

## Article

# Optimizing Glyphosate Removal from Water Using a Peracetic Acid-Assisted Advanced Oxidation Process: A Response Surface Methodology Approach

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**Abstract:** Glyphosate (GLY), one of the most used pesticides in the world, has been frequently detected in water, posing chronic and remote hazards to human health and the environment. Consequently, it has become necessary to develop efficient and sustainable treatment processes able to remove GLY from the polluted aquatic environments. In this context, the use of advanced oxidation processes is of great interest, as it allows for a significant reduction in concentrations of recalcitrant pollutants. In this study, peracetic acid (PAA) was used for the first time to remove GLY from water. In particular, the process parameters (oxidant dose, activation by UV radiation, GLY concentration, process time) were optimized using central composite design (CCD) and response surface methodology (RSM). The degradation of the pollutant, i.e., GLY, was monitored by ion chromatography, optimizing the instrumental parameters. During the process, residual oxidant concentrations were also constantly monitored using reference methods (i.e., UV-visible spectroscopy). Based on the results obtained, the best GLY removals (over 90%) were achieved under the following conditions: a PAA/GLY molar ratio of 3 (concentration of 3.0 mg/L for GLY and 4.0 mg/L for PAA), UV irradiation, and a process time of 45 min. The possibility of achieving total glyphosate removal by using small amounts of oxidant increases the environmental sustainability of the proposed aquatic pollution mitigation strategy.

**Keywords:** glyphosate; peracetic acid; ion chromatography; sustainable wastewater treatment; chemometric approach; pollution mitigation



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## 1. Introduction

Glyphosate (GLY) is a chemical largely employed as herbicide in agriculture for the control of various weeds and it is one of the most used pesticides in the world [1]. Due to its extensive use, this chemical has been frequently detected in water, mainly surface and groundwater nearest to agricultural areas, posing chronic and remote hazards to human health and the environment [2–5]. In Italy, GLY is the pesticide most commonly found in surface and groundwater at concentrations above the environmental quality standard, as reported by the Higher Institute for Environmental Protection and Research [6,7].

As a consequence, the number of studies on the development of efficient treatment processes for the removal of GLY from polluted aquatic environments has increased in recent years. Different technologies were reported in the literature [1,8,9]: adsorption [10–13], biological processes [14], and advanced oxidation processes (AOPs) such as photocatalysis [15–19], Fenton [20–22], and UV-based processes [23–26]. The AOPs are advantageous due to their better ability to remove recalcitrant compounds (total mineralization), with high removal efficiencies in short residence times [8,27–30]. The hydroxyl radical ( $\bullet\text{OH}$ ) plays

a central role in AOPs due to its high standard potentials: the degradation of glyphosate molecule is attributed to the attack of  $\bullet\text{OH}$  that leads to cleavage of the C–N and C–P bonds to yield intermediaries such as its major metabolite, aminomethylphosphonic acid (AMPA), sarcosine, or final degradation products such as nitrate, ammonium and phosphate ions, carbon dioxide, and water [1].

Peracetic acid (PAA) is an organic peroxyacid widely used as disinfectant, sanitizer, sterilizing agent, bleach, and oxidizer [31–34]. PAA, in fact, has become a promising substitute for chlorinated chemicals for water disinfection and microbial inactivation thanks to its advantages such as a high sterilization ability, a lower dependence on pH, an easy technical implementation, and the reduced formation of toxic byproducts in the treated effluent [32]. In addition to this consolidated use, thanks to its high oxidation potential PAA is able to degrade aqueous organic pollutants such as dyes, phenols, and pharmaceuticals [35]. In PAA-based AOPs, the radical formation can be activated by different methods such as light irradiation (mainly UV, but also solar), catalysis (metal ions such as  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ), and also ultrasound exposure [32,36–39]. Moreover, a synergistic effect for degrading organic contaminants and inactivating pathogens in water has also been observed for PAA-based AOPs [40].

Based on these interesting properties of PAA, the aim of this study is to apply for the first time a PAA-assisted AOP for the removal of glyphosate from water. In particular, the process parameters (oxidant dose, activation by light irradiation, GLY concentration, and process time) were optimized using central composite design (CCD) and response surface methodology (RSM). Moreover, this process was always carried out in comparison with the process which uses  $\text{H}_2\text{O}_2$  as an oxidant, since this has already been reported in the literature. Another important and innovative aspect is the use of low oxidant concentrations, close to those used in disinfection processes, as well as glyphosate concentrations closer to those of real contaminated wastewater, to evaluate the use of the proposed processes on a full scale.

## 2. Materials and Methods

### 2.1. Materials

All materials employed in this study (hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution 30%, peracetic acid 40%, glyphosate (PESTANAL<sup>®</sup>, analytical standard), potassium iodide (KI), sodium hydroxide (NaOH), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ), ammonium cerium(IV) nitrate ( $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ ), titanium(IV) oxysulfate solution ~15 wt.% in dilute sulfuric acid, N,N-diethyl-p-phenylenediamine (DPD), ortho-phenanthroline, potassium permanganate ( $\text{KMnO}_4$ )) were purchased from Sigma-aldrich (St. Louis, MO, USA).

