Published in final edited form as:

Water Res. 2012 April 15; 46(6): 1847–1857. doi:10.1016/j.watres.2012.01.002.

Optimization of electrochemical dechlorination of trichloroethylene in reducing electrolytes

Xuhui Mao¹, Ali Ciblak¹, Kitae Baek^{1,2}, Mohammad Amiri¹, Rita Loch-Caruso³, and Akram N. Alshawabkeh^{1,*}

¹Civil and Environmental Engineering Department, Northeastern University, Boston, MA, 02115

²Environmental Engineering Department, Kumoh National Institute of Technology, Republic of Korea

³Environmental Health Sciences Department, School of Public Health, University of Michigan, Ann Arbor, MI 48109-2029

Abstract

Electrochemical dechlorination of trichloroethylene (TCE) in aqueous solution is investigated in a closed, liquid-recirculation system. The anodic reaction of cast iron generates ferrous species, creating a chemically reducing electrolyte (negative ORP value). The reduction of TCE on the cathode surface is enhanced under this reducing electrolyte because of the absence of electron competition. In the presence of the iron anode, the performances of different cathodes are compared in a recirculated electrolysis system. The copper foam shows superior capability for dechlorination of aqueous TCE. Electrolysis by cast iron anode and copper foam cathode is further optimized through a multivariable experimental design and analysis. The conductivity of the electrolyte is identified as an important factor for both final elimination efficiency (FEE) of TCE and specific energy consumption. The copper foam electrode exhibits high TCE elimination efficiency in a wide range of initial TCE concentration. Under coulometric conditions, the optimal conditions to achieve the highest FEE are 9.525 mm thick copper foam electrode, 40 mA current and 0.042 mol L⁻¹ Na₂SO₄. This novel electrolysis system is proposed to remediate groundwater contaminated by chlorinated organic solvents, or as an improved iron electrocoagulation process capable of treating the wastewater co-contaminated with chlorinated compounds.

Keywords

Electrochemical dechlorination; TCE; iron anode; foam electrode; optimization

1. Introduction

Chlorinated solvents, such as trichloroethylene (TCE), tetrachloroethylene (PCE), trichloroethane and methylene chloride, are common contaminants at sites in the United States (Bakke et al. 2007). Many technologies have been developed for in situ and ex situ

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*Corresponding author: Civil and Environmental Engineering Department, Northeastern University, 400 Snell Engineering, 360 Huntington Avenue, Boston, MA 02115, Tel: 617-373-3994, aalsha@neu.edu.

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treatment of these compounds because they are toxic and are suspect human carcinogens (Bakke et al. 2007, Stroo and Ward 2010). Due to the electronegative character of chlorine substituents, most of the chlorinated solvent molecules can be effectively transformed via reductive pathways that are typically achieved by electrochemical (Chen et al. 2003, Li and Farrell 2000), chemical or biological processes (Henry et al. 2003, Lee and Batchelor 2002, Stroo and Ward 2010). Reductive dechlorination by zero valent iron (ZVI) is an example of an electrochemical redox system that has been widely implemented for transformation of chlorinated hydrocarbons (Wilkin et al. 2003, Zhang 2003). This system can be considered to consist of numerous short-circuited, micro-scale electrochemical primary cells. Dechlorination of chlorinated solvents molecules can spontaneously occur on the surface of iron because of its reductive potential. Direct electrolytic reduction is another effective process that uses cathodic reduction to achieve dechlorination. Unlike ZVI system, it provides several advantages for reductive dechlorination because of controlled reductive kinetics and absence of passivation of iron (Liu et al. 1999). Direct electrolytic reduction of chlorinated solvents has been investigated over recent years. Carbon tetrachloride (Li and Farrell 2000, Liu et al. 1999), PCE (Saez et al. 2010), TCE (Chen et al. 2003, Li and Farrell 2000), trichloroethane (Scialdone et al. 2010a) and other chlorinated hydrocarbons (Sonoyama and Sakata 1999) have been investigated as targets of electrolytic reduction in aqueous solution.

Based on thermodynamics data (Wiedemeier et al. 1999), most of chlorinated solvents appear to be susceptible for electrolytic reduction since their standard redox potentials are mostly within the electrochemical window of water decomposition. However, because electrochemical processes always involve mass-transfer of target compounds and the concentration of chlorinated solvents in groundwater is relatively low, the efficiency of direct electrolytic reduction requires improvement for field implementation. Several methods have been investigated to promote the current efficiency or dechlorination rate in electrolytic reduction systems, including (i) using high-performance electrodes and electrolysis cells, (ii) optimization of the operating conditions of the cell, and (iii) application in combination with other remediation processes. Investigating materials with specific electrocatalytic performances for transformation of chlorinated compounds is a routine topic. A variety of carbon materials (Al-Abed and Fang 2006, Saez et al. 2010), elemental metal materials (Liu et al. 1999) and metalized materials (Sonoyama and Sakata 1999) have been investigated as cathode for reduction of chlorinated compounds. Silver is recognized as the best electrocatalytic material, showing less overpotential than other non-catalytic materials for electro-reductive dechlorination of aliphatic chlorides (Rondinini et al. 2009, Scialdone et al. 2010b, Sonoyama and Sakata 1999). Using three-dimensional (3D) electrodes is another approach that was proposed to improve dechlorination rate. Metal foam (He et al. 2004) and metalized carbon fiber electrodes (Sonoyama and Sakata 1999) have shown enhanced dechlorination rate due to their high specific area with respect to 2D electrodes. In addition, improving the cell design can enhance mass transfer, achieve more uniform distribution of current, and decrease the specific energy consumption. Novel cells have been proposed, such as multi-phase iron oxide-packed column cells (Roh et al. 2001), concentric 3D copper reactors (He et al. 2004), and granular graphite-packed reactor (Al-Abed and Fang 2006), and result in improved transformation.

