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Modeling of degradation kinetic and toxicity evaluation of herbicides mixtures in water using the UV/H₂O₂ process

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The UV/H₂O₂ process was applied to the treatment of different mixtures of herbicides in water. Glyphosate, the herbicide most used in the world, was mixed with other hormonal herbicides with residual activity as 2,4-D and dicamba. The main goals of the study were to develop a kinetic model for interpreting the simultaneous oxidation of two mixtures (glyphosate plus 2,4-D and glyphosate plus dicamba). The model is based on a complete reaction mechanism, which comprises hydrogen peroxide photolysis and decomposition of both herbicides in each mixture studied. It takes into account the effect of non-uniform distribution of the local rate of absorbed photons. Good agreement of experimental data and the model is achieved in spite of differences in the reactivity between glyphosate and 2,4-D (or dicamba). Toxicity assays (employing *Vibrio fischeri*) were also performed, indicating that the toxicity of the mixture of glyphosate and 2,4-D was significantly reduced after the treatment.

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1 Introduction

Glyphosate (*N*-phosphonomethyl glycine) is the most widely used herbicide in the world. However, in the last few years, the number of glyphosate-resistant weeds species has increased.^{1,2} This indicates environmental and economic costs, besides productivity losses.³

The main strategy for preventing or delaying the growth of glyphosate resistant weeds is to add glyphosate with herbicides as alternative ways of action and with soil-residual activity.^{4,5} Glyphosate is combined with herbicides such as 2,4-dichlorophenoxyacetic acid (commonly named 2,4-D), atrazine, and dicamba.^{6,7} This is a significant task because pesticides have recently become a considerable environmental problem due to their chemical stability and resistance. In addition, the improper disposal of herbicide containers wastes has led to the contamination of soil, ground and surface waters. Due to the lack of availability of small scale, on-site treatment technologies, only a small amount of this waste is currently annihilated.

Among the different processes for the treatment of pesticides, advanced oxidation processes (AOPs) are a powerful technology for oxidizing this type of contaminants.^{8–11} These processes include technologies such as O₃/H₂O₂, O₃/UV, UV/H₂O₂, O₃/H₂O₂/UV, Fe²⁺/H₂O₂, Fe²⁺/H₂O₂/UV and TiO₂/UV, and

are also efficient processes for removing non-biodegradable and refractory organic compounds. Among various types and combinations of AOPs, the UV/H₂O₂ method has been shown suitable for the degradation of glyphosate in water.¹²

For commercial applications, the UV/H₂O₂ process requires the determination of important design and operational variables such as the optimum oxidant and irradiation dosages within the reactor. The kinetic model provides useful information of the system and is able to predict the decomposition rates of compounds under different operational conditions.

In the literature, kinetic models have been proposed by several research works for predicting the decomposition rate of specific organic compounds using the UV/H₂O₂ process. Liao and Gurol¹³ have developed a kinetic model in continuous-flow stirred reactors to predict the decomposition of a model compound (*n*-chlorobutane) under steady-state conditions. The kinetic model of Glaze *et al.*¹⁴ predicted the decomposition rate of 1,2-dibromo-3-chloropropane (DBCP) in a completely mixed batch reactor. Their model predicted well the concentration of DBCP and hydrogen peroxide, especially at low carbonate concentration levels (free-radical scavengers). The kinetic model of Stefan *et al.*¹⁵ was proposed to predict the degradation rate of acetone, invoking the steady-state assumption. A detailed kinetic model has been developed by Crittenden *et al.*¹⁶ extending the model of Glaze *et al.* by incorporating the effect of natural organic matter (NOM), the pH changes and non-steady state assumption. The model produced good predictions for the degradation of DBCP when tested with the experimental data of Glaze *et al.*

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The work of Song *et al.*¹⁷ has proposed a kinetic model for the decomposition of a pesticide (alachlor) in the presence of NOM and other radical scavengers under different operating conditions.

Chang *et al.*¹⁸ have developed a comprehensive kinetic model to predict the effects of H₂O₂ concentration, solution pH and UV irradiation power on the initial reaction rate of a dye compound. The experimental data and the predicted results are in good agreement.

Kusic *et al.*¹⁹ have developed a mathematical model to predict the system behavior in the degradation of azo dye Orange 7 (AO7) using three photooxidation processes (UV/H₂O₂, UV/S₂O₈²⁻ and UV/O₃).

The mentioned kinetic models for the UV/H₂O₂ process provided a good understanding of the process under different operational conditions. For most of them, the kinetic models are based on complete reaction schemes that take into account scavengers, such as carbonates or NOM, present in natural waters.

In aquatic environments, pesticides usually appear as complex mixtures instead of single contaminants. For this reason, in order to approach the real pollution problems, it is more important to model the mixture of these compounds rather than the individual chemicals separately.

In this work, a mathematical model to interpret the simultaneous oxidation of two herbicides (glyphosate and 2,4-D) in water using the UV/H₂O₂ process is reported. This mixture is formed by compounds with very different chemical structure, and the herbicides were used at the same level of concentration throughout the experiments. The kinetic model is developed from a complete reaction scheme based on the previously cited studies and includes the rigorous modeling of the radiation absorption effects on the rate. In addition, the toxicity during photodegradation was evaluated by employing the Microtox (*Vibrio fischeri*) acute toxicity test.

The model is also evaluated for another mixture of herbicides formed by glyphosate and dicamba.

2. Materials and methods

2.1 Chemicals

The following reagents were used: (a) glyphosate (AccuStandard) as chromatographic standard, (b) glyphosate 95% provided by Red Surcos, (c) 2,4-dichlorophenoxyacetic acid (Sigma-Aldrich) as chromatographic standard, (d) hydrogen peroxide (Cicarelli p.a., >99%), (e) catalase from bovine liver, >2000 units mg⁻¹ (Fluka, 1 unit decomposes 1 mmol H₂O₂ per minute at pH 7.0 and 25 °C), (f) dicamba (Pestanal) as chromatographic standard and (g) dicamba 98% provided by Red Surcos. Distilled water was used in all experiments.

