



Kinetics and statistical approach for 2,5-dichlorophenol degradation in short reaction times by solar TiO₂/glass photocatalysis

Cinética y enfoque estadístico para la degradación de 2,5-diclorofenol en tiempos cortos de reacción por fotocatalisis solar TiO₂/vidrio

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Abstract

Aqueous 2,5-dichlorophenol (2,5-DCP) degradation was studied. Degradation was performed by solar photolysis and heterogeneous photocatalysis on TiO₂ synthesized by sol-gel method. A thin film solar reactor of 1 m² surface area was used. Solution was recirculated for 30 min under a laminar regime, with 20° and 26° surface slopes, under different temperatures and radiation. Samples were taken every 5 min to determine chemical oxygen demand (COD) and absorbance at $\lambda=280$ nm. A 2³ factorial with covariates and repeated measures experimental design was used to determine degradation kinetics of 2,5-DCP in short reaction times, having two response variables: COD and concentration of 2,5-DCP, determined at 280 nm. The factors were: reactor inclination angles (20° and 26°), flow (355 L/h and 407 L/h) and process (photolysis and photocatalysis); and covariates: solar radiation, temperature, evaporation and initial concentration of 2,5-DCP. By comparing the kinetic constants of both processes using Student-t statistic, significant differences ($p < 0.05$) between them were found. Degradation reaction of 2,5-DCP in short times by solar photocatalysis, clearly showed a reaction order $n = 1$, reaching degradation of 75% (20 min), 83% (25 min) and up to 95% (30 min).

Keywords: 2,5-dichlorophenol degradation, solar heterogeneous photocatalysis, short reaction times, kinetics, statistics.

Resumen

Se estudió la degradación de 2,5-diclorofenol (2,5-DCF) en solución acuosa por fotólisis y fotocatalisis solar heterogénea sobre TiO₂ sintetizado por sol-gel, utilizando un reactor solar de cama dura de 1 m² de superficie. Se recirculó la solución durante 30 min bajo régimen laminar, con pendientes de 20° y 26° de la superficie de reacción, bajo distintas temperaturas y radiaciones horarias. Se tomaron muestras cada 5 min para determinar demanda química de oxígeno (DQO) y absorbancia a $\lambda=280$ nm. Se empleó un diseño experimental factorial 2³ con covariables y mediciones repetidas y se determinó la cinética de degradación de 2,5-DCF en tiempos cortos de reacción, teniendo dos variables de respuesta: DQO y concentración de 2,5-DCF, determinada a 280 nm. Los factores fueron: ángulo de inclinación (20° y 26°), flujo (355 y 407 L/h) y proceso (fotólisis y fotocatalisis), y las covariables: radiación solar, temperatura, evaporación y concentración inicial de 2,5-DCF. Al comparar las constantes cinéticas de ambos procesos mediante t-Student, se encontraron diferencias significativas ($p < 0.05$). La degradación de 2,5-DCF en tiempos cortos por fotocatalisis solar, mostró claramente un orden de reacción $n=1$, alcanzando porcentajes de degradación de 75% (20 min), de 83% (25 min) y de hasta 95% (30 min).

Palabras clave: degradación de 2,5-diclorofenol, fotocatalisis solar heterogénea, reacción en tiempos cortos, cinética, estadística.

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1 Introduction

Research advances on the effect of pollutants on life forms and their impact on ecosystems, coupled with the demands of society for better water quality, have materialized in increasingly strict regulations against pollutants disposal in water sources (UNESCO, 2004; Rubiano *et al.*, 2005; Bailón-Salas *et al.*, 2018; Alcázar-Medina *et al.*, 2020).

Chlorophenols are a group of chemicals whose toxicity generally increases as phenol chlorination increases. Even at very low concentrations, chlorophenols give unpleasant smell and taste to water. These compounds may be present in wastewater from municipal drainage, and in drinking water as a result of contamination of natural water sources and chlorination of water containing phenolic products (CDC, 2009).

The 2,5-dichlorophenol (2,5-DCP) can be formed during the process of generation of wood pulp, as well as in its incineration. It is a toxic substance for aquatic organisms with an octanol/water partition coefficient 3.1, so its affinity for animal fatty tissue is medium and it is easily dispersed when is in the form of powder (CDC, 2009). Using organoleptic data for the control of undesirable taste and odor in water, a limit level of 0.5 $\mu\text{g/L}$ for 2,5-DCP has been estimated. However, exposure to this chemical occurs mainly through inhalation of 1,4-dichlorobenzene (1,4-DCB), which is metabolized and excreted in the urine as 2,5-DCP (EPA, 2001).

Advanced oxidation processes (AOPs) are methods used in the degradation of different organic pollutants; they have been extensively used due to the strict regulations of many countries regarding the control of water quality (Vergara-Sánchez *et al.*, 2012). Heterogeneous photocatalysis is one of these technologies. It involves a broadband semiconductor sensitive to light, particularly TiO_2 , on which simultaneous oxidation and reduction photoreactions occur in different areas of the liquid-solid or gas-solid interfacial region (Rincon *et al.*, 2001; Esplugas *et al.*, 2002; Di Paola *et al.*, 2003; Zarazúa-Aguilar *et al.*, 2017).