Operational conditions also impact the performance of an electrolytic reduction system. In addition to the well-known parameters, such as current density, electrode potential and flow-rate of electrolyte, the composition of electrolyte influences dechlorination kinetics at different extents. For example, oxidizing components, e.g. dissolved oxygen (DO) (Mao et al. 2011, Petersen et al. 2007) and nitrate ions (Al-Abed and Fang 2006), could decrease the TCE transformation rate via electron and proton competition. To increase the efficiency of dechlorination, investigators attempted to combine electrolytic reduction with other process.

Because aqueous aliphatic chlorides can be destroyed by some high performance anodes, such as boron doped diamond (BDD) (Carter and Farrell 2009, Scialdone et al. 2010a), integrating transformation at the anode and the cathode has been proven effective for the degradation of aqueous chloroethanes and PCE (Saez et al. 2009, Scialdone et al. 2010a). Electrochemically assisted bioaugmentation are also reported for transformation of chlorinated ethenes (Aulenta et al. 2009).

The electrolytic transformation literature mostly focuses on cathodic reactions. Anodic reactions generate oxidizing condition that does not facilitate the reductive dechlorination of chlorinated hydrocarbons. The most frequent applications use ion exchange membrane or glass frit to spatially separate the anodic and cathodic reaction zone in order to preventing the negative influence of the anodic oxidation on reductive transformation. However a separated cell design for in-situ or ex-situ treatment of chlorinated solvent groundwater results in several challenges from a practical prospective. A separated cell design will be complex, costly and will require higher energy consumption and maintenance problems. This study evaluates a novel electrochemical reduction system that combines the use of reactive iron anode and high specific surface area cathode in an undivided or mixed cell. Iron electrolysis has been extensively applied in wastewater treatment for the removal of a variety of pollutants, such as oil grease, suspended matter, heavy metal ions (Emamjomeh and Sivakumar 2009). Our work (Mao et al., 2011) demonstrated the enhancing effect of iron anode on dechlorination of TCE in batch experiments. The advantage of the iron anode is that it leads to the development of a reducing environment in the mixed electrolyte that enhances direct transformation of chlorinated ethenes on the cathode (Mao et al. 2011). While batch experiments demonstrate enhanced transformation, the significance of the enhancement under flow conditions is not clear. The objective of this study is to further investigate the validity of iron electrolysis under circulation condition, and optimize the operation conditions with a multivariable experiment methodology. The individual impact and interactions of four variables, current, initial TCE concentration, supporting electrolyte concentration and electrode thickness (foam material), are accordingly assessed under a circulated flow condition.

2. Experimental Methods

Chemicals and Materials

The chemicals used include TCE (99.5%, Sigma-Aldrich), *cis*-dichloroethylene (*cis*-DCE, 97%, Sigma-Aldrich), hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethene, acetylene in nitrogen, Supelco), and anhydrous Na₂SO₄ (analytic grade, JT Baker). TCE stock solution was prepared by adding excess pure TCE into 1 liter measuring flask prefilled with 18 ΩM deionized water. The supernatant of the TCE stock solution was used as TCE saturated aqueous solution (1.07 mg mL⁻¹ at 20°C) for preparation of solutions with different TCE concentrations. Three kinds of anode materials, cast iron (McMaster-Carr, USA), mixed metal oxide (MMO, IrO₂ and Ta₂O₅ coating on titanium mesh, 3N International, USA) and PbO₂ electrode, were tested. The PbO₂ electrode (on titanium mesh substrate) was prepared via electrodeposition method (Mao et al. 2008). Five kinds of plate material, copper (99.9%, VWR, USA), nickel (99.9%, VWR, USA), iron (3N5 purity, ESPI metals, USA), glassy carbon (Alfa Aesar, USA) and silver (99.9%, VWR, USA), and four kinds of foam materials, copper foam (99.99 %, 40 PPI, ERG, USA), nickel foam (99%, 100 PPI, Lyrun Ltd., China), iron foam (95% iron, 60 PPI, Aibixi Ltd., China) and vitreous carbon foam (40 PPI, ERG, USA) were tested as cathode for TCE reduction. The plate electrodes were round disk (5 cm diameter and less than 2 mm thick). The foam electrodes had the same diameter as plate electrodes, but their thicknesses increased to 6 to 6.35 mm. For copper foam, electrodes with different thicknesses were investigated. Prior to electrolysis experiments, the plate electrodes were polished using by 1# to 3# emery paper,

sonicated with 2% Micro-90 cleaning solution (Cole Parmer, USA) and distilled water. The cleaning procedure of foam material includes: washing the electrode with diluted acid (1% HCl), and soaking the electrode in 2% Micro-90 cleaning solution for 10 hours, finally washing the electrode with distilled water prior to assembly.

