Non-Thermal Plasma Induced Total Mineralization of Glyphosate in Water in the Presence of Iron II Ions

Moïse Fouodjou, a,b Samuel Laminsi, a Georges Y. Kamgang, a Michele T. Mengue a,c and Nito A. Debacher a,b*

a Mineral Chemistry Laboratory, Department of Inorganic Chemistry, University of Yaoundé 1, P.O. Box 812, Yaoundé, Cameroon
b Chemistry Department, Federal University of Santa Catarina (UFSC), 88040-900 Florianopolis-SC, Brazil
c Département des sciences du bois, Université Laval (UL) 2405, rue de la Terrasse, Quebec City, Canada

The present work focused on the mineralization of herbicide glyphosate (N-(phosphonomethyl) glycine) (C₃H₈NO₅P) in aqueous phase by Glidarc plasma following the orthophosphates released and the reduction of the total organic carbon (TOC). Furthermore, the effect of initial concentration, pH and the degradation process of glyphosate in the presence of Fe²⁺ were also examined. The results showed that the efficiency of degradation increased with the presence of ferrous ions as catalysts in aqueous medium and also the release of orthophosphate is more efficient in acid medium with pH range of 3.5-6.3. The kinetics of the release of orthophosphate and the TOC removal obey the first order rate law. The ninhydrin and orthophosphates tests showed that the degradation of glyphosate in water by Glidarc plasma was mainly by *OH and NO* attacked with C–N and C–P bond cleavage leading to complete mineralization.

**Keywords:** glyphosate, Glidarc discharge, orthophosphate release, mineralization

Introduction

Glyphosate also called N-(phosphonomethyl) glycine (NPG) of chemical formula C₃H₈NO₅P is a nonselective systemic broad spectrum herbicide used for weed control. Glyphosate is absorbed by the leaves and carried by the phloem till the extremities of roots and rhizomes, where it inhibits the biosynthesis of aromatic amino acids by bonding to 5-enolpyruvylshikimate-3-phosphate syntase enzyme.¹ This herbicide was extensively used in European and American agricultural exploitations in the early 1970s. Faced with the problem of famine that characterizes most third-world countries, particularly African countries, the use of this herbicide, based on its ability of fertilizing and destroying annual and perennial weeds was intensified and widespread with leitmotiv the food safety for a growing population. High solubility of glyphosate in water¹ and the fact that less than 1% often reaches the target makes that, a component of herbicide spills unto surface waters. It thus becomes a potential contaminant with harmful effects on the environment.² In water, glyphosate is rapidly dissipated through adsorption on suspended matters and sediments, and has a half-life of 19 to 45 days for the whole system.³ Although recognized to be non toxic for mammals, human beings and birds,⁴ Bolognesis et al.⁵ showed that glyphosate produces positive genotoxic effects in vitro in human peripheral blood, evidenced by sister chromatids exchange and in vivo in mouse. Similarly in their previous works, Clements et al.⁶ reported positive DNA damage for comet assay in erythrocytes of Rana castesbeiana tadpoles following exposure to glyphosate. In the same vein, Poletta et al.⁷ and Manas et al.⁸ respectively revealed DNA damage after performing comet assay and micronucleus test on the erythrocytes of broad-snouted Caiman latirostris and fetal bovin serum exposed to glyphosate. In spite of its hydrolytic decomposition with a greater than 35 days mean half-life at various pH levels and temperatures,⁹ this herbicide is classified among the organic molecules frequently detected in streams and rivers, and generally exceeds the European standard for drinking (1 µg L⁻¹) and surface water (1-3 µg L⁻¹).¹⁰ Although being very sensitive to degradation by microorganisms, glyphosate degradation

*e-mail: nito.debacher@ufsc.br*
in water and soil yields more toxic intermediates, i.e., aminomethylphosphonic acid (AMPA) and sarcosine, which could further be degraded slowly into water, phosphate and carbon dioxide. Within the purview of the relevance of this ecological problem, the control and elimination of glyphosate and other organic pollutants becomes imperative for environmental safety.