Heterogeneous photocatalysis with TiO_2 presents a wide range of applications (Zhao and Yang, 2003; Gaya and Abdullah, 2008; López-Ojeda *et al.*, 2011; Morales-Zárate *et al.*, 2018). The degradation of phenolic compounds in water from the phenolic resin industry or the cellulose industry has been reported

(Parra *et al.*, 2003), as well as the degradation of a wide variety of organochlorine compounds from PVC production plants or wood industries (Thu *et al.*, 2005). In the presence of UV radiation ($<400\text{ nm}$), TiO_2 catalyzes the oxidation of organic compounds reaching, in the ideal case, its complete mineralization and forming CO_2 and H_2O , or transforming them into other organic compounds before mineralizing them, as occurs with a large number of aromatic compounds (Moctezuma *et al.*, 2003; Luna-Sánchez *et al.*, 2013).

In heterogeneous photocatalytic processes, UV radiation triggers the excitation of electrons in the last layer of the photocatalyst, and the generation of a positive gap in the valence band (left by the promoted electron) (Pantoja-Espinoza *et al.*, 2015; Núñez-Núñez *et al.*, 2018). However, the main disadvantage of the use of TiO_2 as photocatalyst, is the recombination of the electron and the hole, which occurs in the absence of electron acceptors. To avoid such recombination, the addition of chemical oxidants has been used in the past; H_2O_2 , for example, reacts with electrons in the conduction band (Malato *et al.*, 2009).

The course of the photocatalytic degradation reaction of organic matter, reaction routes and, consequently, reaction kinetics, depends on a great variety of factors and experimental conditions. Among such factors are the type, nature and properties of the photocatalyst used (Irigoyen-Campuzano *et al.*, 2017), the origin of the effluent to be treated, the magnitude of the pH and its dependence on the isoelectric point (Núñez-Núñez *et al.*, 2018), the selected AOP (photolysis or photocatalysis), the emission source (solar or artificial UV) and its radiation intensity ($\text{UV-C} > \text{UV-B} > \text{UV-A}$) (Malato *et al.*, 2009), and the addition of oxidizing agents to increase the production of $\cdot\text{OH}$ radicals (Moctezuma *et al.*, 2016), which have an oxidation potential of 2.8 eV.

The kinetic parameters of the photocatalytic degradation of organic matter on various types of semiconductors have been widely studied, particularly considering the elements of the reactor dynamics used (Davis and Hao, 1991 and 1992; Wolfrum and Turchi, 1992). Moctezuma *et al.* (2016), studied the reaction routes for the photocatalytic degradation of phenol solutions, demonstrating that both the degradation and the mineralization reactions follow a zero order, also observing that injecting ozone instead of oxygen, as an electron acceptor, accelerates the reaction by favoring the formation of benzoquinone and catechol (Moctezuma *et al.*, 2016).

In our research group, photocatalytic degradation

of various organic compounds classified as recalcitrant and used for pharmaceutical (Salas Ayala, 2018), and industrial uses (González Burciaga, 2013; Morones Esquivel, 2016), has been studied. Such researches, were performed through a thin film solar reactor (TFSR) $\text{TiO}_2/\text{glass}$ at laboratory level (3 L) with sunlight and with the use of fixed bed reactors $\text{TiO}_2/\text{SiO}_2$ at pilot level (50 L) with UV-C radiation, in order to determine the significant interactions of the operation variables, as well as their effect on the kinetics of the degradation reactions of organic matter.

In previous works, degradation of aqueous 2,5-DCP by heterogeneous photocatalysis in this same type of solar reactors has been reported, comparing the efficiency of the supported photocatalyst ($\text{TiO}_2/\text{glass}$) with respect to synthetic photocatalysts of organic nature (conjugated copolymer). Kinetics of the degradation reaction and the effect of pH and the dose of the oxidizing agent (H_2O_2) in the pollutant degradation reaction were also studied (Irigoyen-Campuzano *et al.*, 2017) when taking advantage of the natural conditions of intense solar radiation in Durango, Mexico, with a direct normal insolation reaching $6.5 \text{ kWh/m}^2 \text{ day}$ (Riveros-Rosas *et al.*, 2010).

Subsequently, and taking into account the reactor dynamics (Davis and Hao, 1991 and 1992; Wolfrum and Turchi, 1992; Moctezuma *et al.*, 2016), as well as considering several nano-structural parameters (particle size, specific surface area and crystalline phase of the photocatalyst, TiO_2 , among others), our research group reported the degradation of 2,5-DCP by photocatalysis in long reaction times, using a TFSR, with degradation percentages of up to

98% and demonstrating that the order of reaction, with respect to the concentration of 2,5-DCP, is determined in the interval of both orders (zero and one) and that throughout this transition of the order of reaction, changes in reaction rate are proportional to a magnitude ranging from $1 - \exp(-K_1\Theta_2)$ to K_1 (Morones-Esquivel *et al.*, 2017).

Innovation of this work focusses on the determination of kinetic parameters resulting of 2,5-DCP degradation in high concentration solutions by heterogeneous solar photocatalysis ($\text{TiO}_2/\text{glass}$) and short reaction times (30 min). It is supported by a comparative analysis of the velocity constants of the reaction and in the proposal of an experimental design 2^3 with covariates and repeated measures, in order to determine the significant interactions of the operation variables, which influence the optimization of the reaction.

