

PAPER



Cite this: *Photochem. Photobiol. Sci.*, 2015, **14**, 366

Simplified reaction kinetics, models and experiments for glyphosate degradation in water by the UV/H₂O₂ process

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A simplified mathematical model to describe the oxidative degradation of glyphosate employing hydrogen peroxide and UV radiation was developed based on a sequence of predominant reactions. The kinetics obtained include all the required significant variables. Consequently, not only were concentration dependencies examined but also the influence of a detailed spatial description of the radiation field was included as part of the modeling. The kinetic parameters were obtained by comparing the simulation concentrations obtained with the model with the experimental values gathered in the laboratory reactor, employing a multiparameter non-linear regression analysis. In addition, the potential of the H₂O₂/UV process for treating water polluted with a commercial formulation, which was the glyphosate monoisopropylamine salt plus some additives, was studied. The glyphosate and TOC (total organic carbon) conversions reached were close to 80% and 70% respectively at 12 h (0.66 h actual exposure to radiation). It has been shown that a simple reaction scheme for the degradation of glyphosate acid and glyphosate isopropylamine salt from a commercial formulation can represent with good accuracy the performance of both reacting systems. In addition, the degradation procedure allowed a clear reduction of the toxicity of the glyphosate in the formulation over *Vibrio fischeri* at the end of the experiments. For this reason, reaching complete mineralization might not be necessary.

Received 8th July 2014,
Accepted 5th November 2014

DOI: 10.1039/c4pp00248b

www.rsc.org/pps

1. Introduction

Organophosphorus pesticides are widely used in agriculture. Glyphosate, *N*-(phosphonomethyl) glycine, is a highly effective broad-spectrum, post-emergence, non-selective herbicide. In recent years, its use has remarkably increased due to several factors: an increment in soy production using mainly GR (glyphosate resistant) soy seeds, and the surge of resistant brush, which made it necessary to apply larger doses of this herbicide. Additionally, prices have decreased because as a result of the original patent expiring, new suppliers have emerged on the market.

The countries with the highest production of soybeans are the USA, Brazil and Argentina. According to 2010 statistics, each one commercializes 90, 68, and 18 million tons of soybeans, respectively.¹ Because of the emergence of new demands led by China, international trade has substantially

increased and the soybean crop has accompanied this dramatic growth. This increase has directed a parallel jump on the use of glyphosate, which in countries such as Argentina, for example, a dramatic 18 000% increase from 1997 to 2007 was experienced.²

Due to its extensive use in agriculture, glyphosate has become a major pollutant and studies on its impact on the environment have emerged as it becomes more pertinent. Recent research has documented the environmental occurrence of glyphosate and aminomethylphosphonic acid (AMPA), the major metabolite of glyphosate, associated with use on crops,^{3–5} forests,^{6,7} railway tracks⁸ and even in urban environments.⁹ Glyphosate herbicide is highly soluble in water and it contaminates the environment from various sources, such as agricultural runoff and chemicals spills.^{10,11}

The disposal of pesticide wastewaters, equipment and container rinsates, products derived from fumigations carried out during harvesting, and empty plastic weed killer containers continue to be a problem in many countries. In some cases, disposal legislation is not fully accomplished on the excuse that there is a lack of availability of on-site, small scale, simple remediation technologies. As a result, in some important places of intensive use of glyphosate, only a small amount of this waste is currently treated. The improper disposal of

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such wastes can lead to soil, ground water and surface water contamination.¹²

Pesticide contamination derived from the procedures mentioned above is a potential candidate for the application of Advanced Oxidation Processes (AOPs). Some studies have dealt with the degradation of glyphosate in water using photocatalysis with TiO₂ and different forms of the system Fe(III)/H₂O₂/UV, as well as electrooxidation and ozonation.^{11,13–18}

It is well-known that most of the processes considered AOPs have advantages and disadvantages. Most of them, for example, are not cost effective, but some AOPs, such as O₃, H₂O₂/O₃ and H₂O₂/UV, are already being used for some, commercial applications at a large scale. For example, TROJAN UV® and Atlantic Ultraviolet® Corporation have successfully applied a H₂O₂/UV process in the treatment of polluted wastewaters. Therefore, it is interesting to compare this process with other AOPs already applied.

The oxidation of glyphosate acid (as the active ingredient) treated with the UV/H₂O₂ process was studied in a previous contribution by Manassero *et al.*¹⁹ In that work, the effects of the most significant operating variables on glyphosate degradation were studied. A detailed reaction scheme, according to the intermediates identified, representing the degradation reaction of glyphosate by H₂O₂ and UV irradiation was reported. At first, only very low concentrations of glycine were identified. Afterwards, nitrate and phosphate were found as the final by-products. Sarcosine and AMPA were not identified. On this basis, a “reduced reaction scheme” is proposed in the present work, with the aim of deriving a simpler but useful kinetic model, since it constitutes a good approximation for scaling-up purposes. This outcome results from the methodology used, in which the obtained kinetic constants are independent of the reactor size, shape, and configuration, even if only within the range of the studied operating variables.

It is interesting to note that the degradation of “commercial mixtures of glyphosate” has not been the focus of many research studies yet, according to the information available in the literature. Nevertheless, there should be no doubt that this is a substantial problem to address from an environmental point of view.²⁰ Therefore, the potential of the H₂O₂/UV process for treating water polluted with a commercial formulation is studied. In addition to this, the simplified kinetic model is used to reproduce the experimental data, and the toxicity during the photodegradation was evaluated employing the Microtox (*Vibrio fischeri*) acute toxicity test.

2. Experimental

2.1. Materials

The following reactants were used: (a) glyphosate (AccuStandard) as a chromatographic standard, (b) glyphosate acid 95% provided by Red Surcos, (c) commercial herbicide, 35.6% p/v as acid or 48% as glyphosate monoisopropylamine salt, (d) hydrogen peroxide (Ciccarelli p.a., >99%), (e) isopropylamine (Aldrich >99.5%) and (f) catalase from bovine liver >2000 units

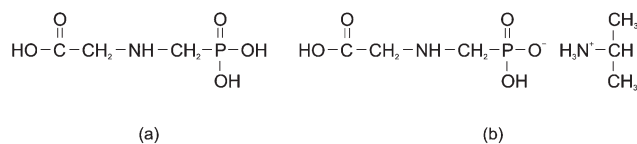


Fig. 1 Structure corresponding to (a) glyphosate acid and (b) glyphosate monoisopropylamine salt.

mg⁻¹ (Fluka, 1 unit decomposes 1 μmol H₂O₂ per minute at pH 7.0 and 25 °C). Purified water (0.055 μS cm⁻¹) was used in all experiments. This water was obtained from an OSMOION™ purification system.

