can induce direct electrolytic reduction of the target compounds and water reduction. Aqueous species can be oxidized or reduced at the electrodes depending on the half-reaction potentials and influence target contaminant degradation pathway and removal rates. Given the highly oxidized nature of TCE, reduction has been considered the preferred degradation mechanism. Therefore, most of the literature has focused on cathodic conversion of chlorinated aliphatic hydrocarbons to the corresponding de-halogenated hydrocarbons (e.g., Petersen et al. 2007, Li and Farrell 2008, Mishra et al. 2008, Mao et al. 2011, Mao et al. 2012a, Mao et al. 2012b). Different cathode (e.g., Petersen et al. 2007, Mao et al. 2012b) and anode materials (Mao et al. 2011) were investigated to improve TCE reduction. Palladized electrodes are reported to significantly improve electrochemical TCE reduction (e.g., Roh et al. 2001, Chen et al. 2003, Li and Farrell 2008).

A few studies focus on electrochemical oxidation for TCE removal (e.g., Yuan et al. 2012b, Lakshmipathiraj et al. 2012, Yuan et al. 2013). Several anodic materials have been tested for chlorinated hydrocarbons electrooxidation, such as Pt, Au, Ebonex®, PbO_2 , boron-doped diamond, graphite, SnO_2 , and mixed metal oxide (MMO) electrodes (e.g., Scialdone et al. 2008, Scialdone et al. 2010). Among the MMO electrodes, IrO_2 -based anodes, and in particular the binary system IrO_2 - Ta_2O_5 , are reported to exhibit good performance in anodic stability and electrocatalytic activity (e.g., Scialdone et al. 2008, Scialdone et al. 2009). TCE is oxidized on the MMO anode surface (above 0.84 V vs. SCE - saturated calomel electrode) according to the following reactions (Lakshmipathiraj et al. 2012),

However, oxygen evolution competes with TCE oxidation at the Ti/IrO₂-Ta₂O₅ electrode surface as given by (Panizza and Cerisola 2009),

Pd can catalyze the decomposition of H₂O₂ in weak acidic conditions to a strong oxidizing •OH radical (Reaction 6) (e.g., Yuan et al. 2012b, Yuan et al. 2013). Furthermore, Pd catalyst can be used to enable electro-Fenton process for TCE oxidation when pH < 4. This is achieved in a flow-through reactor by employing three electrodes with current splitting. Oxidation supported by Pd catalyst is given by,

Electrode polarity reversal is a technique that is based on defined time intervals of operation under reversed electrode polarity (e.g., Pazos et al. 2006, Luo et al. 2005). It has been investigated to control electrokinetic remediation of heterogeneous media. In groundwater treatment, the technique was used (in the presence of an additional electrode) to control electrode fouling due to CaO and CaCO₃ formation (e.g., Gilbert et al. 2010, Duarte et al. 1998). pH profile can be controlled by optimizing the electrode sequence and reversing polarity duration (Pazos et al. 2006). Both H₂ and O₂ could be generated in the Pd catalyst vicinity when changing the electrode polarity. While this process was used to control pH and chemical conditions, it was never evaluated for TCE removal from groundwater.

The objective of this study is to investigate and optimize TCE removal from groundwater using electrode polarity reversal. Two electrodes are used to support TCE removal in the presence of Pd catalysts (Equations 5, 6 and 8). H₂O₂ formation and acidic condition evolution in Pd vicinity were measured to test if polarity reversal could support Fenton reaction in Fe²⁺ presence. The effect of specific parameters including polarity reversal frequency, duration of intervals during polarity reversal, groundwater chemistry, current intensity and TCE concentration is evaluated.

2. Materials and methods

2.1 Chemicals and materials

All chemicals used in this study were analytical grade. TCE (99.5%) and cis-dichloroethylene (cis-DCE, 97%) were purchased from Sigma-Aldrich. H₂O₂ (30%) was

purchased from Fisher Sci. Calcium sulfate was purchased from JT Baker, oxalic acid (anhydrous, 98%) from Acros, sodium chloride and sodium bicarbonate from Fisher Scientific and hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethene, acetylene in nitrogen) from Supelco. Two mesh Ti/MMO electrodes (Ti/IrO₂-Ta₂O₅ -3N International) were used as cathode and anode. The electrodes consist of IrO₂ and Ta₂O₅ coating on titanium mesh with dimensions of 1.8 cm diameter and 1.8 mm thickness. Deionized water (18.0 MΩ·cm) obtained from a Millipore Milli-Q system was used in all the experiments. Palladium on alumina pellets (0.5% wt. Pd, Sigma-Aldrich) with average size of 3.2 mm was used.