2 Methodology

2.1 $\text{TiO}_2/\text{glass}$ solar reactor

A TFSR (Fig.1a) with a 1 m^2 glass plate impregnated with TiO_2 synthesized by the sol-gel method (Djaoued *et al.*, 2002; Sheng *et al.*, 2008) was used (Fig. 1b). TiO_2 photocatalyst was characterized in its microstructural forms by X-ray diffraction (XRD), and its band gap determined by UV-Vis-NIR spectrophotometry, by the Kubelka-Munk method, under previously reported operating conditions (Morones-Esquivel *et al.*, 2017).

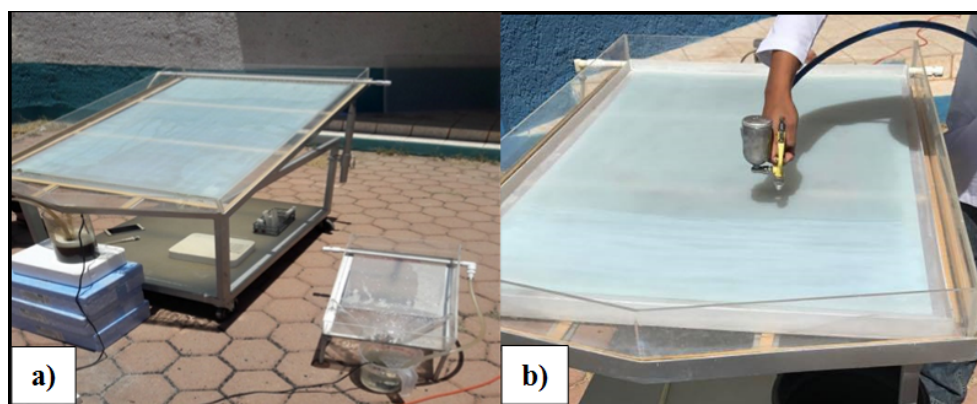


Fig. 1. TiO_2 solar reactor, 1 m^2 contact area ($1.25 \text{ m} \times 0.80 \text{ m}$), adjustable to different inclination angles (18° to 30°) and PVC pipe, keeping constant flow (355 L/h and 407 L/h) with laminar flow regime ($\text{Re} < 1000$). a) 1 m^2 surface and a $1/10 \text{ m}^2$ surface reactors. b) Impregnation of TiO_2 solution over glass surface (1 m^2).

The glass plate has a contact area of 1 m² (1.25 m x 0.80 m) and was adjusted to two different experimental angles (20° and 26°) with respect to the horizontal, close to the latitude of Durango City, Mexico (24° 01' 37" N), with the purpose of capturing the greatest amount of solar energy (Blanco, 2005). Two constant flow rates were tested (355 L/h and 407 L/h), under a laminar regime (Re < 1000), recirculating the solution from a collecting tank (Morones-Esquivel *et al.*, 2017).

2.2 Experimental procedure

Degradation experiments of 2,5-DCP (Aldrich, CAS: 583-78-8, USA) in aqueous solution were carried out taking the initial concentration (C_0) of 2,5-DCP as an experimental covariate and an initial magnitude of pH₀ = 7.3, using deionized water for the preparation of the solution (MAPLA, CAS: 7732-18-5, Mexico). Both photolysis and by photocatalysis experiments were performed to evaluate the effect of the photocatalyst over compound degradation by light (photolysis), using a TFSR on both processes and, as photocatalyst, TiO₂ obtained by the sol-gel method as described by other researchers (Sheng *et al.*, 2008; Morones-Esquivel *et al.*, 2017).

A volume of 2.5 L of 2,5-DCP aqueous solution was recirculated, on the solar reactor plate only (photolysis), or on the reactor glass plate impregnated with TiO₂ (sol-gel) for the case of photocatalysis. Samples of 3 mL were taken every 5 min, including time zero and up to 30 min. The course of reaction was followed by UV-Vis spectrophotometry in a range of 200 to 500 nm (Arellano-Cárdenas *et al.*, 2008), using a HACH spectrophotometer (model DR5000, USA), and performing the corresponding absorbance-concentration calibration curves at 230 and 280 nm (Uchida and Okuwaki, 2003), to determine the residual concentration (mg/L) of 2,5-DCP in aqueous solution. Likewise, COD was determined by the digestion method (HACH, 2000) in a HACH spectrophotometer (model DR2010, USA). Data of the initial and final volume of each experiment were used to determine the levels of evaporation.

Radiation and hourly temperature data were provided by the meteorological station of the Secretaría de Recursos Naturales y Medio Ambiente, measured through a pyranometer (Global Water's, model WE300 Solar Radiation Sensor, USA). Experiments were conducted on cloudless and windless days, under two established hours (9:00 am and 1:00 pm), in low ($\bar{h}v_{average} = 453.6 \text{ W/m}^2$)

and high ($\bar{h}v_{average} = 847.4 \text{ W/m}^2$) solar radiation intensity.

