



Impact of electrode sequence on electrochemical removal of trichloroethylene from aqueous solution



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ARTICLE INFO

Article history:

Received 24 September 2014
Received in revised form 7 January 2015
Accepted 12 March 2015
Available online 21 March 2015

Keywords:

Trichloroethylene
Groundwater
Reduction
Treatment

ABSTRACT

The electrode sequence in a mixed flow-through electrochemical cell is evaluated to improve the hydrodechlorination (HDC) of trichloroethylene (TCE) in aqueous solutions. In a mixed (undivided) electrochemical cell, oxygen generated at the anode competes with the transformation of target contaminants at the cathode. In this study, we evaluate the effect of placing the anode downstream from the cathode and using multiple electrodes to promote TCE reduction. Experiments with a cathode followed by an anode (C → A) and an anode followed by a cathode (A → C) were conducted using mixed metal oxide (MMO) and iron as electrode materials. The TCE removal rates when the anode is placed downstream of the cathode (C → A) were 54% by MMO → MMO, 64% by MMO → Fe and 87% by Fe → MMO sequence. Removal rates when the anode is placed upstream of the cathode (A → C) were 38% by MMO → MMO, 58% by Fe → MMO and 69% by MMO → Fe sequence. Placing the anode downstream of the cathode positively improves (by 26%) the degradation of aqueous TCE in a mixed flow-through cell as it minimizes the influence of oxygen generated at the MMO anode on TCE reduction at the cathode. Furthermore, placing the MMO anode downstream of the cathode neutralizes pH and redox potential of the treated solution. Higher flow velocity under the C → A setup increases TCE mass flux reduction rate. Using multiple cathodes and an iron foam cathode up stream of the anode increase the removal rate by 1.6 and 2.4 times, respectively. More than 99% of TCE was removed in the presence of Pd catalyst on carbon and as an iron foam coating. Enhanced reaction rates found in this study imply that a mixed flow-through electrochemical cell with multiple cathodes up stream of an anode is an effective method to promote the reduction of TCE in groundwater.

Published by Elsevier B.V.

1. Introduction

Trichloroethylene (TCE) is a chlorinated solvent that has been widely used in industrial cleaning solutions and as a “universal” degreasing agent due to its unique properties and solvent effects. TCE is among 29 of the substances most commonly found at the USEPA (United States Environmental Protection Agency) Superfund sites [1]. At many TCE spill sites, residual amounts of TCE persist in a pure liquid phase (known as dense, non-aqueous-phase liquids, DNAPLs) within pore spaces or fractures [2]. The slow dissolution of residual TCE results in a contaminated plume of groundwater. Because of potential health effects, the USEPA has set Maximum Contaminant Levels (MCLs) for TCE in drinking water at very low concentrations ($5 \mu\text{g L}^{-1}$).

Methods that have been proposed to remove TCE from groundwater include microbial degradation [3–5], photochemical oxidation [6,7], sonochemical processes [8–10], and chemical reduction via zero-valent iron (ZVI) [12–15] or palladium-based materials [16–22]. Microbial processes suffer from long reaction time and limiting effects. Due to the thermodynamic instability of ZVI in water, changes in environmental conditions encourage the development of a corrosion surface layer. The formation of this surface layer can inhibit electron transfer and catalytic hydrogenation between any contaminants and the iron. A combination of ultraviolet light (UV) with ozone, hydrogen peroxide, Fenton’s reagent or oxalate-complexes can be effective in degrading TCE [22–28]. Disadvantages of these methods include limitation of dissolved oxygen mass transfer, use of expensive chemicals, high capital costs, lack of mobility of the equipment and the potential formation of toxic byproducts.

Electrochemical treatment offers a significant potential for in situ transformation of TCE [29–31]. Due to their chemical nature,

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attention was focused on cathodic reduction and dehalogenation of TCE and other highly oxidized chlorinated aliphatic hydrocarbons [11,32–37]. Transformation of these compounds at the cathode surface may occur through both direct and indirect mechanisms. Direct reduction occurs by electron tunneling or by formation of a chemisorption complex of the compound with the cathode material [38,39]. Indirect reduction, or hydrodechlorination (HDC), occurs via a reaction with atomic hydrogen and is the main reduction mechanism at hydrogen formation potentials. Atomic hydrogen adsorbed on the cathode can reduce organic compounds through formation of chemisorbed hydride complexes [39]. The reactions that occur at the cathode surface include:



Reduction by HDC is fast on cathodes with low hydrogen overpotentials, such as platinum and palladium, but much slower on metals with high hydrogen overpotentials, such as iron. In some cases, using larger electrode surface area is sufficient in increasing the rate of hydrogen formation [40]. Noble metals (e.g., Ag, Pt and Pd) are often used as working electrodes [41–43] because of the capability of absorbing hydrogen which promotes HDC [44]. Various materials, such as activated carbon fiber/cloth/felt, reticulated vitreous carbon and carbon nanotubes, meshed Ti, Ti/TiO₂ nanotubes, foam Ni, foam Fe and Ebonex[®] were frequently used as cathode substrates supporting Pd catalyst because of the penetrability and advantage for mass transfer in the dechlorination process [44–49]. Palladized electrodes were used for removal of TCE [37,50–52], chlorinated phenols [45,52,53], carbon tetrachloride [37], 4-chlorobiphenyl and 2,4,5-trichlorobiphenyl [47]. These were evaluated in the reactors with divided electrolytes where the anodes and cathodes are separated by ion exchange membranes.

