

# DEGRADATION OF GLYPHOSATE IN WATER USING THE UV/H<sub>2</sub>O<sub>2</sub> ADVANCED OXIDATION PROCESS

Cristina Zalazar, Agustina Manassero, Melisa Mariani, Antonio Negro, Rodolfo Brandi, Alberto Cassano

INTEC - Instituto de Desarrollo Tecnológico para la Industria Química, (U.N.L y CONICET, Güemes 3450 (3000) Santa Fe, Argentina. Fax: +54 342 4511087. E-mail: szalazar@santafe-conicet.gov.ar

## INTRODUCTION

Glyphosate (N-phosphonmethyl glycine) is a non-selective, post-emergence, broad-spectrum organophosphate herbicide, which is the most used in the world. Argentina is the second largest world producer of glyphosate-resistant (GR) soy. This production has been accompanied by an increase in the use of glyphosate (over 160 million L between 2004 and 2005). The United Nations estimates that of all pesticides used in agriculture, less than 1 % actually reaches the crops. The other part ends up contaminating the soil, the air and, mainly, the water. Advanced Oxidation Processes (AOPs) seem to be a suitable option to decrease glyphosate concentration in water within acceptable limits. AOPs are based on the generation of very reactive non-selective oxidizing species, particularly the hydroxyl radical ( $\bullet\text{OH}$ ). The combination of hydrogen peroxide and UV radiation could be a convenient process for the treatment of this type of pollutants.

## METHODS

### Experimental Setup

Figure 1 shows a schematic representation of the experimental setup. Experiments were carried out under different conditions (Table 1).

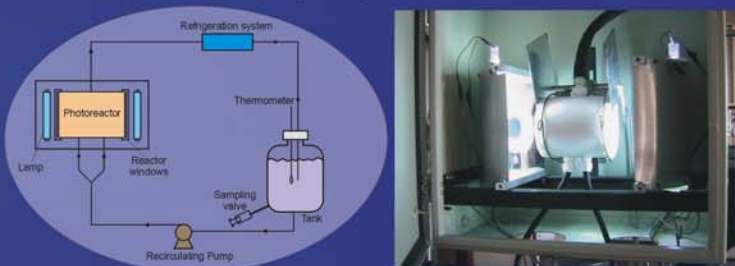


Figure 1: Equipment setup

Irradiated photoreactor

Table 1: Experimental program

Variable	Value
Glyphosate initial concentration (mg/L)	30-90
H <sub>2</sub> O <sub>2</sub> initial concentration (mg/L)	0-402
Incident radiation ( $G_w$ , Einstein $\text{cm}^{-2} \text{s}^{-1}$ ) $\times 10^9$	
Heraeus 40 W Lamp (100 %)	23.3
Heraeus 40 W Lamp (16 %) (with filter)	4.2
Phillips 15 W Lamp	10.4
Reaction time	300 min (5 h)
Initial pH	3.5-7-10

### Analytical methods

Glyphosate was analyzed by ion chromatography with a suppressed conductivity detector employing a Dionex AG4A-SC guard column and an AS4A-SC separating column. A solution of Na<sub>2</sub>CO<sub>3</sub> (9 mM) and NaOH (4 mM) was used as eluent at flow rate 1.5 ml min<sup>-1</sup>. Injection volume was 20  $\mu\text{l}$ . Figure 2 shows a chromatogram of a typical degradation sample under the above chromatographic conditions. The retention time was about 7.6 min. The method was adapted of Zhu et al., 1999.

Hydrogen peroxide was analysed with spectrophotometric methods at 350 nm employing a Cary Bio UV visible instrument. Total organic carbon (TOC) was also analyzed (Shimadzu TOC-5000A) in order to compare the degradation rate of glyphosate with the total mineralization rate to have better information concerning possible reaction intermediates.

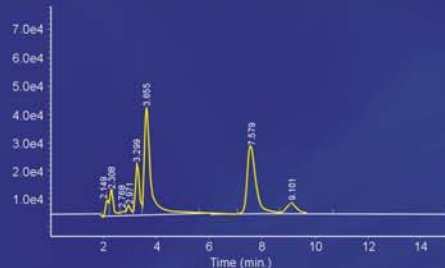


Figure 2: Typical chromatograms of a degradation sample.

## RESULTS

### Effect of initial pH values

The experiments were made with different initial pH: 3.5 (natural), 7 and 10. The results have shown that the best conditions of degradation are at the higher value of pH and there are no significant differences between pH 7 and pH 10 (Figure 3).

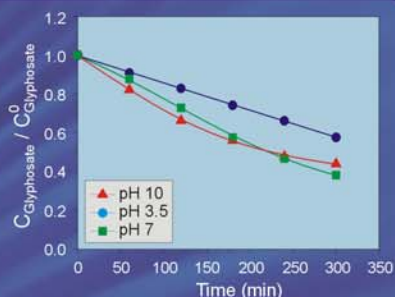


Figure 3: Experiments made under the following conditions:  $C_{\text{Glyphosate}}^0 = 50 \text{ mg/L}$ ;  $C_{\text{H}_2\text{O}_2} = 75 \text{ mg/L}$  at different initial pH and 40 W UV lamp input power.

### Effect of initial H<sub>2</sub>O<sub>2</sub> concentration

There is an optimum concentration of H<sub>2</sub>O<sub>2</sub> in the UV/H<sub>2</sub>O<sub>2</sub> process. The results, for a fixed reaction time (5h), were analyzed in terms of final glyphosate conversion (Figure 4). It is clear that 75-200 mg/L is the range of higher conversions. Under these conditions, conversion of glyphosate was almost 70 % in 5h.

