



Sulfate radicals induced degradation of Triclosan in thermally activated persulfate system



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HIGHLIGHTS

- TCS can be efficiently degraded by TAP oxidation at neutral pH.
- Cl⁻ inhibited TCS degradation at low concentration, while favored degradation at high concentration.
- The degradation performance in a real groundwater sample was studied.
- The ecological risk of TAP oxidation was assessed.

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ABSTRACT

The potential performance of thermally activated persulfate (TAP) oxidation on the degradation of Triclosan (TCS), a widely used antibacterial agent, was investigated under different conditions. TCS degradation by TAP oxidation was found to fit well with an Arrhenius behavior from 50 to 80 °C, yielding apparent activation energy 121.12 kJ/mol. TCS removal was found to be pH-dependent. Acidic conditions (pH 3–5) were beneficial to TCS removal. The performance of TAP oxidation was still promising under circumneutral pH value (pH ~7). The presence of alkaline species (with concentrations ranging from 1 to 50 mM) presented inhibitory effects on TCS degradation. When concentration of fulvic acid (FA) in solution increased to 10 mg/L, the effect on TCS degradation became increasingly negative. Different with alkaline species and FA, chloride ions at relatively low (<10 mM) and high (20–50 mM) concentrations exhibited dual effects on TCS degradation. Both sulfate radicals and hydroxyl radicals were confirmed in the system by Electron Paramagnetic Resonance spectra, and the quenching study indicated that sulfate radicals were the predominant oxidants responsible for the TCS degradation. The major intermediate derived from TCS degradation was identified to be 2,4-dichlorophenol and the reaction scheme was proposed. Additionally, the ecotoxicity of TCS and its degraded samples was assessed by a 4-day zebrafish embryo-larval bioassay, which indicated the capacity of thermally activated persulfate oxidation to decrease ecotoxicity, thus confirmed the sulfate radicals based oxidation a promising alternative of in situ chemical oxidation from the environmental risk standpoint.

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1. Introduction

Triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy) phenol) is a broad-spectrum antibacterial agent extensively used in many personal care products (e.g. toothpaste, cosmetics, soaps, shampoos and deodorants) and consumer products (e.g. plastic kitchenware, athletic clothing and foot ware) [1]. The widespread and long-term usage has resulted in TCS being discharge into wastewater and subsequently, TCS has been detected in surface water, sediments

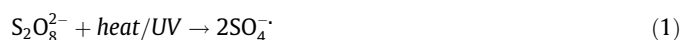
and groundwater [2]. TCS is currently one of the most frequently encountered organic pollutants that pose long-term threats to ecosystem and human health. Because of its hydrophobic nature, with estimated octanol-water partition coefficients ($\log K_{ow}$) of 4.86, TCS is likely to accumulate in aquatic and terrestrial organisms and has been detected in human samples (e.g. urine, plasma and breast milk) [1]. TCS is reported to be of high toxicity to algae and to pose reproductive and developmental effects in some fishes, such as Japanese medaka (*Oryzias latipes*) and zebrafish (*Danio rerio*) [1]. Recently, TCS's potential for endocrine disruption such as thyroid hormone homeostasis disruption has gained increasing concern. However, conventional biological treatment processes is

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hard to completely remove TCS. Furthermore, biotransformation might produce metabolites presenting similar or higher risk to the parent compound such as methyl derivative [1]. Photolysis, another commonly used technique of TCS degradation, might lead to the formation of chlorodioxins [3]. Thus, it is imperative to explore novel methods to remove TCS.

Concerns have been raised over in situ chemical oxidation [4] for the complete degradation and effective mineralization of recalcitrant organic compounds. The well-established oxidants such as Fenton reagents ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), ozone (O_3) and potassium permanganate (KMnO_4) have been used frequently in the last decades [5]. Nonetheless, the above-mentioned oxidizing agents have several demerits in practical application. H_2O_2 may be rapidly depleted in the presence of Fe^{2+} , which makes H_2O_2 hard to reach contaminants and the Fenton reagent works effectively at low pH only [6]. O_3 is sparingly soluble in water (~ 40 mg/L) and the low delivery rates may limit its application, and KMnO_4 is rather selective oxidant towards unsaturated moieties [7]. Recently, persulfate salts ($\text{S}_2\text{O}_8^{2-}$) (PS), as a promising alternative, have received more and more attention owing to its advantages over other common in situ chemical oxidation (ISCO) reagents [4]. PS has high aqueous solubility with a strong redox potential ($E^0 = 2.01$ V). Also, PS is relatively stable at ambient temperature. What's more, PS can be activated by heat, UV light (Eq. (1)), transition metals (Me^{n+}) (Eqs. (2) and (3)), alkaline and H_2O_2 to generate stronger oxidant, sulfate radicals ($\text{SO}_4^{\cdot-}$, $E^0 = 2.60$ V), which have a longer life-time than hydroxyl radicals ($\cdot\text{OH}$, $E^0 = 2.70$ V) [8]. Once $\text{SO}_4^{\cdot-}$ were generated, $\cdot\text{OH}$ can be formed in an indirect way (Eqs. (4) and (5)) [8], which also contributes to the oxidation of contaminants.