The chemical structures of the glyphosate acid and of the glyphosate monoisopropylamine salt as the active ingredient are shown in Fig. 1.

2.2. Analysis

The following analyses were performed: H₂O₂ was analyzed with a spectrophotometric method at 350 nm according to Allen *et al.*²¹ employing a Cary 100 Bio UV-visible instrument. Glyphosate was analyzed by ion chromatography with a suppressed conductivity detector and employing an Ion Pac AG4A-SC guard column, an AS4A-SC separating column, and an ion self-regenerating suppressor (Alltech DS-Plus™). A solution of Na₂CO₃ (9 mM) and NaOH (4 mM) was used as eluent at a flow-rate of 1.5 ml min⁻¹.²²

Total organic carbon (TOC) was measured with a Shimadzu TOC-5000A analyzer. The toxicity evolution of the reacting mixture was assessed by the Microtox® acute toxicity test with *V. fischeri* using a Model 500 Analyzer (Strategic Diagnostics Inc.), according to the ASTM Standard Method D 5660-96.²³

2.3. Reactor, operating conditions and procedure

The reactor was a cylinder sealed with two flat, circular windows made of quartz ($V_R = 110 \text{ cm}^3$). Two tubular cylindrical lamps emitting radiation almost exclusively at 253.7 nm, placed at the focal axis of their respective custom-made cylindrical reflectors of parabolic cross section, provided the required irradiation. The reflectors were made of mirror polished aluminum, with Alzac® treatment provided by ALCOA. Different types of germicidal sources were used: (i) two Philips TUV lamps and (ii) two Heraeus UV-C lamps. Each window permitted to interpose: (1) a shutter to prevent irradiation, and (2) neutral density filters to vary the incident radiant power. The experimental set up also included a storage tank, a heat exchanger to control the temperature, and a high flow rate recirculating pump ($5 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1}$) to constitute a closed operating recycle system ($V_T = 2000 \text{ cm}^3$). Dissolved oxygen values ranged from 8.5 to 8.7 mg L⁻¹ for all experiments. Further details and the corresponding figures can be found in Zalazar *et al.*²⁴

The experiments were carried out at a natural pH (pH = 5.2) and the following variables were changed: (i) initial glyphosate concentration (30.4 to 150 mg a.e L⁻¹), (ii) initial hydrogen peroxide concentration (0 to 403 mg L⁻¹), and (iii) the incident

Table 1 Experimental program

Variable	Value
Glyphosate acid initial concentration	30.4 to 72.7 mg a.e L ⁻¹ (0.18 to 0.43 mM)
Glyphosate acid initial concentration (from commercial formulation)	50.0 to 150 mg a.e L ⁻¹ (0.30 to 0.89 mM)
Isopropylamine	50 to 60 mg L ⁻¹ (0.86 to 1.0 mM)
H ₂ O ₂ initial concentration	0 to 403 mg L ⁻¹ (0 to 11.8 mM)
Lamps: Almost monochromatic emission at 253.7 nm.	
Heraeus UV – C $\left\{ \begin{array}{l} \text{Input power (electrical)} \\ \text{Photon flux} \end{array} \right.$	40 W 16 W (3.4 × 10 ⁻⁵ einstein s ⁻¹)
Phillips TUV $\left\{ \begin{array}{l} \text{Input power (electrical)} \\ \text{Photon flux} \end{array} \right.$	15 W 3.5 W (7.4 × 10 ⁻⁶ einstein s ⁻¹)
Photon fluence rate at the reactor wall	($E_{\text{p,o,w}}$) × 10 ⁹
Heraeus lamp (100%), on amount basis	23.3 einstein cm ⁻² s ⁻¹
Philips lamp, on amount basis	10.4 einstein cm ⁻² s ⁻¹
Heraeus lamp (with neutral filter) (16%), on amount basis	4.2 einstein cm ⁻² s ⁻¹
Initial pH	5.2
Temperature	25 °C

photon fluence rate, ($E_{\text{p,o,w}}$) at the quartz windows (4.2 to 23.3 einstein cm⁻² s⁻¹) (measured with potassium ferrioxalate actinometry^{25–27}) (see Table 1). In order to make the comparison of the experimental data easier, all concentrations are expressed as milligrams of glyphosate acid equivalents per liter (mg a.e. L⁻¹). Each experiment was repeated twice. Significant differences between the obtained values were not found, so the averaged values were informed.

The following protocol was performed for each run: after switching on the lamps, they were allowed 30 min for stabilization. During this time, the shutters at the reactor windows were on to prevent the passage of light. The working solution was then added to the reactor. Immediately after, recirculation was established until the temperature reached a constant reading. The sample at $t = 0$ was taken when the lamp shutters were removed.

Samples were taken every 60 min for the previously described measurements. A typical run lasted 5 h for glyphosate acid, and 6 h for the commercial formulation. It must be noted that due to the type of experimental device configuration used in this work (a recycle with a tank) the irradiation time is not representative of the total reaction volume. Thus, for the actual exposure to radiation it must be taken into account the ratio given by $V_{\text{R}}/V_{\text{T}}$.

3. Mass balance

The mass balances corresponding to glyphosate, isopropylamine and hydrogen peroxide were established and solved in order to obtain the time evolution of the reactant concentrations. In order to accomplish a simple mathematical expression, it was necessary to make a number of assumptions to obtain theoretical simulations of the reaction evolution: (i) the whole system operates under well-stirred conditions; (ii) the ratio $V_{\text{R}}/V_{\text{T}}$ is $\ll 1$; (iii) the recirculating flow rate is high enough so as to have a differential conversion per pass in the photoreactor and, at the same time, to improve mixing; and

(iv) as shown previously,¹⁹ photolysis is neglected. Leaving aside the last one, the most critical assumption is number (iii), because if this condition is not fulfilled, the whole derivation becomes invalid. If the reaction is not too fast and the recirculating flow rate is high, it can be easily satisfied. Under these conditions, it can be seen that changes in concentration in the tank are related to the reaction rates according to eqn (1):²⁸

$$\left. \frac{dC_i(t)}{dt} \right|_{\text{Tank}} = \frac{V_{\text{R}}}{V_{\text{T}}} \langle R_{\text{Hom},i,\lambda}(x,t) \rangle_{V_{\text{R}}}; \quad i = \text{P, Gly, Isop} \quad (1)$$

with the initial condition that $C_i(t = 0) = C_{i,0}$, where C_i is the concentration of glyphosate, hydrogen peroxide or isopropylamine, t is the reaction time, V_{R} is the reactor volume, V_{T} is the total system volume and $R_{\text{Hom},i}$ is the homogeneous reaction rate.

