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This is an **author produced version** of a paper published in:

Journal of Environmental Chemical Engineering 7.5 (2019): 103406

DOI: <https://doi.org/10.1016/j.jece.2019.103406>

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TiO₂-rGO PHOTOCATALYTIC DEGRADATION OF AN EMERGING POLLUTANT: KINETIC MODELLING AND DETERMINATION OF INTRINSIC KINETIC PARAMETERS

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ABSTRACT

An intrinsic kinetic model, derived from a suggested reaction photo-mechanism and with an explicit dependence on the local volumetric rate of photon absorption (LVRPA), was developed to simulate the photocatalytic degradation of clofibric acid and the main reaction intermediates, with a new titania-reduced graphene oxide nanocomposite (TiO₂-rGO). The proposed reaction mechanism takes into account that graphene behaves as an electron acceptor and, therefore, this effect was included in the derivation of the reaction rate expressions and in the parameters estimation of the kinetic model. The photodegradation of clofibric acid was performed in a slurry photoreactor under different irradiation levels and using several loadings of a TiO₂-rGO nanocomposite, prepared by hydrothermal method with a 0.5 wt. % of GO. Absorbed radiation profiles inside the photoreactor were obtained by solving the radiation model with the Monte Carlo method. A photocatalyst loading of 100 mg·L⁻¹ gave place to the best photodegradation results. Mass balances were proposed for the main pollutant and their main detected intermediates: p-benzoquinone and 4-chlorophenol. The intrinsic kinetic parameters were obtained for the complete (6-parameters) and simplified (5-parameters) models by comparing the experimental and the theoretical concentration values of all the organic compounds detected. The model proved to be able to predict with good accuracy the concentration evolution of clofibric acid, 4-chlorophenol and p-benzoquinone under several photocatalyst concentrations and irradiation levels. Finally, a very good correlation between calculated and experimental values of clofibric acid concentration was obtained with root-mean-square errors below 11%.

Keywords: photocatalysis, TiO₂-rGO, kinetic model, LVRPA, Clofibric acid

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1. INTRODUCTION

Heterogeneous photocatalysis is considered a green and sustainable technology; thus in the last decades a lot of research has been focused on gaining knowledge and improving photocatalytic processes and reactors [1-5]. However, to be able to optimize the design and scale-up photoreactors, it is strictly necessary to develop full predictive models. In the case of photocatalytic reactors, mass balances and momentum balances must be solved. Since photocatalytic processes are initiated by the absorption of sufficiently energetic photons by a semiconductor, kinetic equations with an explicit dependency on local radiation absorption must be introduced to solve the mass balances of the main reacting species [6-15].

Great effort has been made to develop radiation models and mathematical tools to obtain the local photon absorption rates inside reactors with different geometries [11, 16-19]. The most popular methods are the discrete ordinate method (DOM) [9-11, 20], the Monte Carlo method (MC) [10, 15-17, 21, 22] and the “two-flux” or “six-flux” radiation models (TFM and SFM, respectively) [8, 18, 23, 24]. The MC method is widely applied because of its simplicity, especially when applied to reactors with complex geometries and configurations. Nevertheless, other methods, such as the method of lines or the control curve method, can be found in the literature [25, 26]. Once the local photon absorption rates are known, intrinsic kinetic parameters of the kinetic equations can be determined by comparing theoretical data obtained from the resolution of the mass balances with experimental data [7-9]. Intrinsic kinetic parameters obtained following this procedure are independent of the hydrodynamic and irradiation conditions and reactor geometry [18, 27]. Hence, they can be employed to reproduce the photodegradation of pollutants in different photoreactors. In addition, intrinsic kinetic parameters are useful to analyze the photocatalytic benefits achieved by modifying TiO_2 , for example, by the addition of metal oxides [25] or silver [24], or the immobilization of TiO_2 on different supports, such as silica particles [7].

In recent years, the addition of graphene and reduced graphene oxide (rGO) to TiO_2 has attracted a lot of attention because of its excellent properties, such as good optical transmittance, chemical stability, large specific surface area and high electrical conductivity [28-30]. Several papers can be found in the literature on the kinetics of the photocatalytic degradation of a wide variety of compounds using TiO_2 -rGO. However, these contributions have proposed Langmuir–Hinshelwood and first-order kinetic expressions to represent the reaction rate, in which the model parameters depend on experimental conditions (radiation flux, catalyst concentration, reactor configuration, etc.) [31-34].