2.2 Analytical methods

TCE and cis-DCE were measured by a 1200 Infinity Series HPLC (Agilent) equipped with a 1260 DAD detector and a Thermo ODS Hypersil C18 column (4.6 × 50 mm) as described in Mao et al. 2011. Dissolved hydrocarbon gases (DHGs) (ethane, ethene and methane) in aqueous solution were calculated according to Henry's law. The DHGs concentrations in gas phase were analyzed by SRI 310 GC with a FID detector (Mao et al. 2011). pH and oxidation-reduction potential (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 (≈0.2 mL). The amount of H₂O₂ produced in the Pd catalyst vicinity was analyzed at 405 nm after coloration with TiSO₄ (Eisenberg 1943).

2.3 Electrochemical flow-through reactor

The electrochemical set-up used for treatments with polarity reversal (PR) is shown in Figure 1. A vertical acrylic column (Ø=3.8 cm; H=10 cm) was used as the electrochemical flow-through column reactor. Sampling ports with 2.5 cm spacing were used (Figure 1). The total column volume was 113 mL. Two Ti/MMO electrodes (E1 and E2) were placed in the column with 2.5 cm spacing and were connected to a DC source. Original electrode polarity is defined with E1 as an anode and E2 as a cathode (A/C arrangement) and vice versa for reversed polarity (C/A arrangement). Each experiment started with reversed polarity (C/A arrangement). The PR was set to the desired frequency using a PR device (DPDT relay, Omron, H3CR-F8-300AC-100/240). A layer of glass beads was placed directly on E2 and a monolayer of Pd pellets (2 g) was placed (when used) on top of the glass beads. Glass beads ensure that Pd pellets do not impact the electro-initiated processes when E2 is employed as anode. The same amount of glass beads was used even when Pd catalyst was not used.

Synthetic TCE solution that represents contaminated groundwater was prepared by dissolving 0.413 g L⁻¹ sodium bicarbonate and 0.172 g L⁻¹ calcium sulfate in deionized water. The concentrations of bicarbonate ions and calcium ions are representative of groundwater from limestone aquifers, resulting in a conductivity range of 800-920 μS cm⁻¹. Excess TCE was dissolved into 18.0 MΩ·cm high-purity water to form a TCE saturated solution (1.07 mg mL⁻¹ at 20°C), which was used as stock solution for preparing aqueous TCE solutions. The temperature during the experiments was kept constant at 20°C. The flow resulted in Darcy's velocity of 0.25 cm min⁻¹ and was maintained constant by a peristaltic pump (Cole Parmer, Masterflex C/L). Prior to treatment, the column was flushed by the

equivalent of 2 column volumes of TCE solution. During treatments current intensity was kept constant by an Agilent E3612A DC power supply.

The testing conditions are given in Table 1. Polarity reversal frequency (PRF) describes the number of cycles with original and reversed electrode polarity within one hour. PRF values applied were calculated as follows:

$$PRF = \frac{60 \text{ min}}{t_0 + t_r} \quad (9)$$

where PRF is polarity reversal frequency (cycles h^{-1}), t_0 is duration of the original electrode polarity (min) and t_r is duration of the reversed electrode polarity (min). Polarity reversal intervals duration ratio (ID) is defined as the ratio of original and reversed polarity interval duration within one cycle:

$$ID = \frac{t_0}{t_r} \quad (10)$$

Values defined in Table 1 as 4/1 and 2/1 mean that A/C arrangement lasted 4 and 2 times longer than C/A, respectively, and for 1/2 and 1/4 C/A arrangement lasted 2 and 4 times longer, respectively.

Aqueous solution was sampled from P1, P2 and P3 sampling ports at defined time intervals, and immediately prepared for analysis. The experiments were conducted for 120 minutes and electrolysis steady state conditions were assumed when change in concentration is less than 0.5% per minute which accounts for other TCE losses, such as adsorption or volatilization. Control experiments without connection to a DC source were conducted to verify the effect volatilization and/or adsorption on TCE concentration. To ensure the reproducibility of the results, experiments were carried out in duplicates. To evaluate the influence of treatment duration on the electrode performance the same experiment was conducted after every 5 experiments (5 h of treatment in total). Long term performance was not evaluated. TCE removal rate was calculated according to following equation:

$$\% = \frac{C_0 - C_t}{C_0} * 100 \quad (11)$$

where c_0 is the initial TCE concentration (mg L^{-1}) and c_t is TCE concentration at defined time during treatment (mg L^{-1}).