### 2.2. Determination of Glyphosate Concentration

The concentration of glyphosate in solution was determined by ion chromatography [12,13], using a Thermo Scientific-Dionex<sup>™</sup> Aquion<sup>™</sup> (Thermo Fisher Scientific Inc., Waltham, MA, USA) ion chromatograph equipped with a conductivity system detector, a self-regenerating suppressor, and a Dionex IonPac<sup>®</sup>AS20 (Thermo Scientific-Dionex<sup>™</sup> Aquion<sup>™</sup> (Thermo Fisher Scientific Inc., Waltham, MA, USA) hydroxide-selective anion-exchange column. In order to achieve proper separations, several experimental conditions were tested: the sodium hydroxide eluent concentration ranged from 10 to 25 mM, the suppressor current from 40 to 100 mA, and the flow rate from 0.8 to 1.2 mL/min. The best results were achieved using a sodium hydroxide concentration of  $20.0 \pm 0.5$  mM, a suppressor current of 80 mA, and a flow rate of 1.0 mL/min. Glyphosate concentrations (expressed as mg/L) were calculated using calibration curves obtained with the standard solution in the range 0.1–30 mg/L (regression line  $y = 0.0445x - 0.0047$ ;  $R^2 = 0.9991$ ). The achieved limit of detection (LOD) and limit of quantification (LOQ), calculated based on the standard deviation of the response and the slope, were 0.03 and 0.1 mg/L, respectively.

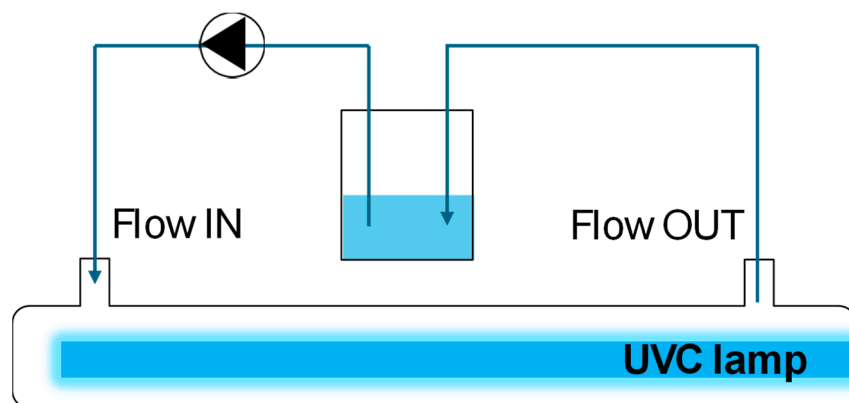
### 2.3. Determination of Oxidant Concentration

Firstly, the commercially available solutions of oxidants were titrated to verify their exact concentration. In detail, the concentration of PAA was determined by iodometric titration with a 0.1 M sodium thiosulphate solution, while the concentration of  $\text{H}_2\text{O}_2$  was measured by permanganometric titration with a 0.02 M solution of potassium permanganate, obtaining concentrations of  $337 \pm 8$  g/L and  $310 \pm 5$  g/L, respectively [41].

Residual oxidant concentrations during the process were determined using UV-visible spectroscopy tests specific to the two oxidants. In particular, the DPD test was used for PAA (absorbance measurement at 565 nm) [41], while the Titanium(IV) oxysulfate test was used for  $\text{H}_2\text{O}_2$  (absorbance measurement at 410 nm) [42].

### 2.4. Experimental Setup

The advanced oxidation process applied to glyphosate solution utilizes  $\text{H}_2\text{O}_2$  and PAA as oxidizing agents, with UV-C radiation generated by an 8 W power lamp (peak at 254 nm) positioned within a closed system. The internal surface of the system was mirrored to maximize UV-C radiation efficiency (Figure 1). The glyphosate solution (1 L) was circulated continuously using a peristaltic pump with a flow rate of 67 mL/min, ensuring each treatment cycle lasted 15 min. Various experimental conditions were examined concerning the oxidizing agent/glyphosate molar ratio. To test the efficiency of UV radiation, experiments in the dark (using only the oxidant species) were performed. During the process, the solution was kept in continuous agitation. For some processes, samples were taken every 15 min until the process was completed (1 h), while for other processes, samples were taken at  $t = 5, 10, 20, 30, 45,$  and 60 min, to observe the kinetics of the AOP at shorter times.



**Figure 1.** Experimental setup for UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  processes.

Preliminary experiments were conducted at high GLY concentrations (20 and 10 mg/L) and a GLY/oxidant molar ratio in the range 1:2–1:4, to explore the experimental setup. The optimization of all experimental parameters was performed at a GLY concentration of 3.0 mg/L, a value closer to the environmental concentration.

Finally, experiments were carried out with sunlight. Specifically, 1 L of glyphosate solution (3.0 mg/L) was transferred into a Pyrex glass bottle, then an appropriate volume of oxidant was added to achieve a GLY/oxidant molar ratio of 1:3 (PAA concentration of 4.0 mg/L and  $\text{H}_2\text{O}_2$  concentration of 1.8 mg/L), and the obtained solution was subjected to sunlight under magnetic stirring for 180 min, taking samples every 30 min.

### 2.5. Experimental Design

In this study, central composite design (CCD) and response surface methodology (RSM) were utilized to identify the optimal conditions for maximizing the removal of GLY at a concentration of 3.0 mg/L. The targeted response for maximization was the GLY percentage removal. The numerical factors adjusted during the RSM were the molar ratio between GLY and the oxidant (GLY/oxidant) ( $X_1$ ) and the reaction time ( $X_2$ ), while

the oxidant type (PAA or H<sub>2</sub>O<sub>2</sub>) was incorporated as a categorical factor (X<sub>3</sub>). These specific factors were judiciously chosen based on their significant impact on the percentage removal of GLY. Based on the outcomes of initial experiments, the levels for X<sub>1</sub> and X<sub>2</sub> were specified to fine-tune the operational parameters, thereby enhancing the efficiency of the oxidation process for the response. The culmination of this preliminary optimization was the establishment of the following kinetic study. The selected ranges and levels of the factors are delineated in Table 1.

