



## Triclosan breakdown by Fenton-like oxidation

Macarena Munoz\*, Zahara M. de Pedro, Jose A. Casas, Juan J. Rodriguez

*Ingenieria Quimica, Universidad Autonoma de Madrid, Crta. Colmenar km 15, 28049 Madrid, Spain*

### HIGHLIGHTS

- ▶ Fenton-like process is an efficient alternative for triclosan breakdown.
- ▶ Triclosan is more susceptible to ·OH attack than chlorophenols.
- ▶ Aromatic byproducts formed during reaction evolved rapidly to organic acids.
- ▶ All the reaction products obtained showed lower ecotoxicity values than triclosan.
- ▶ Fenton oxidation of triclosan leads to a dramatic decrease of ecotoxicity.

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### ABSTRACT

Fenton-like oxidation has proved to be highly efficient for the removal of triclosan, a highly toxic emerging water pollutant. From 10 mg/L starting aqueous solutions complete conversion of triclosan was achieved in less than 1 h at 25 °C and around 20 min at 50 °C with 1 mg/L Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> at the theoretical stoichiometric amount (25 mg/L). From the evolution of byproducts a reaction pathway has been proposed according to which oxidation of triclosan gives rise to several aromatic intermediates (mainly, *p*-hydroquinone of triclosan and 2,4-dichlorophenol) which evolve to short-chain organic acids. These compounds are mineralized except oxalic acid. A dramatic decrease of ecotoxicity was achieved in a relatively short time (more than 95% in 15 min at 35 °C). The evolution of ecotoxicity is intimately related to the disappearance of triclosan, much more toxic than the aromatic oxidation intermediates. This disappearance was successfully described by a simple pseudo-first order rate equation with an apparent activation energy value close to 27 kJ/mol. The apparent rate constant at 25 °C was several orders of magnitude higher than the reported in the literature for other chlorophenolic compounds indicating a higher susceptibility of triclosan to OH radical attack.

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## 1. Introduction

In recent years, there has been increasing concern regarding the emerging pollutants such as pharmaceuticals and personal care products, surfactants, flame retardants, industrial additives, steroids and hormones and disinfection by-products. These pollutants correspond in many cases to unregulated contaminants, which may be candidates for future regulation depending on research on their potential health effects and monitoring data regarding their occurrence. These hardly biodegradable products, resistant to conventional biological treatment in sewage plants, have been found in their effluents at concentrations ranging 0.1–20 µg L<sup>-1</sup> [1,2]. A particularly relevant example of such emerging pollutants is triclosan, 5-chloro-2-(2,4-dichlorophenoxy)phenol, commercially known as Irgasan DP 300 or Irgacare MP [3], a synthetic broad-spectrum antimicrobial agent. Its antibacterial activity is

associated to its capacity to block lipid biosynthesis by specifically inhibiting the enzyme enoyl-acyl carrier protein reductase [4,5]. Due to its high antimicrobial action, triclosan has been incorporated into a vast array of products (toothpaste, mouthwash, soaps and household cleaners), especially in the last 15 years and thus has been detected in municipal wastewater, where in spite of its low levels has been reported as refractory to conventional biological treatments [3,6,7] thus being usually discharged to surface water bodies. This can involve serious environmental implications derived from its toxicity to several water-living organisms such as fish (LC<sub>50</sub> rainbow trout = 0.35 mg/L) [8], algae i.e., *Scenedesmus subspicatus* [3] or microorganisms like *Daphnia magna* (EC<sub>50</sub> = 0.39 mg/L) [8]. Evidences of estrogenic effects have also been observed by several authors [9,10]. Moreover, the presence of triclosan in water can lead to the formation of chloroform and related trihalomethanes as well as chlorinated dioxins from chlorine disinfection [7,11].

In order to complete the treatment of urban wastewaters containing triclosan, several works in the literature have proposed

\* Corresponding author. Tel.: +34 91 497 3991; fax: +34 91 497 3516.  
E-mail address: [macarena.munnoz@uam.es](mailto:macarena.munnoz@uam.es) (M. Munoz).

