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

Bin Yang [a], Guang-Guo Ying [a,*], Jian-Liang Zhao [a], Li-Juan Zhang [a], Yi-Xiang Fang [a], Long Duc Nghiem [b]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] School of Civil Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

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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.

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

* Corresponding author. Tel.: +86 20 85290200; fax: +86 20 85290200.
E-mail addresses: guang-guo.ying@csiro.au, guangguo.ying@gmail.com (G.-G. Ying).

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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.

2.4. Toxicity evaluation

Since algae were found to be very sensitive to triclosan [16,32,33], a freshwater unicellular green alga *P. subcapitata* was used to test toxicity changes during the oxidation of the compound by Fe(VI). The oxidation experiments were conducted at pH 7.0 at room temperature (23 ± 2 °C). In 5 mL reaction mixture solutions, the initial concentration of triclosan was 2 μM while the various concentrations of Fe(VI) were 0, 4, 8, 10, 12, 14, 16, 18, and 20 μM in 10 mL glass tubes (KIMAX, USA) with polytetrafluoroethylene (PTFE) screw caps. The solutions were vortex mixed for 10 s to allow sufficient reaction. Reaction time was 3 h in the darkness. The solution (1 mL) was taken for the algal toxicity test. Another 1 mL was used for the determination of residual triclosan concentrations. All experiments were conducted in triplicate.

Growth inhibition tests of triclosan and its products to *P. subcapitata* over 72 h followed the procedure described by Yang et al. [33]. The EC_{50} value of triclosan was calculated by plotting the log concentration of triclosan versus algal cell counts using logistic regression (Eq. (1)) in the software Origin (OriginLab, Northampton, MA, USA).

$$y = A_2 + \frac{A_1 - A_2}{1 + (x/x_0)^p} = \min + \frac{\max - \min}{1 + ([\mathrm{TCS}]/\mathrm{EC}_{50})^p} \quad (1)$$

where [TCS] is the concentration of triclosan; EC_{50} stands for the calculated concentration at which there was a 50% reduction in cell counts and *p* for the slope; and min and max represent the apparent minimum and maximum values of growth inhibition, respectively.

3. Results and discussion

3.1. Kinetics for the reaction of Fe(VI) with triclosan

The rate expression for the oxidation of organic compound by Fe(VI) follows a first order reaction kinetics with respect to both the organic compound and Fe(VI) [31]. Accordingly, the rate expression for the oxidation of triclosan by Fe(VI) can be expressed as

$$-\frac{d[\mathrm{TCS}]}{dt} = k_{\mathrm{app}}[\mathrm{Fe(VI)}][\mathrm{TCS}] \quad (2)$$

where k_{app} is the overall apparent reaction rate constant and [Fe(VI)] and [TCS] are the concentration of Fe(VI) and triclosan, respectively. Oxidation experiments were conducted as a function of pH and in excess of Fe(VI) to determine the apparent reaction rate constant k_{app}. The pH range of 7.0–10.0 was selected. It is noteworthy that at below pH 7, the reactions would be too rapid due to the instability of Fe(VI) [30,36]. Although the kinetic experiments were designed under pseudo-first-order conditions with Fe(VI) in excess to triclosan ($[\mathrm{Fe(VI)}]_0 = 15 \times [\mathrm{triclosan}]_0$, and $[\mathrm{triclosan}]_0 = 3$ μM), due to the decomposition of Fe(VI) at the setting pH, the concentration of Fe(VI) were not constant during reaction with triclosan. Therefore, it is necessary to account for the decrease in Fe(VI) concentration over the time. Eq. (2) can be rearranged and integrated to yield:

$$\ln\left(\frac{[\mathrm{TCS}]}{[\mathrm{TCS}]_0}\right) = -k_{\mathrm{app}} \int_0^t [\mathrm{Fe(VI)}]\, dt \quad (3)$$

where the term $\int_0^t [\mathrm{Fe(VI)}]\, dt$ represents the Fe(VI) exposure [37], the time integrated concentration of Fe(VI); and k_{app} represents the apparent second-order rate constant. The value of k_{app} could be obtained by plotting the natural logarithm of the triclosan concentration vs. the Fe(VI) exposure.