**Table 1.** Selected ranges and levels of the factors for RSM.

Variables	Code	Range and Levels				
		L [1]	L [2]	L [3]	L [4]	L [5]
Level		L [1]	L [2]	L [3]	L [4]	L [5]
Coded value		−α	−1	0	+1	+α
mol OX: mol GLY	X <sub>1</sub>	0.5	1	2	3	4
Time (min.)	X <sub>2</sub>	10	20	30	45	60
Oxidant type	X <sub>3</sub>	-	PAA	-	H <sub>2</sub> O <sub>2</sub>	-

The response was estimated through a quadratic model according to Equation (1):

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^n b_{ij} X_i X_j + \varepsilon \quad (1)$$

Y is the response of GLY percentage removal, b<sub>0</sub> is the model intercept, b<sub>i</sub> corresponds to the linear coefficient of X<sub>i</sub>, b<sub>ii</sub> is the second order effect on regression coefficients, b<sub>ij</sub> is the interaction coefficient, and ε is the statistical error.

The restriction for the factors was the minimization of the oxidant/GLY molar ratio and the minimization of treatment time. The goal selected for the response was the maximization of GLY percentage removal.

### 2.6. Kinetic Study

Data analysis and kinetics for optimized processes were carried out with the support of OriginLab pro 2021 software. All tests were carried out in triplicate. The error is shown as the standard deviation (SD) of the mean. Kinetic order and k values were obtained from linear fitting. Kinetic equations and t<sub>1/2</sub> were developed according to the following equations (Equations (2) and (3)):

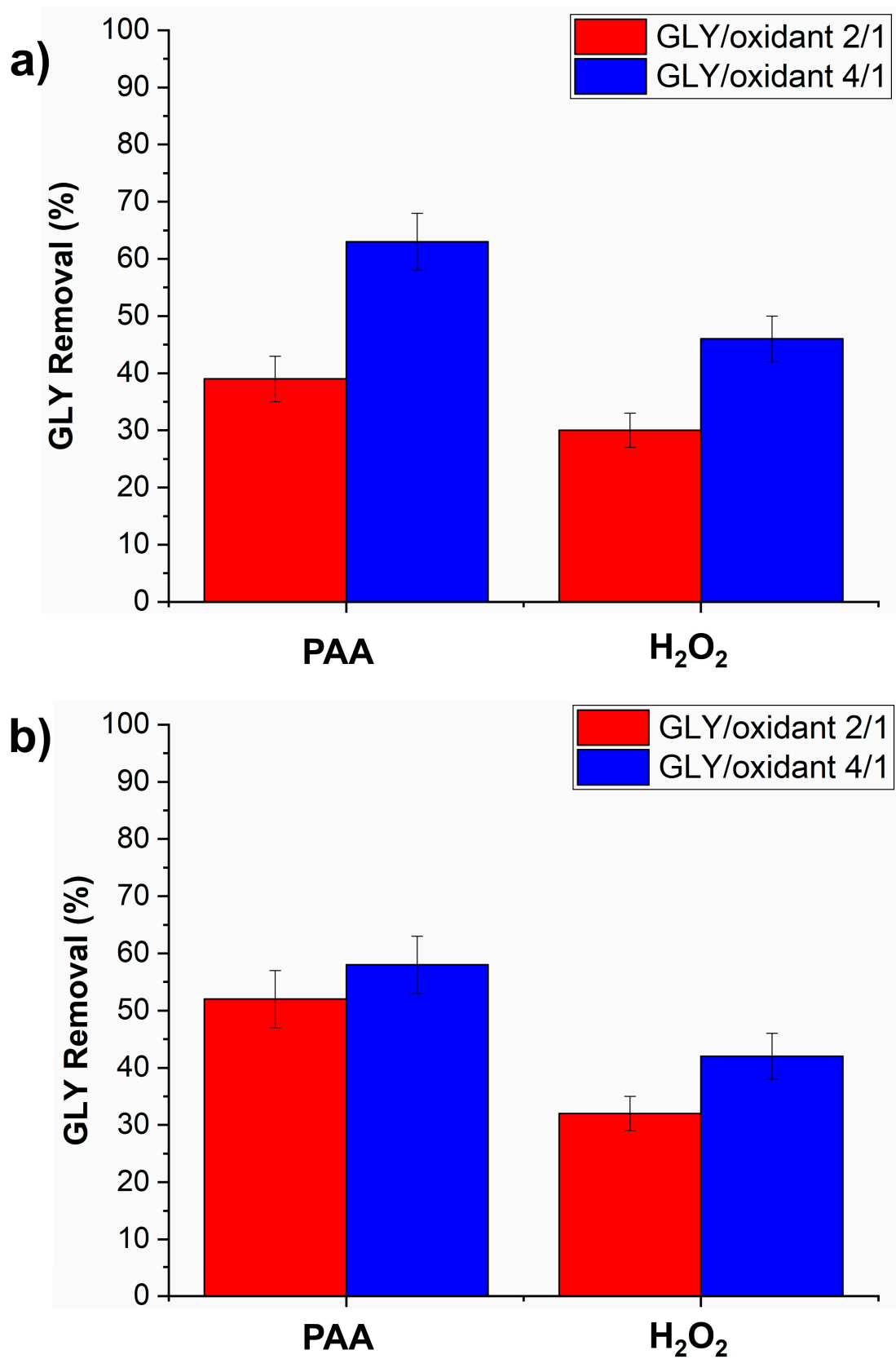
$$\ln\left(\frac{[GLY]_t}{[GLY]_0}\right) = -kt \quad (2)$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \quad (3)$$

## 3. Results and Discussion

### 3.1. Preliminary Results

In this study, PAA was used for the first time to remove GLY from water. To explore the experimental setup, preliminary experiments were conducted at GLY concentrations of 20 and 10 mg/L, higher than environmental ones, in comparison with H<sub>2</sub>O<sub>2</sub>, an oxidant already used for GLY removal (Figure 2).



