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Studies on degradation of glyphosate by several oxidative chemical processes: Ozonation, photolysis and heterogeneous photocatalysis

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Several different Advanced Oxidation Processes (AOPs) including ozonation at pH 6.5 and 10, photolysis and heterogeneous photocatalysis using TiO_2 as semiconductor and dissolved oxygen as electron acceptor were applied to study the degradation of glyphosate (*N*-phosphonomethyl glycine) in water. The degree of glyphosate degradation, the reactions kinetic and the formation of the major metabolite, aminomethyl phosphonic acid (AMPA), were evaluated. Ozonation at pH 10 resulted in the maximum mineralization of glyphosate. It was observed that under the experimental conditions used in this study the degradation of glyphosate followed the first-order kinetics. The half-life obtained for glyphosate degradation in the O_3/pH 10 process was 1.8 minutes.

Keywords: Ozonation; pesticide; advanced oxidation process; heterogeneous photocatalysis; degradation; glyphosate.

Introduction

Organophosphorus pesticides are widely used in agriculture. Glyphosate (N-phosphonomethyl glycine), also known by the trade names Roundup and Rodeo, is a non-selective, post-emergence, broad-spectrum organophosphate herbicide.[1,2] Due to its extensive use in agriculture, it has become a major pollutant and studies of its impact on the environment have become more pertinent. [3,4] Aminomethyl phosphonic acid (AMPA) is the major metabolite of glyphosate and it is produced by microbial degradation on plants and in water and soil. [5] Although this metabolite has low toxicity (DL 8300 mg/kg), it is more persistent than glyphosate.[6] Studies report that the half-life for glyphosate in soil is about three days while for AMPA it is between 119 and 958 days. [6] The chemical structures of glyphosate and AMPA are given in Figure 1.

Like other pesticides, glyphosate could be present, at low levels, in natural water and its occurrence in the disinfection step of drinking water purification is a problematic issue, since the toxicity of any by-product formed during the chlorination step could be greater than that of the parent compounds.[7]

Various treatment processes have been investigated to reduce pesticide concentrations in water and to minimize the potential health risks associated with exposure to these chemicals by consumption of contaminated water. [8,9] Traditional physical techniques (coagulation, adsorption on activated carbon, reverse osmosis, etc.) can generally be used for the removal of such pollutants. Nevertheless, these methods are usually non-destructive and post-treatments of the absorbent materials or solid wastes are necessary and costly.[10] Biodegradation is not usually involved in water treatment to remove trace pesticides. Among the problems encountered in the use of bioremediation are compound specificity, slow rates, incomplete metabolism and biofilm maintenance. [11] Advanced oxidation processes (AOP) are a key technology to solve pesticide contamination problems during both water and wastewater treatments. [12] Degradation of pesticides by AOPs has been studied by many researchers. Degradation of phorate in aqueous solution by ozonation was studied by Ku et al.[13] and results showed that phorate dissolved an aqueous solution had almost completely been decomposed by ozonation to form various species within 10 minutes of reaction time. Studies of the degradation of diuron by ozonation showed that higher pH, increased ozone dosage, use of additives such as Na_2CO_3, $NaHCO_3$ and H_2O_2 were all advantageous to
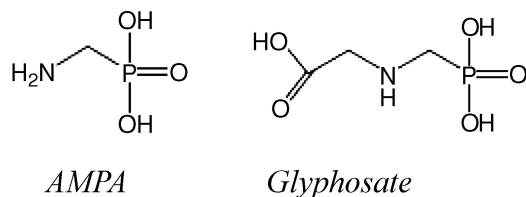
Fig. 1. Chemical structures of glyphosate and aminomethyl phosphonic acid (AMPA).

improve the degradation efficiency of this compound.[9] The photocatalytic degradation of diuron was investigated by Bamba.[8] The results of the kinetic study showed that the kinetic model followed is Langmuir-Hinshelwood. Shifu et al. [2] showed that glyphosate is easily degraded by assisted photocatalysis in aqueous dispersion under radiation by ultraviolet (UV) light. Several parameters such as illumination time, pH and additives were evaluated and the best conditions for the degradation efficiency were obtained.