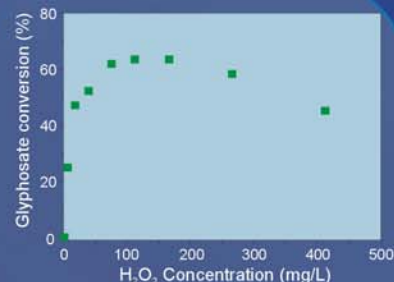


Figure 4: Glyphosate conversion, for a fixed reaction time (5 h) vs. initial H<sub>2</sub>O<sub>2</sub> concentration for  $C_{\text{Glyphosate}}^0 = 50 \text{ mg/L}$ , pH=7 and 40 W UV lamp input power.

### Effect of UV incident radiation intensity

The change on glyphosate concentration under different UV incident radiation rates at the reactor windows are shown in Figure 5. For a reaction time of 5 h, with the 40 W lamp ( $G_w = 2.3 \cdot 10^8 \text{ Einstein cm}^{-2} \text{ s}^{-1}$ ), a glyphosate conversion of 63.5% was reached while the conversions for the 15 W lamp ( $G_w = 10.4 \cdot 10^8 \text{ Einstein cm}^{-2} \text{ s}^{-1}$ ) and 40 W lamp with filter ( $G_w = 4.2 \cdot 10^8 \text{ Einstein cm}^{-2} \text{ s}^{-1}$ ) were 36.3% and 20% respectively.

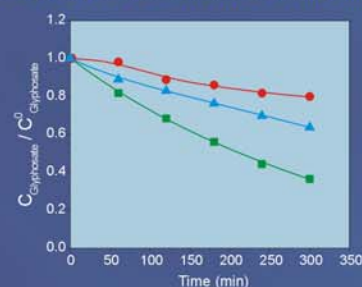


Figure 5: Effect of irradiation rates on the reaction rate. Dimensionless glyphosate concentration vs. time. The parameter is the lamp input power for  $C_{\text{Glyphosate}}^0 = 50 \text{ mg/L}$ ;  $C_{\text{H}_2\text{O}_2} = 11.5 \text{ mg/L}$  and pH=7: (●) 40 W Heraeus with filter, (▲) 15 W Philips, (■) 40 W Heraeus.

### Total organic carbon (TOC) evolution and intermediate reaction products

The results corresponding to TOC conversion indicate that organic intermediates are present. Figure 6 shows the results of a representative run.

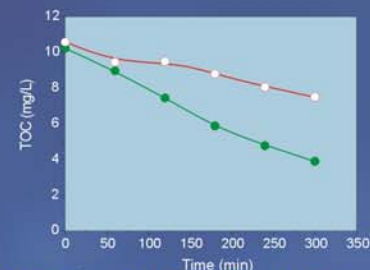


Figure 6: Total organic carbon evolution. Conditions:  $C_{\text{Glyphosate}}^0 = 50 \text{ mg/L}$ ;  $C_{\text{H}_2\text{O}_2}^0 = 80 \text{ mg/L}$  and pH=7: (●) TOC calculated, (■) experimental TOC, pH 7 and 40 W UV lamp input power.

The presence of formic acid in the degradation samples was detected. This is evidence that the principal reaction might be thought of as the cleavage of C-P bond yielding sarcosine and phosphoric acid. Subsequently sarcosine is decomposed into glycine and formic acid (Chen et al., 2007; Barret and McBride, 2005). There are two possible routes for the degradation of glyphosate at low and high pHs (Munier and Boxall, 2008). One of them involves the direct generation of glycine. Considering this information, a sample was analysed employing a specific test for free amino acids. The observed results indicated that only glycine was present.

A possible mechanism of reaction of glyphosate decomposition in UV/H<sub>2</sub>O<sub>2</sub> system was proposed taking into account previous information and the observed experimental results obtained (Figure 7).

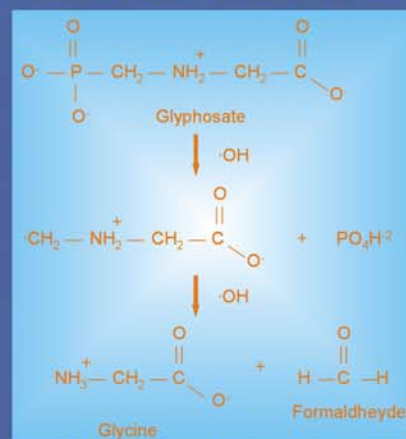


Figure 7: A proposal of a degradation reaction scheme for glyphosate with the UV/H<sub>2</sub>O<sub>2</sub> process.

## CONCLUSIONS

The combination of hydrogen peroxide and UV radiation is a suitable process to remove glyphosate from water. A probable reaction sequence was proposed. This is the first step to work in the derivation of a complete and validated kinetic model having as a final scope scaling-up purposes.

## BIBLIOGRAPHY

Barrett, K. A., McBride, M. B. *Env. Sci. Technol.*, 2005, 39, 9223-9228.  
 Chen, Y., Wu, F., Lin, Y., Deng, N., Bazhin, N., Glebov, E. J. *Hazard. Mater.*, 2007, 148, 360-365.  
 Munier, M., Boxall, C. *Int. J. Photoenergy*. DOI: 10.1155/2008/197346. Published online: 2008.  
 Zhu, Y., Zhang, F., Tong, C., Liu, W. J. *Chromatogr A*, 1999, 850, 297-301