3. Results and discussion

3.1 Influence of the polarity reversal frequency (PRF)

We tested different PRFs at a constant reversed polarity intervals ratio in the presence of Pd catalyst (Table 1). TCE removal rate during different PRFs is shown in Figure 2. Changes in pH and ORP in the effluent (P3) during experiments are shown in Table 2. The overall removal efficacies at steady state (after 60 min) when 6, 10, 15, 30 and 90 cycles h^{-1} were used are: 50.3%, 56.3%, 69.3%, 34.7% and 23.4%, respectively. H_2O_2 and acidic conditions (essential for hydroxyl radical formation via Reaction 7 in presence of Fe^{2+}) were expected

to appear in the system when optimizing the electrode polarity reversal. In the presence of hydrogen (H_2), Pd catalyzes TCE hydrodechlorination (e.g., Chen et al. 2003, Roh et al. 2001, Li and Farrell 2000). However, in the presence of O_2 , Pd catalyst supports Reaction (5) and/or Reaction (12). There was no H_2O_2 detected during the polarity reversal experiments in the presence of Pd catalyst, which indicates the subsequent reduction to H_2O according to Reaction (12) (Gilbert et al. 2010),

ORP values indicate that no sulfate reduction occurs and therefore inactivation of Pd catalyst was not expected during experiments.

TCE removal at steady state in the experiment with and without Pd catalyst (6 cycles h^{-1}) was 50.3% and 49.8%, respectively. This implies that Pd catalyst has no influence on TCE removal efficiency but that different mechanisms will cause TCE removal during electrode polarity reversal. No significant differences were detected in removal efficacies at each sampling port (Figure 3).

TCE removal rate increased with increasing frequency from 6, 10 and 15 cycles h^{-1} and then decreased at 30 and 90 cycles h^{-1} (Figure 2). With increasing the PRF, the polarity duration and time for reactions decrease during one cycle. In this case, 15 cycles h^{-1} produced the best performance, which is similar to that achieved by the electro Fenton reaction in Pd presence without polarity reversal as described in Yuan et al. 2013. For the 30 and 90 cycles h^{-1} , each current interval lasted 60 s and 20 s, respectively. The current interval determines the amount of charge evolved for reduction and oxidation during one cycle. The charge produced within one cycle at the electrode surface influences the removal. According to the results it can be assumed that 60 s and 20 s intervals are not sufficient to evolve conditions on the electrode that favor the reaction. The results under 30 cycles h^{-1} and 90 mA prove that TCE removal is limited by the amount of charge that will evolve by electric current interval (60 s) relative to the advective solution flow rate.

The removal rates in for 30 cycles h^{-1} carried under 60 mA and 90 mA were 34.7% and 69.2%, respectively. Comparing the results for the same charge and frequency but different current (60 min for 60 mA and 40 min for 90 mA), TCE removal was 37.8% and 46.4%, respectively. This supports the conclusion on the influence of the charge evolution (which can be controlled by intervals duration or applied current intensity) and therefore the removal rate. Optimizing the duration of each polarity interval should include time to evolve enough charge for reactions and time for TCE sorption/interaction with electrode surface. Following this analysis, 6 cycles h^{-1} is used to measure the influence of ID on TCE removal rate.

We hypothesize that optimizing the electrode polarity reversal would result in optimal pH for hydroxyl radical formation via Reaction 7. During the course of each treatment, effluent pH values slightly decreased (Table 2). H^+ and OH^- ions produced at the electrodes are neutralized by either direct oxidation or reduction at the electrode opposite in polarity and/or by their reaction to form H_2O . The ORP did not significantly change in the system during

treatment. While Pd catalyst was placed on E2 during treatment to catalyze the H_2O_2 formation, Pd apparently catalyzed Reaction (12) since no H_2O_2 was detected.