4. The kinetic model

4.1. The simplified reaction scheme

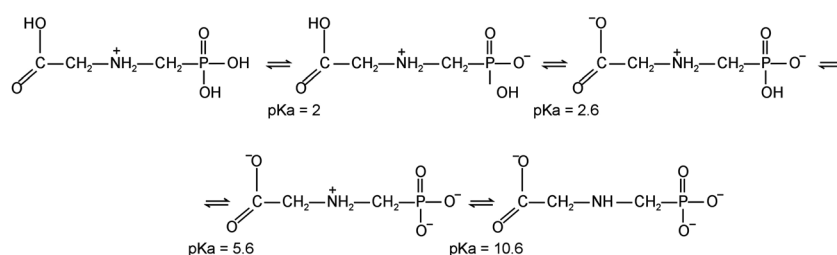
The kinetic model proposed for the degradation of glyphosate acid with H₂O₂/UV is based on the reaction scheme summarized in Table 2. At the working pH (pH = 5.2), the main reactions involving hydrogen peroxide and the free radicals resulting from its photolysis are represented by reactions 1–7.^{29,30} Fig. 2 shows the ionic structure of glyphosate as a function of pH.¹⁷ At a pH between 2.6 and 5.6 glyphosate has a hydroxyl group ionized and the amino group protonated (phosphonic –1, carboxylate –1, amino +1). Therefore, in the reaction scheme the major species considered is [–]O₂CCH₂N⁺HCH₂PO₃H[–]. Also at pH = 5.2, isopropylamine is present as isopropylammonium (C₃H₁₀N⁺).

Reaction 8 corresponds to the reaction of glyphosate acid with hydroxyl radicals, considering that the pathway *via* HO[•] radicals is the dominant reaction step for its oxidation. Likewise, reaction 9 corresponds to the decomposition of the monoisopropylammonium cation.

Table 2 Reaction scheme for the degradation of glyphosate^a

No	Steps	Reaction	Rate constant (M ⁻¹ s ⁻¹)
1		$\text{H}_2\text{O}_2 \xrightarrow{\Phi\nu} 2\cdot\text{OH}$	
2		$\text{H}_2\text{O}_2 + \cdot\text{OH} \xrightarrow{k_2} \text{HO}_2\cdot/\text{O}_2^{\cdot-} + \text{H}^+ + \text{H}_2\text{O}$	4.5×10^7 (i)
3		$\text{H}_2\text{O}_2 + \text{O}_2^{\cdot-} \xrightarrow{k_3} \cdot\text{OH} + \cdot\text{OH} + \text{O}_2$	0.130 (ii)
4		$2\cdot\text{OH} \xrightarrow{k_4} \text{H}_2\text{O}_2$	5.5×10^9 (iii)
5		$\cdot\text{OH} + \text{O}_2^{\cdot-} \xrightarrow{k_5} \cdot\text{OH} + \text{O}_2$	1.1×10^{10} (iv)
6		$\text{O}_2^{\cdot-} + \text{HO}_2\cdot \xrightarrow{k_6} \text{HO}_2^- + \text{O}_2$	6.6×10^9 (v)
7		$\text{HO}_2\cdot \rightleftharpoons \text{O}_2^{\cdot-} + \text{H}^+$	$K = 1.58 \times 10^{-5}$ M (vi)
8	Glyphosate acid:	$\cdot\text{O}_2\text{CCH}_2\text{N}^+\text{HCH}_2\text{PO}_3\text{H}^- + \cdot\text{OH} \xrightarrow{k_7} \text{products}$	
9	Monoisopropylamine:	$\text{C}_3\text{H}_{10}\text{N}^+ + \cdot\text{OH} \xrightarrow{k_8} \text{products}$	

^a (i) (iv) and (vi) taken from Kralik *et al.*,³¹ Kusic *et al.*,³² (ii) taken from Crittenden *et al.*,³³ (iii) taken from Buxton *et al.*,³⁴ and (v) from Schested *et al.*³⁵

**Fig. 2** Different forms of glyphosate as a function of pH.

Furthermore, it has been shown by Manassero *et al.*¹⁹ that the photolytic reaction of glyphosate acid at 254 nm is negligible. In addition to this, no glyphosate degradation was observed by Manassero *et al.*¹⁹ when they studied the effects of H_2O_2 when tested alone. The glyphosate monoisopropylamine salt has a similar behavior. (See section 7.1. Preliminary runs).

In this reaction scheme, we did not take into account all the reaction steps corresponding to the oxidation of different reaction intermediates with the $\text{HO}\cdot$ radical occurring throughout the pathway to the final products. Only the disappearance of the glyphosate acid (step 8) or the glyphosate monoisopropylamine salt (step 8 plus step 9) were considered for this work. This simplification is applicable to low levels of poor UV absorber contaminants. No interaction between the substrate oxidation byproducts and the reactants or with UV radiation is considered (only very low concentrations of glycine were identified by Manassero *et al.*¹⁹). Crittenden *et al.*³³ and Glaze *et al.*³⁶ have applied this approach successfully.

Simplified kinetic models can be derived from the law of mass action and the micro steady state approximation (MSSA) for unstable radicals. Steps 3, 4 and 6 have been assumed as negligible, compared with all the others in the proposed scheme. Indeed, reaction 3 has an extremely low rate constant and the steady-state concentration of the superoxide anion is very low.^{37,38} The recombination of hydroxyl radicals (a short lived intermediate) is undoubtedly negligible as long as there are organic compounds in the solution that trap the hydroxyl

radicals very efficiently. Reaction 7 (disproportionation of superoxide with its conjugated acid) is a very efficient reaction in aqueous solution, producing H_2O_2 ; but it does not contribute to the oxidative degradation of the pollutant, since both the superoxide and its conjugated acid are poorly reactive with organic matter under these conditions.^{39,40} The same assumptions were made in works about the degradation of different pollutants using the UV/ H_2O_2 process in order to obtain simplified kinetic models.^{28,41,42}

Irradiation can be assumed as monochromatic and consequently, the subscript λ may be omitted. The simplified rate equations resulting for the degradation of glyphosate acid, monoisopropylamine and hydrogen peroxide are shown below.