chemical oxidation of this emerging pollutant by means of chlorine [12], ozonation [7] or UV/TiO<sub>2</sub> photocatalysis [13–15] but these techniques have shown some important drawbacks. The former gives rise to the formation of highly toxic byproducts like chlorinated phenoxy-phenols, chlorinated phenols, tetrachloro, pentachloro and trihalomethanes [7,16,17]. Ozonation suffers from the potential generation of carcinogenic byproducts [18] as well as from corrosion problems. On the other hand, exposure of triclosan to sunlight or UV irradiation in photocatalytic processes can lead to the formation of highly toxic and persistent chlorinated byproducts like 2,8-dichlorodibenzo-p-dioxin [17,19–21]. Therefore, other potential solutions need to be investigated. In this context, Fenton oxidation has been studied for chlorobenzenes [22], chlorophenols [23], chlorinated pesticides [24] and PCBs [25]. Fenton's reagent can provide in principle a feasible solution for emerging pollutants which are in general at very low concentrations provided that the total organic load of the effluent to be treated is also within a low range so that the process can be performed at reasonably low H<sub>2</sub>O<sub>2</sub> dosages. Nevertheless, so far there is a lack of information on the potential application of Fenton oxidation as a post-treatment for triclosan and other emerging chlorinated pollutants breakdown. This technique has been employed as a comparative treatment to other AOPs [13,26–29] only regarding the triclosan and COD removal without analyzing the by-products and the evolution of ecotoxicity.

The aim of this work is to study the degradation of triclosan by Fenton-like oxidation (H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>). The effects of the H<sub>2</sub>O<sub>2</sub> dose and temperature have been evaluated. The performance of the process has been followed in terms of triclosan conversion as well as evolution of byproducts and ecotoxicity. A reaction pathway is proposed for triclosan breakdown. Values of the pseudo-first order rate constant for triclosan disappearance within the 25–50 °C range have been calculated and the apparent activation energy is given.

## 2. Materials and methods

### 2.1. Chemicals

All the chemicals were analytical grade reagents and were used without further purification. Triclosan (≥97%) (CAS No.: 3380-34-5), hydrogen peroxide solution (30% w/w) (CAS No.: 7722-84-1) in stable form as well as nitric acid (65%) (CAS No.: 7697-37-2) were purchased from Sigma-Aldrich. Iron (III) nitrate nonahydrate (98%) (CAS No.: 7782-61-8) was purchased from Panreac.

### 2.2. Experimental procedure

Three replicates of each experiment were carried out. The data reproducibility was better than ±10% in all the cases. The oxidation runs were carried out at ambient pressure within the range of 25–50 °C in a glass batch reactor (500 mL), equipped with a magnetic stirrer (700 rpm), and temperature control. The starting concentration of triclosan was always 10 mg/L and the initial pH was adjusted to 3.0 with nitric acid. A low concentration of iron (1 mg/L) was used in order to prevent an uncontrolled generation of radicals and allow an efficient consumption of hydrogen peroxide. Iron was fed as Fe<sup>3+</sup> instead of Fe<sup>2+</sup> giving rise to a Fenton-like process of similar characteristics than the conventional one. With the aim of elucidating the chemical pathway of triclosan Fenton oxidation, hydrogen peroxide was tested at different doses within 20–100% of the theoretical stoichiometric amount for complete oxidation of triclosan to CO<sub>2</sub>, H<sub>2</sub>O and HCl (2.5 mg H<sub>2</sub>O<sub>2</sub>/mg triclosan). The use of substoichiometric conditions allows an easier identification of the reaction byproducts formed at the early stages of the

reaction. Moreover, testing low hydrogen peroxide dosages is of interest regarding the economy of the process.

### 2.3. Analytical methods

In each run, liquid samples (25 mL) were periodically withdrawn in order to follow the progress of the reaction. Triclosan and the main aromatic byproducts were quantified by means of high-performance liquid chromatography (HPLC; Varian Pro-Start 325) equipped with a UV detector and a Microsorb C18 5 μm column (MV 100, 15 cm length, 4.6 mm diameter) as the stationary phase. This analysis was carried out at 270 nm using a 70/30% v/v mixture of acetonitrile and acetic acid aqueous solution (75 mM) as the mobile phase. This method achieves detection limits at or below 0.1 mg/L. Short-chain acids and chloride ion were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a 3.2 mM Na<sub>2</sub>CO<sub>3</sub> aqueous solution as the mobile phase. Detection limits of those analyses were within the range of 0.05–0.1 mg/L. Total Organic Carbon (TOC) was measured using a TOC analyzer (Shimadzu, mod. TOC, VSCH) with a detection limit of 0.2 mg/L. The H<sub>2</sub>O<sub>2</sub> concentration was determined by colorimetric titration using the titanium sulfate method [30], being the detection limit 0.5 mg/L.

