

Degradation of Triclosan by TiO₂ – UV Irradiation in Aqueous Solutions

LUCIAN CONSTANTIN^{1,2}, INES NITOI¹, IONUT CRISTEA¹, PETRUTA OANCEA³, CRISTINA ORBECI², AURELIA CRISTINA NECHIFOR^{2*}

¹National Research and Development Institute for Industrial Ecology – ECOIND Bucharest, 71-73 Drumul Podul Dambovitei Street, 060652, Bucharest, Romania,

²University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

³University of Bucharest, Faculty of Chemistry, 4-12 Elisabeta Av., 030016, Bucharest, Romania

Triclosan (TCS) 5 chloro – 2 – (2, 4 – dichlorophenoxy) phenol is an antimicrobial agent widely used for personal care products. Due to TCS persistence and toxicity, advanced oxidation processes constitute nowadays an alternative to TCS degradation. The UV/TiO₂ degradation of TCS was investigated in the following working conditions: pH domain = 5.3-8.7; initial pollutant concentration [TCS]₀ = 1 – 13.5 mg/L; photocatalyst dose [TiO₂]₀ = 100 – 500 mg/L; irradiation time t = 30 – 180 min; air flow Q_{air} = 50 L/h. The TCS degradation was found to respect the Langmuir – Hinshelwood model. The constant of the degradation rate and the equilibrium constant of TCS adsorption on TiO₂ particles were calculated.

Keywords: triclosan, photocatalysis, TiO₂, anatase, photo-degradation

Triclosan (TCS) 5 chloro – 2 – (2, 4 – dichlorophenoxy) phenol is an antimicrobial agent widely used for personal care products [1]. As a consequence, the effluents and sludge discharged by wastewater treatment plants represent the main sources of TCS for the aquatic environment. TCS removal via conventional wastewater treatment processes presents low efficiencies [2]. Moreover, in the present, there is an increased concern regarding the environmental persistence and potential negative impact of TCS [3]. TCS can undergo direct photo-transformation with the generation of 2, 8 – dichloro – p – dioxin known as carcinogenic [4, 5]. In addition, the methyl triclosan formed by biologic methylation can be more lipophilic and bio accumulative compared with TCS [6]. Environmental risk assessment showed that TCS presence in surface waters can affect aquatic organisms [7]. Due to TCS persistence and toxicity, advanced oxidation processes constitute nowadays an alternative to TCS degradation [8]. This is supported also by the fact that wastewater treatment plants are in general not equipped for the removal of pharmaceuticals and personal care products, being designed and revamped mainly for the removal of carbon, nitrogen, phosphorus easily degradable compounds [9].

The last decades shown a reevaluation of the issue of environmental pollution. Removal of organic compounds of wastewater is a very important subject of research in the field of environmental chemistry. Available technologies dealing with phenolic compounds include the advanced oxidation processes (AOPs), based on the formation of very active hydroxyl radicals, which react quickly with the organic contaminant. AOPs present the advantage of completely removing organic contaminants from the environment, not only from the aqueous phase, by transforming them into other organic compounds with low toxicity and finally into innocuous inorganic species [14-16].

AOPs type procedures can become very promising technologies for treating wastewater containing non-biodegradable or hardly biodegradable organic compounds with high toxicity. In this sense, photocatalysis (UV-TiO₂) is a handy promising technology, very attractive for wastewater treatment [16].

Photochemical processes for the oxidation of organic pollutants, a series of researchers have proposed direct photo-oxidation with ultraviolet light.

TiO₂ is the most used semiconductor because of its higher photocatalytic activity. The anatase form of TiO₂ is reported to give the best combination of photoactivity and photostability. The photocatalytic oxidation of organic compounds in water has been widely discussed in the literature. Many studies shown that are possible different methods for treating the effluents [14-17].