As a representative example, Fig. 1 shows the changes in concentrations of triclosan and Fe(VI) during the oxidation of triclosan (3 μM) by excess Fe(VI) (45 μM) at pH 7.0 and 23 ± 2 °C. The Fe(VI) exposure was obtained by nonlinear regression of the data of the Fe(VI) concentrations and reaction time by Eq. (4)

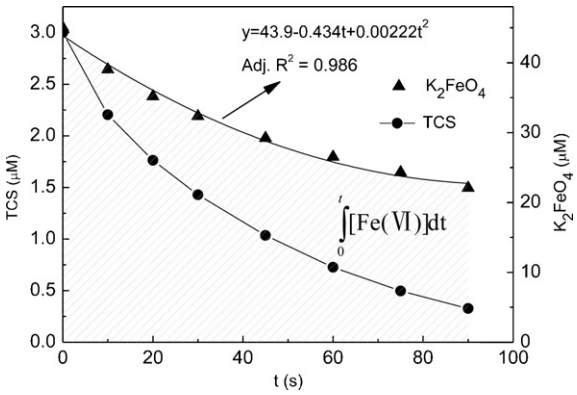


Fig. 1. Fe(VI) degradation of triclosan. $[\mathrm{triclosan}]_0 = 3$ μM, $[\mathrm{Fe(VI)}]_0 = 45$ μM, pH 7.0, 23 ± 2 °C. The shadow represents Fe(VI) exposure.

$$\int_0^t \mathrm{Fe(VI)}]dt = \int_0^t (43.9 - 0.434t + 0.00222t^2)dt \quad (4)$$

Although Fe(VI) was unstable, Fe(VI) was always in excess in comparison to triclosan within the studied reaction time.

The reaction kinetics model presented above successfully describe the oxidation of triclosan by Fe(VI) with R^2 of all regressions consistently above 0.99. The value of k_{app} obtained from the data presented in Fig. 1 was 754.7 M^{-1} s^{-1} (at pH 7.0 and 23 ± 2 °C).

The values of rate constants k_{app} for the reaction of Fe(VI) with triclosan as a function of pH are presented in Fig. 2. The rate constants of the reaction decreased with increasing pH values as observed in previous studies [29,38,39]. These pH-dependent variations in k_{app} could be attributed to the speciations of both ferrate and triclosan. The acid–base speciation of ferrate and triclosan can be expressed in Eqs. (5) and (6)

$$\mathrm{HFeO_4^-} \Leftrightarrow \mathrm{H^+} + \mathrm{FeO_4^{2-}} \quad pK_{a,\mathrm{HFeO_4}} = 7.23 \quad (5)$$

$$\mathrm{TCS\text{-}OH} \Leftrightarrow \mathrm{H^+} + \mathrm{TCS\text{-}O^-} \quad pK_{a,\mathrm{TCSOH}} = 8.1 \quad (6)$$

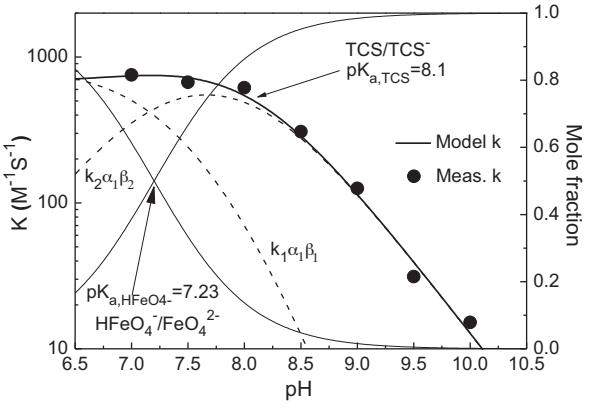


Fig. 2. Apparent second-order rate constants for the reactions of triclosan with Fe(VI) as a function of pH (7.0–10.0) at the room temperature (23 ± 2 °C). $[\mathrm{triclosan}]_0 = 3$ μM, $[\mathrm{Fe(VI)}]_0 = 45$ μM. Symbols represent measured data, and heavy line represents the model calculations. Dashed lines represent the contributions of the specific reactions between $HFeO_4^-$ and the TCS species (protonated and deprotonated form).

Second-order rate law of Fe(VI) degradation of triclosan is expressed by

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_1[\mathrm{HFeO_4^-}][\mathrm{TCS\text{-}OH}] + k_2[\mathrm{HFeO_4^-}][\mathrm{TCS\text{-}O^-}] + k_3[\mathrm{FeO_4^{2-}}][\mathrm{TCS\text{-}OH}] + k_4[\mathrm{FeO_4^{2-}}][\mathrm{TCS\text{-}O^-}] \quad (7)$$

where k_1, k_2, k_3, and k_4 represent species-specific rate constants; α_1 and α_2 represent the fraction of $HFeO_4^-$ and FeO_4^{2-}, respectively; β_1 and β_2 represent the fraction of non-ionisable TCS and ionized TCS, respectively. Because the contribution of FeO_4^{2-} to the overall reactions of Fe(VI) is negligible, therefore the last two terms in Eq. (7) can be neglected [29,38,40,41]. As a result, Eq. (7) can be rewritten as:

$$k_{\mathrm{app}} = k_1\alpha_1\beta_1 + k_2\alpha_1\beta_2 + k_3\alpha_2\beta_1 + k_4\alpha_2\beta_2 \quad (8)$$

$$\alpha_1 = \frac{[\mathrm{H^+}]}{([\mathrm{H^+}] + K_{a,\mathrm{HFeO_4}})} \quad (9)$$

$$\alpha_2 = \frac{K_{a,\mathrm{HFeO_4}}}{([\mathrm{H^+}] + K_{a,\mathrm{HFeO_4}})} \quad (10)$$

$$\beta_1 = \frac{[\mathrm{H^+}]}{([\mathrm{H^+}] + K_{a,\mathrm{TCSOH}})} \quad (11)$$

$$\beta_2 = \frac{K_{a,\mathrm{TCSOH}}}{([H^+] + K_{a,\mathrm{TCSOH}})} \quad (12)$$

The species-specific second-order rate constants, k_1 ($6.7(\pm1.9)\times10^2\ \mathrm{M^{-1}\,s^{-1}}$) and k_2 ($7.6(\pm0.6)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$) were calculated from least-squares nonlinear regressions of the experimental k_{app} data by using the software SigmaPlot 10.0 (Systat Software Inc.). The model could describe very well the experimental k_{app} ($R^2 = 0.97$) (Fig. 2). As can be seen in the speciation of Fe(VI) (Fig. 2), the molar fraction of $HFeO_4^-$ decreases and that of FeO_4^{2-} increases as the solution pH increases. As a result, the k_{app} value decreases as the solution pH increases. The pH dependence of k_{app} for triclosan could also be explained by considering the reactions of $HFeO_4^-$ with the protonated ($k_1 = 6.7(\pm1.9)\times10^2\ \mathrm{M^{-1}\,s^{-1}}$) and deprotonated species of triclosan ($k_2 = 7.6(\pm0.6)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$) at the triclosan's phenolic-moiety (pK_a 8.1). These differences can be explained by the higher activating effect of the hydroxyl groups as a result of their deprotonation [37]. For triclosan, the reaction between $HFeO_4^-$ and the dissociated triclosan ($k_2\alpha_1\beta_2$) controls the overall reaction at pH > 7.5, and the reaction between $HFeO_4^-$ with the undissociated triclosan ($k_1\alpha_1\beta_1$) dominates at pH < 7.5, as shown in Fig. 2 (dashed lines). Moreover, density functional theory (DFT) calculations have shown that the protonated form of Fe(VI) has a larger spin density on the oxo ligands than the unprotonated form of Fe(VI), which increases the oxidation ability of protonated Fe(VI) [42].

The current study appears to be the first to report the rate constants of the oxidation of triclosan by commercial grade ferrate. Nevertheless, values reported here are in good agreement with previous studies, investigating the ozonation and chlorination of triclosan and the oxidation of other phenolic compounds by Fe(VI). The rate constant of ferrate oxidation is several orders of magnitude lower than O_3 but is comparable to that of HOCl [37]. Suarez et al. [22] investigated the oxidation of triclosan by aqueous O_3. These authors reported the pH-dependent apparent second-order rate constant $k_{\mathrm{app,O3}}$ (at pH 7) to be $3.8\times10^7\ \mathrm{M^{-1}\,s^{-1}}$ [22], which is several orders of magnitude higher than the rate constant of ferrate reported in this study. The species-specific rate constant k determined for the ozonation of neutral triclosan was $1.3(\pm0.1)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$, while that measured for anionic triclosan was $5.1(\pm0.1)\times10^8\ \mathrm{M^{-1}\,s^{-1}}$ [22]. On the other hand, the overall second-order rate constant of the chlorination of triclosan was reported to be $5.40(\pm1.82)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$ [20], which is comparable to the apparent rate constant of the oxidation of triclosan by ferrate reported here.

The rate constants of Fe(VI) degradation of triclosan appears to depend on the purity of Fe(VI). With Fe(VI) purity of 40.7% (w/w), the second-order rate constant at pH 7 determined in this study was $750.8\ \mathrm{M^{-1}\,s^{-1}}$. This is lower than the reported value ($1100\ \mathrm{M^{-1}\,s^{-1}}$ at pH 7.0) by Lee et al. [29] who used Fe(VI) purity of 88% (w/w). It is also noted that when unpurified Fe(VI) with purity of 20.9% (w/w) was used, the measured second-order reaction kinetic constant was $275.0\ \mathrm{M^{-1}\,s^{-1}}$ at pH 7.0. Potassium chloride and potassium nitrate as impurities in the solution can accelerate the initial decomposition of the Fe(VI), although these impurities can also stabilize a small quantity of Fe(VI) [43]. Similarly, sodium chloride and hydrous ferric oxide as impurities can cause rapid and complete decomposition of Fe(VI) [43]. In addition, the initial concentration of Fe(VI) in aqueous solution exhibits a significantly influence upon the decomposition of Fe(VI) in solution. It has been established that Fe(VI) is more stable in a diluted solution in comparison to a more concentrated one [43]. The finding presented here suggests that the purity of Fe(VI) should be considered in the determination of degradation rates and efficiency in practical water and wastewater treatment of applications of Fe(VI).