2.2 Analysis

Glyphosate was analyzed by ion chromatography²⁰ with a suppressed conductivity detector and employing an Ion Pac AG2A-SC guard column, an AS2A-SC separating column, and

an ion self-regenerating suppressor (Dionex). A solution of Na₂CO₃ (7.2 mM) and NaOH (3.2 mM) was used as eluent at a flow-rate of 0.6 ml min⁻¹. The injection volume was 20 µl. 2,4-D was analyzed by high performance liquid chromatography (Waters 1525 Binary HPLC Pump) with a UV detector (Waters 2489 UV/Visible Detector) using an analytical column of C18 reverse phase (SUPELCOTM LC-18 – 4.6 × 250 mm). Acetonitrile (49%), water (50%) and acetic acid (1%) were used as the mobile phase,²¹ and the separation was performed at a flow rate of 0.75 ml min⁻¹ and 30 °C. The fixed-wavelength UV absorbance detector was set at 290 nm. The injection volume was 20 µl.

Dicamba was analyzed by high performance liquid chromatography with a UV detector. The mobile phase was acetonitrile (50%), water (50%) and phosphoric acid (0.1%). The separation was performed at 225 nm, with a flow rate of 1.0 ml min⁻¹ and 30 °C.

The pH was measured with a HI 98127 Hanna pH meter (accuracy: ±0.1). Hydrogen peroxide was analyzed using a colorimetric method following the Allen *et al.*²² technique and employing a Cary 100 Bio UV visible spectrophotometer. Total organic carbon (TOC) was analyzed in order to compare glyphosate and 2,4-D degradation rates with the total mineralization rate. The instrument used was a Shimadzu TOC-5000a.

2.3 Toxicity evaluation

The toxicity of the samples was examined using a Model 500 Analyzer (Strategic Diagnostic Inc.) according to the ASTM Standard Method.²³ The toxicity was evaluated with the Microtox Acute Toxicity Test by monitoring changes in the natural emission of the luminescent bacteria *Vibrio fischeri* (freeze-dried strain). Luminescence was recorded after 15 min of incubation. Hydrogen peroxide present in the samples was removed prior to every toxicity analysis using catalase after adjusting the sample pH between 6 and 8.

2.4 Experimental device

The study was carried out in a batch cylindrical photoreactor made of Teflon®, with two parallel, flat windows made of quartz ($V_R = 110 \text{ cm}^3$). Radiation was produced with two low-pressure mercury vapor lamps ($\lambda = 253.7 \text{ nm}$). Each window permitted the interposing of one shutter to block the passage of light when necessary. The reactor was part of a recirculation, batch system complemented with: (i) a peristaltic pump (ii) a heat exchanger for temperature control (iii) a storage tank with provisions for sampling and temperature measurements ($V_{TK} = 1000 \text{ cm}^3$). A detailed description of the photoreactor has been presented in Zalazar *et al.*²⁴

Experiments were carried out by varying the significant experimental variables: (i) initial glyphosate and 2,4-D concentrations in the mixture, (ii) initial hydrogen peroxide concentrations, (iii) initial pH and (iv) spectral fluence rate at the reactor windows measured with potassium ferrioxalate actinometry²⁵ (calculated according to Zalazar *et al.*²⁶).

The experimental conditions are shown in Table 1.

Table 1 Experimental conditions

Variable	Value
Glyphosate initial concentration	15–30 mg L ⁻¹
2,4-D initial concentration	15–30 mg L ⁻¹
H ₂ O ₂ initial concentration	0–800 mg L ⁻¹
Spectral fluence rate at the reactor windows ($E_{p,w}^{\lambda=253.7\text{ nm}}$)	
Lamp Heraeus 40 W	23.3×10^9 (Einstein cm ⁻² s ⁻¹)
Lamp Heraeus 40 W with filter 43%	9.8×10^9 (Einstein cm ⁻² s ⁻¹)
Lamp Heraeus 40 W with filter 18%	4.1×10^9 (Einstein cm ⁻² s ⁻¹)
Time of reaction	6 h
Temperature	20 °C
Initial pH	10

In a previous work, the influence of experimental conditions such as initial hydrogen peroxide dose and initial pH on the degradation of the mixture glyphosate and 2,4-D was examined.²⁷ These results showed that initial pH = 10 is the best value to obtain high degradation levels of 2,4-D and glyphosate mixture while using the UV/H₂O₂ process.

2.5 Degradation procedure

The experimental run was started after every variable of the operating conditions had reached its steady state and/or uniformity. The photoreactor was filled with the working solution, and then recirculation was established. At the same time, the lamp shutters were taken off, and the sample at $t = 0$ was withdrawn. Later, samples (25 ml) were taken at different time intervals. A normal run lasted for 6 h. Once each run was finished, the photoreactor was carefully washed three times with tap water and twice with deionized water.

3. Model formulation

3.1 Reactions scheme and kinetic rate expressions

The proposed reaction path for the simultaneous degradation of glyphosate and 2,4-D with the UV/H₂O₂ process is illustrated in Table 2.

The reaction scheme comprises 14 reactions: the chemical and photochemical reactions known to occur in the UV/H₂O₂ process (reactions 1 to 12), reactions (13) and (14) correspond to the decomposition of glyphosate and 2,4-D, respectively, in the system by the generated hydroxyl radicals. The reaction rates and the equilibrium constants are usually taken from the literature^{16,17,19} (reactions from 1 to 12). It is important to remark that the models proposed by several researches for predicting the decomposition rate of specific organic compound (s) for the UV/H₂O₂ process comprises reaction schemes with the principal interactions between H₂O₂, free radicals and the UV radiation, and taking into account the reactions of equilibrium of H₂O₂ and HO₂[•] radical. However, these models were evaluated for a single contaminant and not for a mixture of compounds, such as the model proposed in this work. This is an important contribution in order to approach the real pollution problems.

