Electrochemical monitoring of the oxidative degradation of glyphosate with UV/H$_2$O$_2$

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Abstract.
A voltammetric method optimized for the sensitive and reliable study of the UV/H$_2$O$_2$ oxidation of glyphosate (N-(phosphonomethyl) glycine) (GPS). The cell consisted of three electrodes in a compartment, silver wire coated with silver chloride as a pseudo reference electrode, platinum electrode as working electrode and stainless steel as auxiliary electrode. GPS cyclic voltammetric analysis suggests the formation of a GPS-Pt complex on the electrode surface, with an enhanced signal in perchloric acid between 1.3 to -1.3V; sensitive to protonation of the amino group, no response observed at pH values greater than 5.0. The oxidative degradation of GPS with UV/H$_2$O$_2$ is evident at pH 3.0, it exhibits first order pseudo kinetics with a half-life of 40 ± 4min. Two degradative routes are estimated depending on the concentration of H$_2$O$_2$: at low concentrations (H$_2$O$_2$/GPS 1:100 ratio), the formation of sarcosine and then glycine is favored; at H$_2$O$_2$/GPS 1:20 and 1:10 ratios predominate the formation of glycine.

1. Introduction
The remediation of water contaminated by toxic organic compounds, such as herbicides, pesticide dyes, pharmaceuticals, detergents, among many has been the subject of many investigations. These organic pollutants are responsible for a large amount of damage to the environment, especially when they accumulate in matrices such as soil and water [1].

The main sources of pollution in Colombia attributed to the petrochemical, chemical, textile, pharmaceutical, and agricultural industry [2]. In particular, growth in agricultural production has led to an increase in the demand for pesticides and herbicides for pest control [3].

The herbicide GPS is broad spectrum, non-selective, with activity for all annual and perennial plants used primarily in agriculture. It inhibits the enzyme 5-enolpiruvilsiquimato 3-phosphate synthase, which acts on the biosynthesis of amino acids, mainly those with aromatic residues in the molecules, fundamental for the development of plants, such as tryptophan, tyrosine and phenylalanine. In plants and some microorganisms, GPS inhibits the pathway of shikimic acid, causing a deficit in aromatic amino acids. The content of shikimic acid increased by 15% and 21% on average in response to the lowest GPS concentrations of 1 and 3 μM, respectively [4].

In Colombia, GPS is widely used in agriculture to accelerate fruit ripening and to inhibit the growth of grasses, broadleaf grasses and woody plants [5] given its effects between 10% to 14% of its application, it’s used for Coca and poppy eradication [6].
A problem of major concern is the resistance of these organic compounds to the technical disposal of wastewater treatment, which culminates in a lower efficiency of removal of contaminants from water currents. Generally, contamination of water or sites where final disposal made by herbicides can occur through fumigation, air or land transportation, leaching through soil and water erosion, disposal of commercial containers and aerosol cleaning [7].

The inadequate cleaning or disposition of the containers that had the herbicide can contaminate the water sources or the places where they are finally disposed of [8]. Among the alternatives and technologies, for the analysis and treatment of persistent toxic organic compounds in the environment are Fenton treatment [9] the advanced oxidation with hydrogen peroxide and UV [10], some herbicides monitored for chromatographic derivatization [11].

This study contributes in the use of electrochemical techniques for the determination and monitoring of oxidative degradation of commercial GPS with UV/H$_2$O$_2$. It determines kinetic aspects of oxidation and its viability to implement with unskilled personnel towards the adequate management of the herbicide residues.

2. Methodology

2.1. Electrochemical cell
Electrochemical measurements for the determination of the platinum electrode area, electrochemical characterization, percentages and degradation kinetics of GPS, selected in this study, were performed on a potentiostat (PG-Tekcorr 4.1 USB) with a three-electrode cell. The working electrode consisted of a Platinum electrode, subjected to a pre-cleaning treatment, a reference electrode of silver wire coated with silver chloride and an auxiliary electrode of stainless steel bar. The platinum electrode was cleaned before each measurement, subjected to ultrasound (Aquasonic 75D, 60 Hz) for 2 minutes in a solution of isopropanol (Merck, 99.5%) and 1:1 distilled water. Finally, it was rinsed with distilled water.