For glyphosate acid:

$$R_{\text{Gly}} = -k_7 C_{\cdot\text{OH}} C_{\text{Gly}} \quad (2)$$

For monoisopropylamine:

$$R_{\text{Gly}} = -k_8 C_{\cdot\text{OH}} C_{\text{Isop}} \quad (3)$$

For hydrogen peroxide:

$$R_{\text{P}} = -\Phi_{\text{P}} \epsilon_{\text{P}}^{\text{a}} - k_2 C_{\text{P}} C_{\cdot\text{OH}} \quad (4)$$

For the free radicals, it can be written:

$$R_{\text{O}_2^{\cdot-}} = k_2 C_{\text{P}} C_{\cdot\text{OH}} - k_5 C_{\cdot\text{OH}} C_{\text{O}_2^{\cdot-}} \quad (5)$$

$$R_{\cdot\text{OH}} = 2\Phi_P e_P^a - k_2 C_P C_{\cdot\text{OH}} - k_5 C_{\cdot\text{OH}} C_{\text{O}_2^-} - k_7 C_{\cdot\text{OH}} C_{\text{Gly}} - k_8 C_{\cdot\text{OH}} C_{\text{Isop}} \quad (6)$$

Taking into account the MSSA, from eqn (5) and (6):

$$C_{\text{O}_2^-} = \frac{k_2 C_P}{k_5} \quad (7)$$

and

$$C_{\cdot\text{OH}} = \frac{2\Phi_P e_P^a}{k_2 C_P + k_7 C_{\text{Gly}} + k_8 C_{\text{Isop}}} \quad (8)$$

The reaction rates results:

$$R_{\text{Gly}} = -\frac{2\Phi_P e_P^a}{\frac{2k_2 C_P}{k_7 C_{\text{Gly}}} + \frac{k_8 C_{\text{Isop}}}{k_7 C_{\text{Gly}}} + 1} \quad (9)$$

$$R_{\text{Isop}} = -\frac{2\Phi_P e_P^a}{1 + \frac{2k_2 C_P}{k_8 C_{\text{Isop}}} + \frac{k_7 C_{\text{Gly}}}{k_8 C_{\text{Isop}}}} \quad (10)$$

$$R_P = -\Phi_P e_P^a - \frac{2\Phi_P e_P^a}{2 + \frac{k_7 C_{\text{Gly}}}{k_2 C_P} + \frac{k_8 C_{\text{Isop}}}{k_2 C_P}} \quad (11)$$

In these equations, Φ_P is the primary quantum yield and e_P^a is the local volumetric rate of photon absorption (LVRPA) also called absorbed local spectral photon flux density (L_P^a). The quantum yield Φ_P and the kinetic constants (k_7 and k_8) are the constants to be determined. The radiation intensity effect was calculated by solving the radiation balance in the experimental reactor as shown below.

Note that when only the glyphosate acid is present, the corresponding kinetic model can be obtained by eliminating step 9 (the monoisopropylamine reaction with hydroxyl radicals). The reaction rates corresponding to the kinetic models for glyphosate acid and glyphosate monoisopropylamine salt are summarized in Table 3.

Table 3 Mathematical expressions for the reactions rates for the different kinetic models

Kinetic models	
Glyphosate acid	Glyphosate monoisopropylamine salt
$R_{\text{Gly}} = -\frac{2\Phi_P e_P^a}{\frac{2k_2 C_P}{k_7 C_{\text{Gly}}} + 1}$	$R_{\text{Gly}} = -\frac{2\Phi_P e_P^a}{\frac{2k_2 C_P}{k_7 C_{\text{Gly}}} + \frac{k_8 C_{\text{Isop}}}{k_7 C_{\text{Gly}}} + 1}$
$R_P = -\Phi_P e_P^a - \frac{2\Phi_P e_P^a}{2 + \frac{k_7 C_{\text{Gly}}}{k_2 C_P}}$	$R_{\text{Isop}} = -\frac{2\Phi_P e_P^a}{1 + \frac{2k_2 C_P}{k_8 C_{\text{Isop}}} + \frac{k_7 C_{\text{Gly}}}{k_8 C_{\text{Isop}}}}$
	$R_P = -\Phi_P e_P^a - \frac{2\Phi_P e_P^a}{2 + \frac{k_7 C_{\text{Gly}}}{k_2 C_P} + \frac{k_8 C_{\text{Isop}}}{k_2 C_P}}$

4.2. The radiation balance

For the one-dimensional radiation field that is applicable to our experimental device, the final equation for the LVRPA takes the following form:²⁸

$$e_P^a(x, t) = \alpha_{P,\lambda} E_{P,\lambda,W} \{ \exp[-\alpha_{P,\lambda}(t)x] + \exp[-\alpha_{P,\lambda}(t)(L_R - x)] \} \quad (12)$$

Eqn (12) includes the assumption that only hydrogen peroxide absorbs radiation. The linearity of the value of $\alpha_{P,\lambda}$ at 254 nm as a function of H_2O_2 concentration was verified spectrophotometrically and compared with values frequently reported in the literature.⁴³ Thus, for low H_2O_2 concentrations, the absorption coefficient is obtained from the value of the molar napierian absorption coefficient ($\kappa_{P,\lambda}$) by applying Beer's equation ($\alpha_{P,\lambda} = \kappa_{P,\lambda} C_P$). The result for this work is $\kappa_{P,\lambda} = 0.389 \times 105 \text{ cm}^2 \text{ mol}^{-1}$.

Eqn (12) gives local values of $[e_P^a(x, t)]$, in this case, in einstein $\text{cm}^{-3} \text{ s}^{-1}$. The experimental values of the rates obtained by measuring averaged concentrations must be compared with the averaged values of the kinetic expressions of the model [eqn (9)–(11)]. With the perfect mixing assumption, the only variable that is a function of position is $e_P^a(x, t)$. With the one-dimensional model, the expression to compute the LVRPA or the absorbed spectral photon radiance ($[L_{P,\lambda}^a(x, t)]_{V_R}$) averaged over the volume of reactor is:

$$\langle L_{P,\lambda}^a(x, t) \rangle_{V_R} = \langle e_P^a(x, t) \rangle_{V_R} = \frac{2E_{P,\lambda,o,W}}{L_R} \{ 1 - \exp[-\alpha_{P,\lambda}(t)L_R] \} \quad (13)$$

where $E_{P,\lambda,o,W}$ is the fluence rate at the reactor wall and α_P is the hydrogen peroxide linear napierian absorption coefficient. The boundary condition $E_{P,\lambda,o,W}$ was evaluated using actinometer measurements using potassium ferrioxalate, and following the experimental procedure suggested by Kuhn *et al.*²⁵ and the mathematical interpretation of the data derived by Zalazar *et al.*²⁷ The results are shown in Table 1.

