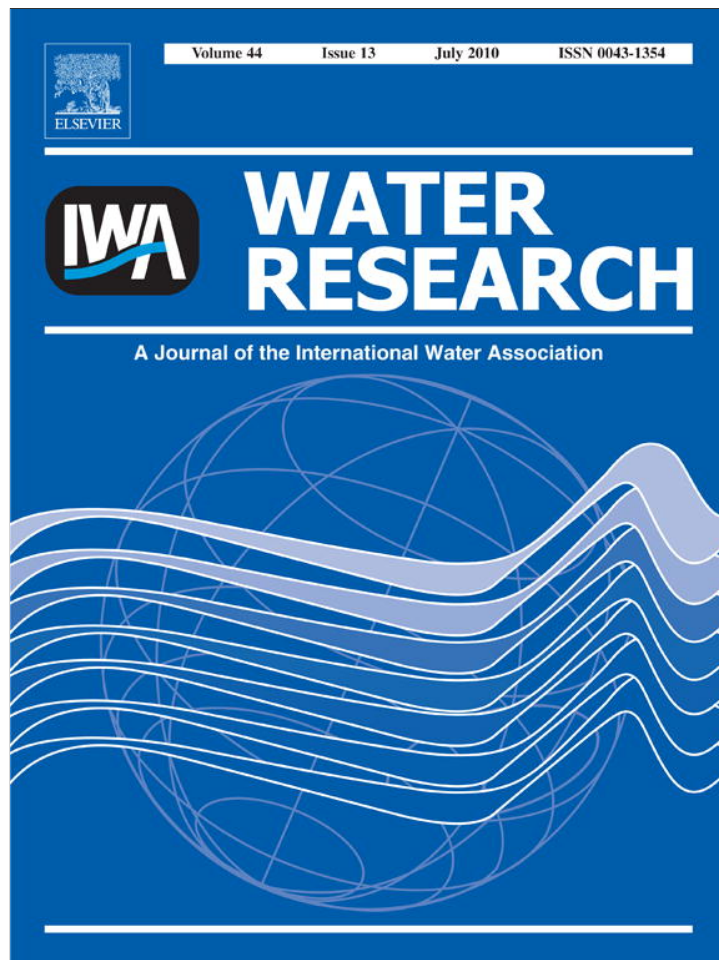


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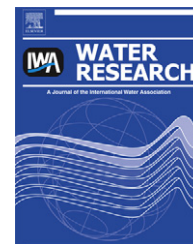


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Glyphosate degradation in water employing the H₂O₂/UVC process

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ABSTRACT

Glyphosate is the organophosphate herbicide most widely used in the world. Any form of spill or discharge, even if unintentional, can be transferred to the water due to its high solubility. The combination of hydrogen peroxide and UV radiation could be a suitable option to decrease glyphosate concentration to acceptable limits. In this work, the effects of initial pH, hydrogen peroxide initial concentration, and incident radiation in glyphosate degradation were studied. The experimental device was a cylinder irradiated with two tubular, germicidal lamps. Conversion of glyphosate increases significantly from pH = 3–7. From this value on, the increase becomes much less noticeable. The reaction rate depends on the initial herbicide concentration and has an optimum plateau of a hydrogen peroxide to glyphosate molar concentration ratio between 7 and 19. The expected non linear dependence on the irradiation rate was observed. The identification of critical reaction intermediaries, and the quantification of the main end products were possible and it led to propose a plausible degradation path. The achieved quantification of the mineralization extent is a positive indicator for the possible application of a rather simple technology for an *in situ* solution for some of the problems derived from the intensive use of glyphosate.

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1. Introduction

Glyphosate (N-phosphonomethyl glycine) is a non-selective, post-emergence, broad-spectrum organophosphate herbicide. It is the active ingredient in herbicides and it is the most widely used in the world (Baylis, 2000; Woodburn, 2000; Shifu and Yunzhang, 2007).

Less than 0.1% of the chemicals applied for pest control reach their target. Thus, more than 99.9% of these substances, when used, move into the environment and contaminate soil, water and the atmosphere of the ecosystem (Pimentel, 1995). Under these conditions, there is no certainty that the rest is, currently, completely annihilated.

The worldwide increase in soy production, in many cases employing glyphosate-resistant (GR) soy, has been

accompanied by an increase in the use of this weed suppressor. In Argentina, for example, the glyphosate consumption increased from 1 million liters in 1991 to 180 million in 2007 (Binimelis et al., 2009). Its impact on the environment is becoming more noticeable. A widespread example is the disposal of herbicide wastes, such as those originated from empty pesticide containers that have not been properly washed. It still remains as an unsolved problem in many countries. The improper disposal of such wastes can lead to soil, ground water and surface water contamination (Huston and Pignatello, 1999).

