

Kinetic modelling of paracetamol degradation by photocatalysis: Incorporating the competition for photons by the organic molecule and the photocatalyst

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ABSTRACT

The design of a photoreactor is a complex task due to the different involved parameters. These parameters are mainly included in the kinetic model and its robustness directly impacts the photoreactor design. In this context, it is a common practice to assume that the reagents, i.e. organic molecules, are transparent to radiation. There are many cases, however, when this is not accurate. In such circumstances, the photons absorbed by the organic molecule should be accounted for in the corresponding kinetic model. This work aimed to achieve so in the Paracetamol oxidation photocatalyzed by TiO₂ at 254 nm. At this wavelength both, TiO₂ and Paracetamol, absorb energy. A kinetic model was developed, and this includes a local volumetric rate of energy absorption function (LVREA) that takes into account that the reagent is capable of interact with radiation thus modifying the radiant field. To simulate the radiant field, the Monte Carlo method described in the literature was modified to consider the competition for energy absorption between the catalyst and Paracetamol. The resulting model allows to predict the effect on Paracetamol degradation of catalyst concentration, initial Paracetamol concentration, intensity of emitted radiation and thickness of the reaction space. The results of computer simulation are in good agreement with experimental data for both, photolytic and photocatalytic degradation using the commercial DP25 catalyst.

1. Introduction

Polluted water has become a worldwide issue due to population growth and decreased availability of this vital resource. Such pollution is produced by several organic compounds like medicines, herbicides, pesticides, dyes, among others [1–6]. Many of these compounds are recalcitrant contaminants that cannot be completely eliminated by conventional biological treatments. In this sense, photocatalysis emerges as a promising advanced oxidation process for wastewater remediation since mineralizes bio-resistant toxic organic compounds via strong oxidant species like hydroxyl radicals [2,5].

Photocatalysis is a process based on the absorption of luminous energy by a solid photocatalyst, usually a semiconductor. When the pho-

tocatalyst is irradiated with light that has an energy greater than the energy of the band-gap of the photocatalyst (E_{BG}), the semiconductor absorbs photons that promote valence band electrons towards the conduction band, e_{CB}^- and this generates holes at the valence band, h_{VB}^+ . Water can then be chemisorbed on these sites and hydroxyl radicals (OH·) are produced. These radicals are responsible for the oxidation of organic matter [7–9]. In the case of TiO₂, it can only be excited with energy greater than 3.2 eV; that is, it can only be excited with light with a wavelength equal or lower than 380 nm. It is worth pointing out that the photocatalytic activity of TiO₂ does not depend only on radiation wavelength but also on structural, morphological, textural, optical and physicochemical characteristics (i.e. surface acidity) [10–12].

Photocatalysis has been extensively studied in recent decades, however, industrial implementation of this technology has been

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Nomenclature	
A	Absorbance
[Cat]	Catalyst concentration (g/m ³)
E _{bg}	Band Gap Energy (eV)
f _{Vol}	Irradiated volume fraction
g	Asymmetric phase function factor of HG equation
I _λ	Intensity of the spectral radiation (W/m ²)
I ₀	Intensity of radiation at lamp wall (W/m ²)
I _{calc}	Calculated radiation intensity (W/m ²)
I _{exp}	Experimental radiation intensity (W/m ²)
k _{ap}	Apparent kinetic constant (s ⁻¹)
k _{photolysis}	pseudo first order kinetic constant of global photolysis (s ⁻¹)
k _{f1}	First apparent kinetic constant of photolysis (m ² /(W s))
k _{f2}	Second kinetic constant of pseudo-first order of photolysis (m ² /(W s))
k _{r1} k _{r2} k _{r3} k _{r4}	Kinetic constants
L	Length of lamp (m)
l	Length of cell (m)
P _{abs}	Probability of radiation absorption
P(Ω' → Ω)	Phase function
[Pam]	Paracetamol Concentration (g/m ³)
s	Direction vector of radiation propagation (m)
T	Transmittance
t	Time (s)
V _{irr}	Irradiated volume (m ³)
V _{Total}	Total volume of reaction space (m ³)
W	Power lamp (W)
x, y, z	Cartesian coordinates (m)
<i>Greek letters</i>	
α ₁ , α ₂ , α ₃ , α ₄	Kinetic coefficients of the degradation model by photolysis and photocatalysis
β _λ	Extinction coefficient
β*	Specific extinction coefficient
λ	Wavelength
κ _λ	Absorption coefficient
σ _λ	Scattering coefficient
Φ _λ	Quantum Yield
θ ₀	Angle formed by incident radiation and scattered radiation
Ω	Solid angle
ω	Albedo coefficient
<i>Acronyms</i>	
Pam	Paracetamol
LVREA	Local volumetric rate of energy absorption
RTE	Radiation Transfer equation
LSSE	Model of the Linear Spherical Source Emission
MC	Monte Carlo method
LHHW	Kinetic model of Langmuir-Hinshelwood-Hougen-Watson

hampered presumably due to the lack of understanding in its design and scaling up [13]. Thus, it is important to develop calculation methods and computational tools to simulate the behavior of photocatalytic reactors [9,13,14]. The performance of a photocatalytic reactor depends on numerous factors such as the lamp radiation intensity, the type of catalyst and its concentration, the initial reagent concentration, reactor dimensions and the stirring rate, among other factors, therefore its analysis becomes complex. Nevertheless, computational simulation together with several statistical tools allow to evaluate the radiation field and the estimation of kinetic parameters [5] as well as the effect of different operation variables on them.

Numerous researchers have investigated the photocatalytic degradation of various organic compounds. In these investigations, the radiant field is evaluated and the kinetic equations have been established under conditions in which organic matter to be degraded is assumed to be transparent to radiation [15,16]. Nevertheless, this condition is not satisfied in all cases, for example, when the reagent also absorbs energy at the wavelength of the radiation source. Therefore, it is important to analyze the photocatalytic process when the reagent absorbs radiation at the wavelength employed, since under these conditions there is a competition for absorption energy between both, the reagent and the catalyst, which modifies the radiant field. Besides, the degradation by photolysis has a significant impact on the degradation process and must be accounted for in any kinetic model. Thus, the aim of this work was to establish and validate a kinetic model able to accurately predict the effect of catalyst loading and initial reagent concentration on conversion. To achieve so, Paracetamol (Pam) was elected. The photocatalytic degradation was experimentally carried out and the Monte Carlo Method was employed to emulate the radiant field. It was established that there is a competition for radiation absorption between the molecule and the catalyst.

Paracetamol (Pam) or Acetaminophen was elected as the molecule to be degraded since is a drug widely used as analgesic and antipyretic. Due to its high demand, its presence has been reported in wastewater, surface and underground water, and even in water for human consumption [17]. In addition, it has been suggested [15] that the absorption of

photons by paracetamol negatively affects the photo-activation of TiO₂. Thus, this work pursues to establish such an effect and incorporate it into the kinetic constant of the proposed kinetic model through a correction of the local volumetric rate of energy absorption (LVREA). Such correction consists in determining the LVREA considering not only the optical coefficients of the catalyst but also including those of paracetamol.

2. Methods

2.1. Paracetamol photocatalytic degradation

The photocatalytic degradation of Paracetamol was experimentally carried out in a cylindrical glass reactor with a reaction volume of 30 mL and a mechanical stirring of 300 rpm. The length of such a reactor was 0.12 m and the diameter 0.02 m. A lamp emitting radiation with a wavelength of 254 nm, 8 W power and 166 W/m² of average radiation intensity was placed at the center of the reactor and it was in contact with the reaction solution during the whole reaction time. The temperature was kept constant at 20 ± 1 °C by using a cooling bath. The Paracetamol solutions (10, 20, 50 and 100 g/m³) were prepared using deionized water. Commercial TiO₂ DP25 was used as catalyst. The catalyst concentration used was within an interval of 0–400 g/m³. The initial pH was 6.0.