4.3. Final equations

Substituting the reaction rate for the stable species given in Table 3 into eqn (1) and introducing $r = C_P(t)/C_{\text{Gly}}(t)$, finally results in:

for glyphosate acid:

$$\frac{d\langle C_{\text{Gly}}(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\frac{2\Phi_P e_P^a(x, t)}{1 + 2\left(\frac{k_2}{k_7}\right)r} \right\rangle_{L_R} \quad (14)$$

$$\frac{d\langle C_P(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\Phi_P e_P^a - \frac{2\Phi_P e_P^a(x, t)}{2 + \frac{k_7}{k_2} \frac{1}{r}} \right\rangle_{L_R} \quad (15)$$

For glyphosate monoisopropylamine salt:

$$\frac{d\langle C_{\text{Gly}}(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\frac{2\Phi_P e_P^a(x, t)}{1 + 2\left(\frac{k_2}{k_7}\right)r + \frac{k_8 C_{\text{Isop}}}{k_7 C_{\text{Gly}}}} \right\rangle_{L_R} \quad (16)$$

$$\frac{d\langle C_{\text{Isop}}(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\frac{2\Phi_P e_P^a(x, t)}{1 + \frac{2k_2 C_P}{k_8 C_{\text{Isop}}} + \frac{k_7 C_{\text{Gly}}}{k_8 C_{\text{Isop}}}} \right\rangle_{L_R} \quad (17)$$

$$\frac{d\langle C_P(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\Phi_P e_P^a - \frac{2\Phi_P e_P^a}{2 + \frac{k_7 C_{\text{Gly}}}{k_2 C_P} + \frac{k_8 C_{\text{Isop}}}{k_2 C_P}} \right\rangle_{L_R} \quad (18)$$

5. Model simulation and experimental results for N-(phosphonomethyl) glycine

The experimental data obtained for N-(phosphonomethyl) glycine or glyphosate acid were qualitatively discussed by Manassero *et al.*¹⁹ and those results will be employed here to validate the kinetic model proposed. Eqn (14) and (15) constitute one system of ordinary differential equations solved by the Runge-Kutta method. The solution of the mathematical system of equations, in fact, constitutes the result of the computer simulation of the model employing the estimated parameters. However, the parameters are still unknown. Therefore, the solution of the system of differential equations must be used together with the experimental information to obtain those

values, resorting to a suitable system of non-linear multi-parameter estimation tool, supported by an optimization program. Thus, the experimental data, the differential equations and the reliable value of the known kinetic constant k_2 ³⁴ can be incorporated into a non-linear multiparameter regression program employing the Levenberg-Marquardt optimization algorithm.^{44,45} The operation is performed by minimizing the sum of the squares of the differences between the experimental and the calculated values of the concentrations. The primary quantum yield Φ_P and the rate constant k_7 were obtained and the results, with a 95% confidence interval, are shown in Table 4.

The kinetic constant k_7 corresponds to the attack of glyphosate acid by the hydroxyl radical, and it was obtained at the working pH (5.2) (see Table 2). The kinetic constant available from bibliography is significantly different but it is important to mention that this constant was obtained with a different process at a different pH value.⁴⁷

The experimental data can be compared with theoretical predictions from the reactor-reaction kinetic model. Fig. 3 is

Table 4 Estimated parameter model for glyphosate acid and published values

Parameter	Estimated value	Reported value
Φ_P	0.42 ± 0.01	$0.5^{29,46}$
$k_7/(\text{cm}^3 \text{mol}^{-1} \text{s}^{-1})$	$(3.37 \pm 0.10) \times 10^{10}$	1.8×10^{11} ⁴⁷

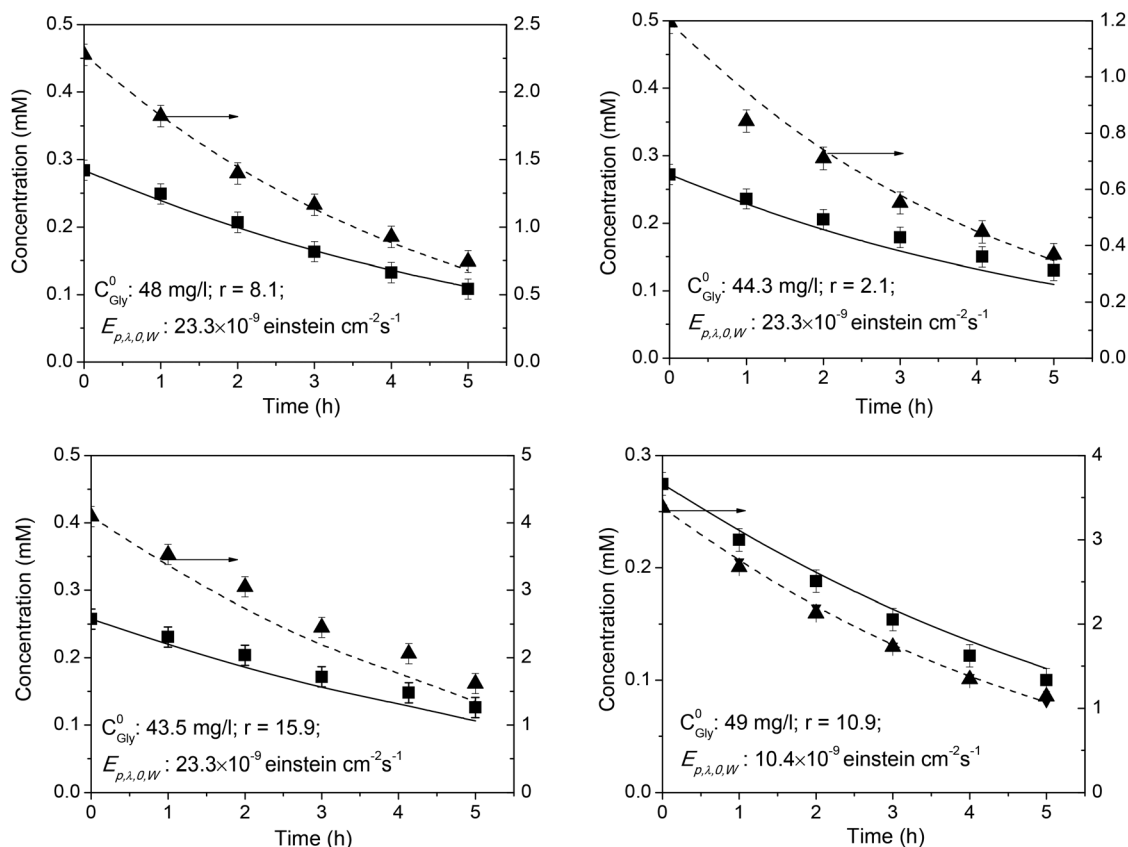


Fig. 3 Glyphosate acid degradation with UV/H₂O₂: simulation results vs. experimental values. ■ Gly experimental, — Gly Model, ▲ H₂O₂ experimental, --- H₂O₂ Model, (r is the initial molar ratio: $r = C_P/C_{\text{Gly}}$).

an example of the quality of the developed kinetic model when it is compared with the experimental results. The relative mean squared error (RMSE) between experimental data and theoretical predictions for both compounds (glyphosate and hydrogen peroxide) were calculated taking into account all the runs performed. The % RMSE was 13% and 11% for glyphosate and hydrogen peroxide respectively.

