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Possible degradation pathways of triclosan from aqueous systems via TiO₂ assisted photocatalysis

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ABSTRACT

Triclosan (TCS) is an antimicrobial agent used for personal care products that cannot be removed by wastewater treatment classical processes. TCS persistence and toxicity is asking for alternative treatment methods such as TiO₂ assisted photocatalyse. Due to the fact that within the literature are presented various pathways for TCS degradation via UV/TiO₂ photocatalysis, some data being contradictory, research work aimed to propose a degradation mechanism supported by as many experimental data. TCS degradation pathways confirmed by experimental results were: addition of hydroxyl radicals at TCS non-phenolic ring, proton extraction by hydroxyl radicals and direct interaction with photo generated electrons.

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Introduction

Triclosan (TCS) 5-chloro-2-(2,4-dichlorophenoxy) phenol is an antimicrobial agent used on a large scale in the composition of personal care products. As a consequence, effluents and sludge discharged from wastewater treatment plants (WWTPs) constitute the main sources of TCS pollution in the aquatic environment. Moreover, TCS is directly photo-transformed generating 2,8-dichloro-dibenzo 1,4-dioxin carcinogenic substance [1,2]. The methyl triclosan formed by biological methylation could be more lipophilic and bio-accumulative than TCS itself [3]. Risk assessment proved that TCS presence on the water surface can affect aquatic organisms [4], so, at the present, there is a growing concern related to the TCS environmental persistence and its potential negative impact on the environment [5].

In general, WWTPs have being mainly designed and modernised for the removal of easily or moderately biodegradable compounds containing carbon, nitrogen and phosphorus [6] and they were not equipped for removal of personal care products and pharmaceuticals active substances. Unfortunately, TCS removal by conventional wastewater treatment processes have had low

efficiencies [7], but advanced oxidation processes (AOPs) could constitute a better alternative for TCS degradation [8–10].

Among AOPs, UV/TiO₂ photo catalysis [11–13] and photo-Fenton [14,15] processes were frequently applied for TCS degradation due to the fact that they were effective methods for in-situ generation of highly oxidizing hydroxyl radicals (\bullet OH). TCS (4–11 mg/L; 15–27 μ mol/L) photo degradation on various TiO₂ types was studied by Rafqah et al. [11]. It was found that Degussa P 25 ($A_{\text{BET}} = 55 \text{ m}^2/\text{g}$) was a more efficient catalyst compared to Millenium PC 50, PC 500 ($A_{\text{BET}} = 45\text{--}250 \text{ m}^2/\text{g}$) because the first one was a mixture of anatase/rutile (80/20) and the others were based only on anatase. The same pattern was reported by Gumy et al. [16] in the case of benzene derivatives photocatalytic degradation, which proved that crystalline structure was an important parameter for an efficient TiO₂ photo activity linked to the organic pollutants degradation. Beside the crystalline phase, other catalysts characteristics such as particle size, aggregate size, specific surface area (A_{BET}) and isoelectric point were parameters that could influence the organic degradation performance or even the pollutant transformation pathways. Yu et al. [12] reported that TCS degradation by TiO₂ Degussa P25 under UV irradiation ($\lambda < 365 \text{ nm}$) took place mostly by addition of \bullet OH radicals to the phenolic fraction. It was found that 2,4-dichlorophenol was the main intermediate compound, while the hydroquinone and quinone species were formed at least 10 folds less than chlorinated phenol derivatives. Dioxin derivatives were not identified during

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this degradation process. Son et al. [13] studied TCS degradation in almost the same experimental conditions as previously reported and the TCS degradation was mostly triggered by $\bullet\text{OH}$ radicals hydrogen abstraction and electron transfer. The results suggested that TCS may also undergo cyclization and dioxin derivatives generation under UV irradiation process which was wavelengths and hydroxyl radicals' concentration dependent. Rafqah et al. [11] proposed other pathways for TCS degradation in which $\bullet\text{OH}$ radicals attack took place on both phenolic and non-phenolic fractions of TCS. Formation of dechlorinated intermediates was attributed to TCS reduction process that involved photogenerated electrons. Dioxin derivatives were not detected among degradation by-products.

In spite of the multiple TCS degradation pathways reported in the literature, some of them contradictory, more information on TCS degradation by-products formed by a photocatalytic treatment is still needed in order to assess their environmental risks and to confirm that the photo catalysis process represent a safe alternative to the conventional wastewater treatment processes. Therefore, the aim of present study was to propose TCS degradation pathways in which TCS degradation by-products could be characterized.

Experimental

The following reagents were used: Triclosan (TCS) (Aldrich); TiO_2 (Merck) pure anatase form ($A_{\text{BET}} = 10 \text{ m}^2/\text{g}$); NaOH (Merck) and H_2SO_4 (Merck) for pH correction; HCl (Merck), anhydrous Na_2SO_4 (Chimreactiv), *n*-hexane (Fluka) for sample preparation.

TCS degradation was performed within a photocatalytic UV reactor – Heraeus type equipped with a medium pressure mercury lamp. Incident photonic intensity of the UV lamp ($\lambda = 300\text{--}400 \text{ nm}$) was determined by actinometrical method and a value of $1.05 \times 10^{-6} \text{ einstein s}^{-1}$ was obtained.