Electrochemical reactor

The setup (Fig. 1) consists of an electrochemical reactor, a recirculation pump and a glass reservoir. The electrochemical reactor was made of acrylic and PTFE material, with a volume of 125 mL. The anode and cathode, with 4 cm spacing, were connected to a power supply (HP 3160, USA) from the back side of the electrodes. Two pieces of stainless steel or copper washers were used for electrical connections of foam materials. The speed of peristaltic pump was fixed at 320 ml min⁻¹ for all experiments. In order to minimize absorption of TCE, glass tube, PTFE tubing (Cole Parmer, USA) and Viton pump tubing (Cole Parmer, USA) were used to connect all parts of the setup. The headspace of the reservoir was connected to a syringe, which allows headspace gas expansion when the internal pressure is higher than 12 kPa. Both headspace gas and liquid samples can be collected from the sampling ports connected to the reservoir. For each experiment, 260 mL aqueous solution of Na₂SO₄ was transferred into the setup and 10 mL TCE saturated solution was injected. For experiments with different initial concentrations of TCE, different volumes of TCE saturated solution were used, but the total volume of electrolyte was maintained at 270 mL for all experiments. The solution was recirculated for 25~30 minutes to allow equilibrium of TCE in the solution. To ensure the reproducibility of the results, experiments were carried out in duplicates or triplicates. TCE loss through absorption or other mechanism in the overall system was between 5% and 8% (depending on the initial concentration), within 4 hours with respect to the equilibrium concentration.

Analytic methods

Aqueous TCE concentration was measured by Gas Chromatography (GC) using 8610GC instrument with purge-trap system (SRI, USA), flame-ionization detector and MXT-VOL stationary column. Hydrocarbon gases (methane, ethene, ethane and acetylene) in the headspace of electrolytic cell were analyzed by Model 310 GC (SRI, USA) with flame ionization detector and Haysep-T column. Detailed information about the temperature programming of these two measurements are reported in our previous work (Mao et al. 2011). Chloride and sulfate ions concentrations were analyzed by Dionex DX-5500 ion chromatograph (IC). Typically, an aliquot 0.5 ml of supernatant was filtered by a 0.45µm pore size PVDF syringe filter and transferred into 5 mL vials for IC testing. The IC instrument was also used for the detection of acetic acid and oxalic acid when inert electrodes were applied, and the samples were alkalized to 10 for measurement. pH, conductivity and oxidation-reduction potential (ORP) of the electrolyte were measured by pH meter, conductivity meter and ORP meter with microprobes (Microelectro, USA). The microprobes allow the measurement of these parameters using a small volume of liquid (≈ 0.2 mL). Experiments were also carried out to monitor changes in dissolved oxygen concentration in the electrolyte. In this case, a DO prober (YSI 5000, USA) was mounted on top of water reservoir to measure the DO concentration in electrolyte.

Final transformation efficiency (FTE) of aqueous TCE, final elimination efficiency (FEE) and specific energy consumption (SEC) of the electrochemical process were determined using the following equations:

$$\text{FTE} = \frac{C_{aq(0)} - C_{aq(t)}}{C_{aq(0)}} \times 100\% \quad (1)$$

$$FEE = 1 - \frac{C_{aq(t)}}{C_{aq(0)}} \left[1 + \frac{H_{TCE} \cdot \Delta V_h}{V_{aq} + H_{TCE} \cdot V_h} \right] \times 100\% \quad (2)$$

$$SEC = \frac{I \cdot U \cdot t}{C_{aq(0)} \cdot (V_{aq} + H_{TCE} V_h) \cdot FEE} \quad (3)$$

where $C_{aq(0)}$ and $C_{aq(t)}$ are aqueous TCE concentration at time zero and time t (mg L^{-1}); V_{aq} and V_h are initial volume of liquid (270 mL) and initial headspace of reservoir (20 mL), respectively. ΔV_h is the expanded volume of headspace gas at time t ; I is the current intensity (ampere); U is the cell voltage of electrolysis cell (Volt); H_{TCE} is the dimensionless Henry Law constant for TCE, and t is the electrolysis time (second). The FTE is only suitable for comparison of the results of tests with similar headspace, while the FEE is used for accurate calculation of TCE elimination from both solution and headspace.

Multivariable experimental design

A statistical experiment design and analysis were used to investigate the effects of four variables on the response function and to determine optimal conditions to maximize the final elimination efficiency of TCE. This design includes two procedures (Costa Ferreira et al. 2007): 1) a series of experiments that follow a certain kind of statistical model are conducted in random chronological order; and 2) variance analysis of the regression results is performed so that the most appropriate model with no evidence of lack of fit can be used to represent the data. The analysis of the experimental data was supported by the statistical software Minitab (Version 14).

3. Results and discussion

3.1 Effect of anode on reductive dechlorination

Constant current electrolysis experiments using silver plate cathode and different anodes were carried out in a closed, recirculated system, and the results are compared in Fig. 2. The decay of aqueous TCE (Fig. 1a) is fastest in the cell using iron anode, followed by the cell using PbO_2 anode and MMO anode. After 4-hours of electrolysis, up to 65.7% of TCE is transformed when silver plate and iron anode are used. PbO_2 anode caused 5.8% increase in TCE transformation when compared to MMO anode, which is due to the higher performance of PbO_2 anode for destroying organic molecules. After 4 hours of electrolysis, acetic ions and oxalic ions were detected in the system using PbO_2 anode, suggesting that oxidation of TCE did occur under this condition. The reductive dechlorination of TCE on cathode is a process that involves electrons and protons transfer, producing less chlorinated ethenes (e.g., *cis*-DCE, vinyl chloride) and eventually non-toxic hydrocarbons, as given by,

Because no chlorinated ethene accumulation is found in the electrolytic cells in this study, Eq. 4 can be further simplified to Eq. 5.