Electrochemical treatment of groundwater in a reactor with mixed anolyte and catholyte has advantages over reactors with divided electrolytes because of lower energy requirements and easier installation and maintenance in the field [33]. In a mixed electrolyte, both reduction and oxidation processes could be optimized for efficient removal of highly oxidized contaminants [53–59]. Electrode materials and electrode arrangements could be selected to achieve specific conditions for the desired redox reactions [29,30,33–35]. For example, a two electrode mixed electrolyte system using an iron anode was successfully implemented for reduction of TCE and other contaminants [34]. The reduction potential of oxygen (1.229 V vs. SHE, standard hydrogen electrode) is higher than that of TCE (0.42 V vs. SHE from TCE to *cis*-DCE) so oxygen is reduced at the cathode along with the H₂O rather than TCE [34]. Employing Fe anode produces ferrous ions instead of oxygen gas and supports the reduction mechanism (Reaction (4)),



Using iron anodes in undivided electrochemical cells eliminates the competition between oxygen and contaminants for reduction at the cathode but may cause precipitation and an increase in pH [34]. Optimizing electrode sequence is an alternative approach to promote the reduction of contaminants at the cathode in a mixed electrochemical cell by minimizing the effects of the anodic processes. We evaluated electrode sequences with an anode downstream from the cathode to diminish the interaction between oxygen and the cathode, therefore promoting TCE reduction. Further, we evaluated using multiple cathodes (iron foam and perforated cast iron), increasing cathode surface area (iron foam cathode) and using Pd catalyst in the cathode vicinity (Pd on

alumina, carbon or iron foam) to enhance the reduction of TCE by the proposed electrode sequence.

2. Materials and methods

All chemicals used in this study were analytical grade. TCE [99.5%] and *cis*-dichloroethylene (*cis*-DCE, 97%) were purchased from Sigma–Aldrich. Calcium sulfate was purchased from JT Baker, oxalic acid (anhydrous, 98%) from Acros Organics, sodium chloride, sodium acetate and sodium bicarbonate from Fisher Scientific. Ti/mixed metal oxide (MMO) mesh (3N International) and gray cast iron (McMaster–Carr) were used as electrode materials. The Ti/MMO electrode consists of IrO₂ and Ta₂O₅ coating on titanium mesh with dimensions of 3.6 cm diameter by 1.8 mm thickness. Perforated cast gray iron disk (Ø=3.6 cm) and iron foam (45 pores per inch, PPI, 98% iron and 2% nickel, Aibixi Ltd. China) perforated with 0.5 cm holes were used as electrodes. Deionized water (18.2 MΩ cm) obtained from a Millipore Milli-Q system was used in all the experiments. Palladium catalyst supported on alumina pellets, Pd/Al (0.5 wt.% Pd, Sigma–Aldrich) with average size of 3.2 mm and on 4–8 mesh activated carbon (4.75–2.36 mm), Pd/C (1 wt.% Pd, Acros Organics) was used. Cast iron electrodes were not subjected to palladization since the high surface area is the most important characteristic of catalyst supporting material [47]. The iron foam electrodes were etched by diluted HCl (10 wt.%) and washed with deionized water. Prior to palladization [52], the iron foam electrodes were immersed in 1 M HCl to remove any foreign metal and the surface oxide layers. After a thorough rinsing of the electrodes with deionized water, the electroless plating of Pd was performed in a closed beaker with a PdCl₂ solution (to ensure 10 mg Pd coating) and 0.1 M HCl, and rotated at 300 rpm until the dark orange PdCl₂ solution turned colorless. The procedure was always performed under exactly the same conditions to ensure the deposition of the same amount of Pd and to achieve the same surface quality on each plate. After palladization, the iron plates were rinsed with deionized water. The exact amount of deposited Pd was calculated from the concentrations of the PdCl₂ solution measured spectrophotometrically at 480 nm, before and after electro plating. Scanning electron microscope (SEM) (Hitachi S-4800 FESEM) was used to prove Pd deposition on the foam iron cathode surface.

TCE and *cis*-DCE concentrations 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). The mobile phase was a mixture of acetonitrile and water [60:40, v/v] at 1 mL min⁻¹. 2 mL samples were collected from the sampling ports for analysis. Concentration of VC in aqueous solution was measured using 8610GC Gas Chromatograph with purge-trap system (SRI, USA), photoionization detector, and MXT-VOL stationary column. The purge-trap autosampler was equipped with carbon-sieve trap and Tenax trap. 50 μL of water sample was injected in 5 mL of deionized water in glass tubes and loaded into the 10-port autosampler. The GC was programmed at 40 °C for 6 min, then ramped to 60 °C in 2 min, and held at 60 °C for 10 min.

Analyses of chloride ions, acetates and oxalates 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⁻¹. The chlorides mass balance during the treatment was calculated to validate TCE reduction. 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 electrochemical reactor with two and three electrodes is shown in Fig. 1. The experimental conditions are given in

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