3.2 Influence of the interval duration (ID)

The influence of the original and reversed electrode polarity intervals duration ratio (ID) on TCE removal rate was investigated. Changes in TCE removal rate in the system at steady state when different IDs were used under 6 cycles h^{-1} are presented in Figure 4. The final TCE removal after 1/1, 2/1, 4/1, 1/2 and 1/4 ID's are 50.3%, 31.7%, 35.3%, 52.7% and 56.8%, respectively. The ID appears to influence TCE removal which is related to duration of A/C and C/A electrode arrangements. In flow-through systems, the A/C arrangement allows substances from the influent to be directly or indirectly oxidized at the anode and then reduced at the cathode. C/A electrodes arrangement allows first reduction at the cathode followed by oxidation at the anode. As TCE is a highly oxidized substance, reduction is the preferred degradation pathway. Since C/A allows reduction first this arrangement improves TCE removal. According to the results, the higher duration of C/A arrangement results in an increase in removal rate. The removal rate during tested IDs did not overcome the one gained with C/A arrangement alone (54.5%).

3.3 Influence of the electrodes arrangements

Experiments with A/C and C/A arrangement were conducted to determine the contribution of different electrode arrangements on the reversed electrode polarity performance and to understand possible mechanism of TCE removal. A similar approach was used to investigate the electrochemical degradation of aqueous phase energetic compounds (Gilbert and Sale 2005) and 1,2-dichloroethane and 1,1,2,2-tetrachloroethane (Scialdone et al. 2010). The removal rates achieved for the target chemicals (hexahydro-1,3,5-trinitro-1,3,5-triazine and 2,4,6-trinitrotoluene) in the reduction-oxidation sequence were less than those of oxidation-reduction (Gilbert and Sale 2005). The combined oxidation and reduction of 1,1,2,2-tetrachloroethane in the divided and undivided cells (Scialdone et al. 2010) resulted in higher concentration reduction than what was obtained under the same amount of charge compared to oxidation or reduction alone. The overall TCE removal after A/C only, C/A only and polarity reversal under 15 cycles h^{-1} were 34.8%, 54.5% and 69.3%, respectively. The changes in TCE concentration during these experiments and 15 cycles h^{-1} PRF in the effluent (P3) are presented in Figure 5a.

Degradation products were measured to understand TCE removal mechanisms. Chloride is a typical degradation product during degradation of TCE. Formation of chlorinated intermediates indicates that reductive dechlorination is the primary degradation mechanism. No chlorinated intermediates were detected during A/C, C/A and 15 cycles h^{-1} at any sampling port. No other halogenated products were detected at the end of the electrolyses when the combined process was performed in an undivided cell in the case of 1,1,2,2-tetrachloroethane (Scialdone et al. 2010). Although MMOs are active types of electrodes (low oxygen overpotential), the oxidation of organic substances at the anode was reported (Scialdone et al. 2008, Lakshmipathiraj et al. 2012). Oxygen formed during the A/C arrangement is driven toward P3 which influences the removal mechanism at the cathode due to the possible formation of hydroxyl radicals and O^{-}_2 (Sawyer and Valentine 1981).

Although it was reported (Li and Farrell 2001) that dissolved oxygen has no effects on the rates of TCE or carbon tetrachloride reduction at the palladized cathode, the formation of hydroxyl radicals and O_2^- at the cathode will contribute to the degradation. Because of the potential for formation of the reactive oxygen species, we concluded that mostly oxidation of TCE occurs in the system when the A/C arrangement is used because of the absence of chlorinated degradation products. After 10 min during the A/C treatment, more than 99% of TCE removed at P2 was in the form of oxalic acid. Figure 5b shows the measured and theoretical mass of chlorides evolved during the course of TCE removal. Continuous release of chlorides is noted during the A/C arrangement.

TCE removal rates by the C/A arrangement are higher than the removal rates by the A/C arrangement (Figure 5). TCE reduction on the cathode contributes to the removal rate in the C/A arrangement. The absence of chlorinated byproducts is due to anodic oxidation (Scialdone et al. 2008, Scialdone et al. 2010, Lakshmipathiraj et al. 2012). The highest removal percentage occurs after 10 min of treatment in both polarity reversal and C/A arrangements.

For polarity reversal under 15 cycles h^{-1} , oxalic acid was detected at P1 after 40 min indicating different removal mechanisms than those for the A/C arrangement. Mass balance calculations show measurement of 93% of the theoretically calculated chlorides in the polarity reversal experiments (15 cycle h^{-1}).

According to the results, there is an optimum frequency for TCE removal by polarity reversal. Using 15 cycles h^{-1} exceeds TCE removal achieved after A/C and C/A arrangements. With 15 cycles h^{-1} , polarity durations are sufficient to optimize both reduction and oxidation on each electrode. By optimizing the frequency, each electrode provides the required reaction zone during each cycle for TCE transformation by both reduction and oxidation. In a two-electrode system with optimum polarity reversal frequency, two reaction zones are active for TCE transformation.