In the present paper, several different AOPs: photolysis, heterogeneous photocatalysis process (using TiO$_2$ as semiconductor and dissolved oxygen as electron acceptor) and ozonation (at low and high pH) were applied to evaluate the degradation of glyphosate in water. The effect of the reaction time on glyphosate removal and the possibility of achieving total mineralization were studied. The possible formation of AMPA, as a result of the application of the chemical oxidative processes, was also evaluated. The efficiencies of these oxidative processes were compared and a kinetic study for photocatalytic degradation and ozone degradation were made.

Materials and methods

Chemicals

Glyphosate (purity 99.8 %) and AMPA (purity 99.1%) were obtained from Monsanto and used without futher purification. Analytical grade organic solvents were used for high performance liquid chromatography (HPLC) analysis. Ultra pure distilled-deionized water from a Milli-Q (Millipore Corp.) system was used throughout this study. Commercially available TiO$_2$ (Degussa P- 25) was obtained from Degussa Chemical. All reagents used were of analytical-reagent grade.

Samples

A stock solution containing 1000 mg/L of glyphosate was prepared in deionized water and diluted to the required concentration (42.275 mg/L) for the degradation experiments. The original pH of this solution was about 6.5. The pH was adjusted to 10 by the addition of a NaOH solution for the ozonation experiment.

Ozonation process

Ozone was generated from pure oxygen using an OZO-CAV ZT-2 generator (Inter Ozone Ingenieria Ecologica, Santiago-Chile). The amount of ozone produced was determined spectrophotometrically at 258 nm ($\in$= 3.000 L/mol cm) in the gas phase by passing the mixture of oxygen and ozone through a flow cell. [14] The system reached a steady-state production of ozone in 10 minutes.[15] An ozone concentration of 14 mg/L was applied for 30 minutes in a batch reactor. Samples (42.275 mg/L glyphosate solution, 400 mL) were submitted to ozonation at pH 6.5 and at pH 10 (pH adjusted with a sodium hydroxide solution) at room temperature, using a tubular 500 mL reactor fitted with a sintered glass dispenser that released the gas from the bottom of the reactor. For all experiments, the excess of ozone was passed from the reactor into a glass flask containing a 2% solution of KI.

Heterogeneous photochemical process

Titanium dioxide (80% anatase and 20% rutile, average particle size of 30 nm and BET Method–Brunauer, Emmett and Teller [BET] surface of 50 $\pm$ 15 m^2/g) was used without any pre-treatment. Aqueous suspensions of 0.1 g of TiO$_2$/L were used in this experiment. A volume of 200 mL of glyphosate solution (42.275 mg/L, original pH) was placed in the 250 mL cylindrical photoreactor. Illumination was provided by a high-pressure mercury lamp (Philips HPL-N, 125 W; λ > 290 nm) with the glass bulb removed. The lamp was fixed in the center of the reactor and cooled by a water jacket, at room temperature. The suspension was bubbled with oxygen (through a sintered glass disk placed in the bottom of the reactor) at a flow rate of about 6 $\pm$ 0.2 L/h for 30 minutes. For analytical control, samples were removed and centrifuged at 3500 rpm.[16]

Photolysis process

The same experimental set up, including the passage of oxygen, was used as in the previous section but without the addition of TiO$_2$ suspension.

Analytical determinations

Mineralization was followed by measuring the total organic carbon (TOC) through direct injection of filtered samples (pore size of 0.45 μm) into a Shimadzu-5000A TOC analyzer provided with a non-dispersive infrared (NDIR) detector and calibrated with standard solutions of potassium phthalate.

The glyphosate and AMPA concentrations were determined by HPLC, with a Merck-Hitachi HPLC system, model D-7000, with fluorescence detection (excitation at 350 nm and emission at 440 nm). [17] A 300 $\times$ 4.6 mm I.D Aminex Glyphosate column and a 100 $\times$ 4.6 mm I.D

HRLC-Glyphosate guard column (both from Bio Rad) were used.