The working conditions applied for TCS degradation from synthetic solutions were the following: pH domain = 5.3-8.7; initial pollutant concentration [TCS]₀ = 1 – 13.5 mg/L; photocatalyst dose [TiO₂]₀ = 100 – 500 mg/L; irradiation time t = 30 – 180 min; air flow Q_{air} = 50 L/h.

Experimental part

Materials and methods

The following reagents were used: triclosan supplied by Aldrich, TiO₂ (Merck) anatase form, NaOH (Merck) and H₂SO₄ (Merck) for pH correction, HCl (Merck), Na₂SO₄anh. (Chimreactiv), n-hexane (Fluka) for samples preparation.

The TCS degradation was carried out in a Heraeus-type laboratory UV reactor equipped with a medium pressure Hg lamp TQ 150. The incident photon flow was I₀ = 1.05 · 10¹⁶ einstein s⁻¹ determined by ferrioxalat actinometry. Prior to irradiation, TiO₂ powder was added to the samples with TCS content and the suspensions were bubbled with air (50 L/h), in the dark, for 30 min, in order to attain the pollutant adsorption equilibrium. For the analysis of TCS, gas chromatography coupled with ion trap mass spectrometry was used. Up to 400 mL of sample were

* email: nechiforus@yahoo.com

pH	[TCS] ₀		[Cl ⁻]		η _{TCS} %	η _{Cl⁻} %
	mg/L	M	mg/L	M		
5.3	0.134	4.63 × 10 ⁻⁷	3.140	8.85 × 10 ⁻⁵	98.53	93.62
6.5	0.100	3.45 × 10 ⁻⁷	3.150	8.87 × 10 ⁻⁵	98.90	98.25
8.7	0.81	6.25 × 10 ⁻⁷	3.050	8.59 × 10 ⁻⁵	98.02	90.94

Table 1
pH INFLUENCE ON TCS
DEGRADATION AND ORGANIC
CHLORINE MINERALIZATION
[TCS]₀ = 9.12 mg/L = 3.15 · 10⁻⁵ M,
[TiO₂] = 100 mg/L, t = 120 min

[TiO ₂] mg/L	[TCS] ₀		[Cl ⁻]		η _{TCS} %	η _{Cl⁻} %
	mg/L	M	mg/L	M		
100	0.100	3.45 × 10 ⁻⁷	3.154	8.89 × 10 ⁻⁵	99.15	98.38
200	0.060	2.07 × 10 ⁻⁷	4.302	1.21 × 10 ⁻⁴	99.49	99.10
500	0.160	5.53 × 10 ⁻⁷	4.172	1.18 × 10 ⁻⁴	98.64	96.11

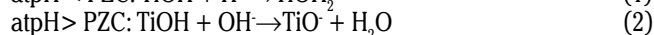
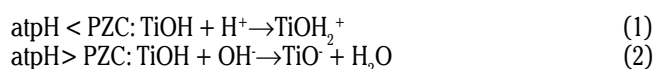
Table 2
PHOTOCATALYST DOSE
INFLUENCE ON TCS
DEGRADATION AND ORGANIC
CHLORINE MINERALIZATION
[TCS]₀ = 11.8 mg/L = 4.08 · 10⁻⁵
M, pH = 6.5, t = 120 min

acidified with 1N hydrochloric acid and then extracted with hexane using a separation funnel. Organic extracts were dried with anhydrous Na₂SO₄ and then concentrated to 1 mL under vacuum. 1 μL of obtained extract was automatically injected to GC. The GC-ITMS conditions were: column: DB-5MS 60 m, 0.25 mm internal diameter, 0.25 μm film thickness; splitless injection; injector temperature 280 °C, flow rate: 1.4 mL/min; carrier gas: helium 6.0; temperature ramp employed: 50 °C (1 min), 5 °C/min to 160 °C, 10 °C/min to 280 °C held 5 min. Mass detector conditions: Ion Trap: 150 °C; Manifold: 40 °C; Transfer line: 270 °C; Ion source: 250 °C. The characteristic ion for TCS (m/z = 218) was recorded in μSIS mode using EI with emission current 30 μAmps. The pH of the irradiated samples was monitored using a Consort C532 pH-meter.

