Radiolytic Degradation of Glyphosate in Aqueous Solution by Co-60 Gamma Radiation in the presence of Hydrogen Peroxide

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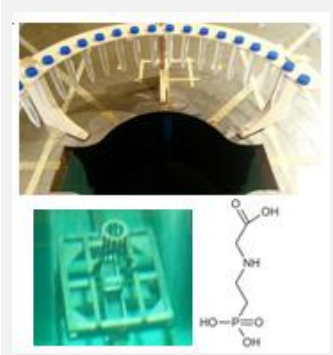

Glyphosate (GLP) is an organophosphorus herbicide widely applied in agriculture. However, its extensive and inadequate use has generated environmental problems. This work aimed to study the degradation of this pollutant using gamma radiation from a Co-60 source with the addition of H_2O_2 in the glyphosate solution. GLP solutions (0.3 mM) were treated in the presence of different concentrations of H_2O_2 (0 - 90 mM) at three gamma radiation doses of 0.5, 1.0 and 1.5 kGy. The results show that a greater degradation of GLP was obtained when the radiation dose and the concentration of H_2O_2 were increased. A GLP removal of 93 % was achieved at 0.5 kGy and 90 mM of H_2O_2. The concentration of the primary GLP degradation product AMPA was monitored. According to the results, the concentration of AMPA increased with the radiation dose and decreased with the addition of H_2O_2 at the same radiation dose.

Introduction

Glyphosate (GLP) is an organophosphorus herbicide widely employed in agriculture for the control of annual and perennial weeds [1]. Although GLP presents low soil mobility, its high solubility, runoff, spraying, spills, and inadequate final disposal are factors that increase its presence in soil and water bodies [2]. Moreover, this pollutant presents toxic effects on the environment and human health. For these reasons, it is necessary to develop strategies to remove this herbicide from water before any discharge takes place.

Traditional treatments such as filtration, adsorption, and biological degradation are not always effective for the removal of recalcitrant pollutants. Therefore, Advanced Oxidation Processes (AOPs) have been applied as feasible technologies for the removal of GLP. These techniques are based on the generation of hydroxyl radicals (•OH), chemical species considered among of the most strong and non-selective oxidizing agents [3]. There are some reports of the treatment of GLP using heterogeneous photocatalysis, photolysis, ozonation, and others [4,5].

Particularly, the application of ionizing radiation (gamma rays) has been proved as an alternative to degrading other organic pollutants, reaching removals higher than 90 % [6]. Gamma rays have high penetration [7], which allows the treatment of different water types. Moreover, it is known that the presence of H_2O_2 in appropiate concentrations by the irradiation process with gamma rays can enhance the generation of •OH [8].

This work aimed to study the removal of GLP in aqueous solutions by Co-60 gamma radiation in the presence of hydrogen peroxide.

Material and Methods

GLP solutions (50 mg/L or 0.3 mM) were prepared using GLP (Sigma Aldrich, 99.0 %) and Milli-Q® water. Samples of the solutions were irradiated using Co-60 gamma radiation at three doses (0.5, 1.0 and 1.5 kGy). Different concentrations of H_2O_2 (Fisher Chemical, 30.0 % w/w) were tested (2, 4, 15, 30 and 90 mM). After the treatment, the concentration of GLP and its primary degradation product, aminomethylphosphonic acid (AMPA), were measured by HPLC (Agilent Technologies 1120 compact LC). The mixture of methanol and ammonium acetate solution 5mM (pH 9) (70:30 v/v) was the mobile phase. Before the injection of the samples into the HPLC equipment, a pre-column derivatization process with 9-fluorenylmethoxycarbonyl chloride (FMOC-Cl) was performed to facilitate the detection and quantification of GLP and AMPA with a fluorescence detector.

Results and Discussion

Figure 1 shows the effect of gamma radiation doses on the removal of GLP. According to the results, there is an increase in the removal of GLP when the radiation dose is higher. The improvement of the degradation with the dose increase can be attributed to a greater generation of reactive species, typically conected with the water radiolysis (i.e. •OH, e_{aq}- and •H) [8]. A GLP removal of 78.7 % was achieved with 5 kGy.

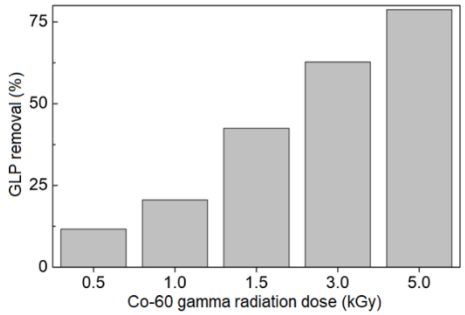

Figure 1. GLP removal as a function of the gamma radiation dose

The effect of the addition of hydrogen peroxide (H_2O_2) was studied. In this case, samples of GLP were irradiated at 0.5, 1.0 and 1.5 kGy in the presence of H_2O_2 (2, 4, 15, 30, 90 mM). Figure 2 shows the influence of the addition of H_2O_2 on the removal of GLP. From the results, it can be observed that the degradation of GLP increased when H_2O_2 was added. This effect was attributed to an increase in the generation of •OH. It was observed that the removal of GLP at 0.5 kGy increased from 11.7 % without H_2O_2 to 94.6 % with H_2O_2 (90 mM).

The concentration of the primary GLP degradation product AMPA was measured. This compound is produced as a consequence of the breakdown of a C-N bond of GLP.

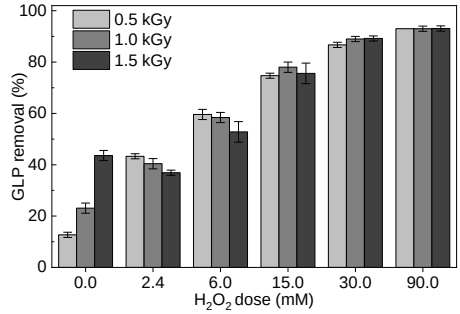

Figure 2. GLP removal as a function of gamma radiation and H_2O_2 doses

The concentrations of AMPA generated under different H_2O_2 and radiation doses are reported in Table 2. As shown in the table, the concentration of AMPA increased with the dose. On the other hand, it decreased with the addition of H_2O_2 at the same radiation dose.

Table 2. Concentration of AMPA (mg/L) generated as GLP was removed

Radiation dose (kGy)	[H_2O_2] (mM)					
	0	**2.4**	**6**	**15**	**30**	**90**
0.5	2.19	0.82	0.55	0.29	0.13	0.05
1.0	4.01	1.60	0.99	0.51	0.35	ND*
1.5	4.72	1.35	0.91	0.57	0.22	ND*

* ND means "no detected". The concentrations are below the Limit of Detection.

The increase in the concentration of AMPA with the radiation dose could be explained by the increment of the removal of GLP. As more GLP is removed, more AMPA is generated. Furthermore, it seems that when H_2O_2 is added not only GLP but also AMPA can be degraded.

Conclusions

Co-60 gamma radiation in the presence of H_2O_2 was applied for the removal of glyphosate (GLP). The results showed that an increase in the removal of GLP was achieved for higher radiation doses, in the range of this study (0.5 – 1.5 kGy). A GLP removal of 78.7 % was reached at 5 kGy. When H_2O_2 was added, an evident increase in GLP removal was observed. The concentration of the primary GLP degradation product AMPA was measured. According to the results, the concentration of AMPA increased with the radiation dose and decreased with the addition of H_2O_2 at the same dose. In other words, when H_2O_2 is added not only GLP but also a certain quantity of AMPA can be degraded.

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