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Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation

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ABSTRACT

The oxidation of triclosan by commercial grade aqueous ferrate (Fe(VI)) was investigated and the reaction kinetics as a function of pH (7.0–10.0) were experimentally determined. Intermediate products of the oxidation process were characterized using both GC–MS and RRLC–MS/MS techniques. Changes in toxicity during the oxidation process of triclosan using Fe(VI) were investigated using *Pseudokirchneriella subcapitata* growth inhibition tests. The results show that triclosan reacted rapidly with Fe(VI), with the apparent second-order rate constant, k_{app}, being 754.7 M^{-1} s^{-1} at pH 7. At a stoichiometric ratio of 10:1 (Fe(VI):triclosan), complete removal of triclosan was achieved. Species-specific rate constants, k, were determined for reaction of Fe(VI) with both the protonated and deprotonated triclosan species. The value of k determined for neutral triclosan was $6.7(\pm1.9) \times 10^2$ M^{-1} s^{-1}, while that measured for anionic triclosan was $7.6(\pm0.6) \times 10^3$ M^{-1} s^{-1}. The proposed mechanism for the oxidation of triclosan by the Fe(VI) involves the scission of ether bond and phenoxy radical addition reaction. Coupling reaction may also occur during Fe(VI) degradation of triclosan. Overall, the degradation processes of triclosan resulted in a significant decrease in algal toxicity. The toxicity tests showed that Fe(VI) itself dosed in the reaction did not inhibit green algae growth.

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1. Introduction

Triclosan (TCS; 5-chloro-2-[2,4-dichlorophenoxy]-phenol) is an antimicrobial agent widely used in a range of personal and health care products. As a result, wastewater effluent discharge and sludge disposal from wastewater treatment plants (WWTPs) are two major pathways for triclosan to reach the aquatic environment. The removal of triclosan by conventional wastewater treatment processes is quite low [1–3]. Indeed, triclosan has been frequently detected in Australian surface water bodies receiving effluent from WWTPs at concentrations up to 75 ng/L [4]. Similarly, in a comprehensive reconnaissance study of 139 streams across 30 states in the USA conducted by the USGS, triclosan was ranked as the seven most frequently detected compound with the median concentration of 140 ng/L [5]. Triclosan was also the most abundant compound among all investigated pharmaceuticals and personal care products (PPCPs) with its mean concentration of 12.6 ± 3.8 mg kg^{-1} in 110 biosolids samples collected from 94 US WWTPs across 32 states in the 2001 National Sewage Sludge Survey [6].

There is a growing concern regarding the persistence of triclosan in the environment and its potential adverse impacts [7–9]. More importantly, triclosan can undergo direct phototransformation to produce 2,8-dichlorodibenzo-*p*-dioxin, which is known to be carcinogenic [10–14]. In addition, methyl triclosan formed by biological methylation process can be more lipophilic and bioaccumulative than the parent compound itself [9]. Risk assessment has shown that triclosan in surface waters could negatively affect a range of aquatic organisms [4,15,16]. It has also been speculated that triclosan resistance can promote the development of concomitant resistance to other clinically important antimicrobials through cross- or co-resistance mechanisms [17]. Given the persistency as well as toxicity of triclosan, the removal of triclosan during wastewater treatment by advanced treatment processes, particularly advanced oxidation, has been the focus of many recent scientific studies.

Oxidation processes of triclosan using oxidizing agents such as free chlorine and ozone have been widely reported. These processes produced various intermediates or by-products [18–21]. For example, with excess free chlorine, 2,4,6-trichlorophenol is formed via electrophilic substitution of 2,4-dichlorophenol which is formed via ether cleavage of triclosan, and chloroform formation was observed [18,20]. Ozone can rapidly oxidize the phenolic moieties of triclosan, and eliminate triclosan's antibacterial activity during wastewater treatment [22]. The oxidation of triclosan by

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permanganate (or Mn(VII)) can also be very effective, often yielding *p*-(hydro)quinine products and 2,4-dichlorophenol [21,23]. TiO_2 is found to degrade effectively triclosan by photocatalysis [19,24,25] with the formation of 2,4-dichlorophenol, chlorocatechol, 5-chloro-2-(4-chlorophenoxyl)phenol as by-products or intermediates [25]. However, with a few exceptions, most studies conducted to date do not assess the changes in toxicity of the reaction solutions [22,26,27].