Prior to irradiation, photocatalyst powder was added to synthetic samples with TCS content and the suspension was bubbled with air (50 L/h), in the dark, for 30 min in order to achieve pollutant's adsorption equilibrium and to avoid the electrons–holes recombination.

A gas chromatograph coupled with an ion trap mass spectrometer (GC-ITMS) was used for TCS detection. About 400 mL of sample was acidified with 1N HCl and afterwards extracted in *n*-hexane ($3 \times 10 \text{ mL}$). Organic extract was dried with anhydrous Na_2SO_4 and concentrated at 1 mL under gentle nitrogen stream. A volume of $1 \mu\text{L}$ from the obtained extract was automatically injected in GC-ITMS in splitless mode, at 280°C .

Identification of TCS degradation intermediates was performed through gas chromatography coupled with mass spectrometry (GC-MS) technique, screening method, on irradiated samples extracted in *n*-hexane ($3 \times 5 \text{ mL}$), at $\text{pH} = 2$, assured through H_3PO_4 addition. An Agilent 7890 gas chromatograph with (5%-phenyl)-methylpolysiloxane capillary column ($\text{ID} \times \text{d}_{\text{film}} \times \text{length} = 0.25$

$\text{mm} \times 0.25 \mu\text{m} \times 60 \text{ m}$), coupled with an Agilent 240 MS ion trap mass spectrometer, with external ionisation (70 eV) was used.

The irradiated samples pH were monitored using a Consort C532 pH-meter.

Results

The various pathways of TCS degradation via UV/ TiO_2 photocatalysis [11–14] showed contradictory data, but we proposed a reliable degradation mechanism based on the identification of newly formed by-products and on the assessment of their concentrations in various monitored experimental conditions. The analyse of TCS degradation kinetic reported in our previous works [17], proved that TiO_2 assisted photocatalysis represent a performant method for this pollutant degradation and its applicability in optimum operation conditions: $\text{pH} = 6.5$; photocatalyst dose $[\text{TiO}_2] = 200 \text{ mg/L}$ could assure a TCS advanced degradation ($\eta \geq 99\%$) up to the concentration level of $\mu\text{g/L}$. It was found that TCS degradation followed a pseudo-first order kinetic with rate constants values of $7.64 \times 10^{-2} - 4.14 \times 10^{-2} \text{ min}^{-1}$ for an initial TCS concentration between 1–13.5 mg/L.

TCS degradation experiments via heterogeneous photocatalysis

TCS photocatalytic degradation experiments via heterogeneous photocatalysis in UV-VIS/ TiO_2 system were performed in the optimum operation conditions described above. Initial pollutant concentration was at 31.80 mg/L. The high level of TCS initial concentration was chosen in order to obtain as many information related to the identification of degradation intermediary products (Table 1).

Formation of degradation intermediates with organic chlorine content was in accordance to the kinetic data obtained through mathematical modelling based on the experimental results, namely $k_{\text{TCS}} > k_{\text{Cl}}$.

TCS degradation experiments via heterogeneous photocatalysis in presence of $\bullet\text{OH}$ radicals scavenger

The degradation of a pollutant by TiO_2 assisted photocatalysis could be performed through hydroxyl radicals as well as through holes and/or photo generated electrons. In order to identify the oxidising specie ($\bullet\text{OH}$, h^+) with a significant contribution to pollutant's conversion, TCS photocatalytic degradation experiments were performed in presence of 2-propanol ($3 \times 10^{-3} \text{ M}$), compound known as a hydroxyl radicals scavenger. The results obtained in presence of 2-propanol (Table 2) were compared with those obtained in the absence of 2-propanol, in similar working conditions.

The analysis of the results showed a decrease of photocatalytic process performances in the presence of 2-propanol. Thus, TCS degradation and organic chlorine mineralization yields decreased

Table 1
TCS degradation via photocatalysis in UV–VIS/ TiO_2 system.

Time, min	[TCS]		[Cl]		η_{TCS} , %	η_{Cl} , %	$-\ln([\text{TCS}]_t/[\text{TCS}]_0)$	$-\ln(1 - [\text{Cl}]_t/[\text{Cl}]_{\text{tot}})$
	mg/L	$\text{M} \times 10^4$	mg/L	$\text{M} \times 10^4$				
0	31.80	1.098	0	0	0	0	0	0
30	8.84	0.305	3.57	0.335	72.22	30.51	1.281	0.364
60	7.15	0.247	4/52	0.424	77.52	38.62	1.492	0.488
120	3.10	0.107	7.51	0.705	90.25	64.21	2.328	1.027
180	0.33	0.012	10.62	0.997	98.90	90.80	4.465	2.386
240	0.09	0.003	10.97	1.030	99.72	93.81	5.968	2.785
							$k_{\text{TCS}} = 4.10 \times 10^{-4} \text{ s}^{-1}$	$k_{\text{Cl}} = 1.93 \times 10^{-4} \text{ s}^{-1}$

$\text{pH} = 6.5$; $[\text{TiO}_2] = 200 \text{ mg/L}$.

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