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Glyphosate degradation in water employing the H_2O_2/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 (•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 Fe (III)/H_2O_2/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 (H_2O_2/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 (≥97.5%, Sigma–Aldrich), (e) glycine (97.3%, Merck), (f) aminometylphosphonic acid, AMPA (≥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 μS/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 TM, with two parallel, flat windows made of quartz ($V_{Reactor} = 110\ cm^3$). Each window was irradiated with a tubular, germicidal lamp ($\lambda = 253.7$ 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 ($V_{Total} = 2000\ cm^3$). 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 ($E_{p,0}$) (Einstein $cm^{-2}\ s^{-1}$) × 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

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