3.2. Oxidation products of triclosan

The intermediate products of Fe(VI) degradation of triclosan were analyzed GC–MS analysis following solvent extraction of the samples. The GC chromatogram presented in Fig. 3a clearly show the detected intermediate products during the oxidation of triclosan by Fe(VI). Four intermediate products were identified in the reaction solution of Fe(VI) with triclosan. Those unspecified peaks in the TIC were mainly phthalates and silica oxides from the GC system. For the product at retention time of 9.632 min (Fig. 3b), the molecular ion peak with m/z of 120 indicated 2-chlorocyclopentanol. The matching degree is 91.4%. The mass spectrum of the peak at retention time of 13.889 min (Fig. 3c) has a molecular ion peak with m/z of 162. Other fragment ion peaks were observed at m/z 126, 98, 63. This compound was assigned as 2,4-dichlorophenol after comparison with a standard. The product at retention time of 18.332 min (Fig. 3d) was identified as 2-chlorobenzoquinone having a molecular ion peak with m/z of 142 and a fragment ion peak with m/z of 114 [19]. Ions m/z 144 and 129 suggest that the product has a chlorophenol structure. The compound at retention time of 29.653 min (Fig. 3e) showed a similar mass spectrum to that of triclosan, with a mass difference of 16 in their molecular ions, and other fragment ions. The substitution of hydroxyl group for a hydrogen atom gave rise to the molecular ion peak m/z 304. This compound was assigned as the hydroquinone of triclosan, 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol. The product was also detected in the photocatalysis and MnO_2 oxidation process [19,21].

The intermediate products were also confirmed using RRLC–MS/MS technique. Table 1 gathers the molecular ions and the primary fragment ions. Chlorophenol, 2-chlorobenzoquinone, 2,4-dichlorophenol and 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol were also be identified by RRLC–MS/MS. In addition, there were evidences of the dimerization of some triclosan degradation intermediate products. For example, 5-chloro-3-(chlorohydroquinone)phenol (Table 1) could be the dimerization of 2-chlorocatechol and o-chlorophenol. Similarly, 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol might be formed from the coupling of 2,4-dichlorophenol (Table 1). It was previously suggested that 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy)phenol (Table 1) with a molecular mass