Table 2 Reaction scheme

N°	Reactions	Constants
(1)	H ₂ O ₂ /HO ₂ ⁻ $\xrightarrow{\Phi_p}$ 2 [•] OH	$\Phi_p = 0.5$
(2)	H ₂ O ₂ + [•] OH $\xrightarrow{k_2}$ HO ₂ [•] + H ₂ O	2.7×10^7 (M ⁻¹ s ⁻¹)
(3)	[•] OH + HO ₂ ⁻ $\xrightarrow{k_3}$ HO ₂ [•] + OH ⁻	7.5×10^9 (M ⁻¹ s ⁻¹)
(4)	H ₂ O ₂ + HO ₂ [•] $\xrightarrow{k_4}$ [•] OH + H ₂ O + O ₂	3 (M ⁻¹ s ⁻¹)
(5)	H ₂ O ₂ + O ₂ ^{-•} $\xrightarrow{k_5}$ [•] OH + O ₂ + OH ⁻	0.13 (M ⁻¹ s ⁻¹)
(6)	2 [•] OH $\xrightarrow{k_6}$ H ₂ O ₂	5.3×10^9 (M ⁻¹ s ⁻¹)
(7)	[•] OH + HO ₂ [•] $\xrightarrow{k_7}$ H ₂ O + O ₂	6.6×10^9 (M ⁻¹ s ⁻¹)
(8)	2HO ₂ [•] $\xrightarrow{k_8}$ H ₂ O ₂ + O ₂	8.3×10^5 (M ⁻¹ s ⁻¹)
(9)	HO ₂ [•] + O ₂ ^{-•} $\xrightarrow{k_9}$ HO ₂ ⁻ + O ₂	9.7×10^7 (M ⁻¹ s ⁻¹)
(10)	[•] OH + O ₂ ^{-•} $\xrightarrow{k_{10}}$ OH ⁻ + O ₂	7×10^9 (M ⁻¹ s ⁻¹)
(11)	H ₂ O ₂ \leftrightarrow H ⁺ + HO ₂ ⁻	$K_{11} = 2 \times 10^{-12}$ (M)
(12)	HO ₂ [•] \leftrightarrow H ⁺ + O ₂ ^{-•}	$K_{12} = 1.58 \times 10^{-5}$ (M)
(13)	-OCCH ₂ NH ₂ ⁺ CH ₂ PO ₃ ⁻² + [•] OH $\xrightarrow{k_{13}}$ products	Present work
(14)	C ₆ H ₃ Cl ₂ OCH ₂ COO ⁻ + [•] OH $\xrightarrow{k_{14}}$ products	Present work

The reactions 2 through 5 comprise reactions between hydrogen peroxide and the generated radicals. Reactions 6 to 10 correspond to free radicals reactions. In reaction 11, the equilibrium between the hydroperoxyl ion and hydrogen peroxide is represented, while reaction 12 describes the equilibrium between the hydroperoxyl radical and the superoxide ionic radical.

Glyphosate contains three chemical groups (phosphonic, amino and carboxylic), all of which can be protonated and deprotonated as a function of pH.^{28,29} At a pH between 5.5 and 10.6, glyphosate has a net charge equal to -2, because it has the three hydroxyl groups ionized and the amino group protonated (phosphonic -2, carboxylate -1, amino +1). Therefore, it can be represented according to this (reaction 13). Reaction 14 represents the reaction between 2,4-D and hydroxyl radicals (2,4-D has a pK_a value = 2.73 and at pH = 10, it is ionized).

The kinetic rate expressions are finally:

For hydrogen peroxide (P):

$$R_P = -\Phi_P e_P^a - k_2 C_P C_{\cdot OH} - k_3 C_{HO_2^-} C_{\cdot OH} - k_4 C_P C_{HO_2^{\cdot}} - k_5 C_P C_{O_2^{\cdot-}} + k_6 C_{OH}^2 + k_8 C_{HO_2^{\cdot}}^2 + k_9 C_{HO_2^{\cdot}} C_{O_2^{\cdot-}} \quad (1)$$

For glyphosate (GF) and 2,4-D:

$$R_{GF} = -k_{13} C_{GF} C_{\cdot OH} \quad (2)$$

$$R_{2,4-D} = -k_{14} C_{2,4-D} C_{\cdot OH} \quad (3)$$

The proposed model invokes the steady state assumption as the kinetic models of Liao and Gurol,¹³ Glaze *et al.*¹⁴ and Stefan *et al.*¹⁵

For unstable species, HO₂[•] and [•]OH, resorting to the micro-steady-state approximation (MSSA):

$$R_{\cdot OH} = 2\Phi_P e_P^a - k_2 C_P C_{\cdot OH} - k_3 C_{HO_2^-} C_{\cdot OH} + k_4 C_P C_{HO_2^{\cdot}} + k_5 C_P C_{O_2^{\cdot-}} - 2k_6 C_{OH}^2 - k_7 C_{\cdot OH} C_{HO_2^{\cdot}} - k_{10} C_{\cdot OH} C_{O_2^{\cdot-}} - k_{13} C_{GF} C_{\cdot OH} - k_{14} C_{2,4-D} C_{\cdot OH} \cong 0 \quad (4)$$

$$R_{\text{HO}_2\cdot} = k_2 C_{\text{P}} C_{\text{OH}} + k_3 C_{\text{HO}_2\cdot} C_{\text{OH}} - k_4 C_{\text{P}} C_{\text{HO}_2\cdot} - k_7 C_{\text{OH}} C_{\text{HO}_2\cdot} - 2k_8 C_{\text{HO}_2\cdot} - k_9 C_{\text{HO}_2\cdot} C_{\text{O}_2\cdot} \cong 0 \quad (5)$$

For the equilibrium reactions:

$$[\text{HO}_2^-] = \frac{K_{11} C_{\text{P}}}{C_{\text{H}^+}} \quad (6)$$

$$[\text{HO}_2\cdot] = \frac{C_{\text{H}^+} C_{\text{O}_2\cdot}}{K_{12}} \quad (7)$$

In the previous equations, R represents molar reaction rates for glyphosate, 2,4-D and H_2O_2 , respectively, where $C_{\text{GF}} = C_{\text{GF}}(t)$, $C_{2,4\text{-D}} = C_{2,4\text{-D}}(t)$, $C_{\text{P}} = C_{\text{P}}(t)$ are the molar concentrations of glyphosate, 2,4-D and H_2O_2 , respectively. Φ_{P} is the primary quantum yield, and $e_{\text{p}}^{\text{a}}(x,t)$ is the local volumetric rate of photon absorption (LVRPA) by H_2O_2 .