To learn more on the potential oxidation byproducts, the samples from reaction were analyzed by SBSE-GC × GC-TOF-MS, a powerful tool for the automatic screening, identification and quantification of priority and emerging organic micropollutants developed by Gómez et al. [31]. It is a novel analytical method based on stir bar sorptive extraction (SBSE) followed by comprehensive two-dimensional gas chromatography (GC × GC-TOF-MS). This method achieves detection limits at or below 1 ng/L and allows identifying masses in the range of 50–450, including dioxins. The extractions were performed with 10 mm × 0.5 mm (length × film thickness) PDMS commercial stir bars obtained from Gerstel (Mülheim a/d Ruhr, Germany). The coated stir bars were thermally desorbed using a commercial thermal desorption unit TDU (Gerstel) connected to a programmed temperature vaporization (PTV) system injector CIS-4 (Gerstel) by a heated transfer line at 300 °C. The PTV injector was installed in a GC × GC-TOF/MS system which consisted of an Agilent 7890A (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph, equipped with a secondary oven to fit the secondary column, and a quad-jets modulator. The first column was a 10 m × 0.18 mm i.d., 0.2 μm film thickness Rtx-5 coated with 5% diphenyl 95% dimethylpolysiloxane from Restek. As second column a 1 m × 0.1 mm i.d., 0.10 μm film thickness coated with a liquid crystalline phase Rt-LC50, also from Restek, was used. The MS system was a Pegasus 4D TOF from LECO Corporation.

### 2.4. Ecotoxicity test

The ecotoxicity of aqueous solutions of triclosan and reaction samples was evaluated by the Microtox toxicity test (ISO 11348-3, 1998). The bioluminescence was measured in a photomultiplier M500 Microtox Analyzer (Azur Environmental). The test was conducted at 15 °C, adjusting the osmotic pressure close to 2% NaCl and the pH within 6–8. The EC<sub>50</sub> was used to quantify the ecotoxicity of each individual compound. It is defined as the effective nominal concentration (mg/L) of the compound that reduces the intensity of light emission by 50% after 15 min contact time. For complex samples IC<sub>50</sub>, defined as the dilution ratio of the sample that yields this 50% reduction, was used. The TU values are inversely proportional to the biological toxicity expressed as IC<sub>50</sub> values.

### 3. Results and discussion

#### 3.1. Oxidation byproducts

With the aim of elucidating the route of triclosan oxidation by Fenton's like reagent, several runs covering from frankly substoichiometric up to stoichiometric  $\text{H}_2\text{O}_2$  to triclosan molar ratios (5–24) were carried out. Fig. 1 depicts the evolution of triclosan and the reaction byproducts under frankly substoichiometric conditions (20% of the theoretical stoichiometric  $\text{H}_2\text{O}_2$  amount). As indicated before, this facilitates identifying the byproducts formed in the early stages of the process. As can be seen, even at these operating conditions triclosan was easily oxidized by hydroxyl radicals and complete conversion of this compound was achieved upon 60 min reaction time. The fact that triclosan reacts rapidly with hydroxyl radical ( $k = 5.4 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) has been reported in the literature [21].

Klamerth et al. [32] showed that emerging pollutants at low concentrations can be successfully reduced up to negligible concentrations with photo-Fenton at low iron concentration (5 mg/L) and relatively low  $\text{H}_2\text{O}_2$  dose (50 mg/L). Yang et al. [33] also achieved complete conversion of triclosan by ferrate oxidation but using an iron/triclosan molar ratio of 10, significantly higher than that used in the current work (0.5).

The main aromatic byproducts identified in the Fenton's oxidation experiments performed with  $\text{H}_2\text{O}_2$  at 20% of the stoichiometric amount were 2-chloro-5-(2,4-dichlorophenoxy)benzene-1,4-diol, known as *p*-hydroquinone of triclosan (HQT), 2-chloro-5-(2,4-dichlorophenoxy)-1,4-benzoquinone (QT), known as *p*-quinone of triclosan and 2,4-dichlorophenol (2,4-DCP). Trace amounts of 4-chlorocathecol (4-CC), 4,6-dichloro-1,2-benzendiol and 4,6-dichloro-1,3-benzendiol were detected by SBSE-GC  $\times$  GC-TOF-MS. The formation of these compounds can be explained due to the director character of OH group which determines the existence of two different positions for hydroxyl radical attack. When that attack occurs in *para*-position HQT is produced. Formation of this compound has been previously reported by Zhang and Huang