**Figure 2.** Results of the preliminary experiments of UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> processes with a GLY/oxidant molar ratio of 1:2 and 1:4 and a GLY concentration of 20 mg/L (a) and 10 mg/L (b).

Starting from a concentration of 20 mg/L, GLY removal values of  $39 \pm 4\%$  and  $63 \pm 5\%$  with PAA, and  $30 \pm 3\%$  and  $46 \pm 4\%$  with  $H_2O_2$ , were achieved after 60 min of treatment, at GLY/oxidant molar ratios of 1:2 and 1:4, respectively (Figure 2a). Reducing the concentration of GLY down to 10 mg/L, GLY removal values of  $52 \pm 5\%$  and  $58 \pm 5\%$  with PAA, and  $32 \pm 3\%$  and  $42 \pm 4\%$  with  $H_2O_2$ , were achieved after 60 min of treatment, at GLY/oxidant molar ratios of 1:2 and 1:4, respectively (Figure 2b). These preliminary results suggest that PAA is able to degrade GLY under the activation of UV light, with only a small difference in terms of removal at varying initial GLY concentrations. Regarding the % of residual oxidant at the end of treatment, results are in line with the observed GLY removals, with a higher % of residual  $H_2O_2$  (range 40–50%) with respect to PAA (range 20–35%).

The results obtained with  $H_2O_2$  are in line with those reported in the literature in terms of % removals obtained for similar GLY/oxidant molar ratios (between 1:2 and 1.4), but at higher glyphosate concentrations (50 mg/L), and much longer treatment times (5 h). Authors reported that the best GLY removals (70% after 5 h and lower than 20% after 1 h of treatment) required higher GLY/oxidant molar ratios (from 1:7 to 1:20), resulting in high reagent consumption [23,25].

### 3.2. Optimization of Process Parameters by Response Surface Methodology

In this work, the AOPs UVC/PAA and UVC/ $H_2O_2$  were optimized using RSM analysis to evaluate their potential as a treatment for the oxidation and the degradation of GLY from the water matrix. The optimization of all experimental parameters was performed at a GLY concentration of 3.0 mg/L, a value closer to the environmental concentration.

Based on the results obtained from the quadratic model (the full experimental design with actual values and the associated results are shown in the Supporting Material, Table S3), the empirical relationships between the response and the independent variables can be described by the following equations showing the actual values of the parameters (Equations (4) and (5)):

$$Y_{PAA} = -36.26 + 28.57X_1 + 2.75 X_2 - 0.01 X_1X_2 - 2.79 X_1^2 - 0.02 X_2^2 \quad (4)$$

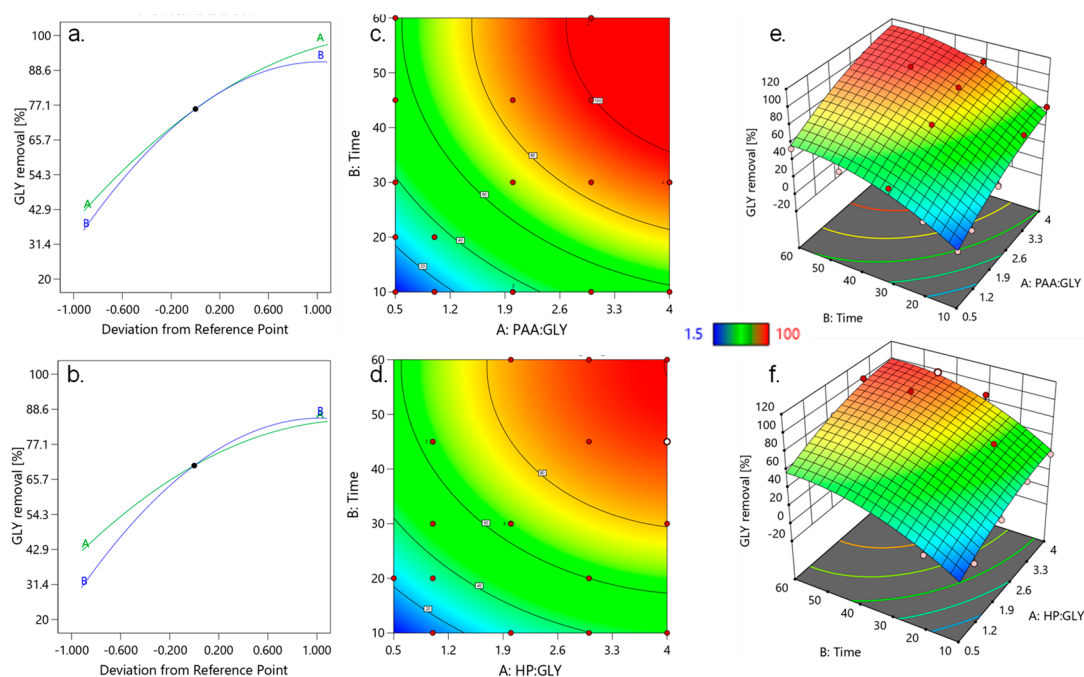
$$Y_{H_2O_2} = -36.4 + 24.9X_1 + 2.81 X_2 - 0.01 X_1X_2 - 2.79 X_1^2 - 0.02 X_2^2 \quad (5)$$

The results of the ANOVA test for GLY removal have been reported and thoroughly discussed in the Supporting Materials (SM) file. In summary, the determination coefficient for GLY removal was  $R^2 = 0.9940$ . The differences between predicted and adjusted  $R^2$  were less than 0.2 in both cases. Importantly, the Lack of Fit tests ( $p$ -value: 0.09) were not significant compared to the pure error.

Concerning the validation of the model assumptions, the residual plots shown in the SM file demonstrate small deviations from the straight line. This indicates that the studentized residuals can be considered to follow a normal distribution for GLY removal. The residual plot displays a random scatter approximately centered on zero across the entire range of predicted values, indicating that the residuals are random and the variance of the observations is constant for all response values. Moreover, no outliers were identified in either case.