Given the volatile nature of TCE and its degradation products, it is likely that gas stripping could contribute to the process due to electro-generated gas bubbles that are uniformly dispersed in the solution (Emamjomeh and Siwakumar 2009). Although it was not feasible to assess the impact of gas formation on TCE removal, it is assumed that the volume of gas generated is the same under applied current, regardless of electrode arrangement and configuration.

3.4 Influence of current intensity

Current intensity influences TCE transformation rates (Figure 6). The final TCE removal rates after 30, 60, 90 and 120 mA (6 cycles h^{-1}) are: 41.2%, 50.3%, 71.9% and 60.9%, respectively. Applying 120 mA decreased TCE removal rate. Ti/IrO₂-Ta₂O₅ electrode is an active type of anode (Panizza and Cerisola 2009) and higher current results in higher hydroxyl radical coverage and formation of oxides on IrO₂ surface that support both target contaminant oxidation and oxygen evolution reactions (Huitle 2004, Lakshmipathiraj et al. 2012). Applying 120 mA decreased the removal rate since gas bubbles covering the

electrode lowers the effective electrode surface area (Wuthrich et al. 2005). This also indicates that the role of gas stripping is limited on the process.

Since electrode polarity reversal has a significant effect on the service life of the MMO electrodes, the electrode performance was evaluated. The changes of final TCE removal after evaluation tests were less than 5%.

3.5 Influence of initial TCE concentration

Initial TCE concentration influence on removal rates when using 6 cycles h^{-1} PRF is shown in Figure 7. Removal rates of 62.7%, 50.3% and 23.6% were achieved for samples with initial TCE concentrations of 2.2 ppm, 5.3 ppm and 10.7 ppm, respectively. Similar amounts of TCE were removed for initial TCE concentrations of 5.3 ppm and 10.7 ppm due to the constant amount of charge that evolves at a constant current intensity.

3.6 Power requirements

The electrochemical treatments require relatively low power levels (e.g., 10 W m^{-2}) compared to other electrically based remediation technologies, such as thermal heating (Gilbert and Sale 2005). The power consumption for similar processes was in the range $1\text{--}35 \text{ W m}^{-2}$ (Gilbert and Sale 2005) and for the optimized polarity reversal technology tested in this study was 13 W m^{-2} . The results indicate that the energy requirements for field scale applications would be low. Additionally, the electrode polarity reversals are necessary during a field application of electrochemical treatments to prevent electrode fouling. The polarity reversal approach may provide an effective electrochemical treatment for TCE removal in terms of maintenance and treatment cost.

4. Conclusions

The electrode polarity reversal technique was investigated to improve treatment of TCE contaminated groundwater in flow-through system. Mixed metal electrodes were used and Pd catalyst was employed to catalyze H_2O_2 formation. However, the results show that TCE degradation mechanism during polarity reversal is not affected by the presence of Pd catalyst.

TCE removal rates by the C/A arrangement (54.5%) are significantly higher than the removal rates by the A/C arrangement (34.8%) since the C/A arrangement induce the reduction of TCE (favorable degradation pathway). The optimized polarity reversal increase TCE removal rates by 99% when compared to constant A/C and 27% compared to C/A (no polarity reversal approach). The higher duration of C/A arrangement during polarity reversal increase TCE removal rate.

Decreasing the duration of polarity reversal (increasing frequency) increases TCE removal efficacy by allowing sufficient oxidation/reduction (anode/cathode arrangement) and reduction/oxidation (cathode/anode arrangement) sequence shifts in the system, as long as the intervals duration are long enough to produce sufficient charge for the reaction. The optimum polarity reversal frequency in this study (15 cycles h^{-1} under 60 mA) enables two

reaction zones formation in the system where reduction/oxidation occur at each electrode surface.

The power consumption for the transformation of TCE by polarity reversal is comparable to the energy requirements for the electrochemical treatments without polarity reversal.