2.3 Determination of kinetic parameters

To determine the kinetics of aqueous 2,5-DCP photocatalytic degradation on the TiO₂/glass plate in short reaction times (up to 30 min), equation 1 was used, considering the following assumptions: a steady state, the magnitude of the pH of the aqueous solution is favorable for degradation, the viscosity and density of the fluid in the reactor are constant, and the flow on the plate is laminar (Re < 1000) (Giménez *et al.*, 1999, Malato *et al.*, 2009):

$$C_t = C_0 e^{-k_{op}t} \quad (1)$$

where k_{op} is the operational constant, given by the slope when plotting $\ln(C_0/C_t)$ against time (t), C_t is the concentration at each time and C_0 is the initial concentration of the organic pollutant (Dijkstra *et al.*, 2001). The photolytic constant (k_{ph}) was determined in the same way.

2.4 Experimental design

Experimental data obtained were analyzed statistically by means of two different models: a factorial design 2³ with covariates and a factorial design 2³ with covariates and repeated measures, having two response variables: COD (mg/L) and the 2,5-DCP concentration (mg/L), determined at 280 nm. The 3 factors, each with 2 levels, were: inclination angle (20° and 26°), flow (355 L/h and 407 L/h) and process (photolysis and photocatalysis). The considered covariates were solar radiation, temperature, evaporation, and initial concentration of 2,5-DCP. The first model is described by equation 2. It was carried out without taking into account the time during the course of the reaction and taking as response variable the degradation percentage that encompasses the entire process. The second model allows us to observe the effect of each factor on the reaction time, plus the effect of the determined covariates, and is described through equation 3:

$$Y_{ijkl} = \mu + P_i + Q_j + A_k + \chi + \lambda + \theta + \eta + PQ_{ij} + PA_{ik} + P_i\lambda + P_i\theta + P_i\eta + QA_{jk} + PQA_{ijk} + PQ_{ij}\lambda + PA_{ik}\lambda + PQA_{ijk}\lambda + \varepsilon_{ijkl} \quad (2)$$

$$Y_{ijklm} = \mu + TP_{il} + TQ_{jl} + TA_{kl} + \chi + \lambda + \theta + \eta + TPQ_{ijl} + TPA_{ikl} + TQA_{jkl} + P_i\lambda + P_i\theta + P_i\eta + TPQA_{ijkl} + PQ_{ij}\lambda + PA_{ik}\lambda + PQA_{ijk}\lambda + \varepsilon_{ijklm} \quad (3)$$

where Y_{ijkl} and Y_{ijklm} are the response variables, μ is the general average of the model, P_i is the process (photolysis $P_i = 1$ and photocatalysis $P_i = 2$), Q_j is the flow (355 and 407 L/h), A_k is the reactor inclination angle (20 and 26°), χ is the initial concentration, λ is the intensity of solar radiation, θ is the temperature, η is the evaporation, ε_{ijkl} and ε_{ijklm} represent the error and T represents the time.

Both models were analyzed in the statistical package SAS 9.1.3 (SAS Institute Inc., USA), taking a level of significance $\alpha = 0.05$. The comparison of the kinetic constants of degradation of 2,5-DCP in aqueous solution was performed using the statistical package Statistica 7 (Stat Soft Inc., USA).

In both models, the Gauss-Markov assumptions for the response variables were verified and the analysis of the general linear model corresponding to the experimental design was made through an analysis of variance, verifying the assumptions of normality, independence and homogeneity, according to the statistical package SAS 9.1.3. The kinetic constants of the degradation of 2,5-DCP in aqueous solution were obtained, as well as the standard errors and the coefficients of determination (R^2), applying a correlation model for first-order reactions and comparing the obtained kinetic constants for each experiment, using the Student-t statistic, through equation 4:

$$t = \frac{(k_1 - k_2)}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}} \quad (4)$$

where t represents the Student-t statistic, k_1 represents the operational photocatalytic constant, k_2 corresponds to the photolytic kinetic constant, σ_1^2 and σ_2^2 represent the variances and n_1 and n_2 , the number of observations.

3 Results and discussion

3.1 Degradation of 2,5-DCP on short reaction times

In Fig. 2, the COD/COD₀ variation as a function of time is presented for the degradation of 2,5-DCP in aqueous solution, both by photolysis (figs. 2a and 2b), and by solar photocatalysis (figs. 2c and 2d), in conditions of high and low intensity of solar radiation. As can be seen, there are no notable variations in the course of the photolytic degradation reaction under high (fig. 2a) and low intensity of solar radiation (Fig. 2b), showing, however, a slight advantage in the average efficiency for the first case, in all photolysis experiments carried out.

The evaporation registered during the 30 min of reaction was, on average, 7% higher in the experiments carried out in conditions of greater intensity of radiation, with respect to those performed in low intensity conditions, generating a greater reconcentration of 2,5-DCP in the aqueous solution.

It is observed a lower efficiency for solar photolysis with respect to the high efficiencies obtained by solar photocatalysis, under high (Fig. 2c), and low intensity of solar radiation (Fig. 2d), which coincides with other reports (Bahnmann, 2004). These results are attributed to better activation of the photocatalyst and, consequently, greater production of ·OH radicals which act in the oxidation of organic matter. For this study, degradation percentages (COD/COD₀) of 75% (20 min), 83% (25 min) and up to 95% (30 min) were reached in conditions of high solar radiation, for the best experiment (20°, 407 L/h) (Fig. 2c); and up to 60% (30 min) for the best case of low radiation (26°, 355 L/h) (Fig. 2d).