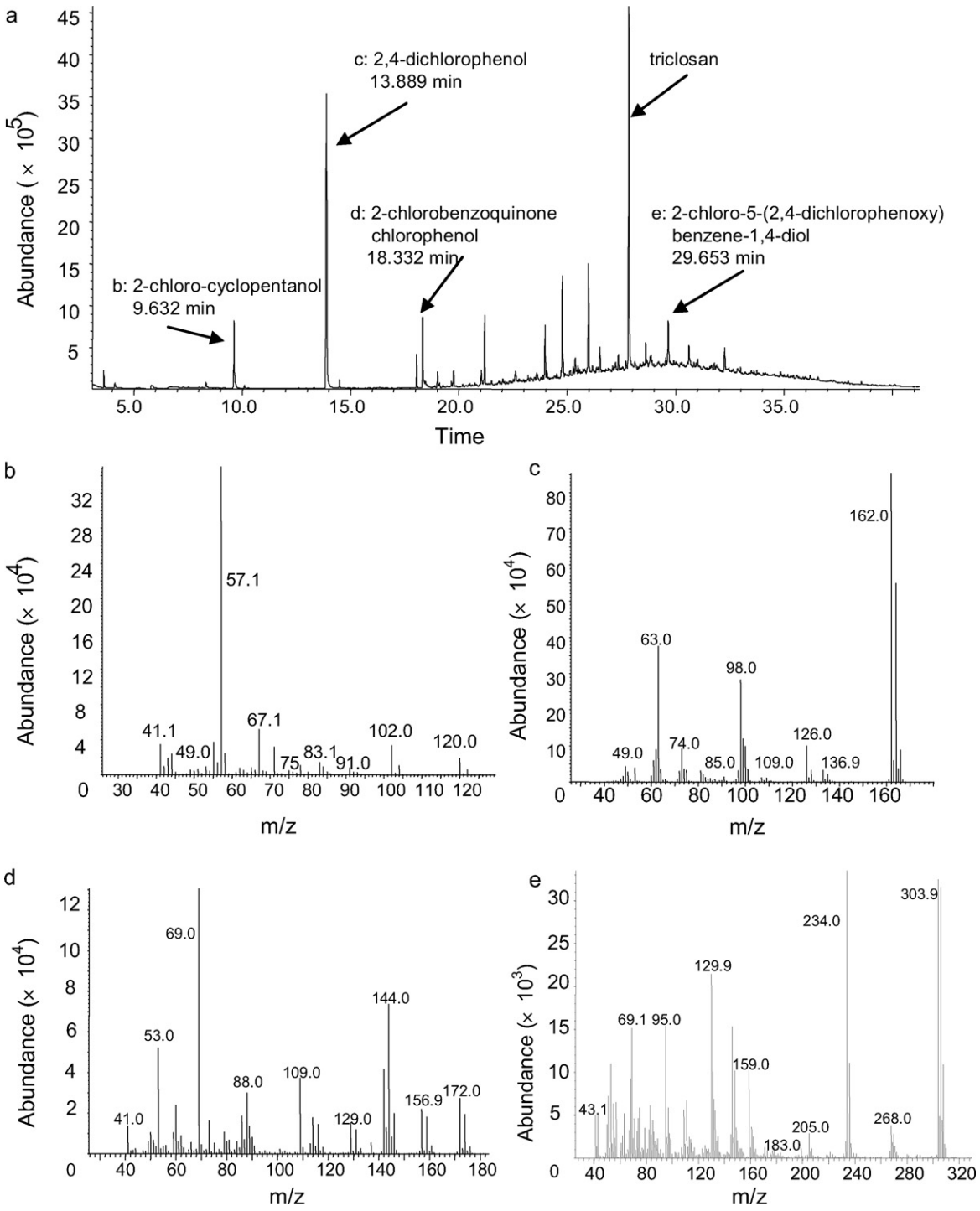


Fig. 3. Intermediate products of triclosan reaction with Fe(VI) analyzed by GC/MS. $[triclosan]_0 = 5\ \mu M$, $[Fe(VI)]_0 = 20\ \mu M$, pH 7.0, $23 \pm 2\ ^\circ C$. (a) Chromatogram of triclosan reaction extract. (b)–(e) Mass spectra of intermediate products.

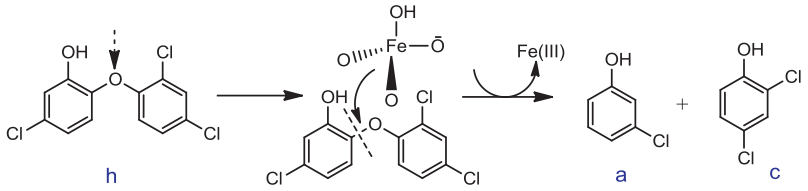
of 449 could be formed by reactions between triclosan and 2,4-dichlorophenol [44].

A plausible reaction scheme for Fe(VI) oxidation of triclosan was proposed in Fig. 4, after taking into account the kinetic information and products identification. The proposed mechanism for the oxidation of triclosan by the Fe(VI) anion involves the scission of ester bond and phenoxy radical addition reaction.

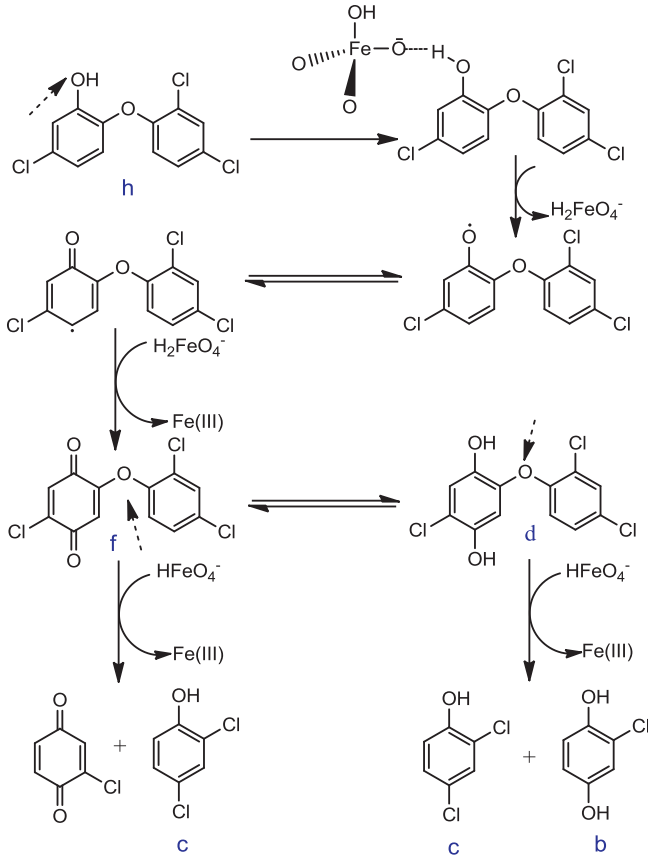
Despite the steric hindrance for triclosan due to its larger *o*-substituents of the phenol ring, the formation of a major product of 2,4-dichlorophenol in triclosan degradation suggested bond-breaking of the ether linkage occurred during the oxidation process (Fig. 4-1). C–O may be attacked by $HFeO_4^-$ through electron oxidation and resulted in the formation of an Fe(III) species, *m*-chlorophenol and 2,4-dichlorophenol. In addition, 2,4-dichlorophenol has also been identified as a intermediate product in the process of photocatalysis [19], transformation by Fe(III)-saturated montmorillonite [44] and oxidation by manganese oxides [21].