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References

- Alshawabkeh AN. Electrokinetic soil remediation: Challenges and opportunities. *Separation Science and Technology*. 2009; 44(10):2171–2187.
- Alshawabkeh AN, Sarahney H. Effect of current density on enhanced transformation of naphthalene. *Environmental Science and Technology*. 2005; 39(15):5837–5843. [PubMed: 16124323]
- Ayyildiz O, Peters RW, Anderson PR. Sonolytic degradation of halogenated organic compounds in groundwater: Mass transfer effects. *Ultrasonic Sonochemistry*. 2007; 14(2):163–172.
- Che H, Bae S, Lee W. Degradation of trichloroethylene by Fenton reaction in pyrite suspension. *Journal of Hazardous Materials*. 2011; 185(2-3):1355–1361. [PubMed: 21071138]
- Chen G, Betterton EA, Arnold RG, Ela WP. Electrolytic reduction of trichloroethylene and chloroform at a Pt/Pd-coated ceramic cathode. *Journal of Applied Electrochemistry*. 2003; 33:161–169.
- Destailhats H, Alderson TW, Hoffmann MR. Applications of ultrasound in NAPL remediation: Sonochemical degradation of TCE in aqueous surfactant solutions. *Environmental Science and Technology*. 2001; 35(14):3019–3024. [PubMed: 11478257]
- Duarte HA, Jha K, Weidne JW. Electrochemical reduction of nitrates and nitrites in alkaline media in the presence of hexavalent chromium. *Journal of Applied Electrochemistry*. 1998; 28:811–817.
- Eisenberg G. Colorimetric determination of hydrogen peroxide. *Industrial and Engineering Chemistry*. 1943; 15(5):327–328.
- Emamjomeh MM, Sivakumar M. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *Journal of Environmental Management*. 2009; 90(5):1663–1679.
- Farooq M, Raja IA, Pervez A. Photocatalytic degradation of TCE in water using TiO₂ catalyst. *Solar Energy*. 2009; 83(9):1527–1533.
- Gilbert DM, Sale TC. Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds. *Environmental Science and Technology*. 2005; 39(23):9270–9277. [PubMed: 16382952]
- Gilbert, DM.; Sale, T.; Petersen, MA. Electrolytic reactive barriers for chlorinated solvent remediation.. In: Stroo, HF.; Ward, CH., editors. *In situ remediation of chlorinated solvent plumes*. Springer Science+Business Media, LLC; 2010. p. 573-590.
- He F, Zhao D, Liu J, Roberts CB. Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Industrial and Engineering Chemistry Research*. 2007; 46(1):29–34.
- Huitle, CAM. Ph.D. Dissertation. University of Ferrara; Italy: 2004. Direct and indirect electrochemical oxidation of organic pollutants..
- Lakshminathiraj P, Bhaskar Raju G, Sakai Y, Takuma Y, Yamasaki A, Kato S, Kojima T. Studies on electrochemical detoxification of trichloroethene (TCE) on Ti/IrO₂-Ta₂O₅ electrode from aqueous solution. *Chemical Engineering Journal*. 2012; 199:211–218.
- Lee Y, Lee W. Degradation of trichloroethylene by Fe(II) chelated with cross-linked chitosan in a modified Fenton reaction. *Journal of Hazardous Materials*. 2010; 178(1-3):187–193. [PubMed: 20129729]