2.2. Analytical methods for the determination of Paracetamol concentration

Aliquots of 500 µL were taken at different time intervals from reacting solution. These samples were centrifuged for 20 min at a speed of 10,000 rpm to remove the catalyst. The samples were subsequently filtered using syringe filters with a pore size of 0.45 µm prior to analysis. The Paracetamol concentration was analyzed by means of absorbance measurements using a Perkin-Elmer spectrophotometer model Lambda 25 UV/vis and by a high performance liquid chromatograph Vanquish Flex, ThermoScientific, equipped with a C18 column and with diodes

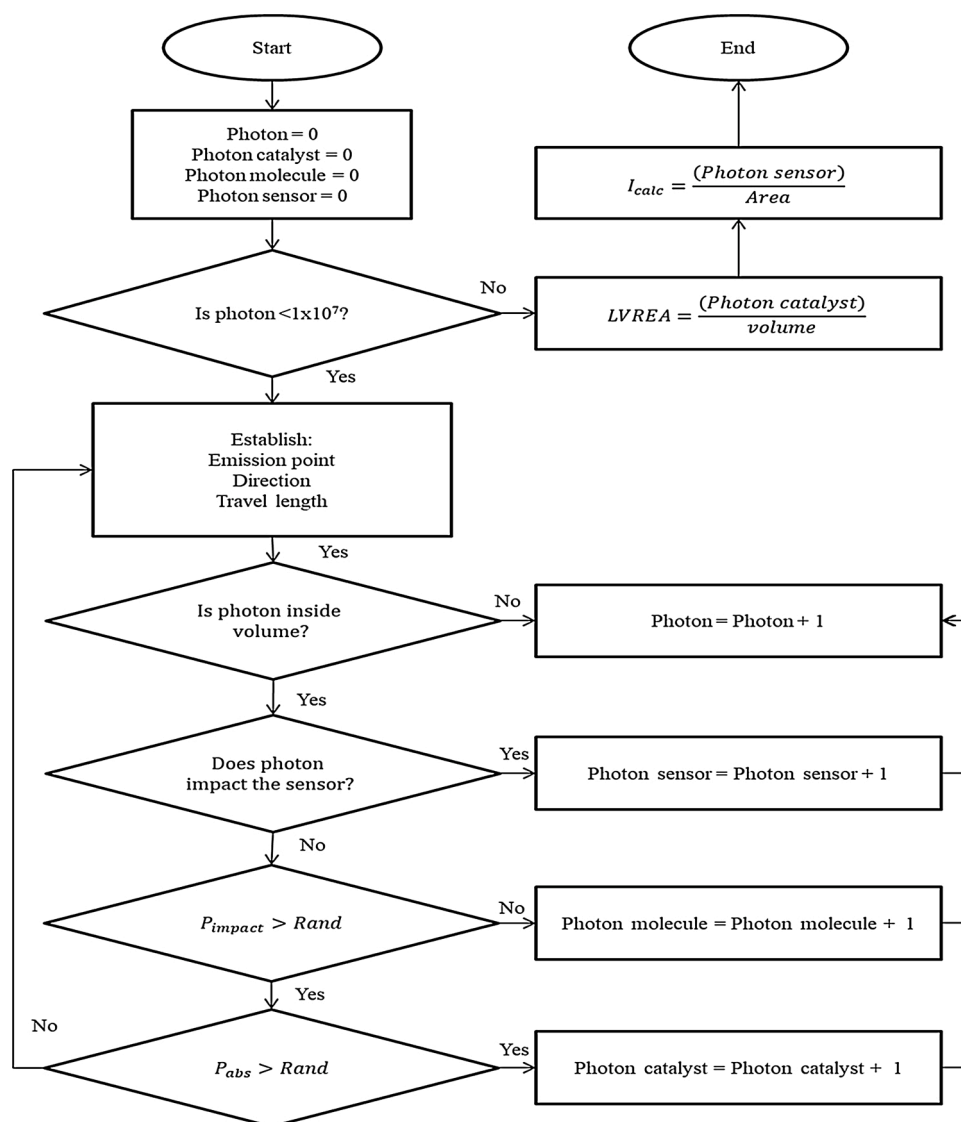


Fig. 1. Flowchart to establish the competitive absorption of radiation between catalyst and the organic molecule by Monte Carlo method.

arrangement detector (DAD). The mobile phase was a methanol-water solution (30:70 v/v) with a mobile phase flow of 1 mL/min and the samples were analyzed for 10 min.

2.3. Radiation transport modelling and simulation

To start the photocatalytic process, it is necessary that a photon with a suitable wavelength, impacts a catalyst particle to excite it. For this reason, it is essential to quantify the *LVREA*, an important component of the photocatalytic reaction rate expression [1,3,14]. The determination of *LVREA* values mainly requires: a) the optical characterization of the reaction space through their optical parameters, extinction coefficients, absorption and scattering of radiation, the scattering albedo and phase function, b) formulation and development of the absorption and dispersion of photons balances from the radiation transfer equation (RTE), which can be expressed as,

$$\frac{dI_{\lambda}(s, \Omega)}{ds} = -\beta_{\lambda}I_{\lambda}(s, \Omega) + \frac{\sigma_{\lambda}}{4\pi} \int_0^{4\pi} I_{\lambda}(s, \Omega') p_{\lambda}(\Omega' \rightarrow \Omega) d\Omega' \quad (1)$$

where I_{λ} is the intensity of the spectral radiation traveling through the medium in the incident direction Ω' along the path s ; λ represents the wavelength; β_{λ} is the volumetric extinction coefficient and describes the

attenuation of the radiation intensity. This parameter is defined as the sum of the scattering volumetric coefficient, σ , and the absorption coefficient, κ , that is $\beta = \sigma + \kappa$. The albedo scattering coefficient, ω , i.e. radiation fraction dispersed in the reaction medium, is defined as $\omega = \sigma / \beta$ [14]. The phase function $p_{\lambda}(\Omega' \rightarrow \Omega)$ can be used to modelling the redistribution of radiation after scattering phenomenon in the direction Ω [18,19]. In the present research, the equation of the phase function proposed by Henyey and Greenstein (HG) was used,

$$p_{\lambda}(\Omega' \rightarrow \Omega) = p_{\lambda}(\theta_0) = \left(\frac{1}{4\pi}\right) (1 - g^2) / (1 + g^2 - 2g \cos\theta)^{\frac{3}{2}} \quad (2)$$

This equation was selected because it takes into account in a relatively simple way the back and forward scattering by employing the parameter, which is the asymmetric phase function factor to describe the distribution of radiation scattering and is in an interval of $-1 < g < 1$, considering in this way the interval of the dispersion completely backward and the dispersion completely forward, respectively. When $g = 0$ is said to be isotropically scattered. The angle between directions Ω' and Ω is defined by θ . RTE is an integro-differential equation difficult to solve analytically, which can be achieved only under certain simplified considerations and situations. Alternatively, it is feasible to employ computational numerical methods.

The radiant field was calculated using the Montecarlo method (MC), implemented according to the methodology described by Moreira [7,20] with some modifications in order to take into account the radiation absorption by the reagent (Pam). In this work, the number of used photons was 1×10^7 . The methodology described by Moreira [3,7] assumes that the radiation interacts only with the catalyst and the molecule to be degraded is transparent. However, in this work, the molecule to degrade absorbs radiation and is liable to degrade by photolysis at the wavelength of the applied radiation. It modifies the radiant field and generates competitive radiation absorption between catalyst and molecule. This is shown in Fig. 1. To describe this competitive radiation absorption, the methodology explained by Moreira was modified according to the following considerations,

- a) The travel length where a photon is likely to be absorbed depends on the extinction coefficients of both, catalyst and molecule, rather than only on the catalyst. This can be mathematically expressed as follows, where *Rand* is a random number

$$l = \left(\frac{1}{\beta_{Cat} + \beta_{Pam}} \right) \log(1 - Rand) \quad (4)$$

- b) Both photon directions of travel, before and after an impact event, were calculated according to the methodology described by Moreira.
c) Thus, the impact probability is also affected by both, catalyst and the organic molecules, and this effect can be accounted for as follows,

$$P_{Impact} = \frac{\beta_{Cat}}{\beta_{Cat} + \beta_{Pam}} \quad (5)$$

If P_{Impact} is greater than a random number, then is assumed that a photon impacts the catalyst and such a photon can then be either absorbed or scattered. To establish whether photon absorption or scattering occurs, the absorption probability was calculated by [7,20],

$$P_{Abs\ cat} = \frac{\kappa_{Cat}}{\beta_{Cat}} \quad (6)$$

If $P_{Abs\ cat}$ is greater than a random number, then it is considered that the photon is absorbed by catalyst. Otherwise, the photon is scattered in a new direction and the travel length is calculated.

