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Electrochemically induced dual reactive barriers for transformation of TCE and mixture of contaminants in groundwater

Xuhui Mao^{1,2}, Songhu Yuan^{1,3}, Noushin Fallahpour¹, Ali Ciblak¹, Joniqua Howard⁴, Ingrid Padilla⁴, Rita Loch-Caruso⁵, and Akram N. Alshawabkeh^{1,*}

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

²School of Resources and Environmental Science, Wuhan University, Wuhan 430079, P. R. China

³State Key Lab of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, P. R. China

⁴Department of Civil Engineering and Surveying, University of Puerto Rico, Mayaguez, Puerto Rico, 00681

⁵Department of Environmental Health Sciences, School of Public Health, University of Michigan, Ann Arbor, Michigan 48109

Abstract

A novel reactive electrochemical flow system consisting of iron anode and porous cathode is proposed for the remediation of mixture of contaminants in groundwater. The system consists of a series of sequentially arranged electrodes, a perforated iron anode, a porous copper cathode followed by a mesh-type mixed metal oxide anode. The iron anode generates ferrous species and a chemically reducing environment, the porous cathode provides a reactive electrochemically reducing barrier, and the inert anode provides proton and oxygen to neutralize the system. The redox conditions of the electrolyte flowing through this system can be regulated by controlling the distribution of the electric current. Column experiments are conducted to evaluate the process and study the variables. The electrochemical reduction on a copper foam cathode produced an electrode-based reductive potential capable of reducing TCE and nitrate. Rational electrodes arrangement, longer residence time of electrolytes and higher surface area of foam electrode improve the reductive transformation of TCE. More than 82.2% TCE removal efficiency is achieved for the case of low influent concentration (< 7.5 mg/L) and high current (> 45 mA). The ferrous species produced from the iron anode not only enhance the transformation of TCE on the cathode, but also facilitates transformation of other contaminants including dichromate, selenate and arsenite. Removal efficiencies greater than 80% are achieved for these contaminants from flowing contaminated water. The overall system, comprising the electrode-based and electrolyte-based barriers, can be engineered as a versatile and integrated remedial method for a relatively wide spectrum of contaminants and their mixtures.

*Corresponding author: Tel: 617-373-3994, aalsha@coe.neu.edu.

Supporting Information.

Supporting information include figure presenting the effluent ORP and pH changes under longer time operation (Figure S1); the decay of the TCE and the generation of products (Figure S2); current efficiency as a function of the cathode thickness (Figure S3); a summary of experimental data (Table S1 and Table S2); detailed information on the analytical method for dissolved hydrocarbon gases, ferrous species and ferric species. This material is available free of charge via the internet at <http://pubs.acs.org>.

Keywords

Electrochemical barriers; redox regulation; mixtures of contaminants; TCE; iron anode

Introduction

Groundwater, a major source for irrigation and drinking water, is susceptible to pollution due to inappropriate disposal of waste or from the higher chemical background concentrations in specific geologic formations. A variety of hazardous substances have been identified as sources of groundwater contamination that pose human health threats, including: 1) toxic organics such as halogenated compounds, benzenes and polycyclic aromatic hydrocarbons (PAHs),^{1–3} 2) inorganic non-metallic ions such as nitrate, perchlorate and fluoride,^{4–6} and 3) heavy metals such as lead, chromium and arsenic.⁷ These contaminants exist in groundwater either as individual species or in mixtures with other contaminants. Presence of mixtures of contaminants is common in the United States (U.S.). Over 40% of all superfund sites include mixtures of organic and heavy metal contaminants,⁸ and other kinds of mixed contaminants are also often reported.^{9–13} Due to co-existence of different contaminants, strategies to address contamination mixtures in groundwater require considering not only the properties of individual contaminants, but also the complexity of their interactions. For example, bioremediation is an attractive technology to transform trichloroethylene (TCE) and other chlorinated ethenes to non-toxic ethenes. However, its utility may be greatly limited by the metal-toxicity of certain heavy metals.^{8, 10} Therefore, remedial technologies are desired for in-situ treatment of mixtures of contaminants in groundwater.