Under alkaline conditions:



Among all of the activation methods, thermally activated persulfate (TAP) oxidation is a very promising and attractive advanced oxidation technology (AOT) to decompose contaminants of concern. What's more, with the application of some emerging energy-efficient in situ thermal remediation (ISTR) [9], a hybrid remediation method can be developed to fully take advantages of these two technologies. So far, the thermal activation method has been applied to degrade some recalcitrant compounds. Gu et al. (2011) demonstrated that TAP oxidation is effective in 1,1,1-Trichloroethane degradation in an aqueous system [10]. Tan et al. (2012) exhibited that heat-activated persulfate oxidation is a promising choice to degrade diuron in water [9]. Simultaneously, the previous studies had taken the influence of groundwater components into account finding that aqueous matrix such as background anions may play different roles in reaction processes.

To our knowledge, however, data is still sparse on the treatment of TCS using $\text{SO}_4^{\cdot-}$ induced advanced oxidation especially TAP oxidation. The main purpose of this work is to elaborate the potential of TCS oxidation using TAP oxidation. Bench-scale experiments were conducted to estimate the activation energy of TCS degradation. Factors affecting the efficiency of $\text{SO}_4^{\cdot-}$ oxidation including elevated temperature, the presence of background anions, natural organic matters (NOM) and solution pH were discussed. In addition, the performance of TAP oxidation in real groundwater was investigated. Using the Electron Paramagnetic Resonance (EPR)

technique, dominant reactive species responsible for TCS degradation were identified. Finally, the complete mineralization of TCS and major intermediates of TCS oxidation were identified and the reaction schemes were proposed. Besides, the ecotoxicity during TCS degradation was assessed via a 4-day zebrafish embryotoxicity bioassay.

2. Materials and methods

2.1. Chemical reagents

TCS (irgasan), acetonitrile, methanol (MeOH), phosphoric acid (HPLC grade, >99.9%), ethyl acetate (Chromatography grade, 99.8%) and 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO, >99.0%, for ESR spectroscopy) were acquired from Sigma-Aldrich, Inc. Analytical grades of sodium chloride (NaCl, 99.5%), potassium chloride (KCl, >99.5%), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, >99.0%), calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99.0–103.0%), sodium bicarbonate (NaHCO_3 , 99.5%), sodium phosphate dibasic dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 99.0%), sodium dihydrogen phosphate dehydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 99.0%), hydrated tri-sodium phosphate (Na_3PO_4 , 98.0%) and potassium iodide (KI, 99.0%) were purchased from China National Medicines Corporation Ltd (Beijing, China). Fulvic acid (FA), analytical grade of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, 99.5%), guarantee reagent sodium hydroxide (NaOH, 99.0%), p-Phthalic acid (99.0%), tert-butyl alcohol (TBA, for HPLC > 99.5%) and dimethyl sulfoxide (DMSO, >99.99%, for Molecular Biology) were purchased from Shanghai Jingchun Reagent Co. Ltd (Shanghai, China). All chemicals were used as received without further purification and all stock solutions were prepared with deionized water.

2.2. Underground water samples

Real samples of underground water were drawn from the well of supplying water source for drinking water in Shanghai. The samples were stored at 4 °C and used for tests within two days without further treatment. Characteristics of underground water samples, which may affect the efficiency of TCS degradation, were determined immediately when received. Inductively Coupled Plasma (ICP, Agilent 720ES, USA) and Ion Chromatography (IC, Dionex DX-500, USA) are used to detect the concentration of metal cations and common anions separately, which are listed as followed:

Underground water sample: pH 8.17, chemical oxygen demand (COD) not detected, Inorganic Carbon 86.86 mg L^{-1} , $\text{NO}_3^- < 2 \text{ mg/L}$, $\text{Cl}^- 33 \text{ mg/L}$, Fe $0.8749 \text{ } \mu\text{g/L}$, Cu $0.0303 \text{ } \mu\text{g/L}$, Co $0.0226 \text{ } \mu\text{g/L}$, Ca $286.9 \text{ } \mu\text{g/L}$, Mn $9.663 \text{ } \mu\text{g/L}$.

2.3. Batch oxidation experimental

TCS oxidation was studied with batch experiments in 100 mL serum bottle incubated in water baths with the temperatures controlled at 50, 60, 70 and 80 °C. The initial concentration of TCS was chosen to be 0.031 mM, which is comparable to the concentration limit of TCS in aqueous environment. Experiments were conducted to determine the appropriate oxidant concentration by adding different amount of $\text{K}_2\text{S}_2\text{O}_8$ to TCS - contained solution. Based on the results shown in Fig. S1, the initial dosage of 0.155 mM $\text{K}_2\text{S}_2\text{O}_8$, i.e. 1:05 M ratio of TCS: PS was selected. The solution was mixed immediately for 10 min with a magnetic stirring prior to heating. Control experiments without $\text{K}_2\text{S}_2\text{O}_8$ addition were also carried out in parallel in 80 °C. The initial pH in all experiments was unadjusted except in tests for investigating the pH effect, where solution pH was maintained with 0.01 mM phosphate buffer (10 mL mixture of 0.1 M KH_2PO_4 and 0.1 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$). The

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