Products identification indicated that triclosan oxidation occurred at its phenol moiety and yielded quinone and hydro-

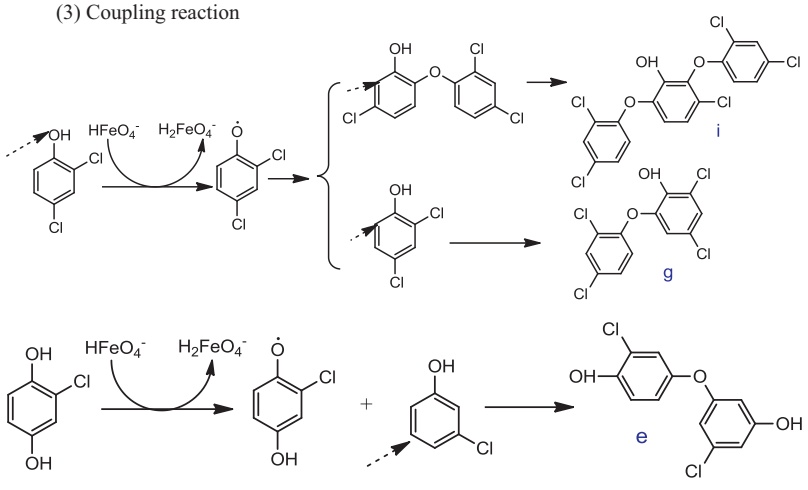
(1) Breaking of the ether bond



(2) Phenoxyl radical reaction



(3) Coupling reaction



(4) Degradation

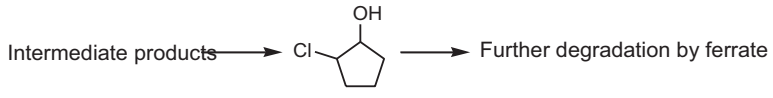


Fig. 4. Proposed reaction schemes for oxidation of triclosan by Fe(VI).

Table 1
Oxidation products of triclosan analyzed by RRLC–MS/MS.

Retention time (min)	m/z[a]	Name	Indication[b]
7.423–7.868	[M+COOH]- **173**/175	Chlorophenol	a
7.922–8.273	[M−H]- **143**/145	Chlorohydroquinone	b
11.416–11.759	[M−H]- **161**/163/164.9	2,4-Dichlorophenol	c
12.492–12.874	[M−H]- **303**/305/306.9	2-Chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol	d
13.077–13.420	[M−H]- **269**/270.9/272.8	5-Chloro-3-(chlorohydroquinone)phenol	e
13.607–13.966	439/381/**305.2**/265.2/157.1/89		
14.215–14.566	394.8(392.9/397)/**303**(305/306.9)/265.2/89		
15.845–16.250	**301.9**(303.9/306)/277.2/160.9/117/89	2-Chloro-5-(2,4-dichlodichlorophenoxy)-[1,4]benzoquinone	f
17.342–17.638	[M+Cl]- 320.9/**322.9**/324.9/326.9	4,6-Dichloro-2-(2,4-dichlorophenoxy)phenol	g
17.958–18.488	[M−H]- **287.0**/288.9/290.9	Triclosan	h
19.377–19.892	378.8/**380.9**/382.9/385		
24.461–25.124	446.9/**448.9**/450.9/452.9	3-Chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy)	i

[a] Each bold number corresponds to the base peak in the mass spectrum.
[b] The compound indication numbers of identified products correspond to those in Fig. 4.