In the U.S., chlorinated solvents appear a group of contaminants that are frequently reported at contaminated sites. Most, if not all, states in the U.S. have TCE contamination and/or other chlorinated ethenes in soil and groundwater.^{14, 15} TCE was recently reclassified by the U.S. Environmental Protection Agency (EPA) as “carcinogenic in humans by all routes of exposure” based on concordant findings of kidney carcinogenesis in humans and laboratory animals, with additional potential risk for noncancer toxicity to the kidney, liver, immune, male reproductive and central nervous systems.¹⁵ Several technologies have been proposed, developed and tested for remediation of groundwater contaminated with chlorinated solvents, such as methods based on phase transfer method, chemical or biological transformation.² Reductive dechlorination of TCE using zero valent iron (ZVI) is an example that has attracted attention for its potential for transforming toxic chlorinated solvent to less or non-toxic products. In situ permeable reactive barriers are the most common applications using ZVI, in which the iron fillers work as numerous short-circuited, micro-scale electrochemical primary cells that induce dechlorination of chlorinated solvent molecules.^{16, 17} ZVI permeable reactive barriers have been evaluated for remediation of TCE contaminated groundwater,^{18–23} and they have also been considered for treatment of other contaminants, such as chromium, arsenic and radionuclides in groundwater.^{17, 19, 21} The drawbacks of ZVI permeable reactive barrier, however, are also evident, and include 1) lack of reactivity manipulation to treat different contaminants, as the reactivity of the system is mostly determined by iron fillers; 2) passivation of iron and precipitation of minerals on iron fillers, which gradually decrease the reactivity and permeability of the system, and limit the removal of contaminants.^{19, 23}

Electrochemical redox systems consisting of an anode and a cathode have been investigated as another option to treat different contaminants, including energetic compounds, chlorinated solvents and chlorobenzene in aquifers or sediments.^{24–27} Energetic compounds like hexahydro-1,3,5-trinitro-1,3,5-triazine and 2,4,6-trinitrotoluene can be decomposed by

electro-oxidation, electro-reduction or electrochemically generated alkaline hydrolysis.^{24, 25} An electrically induced redox barrier was evaluated for in situ remediation of a site contaminated with TCE and trichloromethane.^{25, 28} Compared with ZVI permeable reactive barriers, the electrochemically generated redox conditions can be easily manipulated by varying the potential of electrodes, allowing optimization of transformation rates of target compounds. Furthermore, multiple options of electrode materials and electrode sequences can be arranged to optimize electrochemical treatment for a mixture of contaminants in groundwater.

In this study, we propose an electrochemically induced dual barriers for the remediation of TCE co-contaminated groundwater. A cast iron anode, a mixed metal oxide (MMO) anode and a central cathode are placed to intercept and treat the simulated groundwater. The central cathode provides electrode-based reactive barrier, the iron anode forms an electrolyte-based barrier by injecting ferrous ions to the electrolytes. Both processes contribute to the remediation of contaminants, but target different compounds. The MMO inert anode provides proton and oxygen to neutralize the system, and the electrical currents passing through two anodes can be adjusted and different electrolyte redox conditions can be controlled. Manipulation of groundwater redox conditions is important for this process because it can exert a strong effect on abiotic and biotic transformations of many contaminants in groundwater.^{2, 29, 30} To test the proof-of-concept of the proposed process, TCE, nitrate, chromate, selenate and arsenite are selected as the model contaminants and their transformation is evaluated in flow-through column reactors.