The flow rate of mobile phase (0.68 g/L KH_2PO_4) was adjusted to 0.7 mL/min. After exiting the column, glyphosate and AMPA were then post column derivatized using 1,2 phthalic dicarboxaldehyde and 2-mercaptoethanol. The retention times for glyphosate and AMPA were 17 and 30 minutes, respectively. The limit of detection (LOD) was established at 0.0075 μg/L, using a signal to noise ratio of 3 for glyphosate and AMPA.

Results and discussion

In Brazil, pesticide packaging is considered to be a serious problem. The Legislation establishes that the package must be returned to the manufacturer after use to be cleaned by the producer. Generally, the pesticide after washing is less then 100 μg/mL, therefore the pesticide residues must be monitored and treated.

The different treatment processes were applied for the degradation of glyphosate in aqueous solution. The processes studied were photolysis, heterogeneous photocatalysis (TiO$_2$/UV) and ozonation at two different pH values (6.5 and 10.0). Glyphosate was the only organic compound initially present in the aqueous solutions used in this study.

Ozonation process

A very rapid reaction of glyphosate with ozone in water has been reported.[15] Unlike other organophosphates, the primary reaction site of this compound towards ozone is the amino group, which is highly reactive if not protonated. The pH can affect the nature of the products formed and can influence ozonation efficiency. In general, ozone oxidation pathways include direct oxidation by ozone or indirect oxidation by hydroxyl radicals.[18] The predominance of the oxidation reactions by molecular ozone at a lower pH has already been established while, beyond a critical pH value, hydroxyl radicals become the predominant oxidizing species. The critical pH is expected to differ for
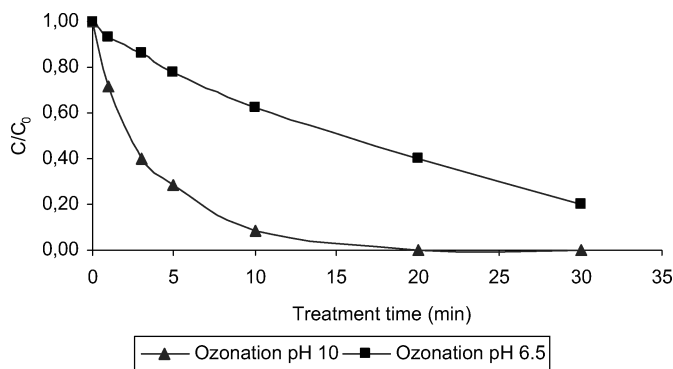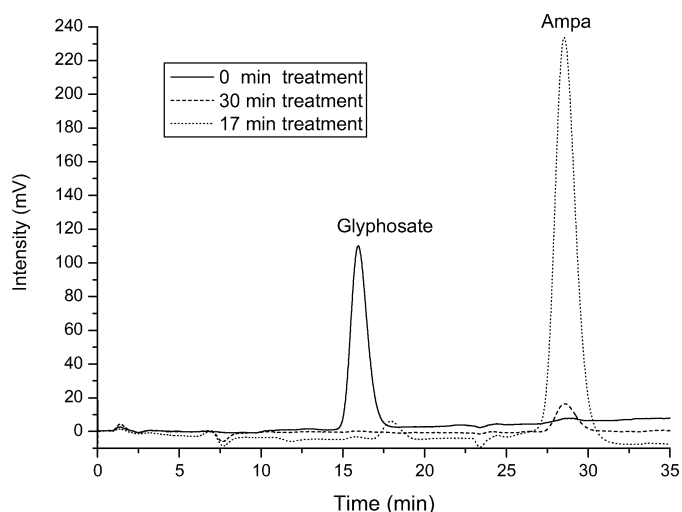

Fig. 3. High performance liquid chromatography (HPLC) chromatograms of samples subjected under O3/pH 10 process at 0, 15 and 30 minutes.