It is interesting to note that these results include experimental data from different initial concentrations of hydrogen peroxide and glyphosate and from different levels of photon fluence rates at the reactor windows.

6. Model simulation and experimental results for isopropylamine

In order to obtain the solution corresponding to the system of ordinary differential equations for glyphosate isopropylamine salt, eqn (16)–(18), it is necessary to know the rate constants k_7 and k_8 . The constant k_7 has been already calculated but it is necessary to obtain the rate constant k_8 (not available in the literature). This constant can be obtained by performing degradation experiments for isopropylamine alone using the UV/ H_2O_2 process, employing the same reactor and the same experimental procedures described before.

In this case, the system of ordinary equations used included eqn (17) and (18) with the glyphosate concentration equal to zero, resulting in eqn (19) and (20):

$$\frac{d\langle C_{\text{Isop}}(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\frac{2\Phi_P e_P^a(x, t)}{1 + \frac{2k_2 C_P}{k_8 C_{\text{Isop}}}} \right\rangle_{L_R} \quad (19)$$

$$\frac{d\langle C_P(x, t) \rangle_{V_R}}{dt} = \frac{V_R}{V_T} \left\langle -\Phi_P e_P^a - \frac{2\Phi_P e_P^a}{2 + \frac{k_8 C_{\text{Isop}}}{k_2 C_P}} \right\rangle_{L_R} \quad (20)$$

Following the same procedure explained in section 5, the constant k_8 was obtained: $(8.99 \pm 0.14) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Fig. 4 is an example of the results obtained from the simplified

model applied to this new reaction system. The % RMSE was 20% and 19% for isopropylamine and hydrogen peroxide, respectively.

7. Model simulation and experimental results for glyphosate isopropylamine salt (commercial formulation)

7.1. Preliminary runs

Two types of the previous experiments were carried out in order to investigate the effects of UV and H_2O_2 separately. After 4 h total reaction time, no noticeable changes in glyphosate concentration were observed. These results confirm those previously obtained by Manassero *et al.*¹⁹ with glyphosate acid tested alone.

7.2. Effects of initial H_2O_2 concentration

As it is already known, there is an optimum concentration of H_2O_2 to carry out the UV/ H_2O_2 reaction.^{30,33,48,49} When the concentration of H_2O_2 is too low, since its radiation absorption coefficient at 253.7 nm is very low, the reaction rate and, more specifically, the rate of the initial step of the H_2O_2 decomposition is extremely slow. But on the other hand, the H_2O_2 is a scavenger of hydroxyl radicals competing with the pollutant degradation reaction and decreasing the rate of the latter (step 2 competes with steps 8 and 9, see Table 2). The dominant pathway depends on the reaction rates, *i.e.* on the concentrations of the other scavengers and on the corresponding rate constants. Because of this phenomenon, unless the information on the optimal ratio is available in the literature, the most favorable concentration, which has important economic implications, usually has to be determined experimentally for each particular case.

The results, examined for a fixed total reaction interval of 5 h (corresponding to an effective irradiation time of 16.5 min) were analyzed in terms of the corresponding final glyphosate

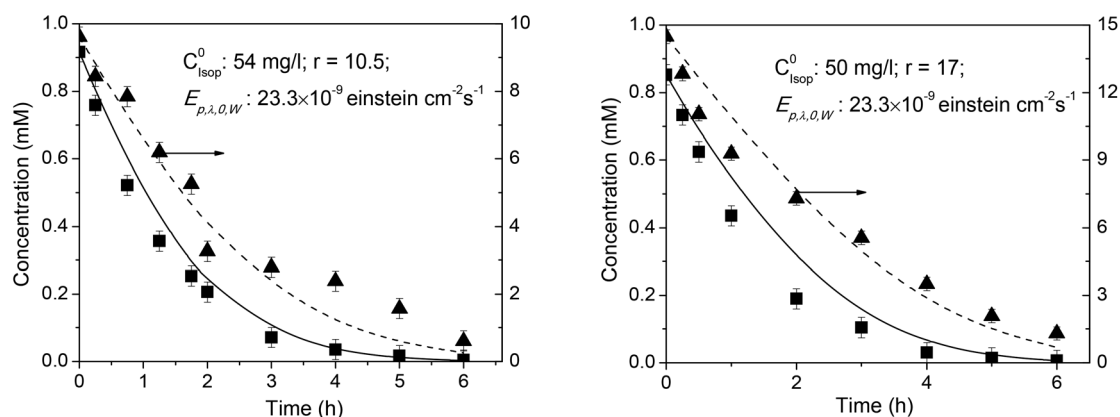


Fig. 4 Isopropylamine degradation with UV/ H_2O_2 : simulation results vs. experimental values. ■ Isopropylamine experimental, — Isopropylamine Model, ▲ H_2O_2 experimental, --- H_2O_2 Model, (r is the initial molar ratio: $r = C_P/C_{\text{Isop}}$).

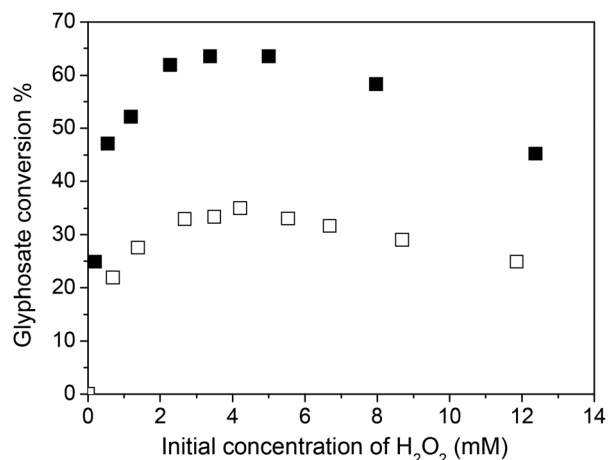


Fig. 5 Glyphosate conversion vs. initial concentration of H₂O₂. $C_{\text{Gly}}^0 = 50 \text{ mg a.e. L}^{-1}$; pH = 5.2; $E_{\text{p.o.w}} = 23.3 \times 10^{-9} \text{ einstein cm}^{-2} \text{ s}^{-1}$; reaction time = 5 h. ■ Glyphosate acid, □ glyphosate monoisopropylamine salt (commercial formulation).

conversion for the commercial formulation (having as a main component the glyphosate monoisopropylamine salt) and for the glyphosate acid previously studied by Manassero *et al.*¹⁹ (Fig. 5). The concentration range between 100–230 mg L⁻¹ produces the highest conversions: 65% and 36% for glyphosate acid and glyphosate monoisopropylamine salt, respectively. This difference is essentially due to the cation of the monoisopropylamine salt, which can be also oxidized by hydroxyl radicals as it was proposed in the degradation scheme (Table 2). Notice that glyphosate monoisopropylamine salt contains three more carbon atoms than glyphosate acid alone. They will also participate in the competition for the attack of [•]OH radicals, which will result in a more complex mixture of oxidation intermediates.