Thus, the increase of chloride ions concentration in the electrolyte should reasonably correspond to the progressive decrease of TCE since all chlorine atoms are transferred to

chloride ions. In Fig. 2b, a higher buildup of chloride ion concentration is found in the cell using iron anode, supporting the observation of aqueous TCE decay. Calculations based on chlorine mass show less than 85% mass recovery for chlorine in the three electrolytic systems. In the system using iron anode, the mass lost in chlorine can be in part explained by the absorption on ferrous hydroxide and formation of ferrous and ferric chloride complexes in solution (Cornell and Schwertmann 2003, Langmuir 1997, Roh et al. 2000). Some chloride ions, derived from dechlorination of TCE, are not detected by the IC for mass recovery calculation. For the inert anodes, the mass lost in chlorine is probably due to the generation of free chlorine (or other chlorinated intermediates) on the anode (Al-Abed and Fang 2007).

The electrolyte pH in the cells using inert anodes did not show (Fig. 2c) any considerable change during electrolysis, indicating the protons (H^+) produced from the anode are quickly neutralized by the hydroxyl ions (OH^-) produced from the cathode. However, the pH of the electrolyte in the cell using iron anode immediately increases once electrolysis starts and stabilizes at a pH of 11.3. The dissolution of ferrous ions from the cast iron anode, instead of proton and oxygen evolution, is the dominant reaction, and the ferrous ions subsequently combine with the hydroxyl ions from the cathode, forming $Fe(OH)_2$ precipitates. However, due to the relatively higher solubility of $Fe(OH)_2$ ($K_{sp}=10e-15$) (Snoeyink and Jenkins 1980), presence of free OH^- in the electrolyte results in an increase in the pH. The generated ferrous species also induce different ORP conditions in electrolytes. The ORP of the electrolyte using inert anodes increases slightly as electrolysis proceed, finally reaching an oxidizing ORP of more than 150 mV. In contrast, when iron anodes were used, the ORP of the electrolyte constantly decreases during electrolysis, indicating buildup of reducing electrolyte conditions.

In this recirculation system, an enhancing effect on TCE dechlorination is observed when iron anodes are used, which is consistent with the results in batch electrolysis system (Mao et al. 2011). As reported in Mao et al (2011), the enhancing effect of iron electrolysis is due to the presence of the ferrous species. $Fe(OH)_2$ or other ferrous species (e.g., $Fe(OH)^+$, $Fe(OH)_4^-$) have a strong tendency to consume other oxidizing chemicals in the electrolyte, especially dissolved oxygen. The dissolved oxygen concentration was monitored in the recirculation system with different anodes (same electrolytic conditions as that in Fig. 2, but in separated experiment). The results show that the dissolved oxygen concentrations in electrolyte (measured in water reservoir) were always maintained at about $10\sim13\text{ mg L}^{-1}$ when MMO anodes or PbO_2 anodes were used. In contrast, when cast iron anode was used, the dissolved oxygen concentration in the electrolyte dramatically decreased to 0.1 mg L^{-1} after thirty minutes of electrolysis. Therefore, although the electrolyte flow condition of this study is different from the batch experiments, an enhancing effect of cast iron on TCE dechlorination is observed. The dissolved oxygen quickly reacted with ferrous hydroxide, and the electron or proton competition effect from oxygen reduction is completely eliminated. Based on the observations in this study, the anodic reactions basically play opposing roles for TCE degradation when inert anodes are typically used. Oxygen generated can disturb the reductive dechlorination on cathode. However, it should be noted that aliphatic chlorides like chloroethanes and TCE can be efficiently degraded by the oxidation process occurring on some specific anodes, such as boron doped diamond film electrode (Carter and Farrell 2009, Scialdone et al. 2010a). Thus, the electrolysis process consisting of BDD anode and copper foam cathode may be another competitive method for TCE degradation if the electro-oxidation of TCE can surpass the adverse effect of the released O_2 .

In addition to the differences in aqueous TCE transformation rates, the products of transformation also reflect the competition effect of O_2 when inert anode is used. Only four hydrocarbon gases (methane, ethene, ethane and acetylene) were detected as the final

products of TCE dechlorination. This is in agreement with previous findings (Chen et al. 2003, Li and Farrell 2000, Mao et al. 2011). In Fig. 3a, the headspace hydrocarbon gases in the water reservoir are compared after 1.5 hours electrolysis. For the iron anode, more methane and ethane are found in the headspace of water reservoir, and the total amount of hydrocarbon gases apparently exceed the amount of the gases generated under the other two conditions (Fig. 3a). Blank experiments (without TCE) with iron anodes did not show formation of these hydrocarbon gases. A parameter, hydrodechlorination index (HI) is proposed for quantitative comparison of the TCE transformation products,