Experimental Section

Chemicals and Materials

The chemical reagents used in the study include trichloroethylene (99.5%, Sigma-Aldrich), potassium dichromate (reagent grade, JT Baker), sodium selenate (99.8%, Alfa Aesar), sodium arsenite (analytical reagent, 0.5% w/v aqueous solution, Riccar chemical), sodium nitrate (reagent grade, JT Baker), sodium sulfate (reagent grade, Fisher chemical), sodium bicarbonate (reagent grade, Fisher chemical) and hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethene, acetylene in nitrogen, Supelco). Excess TCE was dissolved into 18M Ω high-purity water to form a TCE saturated solution, which was used as stock solution for preparing TCE aqueous solutions. The electrode materials include cast iron (Macmaster-Carr, USA), mixed metal oxide (MMO) electrode (IrO₂ and Ta₂O₅ coating on titanium diamond mesh (34 mm $\times$ 76 mm diamond dimensions), 3N international, USA), copper plate (>99.9 purity, VWR) and copper foam (40 pores per inch (PPI), ERG company, USA). The cast iron and copper plate electrodes used in this study were round disks, 6.2 cm in diameter and 4 to 5.5 mm in thickness. Evenly distributed 21 holes (4.6 mm in diameter) were drilled through the plate electrodes to allow for fluid flow. A copper foam electrode, 1.27 cm in thickness, was generally used as the cathode if without otherwise specification. Limestone gravels, 4.75 to 9.5 mm particle size, were used to fill the column. Limestone was specifically selected because of interest in evaluating the process for aquifers in limestone karst deposits.

Column reactors

Two types of column reactors (Column A and Column B), filled with limestone gravels, were set up for testing, as shown in Figure 1. The reactors, constructed of acrylic tube, simulate one-dimensional flow conditions through permeable reactive barriers. One reactor (Column A) is longer and integrates the electrodes arrangement between regions of porous media. The other reactor (Column B) is shorter and integrates the electrodes arrangement at the end of the porous media region. The shorter reactor is designed to achieve steady-state

conditions faster in specific transformation experiments and decrease the axial back-mixing effect after the electrode sets. The void volume of Column A and column B are 0.80 L and 0.55 L, respectively. pH and oxidation-reduction potential (ORP) probes (Fondriest Environmental Company, USA), connected with a computer via the USB interface, were used to monitor the pH and ORP of the effluent. Four stainless steel bolts were used to connect each electrode inside the column, and the bolts were sealed with modified Swagelok® stainless steel nuts and O-rings. All sampling ports were sealed with Swagelok® nuts and septa. Solutions were pumped through the columns from the bottom at a rate of 4 mL/min or 2 mL/min using a peristaltic pump (Masterflex, model 7720060) equipped with Viton tubing. The flow rate results in Darcy's velocities of 1.8 m/day and 0.9 m/day, respectively. Two electrodes (one cathode and one anode) or three electrodes (one cathode and two anodes) were mounted in the columns. When three-electrode arrangement was used, an adjustable resistance was incorporated to allocate the current distribution between the two anodes (Figure 1c). Constant currents ranging from 15 mA to 120 mA were applied using an Agilent E3612A DC power supply. Simulated groundwater was prepared by dissolving 0.413 g/L NaHCO₃ and 0.172 g/L CaSO₄ in de-ionized water or tap water, and was stored in a 10L Tedlar bag. The concentrations of bicarbonate ions and calcium ions are representative of groundwater from karstic aquifer,^{31–33} resulting in a conductivity range of 800–920 µS/cm. The contaminants were injected into the solutions before starting each experiment. Solutions were pumped from the Tedlar bag into the column for thirty minutes before starting the electrical power, to produce homogeneous distribution of contaminants within the column. All experiments were conducted at room temperatures ranging between 19.5 and 21 °C. Control experiments without electrolysis were conducted using the simulated groundwater with the same amount of contaminants (TCE or mixture of contaminants), and the results showed that adsorption of contaminants on limestone gravel was negligible within the duration of all experiments.