[34] upon triclosan oxidation by manganese oxides at room temperature. It has to be noted that dihydroxibenzene and benzoquinones are in redox equilibrium in acid media, which explains the presence of *p*-quinone of triclosan [35]. On the other hand, 2,4-DCP and 4-CC are formed when the OH radical attacks to triclosan in the *ortho*- position leading to the opening of one of the aromatic rings. These results are in good agreement with the reported by other authors [15,34,36] who identified 4-CC and 2,4-DCP upon triclosan oxidation with manganese oxides by photocatalytic processes or electro-Fenton. According to our results, 4-CC is formed in trace amounts, being the formation of 2,4-DCP favored at the operating conditions used in this work. On the other hand, 2,4-DCP can undergo two reaction paths: hydroxylation with dechlorination and hydroxylation without dechlorination. In the first case, it leads to the formation of 4-CC by substitution of the chlorine atom in *para*-position. In the second case, formation of 4,6-dichloro-1,2-benzendiol and 4,6-dichloro-1,3-benzendiol occurs when the hydroxylation of 2,4-DCP takes place in *ortho*- and *meta*-positions, respectively. The hydroxyl radicals attack preferably the *ortho*- and *para*-positions relative to the OH group of the aromatic ring. These results are consistent with the reported in the literature for the oxidation of chlorinated phenols by Fenton's reagent [37].

It is well known that different organic acids such as maleic, malonic, acetic, oxalic and formic are formed from aromatic ring opening upon oxidation by OH radicals [38,39]. These short-chain acids were also identified in this case and their evolution with

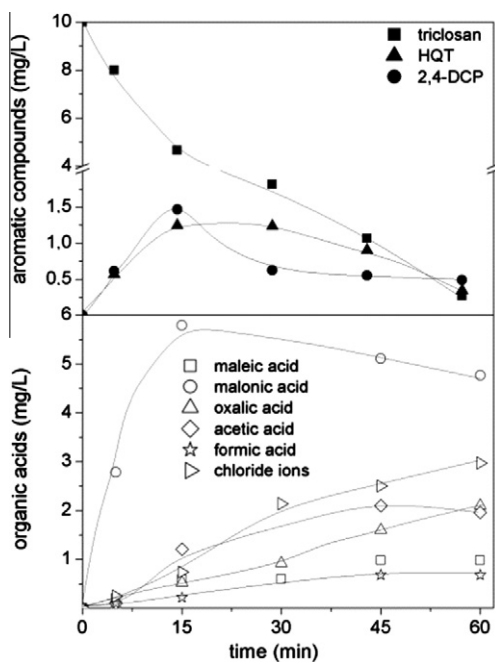


Fig. 1. Time-evolution of triclosan and oxidation byproducts at 20% of the stoichiometric  $\text{H}_2\text{O}_2$  dose.  $[\text{Triclosan}]_0 = 10 \text{ mg/L}$ ,  $[\text{H}_2\text{O}_2]_0 = 5 \text{ mg/L}$ ,  $[\text{Fe}^{3+}]_0 = 1 \text{ mg/L}$ , 25 °C.

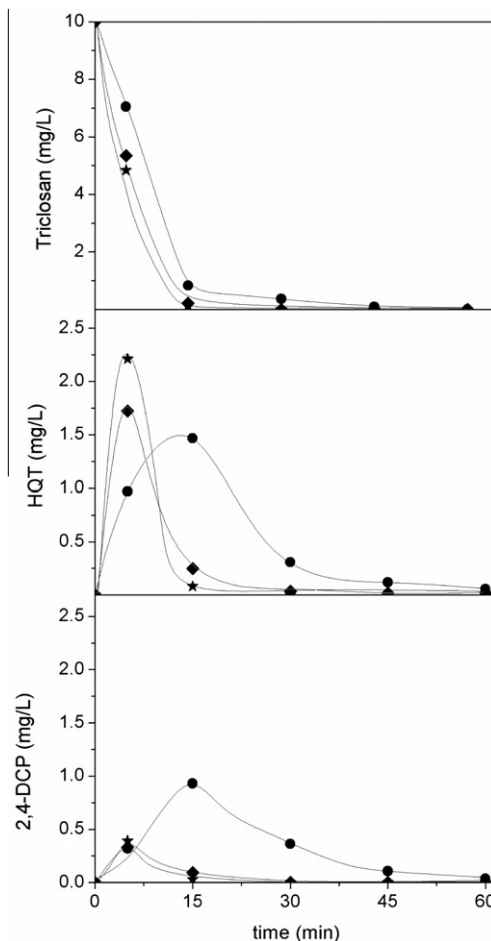


Fig. 2. Time-evolution of triclosan and the aromatic byproducts at different  $\text{H}_2\text{O}_2$  doses: ● 10, ◆ 20 and ★ 25 mg/L.  $[\text{Triclosan}]_0 = 10 \text{ mg/L}$ ,  $[\text{Fe}^{3+}]_0 = 1 \text{ mg/L}$ , 25 °C.