3.2 Mass and radiation balance

The mass balance was solved in order to obtain the theoretical evolution of glyphosate, 2,4-D and H_2O_2 . For this purpose, the following operating conditions must be fulfilled (i) the whole system operates under well-stirred conditions, (ii) the ratio $V_{\text{R}}/V_{\text{T}}$ is $\ll 1$ and (iii) the recirculating flow rate is high ($Q = 3 \text{ L min}^{-1}$) such as to have differential conversion per pass in the photoreactor. Then, the mass balance for the species (i) in the batch, well-mixed stirred tank photoreactor with recycle yields the following ordinary differential equation:³⁰

$$\left. \frac{dC_i(t)}{dt} \right|_{\text{TR}} = \frac{V_{\text{R}}}{V_{\text{T}}} \langle R_{\text{Hom},i}(x,t) \rangle_{V_{\text{R}}} \quad (8)$$

with the initial condition that $\langle C_i(x,0) \rangle_{V_{\text{R}}} = C_i^0$. Where C_i is the concentration of glyphosate, 2,4-D or H_2O_2 , $R_{\text{Hom},i}$ is the homogeneous reaction rate corresponding to glyphosate, 2,4-D and H_2O_2 .

The radiation intensity effect was calculated by solving the radiation balance in the experimental reactor. The local volumetric rate of photon absorption (LVRPA) by the radiation absorption species at a given point in the reactor is given as follows:

$$e_{\lambda}^{\text{a}}(x,t)_{V_{\text{R}}} = \kappa_{\lambda} E_{\text{P}}^{\lambda} \quad (9)$$

where E_{P}^{λ} is the spectral fluence rate, and κ_{λ} is the volumetric absorption coefficient of the reactant absorbing species. In this study, the 2,4-D photolysis by UV radiation was not significant. Therefore, only H_2O_2 absorbs radiation. The value of the absorption coefficient can be obtained by direct application of Beer's equation $\kappa_{\text{P},\lambda} = \alpha_{\text{P},\lambda} \times C_{\text{P}}$, with $\alpha_{\text{P},\lambda} = 0.389 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$.

Considering that the same configuration reactor was used in a previous work,³⁰ the expression employed to compute the averaged LVRPA in the reactor volume is:

$$\langle e_{\text{P},\lambda}^{\text{a}}(x,t) \rangle_{V_{\text{R}}} = \frac{2E_{\text{P},\text{w}}^{\lambda}}{L_{\text{R}}} \{1 - \exp[-\kappa_{\text{P},\lambda}(t)L_{\text{R}}]\} \quad (10)$$

4. Model simulations and experimental results

4.1 Kinetic constants estimation

Eqn (1)–(3) constitute one system of ordinary differential equations, which was solved by the Runge–Kutta method. It must be solved simultaneously with the algebraic equations number (4) and (5). For the last, the Newton–Rawson method was applied. Using the kinetic model, the mass balance for the recycling system and by employing all the experimental values, the solution of the system of differential and algebraic equations mentioned before constitute theoretical predictions that must be compared with experimental data. However, they include two parameters that need to be calculated (k_{13} and k_{14}). Upon application of the Levenberg–Marquard optimization algorithm^{31,32} and working in an iterative manner, the reaction parameters can be obtained (Table 3).

The reported value for glyphosate²⁸ was estimated at pH = 3.8 by a kinetic competition method using the photo-Fenton process.

For the case of 2,4-D, there are two reported values. Mabury and Crosby³³ estimated the rate constant using competition kinetics (pH value was not reported), and Haag and Yao reported a kinetic constant calculated using a predictive correlation.²⁸

Fig. 1a shows the experimental and estimated values of glyphosate concentrations using the kinetic constant obtained with the proposed kinetic model and the reported constant by Haag and Yao.²⁸ With the reported constant, the model over predicts the degradation of glyphosate when compared with experimental values. Instead, a good agreement between the experimental and theoretical values was obtained using the kinetic constant estimated in this work. The difference between the estimated values and the reported values can be attributed to the pH. The reported constant in literature was obtained at pH = 3.8, and the experiences of the degradation of the mixture of glyphosate and 2,4-D were done at initial pH = 10. In fact, in a previous work, the results showed that the initial pH solution had a significant influence on glyphosate oxidation.²⁷ The initial pH = 10 is the best value to obtain high degradation levels of glyphosate in the mixture, while for the initial pH = 3.5, a lower degradation was obtained.

Fig. 1b shows the results for 2,4-D. Using the kinetic constant estimated in this work, the concentration evolution of 2,4-D is better represented.

Table 3 Kinetic constants for glyphosate and 2,4-D^a

Constant	Estimated value	Reported value
$k_{13} (\text{M}^{-1} \text{s}^{-1})$	$(2.49 \pm 0.03) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (pH = 10)	$1.50 \times 10^{8,28}$
$k_{14} (\text{M}^{-1} \text{s}^{-1})$	$(9.67 \pm 0.13) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (pH = 10)	$2.30 \times 10^{9,33}$ $5.00 \times 10^{9,28}$

^a(28) Haag and Yao. (33) Mabury and Crosby.