The aim of the present work is to simulate the photocatalytic degradation of a pharmaceutical in a slurry reactor using TiO_2 -rGO as catalyst. Clofibric acid (CA) was the pharmaceutical chosen as model pollutant. Intrinsic kinetic data of CA photocatalytic degradation in a slurry reactor have been published previously by Manassero and coauthors, 2015, [15] but

employing bare TiO_2 as catalyst. Thus, the reaction mechanism that they have proposed does not take into account the effect of graphene as electron acceptor. Therefore, the reaction rate expressions and the corresponding kinetic parameters obtained in the aforementioned paper will not be useful to properly represent the degradation of CA by using this new TiO_2 -rGO nanocomposite. To the best of our knowledge, no intrinsic kinetic data to simulate CA degradation in a slurry reactor with TiO_2 -rGO as catalyst has been proposed. This kinetic information is essential to optimize, design and scale-up photocatalytic reactors. The photodegradation of CA was performed under different irradiation levels and using several loadings of a TiO_2 -rGO photocatalyst prepared by a hydrothermal process. Radiation distribution inside the reactor was calculated by solving the radiation model using the Monte Carlo method. Mass balances were proposed and kinetic equations were derived according to a kinetic mechanism for CA photocatalytic degradation [35, 36]. Finally, the intrinsic kinetic model was applied to estimate the kinetic parameters and experimental values were compared with predicted results.

2. MATERIALS AND METHODS

2.1. Chemicals

All the chemicals used in this study were analytical grade and used without further purification. They are listed as follows: P25 Aeroxide® (Evonik Company) Graphene Oxide Water Dispersion (0.4 wt%, Graphenea), Clofibric acid (Aldrich, CA>97%), 4-chlorophenol (Aldrich, 4-CP>99%) and p-benzoquinone (Fluka, p-BQ>98%). Through the whole study ultrapure water was used.

2.2. TiO_2 -rGO preparation

P25-rGO 0.5% was synthesized hydrothermally according to the procedure described in our previous study [37].

2.3. Experimental set up and procedure

Photocatalytic runs were conducted in a cylindrical photoreactor of stainless steel. The inside walls of the photoreactor are made of Teflon and the photoreactor windows consisted of circular borosilicate glasses at each side of the reactor. Each glass window was irradiated by a set of four UV-A lamps with an emission peak at 355 nm. The reaction system where photoreactions were carried out and the experimental procedure are described in detailed in a previous study [37]. The dimensions of the reactor and the main characteristics of the lamps are presented in Table 1. Experimental conditions are summarized in Table 1 as well. When the experiments were carried out under different irradiation levels, attenuation filters were placed between the lamps and the reactor.

2.4. Analysis

Concentrations of CA, 4-CP and p-BQ identified during the photodegradation, were quantified by HPLC (a Waters HPLC equipped with a UV detector) and the detailed information about the analytical method was stated previously [37]. Samples were centrifuged and subsequently filtered by using 0.02 μm syringe filters (Anotop 25) prior to analysis.

3. RADIATION PROFILES INSIDE THE PHOTOREACTOR

To calculate the intrinsic reaction kinetics it is essential to obtain the local volumetric rate of photon absorption (LVRPA, $e^a(x)$) by solving the radiation transport equation (RTE) [9, 11]. To calculate LVRPA values it is necessary to know the spectral distribution of the incoming radiation, shown in Figure 1. Calculation of the radiation absorbed in the photoreactor demands the knowledge of the phase function, scattering (σ_λ) and absorption (κ_λ) coefficients of the photocatalytic medium; they were estimated in a previous study [37] and specific scattering (σ_λ) and absorption (κ_λ) coefficients of the P25-rGO 0.5% photocatalyst can be seen in Figure 1.

Given that the photoreactor featured ground glass plates, it was considered that the inlet radiation was diffuse. Therefore, assuming that the radiation was essentially attenuated along the longitudinal axis, a one-dimensional—one-directional model was considered to determine the LVRPA. Thus, the trajectory of the photon will be given by one spatial variable (x) and one angular variable (θ). The Monte Carlo method was applied to obtain the absorbed radiation distribution in the cylindrical photocatalytic reactor. This method consists in generating random numbers (R_i) between 0 and 1 to determine the likelihood of each event. To obtain the solution of the radiation model, the fate of 10^7 photons was evaluated for each wavelength. The spectral distribution of the inlet radiation was divided into eleven wavelengths and 0.0025 cm cells were considered to form the reactor length. The range of emission of the lamps was discretized in 11 wavelengths and the length of the reactor ($L_R=2.5$ cm) was divided into small cells ($\Delta x=0.0025$ cm). The steps followed in the Monte Carlo method are shown schematically in Figure 2 and are detailed hereafter:

- 1) Firstly, it is necessary to know the direction of the photons emitted by the lamp. As it was assumed that the incident radiation was diffuse, all the directions had the same probability [38]. Hence, the zenith angle was determined by :

$$\sin \theta = 2R_1 - 1 \quad (1)$$

- 2) The length travelled by the photon inside the photocatalytic system without interaction is given by:

$$l = -\frac{1}{\beta_\lambda} \ln(1 - R_2) \quad (2)$$

where β_λ ($\beta_\lambda = \sigma_\lambda + \kappa_\lambda$) is the spectral extinction coefficient of the reaction medium for a specific wavelength λ . After travelling a distance l , the new position is determined by:

$$x_{new} = x_{old} + e_x l \quad (3)$$

where x_{old} is the position of the photon in the previous iteration and e_x is $\cos\theta$.