- Li F, Vipulanandan C, Mohanty KK. Microemulsion and solution approaches to nanoparticle iron production for degradation of trichloroethylene. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2003; 223(1-3):103–112.
- Li J, Lei C, Dong S, Shim H. Bioremediation of mixed wastes (BTEX, TPH, TCE, and cis-DCE) contaminated water. *Journal of Hazardous, Toxic and Radioactive Waste*. 2011; 15(Special Issue): 160–165.
- Li T, Farrell J. Reductive dechlorination of trichloroethene and carbon tetrachloride using iron and palladized-iron cathodes. *Environmental Science and Technology*. 2000; 34(1):173–179.
- Lin CJ, Liou YH, Lo SL. Supported Pd/Sn bimetallic nanoparticles for reductive dechlorination of aqueous trichloroethylene. *Chemosphere*. 2009; 74(2):314–319. [PubMed: 18992911]
- Liu CC, Tseng DH, Wang CY. Effects of ferrous ions on the reductive dechlorination of trichloroethylene by zero-valent iron. *Journal of Hazardous Materials*. 2006; 136(3):706–713. [PubMed: 16504392]
- Lowry G, Reinhard M. Pd-catalyzed TCE dechlorination in water: Effect of H₂ (aq) and H₂-utilizing competitive solutes on the TCE dechlorination rate and product distribution. *Environmental Science and Technology*. 2001; 35(4):696–702. [PubMed: 11349280]
- Luo Q, Zhang X, Wang H, Qian Y. The use of nonuniform electrokinetics to enhance in situ bioremediation of phenol-contaminated soil. *Journal of Hazardous Materials*. 2005; 121(1-3):187–194. [PubMed: 15885421]
- Ma H, Huang Y, Shen M, Guo R, Cao X, Shi X. Enhanced dechlorination of trichloroethylene using electrospun polymer nanofibrous mats immobilized with iron/palladium bimetallic nanoparticles. *Journal of Hazardous Materials* 211. 2012; 212:349–356.
- Mao XH, Ciblak A, Amiri M, Alshawabkeh AN. Redox control for electrochemical dechlorination of trichloroethylene in bicarbonate aqueous media. *Environmental Science and Technology*. 2011; 45(15):6517–6523. [PubMed: 21671641]
- Mao XH, Ciblak A, Baek K, Amiri M, Loch-Carusio R, Alshawabkeh AN. Optimization of electrochemical dechlorination of trichloroethylene in reducing electrolytes. *Water Research*. 2012a; 46(6):1847–1857. [PubMed: 22264798]
- Mao XH, Yuan SH, Fallahpour N, Ciblak A, Howard J, Padilla I, Loch-Carusio R, Alshawabkeh AN. Electrochemically induced dual reactive barriers for transformation of TCE and mixture of contaminants in groundwater. *Environmental Science and Technology*. 2012b; 46(21):12003–12011. [PubMed: 23067023]
- Mishra D, Liao Z, Farrell J. Understanding reductive dechlorination of trichloroethene on boron-doped diamond film electrodes. *Environmental Science and Technology*. 2008; 42(24):9344–9349. [PubMed: 19174914]
- Panizza M, Cerisola G. Direct and mediated anodic oxidation of organic pollutants. *Chemical Reviews*. 2009; 109:6541–6569. [PubMed: 19658401]
- Pazos M, Sanroman MA, Cameselle C. Improvement in electrokinetic remediation of heavy metal spiked kaolin with the polarity exchange technique. *Chemosphere*. 2006; 62(5):817–822. [PubMed: 15970309]
- Petersen EJ, Pinto RA, Shi X, Huang Q. Impact of size and sorption on degradation of trichloroethylene and polychlorinated biphenyls by nano-scale zerovalent iron. *Journal of Hazardous Materials*. 2012; 243:73–79. [PubMed: 23122190]
- Petersen MA, Sale TC, Reardon KF. Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes. *Chemosphere*. 2007; 67(8):1573–1581. [PubMed: 17234239]
- Phillips DH, Van Nooten T, Bastiaens L, Russell MI, Dickson K, Plant S, Ahad JME, Newton T, Elliot T, Kalin RM. Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. *Environmental Science and Technology*. 2010; 44(10):3861–3869. [PubMed: 20420442]
- Rashid MM, Sato C. Degradation of trichloroethylene and tetrachloroethylene in simulated groundwater in a flow-through photosono reactor. *Journal of Environmental Engineering*. 2012; 138(12):1179–1185.