Analytical methods

In addition to continuous online measurement of pH and ORP at the outlet of the reactors, 2 mL solutions were sampled at sampling ports throughout the column reactors (Port-S1 to Port-S5 in Figure 1) for ORP and pH measurements using microprobes (Microelectrode company, USA). Aqueous TCE was analyzed using a SRI 8610 gas chromatography (GC) instrument equipped with a purge-trap system and a FID detector. The typical procedure includes collecting a 50 µL water sample using a Hamilton gas-tight syringe, and immediately injecting the water sample into a sealed tube for measurement. When TCE initial concentration was 0.5 mg/L, a sample volume of 0.5 mL was used. The dissolved hydrocarbon gases (DHGs) (ethane, ethene and methane) in aqueous solution were analyzed using SRI 310 GC with a FID detector. Detailed information on DHGs analysis is provided in the SI. The GC operation programs were specified in a previous study.³⁰ Analysis for chloride ions, nitrate ions and selenate ions were performed using an ion chromatography (IC) instrument (Dionex 5000) equipped with an AS20 analytical column. A KOH solution (35 mM) was used as a mobile phase at a flow rate of 1.0 mL/min. For the experiments with mixtures of contaminants, nitrate ions and selenate ions were analyzed simultaneously using IC without mutual interference. The samples for IC measurement were filtered by PVDF syringe filter (0.45 µm pore size, Whatman) before loading to the autosampler. Dichromate ion was measured by diphenylcarbazide method using Hach chroma Ver 3 reagent at 540 nm wavelength (Milton Roy 20D spectrophotometer).³⁴ The total arsenic analysis was performed by a commercial analytical laboratory (Alpha Lab., Westborough, MA, USA). Liquid samples (5 mL) were taken and filtered using a 0.45 µm pore size PVDF syringe filter, and the total arsenic concentration was determined using inductively coupled plasma (ICP) method (EPA 3005A, detection limitation was 20 µg/L in this study). The total ferrous species (Fe(II), including Fe²⁺, Fe(OH)₂ and FeCO₃, etc.) and total ferric species (Fe(III)) in

the effluent were determined using a spectrophotometer (Jasco spectrophotometer V550). The samples for this analysis were collected from effluents without further filtration. More information about this analytical procedure are found in the supporting information.

Results and discussion

ORP and pH changes

Figure 2 shows the effluent ORP and pH changes in Column A, under different electrode configurations and current intensity conditions. When the MMO anode and copper foam cathode are used for electrolysis (Figure 2a), the effluent pH slightly decreases from around 8 to 7.5. The decrease starts within the first 2 hours under 30 and 60 mA, but is delayed for about 5 hours under 120 mA. The pH change appears to be mostly due to the sequential passing of the simulated groundwater flow. The cathodic reaction generates hydrogen and hydroxyl ions, while the anodic reaction produces oxygen and protons. The pH probe measures the electrolytes within the vicinity of the upper cathode first, followed by measurement of the mixed electrolytes from the anodic and cathodic reactions. An increase in the effluent ORP to a steady state value is also noted for this case. Since the ORP is affected by the pH, the ORP changes at 1.8 hours (60 mA) and 5 hours (120 mA) reasonably reflect the pH changes. In Figure 2a, it can be also observed that higher currents produce higher ORP values, indicating that oxidative substances are generated at rates dependent on the current density. Oxygen evolution (eq 1) is the primary electrolytic process on the MMO anode, and dissolved oxygen concentrations higher than 11 mg L⁻¹ were detected in the effluent electrolytes after 6-hours electrolysis for all current conditions due to the effect of anodic O₂. The secondary anodic reaction, the evolution of chlorine in the presence of chloride ions (eq 2), may also contribute to higher positive ORP values at higher currents.

Thus, although the effluent pH values are almost identical under 60 and 120 mA, different ORP values are observed. Furthermore, the hydrogen gas generated from the copper foam cathode (eq 3) seemingly plays a less relevant role on ORP values in this system. As a result, the electrolysis processes using an inert anode and a copper cathode finally increase the ORP value of simulated groundwater due to generation of oxidizing substances, such as active oxygen and chlorine.³⁵

When a cast iron anode is used, the effluent pH and OPR measurement are very different from those obtained when the MMO anode was used. The effluent pH gradually increases (Figure 2b) and maintains alkaline conditions even after 16 hours. A pH peak value appears under 30 mA and 60 mA conditions due to the flow passing through the cathode, however, under 90 mA the effluent maintains very alkaline condition (pH >11). In contrast to the case of the MMO anode, the effluent ORP values continuously decrease to very reducing conditions when iron anodes are used. Although the effluent pH rise results in a drop in the ORP, the ORP profiles do not exactly follow the change of pH (Figure 2b). Thus, the ORP decrease is not only due to the pH change, but also due to the formation of ferrous species from the anodic reaction (eq 4).^{18, 36, 37} Although hydroxyl ions from the cathodic reaction can react with the electrochemically generated ferrous ions (eq 5), free hydroxyl ions still exist in the flowing electrolyte (K_{sp} of Fe(OH)₂ is 10e-15)³⁸.