2.2. Calibration curve
The calibration curve was performed by chronoamperometry in a potential step between 0 and -1.0V vs Ag/AgCl. A standard solution of 0.10mol.L$^{-1}$ GPS was prepared, from which dilutions made up to 0.1µmol.L$^{-1}$, in all cases it diluted with HClO$_4$ pH 3.00. The current graph at ($\tau$ = 3s) vs concentration allowed to determine the linear range and the limit of detection.

2.3. UV/H$_2$O$_2$ oxidation of glyphosate
The monitoring of GPS by degradation of commercial Roundup® glyphosate (745 SG) of 0.10mol.L$^{-1}$ concentration was subjected to UV radiation (wavelength 254 nm) in the presence of hydrogen peroxide (Merck 30%) at different pH adjusted with HClO$_4$ (pH 3.0, 4.0, and 5.0). The effect of the peroxide ratio performed at pH 3.0 and varying concentrations of hydrogen peroxide (0.001, 0.05 and 0.01mol.L$^{-1}$). Chronoamperometric monitoring was performed at -1.0V every 15 minutes for three hours. From the graph of the natural log of current versus reaction time, the degradation rate constant and the reaction order were determined.

3. Analysis of results

3.1. Voltammetric Response
The GPS cyclic voltammetric response exhibits a quasi-reversible redox behavior with $\Delta$Ep of 0.139V, and an $\text{Ipc}/\text{Ipa}$ ratio of 1.3 with adsorption of the reduced compound at the electrode surface. Consecutive voltammetric cycles show a slight decrease in the cathodic peak currents and a greater adsorptive effect on the anodic current. In Figure 1, the cathodic peak A (-0.113V) corresponded to the overpotential of H$^+$ reduction adsorbed on the surface of the electrode to H$_2$ [12]; the cathodic peak B is associated with the reduction of counterions adsorbed at the platinum electrode. The potential can
change depending on the electrolyte used, for the case of perchlorate ion it has a value of -0.592V; It is known in the literature that the phenomenon of adsorption of sulfate and phosphate counterions is strong [13], while that of perchlorate is weak [14]. The cathode peak C is associated with the reduction of the GPS-Pt (II) complex adsorbed on the electrode surface and finally peak D corresponds to the reduction of the GPS-Pt (II) complex to Pt.

Platinum (II) ion with GPS forms a complex with planar square geometry. The monomeric complex exhibits tridentate facial coordination formed by two chelate rings. The coordination of Pt (II) to GPS is relatively soft, and accept electron density of the nitrogen atom. The additional donation from two oxygen atoms helps the formation of two chelate rings with Pt (II), the bite angles caused by the size of the metal ion stabilizes the rings [15].

This mechanism of reduction is analogous to the oxidation of GPS on a copper electrode, where the complexation proceeds by forming a passive layer of Cu$_2$O in buffer solution at a pH greater than 6.5 that oxidized to CuO and the oxide film of Copper (II) is complexed by GPS producing an increase in the oxidation current of copper [16].

Protonation of the GPS amino group is important in order to establish the complex with platinum ions. Experimentally it found that at pH greater than 5.0 the reduction not seen, the redox response is intensified at pH less than 4.0, which is when GPS has protonated its amino group. A decrease of one unit of pH (4.00 to 3.00) generates a 54% increase in current and a displacement of anodic and cathodic peaks about 0.2V, which implies a better analytical performance at lower pH of 3.00. At pH less than 2.0 the cyclic voltammetric response is poorly defined compared to the blank. Repeatability during three days of measurement using cleaning with isopropanol: water, generates similar standard deviations close to 4.0%, a value that guarantees a quantitative analysis at 95% confidence.