Table 1 concentrates the % degradation efficiencies of 2,5-DCP in aqueous solution, determined in conditions of high and low intensity of solar radiation ($\hbar\nu_{average} = 847.4 \text{ W/m}^2$ and $\hbar\nu_{average} = 453.6 \text{ W/m}^2$, respectively), for solar photolysis and photocatalysis. For the solar photocatalysis process, both in low and high intensity solar radiation conditions, the evolution of the characteristic peaks could be followed at 280 nm, which coincides widely with reports by other authors (Labudzińska and Gorczyńska, 1995; Uchida and Okuwaki, 2003).

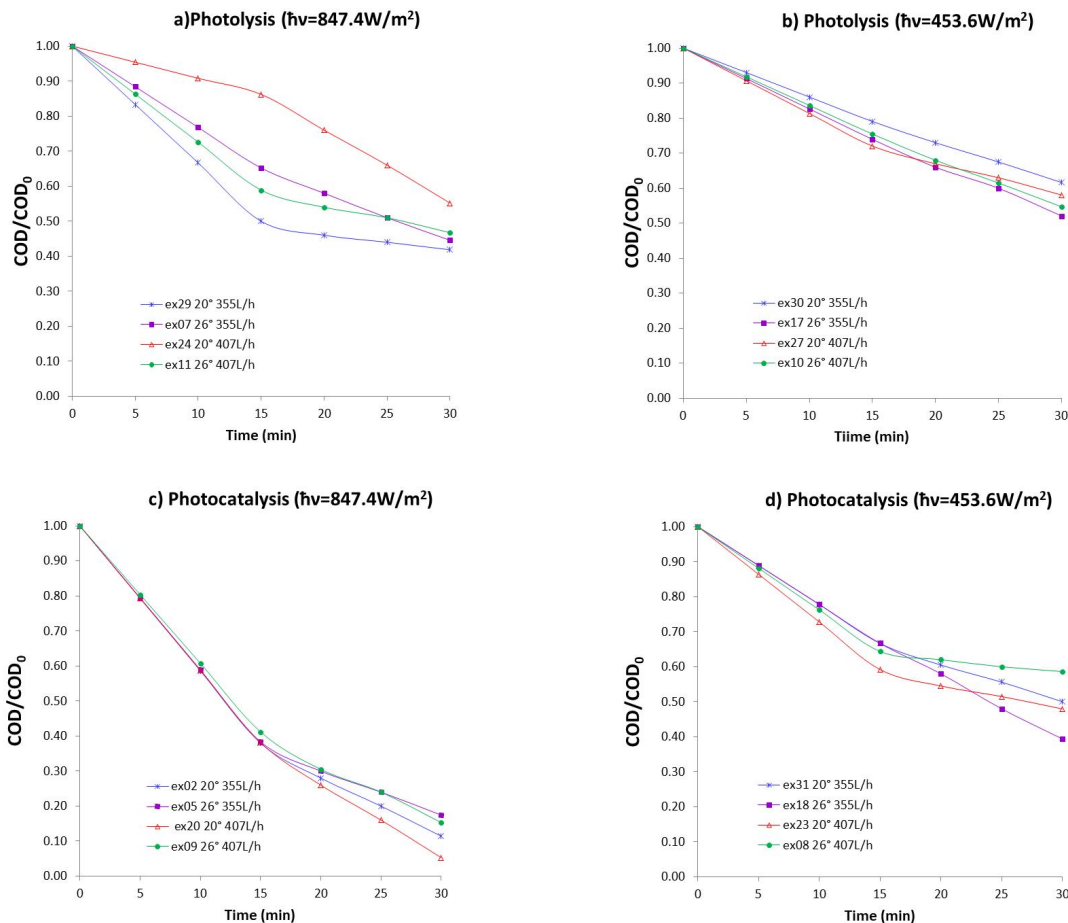


Fig. 2. COD/COD₀ variation over time, at different inclination angles and flows (L/h) in different experiments for: a) photolysis under high radiation intensity, b) photolysis under low radiation intensity, c) photocatalysis under high radiation intensity and d) photocatalysis under low radiation intensity.

Table 1. Aqueous 2,5-DCP degradation efficiencies in short reaction times (30 min) by solar photolysis and photocatalysis, in high and low radiation intensities.

	Photolysis					Photocatalysis			
	Exp ⁱ	$\hbar\nu$ (W/m ²)	C ₀ (mg/L)	COD (%)	$\lambda = 280$ nm (%)	$\hbar\nu$ (W/m ²)	C ₀ (mg/L)	COD (%)	$\lambda = 280$ nm (%)
Low radiation	20°, 355	443	90.0	48.5	50.3	498	84.0	58.2	62.2
	20°, 407	481	93	40	44.1	453	98	53.1	58.8
	26°, 355	479	73	50.8	54.7	476	66	60.3	56.2
	26°, 407	395	80	50	52.3	405	77	52.6	50.4
High radiation	20°, 355	878	86	60	63.4	940	79	91.2	91.9
	20°, 407	763	87	52.3	57	793	76	94.9	96.9
	26°, 355	961	92	56.7	58.1	699	85	89.1	90.1
	26°, 407	810	96	56.6	58.9	935	85	87.3	89

