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Photodegradation performance of 1,1,1-trichloroethane in aqueous solution: In the presence and absence of persulfate

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HIGHLIGHTS

- ▶ 1,1,1-Trichloroethane is frequently detected in contaminated groundwater with recalcitrant characteristics.
- ▶ VUV/$S_2O_8^{2-}$, a novel photochemical technology, is developed and compared with VUV process for 1,1,1-TCA degradation.
- ▶ VUV/$S_2O_8^{2-}$ process is more effective in TCA decomposition, but more sensitive to the solution matrix than VUV process.
- ▶ Several intermediates are detected in VUV/$S_2O_8^{2-}$ process, while none in VUV process.

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ABSTRACT

Photodegradation of 1,1,1-trichloroethane (TCA), a chlorinated solvent, with VUV and VUV/$S_2O_8^{2-}$ processes was investigated. The effects of various parameters including solution pH, Cl^- and HCO_3^- anions, and humic acid (HA) were evaluated. The results indicated that TCA can be effectively removed under VUV irradiation, and the addition of $S_2O_8^{2-}$, significantly enhanced TCA removal. TCA decomposition in both processes follows the pseudo-first-order kinetic model. In the pH adjusted solutions (from pH 3 to 11), maximum TCA degradation rate occurred at pH 3 and remarkable inhibition at pH 11 in the two processes. Both Cl^- and HCO_3^- anions, as well as HA, adversely affected TCA degradation performance. Moreover, TCA degradation in the VUV/$S_2O_8^{2-}$ process was more sensitive to all the influence factors than in the VUV process. The organic chlorine in TCA was released completely to chloride ion as a final product in both processes. Several reaction intermediates, including 1,1-dichloroethylene, 1,1,1,2-tetrachloroethane, perchloroethylene, carbon tetrachloride, chloroform, and dichloromethane were identified during TCA degradation in the presence of $S_2O_8^{2-}$. In summary, it can be concluded that the presence of persulfate was much more effective than the VUV alone, but the latter was more environmentally friendly due to the formation of nontoxic intermediates.

1. Introduction

The chlorinated solvent, 1,1,1-trichloroethane (TCA), has been used widely for several decades as one of the major chemical solvents in adhesives, aerosols, textile processing, extraction solvents, industrial solvent blends, and metal degreasing. As a result of its extensive usage and improper disposal, TCA has been reported as a contaminant in at least 823 of the 1662 National Priorities List sites identified by the U.S. Environmental Protection Agency (USEPA) [1]. The appearance of TCA in soils and groundwater has been of great concern because of its recalcitrant characteristic and potential to cause liver, nervous system and circulatory system problems from the long-term exposure. Hence, currently the maximum contaminant level of TCA in drinking water has been set at 0.2 mg L^{-1} [2]. In contaminated sites TCA in groundwater is susceptible to abiotic and biotic transformations. The biotransformation of TCA is a relatively slow process and can produce even more toxic intermediates, such as 1,1-dichloroethane, 1,1-dichloroethylene (1,1-DCE), and vinyl chloride, as well as the terminal product of TCA dechlorination, chloroethane, through the metabolic reactions of microorganisms [3,4]. Therefore, it is

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urgent to develop a process that is for the fast and effective decomposition of TCA to harmless intermediates.

UV-based advanced oxidation processes (AOPs), such as UV/H_2O_2, UV/O_3, and photoassisted Fenton reaction, are shown to be effective in the degradation of possible chlorinated pollutants in groundwater. Beltrán et al. [5,6] have demonstrated that trichloroethylene (TCE) could be effectively removed in both UV and UV/H_2O_2 processes, but direct UV irradiation did not contribute to TCA removal, and in UV/H_2O_2 process, the rate constant of TCE with $^{\cdot}OH$ was approximately 65 folds higher than that of TCA. Shen and Ku [7] showed that several gas-phase volatile organic compounds including TCA could be oxidized in UV/O_3 process. At the same time, vacuum ultraviolet (VUV) is an alternative promising AOPs in environmental techniques, where water can get dissociated into $H^{\cdot}$ and $^{\cdot}OH$, and O_3 in the presence of O_2 [8]. VUV photons can be generated by either a monochromatic (Xe-excimer) or a polychromatic radiation lamp (VUV-Hg lamp), emitting about 10% of the radiation at 185 nm and 90% radiation at 254 nm [8,9]. Excimer light source has been confirmed to be able to oxidize and mineralize chlorinated hydrocarbons including TCA, carbon tetrachloride (CT), chloroform (CF), dichloromethane (DCM), perchloroethylene (PCE), TCE, and 1,2-dichloroethylene in aqueous solution could be oxidized and mineralized by this technology [10,11]. Considering the equipment cost, VUV-Hg lamps have gained popularity in the degradation of many refractory organic contaminants, including PPCPs (pharmaceuticals and personal care products) [12,13], PFCs (perfluorinated compounds) [14,15], and chlorinated compounds [16]. Shirayama et al. [16] investigated the photodegradation rates of seven chlorinated hydrocarbons (including TCA) under a VUV-Hg lamp and found that all the contaminants could be effectively degraded in the absence of dissolved oxygen.