- d) If P_{Impact} is lower than a random number, then the photon is assumed to impact the molecule. The probability of photon absorption by the molecule can be calculated by using the following equation,

$$P_{Abs\ Mol} = \frac{\kappa_{Mol}}{\beta_{Mol}} \quad (7)$$

If $P_{Abs\ Mol}$ is greater than a random number, it is considered that the photon is absorbed by the molecule. Otherwise, the molecule is transparent to radiation. This implies that the photon travels beyond and a new travel length is calculated to start again the above-described process.

- e) In case the impact does not occur, then it is established that the fate of the photon concurs with the sensor coordinates, and the photon is quantified as detected photon, in order to calculate the radiation reaching the sensor.

The LVREA due to the catalyst is calculated dividing the absorbed photons in each reaction cell by the volume of each cell. Fig. 1 shows the

flowchart of the Monte Carlo process to determine the competitive radiation absorption between catalyst and the organic molecule.

2.3.1. Extinction, absorption and scattering coefficients of radiation

To determine the extinction coefficient of radiation, UV-vis spectrophotometry measurements were performed by using a Perkin-Elmer spectrophotometer model Lambda 25 UV/vis coupled with an integration sphere. Diffuse transmittance spectra were obtained in the UV region for different catalyst concentration solutions. The effect of catalyst concentration was studied in the range of 0–1000 g/m³, within a wavelength interval of 200–400 nm. The solutions prepared at a specific concentration were kept under constant stirring and subsequently subjected to ultrasound to ensure complete dispersion of the catalyst particles in the sample. To obtain the extinction coefficient, the methodology described by Satuf [21] was employed. It is worth to remember that this coefficient represents the capacity of a catalyst or molecule to interact with radiation and it is rather important to consider it while modelling the radiant field.

Some researchers [7,21], have applied MC method and optimization techniques to computationally evaluate the phase function ($p_i(\Omega' \rightarrow \Omega)$) and absorption (κ) and scattering (σ) radiation coefficients. In this research, we used the MC method coupled to the Nelder-Mead function optimization method to estimate these coefficients. Generally speaking, this procedure starts with an experimental value of a variable radiation intensity, (I_{exp}), and values of the absorption and scattering radiation coefficients are also proposed. The MC method is then used to calculate radiation intensity (I_{calc}) with those values. Through optimization techniques the proposed values of the coefficients are adjusted until the values of I_{calc} and I_{exp} converge.

2.4. Kinetic modelling of direct and indirect photolysis

Photolytic degradation phenomenon can occur directly, when a photolabile compound absorbs radiation and decomposes in consequence; or indirectly, when the radiation interacts with other chemical species dissolved in the medium to form radicals ($\cdot\text{OH}$ mainly) which possess a high oxidizing power [22]. Direct photolytic degradation phenomenon or just photolytic degradation of an organic compound depends on its capacity to absorb energy at the wavelength of the employed radiation source. The direct photolytic Pam degradation rate is directly proportional to the amount of radiation absorbed by the molecule [23],

$$\left(-\frac{d[Pam]}{dt} \right)_{direct} = I_0 k_{f1} (1 - 10^{-\tau_{ap}}) [Pam] \quad (8)$$

where I_0 is the emitted radiation intensity by the source, $\tau_{ap} = \beta l [Pam]$ is the apparent optical thickness; β is the extinction coefficient of the molecule to be degraded; l is the thickness of the reaction cell and $[Pam]$ is Paracetamol concentration. k_{f1} is a pseudo first order kinetic constant of direct photolysis. In addition, indirect photolytic degradation is proportional to the amount of radiation capable of interacting with the dissolved substance in the reaction medium. Thus,

$$\left(-\frac{d[Pam]}{dt} \right)_{indirect} = I_0 k_{f2} 10^{-\tau_{ap}} [Pam] \quad (9)$$

k_{f2} is a pseudo first order kinetic constant of indirect photolysis. The net effect of photolytic degradation is the sum of the two rates,

$$\left(-\frac{d[Pam]}{dt} \right)_{direct} + \left(-\frac{d[Pam]}{dt} \right)_{indirect} = I_0 k_{f1} (1 - 10^{-\tau_{ap}}) [Pam] + I_0 k_{f2} 10^{-\tau_{ap}} [Pam] \quad (10)$$

Table 1

Photocatalytic reactions, reaction rate kinetic laws and material balances for the proposed model.

Photocatalytic reactions	Reaction rate laws
$\text{catalyst} + h\nu \rightarrow \text{catalyst}(e_{CB}^- + h_{VB}^+)$	$r_{cat} = \Phi f_{vol} LVREA$ (16)
$e_{CB}^- + h_{VB}^+ \rightarrow \text{heat}$	$k_{r1} [e_{CB}^-] [h_{VB}^+]$ (17)
$h_{VB}^+ + H_2O \rightarrow \cdot OH + H^+$	$k_{r2} [H_2O] [h_{VB}^+] = K_{r2} [h_{VB}^+]$ (18)
$e_{CB}^- + O_2 \rightarrow \cdot O_2^-$	$k_{r3} [e_{CB}^-] [O_2] = K_{r3} [e_{CB}^-]$ (19)
$\text{Pam} + \cdot OH \rightarrow \text{Products}$	$k_{r4} [\cdot OH] [Pam]$ (20)
$\text{Pam} + h\nu \rightarrow \text{Products}$	$r_{photolysis} = k_{fot} [Pam]$ (21)
Material Balances	
$\frac{d[e_{CB}^-]}{dt} = \Phi LVREA_{Cat} - k_{r1} [e_{CB}^-] [h_{VB}^+] - K_{r3} [e_{CB}^-] \approx 0$	$\therefore [e_{CB}^-] = \frac{\Phi LVREA_{Cat}}{k_{r1} [h_{VB}^+] + K_{r3}}$ (22)
$\frac{d[h_{VB}^+]}{dt} = \Phi LVREA_{Cat} - k_{r1} [e_{CB}^-] [h_{VB}^+] - K_{r2} [h_{VB}^+] \approx 0$	$\therefore [h_{VB}^+] = \frac{\Phi LVREA_{Cat}}{k_{r1} [e_{CB}^-] + K_{r2}}$ (23)
$\frac{d[\cdot OH]}{dt} = K_{r2} [h_{VB}^+] - k_{r4} [\cdot OH] [Pam] \approx 0$	$\therefore [\cdot OH] = \frac{K_{r2} [h_{VB}^+]}{k_{r4} [Pam]}$ (24)
$\frac{d[Pam]}{dt} = -k_{r4} [\cdot OH] [Pam] - k_{photolysis} [Pam]$	(25)
$f_{vol} = V_{irr} / V_{Total}$	(26)

$$\frac{d[Pam]}{dt}_{photolysis} = I_0 [k_{f1} + (k_{f2} - k_{f1}) 10^{-\tau_{ap}}] [Pam] = k_{photolysis} [Pam] \quad (11)$$

$$r_{fot} = \frac{d[Pam]}{dt}_{photolysis} = I_0 [\alpha_1 + \alpha_2 10^{-\tau_{ap}}] [Pam] = k_{photolysis} [Pam] \quad (12)$$

Where $k_{photolysis}$ is a pseudo first order kinetic constant of global photolysis, α_1, α_2 are kinetic parameters defined as $\alpha_1 = k_{f1}$, and $\alpha_2 = k_{f2} - k_{f1}$.

2.5. Kinetics of photocatalytic degradation

In order to establish the importance of accounting for the photons absorption by Paracetamol and the catalyst, two base models with three variants each were assessed. These models are below detailed.

2.5.1. Model 1: power law kinetics

It is generally accepted in literature that the kinetic equation obeys a power law model,

$$\frac{d[Pam]}{dt}_{photocatalysis} = k_r [Pam]^m [LVREA]^n \quad (\text{Model 1a}) \quad (13)$$

where $m = 1$ since it corresponds to a pseudo-first order kinetics.

In this work, Eq. 13 was modified to account for the degradation of the organic molecule when is photolabile. To achieve so, the paracetamol oxidation rate due to photolysis was added to Eq. 13 to obtain a global reaction rate model as follows,

$$\frac{d[Pam]}{dt}_{overall} = \left(\frac{-d[Pam]}{dt} \right)_{photocatalysis} + \left(\frac{-d[Pam]}{dt} \right)_{photolysis} \quad (14a)$$

$$\frac{d[pam]}{dt}_{overall} = k_{photolysis} [Pam] + k_r [Pam] [LVREA]^n_{Cat} \quad (\text{Model 1b}) \quad (14b)$$

where $k_{photolysis}$ is the pseudo first order apparent constant of the photolytic degradation (see Eq. 12), which is a function of apparent optical thickness, τ_{ap} . Model 1b considers that LVREA is due to the radiation absorbed only by the catalyst. This implies that the travel length and impact probability were calculated using only the extinction coefficient of the catalyst.