Results and discussions

pH influence

Any semiconductor is characterized by a point of zero charge (PZC) at which its surface is neutral from the electrostatic point of view. For TiO₂ the PZC is situated within the pH domain 6 – 7.5. The semiconductor charge varies with pH as follows:



In other words, at pH > PZC the adsorption of positively charged pollutants is favored and at pH < PZC the adsorption of negatively charged pollutants is favored. The pH also plays a role in the photo catalysis of neutral molecules that tend to dissociate in the charged species [10].

The experiments on the pH influence upon the kinetic and degradation efficiency of TCS were carried out in the following conditions: pH domain = 5.3-8.7; initial pollutant concentration [TCS]₀ = 9.12 mg/L = 3.15 · 10⁻⁵ M; photocatalyst dose [TiO₂] = 100 mg/L; irradiation time t = 120 min. The experimental results are presented in table 1.

The results obtained are explained by the fact that TCS has a pK_a = 7.9. In the alkaline domain there are electrostatic repulsions between the negatively charged surface of TiO₂ and TCS; the rate constant decreasing slowly in the alkaline conditions. Based on the experimental results the optimum selected pH was 6.5.

Influence of photocatalyst concentration

One of the main parameters that influence the efficient TiO₂ photons adsorption and the pollutant degradation is the optimum photocatalyst dose. In order to investigate

this parameter, photooxidation experiments were performed in the following conditions: [TCS]₀ = 11.8 mg/L = 4.08 × 10⁻⁵ M; pH = 6.5; [TiO₂] = 100 – 500 mg/L. TCS and Cl⁻ concentrations were determined for each photocatalyst dose at an irradiation time of 120 min, and pollutant degradation and organic chlorine mineralization efficiencies were calculated. The experimental results are presented in table 2.

The data presented show an ascendant evolution of the TCS degradation and organic chlorine mineralization efficiencies with the increase of photocatalyst dose up to a limit value of [TiO₂] = 200 mg/L. This behavior is a consequence of the phenomenon that occurs during heterogenic photocatalysis, namely the interactions between TiO₂ particles (disperse phase) with incident radiation and surface processes. Thus, at low TiO₂ concentrations (100 – 200 mg/L) the surface processes are prevailing, leading to an increased number of active sites available for pollutant adsorption. At higher photocatalyst concentrations (500 mg/L) the light scattering occurs with a negative effect upon the pollutant photocatalytic degradation.

The data confirm the existence of two domains for pollutant degradation and organic chlorine mineralization rates, depending on the photocatalyst concentration, one with an ascendant profile ([TiO₂] ≤ 200 mg/L) and the other with a descendant profile ([TiO₂] > 200 mg/L). [TiO₂] = 200 mg/L was selected as the optimum dose that assures substrate [TCS]₀ = 4.08 · 10⁻⁵ M degradation with the highest rate 3.38 · 10⁻⁷ M min⁻¹ and a maximum organic chlorine mineralization rate 1.01 · 10⁻⁶ M min⁻¹. The efficiency of TCS degradation was 99.49% and the efficiency of organic chlorine mineralization was 99.10 %, after 120 min irradiation.

Influence of irradiation time and pollutant concentration

The influence of pollutant concentration upon the efficiencies of degradation and organic chlorine mineralization was studied for initial pollutant concentrations within the domain [TCS]₀ = 1.112 ÷ 13.498 mg/L = (0.38 ÷ 4.66) · 10⁻⁵ M. The selection of the concentration domain took into consideration real wastewater cases, for which there are specific concentration values of mg/L. The experiments were carried out at pH = 6.5 and [TiO₂] = 200 mg/L. For each initial pollutant concentration, the irradiation time was varied in the domain 30 ÷ 120 min and the first order rate constants (k_{TCS}) were calculated in respect to TCS degradation as shown in figure 1.