The removal of GLY was investigated under various operating conditions, as outlined by the experimental design using RSM. Figure 3a,b present the perturbation plots for the removal of GLY using PAA and  $H_2O_2$ , respectively. In these plots, the molar ratios of oxidant to GLY (Factor A) and the treatment time (Factor B) are plotted to examine their effects at specific points within the design space. The plots show how the responses vary as each factor deviates from the reference point, which is the center (midpoint) of the experimental design. On the x-axis, the levels of the investigated factors are represented by the values  $-1$ ,  $-0.6$ ,  $-0.2$ ,  $0$ ,  $0.2$ ,  $0.6$ , and  $+1$ . In analyzing the perturbation plots, a positive effect indicates that the response—GLY removal in this case—increases as the level of the

factor increases. Conversely, a negative effect implies that the response decreases with an increase in the factor level.



**Figure 3.** Perturbation plots for the removal of GLY using PAA (a) and H<sub>2</sub>O<sub>2</sub> (b); contour plots for the removal of GLY using PAA (c) and H<sub>2</sub>O<sub>2</sub> (d); three-dimensional response surface of GLY removal efficiencies for PAA (e) and H<sub>2</sub>O<sub>2</sub> (f).

In both processes, assisted by PAA and H<sub>2</sub>O<sub>2</sub>, oxidant dosage and treatment time showed a positive effect until the midpoint, after which the treatment time reached a plateau. The initial positive response can be attributed to the increased concentration of oxidants—PAA and H<sub>2</sub>O<sub>2</sub>. These oxidants generate more reactive species that interact with GLY, thereby enhancing the degradation process. As the levels of these factors approach the midpoint, optimal conditions for glyphosate degradation appear to be reached, as evidenced by the peak in removal efficiency. Beyond this midpoint, the influence of treatment time plateaus. This leveling off suggests a point of diminishing returns, where increasing the treatment time further does not significantly improve GLY removal. This plateau may be due to several factors, such as the depletion of oxidants, the stabilization of reaction intermediates, or the attainment of equilibrium between glyphosate degradation and by-product formation. The contour plots and the three-dimensional response surface of GLY removal efficiencies are shown in Figure 3c,e for the PAA-assisted process and in Figure 3d,f for the H<sub>2</sub>O<sub>2</sub> one.

The results from the comparative analysis of GLY removal using two distinct advanced oxidation processes—UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub>—demonstrate significant efficiencies in the degradation of GLY under optimized conditions (Figure 3). The UVC/PAA system, with a molar ratio of PAA to GLY set at 3:1 and a contact time of 60 min, achieved an exceptional removal efficiency of approximately 99.9% (Figure 3e). This high level of efficiency can be attributed to the strong oxidative potential of PAA, which, when activated by UVC light, generates highly reactive radicals capable of the rapid and extensive degradation of glyphosate molecules. In comparison, the UVC/H<sub>2</sub>O<sub>2</sub> system also showed a high removal efficiency, achieving about 99% GLY degradation under identical conditions of oxidant to GLY ratio and contact time (Figure 3f). While slightly less effective than the PAA system, the H<sub>2</sub>O<sub>2</sub>-based treatment still performs excellently, underscoring the efficacy of hydrogen peroxide as a potent oxidant when paired with UVC radiation. The radicals produced in the UVC/H<sub>2</sub>O<sub>2</sub> system (predominantly HO•), although slightly less reactive than those

generated by PAA ( $\text{HO}^\bullet$  and  $\text{CH}_3\text{COO}^\bullet$ ), still facilitate a substantial breakdown of the GLY structure. From the surface response analysis, PAA not only achieves higher removal rates but also requires comparatively less treatment time to reach peak efficiency than  $\text{H}_2\text{O}_2$ . This can be partly explained by the more robust and rapid generation of radicals by PAA under UVC activation, which enhances the reaction kinetics. Furthermore, the oxidative degradation pathway facilitated by PAA may be more effective at targeting and breaking down the specific chemical bonds of GLY, leading to a more complete mineralization of the molecule. These findings suggest that while both UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  systems are effective for treating glyphosate-contaminated water, the UVC/PAA system might offer a more practical solution in scenarios where treatment time is a critical factor and where achieving near-complete removal is necessary. Moreover, the data indicate the potential for optimizing these AOPs to enhance their practical application in water treatment facilities, particularly for the removal of persistent organic pollutants like GLY. This has significant implications for improving the safety and quality of water, addressing public health concerns, and meeting stringent environmental regulations.

The data obtained from the two processes illustrated can be compared with the results reported in the literature for glyphosate degradation by different processes [1,8]. Adsorption using typical adsorbent (activated carbon, clay, etc.) is a simple technology that can effectively remove glyphosate from wastewater, but it generally requires a long process time (about 24 h) and a post-treatment [8]. Likewise, biological treatments are low-cost and eco-friendly, but they need a pre-treatment for reducing the toxicity of the wastewater, and a long residence time for completely degraded glyphosate. AOPs techniques are more effective for glyphosate degradation, since they require a short process time compared to the other processes mentioned above. However, they have disadvantages such as the consumption of energy and reagents and the production of sludge. For example, with photocatalysis [15–19] and Fenton [20–22], high glyphosate removals can be achieved in a short time (0.5–5 h) but involve the use of catalysts and changes in the pH of the effluent, requiring further treatment, whereas ozonation oxidation is high cost and could generate harmful by-products [8].