different chemical compositions in the aqueous phase.[19] Investigators have commonly controlled pH either by the use of buffers or by addition of acid or alkali. In Figure 2, the variation of the C/C_0 ratio as a function of ozonation treatment time is represented. As can be seen, the ozonation carried out at alkaline pH was more effective for glyphosate degradation. After 17 minutes of treatment the glyphosate was totally removed while, in the ozonation carried out at pH 6.5, after 30 minutes of treatment about 80% of the glyphosate initially present in solution was removed. Due to the oxidation potential of hydroxyl radicals being much higher than that of the ozone molecule, radical oxidation was faster than direct oxidation and higher glyphosate degradation was observed. The HPLC chromatograms of the O$_3$/pH 10 process at 0, 15 and 30 minutes of treatment time were showed in Figure 3.

Aminomethyl phosphonic acid (AMPA) is the major metabolite of glyphosate produced by microbial degradation, and is found in plants, water and soil. The results
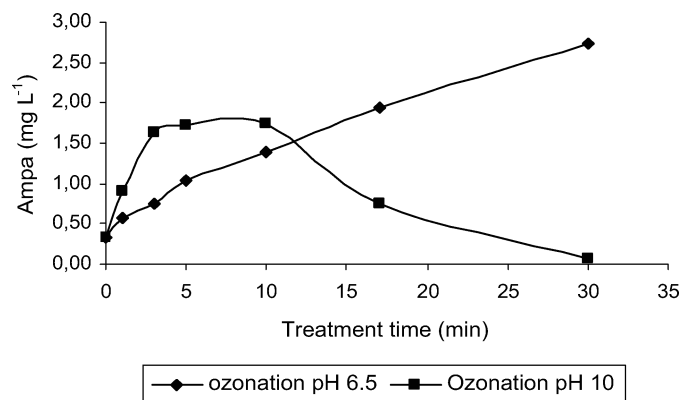

Fig. 2. Glyphosate degradation by ozone (pH 6.5) and ozonation based on the hydroxyl radical (pH 10).

Fig. 4. Aminomethyl phosphonic acid (AMPA) concentration during the ozonation processes.

of the present study indicate that the chemical oxidation processes O_3/pH 6.5 and O_3/pH10 produced this metabolite (Fig. 4). Nevertheless, degradation by hydroxyl radical also removed most of the AMPA produced in 30 minutes of treatment at pH10. For the O_3/pH 6.5 degradation process, this metabolite was continually produced and, apparently, not further degraded.

It is very difficult to determine the degree of pesticide degradation by ozonation based on AOPs due to the complexity of the reactions. The complete disappearance (conversion) of pesticides monitored by high performance liquid chromatography, for example, is often not enough to prove detoxication of the pesticide solution. This is because potentially more toxic degradation products may be present or were produced by the treatment applied and the detection of these compounds depend on the chromatographic conditions. In these cases, the degree of pesticide degradation and mineralization can be measured by the reduction of the total organic carbon content of the solution. The results indicate 20% TOC reduction by application of the O_3/pH 6.5 process. This indicates that other decomposition products, besides AMPA, can be produced during the ozonation process. The ozonation process carried out at pH 10 results in 97.5% TOC removal. These results were very important because they indicate that intermediate compounds (that might be more toxic than the parent compounds) were almost totally removed.

Photolytic and photocatalytic degradation

In order to compare the efficiency of the photocatalytic degradation (UV-TiO₂) with direct photolysis (UV), experiments were carried on using the same initial concentration of pesticide, at pH 6.5. The amount of catalyst used was 0.1 g of TiO_2 L^{-1}.