- 3) Assuming the new position lies within the reactor volume, the photon is assumed to strike a catalyst particle, and it can be either absorbed or scattered. The probability of each event depends on the albedo coefficient (ω_λ), which is the ratio of scattering to extinction coefficients, $\omega_\lambda = \sigma_\lambda / \beta_\lambda$. So, if

$$1 - \omega_\lambda \geq R_3 \quad (4)$$

the photon is absorbed and it is stored in the corresponding cell. If the photon is scattered, the scattering angle is determined using the Henyey and Greenstein (HG) phase function [15, 16, 22, 39].

$$\cos\theta = \frac{1}{2g_\lambda} \left[1 + g_\lambda^2 - \left(\frac{1 - g_\lambda^2}{1 + g_\lambda(2R_4 - 1)} \right)^2 \right] \quad (5)$$

After establishing the new direction, the new length of flight and position are calculated following step 2.

- 4) Providing the new position lies outside the reactor volume, the photon is considered to reach the reactor windows, where it can be reflected or transmitted. If

$$\Gamma_{W,\lambda} > R_5 \quad (6)$$

where $\Gamma_{W,\lambda}$ represents the global window reflection coefficient, the photon is reflected and it returns to the reaction space. Otherwise, the photon leaves the system, the sequence is finished and a new photon is generated.

At last, the LVRPA corresponding to each cell can be obtained by:

$$e^a(x) = \sum_{\lambda=310 \text{ nm}}^{\lambda=420 \text{ nm}} \frac{q_{w,\lambda} n_{ph,\lambda,abs}(x)}{n_{ph,T} \Delta x} \quad (7)$$

where $q_{w,\lambda}$ is the inlet radiation flux of a wavelength λ , $n_{ph,\lambda,abs}(x)$ is the number of photons of a given wavelength absorbed in a cell of position x , $n_{ph,T}$ is the total number of photons considered in the simulation, and Δx is the length of the cell.

4. MASS BALANCES

To model the reaction and obtain the theoretical evolution of the pollutants concentrations, the mass balances of each organic compound were proposed. The conditions assumed to solve these mass balances were: (1) differential conversion per pass in the photoreactor, (2)

the reaction medium is perfectly mixed, (3), reaction occurs at the solid-liquid interface, (4) photolysis is insignificant, and (5) mass transfer limitations can be neglected.

Regarding the reaction scheme considered by Manassero and coauthors [15], CA can be photodegraded by HO• either to produce 4-CP or p-BQ. Then, 4-CP can be further oxidized to generate more p-BQ or other organic intermediates (X_i) that will eventually be turned into HCl, CO₂ and H₂O. In the same way as 4-CP, p-BQ can be photodegraded to generate other organic intermediates (X_j) that will be further oxidized until they are mineralized. Therefore, the following mass balances and their respective initial conditions are proposed:

$$\varepsilon_L \frac{dC_{CA}(t)}{dt} \Big|_{Tk} = -\frac{V_R}{V_T} a_v \{ \langle r_{CA,1}(x,t) \rangle_{A_R} + \langle r_{CA,2}(x,t) \rangle_{A_R} \} \quad (8)$$

$$C_{CA}(t = 0) = C_{CA0}$$

$$\varepsilon_L \frac{dC_{4-CP}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \{ \langle r_{CA,1}(x,t) \rangle_{A_R} - \langle r_{4-CP,1}(x,t) \rangle_{A_R} - \langle r_{4-CP,2}(x,t) \rangle_{A_R} \} \quad (9)$$

$$C_{4-CP}(t = 0) = 0$$

$$\varepsilon_L \frac{dC_{p-BQ}(t)}{dt} \Big|_{Tk} = \frac{V_R}{V_T} a_v \{ \langle r_{CA,2}(x,t) \rangle_{A_R} + \langle r_{4-CP,2}(x,t) \rangle_{A_R} - \langle r_{p-BQ}(x,t) \rangle_{A_R} \} \quad (10)$$