Ferrate (or Fe(VI)) is a supercharged iron molecule in which iron is in the +6 oxidation state. Fe(VI) is a potential water treatment chemical due to its dual functions as an oxidant and a subsequent coagulant [28]. Fe(VI) has recently been shown to effectively remove electron-rich and recalcitrant contaminants such as PPCPs [29–31]. Nevertheless, further studies are still needed to investigate reaction intermediates and toxicity change during the oxidation process of these emerging contaminants such as triclosan by Fe(VI).

This study aims to determine the rate constants and identify intermediates for the reaction of Fe(VI) with triclosan and evaluate the toxicity changes during Fe(VI) oxidation of triclosan using algal toxicity tests. By a systematic examination of the reaction kinetics and intermediate products identifications, the degradation pathway of triclosan due to Fe(VI) oxidation was proposed and discussed. Changes in toxicity of a triclosan solution during Fe(VI) oxidation was also examined using the freshwater unicellular green alga *Pseudokirchneriella subcapitata* species.

2. Materials and methods

2.1. Standards and reagents

Triclosan (99.5%) was obtained from Dr. Ehrenstorfer GmbH (Germany). Diammonium 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS, 98%) was purchased from Aladdin (Shanghai, China). Potassium ferrate (Fe(VI), 20.9%) was purchased from Xian (China). It was purified by the method of Thompson et al. [34] to have a purity of 40.7% as Fe(VI) (w/w), which was determined using the molar adsorption coefficient at 510 nm of $[FeO_4^{2-}]$ of $1150\,M^{-1}\,cm^{-1}$ at pH 9.1 ± 0.1 (5 mM K_2HPO_4/1 mM borate) [29,30]. The purified Fe(VI) was used in the following experiments. All solutions were prepared with Milli-Q water from a Millipore Water Purification System. Others chemicals used for solutions were of analytical grade. Stock solution of Fe(VI) (0.3–0.6 mM) was prepared by dissolving solid potassium ferrate in Milli-Q water (pH ≈ 9.2) and used within 3 h. Stock solution of triclosan was prepared in methanol at concentrations of 100 mg/L. The freshwater unicellular crescent-shaped green alga *Pseudokirchneriella subcapitata* was obtained from the Adelaide Laboratory of the Commonwealth Scientific and Industrial Research Organization (CSIRO, Adelaide, Australia).

2.2. Oxidation of triclosan

Experiments to determine kinetics for the reaction of Fe(VI) with triclosan were carried out in the pH range of 7–10. Reagents containing 10 mM acetic acid/10 mM phosphate and 10 mM borate/10 mM phosphate were used to adjust the pH of reaction solutions. Oxidation of triclosan by Fe(VI) was operated in a 200 mL beaker equipped with a magnetic stirrer (500 rev/min) at room temperature ($23 \pm 2\,^{\circ}C$). The Fe(VI) stock solution was quickly filtered through a 0.45 μm hydrophilic polyethersulfone (PES) syringe filter (Shanghai ANPEL, China) and then standardized spectrophotometrically at 510 nm. Reactions were initiated by adding an aliquot of the Fe(VI) stock solution to suspensions containing triclosan under rapid mixing. In 150 mL reaction mixture solutions, the initial concentration of Fe(VI) was 45 μM while triclosan concentration was 3 μM. Every 10 s, 1 mL of the reaction solution was sampled and quenched with 0.5 mL thiosulfate solution (5 mM) to measure residual triclosan concentrations and 5 mL of the reaction solution with an ABTS solution (2,2′-azinobis(3-ethylbenzthiazoline-6-sulphonic acid)) to measure residual Fe(VI) concentrations using a ABTS method at 415 nm [35]. The absorbance was measured with a Helios Alpha spectrophotometer (Thermo Spectronic, Cambridge, UK). The pH values were determined using a Thermo Orin 5 star pH meter (Thermo Fisher Scientific, USA), which was calibrated using standard buffers (pH 4.0, 7.0, and 10.0, Thermo China).