Previous studies reported the glyphosate degradation using processes such as hydrogen peroxide-based advanced oxidation processes (H\textsubscript{2}O\textsubscript{2}/UV, H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3}/UV, H\textsubscript{2}O\textsubscript{2}/Cl\textsuperscript{•−}) or photo-Fenton (Fe\textsuperscript{III}/Na\textsubscript{2}C\textsubscript{2}O\textsubscript{4}/UV, FeOH/UV, H\textsubscript{2}O\textsubscript{2}/UVC),\textsuperscript{11−13} titanium dioxide-based advanced oxidation processes (TiO\textsubscript{2}/UV)\textsuperscript{14,15} and manganese oxide in aqueous suspension.\textsuperscript{16} Efficiencies obtained with these processes are relative and the costs of set up often expensive. Non-thermal plasma (NTP), an environmental friendly technique, can be a good alternative for organic pollutants abatement in water. For some time in the past, NTP has shown its proofs to be a promising technology for organic pollutants abatement in gaseous, liquid, and solid phases.\textsuperscript{17} Environmental applications of electric discharges are being considered increasingly; they imply the chemical properties of the activated species generated by the discharge.\textsuperscript{18} There are many types of non-thermal plasmas,\textsuperscript{19} but in this work, we focused on gliding arc discharge commonly called Glidarc. The Glidarc device is an inexpensive source of NTP, which operates at conditions close to atmospheric pressure and room temperature. The analysis with spectroscopy emission has identified \( \bullet\)OH and NO\textsuperscript{•} radicals as responsible of oxidative properties of Glidarc plasma plume when humid air is used as feeding gas.\textsuperscript{20} These radicals are precursors of other active species, which endow the reaction medium a very high enhanced chemical reactivity.\textsuperscript{19} The chemical reactivity of Glidarc has been utilized with success in both the degradation of several dissolved organic compounds\textsuperscript{21,22} and industrial effluents.\textsuperscript{23}

The present work focused on the study of the mechanism of mineralization of glyphosate in aqueous phase by Glidarc plasma. Mineralization via the orthophosphates released and the total organic carbon (TOC) was studied. Furthermore, the effect of initial concentration, initial pH and the degradation process of glyphosate in the presence of Fe\textsuperscript{II} were also examined. The kinetics was studied and a plausible degradation pathway of glyphosate in water by NTP was proposed.

Experimental

Materials and reagents

Glyphosate (Figure 1) 98.5% was purchased from Dr Ehrenstorfer Gmbh (Bgm Schlosser-Str., Augsburg, Germany). Aqueous solutions of glyphosate were prepared by dissolving 6.0 mg of highly soluble glyphosate salt in distilled water. All other reagents were of analytical grade and were used without purification. Molar solutions of NaOH and H\textsubscript{2}SO\textsubscript{4} were used to adjust the pH values to study the influence of initial pH on glyphosate degradation by humid air plasma. 4.0 mol L\textsuperscript{−1} acetic acid-sodium acetate buffer (HAc-NaAc; pH 5.5) was prepared for ninhydrin method,\textsuperscript{24} which involves the reaction of alpha-amino acid and ninhydrin resulting in a colored solution absorbing in 570 nm.

![Figure 1. Chemical structure of glyphosate.](image)

