Simultaneous degradation of 1,1,1-trichloroethane and solvent stabilizer 1,4-dioxane by a sono-activated persulfate process

Bingzhi Li, Jiang Zhu *

Shanghai Academy of Environmental Sciences, Shanghai 200233, China

HIGHLIGHTS

- Degradation kinetics of TCA and concomitant 1,4-D were first studied.
- All pollutants followed the pseudo-first-order kinetics model.
- The generated radical species were identified by EPR.
- The pollutants' degradation was affected by reaction process, PS dose, pH and anions.
- The degradation products of the pollutants were determined by P&T–GC/MS, HPLC and IC.

ARTICLE INFO

ABSTRACT

Increasing attention has been paid to persulfate activation for the degradation of organic contaminants due to its high efficiency and low cost. However, most previous studies have overlooked the detection of generated reactive oxygen species (ROS), which plays an important role in the transformation of contaminants. In this study, the activation of persulfate by ultrasonic field (UF) for the degradation of 1,1,1-trichloroethane (TCA) and solvent stabilizer 1,4-dioxane (1,4-D), and the possible reaction mechanism were investigated. The results showed that the contaminants can be efficiently degraded under the optimal conditions of $pH_0 = 7.0$, Temp. $15 \pm 2\,°C$, persulfate 1.50 mmol/L, ultrasonic frequency 400 kHz, power 100 W and ultrasonic density 2.67 W/cm^2 with initial TCA $\sim$20 mg/L and 1,4-D $\sim$1.0 mg/L. Coexisting 10 mmol/L inorganic anions slowed down the contaminant degradation to different degrees, and the inhibiting effect followed the order of $CO_3^{2-} > HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. The electron paramagnetic resonance (EPR) technique was used to detect and identify the ROS. Results show that the applied UF could effectively activate persulfate and produce more hydroxyl radicals ($\cdot$OH) and sulfate radicals ($SO_4^{\cdot-}$), accordingly resulting in the enhanced degradation of the contaminants. Twenty-three and eight degradation intermediates were detected and identified for TCA and 1,4-D, respectively. Results indicate that the sono-activated persulfate process is a promising technique to simultaneously eliminate of TCA and 1,4-D from water or groundwater.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

As an emerging groundwater contaminant by the United States Air Force (USAF) and also a Group 2B possible human carcinogen by the International Agency for Research on Cancer (IARC), 1,4-dioxane (1,4-D) is attracting considerable attention in part because of its potential for widespread occurrence in groundwater that has been impacted by chlorinated solvents [1–3]. Generally, 1,4-D was used as a stabilizer for industrial solvents, typically 1,1, 1-trichloroethane (TCA), in the range of 2–8% by weight to neutralize hydrochloric acid, thus lengthening the lifetime of the solvent [1]. The EPA's Toxic Chemical Release Inventory (TRI) estimated that a total of 1.15 million pounds of 1,4-D and 273,693 pounds of TCA containing 1,4-D were released in 2002 [4]. Nevertheless, for a long time, 1,4-D was not analyzed in the site investigation/remedial design process at some chlorinated solvent sites, primarily because the standard EPA Method 8260 analysis had difficulty in detecting it at the levels below 100 parts per billion (ppb). In addition, the EPA list of priority compounds did not include 1,4-D. The removal of 1,4-D was not economically feasible using traditional physiochemical methods [5]. Recently, a series of reports highlighted the co-occurrence of 1,4-D and chlorinated solvents in

* Corresponding author. Tel.: +86 21 64085119x2809; fax: +86 21 64085119x3112.

E-mail address: jzh@sjtu.edu.cn (J. Zhu).

the environment [2,6–10], which makes us rethink and reexamine whether previous site investigations and remediation strategies for solvent sites are appropriate or not under the new situation that 1,4-D is recently listed as an emerging groundwater contaminant [11]. It further implies the necessity of expanding monitoring networks in future site investigations and exploring new cost-effective remediation technologies that can adequately treat both chlorinated solvents and 1,4-D.

Although 1,4-D and chlorinated solvents coexist in the environment, few studies have documented the combined remediation of them in the laboratory scale. Using the ozone/H_2O_2 process, Yunker [12] carried out a pilot-scale field evaluation and found that the process could significantly reduce the concentrations of trichloroethene, *cis*-1,2-dichloroethylene, 1,1-dichloroethane, and 1,4-D. In contrast to chlorinated solvents, air stripping and liquid-phase granular-activated carbon adsorption are not effective for the removal of 1,4-D [7,13]. On the other hand, advanced oxidation techniques involving ultrasound, hydrogen peroxide, ultraviolet light, ozone, and persulfate have been applied successfully to degrade the individual contaminant [14–19].

In a previous study, we effectively decomposed TCA in the aqueous solution utilizing a sono-activated persulfate process, and the nearly complete elimination of TCA was achieved under the following optimal conditions: initial pH 7.0; ultrasonic frequency, 400 kHz, power, 100 W; $T = 20 \pm 2\ ^{\circ}C$; and a molar ratio of persulfate/TCA = 10:1 [20]. Previous study was only focused on the TCA degradation but not involved the detection of solvent stabilizer 1,4-D, thus, the effect of the concurrence of these contaminants was not well elaborated. At present, there is now indirect evidence suggesting that the persulfate activation by UF can produce reactive oxygen species (ROS), most of these studies only drew conclusions based on the quenching studies for detecting the type of ROS [21], but could not provide direct evidence, such as electron paramagnetic resonance (EPR) investigations, for the formation of ROS in these processes. Therefore, the main purposes of this study were (i) to investigate the degradation of TCA and the solvent stabilizer 1,4-D in aqueous solution with different processes and conditions; (ii) to identify the radical species generated in the systems using the EPR technique, and to determine the effects of persulfate dosage, initial solution pH, and the reaction time on the degradation of the contaminants and on the generation of radical species in detail; and (iii) to analyze the intermediates of TCA and solvent stabilizer 1,4-D degradation by the P&T–GC/MS, HPLC and IC methods during the sono-activated persulfate process, and then deduce possible degradation pathways. To the best of our knowledge, this is the first study that focuses on the simultaneous degradation of TCA and 1,4-D by the sono-activated persulfate process. This study is part of a wider ongoing project on the remediation of contaminated water or groundwater with chlorinated hydrocarbons (CHCs) by a sono-activated persulfate process [20]. Through this research, we intended to provide a theoretical basis and practical guidance for the remediation of water or groundwater that is concurrently contaminated by TCA and 1,4-D.