$$C_{p-BQ}(t = 0) = 0$$

Where $r_{CA,1}$ represents the photodegradation rate of clofibric acid to form 4-chlorophenol, $r_{CA,2}$ represents the reaction rate of clofibric acid to produce p-benzoquinone, $r_{4-CP,1}$ is the rate of 4-chlorophenol that is converted into organic intermediates, $r_{4-CP,2}$ is the photodegradation rate to produce p-benzoquinone and r_{p-BQ} is the photodegradation rate of p-benzoquinone. A_R is the reaction area and all the reaction rates are mean surface reaction rates. The catalyst interfacial area per unit of suspension volume is a_v , $a_v = S_g C_{cat}$, where S_g represents the catalyst specific surface area and C_{cat} is the mass catalyst loading. The liquid hold-up, ε_L , was assumed to be 1. C_i indicates the molar concentration of the organic compound; V_R is the reactor volume, V_T is the total volume of the experimental set-up where photoreactions were carried out and Tk refers to the storage tank.

5. KINETIC MODEL

Once the mass balances were proposed, the kinetic equations were deduced using the reaction mechanism shown in Table 2 which was based on previous studies [35, 36, 38]. The following steps were considered in the reaction scheme: (1) activation of the photocatalyst by

absorbing a photon with enough energy to generate an electron-hole pair, (2) adsorption of the different species on the photocatalyst surface, (3) recombination of the formed electron and hole, (4) electron transfer from TiO₂ to rGO, (5) reduction of oxygen by photogenerated electrons, (6) hole trapping by adsorbed water or hydroxyl ions, and (7) hydroxyl radical attack (HO•) to react with the different organic compounds, finally generating organic intermediates from 4-CP (X_i) and p-BQ photodegradation (X_j), or with inorganic species (Y) that can compete for hydroxyl radicals. It is important to point out that the production of hydroxyl radicals from photogenerated electrons was considered since it was reported that rGO can act as electron acceptor, favouring the transference of conduction band electrons and reduction of adsorbed oxygen to form superoxide radicals (O₂^{•-}) [29, 40-42]. These radicals can further react to finally obtain hydroxyl radicals. In order to deduce the kinetic equations several assumptions were made: photocatalytic reaction takes place among adsorbed species on the photocatalyst surface and a dynamic equilibrium between adsorbed and bulk species was considered; oxygen is adsorbed at different active sites than the organic compounds; since clofibric acid and its intermediates are adsorbed at the same type of sites, competitive adsorption was considered.

A complete procedure to derive the equations of the kinetic model can be found in the Appendix. Thus, the following final expressions were obtained:

$$r_{CA}(x, t) = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA}(x, t)}{1 + \alpha_3 C_{CA}(x, t) + \alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \quad (11)$$

$$r_{4-CP}(x, t) = \frac{(\alpha_{4,1} + \alpha_{4,2})C_{4-CP}(x, t)}{1 + \alpha_3 C_{CA}(x, t) + \alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \quad (12)$$

$$r_{p-BQ}(x, t) = \frac{\alpha_5 C_{p-BQ}(x, t)}{1 + \alpha_3 C_{CA}(x, t) + \alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a(x)}{S_g C_{cat}}} \right\} \quad (13)$$

where α_i are the intrinsic kinetic parameters.

The model agrees with the dependence of photoreaction rate on radiation absorbed experimentally observed in previous research [1, 43]. When the photoreactor is subjected to low volumetric rates of photon absorption $\frac{\alpha_1 e^a}{S_{BET} C_{cat}} \ll 1$, the square root can be approximated by the first term of the Taylor series expansion ($\sqrt{1+x} = 1 + x/2$), which leads to a linear dependence of the photoreaction rate on the LVRPA. On the other hand, when the volumetric rate of photon absorption is high $\frac{\alpha_1 e^a}{S_{BET} C_{cat}} \gg 1$, which involves a square-root dependence of the photodegradation reaction rate on the radiation absorption profiles (LVRPA) as it is shown below.

Therefore, thanks to the electron transfer from TiO_2 to rGO, recombination of charge carriers might be decreased, and therefore more holes could be available to oxidize water [40, 44]. Furthermore, the presence of rGO facilitates charge transfer to electron acceptors, which increases oxygen reduction [42].

6. RESULTS AND DISCUSSION

6.1. LVRPA profiles

LVRPA profiles along the longitudinal axis of the photoreactor using different catalyst loadings of P25-rGO 0.5% are depicted in Figure 3. Regardless of the photocatalyst concentration, it could be clearly observed that no radiation was absorbed by the suspension at the center of the photoreactor. However, a rise of the photocatalyst loading led to a sharp increase of the radiation absorbed near the reactor windows. Thus, attenuation of light became more significant when using higher concentration of the nanocomposite.