As a result, the pH reaches alkaline condition and ORP decreases to reducing values. This trend is further enhanced under higher current since the electrochemical process is accelerated. In these reducing electrolytes containing ferrous species, the dissolved oxygen decreases from more than 8 mg/L in the influent to less than 1 mg L⁻¹ in the effluent. In turn, ferric species generated in the solution and the ratio of Fe(II)/Fe(III) in the effluents varied. The measurements showed that the Fe(II)/Fe(III) ratios were 0.82 under 90 mA, 0.48 under 60 mA, and 0.24 under 30 mA after 18 hours operation.

Figure 2c depicts the pH and ORP changes of the effluents from the electrolytic system with three electrodes (two anodes and one cathode). The effluent pHs follow a similar “increasing-decreasing” trend, and the final pHs after 21-hours operation range from 8.5 to 9. Different from the two-electrodes system, the two anodic processes including iron dissolution (eq 4) and oxygen evolution (eq 1) contribute in this three-electrodes system. Production of protons on the MMO electrode limits the generation of alkaline conditions in the effluent. While the pH is being neutralized, the ORP profiles (Figure 2c) still decrease and reach relatively steady state reducing conditions at values ranging from -310 to -150 mV vs. Ag/AgCl. Moreover, the final effluent pH and ORP values are dependent on the current distribution between the two anodes: a larger current passing through the inert anode induces higher ORP value, while a larger current passing through the cast iron anode induces lower ORP value. The ratio of Fe(II) and Fe(III) concentrations further supports the observation on ORP. After 20 hours, the ratios of Fe(II) concentration to Fe(III) concentration are 0.15 (60 mA MMO anode : 30 mA iron anode), 0.83 (60 mA MMO anode : 60 mA cast iron anode), and 0.96 (30 mA MMO anode : 60 mA cast iron anode), respectively. Generally, the data demonstrate that the redox conditions of electrolytes can be regulated by varying the currents on the two anodic reactions. This is further validated by an experiment with longer time of operation (47 hours) (Figure S1 in the supporting information (SI)). The electrolysis using an iron anode not only shifts the redox condition in the immediate vicinity of electrode, but also provides reducing substances like ferrous species to electrolytes, which also contribute to the transformation of contaminants.

TCE reduction on cathode

Electrochemical transformation of TCE in simulated groundwater flow is investigated in Column B (faster evaluation of TCE steady-state concentrations). The transformation occurs at the electrodes through electrochemical reduction on the cathode and the degradation products include chloride ions, ethene, ethane (see Figure S2 in the SI), indicating that reductive β-elimination reactions of TCE were negligible under the experimental conditions.^{30, 39} Figure 3a shows the decay of TCE in the experiments using Column B. The TCE concentrations decrease after the water passes through the electrodes (measured at Port-S4 of Column B) and reach steady-state values within 3.5-hours. The removal efficiency (RE) of aqueous TCE (eq 6), and the treating capacity (TC, mg/h) of TCE (eq 7), defined as:

$$\text{RE} = (C_{\text{in}} - C_{\text{en}}) / C_{\text{in}} \times 100\% \quad (6)$$