Expⁱ: reactor inclination (°), and flow (L/h)

$\hbar\nu$: solar radiation

C₀: 2,5-DCP initial concentration

Experiments performed by triplicate, for each one of experimental conditions

As it is observed (Table 1), the efficiencies of 2,5-DCP degradation (degradation %) by solar photocatalysis, measured both by COD and UV-visible at 280 nm, for conditions of high intensity of solar radiation, are always superior to those obtained at low intensity, independently of the photocatalyst/support surface slope (TiO₂/glass) and the flow (L/h) chosen. These results coincide with theories of maximum efficiency of degradation of organic matter on TiO₂, by heterogeneous solar photocatalysis (Feitz *et al.*, 2000; Zhao and Yang, 2003). Furthermore, average degradation efficiencies of up to 95% for conditions of high solar radiation in short reaction times (30 min) were reached, and are similar to those reported by Ba-Abbad *et al.* (2010), who degraded 2,4-DCP in aqueous solution (50 mg/L) by solar photocatalysis on ZnO, obtained also by the sol-gel method, determining a degradation efficiency greater than 98% during 60 min of reaction and measuring pollutant concentration by molecular absorbance ($\lambda = 285$ nm).

The best efficiencies obtained (Table 1), are also very close to those achieved by other authors (Morones-Esquivel *et al.*, 2017), who under identical operating conditions to those followed in this work, reached up to 98% degradation of 2,5-DCP by solar

photocatalysis, after 60 min of reaction. The 2,5-DCP degradation % in short reaction times (30 min, table 1), obtained by means of both response variables (COD and absorbance at 280 nm), are close to each other for the particular case of the degradation of 2,5-DCP in short reaction times (30 min) by solar photocatalysis and high intensities of solar radiation ($\bar{h\nu}_{average} = 847.4$ W/m²) (Table 1).

3.2 2,5-dichlorophenol degradation kinetics

Table 2 shows the kinetic constants for the degradation of 2,5-DCP in aqueous solution by photolysis (on a glass plate) and by solar photocatalysis (TiO₂/glass), when considering the initial concentration of 2,5-DCP in aqueous solution, the intensity of solar radiation and temperature, as covariates in the experimental design.

Degradation follows a first order reaction ($n = 1$), similar to that reported by other authors (Irigoyen-Campuzano *et al.*, 2017), who studied the degradation of 2,5-DCP by heterogeneous photocatalysis, using solar reactors with P-25 TiO₂ supported on glass (1/100 m²), under different magnitudes of pH (3-10) and obtaining an average $k_{op} = 0.0054$ min⁻¹.

Table 2. Aqueous 2,5-DCP kinetic degradation rates in short reaction times (30 min) by solar photolysis and photocatalysis, compared in terms of COD through Student-t test.

	Photolysis				Photocatalysis			
	Exp ⁱ (°), L/h	$\bar{h\nu}$ (W/m ²)	k_{ph} (min ⁻¹)	τ (min)	$\bar{h\nu}$ (W/m ²)	k_{op} (min ⁻¹)	τ (min)	p
Low radiation	20°, 355	443	0.0130±0.0051	53.32	498	0.0234±0.0069	29.62	0.0138
	20°, 407	481	0.0122±0.0018	56.81	453	0.0282±0.0020	24.58	0.0145
	26°, 355	479	0.0172±0.0028	40.30	476	0.0203±0.0022	34.14	0.0400
	26°, 407	395	0.0125±0.0023	55.45	405	0.0177±0.0023	39.16	0.0034
High radiation	20°, 355	878	0.0146±0.0037	47.47	940	0.0999±0.0268	6.94	0.0005
	20°, 407	763	0.0124±0.0017	55.90	793	0.0880±0.0017	7.88	0.0001
	26°, 355	961	0.0195±0.0022	35.55	699	0.0674±0.0164	10.28	0.0000
	26°, 407	810	0.0158±0.0035	43.87	935	0.0615±0.0225	11.27	0.0010

Expⁱ: reactor inclination (°) and flow (L/h)

$\bar{h\nu}$: solar radiation

k_{ph} : photolytic constant

k_{op} : operational constant (photocatalytic)

τ : half-life period

p : significance level

Experiments performed by triplicate, for each one of experimental conditions

As can be observed in table 2, the best results obtained (k_{op}) always correspond to experiments carried out by photocatalysis under conditions of high solar radiation intensity ($\hbar\nu_{average} = 847.4 \text{ W/m}^2$), surpassing, in all cases, the corresponding magnitudes obtained under conditions of low radiation intensity, as well as by photolysis (k_{ph}) in both levels of solar radiation.

When kinetic constants (k_{ph} vs k_{op}) obtained under similar conditions of slope and reactor flow are compared through Student-t statistic, significant differences ($p < 0.05$) were found between the photolysis and the photocatalysis (Table 2). Such observation is consistent with reported by Stintzing (2003), who used $\text{TiO}_2/\text{concrete}$ reactors, with slope of 20° and laminar flow ($< 500 \text{ L/h}$) to degrade organic matter by solar photocatalysis.