$$\text{Hydrodechlorination Index} = \sum_{j=\text{hydrocarbon compounds}} n_j \chi_j \quad (6)$$

where the n_j is the number of the hydrogen atoms by which TCE is transformed to hydrocarbon compound j (e.g., $n_{\text{acetylene}}=1$, $n_{\text{ethene}}=3$, $n_{\text{ethane}}=5$, $n_{\text{methane}}=3.5$), χ_j is the molar percentage of species j in the total hydrocarbon gases of headspace. The HI values of the headspace hydrocarbon gases in three electrolytic cells are summarized in Fig. 3b. The HI value for iron anode electrolysis starts at 4.04 after thirty minutes and stabilizes at 4.2, being higher than the HI value of inert anode electrolysis. Under identical electrolysis condition, higher HI value means that more hydrogen atoms are acquired in the dechlorination process. In other words, it means the cathodic process can provide more atomic hydrogens ($\text{H}_2\text{O} + \text{e} = \text{H}^\bullet + \text{OH}^-$) (Li and Farrell 2001) for TCE reduction because the competition process from O_2 reduction is avoided (or eliminated) in the iron anode electrolysis.

3. 2 Effect of cathode material

The performances of different cathode materials on TCE dechlorination are compared using galvanostatic electrolysis experiments under flow. The headspace gas expansion volumes in all experiments varied from 136 mL to 143 mL after 4 hours electrolysis at 100 mA. The decay of normalized aqueous concentration of TCE is shown in Fig. 4. Silver and copper materials exhibit better electrocatalytic performances in comparison with other plate materials by achieving more than 70% aqueous TCE transformation (FTE). The iron, glassy carbon and nickel plate cathodes show similar performance on TCE dechlorination with FTE less than 60%. Foam materials, such as copper foam cathode (Fig. 4b), increased the FTE to 92.3% or 21.1% higher than that of copper plate electrode. Iron foam and vitreous carbon foam also show enhancing effect in comparison to the corresponding plate materials. Only nickelfoam show inferior performance with respect to plate materials.

The TCE hydrogenation (Eq. 1) and hydrogen evolution (Eq. 7 and Eq. 8) are ompetitive reactions that proceed simultaneously on the surface of cathode.

The electrodes' catalytic activity on hydrogen evolution may explain their different TCE dechlorination rates. For materials with higher hydrogen evolution overpotential, such as silver, copper and lead (Halmann 1993), the kinetics of Eq.8 may be relatively slow, and TCE molecules have better chances to acquire the atomic hydrogen from the cathode. On the contrary, electrodes with lower hydrogen evolution overpotential, such as nickel (Halmann 1993), may represent faster kinetics for Eq. 8 (Jeremiasse et al. 2010), which will lower the

probability of TCE molecules acquiring atomic hydrogen. Therefore, when the working area of nickel significantly increase from plate to foam, less degradation of TCE was observed since nickel foam results in lower hydrogen evolution overpotential and facilitates hydrogen release (Jeremiasse et al. 2010).

Although oxygen reduction is eliminated in the cell by using iron anode, the reduction of sulfate is another concern for dechlorination of TCE. Based on the standard potential data and previous studies, sulfate can be reduced by atomic hydrogen in aqueous solution (Bilal and Tributsch 1998, Yang et al. 2007). A batch electrolysis experiment using copper foam cathode and separated cell (by Nafion® membrane) was carried out to understand the impact of sulfate reduction on cathode. Only 1.8% of sulfate ions concentration decreased in the catholyte after 4-hour electrolysis (200 mL catholyte, 100 mA, 0.01 M Na₂SO₄, without TCE). Thus, it is reasonable to assume that sulfate reduction on the cathode does not have an appreciable effect on TCE reduction under the testing conditions of this study.

3.3 Optimization of electrolysis process

3.3.1 Regression model and assessment of the main factors—The combination of iron anode and copper foam cathode result in the highest TCE dechlorination performance compared to other materials tested. Due to cast iron anode, the cathodic reduction of aqueous TCE can be further optimized under reducing electrolyte condition, using a multivariable experiment design (Rezzoug and Capart 2003, Wei et al. 2011). In addition to the electrode type, the process can be affected by other operating variables, such as flow rate of aqueous solution, current, temperature, and supporting electrolyte. However, given the time frame and scope of this study, it was not feasible to carry out an experimental design that includes all these factors. In this study, four variables including (A) initial concentration of TCE, (B) surface area represented by thickness of copper foam electrode, (C) current intensity and (D) concentration of supporting electrolyte (Na₂SO₄) are selected for further investigation. The experimental range and levels of variables used in the factorial design are listed in Table 1. Among these factors, thickness of the electrode is proportional to the surface area of electrode, and conductivity of electrolyte increases almost linearly with the concentration of Na₂SO₄. Different electrolysis times (2, 3, and 6 hours) were selected to maintain identical total applied charge (240 mA h) for all experiments. The experimental design matrix, listed in Table 2, consists of three series of experiments (Deepak et al. 2008, Wei et al. 2011): (i) a two-level full factorial design 2⁴ (all possible combinations of codified values +1 and -1); (ii) six central, replicates of central point (0); and (iii) eight axial or star point located at the center and both extreme levels of the experimental models. Experiments were conducted in random order and the results are summarized in Table 2. Using the factorial experiment analysis in MINITAB software, semi-empirical expressions at 95% of confidence level can be obtained for the response of final elimination efficiency (Y1(FEE)) and the response of specific energy consumption (Y2 (SEC)),