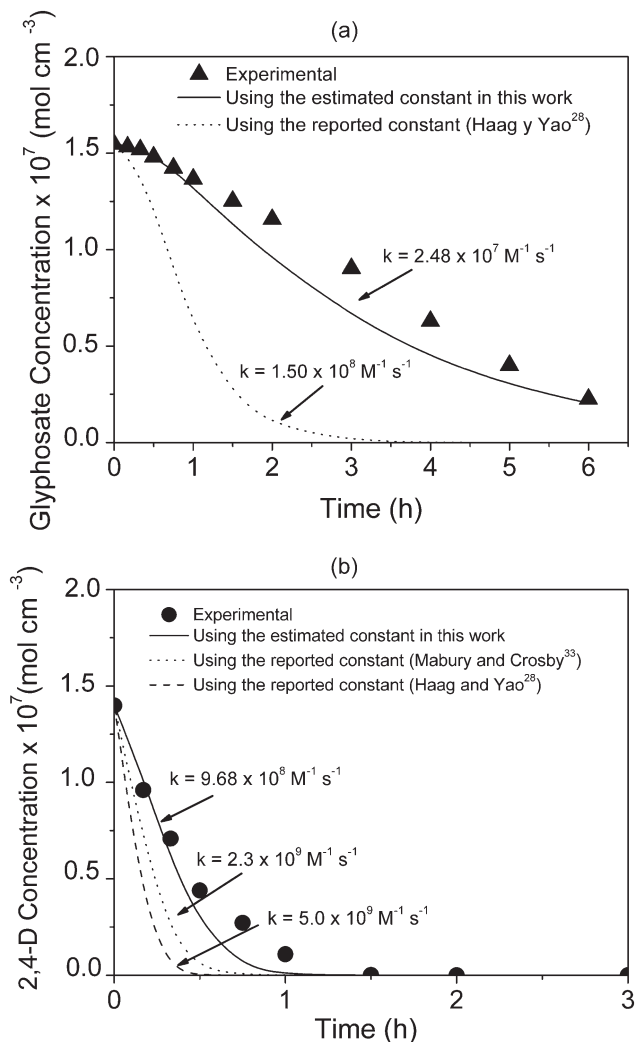


Fig. 1 Model prediction and experimental values. (a) glyphosate (b) 2,4-D $C_{GF}^0 = 30 \text{ mg L}^{-1}$; $C_{2,4-D}^0 = 30 \text{ mg L}^{-1}$; initial pH = 10; Lamp 40 W.

Wols and Hofman-Caris,³⁴ in a review of the photochemical reaction parameters (quantum yield, molar absorption and OH radical reaction rate constant) of more than 100 organic micro-pollutants, exposed that the same compound may show differences in the reported constants. These differences are mainly attributed to the pH, which could change the compounds and/or radical's conjugate acid or base concentration, which may affect the degradation rate. The reactivity of a particular pollutant towards the $\cdot\text{OH}$ radical depends on its ionized form, which is determined by the pH of the solution.

4.2 Effect of initial concentration of H₂O₂ and reactant concentrations

The comparison between the model corresponding to the mixture and the experimental data for different hydrogen peroxide initial concentrations is presented in Fig. 2. The model proposed was able to predict quite acceptably the concentration evolution of all of the reactants.

It must be noted that the model includes the simulation of concentration evolution for three species in mixture: the herbicides glyphosate, 2,4-D and the oxidant H₂O₂. Crittenden *et al.*¹⁶ proposed a reaction scheme with two organic generic compounds (R1 and R2), but in the model verification, only one compound was used (the model compound was DBCP). In this work, the model takes into account a mixture of two herbicides of different chemical structures and reactivities.

In addition, the model is able to predict the very different behavior in the degradation rates (note that for glyphosate, the decay rate was significantly lower than that for 2,4-D).

Fig. 3 shows the experimental and predicted values for different reactant initial concentrations.

It can be seen that 2,4-D is completely degraded before 2 hours of treatment. However, for glyphosate, the decay rate was significantly lower than that for 2,4-D, which indicates that 2,4-D is easily degraded during the first stages of the reaction. Higher rates are observed for compounds exhibiting aromatic rings. Significantly slower rates are found only for compounds that do not exhibit any aromatic ring or carbon-carbon double bond, and for aliphatic compounds, without easily abstractable H-atoms. Such H-atoms include those that are bound to carbon atoms carrying one or several electronegative heteroatoms or groups. Thus, the differences in the reactivity between glyphosate and 2,4-D could be explained by their structure differences. In spite of this, the model predictions and the experimental values agree very well.

4.3 Effect of the incident radiation at the reactor windows

The experimental and simulated values of each component of the mixture of glyphosate and 2,4-D, applying the UV/H₂O₂ process with the same lamps, but using neutral density filters that permitted the passage of 43% and 18% of the incident radiation at the reactor wall are shown separately in Fig. 4(a) and (b), respectively.

These results also confirmed the capacity of the model to predict the system behaviour under different incident radiations at the reactor windows. The proposed kinetic model takes into account the effect of non-uniform distribution of the local rate of absorbed photons, similar to other studies.¹⁴⁻¹⁹ However, in this case, the mathematical model can interpret the simultaneous oxidation of two herbicides and hydrogen peroxide in water by the UV/H₂O₂ process.

5. Toxicity evaluation during the degradation of the mixture of glyphosate and 2,4-D

Toxicity measurements are very important in AOPs, because, sometimes, the treatment could produce a variety of organic intermediates, which can be more toxic than the parent compound.³⁵ Bacterial assays are relatively quick and simple for monitoring the toxicity of environmental samples.