For all the k_{op} magnitudes (Table 2) in the degradation of 2,5-DCP by solar photocatalysis at high radiation intensities ($0.0615 \text{ min}^{-1} \leq k_{op} \leq 0.0999 \text{ min}^{-1}$), dependence of k_{op} on the process is shown with respect to the radiation intensity and the experimental conditions (flow and slope of the surface), maintaining the initial concentration (C_0) as a covariate and showing very high degradation rates and very short half-life times (τ). It is important to note that the covariate evaporation does not play a significant role in the course of these experiments, as confirmed statistically in this work (Tables 3 and 4), since the half-lives of the reagent (6.94 - 11.27 min) are very short (Table 2).

3.3 Statistical analysis

In the 2^3 factorial design with covariates, for the case of the response variables COD and concentration of 2,5-DCP read at 280 nm, the assumption of normality of the residuals, verified with the Kolmogorov-Smirnof, Lilliefors and Shapiro Wilk tests, showed that they are greater than 0.05, so the assumption is fulfilled (Daniel and Cross, 2013). Linearity was checked with the graph of predicted against standardized residuals, observing that all the residuals are within 2 standard deviations, both in terms of COD (Fig. 3a), and concentration of 2,5-DCP (Fig. 3b).

For the 2^3 factorial design with covariates and repeated measures, the assumption of normality of the residuals was also verified by the Kolmogorov-Smirnof, Lilliefors and Shapiro Wilk tests (Daniel and Cross, 2013). Independence was verified by the standardized residuals chart, in which only one data is observed outside two standard deviations (Fig. 3c).

For the kinetic constants of degradation, the statistical analysis of the linear regression model showed, for the adjusted coefficients of determination, magnitudes between 0.900 and 0.992, all of them being significant and fitting to a line with a positive slope, validating the kinetic constants.

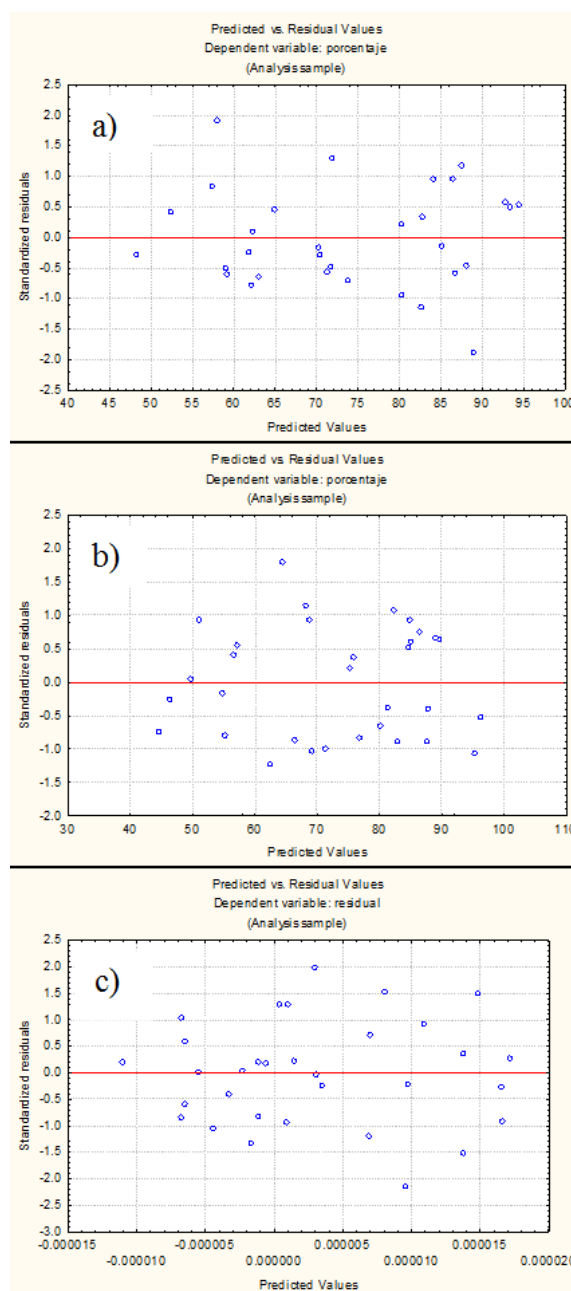


Fig. 3. Predicted vs standardized residuals graph in terms of COD (a), and in terms of 2,5-DCP at 280 nm (b), from 2^3 factorial design with covariates; and in terms of COD (c), from 2^3 factorial design with covariates and repeated measures.

3.3.1 2³ factorial design with covariates

The analysis, through equation 2, of the general model used, shows that the degradation percentage of 2,5-DCP measured at 280 nm presents significant differences calculated through the Tukey HSD test in all the model means (Daniel and Cross, 2013). In the general model, there are differences when there is interaction between process*flow*angle and process*flow*angle*radiation. For the degradation % in terms of COD, it is observed that the mean difference is significant for the Tukey test, and the model shows that when there is an interaction between the process factor and the angle and flow factors, as with the covariates radiation intensity and temperature, there are significant differences ($p < 0.05$)

between both oxidation processes (photolysis and photocatalysis). The covariate solar radiation intensity is decisive and the results obtained for it show that, in fact, there are significant differences when performing experiments with high or low radiation ($\hbar\nu_{average} = 847.4 \text{ W/m}^2$ and $\hbar\nu_{average} = 453.6 \text{ W/m}^2$).