Apparatus

The gliding arc device used for this study was described previously.\textsuperscript{17} It derived from the original device described by Czernichowski et al.\textsuperscript{25} Figure 2 presents a scheme of the experimental device. When a suitable voltage (5-10 kV) and electric current (160 mA)\textsuperscript{25} are applied between two aluminum divergent electrodes, an electric arc forms at the shortest electrode gap (3 mm) and glides along the electrode’s axis pushed on by a gas flow (humid air). The arc length increases on moving and its temperature decreases, so that the arc turns from thermal plasma to quenched plasma on breaking into a plume. A new arc then forms at the narrowest gap and the cycle resumes as a large plasma plume. The plasma plume leaks the liquid target brought to its contact at overall room temperature and pressure, close to atmospheric conditions.\textsuperscript{17} The electric energy is transferred to gas molecules, which become excited and are broken into radicals giving highly reactive species such as \( \bullet\)OH and NO\textsuperscript{•} according to the following equations.\textsuperscript{18}

\[
\begin{align*}
H\textsubscript{2}O + e^- &\rightarrow H^* + OH^* + e^- \\
O_2 + e^- &\rightarrow O(3P) + O(1D) + e^- \\
N\textsubscript{2} + e^- &\rightarrow N(4S) + N(2D) + e^- \\
N(2D) + O_2 &\rightarrow NO^* + O \\
H^* + O_2 &\rightarrow HO^*_2 \\
HO^*_2 + NO^* &\rightarrow NO_2 + OH^*
\end{align*}
\]

The diffusion process in the liquid is improved by convection in the liquid phase due to the airflow and magnetic stirring. Treatments were carried out in a closed batch reactor for different plasma-exposure time. The reactor is equipped with a cooling system to avoid
evaporation and the temperature was kept constant at 24 ± 0.1 °C for all treatments.

Analytical methods

The pH adjustment was followed using a multifunctional digital pH-meter branded HANNA. FeSO₄ was added to the solution as a ferrous ions (Fe²⁺) catalyst source. The monitoring of reduction of glyphosate concentration in solution after Glidarc plasma treatment, proceeded as follows: glyphosate solution (1 mL) and ninhydrin solution (1 mL) were put in screw-capped test tubes and heated in a boiling water bath for a pre-determined period of time. After heating, the tubes were immediately cooled in an ice-bath, then; 5 mL of 50% ethanol was added into each tube and thoroughly mixed with a Vortex mixer for 30 s. The residual glyphosate was followed by spectrophotometry at 570 nm. The reduction product obtained from ninhydrin then reacts with NH₃ and excess ninhydrin to yield a blue colored substance.

Orthophosphates (PO₄-P) formed as result of degradation of glyphosate were measured according to the standard methods with a spectrophotometer at 700 nm, based on the formation of a blue molybdenum complex and after digestion using peroxodisulfate (K₂S₂O₈), respectively. All experiments (manipulations and analysis) were duplicated. Glyphosate degradation was also evaluated by analyzing the TOC content of the samples using a Shimadzu TOC-VE analyzer equipped with a nonselective infrared detector. Calibration was done before, and destruction of the parent pesticide (glyphosate) was then confirmed by measuring its TOC in both untreated and treated samples by comparison with pure glyphosate standards.

Calculations

The release of orthophosphates in the solution [%(PO₄-P)] and the TOC abatement rate were respectively calculated using equations 7 and 8.

\[\%(PO_4 - P) = \frac{[PO_4 - P]_t - [PO_4 - P]_0}{[PO_4 - P]_{tot}} \times 100 \]  

\[\eta = \frac{(TOC_0 - TOC_t)}{TOC_0} \times 100 \]  

%(PO₄-P) is the orthophosphates release efficiency, [PO₄-P] in mg L⁻¹ the orthophosphates concentration at treatment time t, [PO₄-P]₀ the residual concentration of orthophosphate found before treatment and [PO₄-P]tot the total concentration of orthophosphate releasable calculated considering that each molecule of glyphosate releases one molecule of orthophosphate. \(\eta\) is the TOC reduction percentage, TOC₀ the initial total organic carbon and TOCₜ the TOC at treatment time, t.

Results

The study of the degradation of glyphosate by Glidarc humid air plasma was followed by measuring the orthophosphates released and the TOC values as a function of exposure time together with ninhydrin test to highlight the breaking of C–N bond.

\[NPG + OH^- \rightarrow oxidation\ products \]  

The working parameters fixed were: the distance between the ends of the electrodes and the liquid surface (1.5 cm), the lengths of the electrodes (6.0 cm), the nozzle diameter by which the plasmogen gas flows (1 mm) and the gas flow rate (800.0 L h⁻¹).