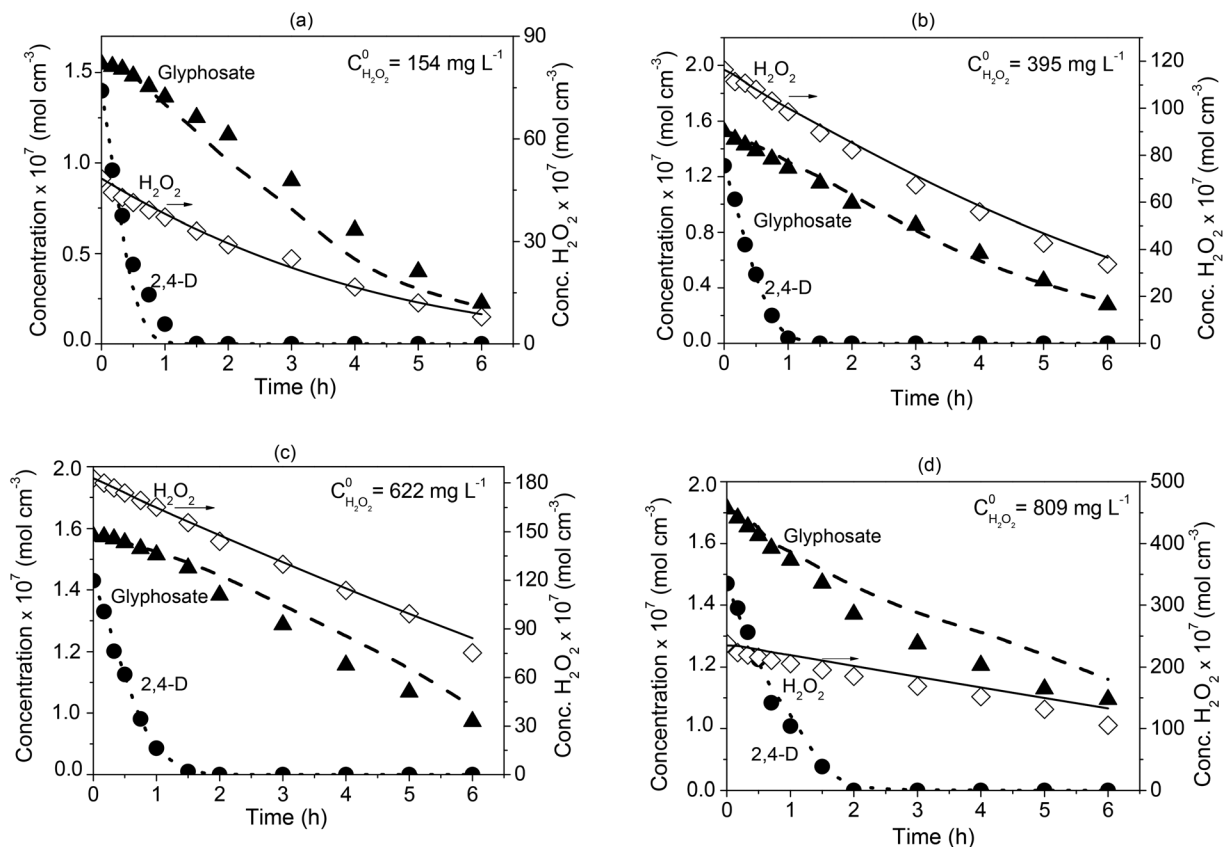


Fig. 2 Model prediction and experimental values (▲) C_{GF} experimental, (---) C_{GF} model; (●) $C_{2,4\text{-D}}$ experimental, (....) $C_{2,4\text{-D}}$ model, (◇) $C_{\text{H}_2\text{O}_2}$ experimental, (—) $C_{\text{H}_2\text{O}_2}$ model. Lamp 40 W, $C_{\text{GF}}^0 = 30 \text{ mg L}^{-1}$, $C_{2,4\text{-D}}^0 = 30 \text{ mg L}^{-1}$; initial pH = 10.

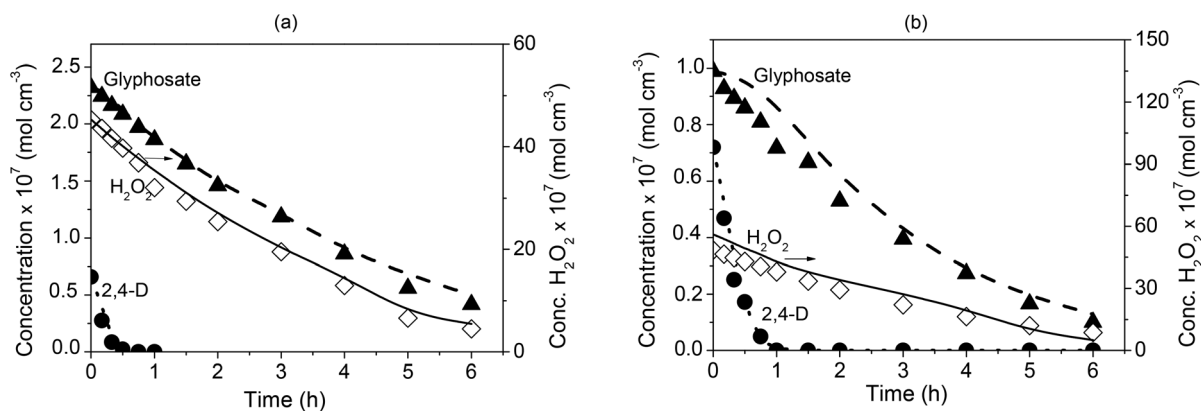


Fig. 3 Model prediction and experimental values. (▲) C_{GF} experimental, (---) C_{GF} model; (●) $C_{2,4\text{-D}}$ experimental, (....) $C_{2,4\text{-D}}$ model, (◇) $C_{\text{H}_2\text{O}_2}$ experimental, (—) $C_{\text{H}_2\text{O}_2}$ model. (a) $C_{\text{GF}}^0 = 30 \text{ mg L}^{-1}$, $C_{2,4\text{-D}}^0 = 15 \text{ mg L}^{-1}$, $C_{\text{H}_2\text{O}_2}^0 = 153.9 \text{ mg L}^{-1}$; initial pH = 10. (b) $C_{\text{GF}}^0 = 15 \text{ mg L}^{-1}$, $C_{2,4\text{-D}}^0 = 15 \text{ mg L}^{-1}$, $C_{\text{H}_2\text{O}_2}^0 = 190.7 \text{ mg L}^{-1}$; initial pH = 10.