$$\text{TC} = Q \times (C_{\text{in}} - C_{\text{en}}) \quad (7)$$

are used for analysis, where C_{in} and C_{en} are the TCE concentration (mg/L) in the influent and in the effluent, respectively; and Q is the flow rate of groundwater solution (L/h). For the flow rates specific to this study, using a pair of cast iron electrodes (No. 1) or a pair of MMO electrodes (No. 2) produce limited TCE removal (Figure 3a), indicating the surface area of cathode is essential for improving the removal efficiency. When a copper foam cathode is used with an MMO anode, the electrode sequence appears to affect the removal efficiency. For the Anode-1 || Cathode sequence (No. 3), the oxygen released from the MMO anode decrease the TCE removal efficiency through the electron competition effect on the electro-reduction reaction. Therefore, only 23.1% RE and 1.93 mg/h treating capacity are obtained for this case (also see the summary in Table S1 in the SI), which is lower than the 33.7% RE and 2.82 mg/h TC under the Cathode || Anode-2 sequence (No.4). Using a copper foam cathode with cast iron anode (No.5), further decreased the steady-state concentration of TCE to 23.1 mg/L and increased the RE to 40.5%. Based on the literature, the ferrous species like ferrous hydroxides are not capable of reducing TCE at a such fast rate,^{40, 41} and the improvement of the RE is due to the deoxygenating effect from the ferrous species,³⁰ which are produced by the iron anode. Measurements of the solution ORP after the anode and before the cathode (Port-S3) show that the iron anodes (Cases No. 5 and No. 7 in Figure 3b) generate a reducing environment. Consequently, the dissolved oxygen in the influents is scavenged by the ferrous species, promoting the TCE removal efficiency. DO concentration in the electrolytes between iron anode (Anode-1) and cathode were measured to be lower than 1 mg/L after 3.5-hours operation. To further verify this observation, a deoxygenated solution containing TCE was used as the influent for column experiment No. 6. The removal efficiency was as high as that of No. 5, suggesting that the enhancing effect of iron anode is due to the disappearance of the dissolved oxygen (8.5–8.8 mg/L in the influent in this study).

In addition to using iron anode before the cathode, the introduction of secondary anode (Anode-2 position) after the cathode further improves the TCE RE and decreases the cell voltages and energy consumption (see RE, cell voltages and energy consumption in Table S1 in the SI). In comparison with the two electrode systems, three electrodes arrangement is believed to facilitate more effective current distribution on the cathode,⁴² thereby the removal efficiency (No. 7) surpasses that of No. 5 experiment by 4.9%. The addition of an MMO electrode at Aonde-2 position is not expected to negatively impact the TCE reduction on cathode (also see No.7 and No.8 experiment in Table S1 in the SI) because any oxygen gas generation is occurring downstream from the cathode. Thus, the three-electrodes arrangement (No.7) is adopted for further analysis.

A higher TCE removal efficiencies are observed for a flow rate of 2 mL/min when compared with 4 mL/min flow rate (Figure 4a), indicating that longer residence time of electrolyte improves the removal efficiency. In contrast, the treating capacity of the electrolytic flow system exhibits higher values for the 4 mL/min flow rate, as shown in the inset of Figure 4a, which is due to the better mass transfer of TCE at this flow rate. Likewise, the current efficiencies were roughly estimated to be higher at 4 mL/min flow rate (see Figure S3 in the SI). Under the two flow rate conditions, the TCE removal efficiencies gradually increase with the increasing thickness of the cathode. At 2 mL/min flow rate, the TCE removal efficiency can reach 85% with a higher thickness or surface area. At the same time, observation of RE profiles indicates that the relationship between RE and thickness of foam cathode is not linear. For 2 mL/min flow rate, the RE relatively plateaued when the foam cathode thickness increased beyond 1.9 cm. It is possible that the uneven current distribution from the surface to the inside of electrode results in the non-linear relationship between RE and thickness of foam. Specifically, because the current distributes mostly on the outmost layer of the foam electrode, the improvement on TCE RE is limited when the surface area of the cathode (or thickness of foam cathode) reaches a certain value.^{42, 43}

The effect of applied current intensity and TCE concentration is depicted in Figure 4b using a contour plot. The data used for preparing this plot are summarized in Table S2 in the SI. The highest removal efficiency (> 82.18%) can be obtained for low influent TCE concentration (0.5 to 7.5 mg/L) and high current intensity (> 45 mA). At high influent TCE concentration ranging from 20 to 35 mg/L, the RE does not increase beyond 73.50%, even though higher current is imposed. By contrast, at low concentration of 0.5 and 5 mg/L, 15 mA current still achieves more than 71.50% RE. It is concluded that the TCE RE depends upon the current and influent TCE concentration, and the electrochemical reactive flow process allows for convenient and effective manipulation of the current to optimize reaction rates for target contaminants.