Although Shifu et al. [2] concluded that acidic or alkaline medium favors glyphosate degradation by photocatalytic processes, this study showed that the pH 6.5 also was effective for degradation of glyphosate. Figure 5 shows the disappearance of glyphosate by photocatalysis and photolysis in relation to illumination time. As expected, the direct pho-
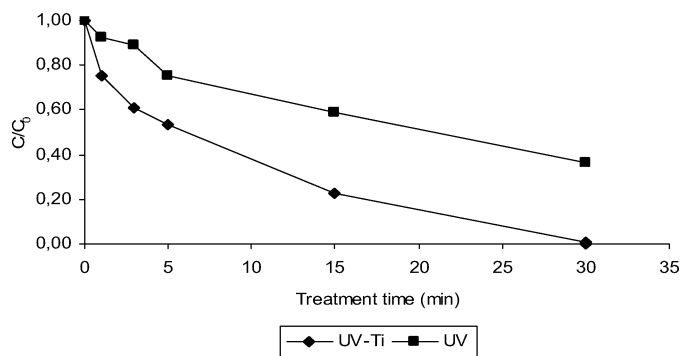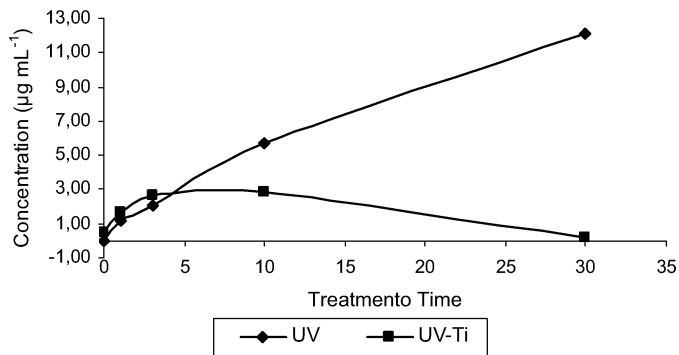

Fig. 6. Aminomethyl phosphonic acid (AMPA) concentration during the ultraviolet (UV) and UV/TiO₂ processes.

tolysis was less effective than photocatalysis for glyphosate removal. After 3 minutes of irradiation without TiO₂, only 10.9% of the initial amount of the compound was degraded while the glyphosate degradation for the same treatment time was 38.7% for the photocatalytic process. The literature reports that direct photolysis is usually not an option due to the low quantum efficiency for most pesticides.[13] After 30 minutes of UV irradiation in the presence of TiO₂, the residual concentration of glyphosate was 0.06 mg/L (99.9 % efficiency removal). TOC removal for the UV/TiO₂ process achieved 92 % after 30 minutes of treatment time.

For both photo-induced processes formation of the AMPA intermediate was also observed (Fig. 6). The amount AMPA formed during the photocatalytic process was less than the amount formed during the UV process, 2.85 mg/L after 10 minutes of treatment, but this was completely degraded after 30 minutes. For the UV process, the amount of AMPA formed increased during the treatment. At the end of the UV treatment without TiO₂(30 minutes) the AMPA concentration was 12.1 mg/L indicating that this compound is less easily degraded by UV radiation than is glyphosate.

It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of TiO₂ and that O_2 and H_2O are necessary for photocatalytic degradation. Under UV illumination, electron-hole pairs are created on the TiO₂ surface. Oxygen adsorbed on the TiO₂ surface prevents the electron-hole pairs from trapping electrons. Superoxide radical-ions ($^\bullet O_2^-$) are thus formed. The $^\bullet OH$ radicals are formed from holes reacting with either H_2O or OH^- adsorbed on the TiO₂ surface. $^\bullet OH$ and $^\bullet O_2^-$ are widely accepted as primary oxidants in heterogeneous photocatalysis. The oxidizing power of the $^\bullet OH$ radicals is strong enough to completely oxidize glyphosate adsorbed on the surface of TiO₂.[2,21]

Comparison between O₃/pH 10 and TiO₂/UV processes

The processes that showed the highest rates for degradation of glyphosate in water were O_3/pH 10 and TiO₂/UV. Both processes were able to remove glyphosate and also

Fig. 5. Glyphosate degradation by the ultraviolet (UV) and TiO₂/UV processes.