The luminescent bacteria toxicity test is most frequently used when the UV/H₂O₂ process applied is the Microtox test.^{36–38}

Toxicity was measured based on the inhibition of the luminescence emitted by the bacteria *Vibrio fischeri* upon contact times of the samples at 15 min. Fig. 5a shows the percentage of inhibition of *Vibrio fischeri* for a typical run. At the beginning, the toxicity was approximately 85%. This might be due

to the presence of the herbicides glyphosate and 2,4-D in the solution and the fast formation of 2,4-dichlorophenol (2,4-DCP), which has been described as toxic and more resistant to oxidative degradation than 2,4-D (Fig. 5b).

In the experiments with *Vibrio fischeri* where glyphosate was used, Bonnet *et al.*³⁵ obtained an $\text{EC}_{50,30 \text{ min}} = 21.25 \text{ mg L}^{-1}$ after 30 min of incubation. However, Hernando *et al.*³⁹ found

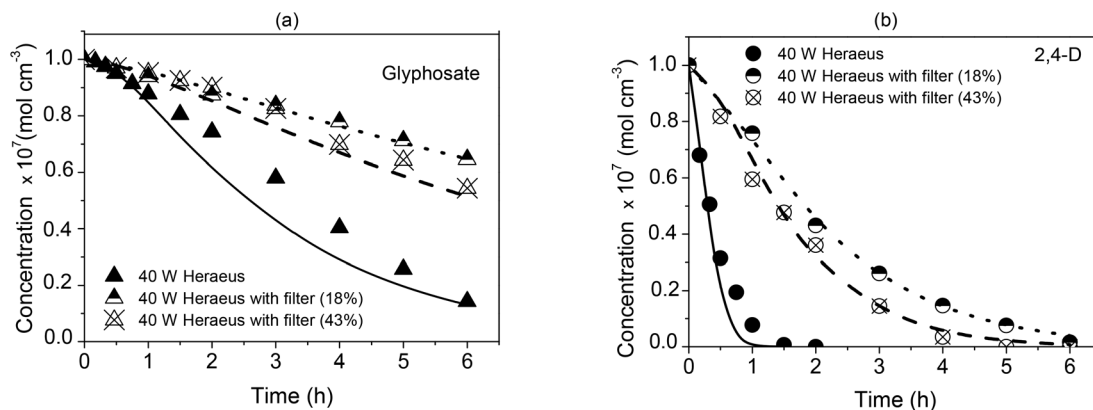


Fig. 4 Model prediction and experimental values for different irradiation conditions. (a) Glyphosate (b) 2,4-D. $C_{\text{GF}}^0 = 30 \text{ mg L}^{-1}$; $C_{2,4\text{-D}}^0 = 30 \text{ mg L}^{-1}$; $C_{\text{H}_2\text{O}_2}^0 = 150 \text{ mg L}^{-1}$ initial pH = 10.

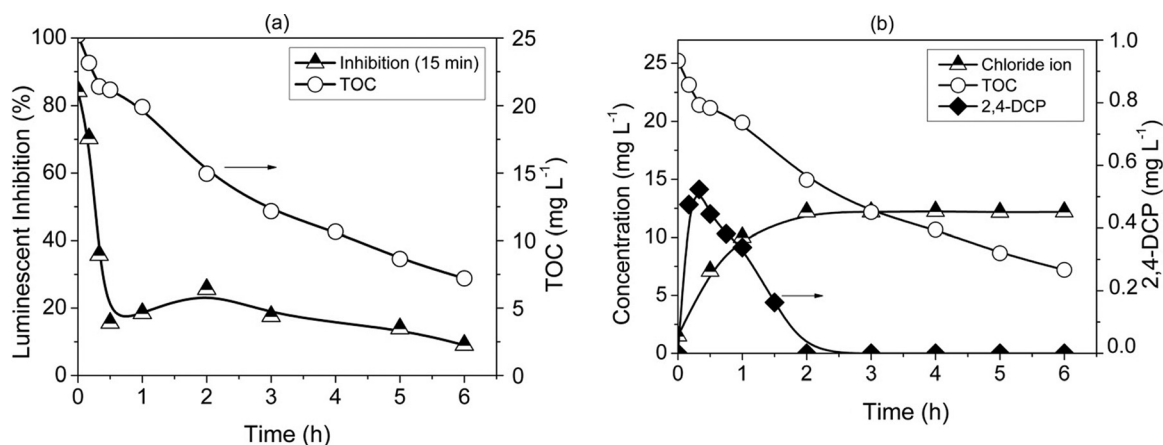


Fig. 5 (a) Toxicity (percentage of inhibition of *Vibrio fischeri*) of samples treated by the UV/H₂O₂ process. (b) 2,4-DCP, chloride ion and TOC evolution during degradation of the herbicide mixture. $C_{\text{GF}}^0 = 30 \text{ mg L}^{-1}$; $C_{2,4\text{-D}}^0 = 30 \text{ mg L}^{-1}$; $C_{\text{H}_2\text{O}_2}^0 = 150 \text{ mg L}^{-1}$; initial pH = 10.

that glyphosate was “harmful” (according to the toxicity categories established in the European Community legislation) for *Vibrio fischeri* with an $\text{EC}_{50,30 \text{ min}} = 44.2 \text{ mg L}^{-1}$.

Zona *et al.*⁴⁰ reported that the herbicide 2,4-D is a moderately toxic compound with an $\text{EC}_{50,30 \text{ min}} = 59 \text{ mg L}^{-1}$ for *V. fischeri*. Instead, 2,4-DCP, is more toxic than 2,4-D with an $\text{EC}_{50,30 \text{ min}} = 5 \text{ mg L}^{-1}$ determined by the Microtox bioassay.⁴¹

After 30 min of treatment, the percentage of inhibition decreased to 20%. Between 1 and 2 h of treatment, a slight rise in toxicity can be observed. It could be attributed to the accumulation of chlorinated oxidation intermediates. In this study, toxicity tends to decrease rapidly until 2 hours of treatment, when total dechlorination has been achieved. Then, the toxicity decreases gradually, following the TOC changes and reduces up to approximately 10% inhibition, confirming the capability of the UV/H₂O₂ process to detoxify the herbicide mixture. At the end of the process, nearly 76% of TOC removal was achieved. From these results, it can be concluded that it is not necessary to complete the mineralization of the mixture, because intermediate compounds present after 6 h of treatment have very low toxicity.