The third variant of Model 1 was obtained by correcting the LVREA with MC considering that there is a competition between catalyst and reagent to absorb photons,

$$\frac{d[pam]}{dt}_{overall} = k_{photolysis} [Pam] + k_r [Pam] [LVREA]^n_{Corr} \quad (\text{Model 1c}) \quad (15)$$

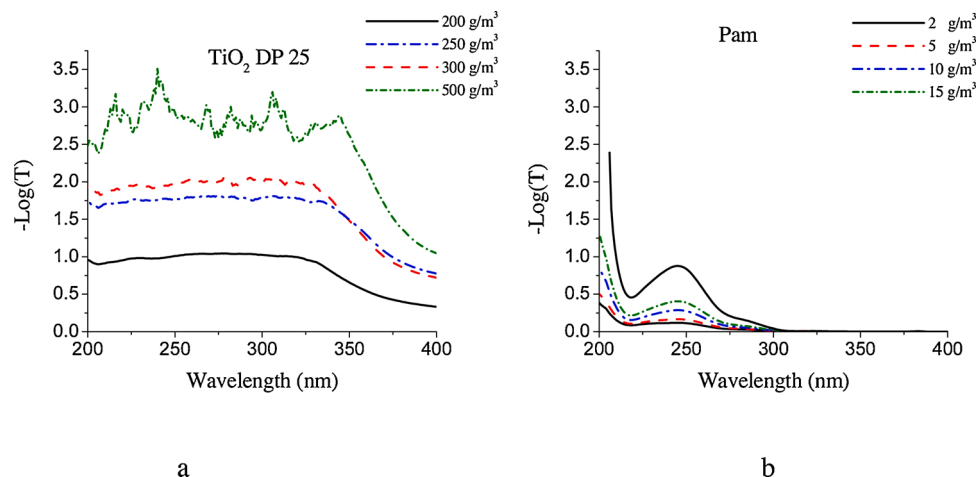


Fig. 2. Profiles of $-\text{Log}(T)$ depending on the wavelength at different concentrations for a) catalyst TiO_2 DP25 and b) Paracetamol solutions.

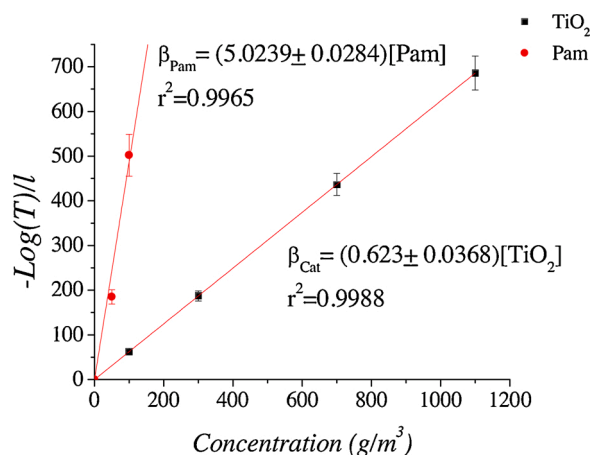


Fig. 3. Linear regression graph to estimate the specific extinction coefficients of catalyst (TiO₂ DP25) and reagent (Paracetamol).

2.5.2. Model 2: mechanistic kinetic equation

To establish the reaction rate equation for the Paracetamol photocatalytic degradation, a more detailed mechanism was proposed to include direct and indirect oxidation, radiation absorption by the catalyst, the generation and recombination of electron-hole pairs, the generation and propagation of radicals. Reactions involved, reaction rate laws and material balances are summarized in Table 1.

After performing the balances described by equations (16) to (26) and excluding photolysis (Eq. 21), the following expression is obtained,

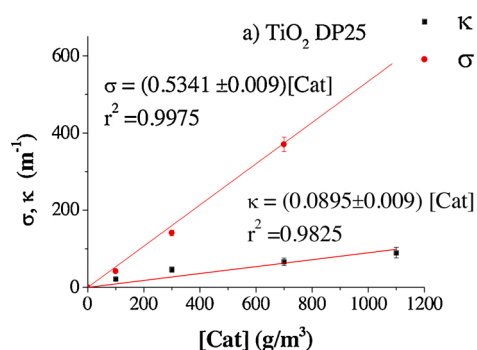
$$\frac{d[Pam]}{dt} = - \left(\frac{\left(-\frac{K_{r2}K_{r3}}{2k_{r1}} + \frac{K_{r2}K_{r3}}{2k_{r1}} \sqrt{\frac{4k_{r1}\Phi LVREA_{Cat} + 1}{K_{r2}K_{r3}}} \right)}{[Pam]} \right) [Pam] \quad (27a)$$

$$\frac{d[Pam]}{dt} = - \left(\frac{\alpha_3 (-1 + \sqrt{\alpha_4 LVREA_{Cat} + 1})}{[Pam]} \right) [Pam] \quad (Model\ 2a) \quad (27b)$$

This is Model 2a, where $\alpha_3 = K_{r2}K_{r3}/2k_{r1}$ and $\alpha_4 = 4k_{r1}\Phi/K_{r2}K_{r3}$ represent the kinetic coefficients of the model, which were evaluated and statistically verified based on the experimental data, adjusting them by a nonlinear regression.

Another model (model 2b) was established, considering once again, that the overall reaction is due to both, photolysis and photocatalysis. Therefore, to obtain model 2b, the kinetic constant of the photolytic process, $k_{photolysis}$, was added to Model 2a,

$$\frac{d[Pam]}{dt} = - \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 LVREA_{Cat} + 1})}{[Pam]} \right) [Pam] \quad (Model\ 2b) \quad (28)$$



where $LVREA_{Cat}$ was calculated assuming that only the catalyst absorbs radiation. Model 2b was also solved assuming that the reagent competes with the catalyst to absorb radiation, thus $LVREA_{Corr}$ is used instead of $LVREA_{Cat}$.

$$\frac{d[Pam]}{dt} = - \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 LVREA_{Corr} + 1})}{[Pam]} \right) [Pam] \quad (Model\ 2c) \quad (29)$$

3. Results and discussion

Fig. 2 shows the profiles of the negative logarithm of the transmittance at different wavelengths for: a) catalyst TiO₂ DP25 and b) Paracetamol solutions. It can be observed that Pam absorbs radiation at 254 nm (Fig. 2b), even at low Pam concentration. Hence, at this wavelength it cannot be assumed that the reagent is transparent to radiation. This phenomenon might be evident with other molecules by their concentration causing a change in the kinetic constant. In the system under study, this wavelength (254 nm) actually characterizes the radiation emitted by the lamp placed inside the reactor.

Table 2

Specific extinction, absorption and scattering coefficients and phase function coefficient.

	*β (m ⁻¹)	*κ (m ⁻¹)	*σ (m ⁻¹)	g
TiO ₂ DP25	0.6236	0.0895	0.5341	0.01
Paracetamol	5.0239	0.5080	4.3638	0.00

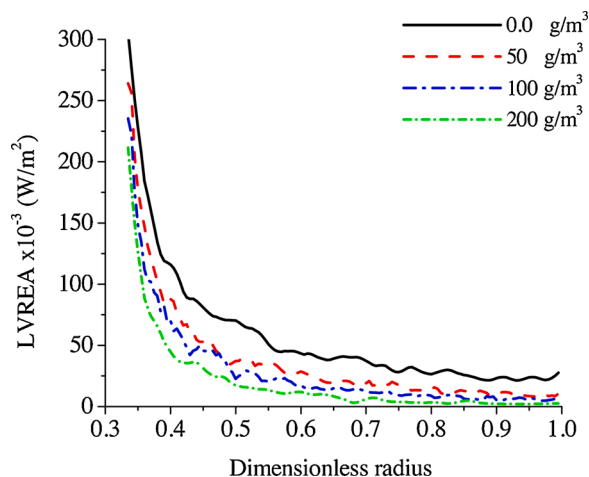


Fig. 5. Effect of reagent concentration on LVREA radial profiles. [Cat] = 100 g/m³.