The advantages of the process studied over other AOP processes reported in the literature are firstly that it allows quantitative glyphosate removals to be achieved in a shorter time (1 h) and using only one reagent, which is the oxidizing species, i.e., PAA, and secondly that it is used in low concentrations (1–5 mg/L), which are close to those used in disinfection processes, suggesting easy full-scale use. Moreover, high reagent consumption (GLY/oxidant molar ratios from 1:7 to 1:20) is required for the UVC/ $\text{H}_2\text{O}_2$  process reported in the literature to only achieve a GLY removal of about 20% after 1 h of treatment starting from a higher GLY concentration (50 mg/L) [23,25].

### 3.3. Kinetic Study

According to the RSM analysis, the optimal conditions for effectively removing GLY in UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  processes are as follows:

- (i) PAA/GLY = 3/1 and 45 min of treatment time
- (ii)  $\text{H}_2\text{O}_2$ /GLY = 3/1 and 45 min of treatment time

These optimal conditions were applied to solutions of 3 mg/L of GLY in the UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  processes. Figure 4 shows the kinetics for UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  for GLY removal.

The optimized UVC/PAA and UVC/ $\text{H}_2\text{O}_2$  processes achieved remarkable glyphosate reduction efficiencies, reaching a final concentration lower than 30  $\mu\text{g/L}$ , which corresponds to reductions greater than 99% for both processes. This demonstrates the high efficacy of these treatments in reducing glyphosate to very low levels. Additionally, the consumption rates of PAA and  $\text{H}_2\text{O}_2$  were approximately 80% and 65%, respectively, indicating a significant utilization of the oxidants during the treatment.



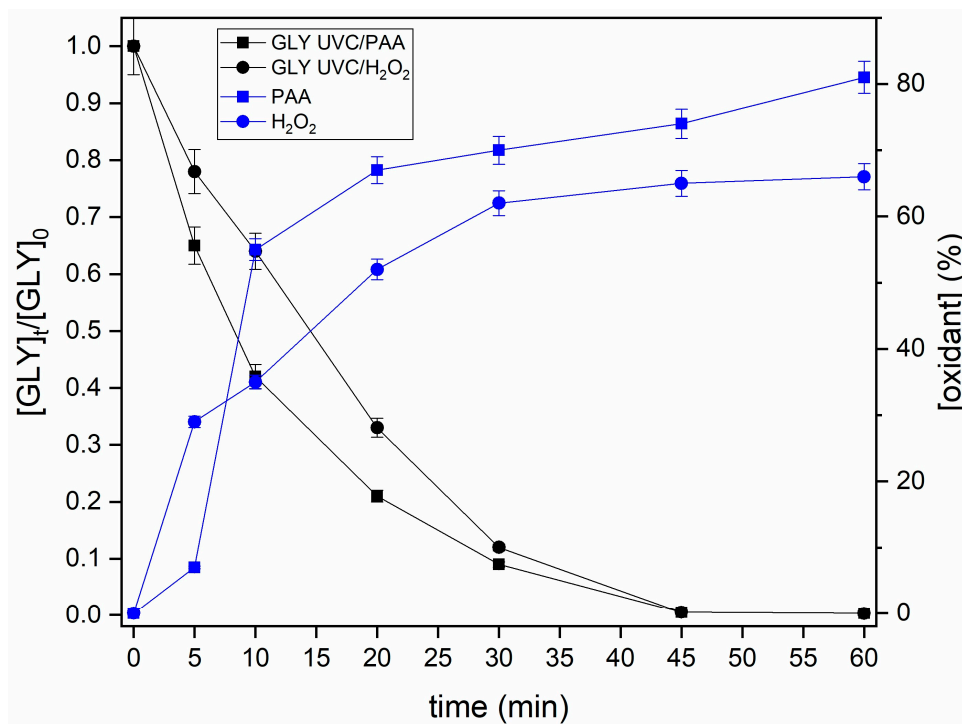


Figure 4. Kinetics for UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> for GLY removal.

The first-order kinetic models proved to be suitable to describe both processes since R<sup>2</sup> was >0.95. The kinetic constant *k* was 0.099 and 0.096 whereas the *t*<sub>1/2</sub> was 7 min for both processes (Table 2).

Table 2. Parameters obtained from the kinetic study.

Parameter	Kinetic Order	<i>k</i> (min <sup>-1</sup> )	<i>t</i> <sub>1/2</sub> (min)	R <sup>2</sup>
UVC/PAA	First	0.099	7	0.98
UVC/H <sub>2</sub> O <sub>2</sub>	First	0.096	7	0.96

The kinetic graph (Figure 4) illustrates the reaction kinetics for GLY removal under UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> treatments. The normalized concentration of GLY (*C*/*C*<sub>0</sub>) depicted by the black lines shows a marked reduction over time, indicative of GLY degradation. UVC light activates PAA and H<sub>2</sub>O<sub>2</sub> through photolysis, leading to the generation of hydroxyl radicals (\*OH) and other reactive species. Specifically, UVC irradiation causes the decomposition of PAA into hydroxyl and acetate radicals, while H<sub>2</sub>O<sub>2</sub> undergoes homolytic cleavage to produce two hydroxyl radicals. These radicals are highly reactive and significantly enhance the degradation of pollutants by breaking down their molecular structures.

In the UVC/PAA treatment, a pronounced decline in GLY concentration is observed within the initial 15 min, suggesting rapid degradation kinetics. This could be associated with an efficient generation of reactive oxidative species by PAA when activated by UVC radiation, which results in a quicker reduction in GLY levels.

By comparison, the UVC/H<sub>2</sub>O<sub>2</sub> treatment displays a more gradual initial decline in GLY concentration yet maintains a consistent degradation rate throughout the treatment duration. This indicates that despite a slower onset, the process continues to effectively reduce GLY levels.

Both treatment processes approach and achieve the near-complete removal of GLY, with the UVC/PAA system reaching negligible levels at a faster rate. This is consistent with the optimal treatment time of 45 min, as previously determined by RSM analysis, validating the efficacy of the established conditions.