quinone intermediates (Fig. 4-2). Initially the reaction mixture is becoming more organized as it goes from reactant to transition state or that the reaction proceeds through an associative type of mechanism and may involve hydrogen bond formation in the activated complex accompanied by intermolecular electron transfer. Consequently Fe(VI) oxidizes phenol by one electron transfer generating a phenoxyl radical and Fe(V) as the first step [45]. The phenoxy radical is stabilized by electron resonance within the phenol ring. In terms of electronic influence, triclosan's *o*-dichlorophenoxy group provides strong resonance and weak electron-withdrawing effects, thus overall an activating effect. Therefore para-position of the phenol was more readily attacked by Fe(V) or Fe(VI) than ortho position. This attack was also facilitated by the ortho orientation of the ring chlorine. It has been proposed that the phenoxyl radical transferred to the para-position and reacts with Fe(V) generating 2-chloro-5-(2,4-dichlodichlorophenoxy)-[1,4] benzoquinone through two-electron oxidation. It can be converted into 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol. Fe(VI) then goes on to break C–O bond leading to the formation of 2,4-dichlorophenol and chlorocatechol or 2-chlorobenzoquinone. Similarly in the case of ethinyl estradiol (EE2), 2,3-quinone EE2 and 3,4-quinone EE2 are expected to be the main initial transformation products during the oxidation of EE2 by Fe(VI) [46].

Coupling reaction may also occur during Fe(VI) oxidation of triclosan. This is especially likely given the large excess of phenol in the reaction mixture. Phenoxyl radical of 2,4-dichlorophenol reacted with another triclosan and 2,4-dichlorophenol forming products 3-chloro-2-(2,3-dichlorophenoxy)-6-(2,4-dichlorophenoxy) and 4,6-dichloro-2-(2,4-dichlorophenoxy)phenol (Fig. 4-3). Phenoxyl radical of 2-chloro catechol and m-chlorophenol produced 5-chloro-3-(chlorohydroquinone)phenol. Overall, phenol ring opening is expected to produce 2-chloro-cyclopentanol (Fig. 4-4). Intermediates could undergo further reactions with Fe(VI), yielding low molecular weight organic compounds.

3.3. Elimination of triclosan toxicity by reaction with Fe(VI)

Under different molar ratios between triclosan and Fe(VI), the degradation efficiency of triclosan was investigated (Fig. 5). The residual concentration of triclosan decreased as the dosage of Fe(VI) gradually increased. With the molar ratio of Fe(VI) over triclosan increasing up to 10:1, the removal rate of triclosan reached 100%. As can be seen from Fig. 5, about 10.53 mole of Fe(VI) is required for complete degradation of one mole of triclosan at pH 7. In comparison, approximately 0.4 mole of triclosan was consumed per mole of O_3 at pH 8.0 [22]. In consistent with the above discussion, this also suggests that the reactivity of Fe(VI) is lower than ozone.

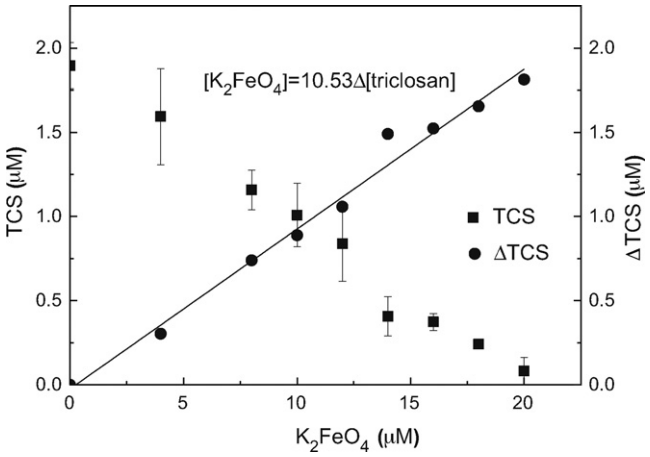


Fig. 5. Reaction stoichiometry for 2 μM triclosan treated with increasing Fe(VI) doses at pH 7.0 and 23 ± 2 °C. The reaction time was 3 h. ΔTCS represents the difference in concentration between reactions with and without ferrate.

Changes in toxicity of a triclosan solution during Fe(VI) oxidation was evaluated by using green algae. In the triclosan toxicity tests, the Fe(VI) treated samples were diluted 50-fold to yield triclosan concentrations ranging from 1.65×10^{-9} M to 3.79×10^{-8} M. Triclosan standards with known concentration ranging from 0 M to 1.11×10^{-7} M were used in parallel with these treated samples. The dose–response relationships observed for the Fe(VI) treated samples and the standard series (in terms of cell amount vs. in vitro triclosan concentration) are shown in Fig. 6. The cell counts for the Fe(VI) treated samples are consistent with the dose–response