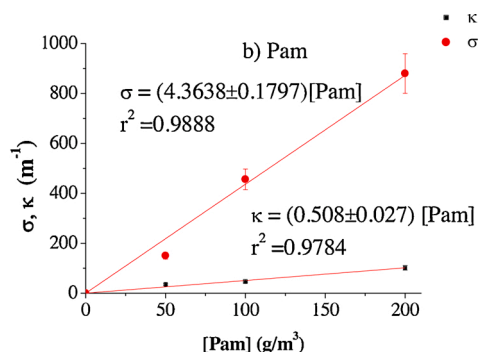


Fig. 4. Specific absorption (κ) and scattering coefficients (σ) as a function of concentration for a) TiO₂ DP25 Catalyst and b) Paracetamol.

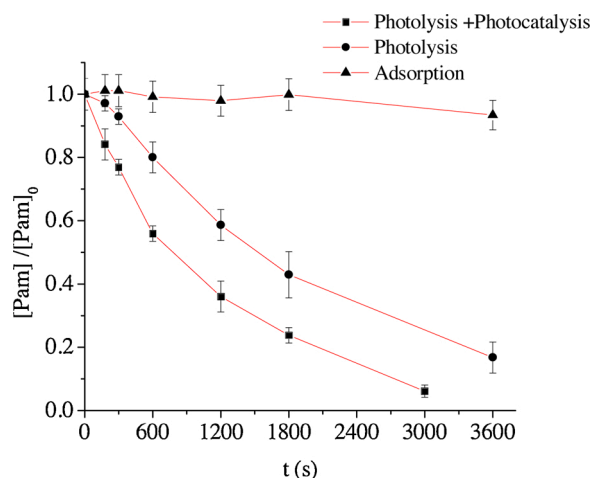


Fig. 6. Paracetamol removal by adsorption, photolysis and photocatalysis. $[Pam]_0 = 20 \text{ g/m}^3$.

3.1. Calculation of optical properties of the catalyst

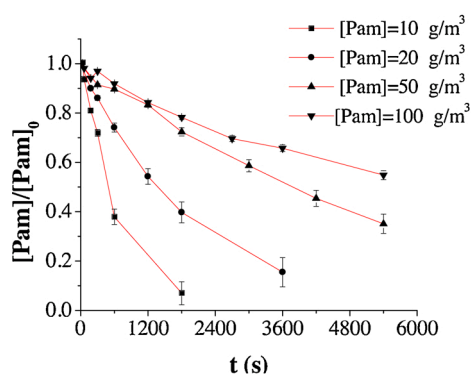
3.1.1. Specific extinction coefficient (β)

Specific extinction coefficients at 254 nm were obtained by plotting $-\log(T)/l$ against concentration (Fig. 3). In Fig. 3, the slope of each line represents the specific extinction coefficient.

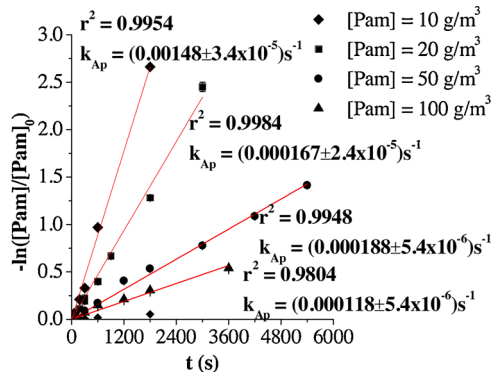
Optical coefficients were obtained by comparing the experimental data against incident radiation measurements data calculated by the MC method, using the method of Nelder - Mead for parameter optimization. There are in Fig. 4, the optical coefficients plotted versus concentration to obtain the specific coefficients for both, TiO_2 DP25 catalyst and Pam. The optical specific coefficients are summarized in Table 2.

3.2. Simulation of radiant field by Monte Carlo Method

Fig. 5 shows the radial profile of LVREA computationally obtained at the middle of reactor length. The continuous line represents the LVREA when radiation is considered only absorbed by the catalyst. The dash lines represent the LVREA when Pam is in solution. It can be observed that an increase in Pam concentration diminishes the LVREA values. This is due to a competition between the catalyst and the reagent for photons at the employed wavelength. This was taken into account in Eq. 29 by using the $\text{LVREA}_{\text{corr}}$ instead of the $\text{LVREA}_{\text{cat}}$. It is worth keeping in mind that the latter does not consider the absorption of photons by Pam.



a



b

Fig. 7. a) Effect of initial Paracetamol concentration on normalized concentration profiles under UV light only; b) First order kinetics test by integral method.

3.3. Modeling of paracetamol photocatalytic degradation

3.3.1. Adsorption of Paracetamol on the catalyst surface

To test the ability of the catalyst to adsorb the Pam molecule, a solution of Pam was prepared with an initial concentration of 20 g/m^3 . Separately, the catalyst was added until a concentration of 200 g/m^3 was obtained. The Pam solution with the catalyst was kept in the dark under continuous stirring for 30 min. Pam concentration in solution was determined prior catalyst addition, $[Pam]_0$, and after being in contact with the catalyst, $[Pam]_{\text{End}}$. The adsorption percentage was determined by means of,

$$\% \text{Adsorption} = \frac{[Pam]_0 - [Pam]_{\text{End}}}{[Pam]_0} \times 100 \quad (30)$$

Fig. 6 shows the $[Pam]$ profiles under the following conditions: a) Pam solution with catalyst in darkness conditions (adsorption), b) Pam solution under UV radiation without catalyst (photolysis), and c) Pam solution with catalyst under UV radiation (photocatalysis). These profiles were experimentally obtained. Due to low adsorption of Pam on the TiO_2 surface when the lamp is off, the removal of Pam by adsorption is considered negligible, thus this phenomenon is not taken into account in the proposed models describing the kinetics of Pam oxidation. When the light is on, then the hole-electron pairs are generated on the photocatalyst surface and under these circumstances, Pam chemisorption and consequent oxidation on the photocatalyst surface (direct oxidation) cannot be ruled out.

3.3.2. Kinetic equation for degradation by photolysis

The effect of initial Pam concentration on Pam normalized concentration profiles under photolysis is shown in Fig. 7a. After applying the integral method (Fig. 7b), it can be concluded that the Pam degradation rate obeys a pseudo-first order kinetics and the estimated parameters along with correlation coefficients are summarized in Table 3.

It can be observed in Table 3 that the apparent constant, $k_{\text{photolysis}}$, decreases when $[Pam]_0$ increases. This can be attributed to the following phenomena: a) when the initial Pam concentration increases, the

Table 3

Apparent constant of pseudo-first reaction order of photolytic degradation of Paracetamol.

$[Pam]_0$ (g/m^3)	$k_{\text{photolysis}}$ (s^{-1})	r^2
10	0.001480	0.9954
20	0.000167	0.9984
50	0.000188	0.9948
100	0.000118	0.9804

Table 4
Estimated parameters for photolysis model.

Parameter	Estimation	Confidence intervals	p-Value	r^2
α_1	1.329×10^{-06}	$\{1.403 \times 10^{-07}, 2.516 \times 10^{-06}\}$	0.037730	0.9984
α_2	2.194×10^{-05}	$\{1.529 \times 10^{-05}, 3.029 \times 10^{-05}\}$	0.002375	

extinction coefficients increases too (see Fig. 3) and the travel length of the photon is reduced, therefore the effective irradiated volume decreases and this reduces reaction rate; and b) indirect photolysis occurs when radiation is absorbed by other species of the reaction medium such as dissolved oxygen and carbonates; therefore, increasing the initial concentration of reagent promotes competition for the absorption of radiation between these species and the Pam molecule, decreasing the specific reaction rate [20]. The developed model is described by Eq. (12), where

$$I_0(\alpha_1 + \alpha_2 10^{-\beta[Pam]_0 l}) = k_{photolysis} \quad (31)$$

The conditions employed for the degradation of Paracetamol by photolysis are:

- Intensity of radiation emitted by the lamp: $I_0 = 166 \text{ W/m}^2$, (Experimentally determined by radiometric measurements)
- Thickness of the annulus of the reaction zone, $l = 0.01 \text{ m}$
- Paracetamol extinction coefficient $\beta = 5.0239 \frac{\text{m}^2}{\text{g}}$ (Fig. 3)

Thus, the expression that relates the pseudo first order constant with the initial reagent concentration is,

$$166 \times (\alpha_1 + \alpha_2 10^{-5.0239[Pam]_0 0.01}) = k_{photolysis} \quad (32)$$