There is a wide controversy about the importance of the effects of the changes in agricultural practices on the environment. Many manufactures and other existing reports claim that the use of glyphosate is safe for the environment, like the extensive review by Williams et al. (2000) in collaboration with

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Monsanto and the USEPA (1993). But, several studies have shown no definitive data (Bradberry et al., 2004; Botta et al., 2009), and other studies have shown that glyphosate, whether alone or mixed with the additives used in commercial formulations, may damage aquatic biota. A recent study has showed that glyphosate may affect phytoplankton and periphyton community composition. Therefore it is quite likely that current agricultural practices may alter the structure and function of many natural aquatic environments (Pérez et al., 2007). A similar work has been carried out to evaluate the genotoxic potential of the herbicide formulation of Roundup® (glyphosate) on erythrocytes of broad-snouted caiman (*Caiman latirostris*) after *in ovo* exposure. This research has demonstrated its adverse effects on DNA of *C. latirostris* (Polleta et al., 2009). Lajmanovich et al. (2003) has shown that glyphosate formulations can affect native populations of neotropical tadpoles. The above mentioned researches are relevant to this work, as the region studied is an area of intensive production of genetically modified soy, in a country (Argentina) that is the second largest consumer of Roundup in the world (Binimelis et al., 2009).

Advanced Oxidation Technologies (AOTs) seem to be potential options to reduce glyphosate concentration to acceptable limits. The major active species in such systems is the hydroxyl radical ($\cdot\text{OH}$), which is strongly oxidative (2.8 V oxidation potential) and many compounds are potentially mineralized to CO_2 , H_2O and to inorganic ions (Malato et al., 2000).

There are some studies which deal with the degradation of glyphosate in water with AOTs. These studies may include photocatalysis with TiO_2 as well as the different forms of the system $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$ (Chen et al., 2007; Shifu and Yunzhang, 2007; Muneer and Boxall, 2008; Echavia et al., 2009). In these works, it has been shown the efficiency of these processes to degrade this herbicide. The combination of hydrogen peroxide and UV radiation ($\text{H}_2\text{O}_2/\text{UV}$) could be a simple and convenient process for the treatment of this type of pollutants. However, the degradation of glyphosate by this method has been seldom investigated (Ikehata and Gama El-Din, 2006). In this work the effects of hydrogen peroxide initial concentration, initial pH, and irradiation rates in the glyphosate degradation in water were studied. In addition to this, the extent of mineralization was quantified and the main reaction intermediaries were identified as well as the oxidation end products. All this information led us to suggest a tentative, feasible reaction pathway to the glyphosate degradation in water.

2. Experimental section

2.1. Chemicals

The following reagents were used: (a) glyphosate (AccuStandard) as standard chromatographic, (b) glyphosate 95% provided by Red Surcos, (c) hydrogen peroxide (Ciccarelli p.a., >99%), (d) sarcosine ($\geq 97.5\%$, Sigma–Aldrich), (e) glycine (97.3%, Merck), (f) aminomethylphosphonic acid, AMPA ($\geq 99\%$, Sigma–Aldrich), (g) formic acid (98–100%, Merck), (h) acetic acid (100%, Merck), (i) glycolic acid (solution 70% in water, Merck) and (j) catalase from bovine liver, >2000 units/mg (Fluka, 1 unit decomposes 1 μmol H_2O_2 per minute at pH 7.0 and 25 °C). Ultra pure water (0.055 $\mu\text{S}/\text{cm}$) was used in all experiments. This

water was obtained from an OSMOION™ purification system made of several filters to eliminate particulate matter, chlorinated compounds, and low molecular weight organic substances. Two reverse osmosis membranes and an ion exchange resin completed the equipment.

2.2. Experimental setups and procedures

The photodegradation of glyphosate was carried out in a cylindrical reactor made of Teflon™, with two parallel, flat windows made of quartz ($V_{\text{Reactor}} = 110 \text{ cm}^3$). Each window was irradiated with a tubular, germicidal lamp ($\lambda = 253.7 \text{ nm}$) placed at the focal axis of a parabolic reflector made of mirror finished aluminum. The small reactor operates in the loop of a batch recycling system that includes a pump, a heat exchanger (for temperature control) and a large volume, well stirred tank with provisions for sampling, temperature control and pH measurements ($V_{\text{Total}} = 2000 \text{ cm}^3$). Further details on the experimental device can be found in Zalazar et al. (2007).

Experiments were carried out changing the following variables: (i) initial glyphosate concentrations, (ii) initial hydrogen peroxide concentrations, (iii) initial pH and (iv) incident radiation on the windows of radiation entrance (or, according to IUPAC, the photon fluence rate, $E_{p,0}$) measured with potassium ferrioxalate actinometry (Zalazar et al., 2005) (Table 1). Most of the experiments were done at 0.30 mM of glyphosate initial concentration. Lower and higher concentrations were used to study the behavior of glyphosate degradation at different initial concentrations. Values between 0.30 and 0.45 mM are important from an environmental point of view since they are the average values of glyphosate concentrations found in wastewaters which result from rinsing herbicide containers.

2.3. Analytical methods

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™) with electrochemical methods. A solution of Na_2CO_3 (9 mM) and NaOH (4 mM) was used as eluent at a flow-rate of 1.5 ml/min (Zhu et al., 1999). The injection volume was 20 μl . Under this

Table 1 – Experimental program.