Cleanup of mixture of contaminants

The electrolysis process using an iron anode generates reducing electrolytes containing ferrous species, which also contribute to the transformation of other contaminants in groundwater. Figure 5 shows the validity of the system for cleanup of other contaminants including nitrate, Cr (VI), selenate and As(III). These contaminants are selected for the test because they are, together with chlorinate solvents, frequently encountered and priority groundwater pollutants.⁴⁴ Using a three-electrodes system in Column B, the Cr(VI) concentrations monitored at Port-S4 decrease rapidly after the beginning of electrolysis. For the 0.35 mg/L influent concentration, a steady-state concentration close to zero (under detection limit) is achieved at all current conditions within 150-minutes electrolysis. Furthermore, the decay profiles are not affected by the cathode type. For 2.4 mg/L influent concentration, the decrease of Cr(VI) concentration slows down at 30 mA, indicating the ferrous species generated at this current becomes the limiting factor for the cleanup of Cr(VI). When electrocoagulation is applied under low currents (0.05~0.1 A), it is reported that the removal of Cr(VI) from wastewater is mostly due to chemical reduction by electrogenerated ferrous, instead of direct electrochemical reduction on the cathode.⁴⁵ Our results further support this point of view.

In order to evaluate the potential efficacy of the current system on a mixture of several contaminants, an electrolysis experiment using Column A was conducted. The concentration profiles of five contaminants were measured after 7-hours electrolysis (Figure 5b). Transformation is observed for the five contaminants along the flow direction of electrolytes, but the decay behaviors are different. For the dichromate, arsenite (total As) and selenate ions, a sharp concentration decrease appears in the simulated groundwater after the Anode-1 position (the iron anode), suggesting the removal of these contaminants is due to formation of ferrous species from the iron anode. In contrast, the nitrate and TCE concentrations do not show a considerable decline at the Port-S3 after the Anode-1 position. Instead, their concentrations decay after the foam cathode and the MMO (Anode-2). Because the MMO anode has negligible effect on the transformation of TCE and nitrate, the declines of TCE and nitrate from Port-S3 to Port-S4 are associated with the electrochemically reductive processes on the foam cathode. When the steady-state condition is reached, the removal efficiencies of TCE and nitrate are approximately 53% and 85% after the electrodes with respect to the influent concentrations. Due to the electron competition from nitrate and possible other co-contaminants like dichromate ions, the TCE RE decrease by around 30% compared to the RE reported in Figure 4b. The standard reduction potentials of nitrate and dichromate are both more positive than that of TCE,⁴⁶ hence, similar competition effect of nitrate and dichromate was also reported in ZVI column experiments.¹³ Generally, the concentration profiles in Figure 5b suggest that two kinds of cleanup mechanisms proceed in the system. TCE and nitrate are removed through the electrode-based electrochemical processes, therefore their removal efficiencies are subject to the factors that are related to the mass transfer effect of contaminants on the electrode /

liquid interface, such as the hydraulic residence time of the synthetic groundwater and the surface area of electrode. On the other hand, the removal of Cr(VI), selenate ions and As(III) primarily relates to the iron anode and the reducing electrolyte containing ferrous species. Ferrous hydroxides and ferrous carbonates can react with dissolved oxygen,³⁷ moreover, they are reportedly capable of adsorbing or reducing these targeting contaminants.^{47–51} Iron oxyhydroxides produced by chemical coagulation or electrocoagulation can adsorb aqueous arsenite effectively,^{47, 48} meanwhile the ferrous hydroxide can reduce selenate and further co-precipitate the produced elemental selenium.⁴⁹ Studies are ongoing in our lab to further identify the specific mechanisms of their removal by the iron species derived from iron electrolysis.