The absorbed radiation profiles obtained for different irradiation levels are shown in Figure 4. These LVRPA profiles were calculated using the optimum concentration of P25-rGO 0.5% ($100 \text{ mg}\cdot\text{L}^{-1}$) and different attenuation filters that allowed the pass of 62% and 30% of the incoming radiation. This photocatalyst loading was chosen because of the higher activity achieved compared to other photocatalyst loadings and other initial GO/ TiO_2 weight ratios analyzed previously [37]. It could be noted that the lower the radiation level, the lower the radiation absorbed near the window.

6.2. Mass balances and kinetic model

A non-linear regression method based on the Levenberg–Marquardt algorithm was applied to estimate the kinetic parameters by comparing experimental values of clofibric acid, 4-chlorophenol and p-benzoquinone with those values obtained from the mass balances averaged over the whole reactor volume. Since values of the term $[\alpha_3 C_{CA}(x, t) +$

$\alpha'_3 C_{4-CP}(x, t) + \alpha''_3 C_{p-BQ}(x, t)] \ll 1$, they were not considered and the denominator of the photodegradation rate expressions were disregarded.

On the other hand, since the value of α_1 was so high, it was assumed that $\alpha_1 e^{\alpha(x)} \gg 1$ for the different irradiation conditions, and therefore the kinetic equations could be simplified to obtain the following expressions:

$$r_{CA}(x, t) = (\alpha'_{2,1} + \alpha'_{2,2}) C_{CA}(x, t) \sqrt{\frac{e^{\alpha(x)}}{S_g C_{cat}}} \quad (14)$$

$$r_{4-CP}(x, t) = (\alpha'_{4,1} + \alpha'_{4,2}) C_{4-CP}(x, t) \sqrt{\frac{e^{\alpha(x)}}{S_g C_{cat}}} \quad (15)$$

$$r_{p-BQ}(x, t) = \alpha'_5 C_{p-BQ}(x, t) \sqrt{\frac{e^{\alpha(x)}}{S_g C_{cat}}} \quad (16)$$

where $\alpha'_{2,1} = \alpha_{2,1} \sqrt{\alpha_1}$, $\alpha'_{2,2} = \alpha_{2,2} \sqrt{\alpha_1}$, $\alpha'_{4,1} = \alpha_{4,1} \sqrt{\alpha_1}$, $\alpha'_{4,2} = \alpha_{4,2} \sqrt{\alpha_1}$ and $\alpha'_5 = \alpha_5 \sqrt{\alpha_1}$.

The values of the kinetic parameters which provided the best fittings for both the complete (6-parameters) and simplified (5-parameters) kinetic models are shown in Table 3. From the values obtained with the 6-parameter and 5-parameter models, it could be observed that the kinetic parameter that represents the photodegradation of clofibric acid to form p-benzoquinone, $\alpha_{2,2}$, is slightly higher than that to generate 4-chlorophenol, $\alpha_{2,1}$. However, because of the higher value of the parameter related to p-benzoquinone photo-oxidation, α_5 , p-benzoquinone concentration was always very low. On the other hand, p-benzoquinone formation from 4-chlorophenol photo-oxidation was not kinetically favoured and other intermediates (X_i) would be preferentially produced, as indicated the value of $\alpha_{4,2}$, which was far lower than $\alpha_{4,1}$.

Figure 5 presents photodegradation experiments carried out employing different photocatalyst concentrations with 100% of the irradiation level. It can be observed that clofibric acid concentration was lower than $0.01 \text{ mmol}\cdot\text{L}^{-1}$ after 6 h of irradiation in all cases. 4-Chlorophenol concentration was much higher than p-benzoquinone concentration, which was always below $0.003 \text{ mmol}\cdot\text{L}^{-1}$. Concerning both intermediate products, their concentration reached a peak after approximately 2 h of irradiation. The organic compound concentrations followed the same trend for the different photocatalyst loadings. It can be observed that $100 \text{ mg}\cdot\text{L}^{-1}$ of photocatalyst led to the best photodegradation results. Afterwards, the optimum photocatalyst loading ($100 \text{ mg}\cdot\text{L}^{-1}$) was chosen and experiments

with different irradiation levels are presented in Figure 6. When the irradiation level was decreased from 100% to 62%, 4-chlorophenol reached higher concentrations and, at the end of the experiment, 4-chlorophenol concentration exceeded the residual concentration of clofibric acid. Using an irradiation level of 30%, clofibric acid conversion after 2 h of treatment only reached 41%, while this value increased up to 73% for 100% irradiation. No meaningful differences in the evolution of p-benzoquinone concentration were detected under different irradiation levels.