It is important to bear in mind that in this work two solutions of “glyphosate” were used; a solution of glyphosate acid (see Fig. 1a), and a solution of a commercial formulation consisting of the monoisopropylamine salt (see Fig. 1b) plus other additives that are not specified by the provider. Fig. 5 compares the results obtained from both solutions. As can be seen in the figure, both curves have the same form. In fact, in the case of the salt, the cation competes with the moiety of glyphosate for scavenging the hydroxyl radicals, slowing down glyphosate oxidation, independently of the initial concentration of H₂O₂. Nevertheless, the optimal concentration of the latter remains unchanged compared to the glyphosate acid. This can be explained by the fact that hydroxyl radicals are reactive but not selective species and the initial concentration of the cation is of course always equal to the concentration of the moiety of glyphosate. It could be considered that the rest of the compounds that form the commercially formulated solution do not have a great influence on the kinetics of the reaction studied in this paper.

From this information, it is possible to verify the importance of the contribution to the TOC that results from the presence of the additives in the corresponding solution of the

mixture. It was found by difference, because the concentration of the glyphosate acid is always well-known, that its contribution to the TOC is lower than 1 mg L⁻¹. This very low value is at least partially linked to the concentrations of the additives present, and it is an additional contribution to explain the absence of significant differences in the kinetic behavior found in both cases.

Summarizing, the fact that the two curves shown in Fig. 5 present the same “shape” is indeed significant. It shows that all organic compounds contained in the reaction system present approximately the same reactivity towards hydroxyl radicals. The shape of the curves is therefore, in a first approximation, dependent only on the concentration of hydrogen peroxide and, consequently, on the availability of hydroxyl radicals for the oxidation of the substrates and their subsequent intermediates in the scheme proposed for oxidative degradation.

7.3. Experimental runs for an extended reaction time. Mineralization and toxicity evaluation

For an extended degradation time under the best operating conditions for the formulation degradation, Fig. 6 shows the temporal progression of the participating species concentrations. The initial pH was 5.2 and this value did not change significantly during the process. The glyphosate and TOC conversions reached were 76% and 68% in 12 h respectively.

The changes in the toxicity of the treated solution for *V. fischeri* are shown in Fig. 6. The toxicity of the samples is represented by the percentage inhibition of the natural bioluminescence of *V. fischeri*. The sample at time $t = 0$ causes an inhibitory effect of almost 50%. A slight rise in toxicity is observed at approximately 4 h reaction time. Nevertheless, as the treatment progresses, the toxicity diminishes. At the end of the photodegradation, inhibition was reduced to 32%. It is important to mention that according to the toxicity categories established in the EU legislation, glyphosate is harmful to

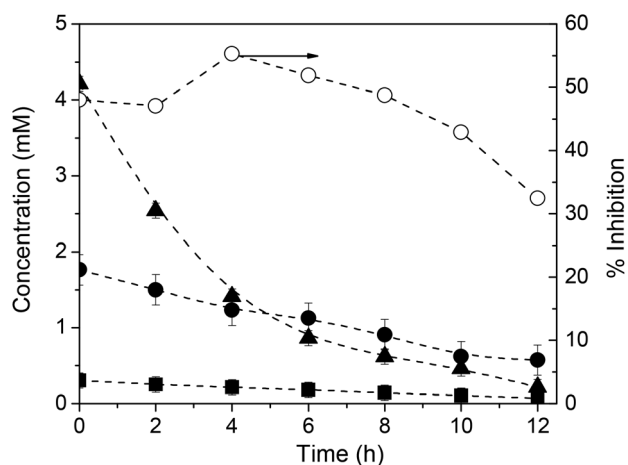


Fig. 6 Degradation of glyphosate monoisopropylamine salt (commercial formulation). Evolution of glyphosate (■), H₂O₂ (▲), TOC (●) and toxicity (○) % inhibition *Vibrio fischeri*. $C_{\text{Gly}}^0 = 50 \text{ mg a.e. L}^{-1}$, $C_{\text{H}_2\text{O}_2}^0 = 140 \text{ mg L}^{-1}$.

V. fischeri (EC_{50} , 30 min = 44.2 mg L⁻¹) where the EC_{50} is the effective concentration of a chemical that causes a 50% reduction in the bioluminescence of the bacteria.⁵⁰

Notably, nearly 30% of the initial TOC content of the sample remains after 12 h, which corresponds to a glyphosate concentration of 12 a.e. mg L⁻¹.

In addition to this, Junges *et al.*⁵¹ used ecotoxicity assays employing *V. fischeri* and *Rhinella arenarum* tadpoles to show that the concentration of 11 ± 1 mg a.e. L⁻¹ glyphosate from the Eskoba® commercial formulation could be used as a final point for glyphosate treatment with the UV/H₂O₂ process. However, the toxicity to *V. fischeri* can be reduced further (17% inhibition) if a concentration of 4 ± 1 mg a.e. L⁻¹ glyphosate is reached.⁵¹

7.4. Comparison of model simulation and experiments for glyphosate isopropylamine salt (commercial formulation)

The set of experimental data described in Table 1 was used to evaluate the quality of the mathematical model (represented by the system of ordinary differential equations for glyphosate isopropylamine, eqn (16)–(18) with the rate constants previously determined, k_7 and k_8).

Fig. 7 shows that, in this case, the developed kinetic model is also valid for the glyphosate monoisopropylamine salt degradation. The % RMSE was 12% and 18% for glyphosate

and hydrogen peroxide respectively. In spite of this, the model predicts a greater disappearance of glyphosate in the cases $r = 2.3$ and 39.2. The difference could be due to the low conversions reached in these cases (23% and 30% respectively).

8. Comparison of various AOPs

It is very difficult to compare processes using experimental values obtained from studies carried out under different operating conditions (for example, different pH values). Nevertheless, the comparison could bring some useful semi-quantitative estimates that may be helpful to evaluate the relative efficiency of different technologies. A few research publications presented the half-life data obtained from glyphosate degradation employing different AOPs. In Assalin *et al.*¹⁴ ozonation at pH 6.5 and 10, photolysis and heterogeneous photocatalysis using TiO₂ were applied to study the degradation of this pollutant in water. The half-lives for glyphosate degradation were 1.8 and 6.2 minutes for O₃/pH 10 and TiO₂/UV, respectively. In another study, titania nanotubes doped with cerium were used to test the photocatalytic activity for glyphosate degradation in water. From the data published in this work, it is possible to calculate that a half-life of approximately 20 min⁵² was obtained.