3.3.2 2³ factorial design with covariates and repeated measures

The general analysis of variance of the model used, through equation 3, is shown in Table 3, confirming the aforementioned in section 3.3. For the 2,5-DCP degradation significant differences are found with the interaction of the factors flow, inclination angle and radiation intensity.

Table 3. Variance analysis for aqueous 2,5-DCP degradation % in short reaction times (30 min) by solar photolysis and photocatalysis, performed according to a 23 factorial design with covariates and repeated measures, in terms of COD and 2,5-DCP concentration determined at 280 nm.

Response variable: 2,5-DCP concentration determined at 280 nm					
Factors	d.f.	SS	SM	F	p
Time*AOP*Q	3	2251.61259	750.537529	2.8	0.0553
Time*Q*IA	3	2335.17639	778.392129	2.9	0.0494
Time*AOP*Q*IA	3	2333.28099	777.760331	2.9	0.0496
Time*rad*AOP*Q*IA	6	4747.18011	791.196685	2.95	0.0204
Time*rad*AOP*Q	6	3265.09601	544.182667	2.03	0.0896
Response variable: COD (mg/L)					
Factors	d.f.	SS	SM	F	p
Time*AOP	3	631.179445	210.393148	3.98	0.0159
Time*rad	3	723.705546	241.235182	4.57	0.0088
Time*te	3	518.396495	172.798832	3.27	0.0333
Time*AOP*Q*IA	3	620.635229	206.87841	3.92	0.017
Time*rad*AOP	3	451.917913	150.639304	2.85	0.0522
Time*te*AOP	3	550.996346	183.665449	3.48	0.0268
Time*rad*AOP*Q*IA	6	807.723796	134.620633	2.55	0.0387

Q: flow

IA: reactor Surface inclination angle

AOP: Advanced Oxidation Process (photolysis or photocatalysis)

rad: solar radiation intensity

te: temperature

*: interactions among factors and/or among factors and covariates

d.f: degrees of freedom

SS: sum of squares

SM: squared means

F: Fisher statistic

p: significance level

For the COD response variable, it is observed through the Tukey test that the means are different and the general analysis of time with respect to all the factors shows that there are highly significant differences with respect to the factors process ($p = 0.0159$) and solar radiation intensity ($p = 0.0088$); as well as with respect to the interactions process*flow*angle ($p = 0.017$), radiation*process*flow*angle ($p = 0.0387$), temperature*process ($p = 0.0268$), as shown in Table 3.

The above demonstrates the high significance of all the factors considered in the model, as well as the main covariate, radiation intensity, and the determining interactions: radiation*process*flow*angle, radiation*process and process*flow*angle, fulfilling the objective of this work.

Conclusions

The degradation follows a first order reaction ($n = 1$), and the best results obtained (k_{op}) always correspond to experiments carried out by photocatalysis under conditions of high intensity of solar radiation ($\bar{h\nu}_{average} = 847.4 \text{ W/m}^2$).

When comparing the kinetic constants (k_{ph} vs k_{op}) using the Student-t statistic, significant differences were obtained ($p < 0.05$) between photolysis and photocatalysis. The maximum efficiency of degradation obtained was 95% during 30 min of reaction, for high solar radiation conditions and the operational constants ($0.0615 \text{ min}^{-1} \leq k_{op} \leq 0.0999 \text{ min}^{-1}$) show dependence of k_{op} regarding the process (photolysis or photocatalysis), radiation intensity (high or low) and experimental conditions (flow and slope of the surface).

The analysis of variance for degradation % at 280 nm using factorial design 2^3 with covariates showed significant differences ($p < 0.05$) in all means with the Tukey HSD test. Differences are also shown between process*flow*angle and process*flow*angle*radiation interactions and, for degradation % in terms of COD, it is observed that the difference of means is significant for the Tukey test.

The model showed that when there is interaction between the process factor with the angle and flow, as well as with the covariates of radiation intensity and temperature, there are significant differences ($p < 0.05$)

between photolysis and photocatalysis.

For the COD response variable (mg/L), it was observed through the Tukey test that the means are different and the general analysis of time with respect to all the factors showed highly significant differences with respect to the process ($p = 0.0159$), the intensity of solar radiation ($p = 0.0088$) and temperature ($p = 0.033$); as well as with respect to the interactions process*flow*angle ($p = 0.017$), temperature*process ($p = 0.0268$) and radiation*process*flow*angle ($p = 0.0387$).

The results of this work suggest the use of AOPs, particularly of heterogeneous solar photocatalysis, in geographical zones characterized by a high incidence of solar radiation. The population of these areas can become potential users of these technologies in the treatment of their wastewater.

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Nomenclature

C_0	2,5-dichlorophenol concentration, mg/L	initial
COD	chemical oxygen demand, mg/L	
RXD	x-ray diffraction	
EPA	Environmental Protection Agency	
GLM	general linear model	
k_{ph}	photolytic constant rate, min^{-1}	
k_{op}	photocatalytic operation constant, min^{-1}	
LSD	least significant difference	
R^2	determination coefficient	
TFSR	thin film solar reactor	
τ	half life time, min	
1,4-DCB	1,4-dichlorobenzene	
2,5-DCP	2,5-dichlorophenol	

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