Variable	Value
Glyphosate initial concentration (mM)	0.16–0.54
H_2O_2 initial concentration (mM)	0–11.82
Photon fluence rate ($E_{p,0}$) ($\text{Einstein cm}^{-2} \text{ s}^{-1}$) $\times 10^9$	
Heraeus 40 W lamp (100%)	23.3
Philips 15 W lamp	10.4
Heraeus 40 W lamp (with filter) (16%)	4.2
Reaction time	5 h
Initial pH	3.5–7–10
Temperature	25 °C

condition the retention time for glyphosate was 4.77 min. The aminomethylphosphonic acid (AMPA) standard could be identified under the same operating conditions. pH was monitored with a HI 98127 Hanna pHmeter. Hydrogen peroxide was analyzed using a colorimetric method following Allen et al. (1952) techniques, and employing a Cary 100 Bio UV visible spectrophotometer. Total organic carbon (TOC) was analyzed in order to compare glyphosate degradation rate with total mineralization rate and also in order to provide more accurate information about possible reaction intermediates. The instrument used was a Shimadzu TOC-5000A. End products were monitored by ion chromatography, and following a procedure similar to the one employed for glyphosate analysis. The identification of glycine, sarcosine and NH_3 was done employing a specific test for free amino acids according to Bergamini et al. (2009). More information about these methods can be found in the [Supplementary Data Section](#). The presence of formaldehyde was also confirmed using a specific colorimetric method (NIOSH, 1994). Though the possible degradation products monitored were: glycine, sarcosine, AMPA, formaldehyde, acetic acid, formic acid, nitrate anion, ammonium and phosphate anion only nitrate and phosphate ions were quantified.

2.4. Operation

The experimental run was started after every variable of the operating conditions had reached its steady-state and/or uniformity: concentrations, temperature, irradiation rates, etc. The employed equipment permitted to isolate the reactor from the irradiating system until the starting time was reached. It must be noticed that due to the type of equipment used in this work (an irradiated reactor in a recycle that includes a large volume tank) the reaction time plotted in the figures, does not represent the irradiation time of the active reaction volume. The real reaction time is the reaction time measured in every experiment and multiplied by the ratio $V_{\text{Reactor}}/V_{\text{Total}}$ which is a factor $\ll 1$.

3. Results and discussion

3.1. Preliminary runs

Two types of previous experiments were carried out in order to investigate the effects of UVC and H_2O_2 separately. The first run was performed employing $C_{\text{Glyph.}}^0 = 0.30 \text{ mM}$, (50 mg/L); $C_{\text{H}_2\text{O}_2}^0 = 2.20 \text{ mM}$; (75 mg/L) and without UV radiation. After 3 h of total time, no noticeable changes in glyphosate concentration were observed. A similar run was performed with $C_{\text{Glyph.}}^0 = 0.30 \text{ mM}$ (50 mg/L) and using 40 W Heraeus UVC lamps turned on during 3 h of total time. No signs of direct photolysis were observed, as it had been previously reported by Rueppel et al. (1977). This is in agreement with the absorption spectrum of glyphosate, at least in the range from 200 to 400 nm.

3.2. Effect of initial pH values

The experiments were carried out at different initial pH: 3.5 (which results from the preparation of the reacting mixture), 7

and 10, and at initial concentrations of glyphosate and hydrogen peroxide of 0.30 mM and 2.20 mM respectively. pH adjustment was accomplished by the addition of the required amount of NaOH 1 N. The results have shown that the best condition for degradation took place at the highest value of pH. However, there are no significant differences between pH 7 and pH 10 (Fig. 1).

3.3. Effects of initial H_2O_2 concentration

It is known that there is an optimum concentration of H_2O_2 in the UV/ H_2O_2 process (Glaze et al., 1995; Stefan et al., 1996; Zalazar et al., 2008). The results, for a total reaction time of 5 h, were analyzed using the final glyphosate conversion under the following operating conditions: $C_{\text{Glyph.}}^0 = 0.30 \text{ mM}$ (50 mg/L), pH = 7, two 40 W lamps and H_2O_2 concentration range from 0 to 12.4 mM (Fig. 2a). It is clear that 2.2–5.9 mM (75–200 mg/L) is the range of higher reaction rates. These values are related to the H_2O_2 /glyphosate molar ratio between 7.3 and 19.7. Within this plateau, conversion of glyphosate after 5 h was almost 70%.

For a run under the best operating conditions for degradation, Fig. 2b shows the temporal progression of the participating species concentrations. The existence of this optimum is a well-known phenomenon which results from the scavenging effect of the excess of $\cdot\text{OH}$ radicals on the hydrogen peroxide.

The glyphosate decay follows a first-order kinetics with an observed rate constant $k = 0.20 \text{ h}^{-1} \pm 0.01$ (3.68 h^{-1} total process time) with a correlation coefficient of 0.9986. Also, the half-life value was calculated, resulting $t_{1/2} = 0.19 \text{ h}$ (3.5 h total process time).