$$Y1(FEE)=88.603+1.02A+4.002B - 4.916C+4.907D - 0.265AB+0.057AC - 0.256AD+1.273BC-1.061BD+1.988CD+0.875ABC+0.059ABD - 0.331ACD - 1.109BCD+0.264ABCD \quad (R^2=0.994)^{(9)}$$

$$Y2(SEC)=178.4 - 78.8A - 22.5B+156.1C - 229.5D+10.2AB - 59.9AC+78.8AD - 18.5BC+23.4BD-167CD+9.3ABC - 10.3ABD+58.4ACD+18.9BCD - 9.4ABCD \quad (R^2=0.890)^{(10)}$$

where A, B, C and D take values between -1 and 1, representing the level of a factor. The model produced R-squared values of 0.994 and 0.890 for FEE and SEC, respectively. The *p*-value of lack-of-fit shows that the model of the FEE response is significant (*p*-value > 0.05);

while the model on SEC response is insignificant. It is not surprising that SEC model is insignificant since the variation of the potential of anode also contributes to the cell voltage, which is crucial to the SEC calculation. To visualize the importance sequence of the calculated factors, the single factor and interaction factors are depicted in rank order in the form of Pareto chart (Fig. 5). The absolute value of the standardized effect of a factor overpassing the significance line (the vertical line at 2.14 and 2.145 in Fig. 5) means it exerts a statistically significant influence on the response. The signs + and – represent positive and negative effects, respectively. Positive effect means the increases of response in the presence of high levels of the respective factors within the range studied, while the negative effect indicates the decrease of response in the presence of high levels of the factors. Positive quadratic or third order polynomial coefficients indicate a synergistic effect, while negative coefficients represent a negative effect between or among the factors. In Fig. 5a, the most significant individual factor for FEE is the applied current (C), followed by the Na_2SO_4 concentration (D) and the thickness of electrode (B), whereas the initial concentration of TCE showed much less importance. On the other hand, the analysis shows that the FEE is also affected by some quadratic interaction factor (CD, BC, BD) and third order polynomial factors (BCD, ABC). For the specific energy consumption, as shown in Fig. 5b, five factors are statistically significant based on 95% confidence intervals: the Na_2SO_4 concentration, the current, the initial TCE concentration, and two quadratic factors (CD and AD).

Effect of Na_2SO_4 concentration: Among these four individual factors, the Na_2SO_4 concentration is important for both FEE and SEC. As mentioned above, Na_2SO_4 is almost an inert supporting electrolyte and it will not exert appreciable effect on the degradation of TCE through chemical route, because of its low reactivity on either cathode or anode. However, the Na_2SO_4 concentration significantly changes the conductivity of electrolyte, which can impact the electrochemical process when a 3D porous electrode is adopted. When the copper foam is working as a cathode, the potential of the metal phase (E) is constant throughout the network of copper foam due to the excellent electron conductivity of copper. This potential is composed of four parts (He et al. 2004), as shown in Eq. 11, the equilibrium potential of the rate-limiting reaction step (E_{eq}), the electron transfer overpotential (η_e), the concentration overpotential (η_c), and solution potential (φ_s).

$$E = E_{\text{eq}} + \eta_e + \eta_c + \varphi_s \quad (11)$$

When a cathodic reaction is in progress, solution potential is related to solution electrolytes conductivity and shows increasing trend from the surface to the inner part of foam electrode, hence the electron transfer overpotential (η_e) of the inner part decreases to maintain constant electrode potential (E). As a result, the current (or electron discharge) mostly distribute on the outmost layer of foam electrode (with respect to anode direction), which causes strong hydrogen evolution on the surface layer and lower the real reaction area for TCE reduction. In contrast, high ionic conductivity of the electrolyte will bring more homogenous solution potential and electron discharge in the network of the foam electrode, increasing the probability of TCE acquiring the atomic hydrogen. As for the specific energy consumption, apart from the high FEE at higher Na_2SO_4 concentration, higher ionic conductivity decrease the cell voltage greatly (see Table. 2), resulting in less energy consumption (negative effect in Fig. 5b).

Effect of current: In the range of 40 to 120 mA, the electrical current significantly impacts the FEE and SEC not only at first order but also at quadratic level. Under the constant-charge but different current condition, the headspace gas expansion volume in these 30 experiments varied around 80 mL and did not show remarkable difference, indicating that

the current level did not change the primary reaction process on the cathode (hydrogen evolution). Based on the results of the FEE, the advantages of applying lower current can be concluded as follows: 1) the lower level of current will not cause excessive release of hydrogen gas and decrease the effect of mass-transport limiting; 2) lower current means more detention time and reaction time; 3) lower current brings out less iR drop in solution, favoring a more homogenous current distribution. Therefore, from a perspective of engineering operation, low current is much more preferred if the detention time of the contaminated water is not a primary factor.

Thickness of foam electrode: As expected, the thickness of foam electrode is an essential factor that influences the FEE of TCE positively, even if it is less important than the current and the Na_2SO_4 concentration. Although the surface area increase linearly with increasing electrode thickness (see note in Table 1), there is no significant increase in TCE removal efficiency. When other factors are at middle level, 9.525 mm electrode exhibited 93.56 % FEE of TCE, being only 9.87% higher than that of 0.125 mm thickness electrode. This suggests that a large area of the foam electrode did not contribute at the same rate when the surface area increased significantly. While thicker electrodes have larger surface area, it may be more difficult to achieve sufficient electron-transfer potential for the inner part of the foam electrode because of the increasing iR drop.