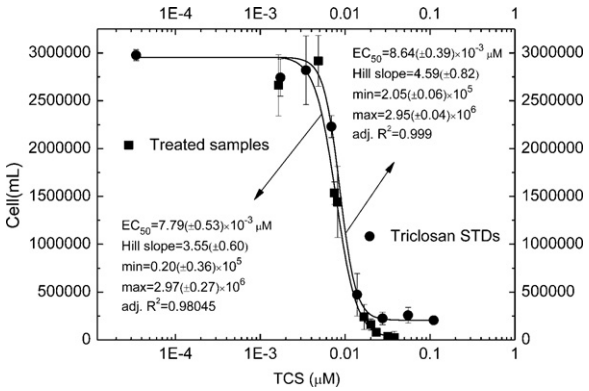


Fig. 6. Dose–response relationships for triclosan samples and triclosan standards obtained from *Pseudokirchneriella subcapitata* growth inhibition test.

curve acquired from the standard series (Fig. 6). Results reported here demonstrate that the inhibitory capacity of the Fe(VI) treated samples are fundamentally the same as their residual triclosan concentrations. The EC_{50} value for the Fe(VI) treated triclosan was identical to that of the triclosan standards. In addition, the toxicity of the Fe(VI) treated triclosan relative to the triclosan standards closely parallels the relative decline in triclosan concentrations. Moreover, the dose–response relationships of the Fe(VI) treated samples and triclosan standards are almost the same, clearly indicating that the degradation products generated by Fe(VI) treated triclosan do not exhibit any appreciable degree of inhibitory effect relative to triclosan itself. These results suggest that the residual triclosan concentration was the major factor in determining the toxicity of the treated samples. This is indeed, in good agreement with previous studies investigating the ozone oxidation [22], photolysis [27], and electrochemical [47] inactivation of triclosan.

Aquatic toxicity of triclosan is related to the structure itself. The transformation and degradation of triclosan lead to depression of toxicity. According to Levy et al. [48], the antibacterial activity of the triclosan molecule is derived primarily from its phenol ring, via van der Waals and hydrogen-bonding interactions with the bacterial enoyl–acyl carrier protein reductase enzyme. Consequently, oxidation of the triclosan molecule by Fe(VI) lead to break of C–O bond or phenol ring opening, which is considered to reduce or eliminate its toxicity. Similarly, Fe(VI) treatment of the steroid hormone EE2 has been found to yield nearly complete, stoichiometric elimination of the estrogenic activity, via oxidation of its phenol ring [46]. In addition, a major intermediate product of Fe(VI) degradation of triclosan is 2,4-dichlorophenol. The acute toxicity of 2,4-dichlorophenol to *P. subcapitata* in terms of EC_{50} is 14,000 μg/L [49], which is much less potent than that of triclosan (EC_{50} 2.5 μg/L or 8.64×10^{-3} μM). In fact, Wammer et al., examined the ability of 2,4-dichlorophenol to inhibit *Escherichia coli* DH5α growth and observed no antibacterial activity of this compound [27]. Moreover, the Fe(VI) dosage used in this study did not by itself appear to inhibit green algae growth. This reconfirms previous assumption that Fe(VI) can be an "environmentally friendly" oxidant for water and wastewater treatment applications [30].

4. Conclusions

This study demonstrated that ferrate (Fe(VI)) could be applied to effectively oxidize triclosan in wastewater. Triclosan reacted rapidly with commercial product potassium ferrate Fe(VI), with an overall apparent second-order rate constant (k_{app}) of $754.7\,M^{-1}\,s^{-1}$ at pH 7.0. Triclosan was completely degraded by Fe(VI) with a stoichiometric ratio of 10:1 (Fe(VI):triclosan). The species-specific rate constants determined for the reaction of $HFeO_4^-$ with neutral triclosan and with anionic triclosan were $6.7(\pm1.9) \times 10^2$ and $7.6(\pm0.6) \times 10^3\,M^{-1}\,s^{-1}$, respectively. The apparent second-order rate constants for Fe(VI) oxidation of triclosan were found related to the purity and constituents of Fe(VI) solution.

Based on the intermediate products identified by GC–MS and RRLC–MS/MS, a plausible mechanism for the oxidation of triclosan by the Fe(VI) was provided, which involves the scission of ester bond and phenoxy radical addition reaction. Triclosan oxidation occurred at the phenol moiety and yielded quinone and hydroquinone intermediates. Coupling reaction may also occur during Fe(VI) oxidation of triclosan. More importantly, the oxidation of triclosan by Fe(VI) led to the loss of its toxicity according the growth inhibition tests with alga *P. subcapitata*. It was also confirmed that at the required dosage for complete removal of triclosan, Fe(VI) did not inhibit green algae growth.

Acknowledgments

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