6 Model evaluation for the mixture of glyphosate and dicamba

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a widely used chlorobenzoic herbicide for controlling annual and perennial weeds in grain crops and highlands. This herbicide is frequently used in combination with glyphosate for increase in the control of weeds.

The kinetic model previously developed for the mixture of glyphosate and 2,4-D was applied for a new mixture (glyphosate and dicamba). Step 14 in Table 2 was replaced by the reaction of dicamba with $\cdot\text{OH}$ radicals:



where k_{14} is the kinetic constant to be obtained in this case (not reported in the literature). The experimental conditions (herbicide concentrations, H₂O₂ initial concentrations, radiation and initial pH) were similar to those used for the first mixture.

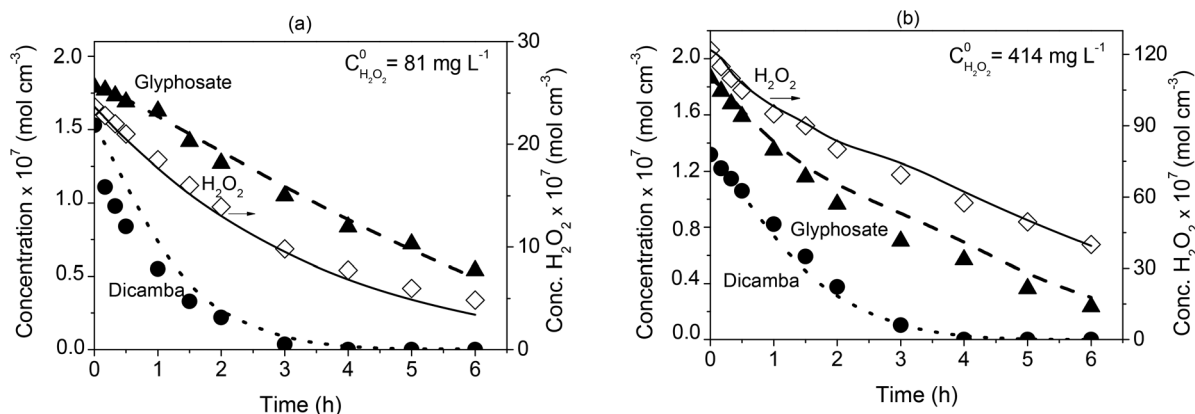


Fig. 6 Model prediction and experimental values. (▲) C_{GF} experimental, (---) C_{GF} model; (●) $C_{Dicamba}$ experimental, (....) $C_{Dicamba}$ model (◇) $C_{H_2O_2}$ experimental, $C_{H_2O_2}$ (—) model. $C_{GF}^0 = 30 \text{ mg L}^{-1}$; $C_{Dicamba}^0 = 30 \text{ mg L}^{-1}$; initial pH = 10.

The value of k_{14} was estimated following the same procedure explained in section 4:

$$k_{14} = (2.90 \pm 0.12) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}.$$

Fig. 6 is an example of the quality of the developed model for different hydrogen peroxide concentrations.

It can be seen that dicamba is completely degraded before 4 hours of treatment. Instead, for glyphosate, the decay rate was lower, presenting the same behavior as in the mixture with 2,4-D. This is because dicamba has a similar structure to 2,4-D, exhibiting an aromatic ring, and as mentioned before, higher degradation rates are found for these compounds.

Furthermore, these results showed that the proposed kinetic model successfully predicts the degradation of other mixtures of herbicides such as that of glyphosate and dicamba.

7. Conclusions

The proposed kinetic model showed a rather high accuracy in predicting the degradation of the mixture of glyphosate and 2,4-D, employing UV radiation and H_2O_2 . Simulation results of concentration evolutions of glyphosate, 2,4-D and H_2O_2 from the model are in good agreement with the experimental data under different operating conditions. The Microtox assays performed indicated that the toxicity of the mixture of glyphosate and 2,4-D was significantly reduced after the treatment. From this result, it can be concluded that it is not necessary to complete the mineralization of the mixture.

Moreover, the kinetic model allowed representing successfully the degradation of other mixtures of herbicides, such as glyphosate and dicamba. Therefore, the methodology developed in this work could be applied for representing the degradation kinetics of other mixtures of herbicides or pollutants. However, to widen the methodology to increasingly complex systems, it would be necessary to take into account additional characteristics that may appear in practical applications, not included in this work. For example, scavengers of hydroxyl rad-

icals, such as carbonate/bicarbonate ions, and the presence of NOM that can affect the degradation rate, and their effects must be considered in future works.

Notation

C	Concentration, mole L^{-1} (M)
e^a	Local volumetric rate of photon absorption (LVRPA), Einstein $cm^{-3} s^{-1}$
E	Spectral fluence rate, Einstein $s^{-1} cm^{-2}$
k	Kinetic constant, $M^{-1} s^{-1}$
K	Equilibrium constant, M
L	Length, cm
Q	Flow rate, $L min^{-1}$
R	Reaction rate, mole $L^{-1} s^{-1}$
t	Time, h
V	Volume, cm^3
X	Rectangular cartesian coordinate, cm

Greek letters

κ	Volumetric absorption coefficient, cm^{-1}
α	Molar Napierian absorption coefficient, $cm^{-2} mol^{-1}$
λ	Wavelength, nm
Φ	Primary quantum yield

Subscripts

GF	Relative to glyphosate
2,4-D	Relative to 2,4-D
Hom.	Relative to the homogeneous phase
i	Relative to species i
P	Relative to hydrogen peroxide
R	Denotes reactor volume
T	Denotes total reaction volume
Tk	Relative to tank
t	Time, h
w	Relative to the reactor wall

λ Relative to monochromatic radiation of wavelength λ

Superscripts

0 Relative to an initial condition

Special symbols

$\langle \rangle$ Average value over a defined space

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