In Figures 5 and 6 the theoretical values obtained with the 6-parameter model, for a wide range of operational conditions, were depicted for the three organic compounds detected. Concentrations predicted with the 5-parameter model were plotted in Figures S1 and S2 of the Supporting Information. It could be noted that good correlations between theoretical and experimental results were always obtained. To compare the ability of the model to predict the evolution of concentrations, total root-mean-square errors (RMSE) were calculated:

$$RMSE (\%) = \sqrt{\frac{\sum_{i=1}^N \left(\frac{C_{Exp}^i - C_{Mod}^i}{C_{Exp}^i} \cdot 100 \right)^2}{N}} \quad (17)$$

Values of RMSE can also be seen in Table 3. RMSE values of 10.8% and 16.3% were calculated for clofibric acid using the 6-parameter and 5-parameter models, respectively. Since concentrations lower than 0.01 mmol·L⁻¹ are within the experimental error, these low concentrations were not considered for the calculation of the RMSE. From these data, it can be concluded that, although simplified models with a small number of parameters are always preferred, the simplification leads to an increase in the error of the predicted values. Thus, the 6-parameter model was chosen to simulate the concentrations of the pollutants.

The proposed kinetic model was able to simulate accurately the experimental results of clofibric acid photodegradation using rGO-TiO₂ based photocatalysts.

7. CONCLUSIONS

In this work, an intrinsic kinetic model with an explicit dependence on radiation absorption was developed to model the photodegradation of clofibric acid and the main photogenerated intermediates, considering also the formation of hydroxyl radicals from photogenerated electrons. Firstly, the radiation absorbed by a nanocomposite, P25-rGO 0.5%, was computed for different catalyst loadings and irradiation levels. The LVRPA was calculated by solving the RTE using the Monte Carlo method. Most radiation was absorbed near the photoreactor windows and it was not able to reach the centre of the reactor even using only 50 mg·L⁻¹ of photocatalyst. The intrinsic kinetic parameters were obtained for the complete (6-parameters)

and simplified (5-parameters) models by comparing the experimental values and the theoretical concentrations of the organic compounds. The model proved to be able to predict with good accuracy the concentration evolution of clofibric acid, 4-chlorophenol and p-benzoquinone, under several photocatalyst concentrations and irradiation levels. A very good correlation between calculated and experimental values of CA concentration was obtained with root-mean-square errors below 11%.

Appendix. Derivation of the kinetic model

Firstly, competitive adsorption among the main pollutant, clofibric acid, and the intermediates was considered. The following equations can be written:

$$[CA_{ads}] = K_{CA}[site_{CA}]C_{CA} \quad (1)$$

$$[4 - CP_{ads}] = K_{4-CP}[site_{CA}]C_{4-CP} \quad (2)$$

$$[p - BQ_{ads}] = K_{p-BQ}[site_{CA}]C_{p-BQ} \quad (3)$$

where $[i_{ads}]$ is the superficial concentration of the adsorbed species, K_i is the equilibrium adsorption constant of each species, $[site_i]$ indicates the surface concentration of vacant sites and C_i represents the concentration of i in the bulk. The adsorption equation for oxygen can be expressed as:

$$[O_{2,ads}] = K_{O_2}[site_{O_2}]C_{O_2} \quad (4)$$

The total concentration of sites $[site_{i,T}]$ could be related to the concentration of vacant sites and concentration of occupied sites $[site_{i,oc}]$, by oxygen or organic compounds, by making a balance of sites:

$$[site_{O_2,T}] = [site_{O_2,oc}] + [site_{O_2}] \quad (5)$$

$$[site_{CA,T}] = [site_{CA,oc}] + [site_{CA}] \quad (6)$$

Introducing equation 4 into equation 5 and equations 1-3 into equation 6:

$$[site_{O_2}] = \frac{[site_{O_2,T}]}{1 + K_{O_2}C_{O_2}} \quad (7)$$

$$[site_{CA}] = \frac{[site_{CA,T}]}{1 + K_{CA}C_{CA} + K_{4-CP}C_{4-CP} + K_{p-BQ}C_{p-BQ}} \quad (8)$$

Since it was assumed that the organic compounds are mainly attacked by hydroxyl radicals and taking into account the photoreaction mechanism, the following photodegradation rates are proposed:

$$r_{CA} = k_{8,1}[HO^\cdot][CA_{ads}] + k_{8,2}[HO^\cdot][CA_{ads}] \quad (9)$$

$$r_{4-CP} = k_{9,1}[HO^\cdot][4 - CP_{ads}] + k_{9,2}[HO^\cdot][4 - CP_{ads}] \quad (10)$$

$$r_{p-BQ} = k_{10}[HO^\cdot][p - BQ_{ads}] \quad (11)$$

where k_i represents the kinetic constant of the reaction between the organic compounds and hydroxyl radicals.