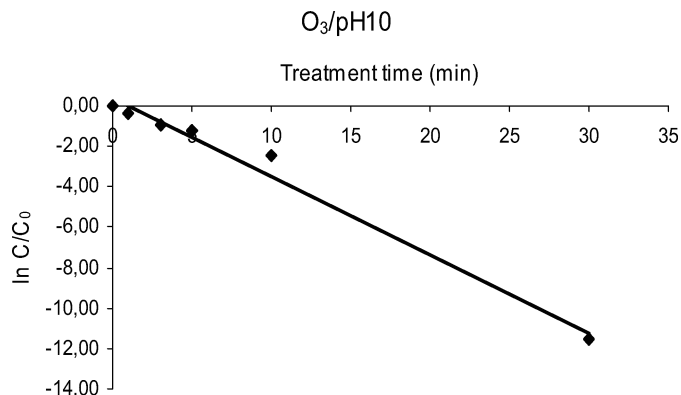## O₃/pH10

Treatment time (min)

Fig. 7. The pseudo-first-order decay of glyphosate by ozonation at pH 10.

the AMPA generated during the degradation processes with efficiency. Knowledge of the kinetics and direct comparison of chemical oxidants are required to assess the efficiency of systems engineered for the oxidation of a variety of pollutants. Reliable kinetic studies require obvious substrate decay measurements. Thus, for comparison of the efficiency of these treatment processes, kinetic studies of glyphosate decomposition were carried out.

As several authors have previously reported, the reaction of ozone with organic compounds is second order, first order with respect to each reactant.[22] Therefore, the glyphosate disappearance rate equation can be expressed as:

$$\frac{d[glyphosate]}{dt} = k[O_3][glyphosate] \qquad (1)$$

where k is the second order rate constant. In addition, as the initial ozone concentration was in excess with respect to glyphosate, the ozone concentration through each experiment can be considered almost constant.[23] Then, the reaction rate can be reduced to pseudo-first-order kinetics with respect to the ozone concentration. In order to evaluate this pseudo rate constant, the data obtained for
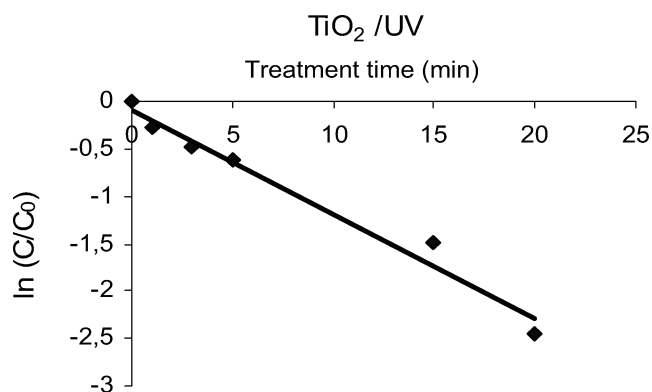
TiO₂ /UV

Treatment time (min)

Fig. 8. The pseudo-first-order decay of glyphosate by TiO₂/UV process.

glyphosate degradation by O_3/pH 10 were plotted as ln (C/C_0) versus reaction time, and after linear regression analysis ($R^2 = 0,9836$), the slope can be attributed as the apparent first-order constant $k\prime$.(Fig. 7)

Several experimental results have indicated that the photocatalytic degradation rates of pesticides over illuminated TiO₂ follow the Langmuir-Hinshelwood kinetic model.[24] In our investigation, by plotting ln $[C/C_0]$ as a function of time, a straight line was obtained (Fig. 8) that confirms the apparent first-order kinetic law ($R^2 = 0.9743$).

The half - life obtained for glyphosate was 1.8 and 6.2 minutes for O₃/pH 10 and TiO₂/UV, respectively. This indicates that for the ozonation carried out at pH 10 a faster rate of glyphosate decomposition was observed under the experimental conditions studied.

Conclusions

The degradation of aqueous solutions containing glyphosate can be realized by oxidative advanced processes. Processes based on the formation of hydroxyl radical, such as Ti/UV and O₃/pH 10, were effective for the degradation of glyphosate and its degradation intermediates, AMPA, after a short treatment time. Under the experimental conditions used in this study the degradation of glyphosate followed a pseudo first-order kinetic law for both processes studied. The half–lives obtained for glyphosate degradation were 1.8 and 6.2 minutes for O₃/pH 10 and TiO₂/UV, respectively.

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