Chronoamperometric experiments of standard GPS in HClO$_4$ pH 3.00 show two linear regions. The high range is between 85 $\mu$mol.L$^{-1}$ and 93mmol.L$^{-1}$ and its ratio has a correlation coefficient of 0.9898, a slope of 3552.2mA.L/mol and an intercept of 62.98mA. On the other hand, the correlation at low range is between 8.6 $\mu$mol.L$^{-1}$ and 80 $\mu$mol.L$^{-1}$ with $R^2 =0.9971$, the slope is 0.276$\mu$A.L.$\mu$mol$^{-1}$ and the intercept is 32.9$\mu$A.

The analytical ranges with platinum electrode are better than those obtained with a Copper or Nickel electrodes [17], although it does not exceed modified electrodes such as electrochemical sensor on the hierarchically porous Cu-BTC MOF platform [18] or to the carbon nanotube electrode with copper.
Our LOD $55.0 \mu\text{g L}^{-1}$ results is lower than that required for environmental monitoring of GPS in surface water regarding EPA reference of $700\mu\text{g.L}^{-1}$.

3.2. UV/H$_2$O$_2$ oxidation of glyphosate

Several reaction mechanisms for GPS oxidation known; in the degradation with manganese oxide, sarcosine is an intermediate, which is then broken down into glycine and formic acid [20]. Another recent research work on photocatalytic degradation of organophosphorus pesticides and phosphonom glycine, in immobilized TiO$_2$, considered the generation of sarcosine and, as an alternative route, aminomethylphosphonic acid (AMPA) and the production of glycolic acid [21].

A particular study associated with the oxidation of GPS with H$_2$O$_2$/UV [22], establishes the formation of the •OH radical which attacks GPS to form a carbon-centered radical •CH$_2$-NH$_2$-\text{-CH}=\text{COO}^- and phosphate; that can react with the molecular oxygen present in the medium at high concentration, to give a new radical that reacts directly with water to form glycine, formaldehyde and the radical HO$_2$• without the presence of sarcosine in correspondence to biodegradative processes [23].

Studies on the behavior of glycine in acidic medium indicate that glycine and sarcosine (Figure 2) reversibly adsorbed on the platinum electrode, whereby adsorbates attached to the surface of the electrode through the carboxyl group and it indicates that the presence of the protonated amino group does not interfere with the redox behavior of glycine and sarcosine.

![Figure 3](image-url)

**Figure 3.** Monitoring of GPS oxidation with H$_2$O$_2$ / UV.

A. pH Effect. [GPS]$_{\text{initial}}$ 0.10mol.L$^{-1}$; 254 nm lamp, [H$_2$O$_2$] 10.0mmol.L$^{-1}$

B. Peroxide concentration effect; 254nm lamp, pH 3.00. [GPS]$_{\text{initial}}$ 0.10mol.L$^{-1}$, [H$_2$O$_2$] 0.010mol.L$^{-1}$, 0.005mol.L$^{-1}$, 0.001mol.L$^{-1}$

The cyclic voltammetric GPS responses in the presence of UV /H$_2$O$_2$, obtained in this study, show that in addition to the decrease in current, a peak potential shift is evidenced, which may be associated with the generation of ammine species in the system which can also complex with platinum.

According to the voltammetric response of glycine, sarcosine, and GPS (Figure 2), if oxidation follows the path of sarcosine and subsequent glycine, a decrease in the cathodic peak current should be seen and subsequently an increase thereof. On the contrary, if oxidation follows the glycine route, the current should stabilize for a while and then increase.