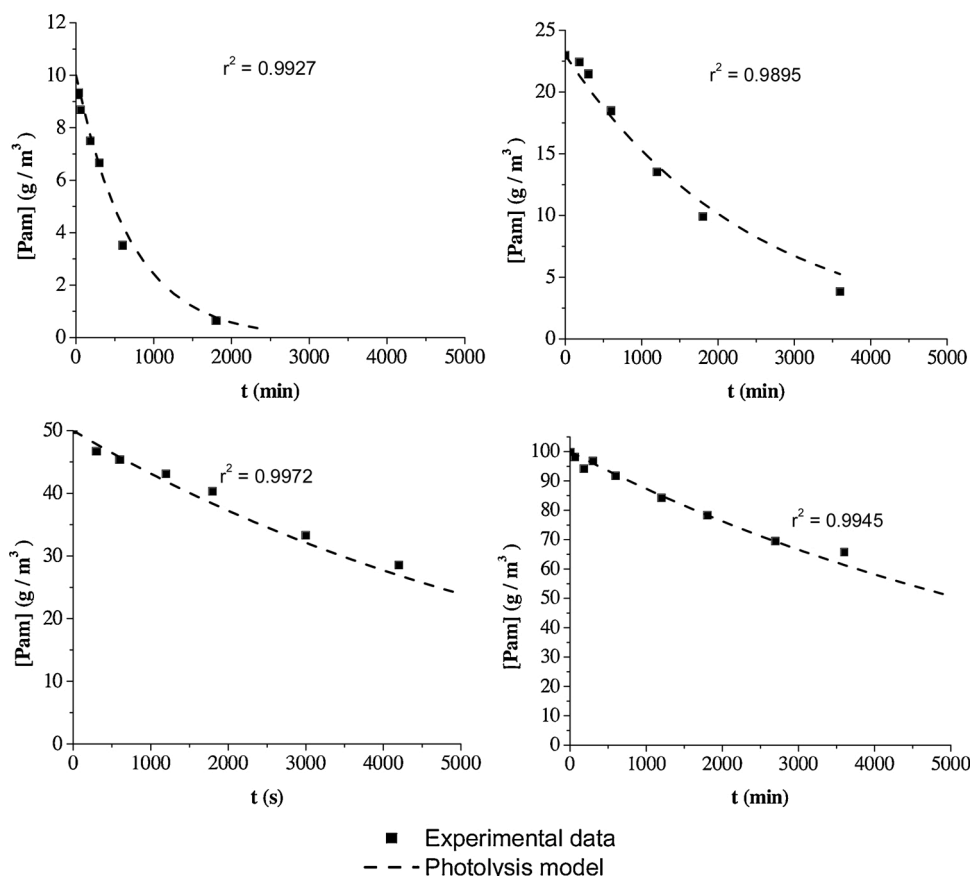


Fig. 8. Comparison of the experimental degradation profiles (marker points) with the photolysis model (dash line) at different initial Pam concentration.

Taking into account each value of $[Pam]_0$ in Table 3 and its corresponding $k_{photolysis}$, the coefficients of Eq. (32) were obtained by nonlinear regression method. The results are listed in Table 4.

If the rejection criterion is the comparison between the observed significance (p -Value) and predefined significance (95 % confidence), then it can be observed that the kinetic coefficients of the photolytic model are significant since p -Values are lower than the predefined significance level.

Fig. 8 shows the comparison of the experimental data of the degradation by photolysis of Pam against the results from the proposed model. It is observed at all cases that the correlation coefficient is high, which

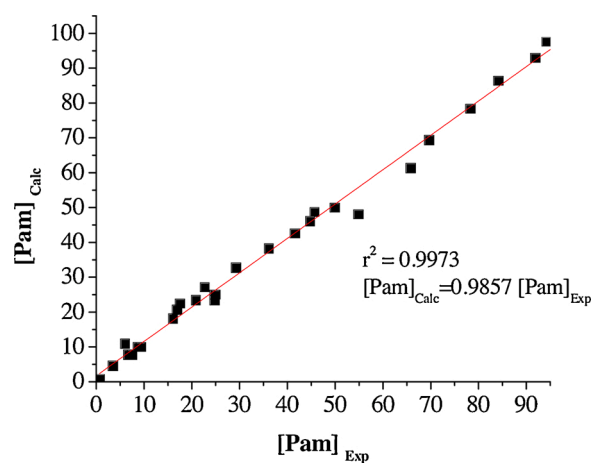


Fig. 9. Parity plot of calculated and experimental data of photolytic degradation of Paracetamol.

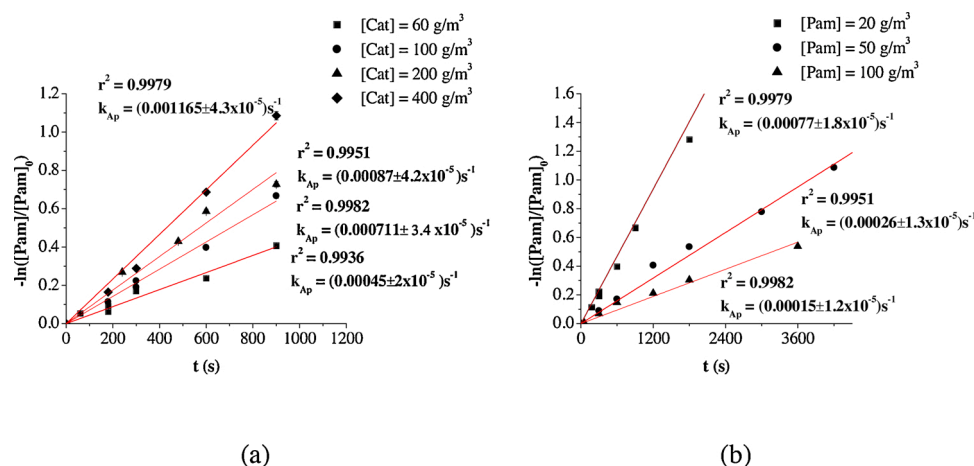


Fig. 10. a) Effect of catalyst concentration on apparent kinetic constant. $[Pam]_0 = 20 \text{ g/m}^3$; b) Effect of the initial Paracetamol concentration on apparent kinetic constant. $[Cat] = 100 \text{ g/m}^3$ of TiO_2 DP25 as a catalyst.

Table 5

Apparent constants and LVREA of photocatalytic degradation of Paracetamol.

$[Pam]_0$ (g/m^3)	$[Cat]$ (g/m^3)	LVREA _{CAT} (W/m^2)	LVREA _{CORR} (W/m^2)	k_{Ap} (s^{-1})	r^2
10	65.0	27,127	23,523	0.001875	0.9897
20.0	65.0	27,127	21,220	0.000445	0.9905
20.0	100.0	36,112	29,484	0.000711	0.9659
50.0	100.0	36,112	23,773	0.000265	0.9929
100.0	100.0	36,112	18,564	0.000165	0.9916
20.0	200.0	58,220	49,726	0.000876	0.9914
20.0	400.0	92,900	82,997	0.001148	0.9712

indicates that there is an excellent agreement between experimental and predicted data. At this point, it is worth pointing out that when indirect photolysis is not taken into account in the model, i.e. only direct photolysis given by Eq. 8 is considered in the model, then the fitting is not as good as when both types of photolysis are included.

Fig. 9 shows the parity plot of the experimental data of Pam degradation by photolysis against data calculated with the proposed photolysis model (Eq. 31). It is observed that the experimental and calculated

Table 6

Kinetic models for degradation of Paracetamol and the expression for apparent pseudo first order kinetic constants.