Initial TCE concentration: For the experimental range of 28 to 56 mg L^{-1} , the initial TCE concentration had an impact on both FEE and SEC. Although initial TCE concentration was doubled from 28 mg L^{-1} to 56 mg L^{-1} ; except for Exp. No. 4, the final aqueous TCE concentrations for all experiments were all below 10 mg L^{-1} (not shown). At high initial concentration, due to the large surface area of foam cathode, the chemisorption of TCE on foam electrode is accordingly enhanced. This ensures that foam maintains relatively high efficiency for a wide range of TCE concentration. Therefore, a positive impact on FEE and a negative impact on SEC (higher initial concentration gives less energy consumption) are observed in the multivariable experiments.

3.3.2 Contour diagrams and optimum conditions—After screening the controlling factors, the response surface analysis using contour diagram can be generated, in order to determine the optimum conditions for removal of TCE. In Fig. 6, three important pairs of factors are displayed in contour plots of FEE of TCE: Na_2SO_4 concentration of versus current (Fig. 6a), current versus thickness of electrode (Fig. 6b), and Na_2SO_4 concentration versus thickness of electrode (Fig. 6c). Each contour plot has an infinite number of combinations based on two selected factors while maintaining the two other factors constant at their middle values (level “0”). The obliquely orientated contours in these three plots indicate that the interactions between the corresponding factors were always significant in the experimental range. The optimal conditions for highest FEE are depicted by the dark green zones in these plots. As shown in Fig. 6a, the highest FEE (> 96%) can be achieved when the concentration of Na_2SO_4 is higher than $0.0388 \text{ mol L}^{-1}$ (0.84 in Fig. 6a) and the current is lower than 46 mA (− 0.85 in Fig. 6a). The foam electrode features very large surface area, and the conductivity of electrolyte determines the extent of effective utilization of the real surface area. Lower current, but same amount of total electrical charge, means more reaction time and facile hydrogen evolution. Thus, these two factors and their interaction are important for the FEE. In Fig. 6b, the optimal range for the highest FEE (> 95.3%) is that current is lower than 50 mA and thickness of electrode exceeds 8.41 mm. As seen in Fig. 6c, more than 95.3% of FEE can be obtained when the Na_2SO_4 concentration exceeds 0.036 mol L^{-1} and the electrode is thicker than 8.34 mm. Generally, based on the results of the multivariable experiments, the optimal combination of the operation conditions for response FEE is: 40 mA current, 9.525 mm foam electrode and 0.042 mol L^{-1} Na_2SO_4 .

The TCE initial concentration is a less important efficiency-determining factor, indicating that the large surface area of foam electrode enables it to adapt to a wide range of TCE concentration.

It is also noteworthy that, even at low conductivity ($0.002 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$) solution, high TCE removal efficiency still can be achieved if the current is applied at low level (see Fig. 6a). Considering that the ionic conductivity of groundwater is usually more than $500 \mu\text{S cm}^{-1}$, being higher than the conductivity of $0.002 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, the present electrolysis system of copper foam cathode and cast iron anode is applicable to groundwater remediation. The implementation of the present system can be flexible: it can be powered by either normal electrical power for an ex-situ remediation, or a photovoltaic power for an in-situ remediation of groundwater contaminated by chlorinated solvents.

4. Conclusions

TCE in recirculated aqueous solution is rapidly removed through an electrolysis system that consists of cast iron anode and copper foam electrode. The cast iron anode generates a reducing electrolyte and prevents the electron and proton competition from dissolved oxygen, thus the reduction of TCE on the cathode is enhanced. The Hydrodechlorination Index reflects that fast TCE transformation occurs in the reducing electrolyte due to highly available atomic hydrogen on cathode. In screening of different cathode materials in a recirculated system, copper foam electrode exhibits superior performance on TCE transformation. Through a multivariable experiment design; the electric current, Na_2SO_4 concentration (representing conductivity), thickness of foam electrode (or surface area of electrode), and initial TCE concentration were identified as the individual factors that impact TCE removal efficiency. Higher electrolyte conductivity facilitates better current distribution on the foam electrode, promoting electrochemical dechlorination of TCE. The copper foam electrode exhibits high TCE removal efficiency in a wide range of initial concentration and Na_2SO_4 concentration. The optimal combination for aqueous TCE elimination is high electrolyte conductivity, high surface-area electrode and lowest applied current for a specific electric charge application. With the optimal condition, the final elimination efficiency of TCE can reach up to 98 %, and the corresponding energy consumption is 6.49 kWh kg^{-1} .

Although the technology described in this study can be applied to wastewater treatment or groundwater; the pH increase of electrolyte should be carefully addressed, especially for remediation of contaminated sites. pH increase from the process may impact the chemical and biological characteristics of the groundwater and aquifer. Research work aiming at assessing and resolving this issue is underway.

Acknowledgments

The project described was supported by Award Number P42ES017198 from the National Institute of Environmental Health Sciences (NIEHS) of US. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the National Institutes of Health.