The prolonged irradiation time has a positive effect on the efficiency of the pollutant's degradation. The optimum

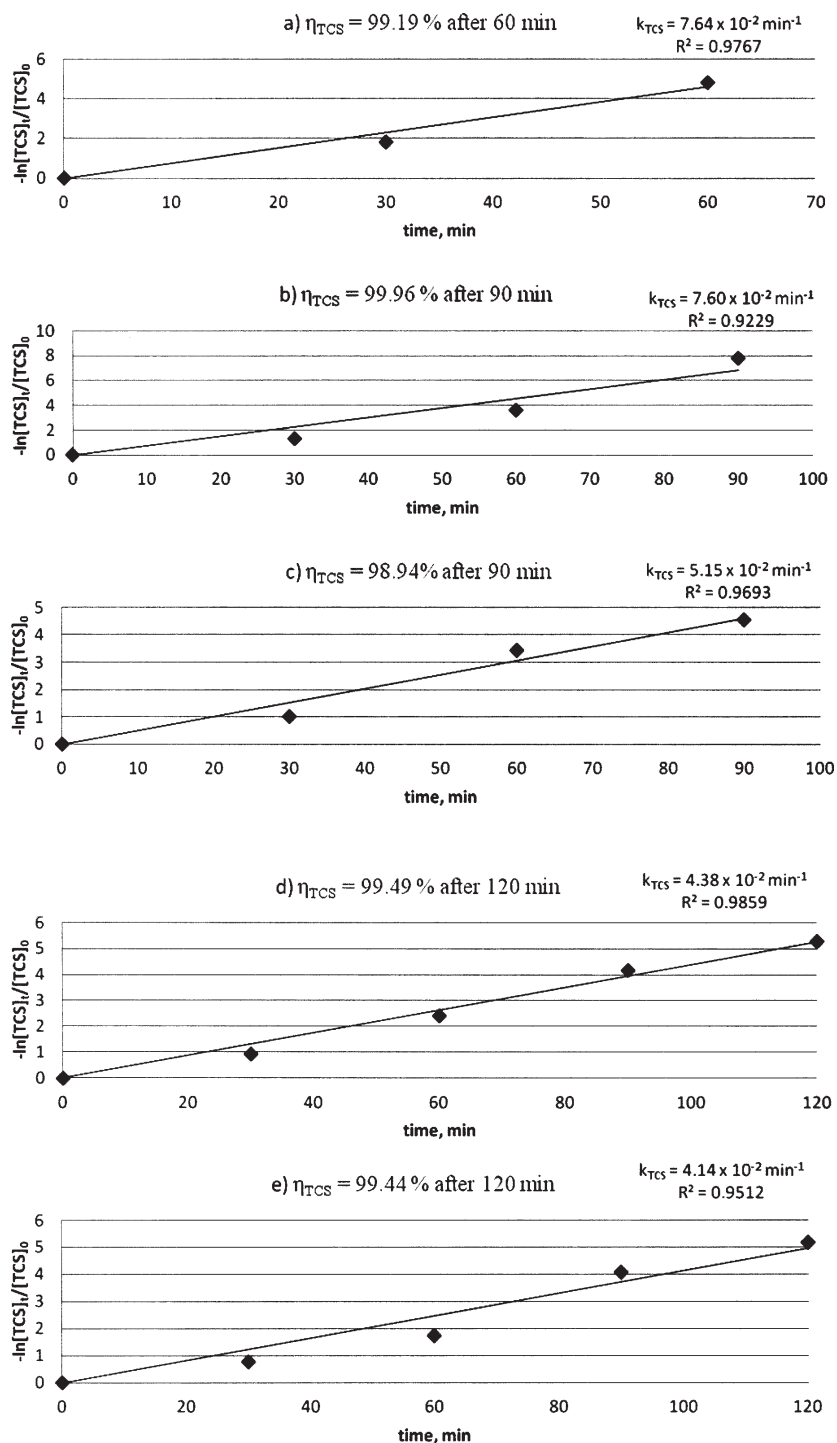


Fig. 1. Efficiency of TCS degradation using UV/TiO₂ system
 a) [TCS]₀ = 1.112 mg/L, b) [TCS]₀ = 4.81 mg/L, c) [TCS]₀ = 7.552 mg/L, d) [TCS]₀ = 11.8 mg/L, e) [TCS]₀ = 13.498 mg/L