3.4. Effects of glyphosate initial concentration

The glyphosate degradation for different initial glyphosate concentrations – between 0.16 and 0.54 mM – and the same hydrogen peroxide initial concentration is shown in Fig. 3. The degradation rate is pseudo-first order with respect to initial concentration.

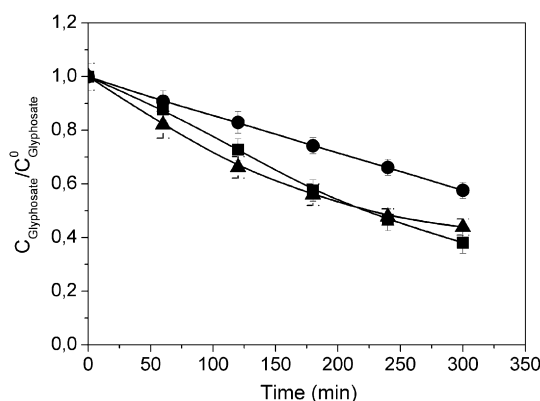


Fig. 1 – Experiments made under the following conditions: $C_{\text{Glyph.}}^0 = 0.30 \text{ mM}$; (50 mg/L), $C_{\text{H}_2\text{O}_2}^0 = 2.20 \text{ mM}$; (75 mg/L) at different initial pHs and using a UV lamp of 40 W input power: ●, pH 3.5; ■, pH 7 and ▲, pH 10.

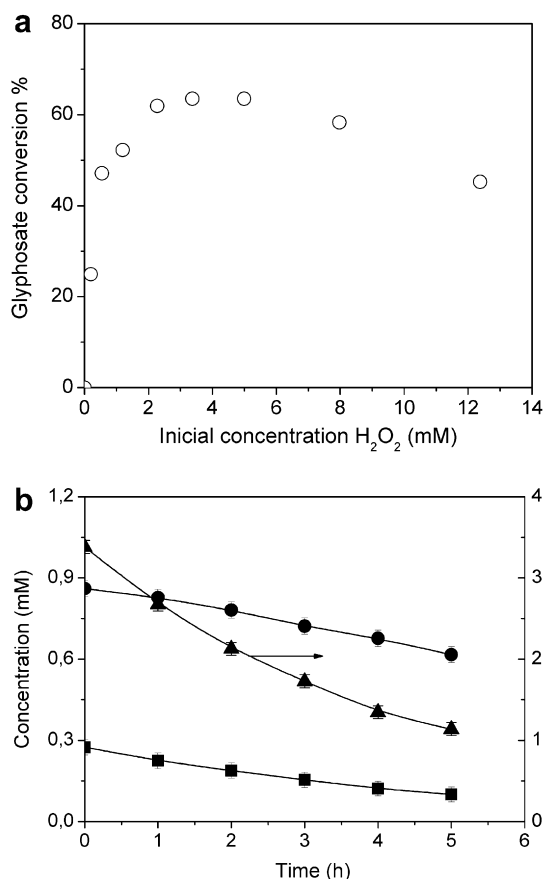


Fig. 2 – (a) Glyphosate conversion, for a fixed reaction time (5 h) vs. initial H₂O₂ concentration. $C_{\text{Glyph}}^0 = 0.30$ mM; (50 mg/L), pH = 7 and UV lamp of 40 W input power. (b) Glyphosate, H₂O₂ and TOC concentration evolution as a function of time. $C_{\text{Glyph}}^0 = 0.27$ mM; (46.4 mg/L), $C_{\text{H}_2\text{O}_2}^0 = 3.38$ mM; (114.9 mg/L) and UV lamp of 40 W input power: ■, glyphosate, ▲, H₂O₂ and ●, TOC.

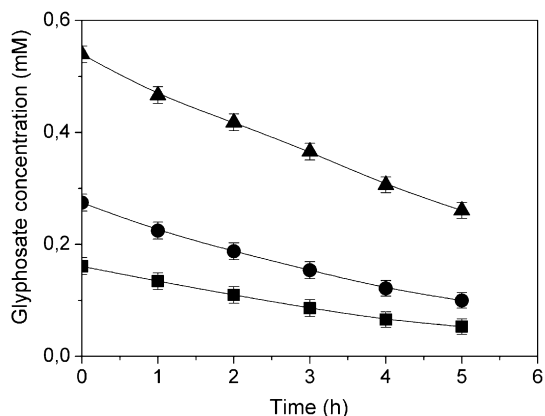


Fig. 3 – Glyphosate concentration as a function of time. Initial glyphosate concentration is the parameter: ▲, $C_{\text{Glyph}}^0 = 0.54$ mM; ●, $C_{\text{Glyph}}^0 = 0.27$ mM, ■, $C_{\text{Glyph}}^0 = 0.16$ mM; UV lamp of 40 W input power and pH = 7.