By applying the kinetic steady state approximation, the following superficial formation rates for electrons, holes, hydroxyl radicals, superoxide radicals, hydroperoxyl radicals and hydrogen peroxide were proposed:

$$r_{e^-} = r_{gs} - k_2[e^-][h^+] - k_3[e^-][O_{2,ads}] \cong 0 \quad (12)$$

$$r_{h^+} = r_{gs} - k_2[e^-][h^+] - k_4[h^+][H_2O_{ads}] \cong 0 \quad (13)$$

$$\begin{aligned} r_{HO^\cdot} = & k_4[h^+][H_2O_{ads}] + k_7[O_2^{\cdot-}][H_2O_2] - (k_{8,1} + k_{8,2})[HO^\cdot][CA_{ads}] - (k_{9,1} \\ & + k_{9,2})[HO^\cdot][4 - CP_{ads}] - k_{10}[HO^\cdot][p - BQ_{ads}] - \sum_l k_l[HO^\cdot][Y_{l,ads}] \\ & \cong 0 \end{aligned} \quad (14)$$

$$r_{O_2^{\cdot-}} = k_3[e^-][O_{2,ads}] - k_5[H^+][O_2^{\cdot-}] - k_7[O_2^{\cdot-}][H_2O_2] \cong 0 \quad (15)$$

$$r_{HO_2^\cdot} = k_5[H^+][O_2^{\cdot-}] - k_6[HO_2^\cdot]^2 \cong 0 \quad (16)$$

$$r_{H_2O_2} = k_6[HO_2^\cdot]^2 - k_7[O_2^{\cdot-}][H_2O_2] \cong 0 \quad (17)$$

where r_{gs} is the surface rate of electron-hole generation. Rearranging equations 12-17:

$$[e^-] = \frac{r_{gs}}{k_2[h^+] + k_3[O_{2,ads}]} \quad (18)$$

$$[h^+] = \frac{r_{gs}}{k_2[e^-] + k_4[H_2O_{ads}]} \quad (19)$$

$$[HO\cdot] = \frac{k_4[H_2O_{ads}][h^+] + k_7[O_2^-][H_2O_2]}{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}] + \sum_l k_l[Y_{l,ads}]} \quad (20)$$

$$[H_2O_2] = \frac{k_5[H^+]}{k_7} \quad (21)$$

$$[O_2^-] = \frac{k_3[e^-][O_{2,ads}]}{2k_5[H^+]} \quad (22)$$

From equations 18 and 19, the hole and electron concentrations could be obtained and operating with equation 20-22 the hydroxyl radical concentration is:

$$[HO\cdot] = \frac{3k_3k_4[H_2O_{ads}][O_{2,ads}] \left\{ -1 + \sqrt{1 + \frac{4k_2r_{gs}}{k_3k_4[H_2O_{ads}][O_{2,ads}]}} \right\}}{4k_2\{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}] + \sum_l k_l[Y_{l,ads}]\}} \quad (23)$$

Assuming that $[H_2O_{ads}]$ and $[O_{2,ads}]$ are constant and considering that mass transfer limitations can be neglected, the obtained photodegradation rate of clofibric acid was:

$$r_{CA} = \frac{(\delta_{2,1} + \delta_{2,2})[CA_{ads}]\{-1 + \sqrt{1 + \delta_1 r_{gs}}\}}{\delta_3\{(k_{8,1} + k_{8,2})[CA_{ads}] + (k_{9,1} + k_{9,2})[4 - CP_{ads}] + k_{10}[p - BQ_{ads}]\} + 1} \quad (24)$$

where:

$$\delta_1 = \frac{4k_2}{k_3k_4[H_2O_{ads}][O_{2,ads}]}$$

$$\delta_{2,1} = \frac{3k_3k_4k_{8,1}[H_2O_{ads}][O_{2,ads}]}{4k_2 \sum_l k_l[Y_{l,ads}]}$$

$$\delta_{2,2} = \frac{3k_3k_4k_{8,2}[H_2O_{ads}][O_{2,ads}]}{4k_2 \sum_l k_l[Y_{l,ads}]}$$

$$\delta_3 = \frac{1}{\sum_l k_l [Y_{l,ads}]}$$

Substituting equations 1-3 and 8 into equation 24 and rearranging:

$$r_{CA} = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA}\{-1 + \sqrt{1 + \delta_1 r_{gs}}\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (25)$$