**Table 1**

Residual concentration of triclosan after 1 h reaction time at different H<sub>2</sub>O<sub>2</sub> doses. [Triclosan]<sub>0</sub> = 10 mg/L, [Fe<sup>3+</sup>]<sub>0</sub> = 1 mg/L, 25 °C.

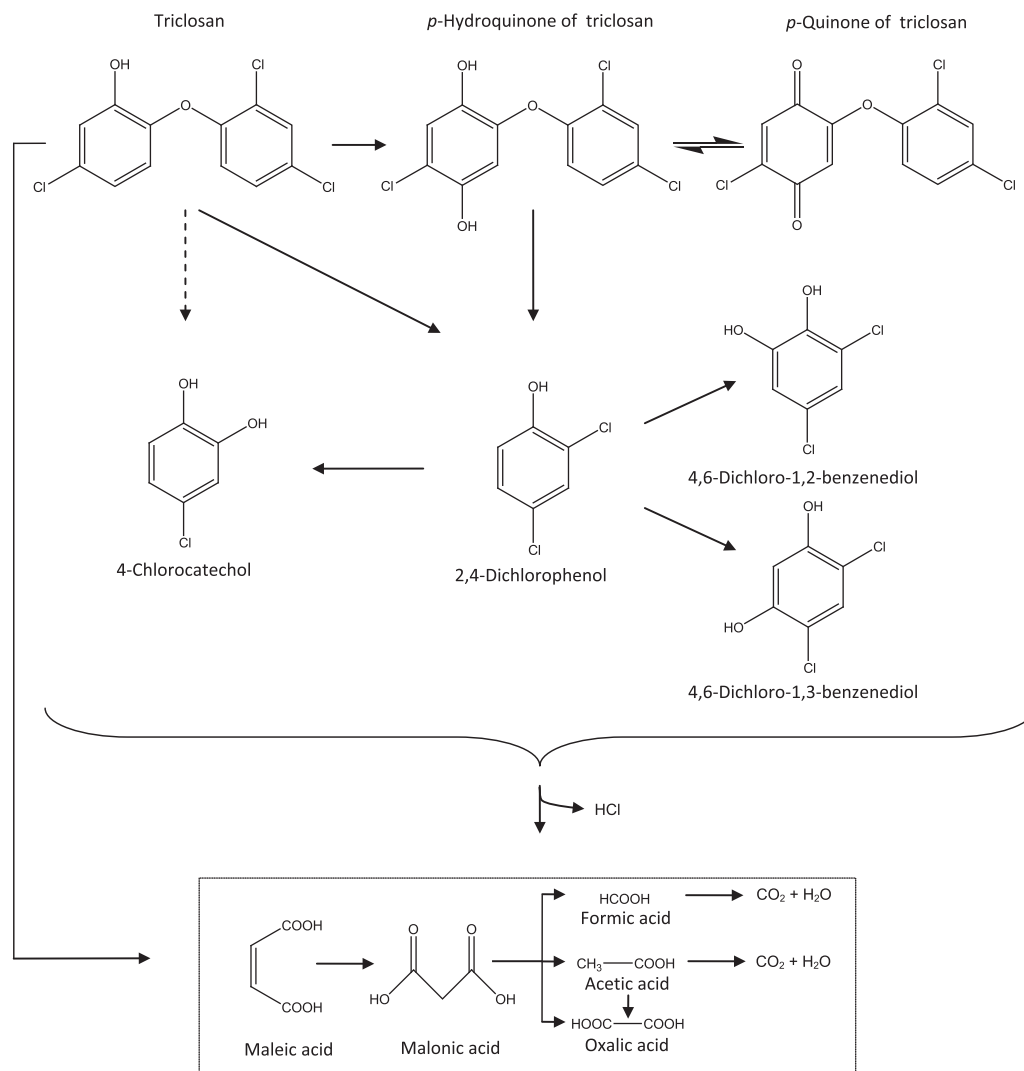
H <sub>2</sub> O <sub>2</sub> dose (% of the stoichiometric molar amount)	Concentration of triclosan (ng/L)
20	2991
40	138
60	102
80	63
100	25

reaction time at the lowest H<sub>2</sub>O<sub>2</sub> dose tested (20% of the stoichiometric) is reported as well in Fig. 1.