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Fig. 1.
A schematic of the experiment setup including 1) DC power source; 2) electrolysis reactor; 3) cooling water (20 °C); 4) peristaltic pump; 5) liquid sampling port; 6) water reservoir; 7) gas sampling port; and 8) headspace gas expandable syringe (180 mL).

Fig. 2.

Comparison of electrolytic dechlorination results using different anodes: (a) aqueous TCE concentration; (b) chloride ions concentration; (c) pH change; and (d) ORP change during electrolysis. Experiments were conducted with silver plate cathode and 80 mA current. The headspace gas expansion volumes (ΔV_h) after 4-hour electrolysis were 118 ± 1.5 mL for cast iron anode, 106 ± 1.0 mL for PbO_2 anode and 108 ± 1.0 mL for MMO anode. Error bars represent the standard error of the mean of duplicated experiments.

Fig. 3. (a) Mass of headspace hydrocarbon gases after 1.5 hours electrolysis, and (b) hydrodechlorination index of the headspace hydrocarbon gases using different anode materials. All gas samples were collected from the headspace of water reservoir.

Fig. 4. Decay of the normalized aqueous TCE concentration using iron anode and different (a) plate cathodes and (b) foam cathodes. The initial concentration of aqueous TCE was 38 mg L^{-1} .

Fig. 5. Pareto chart: standardized effects of individual factors and interactions on (a) the FEE of TCE and (b) SEC.

Fig. 6. Contour plots of the FEE for three most significant pairs of factors: (a) $[Na_2SO_4]$ vs. current, (b) Current vs. Thickness (Thk) of electrode, (c) $[Na_2SO_4]$ vs. Thickness of electrode

Table 1

Range of variation of the parameters used in the experimental design

Parameter	Notation	Low (-1)	Center (0)	High (+1)
A ^a	[TCE] (mg L ⁻¹)	28	42	56
B ^b	Thickness of foam cathode (Thk) (mm)	3.175	6.35	9.525
C ^c	Current (mA)	40	80	120
D ^d	[Na ₂ SO ₄] (mol L ⁻¹)	0.002	0.022	0.042

^aThe initial concentrations of aqueous TCE were obtained by spiking 8 mL, 12 mL and 16 mL TCE saturated solution.

^bThe surface area of foam electrodes (provided by manufacturer) are 145 cm² (3.175 mm), 290 cm² (6.35 mm), 435 cm² (9.525 mm).

^cElectrolysis time at three levels were 6 hours (40 mA), 3 hours (80 mA) and 2 hours (120 mA).

^dThe ionic conductivity of the electrolyte at three levels were 480 μS cm⁻¹, 4.31 mS cm⁻¹ and 7.60 mS cm⁻¹.

Table 2

Experimental data of the multivariable experiment design^{*}

Exp. No.	Variable levels				Expended gas volume (ml)	Cell voltage (V)	YI (FEE) (%)	Y2 (SEC) (kW h kg ⁻¹)
	A [TCE]	B Thk	C I	D [Na ₂ SO ₄]				
1	-1	1	-1	1	77	0.51	99.01	15.43
2	1	1	1	1	82	0.82	94.84	13.35
3	1	1	-1	-1	80	5.1	93.02	84.45
4	1	-1	1	-1	87	27.1	70.87	580.47
5	1	-1	1	1	83	0.88	87.00	15.45
6	1	-1	-1	-1	78	5.9	89.74	102.19
7	0	0	0	0	81	2.9	88.58	72.98
8	-1	-1	-1	-1	80	5.6	86.00	196.16
9	0	0	0	0	81	2.9	88.94	69.81
10	-1	-1	1	1	84	0.85	87.79	29.81
11	-1	1	-1	-1	80	5.2	93.05	171.34
12	-1	-1	1	-1	85	27.7	68.02	1222.46
13	1	1	-1	1	80	0.42	98.49	6.49
14	-1	1	1	-1	84	27.0	82.10	972.92
15	-1	-1	-1	1	81	0.55	91.01	18.69
16	0	0	0	0	82	2.9	88.54	68.65
17	1	1	1	-1	80	27.1	86.10	488.01
18	1	-1	-1	1	83	0.6	95.87	9.66
19	-1	1	1	1	78	0.86	91.90	28.67
20	0	0	0	0	81	3.0	89.10	71.77
21	0	0	0	0	82	2.9	89.74	69.27
22	0	0	0	-1	84	20.0	82.75	493.18
23	0	-1	0	0	81	3.0	83.69	74.51
24	0	0	1	0	82	4.0	82.97	100.33
25	0	0	0	0	80	3.0	88.85	71.75
26	0	0	0	1	80	1.9	94.02	42.49
27	0	1	0	0	81	2.9	93.56	63.86

Exp. No.	Variable levels				Expend gas volume (ml)	Cell voltage (V)	Y1 (FEE) (%)	Y2 (SEC) (kW h kg ⁻¹)
	A [TCE]	B Thk	C I	D [Na ₂ SO ₄]				
28	-1	0	0	0	81	3.0	88.69	112.13
29	1	0	0	0	80	2.9	89.96	49.42
30	0	0	-1	0	80	1.7	93.97	36.60

* The cell voltage is the mean of five cell voltage values recorded, with equal time intervals, from start to the end of electrolysis. Values in each trial were average of duplicates.