3.5. Effect of UV incident radiation intensity

The change on glyphosate concentration under different UV incident radiation rates at the reactor windows, at pH = 7, and for initial glyphosate and hydrogen peroxide concentrations of 0.30 mM and 3.38 mM respectively is shown in Fig. 4. For a reaction time of 5 h, with two 40 W lamps (Photon fluence rate, $E_{p,0} = 2.3 \times 10^{-8}$ Einstein $\text{cm}^{-2} \text{s}^{-1}$), a glyphosate conversion of 63.5% was reached while conversions with two 15 W lamps ($E_{p,0} = 10.4 \times 10^{-9}$ Einstein $\text{cm}^{-2} \text{s}^{-1}$) and two 40 W lamps with neutral density filters ($E_{p,0} = 4.2 \times 10^{-9}$ Einstein $\text{cm}^{-2} \text{s}^{-1}$) were 36.3% and 20% respectively.

Please note that this is not a direct indicator of the reaction rate dependence with respect to the absorbed photons because, from the kinetic point of view, the exact information is provided by the average value of the local volumetric rate of photon absorption by H₂O₂ (sometimes called photon absorption rate) and not the fluence rate at the reactor walls.

3.6. Total organic carbon (TOC) evolution

The total organic carbon (TOC) concentration at every elapsed time is important from two points of view: (i) because it is one of the best indications to conclude that complete mineralization has been achieved. When the TOC concentration is zero, it is certain that the glyphosate and all the reaction byproducts have been entirely degraded. (ii) Because it is always possible to calculate the equivalent theoretical TOC value from the experimentally measured glyphosate concentration at each reaction time. This result can be compared with the above-mentioned experimental TOC. This information is very useful to have an indicator of the existence of stable reaction intermediates; i.e., other organic, carbon-containing compounds, during the progress of the reaction. Fig. 5 depicts the result of a representative run. It proves the existence of different reaction intermediates. It was also observed that, under these experimental conditions, TOC conversion after 5 h was 29%.

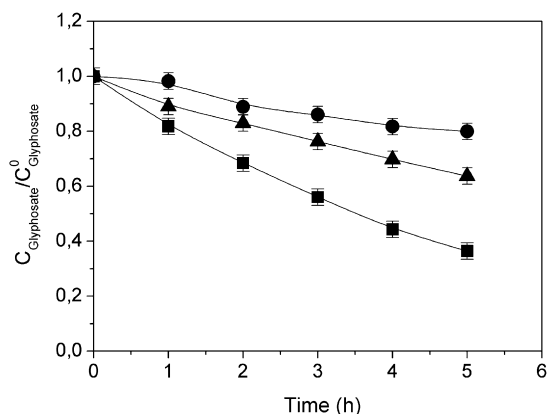


Fig. 4 – Effect of irradiation rates on the reaction rate. Dimensionless glyphosate concentration vs. time. The parameter is the lamp input power for $C_{\text{Glyph}}^0 = 0.30$ mM; (50 mg/L), $C_{\text{H}_2\text{O}_2}^0 = 3.38$ mM; (115 mg/L) and pH = 7: ●, Heraeus, 40 W input power with filter, ▲, Philips, 15 W input power, ■ Heraeus, 40 W input power.

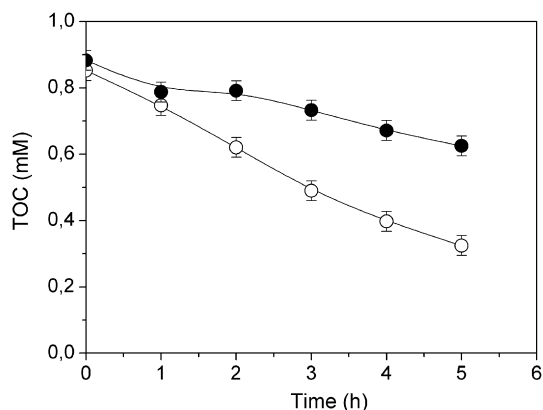


Fig. 5 – Total organic carbon evolution at pH 7 and UV lamps of 40 W input power. Conditions: $C_{\text{Glyph}}^0 = 0.30$ mM; (50 mg/L), $C_{\text{H}_2\text{O}_2}^0 = 2.35$ mM; (80 mg/L). ○, calculated TOC ●, experimental TOC.

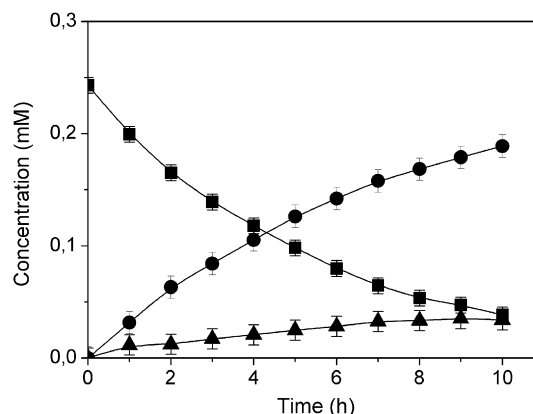


Fig. 6 – Evolution of glyphosate and end products during an extended run made under the best operating conditions for degradation: ■, glyphosate; ●, phosphate and ▲ nitrate. Conditions: $C_{\text{Glyph}}^0 = 0.24$ mM; (41 mg/L), $C_{\text{H}_2\text{O}_2}^0 = 2.4$ mM; (83 mg/L).