Fig. 2 shows the evolution of triclosan, HQT and 2,4-DCP upon reaction time at different H<sub>2</sub>O<sub>2</sub> doses within 40% and 100% of the stoichiometric. Increasing the H<sub>2</sub>O<sub>2</sub> dose leads to a faster disappearance of triclosan being necessary only 15 min of reaction time to achieve complete conversion at the stoichiometric H<sub>2</sub>O<sub>2</sub> amount. A similar situation occurs with the main aromatic byproducts, HQT and 2,4-DCP, which only at the lowest H<sub>2</sub>O<sub>2</sub> dose remained in the reaction medium after 60 min. The occurrence of

the concentration maxima displaces to shorter reaction times as the H<sub>2</sub>O<sub>2</sub> dose increases as expected from a faster conversion of triclosan and these two intermediates due to the higher rate of OH radicals generation. The evolution of the HQT and 2,4-DCP curves indicates that both compounds are primary products from triclosan oxidation. Moreover, 2,4-DCP could also be formed as a secondary product from HQT. The chlorine balance at the earlier stages of reaction matched around 90% and the difference between the measured TOC and the calculated from the organic compounds quantified was lower than 10%. This difference is in part related with the formation of 4-CC, 4,6-dichloro-1,2-benzenediol and 4,6-dichloro-1,3-benzenediol which were detected in trace amounts by SBSE-GC × GC-TOF-MS. These byproducts must have disappeared completely after 60 min reaction time since they were not detected by SBSE-GC × GC-TOF-MS (detecting sensibility: 1 ng/L). After that reaction time the chlorine balance matched always around 95% and the difference between the measured TOC and the calculated from the identified species was less than <5% at all the H<sub>2</sub>O<sub>2</sub> doses tested.

In order to learn more on the degradation of triclosan upon Fenton-like oxidation the effluents resulting from the experiments performed at all the H<sub>2</sub>O<sub>2</sub> doses tested were analyzed by SBSE-GC × GC-TOF-MS. As can be seen in Table 1, the residual



**Fig. 3.** Proposed reaction pathway for Fenton-like oxidation of triclosan.

concentrations of triclosan after 1 h reaction time were always very low, decreasing as the  $H_2O_2$  dose was increased. From these results, it can be concluded that Fenton-like oxidation is a really efficient technique for triclosan abatement.

The formation of dioxins from triclosan upon sun-light exposition has been reported in the literature [17,19–21]. In order to investigate in depth the possible occurrence of these compounds upon Fenton-like oxidation in our working conditions the final effluents after one-hour reaction time were analyzed by SBSE-GC  $\times$  GC-TOF-MS. These highly toxic chlorinated species were not detected by this method which allows detection limits at or below 1 ng/L.

From the results obtained, the reaction pathway depicted in Fig. 3 is proposed for Fenton-like oxidation of triclosan. According to this scheme, hydroxylation of the aromatic ring would lead to the formation of HQT and to the breakdown of the ether bond giving rise to 2,4-DCP or 4-CC. Further attack of OH radicals to 2,4-DCP would result in the formation of 4-CC and dichlorobenzenediols (4,6-dichloro-1,2-benzenediol and 4,6-dichloro-1,3-benzenediol). On the other hand, different short-chain organic acids would be produced from the ring-opening of the aromatic intermediates releasing chlorine as HCl. All the intermediates would be finally oxidized to  $CO_2$  and oxalic acid, which shows quite refractory to further oxidation confirming the generally observed resistance of this acid to Fenton oxidation.

### 3.2. Influence of temperature

Fig. 4 shows the evolution of triclosan and the aromatic reaction byproducts upon Fenton-like oxidation at different temperatures using the stoichiometric  $H_2O_2$  dose. As can be seen, the temperature has a significant effect so that the rate of disappearance of triclosan is approximately doubled from 25 to 50 °C and further conversion of the main aromatic intermediates (HQT and 2,4-DCP) is also strongly enhanced. After 20 min reaction time the remaining concentrations of triclosan and the aromatic intermediates were negligible even at the lowest temperature tested. At 50 °C HQT was barely detected and the maximum concentration of 2,4-DCP showed a very low value. Thus, the increase of temperature has a more pronounced effect on the rate of conversion of these aromatic intermediates into organic acids than on their respective rates of formation. That was confirmed by the evolution of short-chain organic acids, which showed higher concentrations at shorter reaction times as the temperature increased (Supplementary data). All the acids were mineralized except oxalic which showed to be refractory to Fenton oxidation even at those higher temperatures. Zazo et al. [40] reported that oxalic acid can be mineralized upon Fenton oxidation at around 100 °C.