2. Materials and methods

2.1. Materials

All of the chemicals that were used in this study were of analytical grade and were used without further purification. 1,1,1-Trichloroethane (TCA, $\geqslant$99.0%), 1,4-dioxane (1,4-D, $\geqslant$98%), sodium persulfate ($Na_2S_2O_8$, $\geqslant$98.0%), sodium chloride (NaCl, $\geqslant$99.5%), sodium nitrate ($NaNO_3$, $\geqslant$99.0%), sodium sulfate (Na_2SO_4, $\geqslant$99.0%), sodium carbonate (Na_2CO_3, $\geqslant$99.8%), sodium bicarbonate ($NaHCO_3$, $\geqslant$99.8%), formic acid (98%), acetic acid ($\geqslant$99.9%), glycolic

acid ($\geqslant$98.0%), oxalic acid ($\geqslant$99.5%), formaldehyde solution (wt. 36.0%), acetaldehyde ($\geqslant$99.5%), oxalaldehyde solution (wt. 40.0%), 2,4-dinitrophenylhydrazine (DNPH, $\geqslant$99.0%), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%) were purchased from Shanghai Jingchun Reagent Co., Ltd. (Shanghai, China). 1,1,1-Trichloroethane (2,2,2-d3, 99.0%) was obtained from Chem Service Inc. (Pennsylvania, USA), and 1,2-ethanediol diformate (90.0%) was provided by Shanghai Tongyuan Chemical Co., Ltd. (Shanghai, China). All of the solutions that were used in the experiments were prepared using Watsons Water (Pure Distilled). For pH adjustment, HNO_3 and NaOH solutions (0.1 mol/L and 1.0 mol/L) were used. A stock solution of TCA and 1,4-D was prepared by allowing the pure NAPL TCA and 1,4-D to equilibrate with Watsons Water in the dark with violent stirring and sealing via Parafilm and PTFE thread seal tape. The solution was then diluted to the desired concentration. The required amount of $Na_2S_2O_8$ was freshly prepared in Watsons Water just prior to the experiments.

2.2. Experimental procedure

A precalculated amount of $Na_2S_2O_8$ (0.075–7.5 mmol/L) was added to the TCA and 1,4-D containing solution, immediately mixed for a few minutes, and used to completely fill a group of 40 mL capacity screw-cap borosilicate glass reaction vials with TFE/silicone liners. All of the vials were installed in the transducers of a 100 W ultrasound generator operating at an 400 kHz ultrasound frequency (Shanghai Acoustics Laboratory, Chinese Academy of Sciences, Shanghai, China; diameter of oscillator: 80 mm). The temperature was maintained at $15 \pm 2\ ^{\circ}C$ with a Haake A80 refrigerated bath and circulator (Gulf Breeze, FL, United States). At different time intervals, the vials were taken out and then cooled at $4\ ^{\circ}C$ in an ice bath for approximately 5 min to further quench the reaction before the analysis of TCA and 1,4-D [20]. All of the batch tests were performed in triplicates, and control tests were performed in parallel without the addition of $Na_2S_2O_8$ or ultrasound intervention.

2.3. Analytical methods

For the analysis of aqueous samples containing TCA and 1,4-D, the concentrations were analyzed by an ATOMX Purge and Trap Sample Concentrator (Teledyne Instruments, Ohio, USA) that was coupled to an Agilent 6890/5973N gas chromatograph mass spectrometry (P&T–GC/MS) using the US EPA Method 8260C.

The EPR spectra were obtained using a Bruker EMX – 8/2.7 spectrometer (Germany) with a resonance frequency of 9.77 GHz, a microwave power of 20.02 mW, a modulation frequency of 100 kHz, a modulation amplitude of 1.0 G, a sweep width of 200 G, a time constant of 40.96 ms, a sweep time of 83.87 s, and a receiver gain of 1.0×10^4.

To analyze the degradation intermediates of TCA and deuterium-labeled TCA, an Agilent 7890/5975 GC/MS coupled to a Tekmar 3000 purge and trap concentrator by means of a transfer line that was maintained at 200 °C was used. The purge and trap conditions used in the experiments are summarized as follows: 40 mL purge vessel and 40 mL/min helium purge flow, purge-ready temperature: 140 °C, purge time: 11 min, desorb preheat: 245 °C, desorb temperature: 250 °C, desorb time: 2 min, desorb flow 300 mL/min, bake temperature: 280 °C, and bake time: 0.25 min. GC/MS analysis was performed using a DB-624 column (60 m × 1.25 mm × 1.4 μm; Agilent Technologies, USA) and helium as carrier gas. GC was operated under the following settings: injection temperature 220 °C; total flow rate: 14 mL/min; column flow rate: 1 mL/min; and split ratio: 10:1. The oven temperature was programmed from 35 to 80 (6 °C/min) and then from 80 to 120 (8 °C/min) holding for 3 min, then to 200 (12 °C/min)