3.7. Formation of byproducts

In order to confirm the extent of glyphosate oxidation and to obtain a better understanding of the reaction mechanism involved, a byproduct evaluation is needed. However, given the complex variety of photoproducts that can be produced, an exhaustive identification and quantification of all intermediate products would be very difficult. Hence, this study is primarily focused on the major stable byproducts of the reaction.

As shown in Fig. 6, the mineralization of glyphosate under a longer run time using UV/H₂O₂ process is evidenced by the evolution of inorganic anions at the highest oxidation states, i.e., phosphate and nitrate. For each mol of glyphosate that is decomposed, one mol of phosphate appears at each reaction time (in the run shown in Fig. 6, after 10 h of total reaction

time, the difference between the theoretical and the experimental phosphate concentration was 7%). However, for nitrate ion the concentration of this end product was below the expected stoichiometric value. In fact, under the operating time shown in Fig. 6, less than 20% of initial nitrogen is under the nitrate form. In addition to mineral ions, formic acid was detected in the degradation samples. However, other organic acids such as acetic and glycolic acids were not found in this study.

3.8. A reaction pathway proposal

Several possible reaction paths have been proposed for the oxidation of glyphosate in recent studies. In one of them, the degradation is achieved by using manganese oxide and the

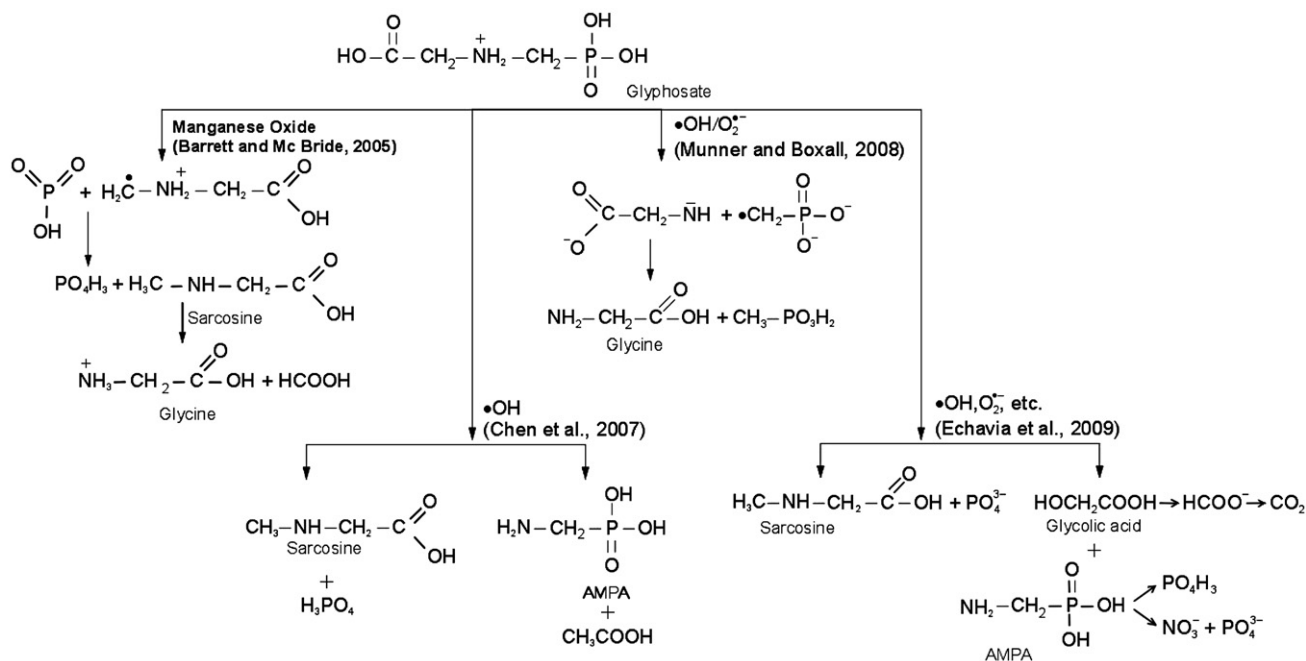


Fig. 7 – Possible oxidation path of glyphosate under different processes.