Model	Considerations	Mathematical expression
Model 1a Power Law	Photocatalysis	$\frac{-d[Pam]}{dt} = k_r [Pam] [LVREA]_{Cat}^n$ $k_{Ap} = k_r [LVREA]_{Cat}^n$
Model 1b Power Law	Photocatalysis and photolysis	$\frac{-d[Pam]}{dt} = k_{photolysis} [Pam] + k_r [Pam] [LVREA]_{Cat}^n$ $k_{Ap} = k_{photolysis} + k_r [LVREA]_{Cat}^n$
Model 1c Power Law	Photocatalysis and photolysis LVREA corrected	$\frac{-d[Pam]}{dt} = k_{for} [Pam] + k_r [Pam] [LVREA]_{Corr}^n$ $k_{Ap} = k_{photolysis} + k_r [LVREA]_{Corr}^n$
Model 2a Mechanistic kinetic equation	Photocatalysis	$\frac{d[Pam]}{dt} = - \left(\frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Cat} + 1})}{[Pam]_0} \right) [Pam]$ $k_{Ap} = \left(\frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Cat} + 1})}{[Pam]_0} \right)$
Model 2b Mechanistic kinetic equation	Photocatalysis and photolysis	$\frac{d[Pam]}{dt} = - \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Cat} + 1})}{[Pam]_0} \right) [Pam]$ $k_{Ap} = \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Cat} + 1})}{[Pam]_0} \right)$
Model 2c Mechanistic kinetic equation	Photocatalysis and photolysis LVREA corrected	$\frac{d[Pam]}{dt} = - \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Corr} + 1})}{[Pam]_0} \right) [Pam]$ $k_{Ap} = \left(k_{photolysis} + \frac{\alpha_3 (-1 + \sqrt{\alpha_4 f_{vol} LVREA_{Corr} + 1})}{[Pam]_0} \right)$

points fit properly to the 45° line, i.e. $[Pam]_{Calc} = [Pam]_{Exp}$, indicating that the calculated data show an excellent agreement with experimental data.

3.3.3. Kinetic equation for the photocatalytic degradation of Paracetamol

Fig. 10a shows the test of the integral method of analysis for the photocatalytic degradation of Pam with an initial concentration of reagent $[Pam]_0 = 20 \text{ g/m}^3$. It can be seen that Pam degradation rate adjusts to a pseudo-first order kinetics. It is also noted that increasing the catalyst concentration increases reaction rate; however, at high catalyst concentrations the slope tends to remain constant, which indicates that after a certain catalyst concentration the reaction rate does not significantly increase anymore. Fig. 10b shows the effect of the initial concentration of reagent on the photocatalytic degradation rate using a catalyst concentration of 100 g/m^3 . It is observed that the increase in the $[Pam]_0$ decreases reaction rate. This can be ascribed to the fact that the number of active sites on the catalyst surface at a given catalyst concentration is constant and increasing the reagent concentration increases the competition for adsorption at the active sites, causing lower reaction rates. It can also be due to Pam also absorbing radiation, thus an

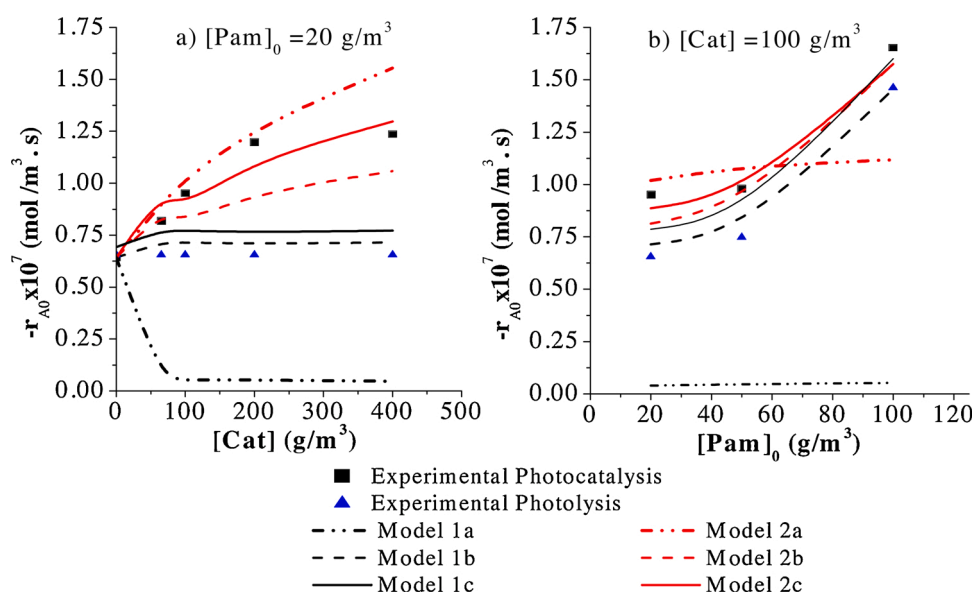


Fig. 11. Comparison of experimental initial reaction rates with those obtained by photolytic and photocatalytic models: a) with [Pam] constant; b) with [Cat] constant.

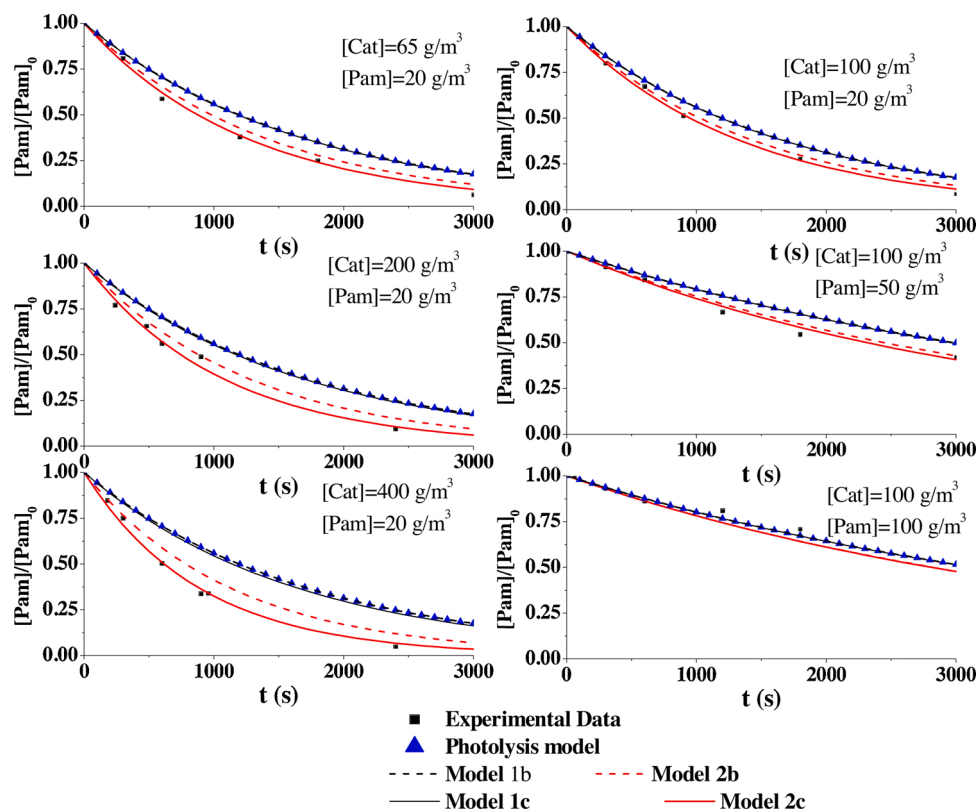


Fig. 12. Comparison of experimental normalized Paracetamol concentration with profiles predicted by photolysis and photocatalytic models, at different catalyst concentration and initial Paracetamol concentration.

increase in the reagent concentration decreases apparent optical thickness, which decreases the amount of effectively irradiated catalyst. The pseudo-first order constants obtained from Fig. 10 are listed in Table 5 together with the LVREA values considering that only the catalyst absorbs radiation ($LVREA_{cat}$) and LVREA values obtained considering a radiation absorption competition between catalyst and Paracetamol ($LVREA_{corr}$). To obtain the values of $LVREA$, the MC method was applied for each catalyst concentration used in the optical coefficients