For the study, the pH of the pristine solution was 6.3 and the initial concentration of glyphosate 33.0 µmol L⁻¹. The TOC found was 215.0 mg L⁻¹ and the residual concentration of orthophosphates 0.097 mg L⁻¹.

Glyphosate degradation

Figure 3 shows the visible spectrum of glyphosate degradation after ninhydrin colorimetric assay. From
this figure, it is clear that, just after 5 min of exposure, the intensity of the signal decreases substantially and disappears after 30 min of treatment.

Figure 3. The visible absorbance spectra of glyphosate after ninhydrin colorimetric test. (a) 0 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 30 min. [NPG]₀ = 33.0 µmol L⁻¹, pH 6.3.

Release of orthophosphates by cleavage of C–P bond

Figure 4 shows that glyphosate exposed to Glidarc plasma released orthophosphates (PO₄⁻P). It also shows the variations of orthophosphates formed for various exposure times. Orthophosphate release is continuous and increases with exposure time. The curve leveled off after 30 min of treatment.

Figure 4. Profile of orthophosphates formation against exposure time during plasma treatment under the following conditions (initial concentration [NPG]₀ = 33.0 µmol L⁻¹, pH 6.3). Zone I is characterized by first-order in relation to substrate. Zone II the orthophosphate production rate decreases and tends to zero.

Kinetics of orthophosphate released

From Figure 4, it can be observed that, the kinetics of release of orthophosphates obey the first-order rate law with a rate constant of $7.83 \times 10^{-2}$ min⁻¹. The interval of time ($0 \leq t < 30$ min) is the most significant and relevant because 93.72% of orthophosphates were released within this period. After 30 min, a landing is observed showing the decrease in the degradation rate of glyphosate (Figure 4).

Influence of initial pH on the release of orthophosphates

Figure 5 shows the plasma degradation of glyphosate with formation of orthophosphates in the range of pH 3.5-11.0. Glyphosate can be efficiently transformed into orthophosphates at pH 3.5-6.3. It also shows that the degradation was slow for the higher values of pH (pH > 6). Initial pH values governed the degradation of glyphosate by plasma.

Figure 5. Effect of initial pH (★ 3.5; ▼ 5.0; ▲ 6.3; △ 7.5; ● 9.0; ■ 11.0) on the degradation of glyphosate ([NPG]₀ = 33.0 µmol L⁻¹) by plasma.

Effect of initial concentrations on the release of orthophosphates

As shown in Figure 6, the efficiency of orthophosphate released increases with the increase in the initial concentrations. For example, when the initial concentration of glyphosate is 33.0 µmol L⁻¹ and pH 3.5, 93.72% of orthophosphates was produced after 30 min of exposure, whereas under the same conditions with an initial concentration of 5.5 µmol L⁻¹, only 75.78% of orthophosphates was released. It is observed that as for higher initial concentration, higher degradation occurred.

Effect of Fe²⁺ catalysis

Figure 7 shows that the formation of PO₄⁻P increased with the presence of ferrous ions acting as catalyst in the aqueous medium. Addition of Fe²⁺ 0.1 mmol L⁻¹ permitted to obtain 90.60% of orthophosphate release after 15 min.
of plasma exposure compared to 60.61% obtained for the plasma treatment alone. It is also noticed that an increase in the concentration of ferrous ions increased the formation of PO$_4$-P. With an initial concentration [NPG]$_0$ = 33.0 µmol L$^{-1}$ and an pH 6.3, the formation of orthophosphate was fast in the presence of Fe$^{2+}$ and equilibrium was attained after 40 min of exposure. However, it is observed that excessive addition of catalyst acts negatively on the glyphosate degradation: the uses of 0.2 mmol L$^{-1}$ ferrous ions diminished the efficacy of PO$_4$-P release from 90.60% to 80.44% after 15 min of exposure to Glidarc plasma.