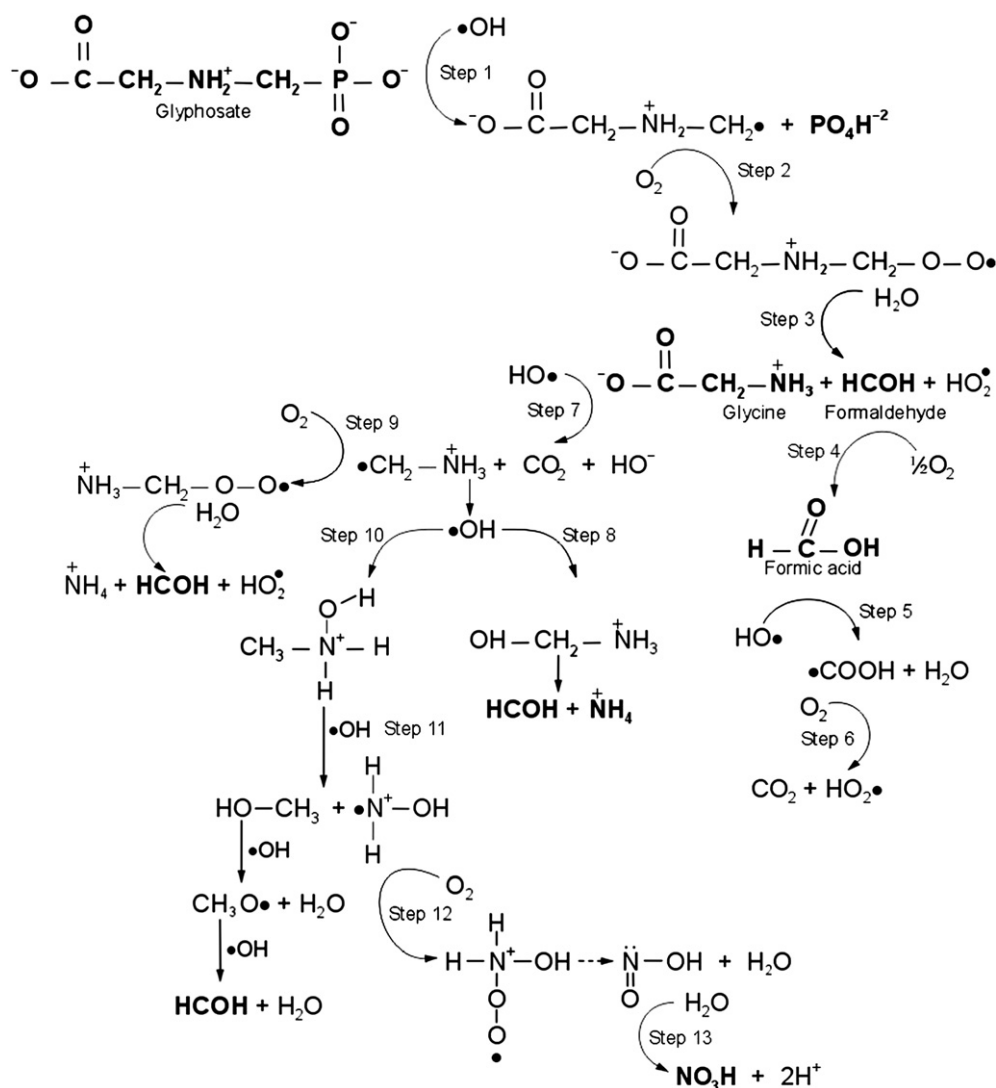


Fig. 8 – A proposal of a reaction scheme for glyphosate degradation with the UV/H₂O₂ process.

intermediate produced is sarcosine. Then, sarcosine is decomposed into glycine and formaldehyde (Barrett and McBride, 2005). In a different work, employing the Fe (III)/H₂O₂/UV process, two degradation paths have been proposed. The cleavage of C–N and C–P bonds is attributed to the existence of hydroxyl radicals. In the first case, glyphosate splits into AMPA and acetic acid while in the second, it is broken down into sarcosine and phosphoric acid (Chen et al., 2007).

In addition to these reports, the photocatalytic degradation of glyphosate has been investigated in aqueous suspensions of titanium dioxide at different pH values. Basically, two possible ways to degrade glyphosate at low and high pH have been proposed. One of them involves sarcosine formation while the other proposes the direct generation of glycine (Muneer and Boxall, 2008). In a recent research on the photocatalytic degradation of organophosphate and phosphonoglycine pesticides, where TiO₂ immobilized was used, a tentative path for the degradation of glyphosate has been proposed. This mechanism proposes the sarcosine generation and, as an alternative path, the AMPA and the glycolic acid production (Echavia et al., 2009).

The existing literature on oxidation pathways of glyphosate under different processes is summarized in Fig. 7.

A different, plausible reaction pathway of glyphosate decomposition with the H₂O₂/UV system is proposed here. The previously cited studies and the observed experimental results in this work were considered for this proposal. This pathway is illustrated in Fig. 8.