However, the potential of alternative AOPs in improving the removal performance of the recalcitrant contaminants is always of interest and persulfate ($S_2O_8^{2-}$), a strong oxidant ($E^0 = 2.1$ V), has emerged to have great potential for pollutants oxidation through the activation by means of heat, ultraviolet irradiation, chelated or unchelated transition metals, hydrogen peroxide, and alkaline pH to generate sulfate radicals ($SO_4^{-\cdot}$) and other reactive species [17–19]. The various activation methods are proved effective in most prevalent organic contaminants remediation, e.g. halogenated aliphatics, chlorinated aromatics, fuel hydrocarbons, polycyclic aromatic hydrocarbons, and pesticides [19]. Significant degradation of TCA was observed by heat activation [20,21], as well as alkaline and hydrogen peroxide activation reported by Block et al. [22]. Moreover, photolysis of $S_2O_8^{2-}$ has recently gained much attention and there have been a few investigations on the photochemical decomposition of environmentally harmful substances with the help of $SO_4^{-\cdot}$ [23–27]. However, to our knowledge, only one study was conducted so far that combined VUV and $S_2O_8^{2-}$ for the degradation of perfluorodecanoic acid [14]. Although TCA degradation under VUV irradiation has been previously reported, the influence of complex solution matrix encountered in contaminated groundwater and TCA degradation mechanism were not well considered [10,11,16]. In addition, there is no report on direct comparison of VUV and VUV/$S_2O_8^{2-}$ processes under controlled conditions. Therefore, the objective of this work was to methodically investigate and compare TCA degradation efficiency by VUV and VUV/$S_2O_8^{2-}$ processes in aqueous solution. Because the oxidant dosage and solution pH are important in persulfate chemistry, and the background anions and dissolved organic matter (DOM) are commonly found in natural waters with potential to consume the reactive species generated during AOPs. The effects of solution conditions, such as the molar ratios of $S_2O_8^{2-}$/TCA, solution pH, Cl^- and HCO_3^- anions, and DOM, on TCA removal performance are evaluated. The intermediates in TCA degradation in both processes are detected by gas chromatography–mass spectrometry (GC/MS), and a possible TCA degradation pathway is proposed. The purpose of this investigation is to elucidate the mechanisms of TCA photodegradation based on direct VUV photolysis (in the absence of persulfate) and AOPs containing $^{\cdot}OH$ and $SO_4^{-\cdot}$ (in the presence of persulfate), and therefore provide theoretical support for the remediation of the TCA-contaminated groundwater.

2. Materials and methods

2.1. Materials

1,1,1-trichloroethane (TCA, 99.0%), sodium persulfate ($Na_2S_2O_8$, 98.0%), sodium chloride (NaCl, 99.5%), sodium bicarbonate ($NaHCO_3$, 99.5%), sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$, 99.0%), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, 99.0%), sodium phosphate (Na_3PO_4, 99.0%), potassium iodide (KI, 99.0%), and humic acid (fulvic acid > 90.0%), hexane (C_6H_{14}, 97.0%) were purchased from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). Ultrapure water from a Milli-Q water process (Classic DI, ELGA, Marlow, UK) was used for preparing aqueous solutions.

2.2. Experimental procedures

Irradiation experiments were conducted in a 1 L cylindrical glass reactor (an inner diameter of 7.0 cm and a height of 25 cm) with a quartz tube in the center of the reactor. A 10 W, low-pressure mercury vapor lamp (Guangdong, China), emitting at combined 254 nm (90%) and 185 nm (10%) wavelengths (hereafter referred to as VUV), was placed in the quartz tube with a photon flux of 2.09×10^{-5} Einstein cm^{-2} s^{-1}. The TCA concentration in all tests was prepared in an aqueous solution at 20 mg L^{-1}, except for the intermediate investigation where 114 mg L^{-1} TCA was used. The joint of the reactor and quartz tube was ground, and the sampling plot equipped with a ground glass stopper to avoid the loss of TCA through volatilization. The aqueous solution was filled into the reactor and the temperature was kept constant at 20 °C during all experiments with a cooling water jacket using a thermostat circulating water bath (SCIENTZ SDC-6, Zhejiang, China). A magnetic stirrer was located at the base of the reactor to maintain the solution homogeneity. Aqueous samples were taken at desired time intervals and analyzed immediately. The initial pH in all experiments was unadjusted except in the tests for investigating the influence of pH. All experiments were conducted in triplicate with the standard deviation $\leqslant$ 5%, and the mean values reported.

2.3. Analytical methods

The concentration of TCA was quantified by a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with an electron capture detector (ECD), an autosampler (Agilent 7693) and a DB-VRX column (60-m length, 320-μm i.d., 1.4-μm thickness). The method detection limit (MDL) for TCA is 5 μg L^{-1}. The temperatures of the injector and detector were 240 °C and 260 °C, respectively, and the oven temperature was isothermal at 75 °C. The amount of sample injected was 1 μL with a split ratio of 20:1. Aqueous samples were analyzed after extraction with hexane. The volatile organic intermediates formed in TCA degradation were identified by the EPA SW-846 Method 8260B using an automatic purge and trap (Tekmar Atomx, Mason, OH) coupled to a GC/MS (Agilent 7890/5975) with the same DB-VRX column. The MDL for the intermediates is 0.5 μg L^{-1}. The concentration of $S_2O_8^{2-}$ was determined by a spectrophotometric method using potassium