- Roh Y, Cho KS, Lee S. Electrochemical remediation of trichloroethene-contaminated groundwater using palladized iron oxides. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*. 2001; 36(6):923–933.
- Sawyer DT, Valentine JS. How super is superoxide? *Accounts of Chemical Research*. 1981; 14:393–400.
- Scialdone O, Galia A, Filardo G. Electrochemical incineration of 1,2-dichloroethane: Effect of the electrode material. *Electrochimica Acta*. 2008; 53(24):7220–7225.
- Scialdone O, Galia A, Gurreri L, Randazzo S. Electrochemical abatement of chloroethanes in water: Reduction, oxidation and combined processes. *Electrochimica Acta*. 2010; 55(3):701–708.
- Scialdone O, Randazzo S, Galia A, Filardo G. Electrochemical oxidation of organics at metal oxide electrodes: The incineration of oxalic acid at IrO₂–Ta₂O₅ (DSA–O₂) anode. *Electrochimica Acta*. 2009; 54(4):1210–1217.
- Semkiw ES, Barcelona MJ. Field study of enhanced TCE reductive dechlorination by a full-scale whey PRB. *Ground Water Monitoring and Remediation*. 2011; 31(1):68–78.
- Teel AL, Warberg CR, Atkinson DA, Watts RJ. Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Research*. 2001; 35(4):977–984. [PubMed: 11235893]
- Tiehm A, Schmidt KR. Sequential anaerobic/aerobic biodegradation of chloroethenes-aspects of field application. *Current Opinion in Biotechnology*. 2011; 22(3):415–421. [PubMed: 21377349]
- Tsai TT, Kao CM, Wang JY. Remediation of TCE-contaminated groundwater using acid/BOF slag enhanced chemical oxidation. *Chemosphere*. 2011; 83(5):687–692. [PubMed: 21377186]
- Waldemer R, Tratnyek PG, Johnson RL, Nurmi JT. Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products. *Environmental Science and Technology*. 2007; 41(3):1010–1015. [PubMed: 17328217]
- Wu L, Ritchie SMC. Removal of trichloroethylene from water by cellulose acetate supported bimetallic Ni/Fe nanoparticles. *Chemosphere*. 2006; 63(2):285–292. [PubMed: 16226292]
- Wuthrich R, Comninellis Ch, Bleuler H. Bubble evolution on vertical electrodes under extreme current densities. *Electrochimica Acta*. 2005; 50:5242–5246.
- Yamazaki S, Matsunaga S, Hori K. Photocatalytic degradation of trichloroethylene in water using TiO₂ pellets. *Water Research*. 2001; 35(4):1022–1028. [PubMed: 11235867]
- Yuan B, Chen Y, Fu ML. Degradation efficiencies and mechanisms of trichloroethylene (TCE) by controlled-release permanganate (CRP) oxidation. *Chemical Engineering Journal*. 2012a; 192:276–283.
- Yuan SH, Chen MJ, Mao XH, Alshawabkeh AN. A three-electrode column for Pd-catalytic oxidation of TCE in groundwater with automatic pH-regulation and resistance to reduced sulfur compound foiling. *Water Research*. 2013; 47(1):269–278. [PubMed: 23121896]
- Yuan SH, Mao XH, Alshawabkeh AN. Efficient degradation of TCE in groundwater using Pd and electro-generated H₂ and O₂: A shift in pathway from hydrodechlorination to oxidation in the presence of ferrous ions. *Environmental Science and Technology*. 2012b; 46(6):3398–3405. [PubMed: 22315993]
- Yue-hua Z, Chun-Mei X, Chang-Hong G. Application sodium percarbonate to oxidative degradation trichloroethylene contamination in groundwater. *Procedia Environmental Sciences*. 2011; 10(B): 1668–1673.

Highlights

- Polarity reversal frequency influences trichloroethylene removal
- Intervals duration needs to provide sufficient charge for the reactions
- Optimized polarity reversal frequency enables two reaction zones in the system

Figure 1. Electrochemical flow-through reactor: (1) DC source; (2) PR device; (3) synthetic groundwater reservoir, (4) peristaltic pump and (5) effluent; E1, E2 and E3 are MMO mesh electrodes; P0, P1, P2 and P3 are sampling ports.

Figure 2.
Changes in TCE concentration values during treatments with different PRF

Figure 3.
Changes in TCE concentration at different sampling ports at steady state (60 min) after treatments with different PRF

Figure 4.
Changes in TCE concentration during treatments with different PR intervals duration

Figure 5. Changes in a) TCE concentration and b) normalized chloride content in solution during treatments with different electrode arrangements

Figure 6.
Changes in TCE concentration with different current intensities

Figure 7.
Changes in TCE concentration during treatments with different initial TCE concentrations

Table 1

Experimental conditions

Variable	Unit	Values	Conditions
PRF	cycles h ⁻¹	6 ^a ; 10; 15; 30; 90	1/1, 5.3 ppm TCE, 60 mA
PR	-	A/C; C/A; 3 electrodes	5.3 ppm TCE, 60 mA
ID	-	4/1; 2/1; 1/2; 1/4	5.3 ppm TCE, 6 cycles h ⁻¹ , 60 mA
Current intensity	mA	30; 90; 120	1/1, 5.3 ppm TCE, 6 cycles h ⁻¹
TCE concentration	ppm	2.2; 10.7	1/1, 6 cycles h ⁻¹ , 60 mA

^a was also tested without Pd catalyst

Table 2

Changes in pH and ORP in the effluent (P3) at steady state (60 minutes)

Experiments	pH	ORP (mV)
Initial	8.0±0.3	235±5
6 cycles h ⁻¹	7.2	211
10 cycles h ⁻¹	7.7	144
15 cycles h ⁻¹	7.0	178
30 cycles h ⁻¹	7.2	184
90 cycles h ⁻¹	6.4	172
A/C	7.6	214
C/A	8.1	140
2/1	6.8	230
4/1	6.4	210
1/2	7.1	199
1/4	7.4	223
30 mA	7.2	173
90 mA	7.4	151
120 mA	8.1	141