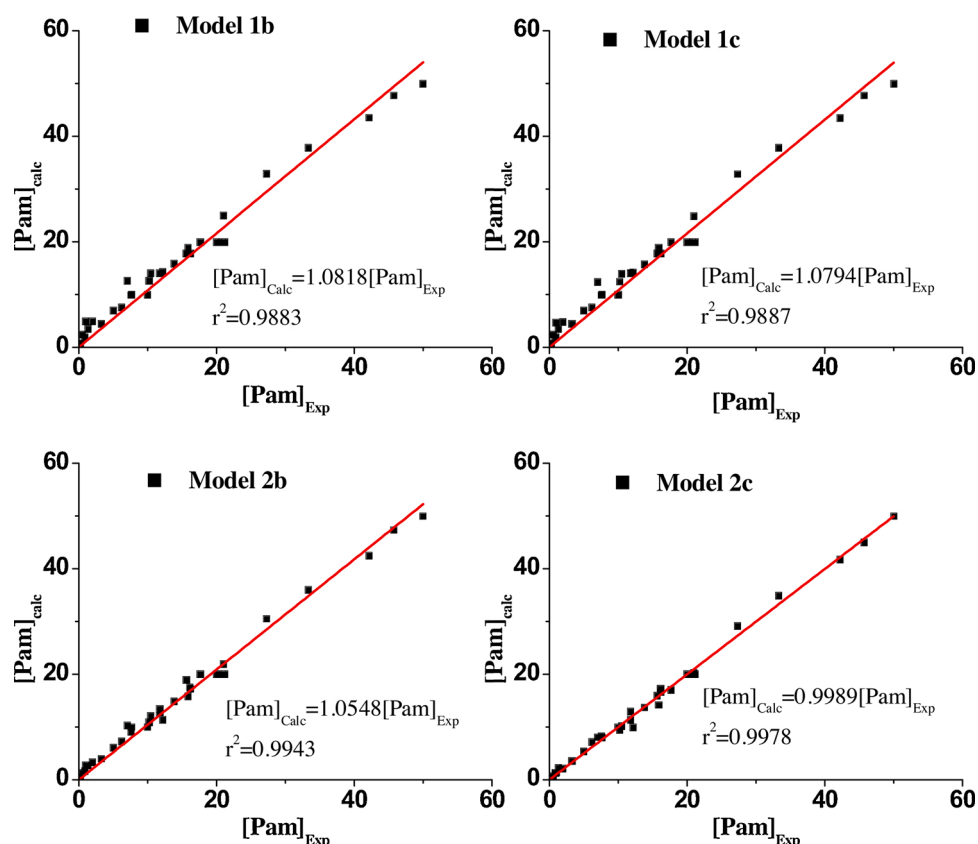
calculation.

The kinetic models considered in this study are summarized in Table 6 along with the expression for apparent pseudo first order kinetic constant for each model. The expression for $k_{photolysis}$ is Eq. 32 with their corresponding constants listed in Table 4. Taking into account each value of $[Pam]_0$ and $[Cat]$ in Tables 3 and 5, with its corresponding k_{Ap} and LVREA values.

Table 7

Kinetic constants and regression statistics for tested models.

Model	Parameter	Value	Standard Error	Confidence Interval	P-Value	r^2
Model 1a	k_r	0.001137	0.00426	-0.00929, 0.01156	0.7986	0.69
	n	-0.037207	0.363391	-0.92630, 0.85197	0.9217	
Model 1b	k_r	2.486×10^{-13}	4.414×10^{-13}	-7.621×10^{-12} , 8.041×10^{-12}	0.9467	0.93
	n	1.8850	1.2107339	-0.907, 4.675	0.1582	
Model 1c	k_r	3.323×10^{-11}	2.5764×10^{-10}	-5.531×10^{-10} , 6.182×10^{-10}	0.9000	0.94
	n	1.481	0.6895	-0.0109, 3.0789	0.0640	
Model 2a	α_3	7.955×10^{-10}	1.032×10^{-10}	5.429×10^{-10} , 1.048×10^{-9}	0.0003	0.90
	α_4	1.252×10^{10}	3.279×10^{-20}	1.252×10^{10} , 1.252×10^{10}	0.0000	
Model 2b	α_3	46.917	1.187×10^{-19}	48.917, 48.917	0.0000	0.96
	α_4	4.942×10^{-9}	1.126×10^{-9}	2.287×10^{-9} , 7.621×10^{-9}	0.0030	
Model 2c	α_3	56.217	7.784×10^{-20}	56.217, 56.217	0.0000	0.98
	α_4	4.952×10^{-9}	8.737×10^{-10}	2.938×10^{-9} , 6.967×10^{-9}	0.0004	

**Fig. 13.** Parity plots of calculated data and experimental data of photocatalytic degradation of Paracetamol.

3.3.4. Validation of the photocatalytic model

The photolysis and photocatalysis models were algorithmically solved and coupled with MC method results that describe the radiation field.

Fig. 11 shows the initial reaction rate obtained with experimental data as a function of catalyst loading (Fig. 11a) and initial paracetamol concentration (Fig. 11b). There are plot also in Fig. 11 the predicted initial reaction rates by all assessed models. According to Fig. 11a, the initial reaction rate tends to increase with catalyst loading up to 200 g/m^3 where a plateau is reached. This trend is better emulated when the mechanistic kinetic models (models 2) are applied than when the models based on power-law kinetics (models 1) are applied. Nevertheless, the model that best fits the initial Pam reaction rate is model 2c and this supports the importance of including the competition for radiation absorption by the organic molecule. Model 2a (only catalyst absorbs

radiation and there is not photolysis) predicts higher reaction rates than the experimental ones and Model 2b predicts lower reaction rates than experimental ones. Fig. 11b, shows the effect of initial Pam concentration on initial Pam oxidation rate at a constant catalyst concentration $[\text{Cat}] = 100 \text{ g/m}^3$. It can be seen that at any time, the initial reaction rate with the catalyst is higher than with photolysis only. Nevertheless, it is worth noticing that the gap among these values becomes narrower as initial Pam concentration increases. This fact also justifies the inclusion of the radiation absorption by Pam since is not negligible and thus affects the radiant field. This explains the good fitting of model 2c in both cases, when the catalyst loading and the initial Pam concentration change.

Fig. 12 shows the comparison of normalized Pam experimental concentration profiles with those predicted by the proposed models, as a function of catalyst loading, initial Pam concentration and time. Table 7

summarizes the kinetic constants (obtained by a non-linear regression method) and the regression statistics for each model presented in Table 6. According to Table 7, model 1a exhibits a rather low correlation coefficient. By contrasting this statistic parameter with the ones obtained for the other models, the importance of including the photolysis term can be established. Model 2a also exhibits a low correlation coefficient and this is the reason for not being included in Fig. 12. It can also be observed that Model 2c with $LVREA_{CORR}$ has the kinetic coefficients with the most narrow confidence intervals and the observed significance (p -Value) is lower than the predefined significance (95 % de confidence), then it can be concluded that the kinetic coefficients estimated for photocatalytic Model 2c are significant. Indeed, it is observed in Fig. 12 that the data predicted by Model 2c (LVREA corrected) are in good agreement with experimental data. Model 2c (LVREA corrected). Although model 2b also presents a reasonable correlation coefficient and concordance with experimental data (Fig. 12), this model was discarded due to the poor prediction of initial reaction rates plotted in Fig. 11.

Fig. 13 shows the parity diagrams of the experimental data of photocatalytic degradation of Pam versus the data obtained by the proposed Models studied in this paper. It can be seen that data obtained by the simulation of Model 2 with $LVREA_{CORR}$ (Model 2c) which considers that there is a competition between the catalyst and the reagent, correctly fits the line $[Pam]_{Calc}=[Pam]_{Exp}$, and its Pearson correlation is the closest to 1, which indicates that the proposed model is adequate to estimate the concentration of Pam in the photocatalytic degradation using the catalyst TiO_2 DP25.

4. Conclusions

The kinetic modelling of Paracetamol oxidation was carried out. Six kinetic models were assessed, three of them based on power law kinetics and the other three based on a mechanistic approach. It was concluded that not taking into account Paracetamol photolysis and the effect of Paracetamol concentration on LVREA in the proposed model, leads to a rather poor fitting ($r^2 = 0.69$). It can also be concluded that the model that best represents the experimental data ($r^2 = 0.98$) is the one that was obtained from a mechanistic point of view and that incorporates the observed competition between catalyst and the paracetamol by correcting the LVREA and including a term accounting for photolysis contribution. For best results, the photolytic term should include both, direct and indirect photolysis. The resulting model allows predicting the effect on Paracetamol degradation of catalyst concentration, the initial reagent concentration, the intensity of emitted radiation and thickness of the annulus of the reaction space.

It was also concluded that an increase in paracetamol concentration leads to a decrease in LVREA due to the radiation absorption by the organic molecule and this explains why the kinetic constant decreases when paracetamol concentration increases. This effect is taken into account by incorporating the $LVREA_{CORR}$ in the kinetic model.

Author statement

Dr. O. Alvarado-Rolon performed the experiments, data collection and the writing of the initial draft. Dr. Jorge Ramírez conducted the chemical analysis. Dr. Jorge Orozco and Dr. Jose A. Hernandez-Servin contributed with the conceptualization and formal analysis. Dr. Reyna Natividad and Dr Armando Ramírez contributed with the funding acquisition, project administration, supervision, visualization, review and editing of the initial draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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