Fig. 5 depicts the evolution of TOC upon reaction time at different temperatures in the experimental conditions of Fig. 4. Some small differences (<5%) between the measured TOC and the calculated from the species identified were found within the early stages of reaction. These differences can be attributed in part to the aforementioned chlorinated aromatic species (4,6-dichloro-1,2-benzenediol, 4,6-dichloro-1,3-benzenediol and 4-CC) which were detected in trace amounts (<1  $\mu g/L$ ). Although the occurrence of polymerization reactions has been commonly reported in Fenton oxidation of phenolic compounds [33,39,41,42], condensation byproducts have not been detected in this study. The chlorine balances matched always around 95%.

### 3.3. Evolution of ecotoxicity

High ecotoxicity values (TU = 40) were measured for the triclosan solution (10 mg/L) which correspond to an effective  $EC_{50}$  of 0.25 mg/L. This is in good agreement with the results reported by

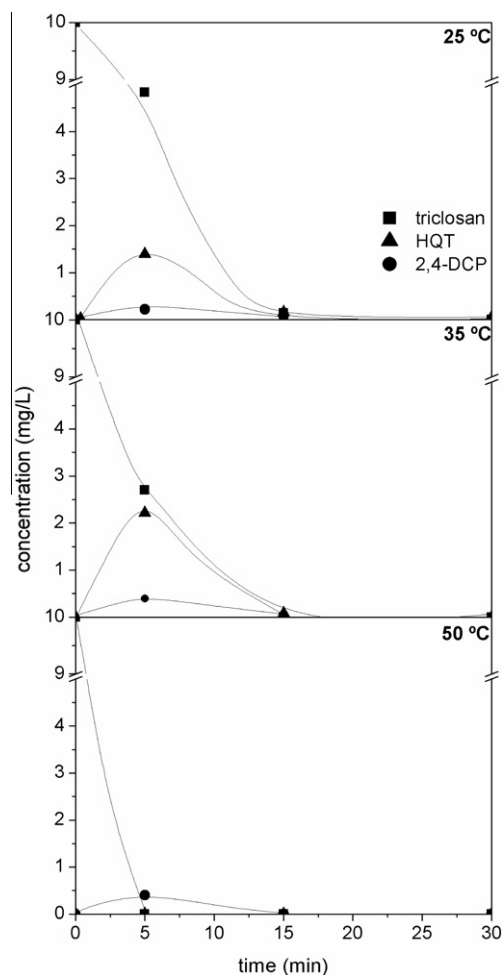


Fig. 4. Effect of temperature on the evolution of triclosan and the aromatic byproducts upon Fenton-like oxidation.  $[Triclosan]_0 = 10$  mg/L,  $[H_2O_2]_0 = 25$  mg/L,  $[Fe^{3+}]_0 = 1$  mg/L.

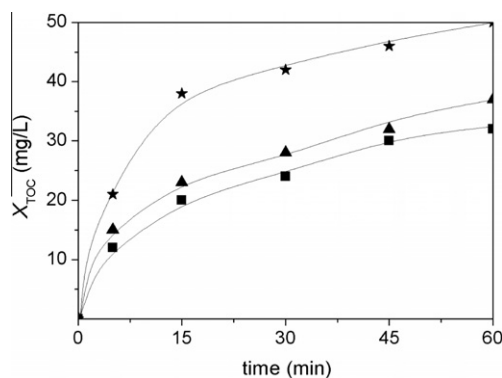


Fig. 5. TOC conversion upon reaction time at different temperatures (■ 25, ▲ 35, and ★ 50 °C). Operating conditions of Fig. 4.

Farre et al. [43] and Stasinakis et al. [44] who obtained  $EC_{50}$  values of 0.28 and 0.22 mg/L, respectively. The high ecotoxicity of triclosan must be related with its antimicrobial properties [45].

Fig. 6 shows the evolution of ecotoxicity at three different  $H_2O_2$  doses and an intermediate temperature (35 °C) within the range tested. As can be observed Fenton-like oxidation allows a dramatic reduction of ecotoxicity leading to values below 5% of the initial in 15 min reaction time with the stoichiometric dose of  $H_2O_2$ .