The percentage of GPS oxidation efficiency is greater at pH 3.0 (75.6%), with a decrease as pH increases. Figure 3A shows the monitoring of GPS peak current over time at different pH and at 1:100 ratio between peroxide and GPS. In general, it observed that the current decreases, then increases, then decreases again, consistent with the oxidation route proposed by Barret and Mc Bride (2005), where
sarcosine formed as an intermediate and subsequently glycine. At pH 5.00 it is not possible to see the degradation of glycine.

On the other hand, by decreasing the $\text{H}_2\text{O}_2$: GPS ratio from 1:20 to 1:100, there is a decrease in maximum cathodic current, related to the formation of sarcosine and GPS is the species that dominates the reaction rate. Nevertheless, increasing the ratio to 1:10 it discovered that the oxidation rate dominated by $\text{H}_2\text{O}_2$ and does not pass through sarcosine; but occurs directly by the formation of glycine, mechanism proposed by Munner and Boxall [24]. Thus, after 15 minutes of reaction, the glycine intermediate begins to form and an increase in the current is evident, which subsequently (45-135min) decreases due to its oxidation (Figure 3B). After 210 minutes, the current changes dramatically and does not increase again due to the non-presence of electroactive species produced in the oxidation.

Table 1. Kinetic data for degradation of Glyphosate with UV/$\text{H}_2\text{O}_2$

| pH $^a$ | $K$ (min$^{-1}$) | $t_\frac{1}{2}$ |
|--------|----------------|---------------|
| 3.00   | -0.0138        | 50.22 min     |
| 4.00   | -0.0106        | 65.38 min     |
| 5.00   | -0.0041        | 169.02 min    |

| Relation $\text{H}_2\text{O}_2$: Glyphosate $^b$ |
|------------------------------------------------|
| 1:10 | -0.019 | 36.47 min |
| 1:20 | -0.016 | 42.52 min |
| 1:100 | 0.017 | 40.76 min |

Kinetic data for a first order reaction

$^a$ Relation $\text{H}_2\text{O}_2$: GPS: 1:100, $^b$ pH 3.00

The degradation of GPS with time often described according to first-order kinetics, congruent with previously reported data [25]. When peroxide concentrations are low below 5.0mmol.L$^{-1}$, the half-life in sarcosine formation becomes faster when the GPS vs $\text{H}_2\text{O}_2$ ratio increases (36.47min). On the other hand, when $\text{H}_2\text{O}_2$ exceeds 0.01mol.L$^{-1}$, the oxidative process is more efficient since it occurs due to the formation of glycine and its half-life (40.76 min) is similar to the process when sarcosine obtained.

The kinetic scopes obtained by Manasero, indicate a half-life of 11.4min and a total oxidation time of 3.5 hours at pH 7.00; values that are not far from those obtained in this study taking into account that they always worked with an excess of $\text{H}_2\text{O}_2$ and oxidation becomes faster under these conditions.

4. Conclusion

The cyclic voltammetric analysis of GPS at platinum electrode, the redox process, presented which involves the formation of a GPS-Pt (II) complex. The redox behavior of this complex shows better performance in perchloric acid and is sensitive to protonation of the amino group; no response observed at pH values greater than 5.0. The electrode surface requires cleaning between measurements to ensure reproducible results. The herbicide has two linear ranges, one between 85 μmol.L$^{-1}$ and 93mmol.L$^{-1}$, the high range and the second, a low range, between 8.6μmol.L$^{-1}$ and 80μmol.L$^{-1}$, a detection limit of 0.326μmol.L$^{-1}$ and a quantification limit of 14.53μmol.L$^{-1}$, that allow to measure concentrations below 0.7ppm, maximum value established by the EPA.

The oxidation of GPS with UV/$\text{H}_2\text{O}_2$ can be an alternative for the treatment of wastes of this pesticide, it is favored at pH 3.0 with a first order pseudo kinetics and a half-life of 40 ± 4min. Two degradative pathways are estimated depending on $\text{H}_2\text{O}_2$ concentration: at low concentrations sarcosine formation is favored over glycine and at high concentrations glycine formation is favored.

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