irradiation time was set at 120 min. The increase of the initial TCS concentration determines the decrease of the efficiency of the pollutant degradation at the same irradiation time. That is explained by the competition between TCS and its degradation byproducts for the consumption of hydroxyl radicals involved in the photooxidation reactions.

Kinetics

In order to describe the effect of the organic pollutant concentration upon the degradation rate, the Langmuir – Hinshelwood model is used [11-13].

The degradation rate can be described by the following equation:

$$r_0 = \frac{k_r K_{ad} [TCS]_0}{1 + K_{ad} [TCS]_0} \quad (3)$$

where: r_0 is the initial degradation rate of TCS, $[TCS]_0$ is the initial concentration of the substrate, k_r is the rate constant

for TCS degradation and K_{ad} is the equilibrium constant of TCS adsorption on TiO₂ particles. By rearranging equation (3) a linear equation can be obtained between the inverse of the initial degradation rate and the inverse of the pollutant initial concentration.

$$\frac{1}{r_0} = \frac{1}{k_r K_{ad} [TCS]_0} + \frac{1}{k_r} \quad (4)$$

From the equation (4) plot the values of rate constant k_r and equilibrium constant K_{ad} can be calculated: $1/k_r$ represents the intercept and $1/k_r K_{ad}$ represents the slope of the plotted equation (4).

The experimental data for the first 30 min of irradiation were used in order to plot equation (4). The linearization of the Langmuir – Hinshelwood equation is presented in figure 2.

The equilibrium constant of TCS adsorption on TiO₂ particles was calculated from the slope $K_{ad} = 12989 \text{ M}^{-1}$

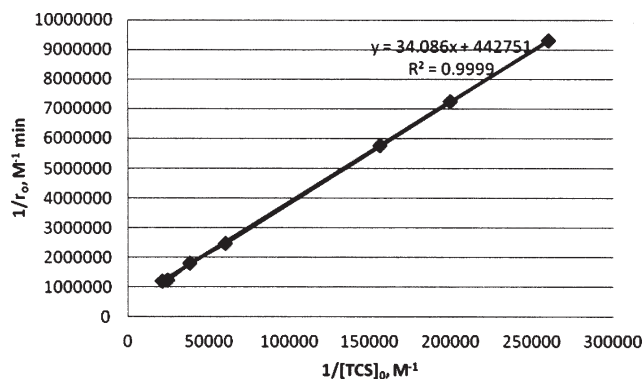


Fig. 2. Linearization of Langmuir – Hinshelwood equation

and the rate constant was calculated from the intercept $k_p = 2.258 \cdot 10^{-6} \text{ M min}^{-1}$.

The verification of equation (2) shows that the degradation of the adsorbed pollutant takes place at the TiO_2 particle surface where radical species generated by photocatalyst irradiation are also adsorbed.

Conclusions

The Langmuir – Hinshelwood kinetic that describes the pollutant degradation explains the inverse dependence of the rate constant and the initial pollutant concentration if the following aspects are taken into consideration:

- the main stage of the photocatalytic degradation is represented by the surface process favored by the photocatalyst high adsorption capacity;
- the photogeneration and charge transfer (electrons – holes) at the photocatalyst surface as well as their interactions with the pollutant are phases that occur in series, each of them with the capacity to be the rate determining step;
- the concentration of adsorbed intermediates increases with the initial pollutant concentration, TCS being in competition with its degradation intermediates for hydroxyl radicals consumption, determining the decrease of the pollutant degradation rate.

Acknowledgments: The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398 and Programme Nucleu 13N/2009, Project PN 09 – 13 03 15.

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Manuscript received: 14.10.2014