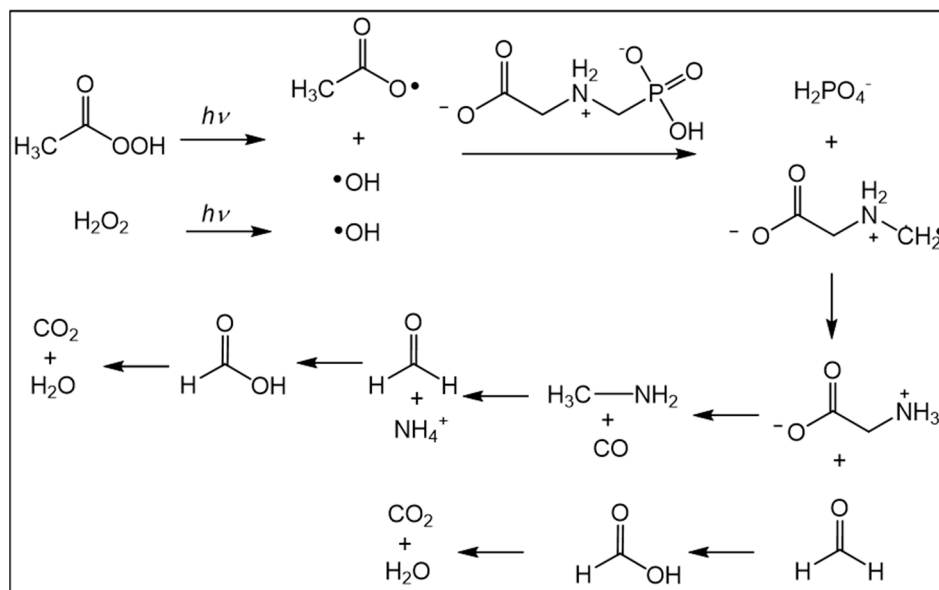
The concurrent reduction in PAA and H<sub>2</sub>O<sub>2</sub> concentrations, depicted by the blue lines, reflects the oxidants' consumption. The steeper decrease in PAA aligns with the higher removal efficiency of GLY, whereas the more gradual decrease in H<sub>2</sub>O<sub>2</sub> concentration corresponds with the less aggressive decline of GLY concentration.

Notably, the concentrations of PAA and H<sub>2</sub>O<sub>2</sub> do not diminish to zero, indicating that the applied oxidant dosages were more than sufficient to achieve GLY degradation without the complete depletion of the oxidants. This observation is relevant for optimizing the process, ensuring that oxidant usage is both effective and economical.

The adherence of the glyphosate degradation process to first-order kinetics is substantiated by high correlation coefficients ( $R^2 > 0.95$ ). The kinetic constants ( $k$ ) for UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> treatments are closely matched, reinforcing the notion that both systems, while exhibiting different rates of reaction initiation, are competent for GLY degradation within the determined optimal treatment timeframe.

This kinetic analysis confirms the effectiveness of the UVC/PAA system in rapidly reducing GLY concentrations, with the UVC/H<sub>2</sub>O<sub>2</sub> system also demonstrating substantial degradation capability. These results corroborate the optimal conditions derived from RSM analysis and highlight the potential of both advanced oxidation processes in wastewater treatment applications, with positive implications for environmental management and public health safety.

Based on what has been reported in the literature for the degradation process of glyphosate in the presence of hydrogen peroxide and UVC radiation [25], we can assume that the processes reported in this study follow the mechanism shown in Figure 5. Given the few differences between the kinetics observed with H<sub>2</sub>O<sub>2</sub> and PAA, we can assume that the reaction steps are similar for the two processes. Therefore, only one reaction pathway is illustrated in Figure 5.



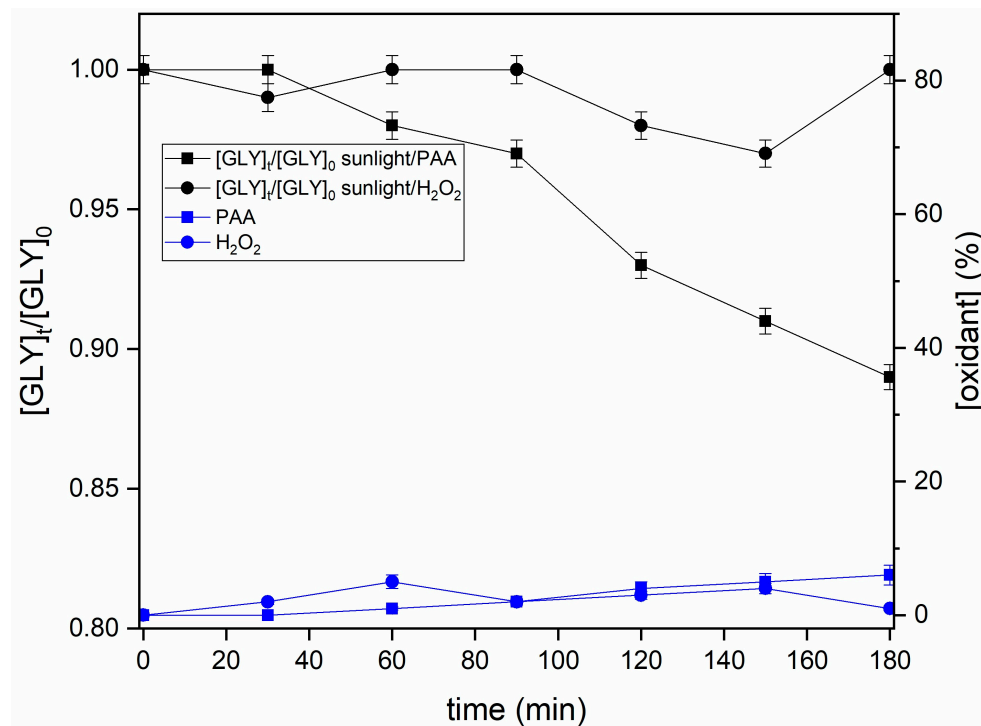
**Figure 5.** Proposed reaction mechanism for glyphosate degradation with the UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> process.