Triclosan was analyzed on an Agilent 1200 series high performance liquid chromatograph (HPLC) fitted with a diode array detector. A SGE C18 RS column (100 × 4.6 mm, 5 μm) with a guard column (C18, 4.6 × 7.5 mm, 5 μm) was used for the separation of triclosan. Acetonitrile (ACN) and water were used as the mobile phase, which was programmed from 70% ACN at 0 min to 85% ACN at 6 min, 70% ACN at 8 min and post time was 2 min. The injection volume was 100 μL and the flow rate was set at 1 mL/min. The UV wavelength for detection was 205 nm. The retention time for triclosan was 5.0 min. The limit of quantification for triclosan was 5 μg/L.

2.3. Identification of intermediate products

For intermediate products identification, 100 mL of reaction suspensions containing the 5 μM triclosan and 20 μM Fe(VI) were reacted at pH 7.0 at room temperature ($23 \pm 2\,^{\circ}C$). Samples were adjusted to pH value of about 2 with 1 M HCl and saturated with NaCl. Intermediate products were extracted by vigorous shaking with 3× 10 mL dichloromethane. Each extract was passed through an anhydrous Na_2SO_4 column to remove water. The extract was concentrated under a gentle nitrogen stream and re-dissolved in 1 mL methanol. Each final extract was then filtered through a 0.22 μm nylon syringe filter (Shanghai ANPEL, China) into a 2 mL amber glass vial which was kept at $-20\,^{\circ}C$ until analysis.

Intermediates and by-products of the oxidation of triclosan by Fe(VI) were independently determined by gas chromatography–mass spectrometry (GC–MS) and rapid resolution liquid chromatography–tandem mass spectrometry (RRLC–MS/MS). The GC–MS instrument used in this study was an Agilent 6890N gas chromatograph (Agilent, USA) connected to an Agilent 5975B MSD mass spectrometer with a DB-5MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness) (J&W, USA). The GC conditions were given as follows: a sample volume of 5 μL injected in the splitless mode at 250 °C and the oven temperature programmed from 50 °C (5 min) to 300 °C at 8 °C/min followed by a 5 min hold at 280 °C, and helium used as the carrier gas at a flow rate of 1.0 mL/min. Mass spectrometer was operated under electron ionization mode at 70 eV with mass scan range of 40–500 amu. The temperatures of the ion source and interface were 250 °C and 300 °C.

The RRLC–MS/MS instrument used in this study was an Agilent 1200 series RRLC (Agilent, USA) connected to an Agilent 6460 triple quad mass spectrometer with a Zorbax SB-C18 column (3.0 mm × 100 mm, 1.8 μm). The mobile phase consisted of (A) Milli-Q water with 0.1% acetic acid and (B) acetonitrile, which was run at a flow rate of 0.3 mL/min. The gradient was programmed as follows: 10% B at 0 min, increased to 60% at 10 min, increased to 70% at 25 min and to 100% at 30 min and then decreased to 10% B at 35 min. The column temperature was set at 40 °C. The mass spectrometer was operated under electrospray negative ionization at a fragmentor voltage of 100 V with mass scan range of 50–1000 amu. The ionization source conditions were listed as follows: the drying gas flow 3 mL/min at 325 °C, sheath gas flow 12 mL/min at 350 °C and the nebulizer pressure 40 psig.

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