At pH 7 the glyphosate has the three hydroxyl groups ionized and the amino group protonated. The •OH formation follows the classical mechanism related to hydrogen peroxide decomposition under illumination (Liao and Gurol, 1995). The •OH radical attacks glyphosate, which leads to the formation of a carbon centered radical $\cdot\text{CH}_2\text{-NH}_3^+\text{-CH}_2\text{-COO}^-$ and phosphate. Since evolution of phosphate occurred during the initial stages of glyphosate decomposition, it may be inferred that C–P cleavage led to formation of phosphate (Step 1). The generated radical can react with molecular oxygen present in the medium at high concentration to give a new radical $\text{COO}^-\text{-CH}_2\text{-NH}_3^+\text{-CH}_2\text{-O-O}\cdot$ (Step 2), which reacts directly with water to form glycine, formaldehyde and HO₂• radical (Step 3). The direct formation of glycine without the sarcosine

generation was proposed due to verified absence of this compound in the described analytical procedures. The experimental results indicated that when this process was applied, only glycine was present. Furthermore, the absence of AMPA in all samples was confirmed. The generation of formaldehyde was also confirmed as described before. The formaldehyde generated (in all steps) can be directly oxidized to formic acid by the dissolved oxygen under UV light as it is proposed by Stefan et al. (1996). The steps corresponding to formic acid degradation have been proposed taking into account that the hydroxyl radical formed produces a hydrogen abstraction from the H–C bond to give rise to a $\cdot\text{COOH}$ radical. This radical, combined with the existing oxygen in the medium, result in CO_2 and the hydroperoxyl radical HO_2 (Step 5). A similar mechanism has been suggested for the degradation of formic acid that employs the UV/ TiO_2 process (Dijkstra et al., 2002; Krýsa et al., 2006).

For the next oxidation step of glycine in aqueous solution, it is proposed the decarboxylation of the α -amino acids due to the presence of the $\cdot\text{OH}$ radical. It results in CO_2 and $\cdot\text{CH}_2\text{NH}_3^+$ radical (Step 7). This step is suggested by Hidaka et al. (1997) to degrade amino acids upon exposure to aqueous titania suspensions and irradiated with UV. The combination of $\cdot\text{CH}_2\text{NH}_3^+$ and $\cdot\text{OH}$ radicals produces formaldehyde and NH_4^+ (Step 8). The generation of NH_3 has been detected as mentioned in the analytical section. There is also another possible step: the addition reaction of molecular oxygen to the $\cdot\text{CH}_2\text{NH}_3^+$ radical to produce NH_4^+ , formaldehyde and HO_2 radical (Step 9).

The nitrate formation would follow an alternative path to the NH_4^+ formation. The nitrogen radical also reacts with $\cdot\text{OH}$ radical in Step 10 to give a protonated hydroxylamine intermediate. This oxidation path is proposed by Hidaka et al. (1997) as one of various steps during the photodegradation of an amino acid catalyzed by irradiated TiO_2 . Afterwards, a possible reaction way is that the protonated hydroxylamine reacts with $\cdot\text{OH}$ radical to produce methanol and $\cdot\text{NH}_2\text{—OH}$ radical (Step 11). This nitrogen radical can react with molecular oxygen to generate $\cdot\text{O—O—NH}_2\text{—OH}$ nitrogen radical. A similar step is proposed by Leitner et al. (1999) in the removal of hydroxylamine by means of processes which generate $\cdot\text{OH}$ radicals in aqueous solution. The $\cdot\text{O—O—NH}_2\text{—OH}$ radical, under reorganization, yields nitrous acid (or nitrite) (Step 12). Then, the nitrous acid, by means of hydrolysis, is transformed into nitric acid (or nitrate) (Step 13). The nitrite and nitrate formation from hydroxylamine is also proposed by Hidaka et al. (1997). The nitrate evolution for the longer run time shows that other forms of nitrogen compounds, such as glycine and nitrite, may be present.

The methanol formed in Step 11 can be oxidized by $\cdot\text{OH}$ radical to generate, first, the $\text{CH}_3\text{O}\cdot$ radical and then, formaldehyde. This oxidation pathway is described by Chen et al. (1999) as a possible mechanism where methanol is oxidized by the free $\cdot\text{OH}$ in solution.

In summary, the glyphosate decomposition stable compounds identified in this study were: glycine, formaldehyde, formic acid, nitrate anion, ammonium and phosphate anion (see compounds in bold face in Fig. 8).

Perhaps one of the most interesting outputs of this process is that, at a first glance, it seems that none of the formed byproducts is toxic. This hypothesis should be always

confirmed by specific toxicity studies, particularly considering the possible existence of small concentrations of other undetected reaction intermediates. It must be noticed that this study was made using glyphosate alone, without other compounds existing in commercial formulations.

This first step is the basis to develop a workable, validated and reliable reaction kinetics model. Degradation tests on commercial formulations should be carried out in order to determine the influence of the additives on the degradation process.

4. Conclusions

1. As shown in this work, the study of the resulting effects of the most significant operating variables on glyphosate degradation would indicate that the combination of hydrogen peroxide and UV radiation may become a suitable and very simple process to remove glyphosate from water.
2. A proposal of a degradation path based on the observed experimental data has been possible.
3. In a first approach, it seems that glyphosate degradation does not lead to stable toxic end products. Moreover, it could be not necessary to reach complete mineralization in order to have non toxic end products.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.watres.2010.05.004](https://doi.org/10.1016/j.watres.2010.05.004).

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