The electron-hole pair formation rate per unit catalytic area can be described by:

$$r_{gs} = \frac{\bar{\phi} e^a}{a_v} \quad (26)$$

where e^a corresponds to the local volumetric rate of photon absorption (LVRPA), $\bar{\phi}$ is the primary quantum yield averaged over all wavelengths and a_v is the interfacial area per unit suspension volume ($a_v = S_g C_{cat}$). Thus, the final expression is:

$$r_{CA} = \frac{(\alpha_{2,1} + \alpha_{2,2})C_{CA} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-Bzq}} \quad (27)$$

where:

$$\alpha_1 = \delta_1 \bar{\phi}$$

$$\alpha_{2,1} = \delta_{2,1} K_{CA} [site_{CA,T}]$$

$$\alpha_{2,2} = \delta_{2,2} K_{CA} [site_{CA,T}]$$

$$\alpha_3 = \delta_3 (k_{8,1} + k_{8,2}) K_{CA} [site_{CA,T}] + K_{CA}$$

$$\alpha'_3 = \delta_3 (k_{9,1} + k_{9,2}) K_{4-CP} [site_{CA,T}] + K_{4-CP}$$

$$\alpha''_3 = \delta_3 k_{10} K_{p-BQ} [site_{CA,T}] + K_{p-BQ}$$

Following the same procedure, the expressions of the 4-chlorophenol and p-benzoquinone were obtained:

$$r_{4-CP} = \frac{(\alpha_{4,1} + \alpha_{4,2})C_{4-CP} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (28)$$

$$r_{p-BQ} = \frac{\alpha_5 C_{p-BQ} \left\{ -1 + \sqrt{1 + \frac{\alpha_1 e^a}{S_g C_{cat}}} \right\}}{1 + \alpha_3 C_{CA} + \alpha'_3 C_{4-CP} + \alpha''_3 C_{p-BQ}} \quad (29)$$

where:

$$\alpha_{4,1} = \frac{3k_3 k_4 k_{9,1} [H_2 O_{ads}] [O_{2,ads}] K_{4-CP} [site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

$$\alpha_{4,2} = \frac{3k_3 k_4 k_{9,2} [H_2 O_{ads}] [O_{2,ads}] K_{4-CP} [site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

$$\alpha_5 = \frac{3k_3 k_4 k_{10} [H_2 O_{ads}] [O_{2,ads}] K_{p-BQ} [site_{CA,T}]}{4k_2 \sum_l k_l [Y_{l,ads}]}$$

Acknowledgements

Thanks are due to the Spanish Plan Nacional I+D+i (projects CTM2015-64895-R and CTM2016-76454-R) and Universidad Nacional del Litoral (UNL), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) for financial support. We would also like to thank Antonio C. Negro for his valuable help during the experimental work. Alvaro Tolosana-Moranchel acknowledges to Ministerio de Educación, Cultura y Deporte for his FPU grant (FPU14/01605) and (EST17/00110).

NOMENCLATURE

a_v = interfacial area per unit suspension volume, m^{-1}

C_{cat} = mass catalyst concentration, $g \cdot cm^{-3}$

C_i = molar concentration of compound i in the bulk, $mmol \cdot L^{-1}$

CA = clofibric acid

e^a = averaged volumetric rate of photon absorption, $\text{Einstein} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$

$e^a(x)$ = local volumetric rate of photon absorption, $\text{Einstein} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$

4-CP = 4-chlorophenol

g = asymmetry factor

k = kinetic constant, its units depend on the step considered

K = equilibrium constant

LVRPA = local volumetric rate of photon absorption, $\text{Einstein} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$

p = phase function, dimensionless

p-BQ = p-benzoquinone

q = radiation flux, $\text{Einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$

r_{gs} = surface rate of electron-hole generation, $\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$

r_i = photodegradation rate of compound i , $\text{mmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$

S_g = catalyst specific surface area, $\text{m}^2 \cdot \text{g}^{-1}$

t = time, h

V = Volume, L

VRPA = volumetric rate of photon absorption, $\text{Einstein} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$

X_i, X_j = secondary organic intermediates

Y_I = inorganic species

Greek letters

α_i = kinetic parameter

β = extinction coefficient, cm^{-1}

ϕ = primary quantum yield, $\text{mol} \cdot \text{Einstein}^{-1}$

$\bar{\phi}$ = wavelength averaged primary quantum yield, $\text{mol} \cdot \text{Einstein}^{-1}$

κ = absorption coefficient, cm^{-1}

λ = wavelength, nm

Γ = global reflection coefficient of the reactor windows

θ = spherical coordinate, rad

σ = scattering coefficient, cm^{-1}

ω = spectral albedo

Subscripts

4-CP = relative to 4-chlorophenol

0 = initial value or relative to the reactor window at $x=0$

λ = indicates a dependence on wavelength

CA = relative to clofibric acid

Cat = relative to catalyst

Exp = experimental value

L = relative to the reactor window at $x = L$

Mod = simulated value

p-BQ = relative to p-benzoquinone

R = reactor

T = total

Tk = tank reservoir

V_R = relative to reactor volume

W = wall

Special symbols

$\langle \rangle$ = average value over a defined space

$[]$ = relative to surface concentration

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