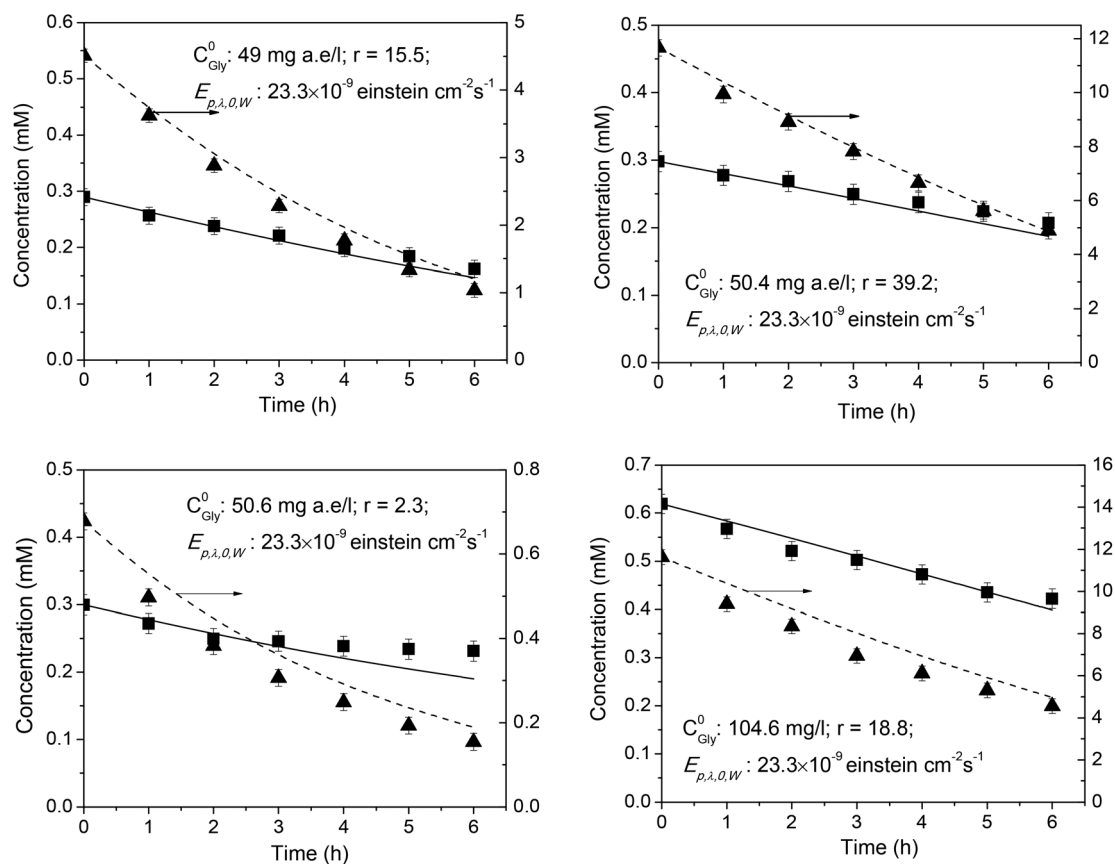


Fig. 7 Glyphosate monoisopropylamine salt degradation with UV/H₂O₂: simulation results vs. experimental values, ■ Gly experimental, — Gly Model, ▲ H₂O₂ experimental, --- H₂O₂ model, (r is the initial molar ratio, $r = C_P/C_{Gly}$).

For the UV/H₂O₂ process utilized in this work, a half-life value of 11.4 min¹⁹ was calculated. This time is larger than some of those previously mentioned, but the equipment cost of ozonation and the operating difficulties of photocatalysis, compared with UV/peroxide should be taken into account. In addition, it is important to mention that AMPA, a metabolite more persistent than glyphosate, was not found when the UV/H₂O₂ process was adopted.¹⁹

9. Conclusions

It has been shown that a simple reaction scheme for the degradation of glyphosate acid and glyphosate isopropylamine salt from a commercial formulation can represent the performance of both reacting systems accurately. Considering the methodology employed to obtain these results, the kinetic expressions derived throughout this work are valid for any reactor configuration.

Additionally, it has been shown that the combination of hydrogen peroxide and UV radiation may become a suitable and very simple process for treating wastewater originating from glyphosate commercial formulations. Consequently, it can be concluded that this process may be effective in treating equipment rinsates or diluted unused products, such as wastewaters resulting from rinsing herbicide containers.

However, in practical applications, there are additional factors that should be taken into account. For example, the presence of organic matter or some inorganic salts in water, not included in this experiments, can produce important changes in the reaction environment and their effects must be considered in future works.

Notation

C	Concentration, mol cm ⁻³
$e^a = L_p^a$	Local volumetric rate of photon absorption or absorbed local radiance, einstein cm ⁻³ s ⁻¹
$E_{p,\lambda,o,w}$	Spectral fluence rate at the reactor windows, einstein s ⁻¹ cm ⁻²
K	Kinetic constant, units depend on the reaction step
L	Length, cm
P	Hydrogen peroxide
R	Reaction rate, mol s ⁻¹ cm ⁻³
R	Molar concentration ratio
T	Time, s
V	Volume, cm ³
X	Rectangular Cartesian coordinate, cm

Greek letters

K	Molar napierian absorption coefficient, cm ² mol ⁻¹
A	Linear napierian absorption coefficient, cm ⁻¹
λ	Wavelength, nm
Φ	Primary quantum yield, mol einstein ⁻¹

Subscripts

Gly	Relative to glyphosate
Hom.	Relative to homogeneous phase
I	Relative to species i
Isop	Relative to isopropylamine
P	Relative to hydrogen peroxide
R	Denotes reactor volume
T	Denotes total reaction volume
T	Time, s
W	Relative to the wall
λ	Relative to monochromatic radiation of wavelength λ

Superscripts

0	Relative to an initial condition
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Special symbols

$\langle \rangle$	Means average value over a defined space
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Acknowledgements

Thanks are given to Universidad Nacional del Litoral, Consejo Nacional de Investigaciones Científicas (CONICET) and Agencia Nacional de Promoción Científica y Tecnológica for the financial support. We would like to thank Silvana Neder for her help in part of the experimental work. Also to Margarita Herman for the English language editing. The technical assistance of Eng. Claudia Romani is gratefully appreciated.

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