Firstly, UV radiation activates the homolytic cleavage of the two oxidizing species with the formation of hydroxyl radical •OH in both cases and also the acetate radical CH<sub>3</sub>COO• in the case of PAA. In the presence of glyphosate, these radicals react, leading to the formation of phosphate and a carbon centered radical •CH<sub>2</sub>-NH<sub>2</sub><sup>+</sup>-CH<sub>2</sub>-COO<sup>-</sup>. The subsequent reactions of this carbon radical can promote the formation of glycine <sup>-</sup>OOC-CH<sub>2</sub>-NH<sub>3</sub><sup>+</sup> and formaldehyde (HCOH). Glycine undergoes decarboxylation with the subsequent formation of further formaldehyde and ammonia. The formaldehyde can

be directly oxidized to formic acid (HCOOH), and finally to CO<sub>2</sub> and water. Obviously, further experiments are needed to verify the proposed mechanism.

### 3.4. Sunlight-Activated Processes

UVC/PAA and UVC/H<sub>2</sub>O<sub>2</sub> processes were compared to sunlight/PAA and sunlight/H<sub>2</sub>O<sub>2</sub> processes (Figure 6) for GLY removal under the same oxidant concentration but for a longer treatment time (180 min), to assess the feasibility of applying a more eco-friendly process.



**Figure 6.** Kinetics for sunlight/PAA and sunlight/H<sub>2</sub>O<sub>2</sub> for GLY removal.

The data indicate a notably less pronounced reduction in GLY concentration when sunlight is used as the irradiation source compared to the UVC light processes. The sunlight/PAA and sunlight/H<sub>2</sub>O<sub>2</sub> treatments show minimal changes in GLY concentration over time, suggesting that these processes are significantly less effective under the conditions tested. The kinetics for the sunlight-driven processes indicate a discernible disparity in the removal efficiency of GLY using PAA and H<sub>2</sub>O<sub>2</sub>. Under the conditions tested, the sunlight/PAA treatment achieved a GLY removal efficiency of approximately 11%, as represented by the marginal decline in the glyphosate concentration ( $C/C_0$ ). Conversely, the sunlight/H<sub>2</sub>O<sub>2</sub> treatment did not exhibit any noticeable reduction in GLY levels, indicating an absence of removal under the same conditions. The modest 11% removal efficiency observed with sunlight/PAA suggests that, while some activation of PAA occurred, it was not sufficient to facilitate significant degradation of glyphosate. This outcome could be attributed to the lower activation potential of PAA by the solar UV light components, which are less intense compared to artificial UVC light sources. In contrast, the complete lack of efficacy in the sunlight/H<sub>2</sub>O<sub>2</sub> process points to an even more pronounced limitation of sunlight to initiate the required photochemical reactions for GLY degradation with H<sub>2</sub>O<sub>2</sub>. The disparity between the PAA and H<sub>2</sub>O<sub>2</sub> processes could be related to the different mechanisms by which these oxidants produce reactive oxidative species when activated by UV light. It is possible that PAA is somewhat more responsive to the available solar UV radiation than H<sub>2</sub>O<sub>2</sub>, leading to the observed minimal GLY removal. These findings emphasize the challenges in employing sunlight for AOPs in contaminant degradation, particularly in the case of H<sub>2</sub>O<sub>2</sub>, which appears to be significantly less reactive under solar irradiation as opposed to controlled UVC light. This is a crucial consideration for the application of such

eco-friendly processes in real-world scenarios, where the efficiency of solar-driven chemical reactions can be significantly lower than those driven by more intense and focused UVC light. To enhance the feasibility of sunlight-based treatment methods, it may be necessary to explore the use of solar concentrators, which could increase the intensity of the effective UV light spectrum, or to investigate alternative catalysts that can better harness solar energy. Furthermore, optimizing the treatment duration and oxidant concentration in accordance with the variable nature of sunlight may also be key to improving the removal efficiency of contaminants like glyphosate.

#### 4. Conclusions

In this study, PAA-based AOPs was employed for the first time to remove GLY from water, in comparison with  $H_2O_2$ , an oxidant already used for GLY removal. Process parameters such as oxidant dose, activation by UV radiation, GLY concentration and process time were optimized using a response surface methodology approach. According to the RSM analysis, the optimal conditions for effectively removing GLY in UVC/PAA and UVC/ $H_2O_2$  processes are a PAA/GLY molar ratio of 3 (concentration of 3.0 mg/L for GLY, 4.0 mg/L for PAA, and 1.8 mg/L for  $H_2O_2$ ), and a process time of 45 min, reaching final concentrations of GLY lower than 30  $\mu\text{g/L}$ , which corresponds to reductions greater than 99% for both processes. The comparison of these UVC-activated processes with the eco-friendlier sunlight/PAA and sunlight/ $H_2O_2$  shows that sunlight is not sufficient to activate the degradation process of glyphosate, which, after 180 min of treatment, only reaches 11% with PAA and zero degradation with  $H_2O_2$ .

In conclusion, the proposed AOPs achieve total glyphosate removal using low concentrations of oxidants, in the range of those currently used in disinfection processes in wastewater treatment plants, in short treatment times (45 min), resulting in a sustainable aquatic pollution mitigation strategy.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su16135741/s1>, Table S1. ANOVA results. Table S2. Fit statistics. Table S3. Full experimental design and results in actual values. Figure S1. Predicted vs Actual values. Figure S2. residuals vs predicted.

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