Implications for groundwater remediation

In this study, an electrochemical reactive flow system is evaluated for the remediation of groundwater with mixture of contaminants. The cathode serves as an electrode-based permeable reactive barrier for the transformation of specific contaminants like chlorinated solvents and nitrates, while the anode design is optional. The system is different from conventional electrochemical processes that only use inert anodes such as MMO or carbon materials, because the iron anode generates ferrous species, which can serve either as electron donors for the reduction of contaminants or as adsorbents for the immobilization of contaminants. Unlike the zero valent iron permeable reactive barriers, the reactivity of the dual reactive barriers here can be controlled by varying the applied current in term of the type and level of the contaminants. Introducing iron anode and MMO anode simultaneously (or individually) provides a way for the in situ regulation of the redox condition of groundwater. The redox conditions can be varied based on the properties of target contaminants. Suitable redox condition, in combination with the electrochemically generated gases (H₂, O₂), may stimulate the anerobic or aerobic activities of the bacteria in the groundwater, facilitating the degradation of contaminants.^{29, 52, 53}

Although the results presented here demonstrate the effectiveness of the current system on the cleanup of TCE and mixed contaminants, the long-term performance of the electrolysis on a mixture of different contaminants still needs to be evaluated. Furthermore, although the present process is intrinsically convenient to combine with solar energy, it can be expected that a field implementation of the dual electrochemical barriers will meet with a series of technical and engineering challenges, such as the scale formation of carbonates deposition on electrodes,²⁸ the scaling of electrode to the field and the engineering design for minimum energy consumption, etc. Although there are some options to address these problems, such as periodic polarity reverse for preventing electrodes from scale formation, research is still needed to identify and address these possible issues that this remedial strategy may encounter in full-scale implementation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Schema of (a) Column A, (b) Column B and (c) electric connections for the three electrodes. The dimensions are in centimeters.

Figure 2.

Effluent ORP and pH changes under different electrode configurations and currents. (a) MMO anode (Anode-1 in Column A) and copper foam cathode; (b) Cast iron anode (Anode-1 in Column A) and copper foam cathode; (c) cast iron anode (Anode-1), MMO anode (Anode-2) and copper foam cathode, with different current distributions on the two anodes. Electrolytes were made by dissolving salts in tap water (containing around 20 mg L⁻¹ chloride ions). Flow rate of 2 mL/min for all the experiments.

Figure 3.

(a) Decay of the aqueous TCE concentration in the effluent (samples collected from Port-S4 of Column B), under different electrode configurations. (b) The ORP values of the electrolytes before the cathode (samples from Port-S3 of Column B). 90 mA current and 4 mL/min flow rate were applied in all the experiments. For the two anode experiments, the current was equally divided (45 mA for each of the cast iron and MMO anodes). A-1 and A-2 in the legend refer to the Anode-1 and Anode-2 position, respectively. The letter C refers to the cathode. The symbol “||” denotes the electrolytes between the electrodes. Data points are average for duplicate set of experiments.

Figure 4.

(a) TCE removal efficiency for different flow rates, as a function of the thickness of foam electrode. 90 mA current and influent containing 20 mg/L TCE are applied. Samples were collected from Port-S4 of Column B when steady-state concentration was reached. Iron (A-1)||Cu foam(C)||MMO(A-2) electrode configuration and equal current distribution on the two anodes (45 mA for each) were used. (b) Contour plot for the TCE removal efficiency when steady-state conditions was reached at Port-S4 as a function of applied current and influent TCE concentration. 2 mL/min electrolyte flow rate, 1.27 cm thick copper foam electrode and equal current distribution on the two anodes (iron anode and MMO electrode) were applied. Data points are average of duplicate set of experiments.

Figure 5.

(a) Normalized Cr(VI) concentrations at Port-S4 of Column B. Two-anodes (iron anode and MMO electrode) configuration with equal current distribution. The cathode is Cu plate if not otherwise specified. The electrolytes contained dichromate and 5.0 mg/L TCE with 2 mL/min flow rate. Data points are average of duplicate set of experiments. (b) Normalized concentration profiles of Cr(VI), selenate, total As, nitrate and TCE when steady-state conditions are reached (7 hours after the start of electrolysis). Column A is used for this experiment. 60 mA current and Iron (A-1)||Cu foam(C)||MMO(A-2) electrode configuration. The influents include 0.5 mg/L $\text{Cr}_2\text{O}_7^{2-}$, 0.75 mg/L AsO_2^- , 2.2 mg/L SeO_4^{2-} , 20 mg/L NO_3^- and 5.4 mg/L TCE. 2 mL/min electrolyte flow rates for all the experiments in (a) and (b). Data points are average of duplicate measurements.