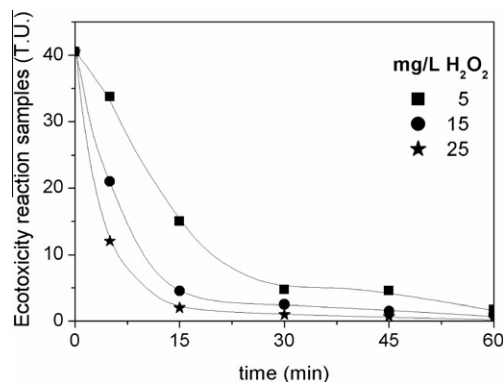


Fig. 6. Evolution of ecotoxicity upon Fenton-like oxidation of triclosan at different  $\text{H}_2\text{O}_2$  doses (■ 5, ▲ 15, and ★ 25 mg/L  $\text{H}_2\text{O}_2$ ). [ $\text{Triclosan}$ ]<sub>0</sub> = 10 mg/L, [ $\text{Fe}^{3+}$ ]<sub>0</sub> = 1 mg/L, 35 °C.

Triclosan is by far the determining species in terms of ecotoxicity in the reaction pathway describing its oxidation by Fenton-like reagent. The  $\text{EC}_{50}$  values of the aromatic intermediates are much higher and the contribution of the organic acids to ecotoxicity is of very low significance. For 2,4-DCP an  $\text{EC}_{50}$  value of 4.9 mg/L was determined, almost twenty times higher than that of triclosan, which indicates the lower ecotoxicity of this compound compared to triclosan (the  $\text{EC}_{50}$  value of HQT could not be determined since commercial standards are not available). The ecotoxicity of 4-CC, detected in trace amounts (<1  $\mu\text{g/L}$ ), was even lower, with a measured  $\text{EC}_{50}$  value of 15.3 mg/L. On the other hand, as has been seen, the evolution of these aromatic intermediates up to organic acids is quite fast so that the maximum concentration values reached were always very low. Thus, the evolution of ecotoxicity is intimately related to the disappearance of triclosan. This was usefully described by a simple pseudo-first order rate equation. The values obtained for the apparent kinetic constants with the stoichiometric dose of  $\text{H}_2\text{O}_2$  ranged from  $0.298 \pm 0.052 \text{ min}^{-1}$  at 25 °C to  $0.675 \pm 0.025 \text{ min}^{-1}$  at 50 °C. The resulting apparent activation energy was in the vicinity of 27 kJ/mol. Zhang and Huang [34] reported a substantially lower value of the first-order rate constant ( $0.029 \text{ min}^{-1}$ ) for the oxidation of triclosan with manganese oxides at 22 °C. Son et al. [29] reported values of  $0.115 \text{ min}^{-1}$  and  $0.286 \text{ min}^{-1}$  for the photolytic degradation of triclosan by UV-A ( $\lambda_{\text{max}}$ : 365 nm) and UV-C ( $\lambda_{\text{max}}$ : 254 nm), respectively at 20 °C.

The kinetic constants reported in the literature for Fenton oxidation of chlorophenols at 25 °C are several orders of magnitude lower than that obtained in this work for triclosan:  $5 \times 10^{-4} \text{ min}^{-1}$  for 2,4,6-TCP,  $7 \times 10^{-4} \text{ min}^{-1}$  for 2,4-DCP and  $7 \times 10^{-3} \text{ min}^{-1}$  for 4-CP [46]. These results are in good agreement with the reported by Zhang and Huang [34] who concluded that triclosan has comparable or higher reactivities than the related substituted phenols resulting from its oxidative transformation with manganese oxides (i.e. triclosan  $\sim$  2-methyl-4-chlorophenol > 2,4-dichlorophenol > phenol > 3-chlorophenol).

#### 4. Conclusions

Fenton-like oxidation has shown to be an efficient solution for the removal of triclosan, an emerging water pollutant with antimicrobial activity. Complete triclosan disappearance was achieved from 10 mg/L starting aqueous solutions at very low iron and  $\text{H}_2\text{O}_2$  doses (1 mg/L and 5 mg/L, respectively) and room temperature. Although aromatic byproducts were formed upon reaction, the ecotoxicity of these compounds is significantly lower than that of triclosan and, on the other hand, they evolve rapidly to organic acids. Fenton-like oxidation allowed a dramatic reduction of ecotoxicity and the formation of dioxins can be discarded in the

operating conditions tested in this work. That dramatic reduction of ecotoxicity is essentially associated to triclosan disappearance which proceeds rapidly up to almost negligible residual concentrations upon Fenton-like oxidation at near-ambient temperature with  $\text{H}_2\text{O}_2$  doses below the stoichiometric and very low  $\text{Fe}^{3+}$  concentration (1 mg/L).

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2012.05.097>.

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