Figure 6. Effect of initial concentrations of glyphosate: ■ 5.5; ● 11.0; ▲ 22.0; ▼ 33.0 µmol L$^{-1}$ on the release of orthophosphates at initial pH 3.5.

Figure 7. Influence of ferrous ions concentration: ■ 0.0; ● 0.02; ▲ 0.05; ▼ 0.1; ★ 0.2 mmol L$^{-1}$ on the catalysis of PO$_4$-P released ([NPG]$_0$ = 33.0 µmol L$^{-1}$, pH 3.5).

TOC content

Figure 8 shows that glyphosate exposed to plasma can be mineralized into CO$_2$. The TOC concentration decreased with time and an abatement of 68.8% was reached after 90 min of treatment in the absence of iron II ions.

The degradation was slow between 0-10 min. Figure 8 also shows the plot of ln(TOC) versus exposure time and suggests that the kinetics of TOC reduction is first-order with a kinetic constant $k = 1.39 \times 10^{-2}$ min$^{-1}$.

Figure 8. Plot of total organic compound (TOC) against exposure time. The insert shows a linear correlation between ln(TOC) and exposure time which fit the first order rate law, ($k = 1.39 \times 10^{-2}$ min$^{-1}$).

Figure 9 shows the combined effect of plasma and ferrous ions on glyphosate degradation. The mineralization of glyphosate is more efficient when ferrous ions are added to the target solution. Table 1 gives the rate constants for each concentration of ferrous ions added to the medium.

Figure 9. Influence of ferrous ions concentration: ■ 0.0; ● 0.02; ▲ 0.05; ▼ 0.1; ★ 0.2 mmol L$^{-1}$ on the mineralization of glyphosate ([NPG]$_0$ = 33.0 µmol L$^{-1}$, pH 3.5).

Glyphosate degradation pathway

As mentioned previously, glyphosate can be degraded by Glidarc plasma via C–N and C–P bond cleavages.
leading to mineralization (Figure 10). The ninhydrin method based on the formation of the colored Ruhemann purple compound of primary amine showed that glyphosate possibly underwent C–N bonds breakage. The C–P bond cleavage also occurred and was evidenced by the formation of orthophosphates and TOC removal.

**Discussion**

The above results showed that glyphosate is effectively degraded by humid air plasma. The formation of orthophosphates and decrease in the TOC concentration are proofs of the degradation of this compound and can be considered as the results of the interaction between the strong oxidizing agents present in humid air plasma and the solute at the plasma-liquid interface. Previous work suggested that \(^{\cdot}\)OH and NO\(^{\cdot}\) were the main activated species present in humid air plasma plume.\(^{21}\) \(^{\cdot}\)OH is the most powerful oxidizing agent and, as other radicals, it has a very short half-life (1 ms).\(^{28}\) Therefore, the entire \(^{\cdot}\)OH formed by conventional electron impact dissociation of water molecules could not, during that short time, react with target molecules. Consequently, part of radicals, which did not react because of the dilution of the target, combine together to form \(\text{H}_2\text{O}_2\) in aqueous phase. This was evidenced and measured by previous works.\(^{29,30}\) Since \(^{\cdot}\)OH is a stronger oxidizing agent after fluorine with a standard potential \((^{\cdot}\text{OH}/\text{H}_2\text{O}) = 2.72\ \text{V}\),\(^{31}\) it likely participated in the plasma-chemical degradation processes of organic compounds. Apart from \(^{\cdot}\)OH and \(\text{H}_2\text{O}_2\), some other species such as \(\text{HO}_2^{\cdot}\), ONOO\(^{-}\), \(\text{O}_3\) and \(\text{O}_2\)\(^{30,32}\) are formed and are also thermodynamically able to oxidize organic compounds. Previous investigation on the degradation of glyphosate also showed that the mechanism path involves many radical steps.\(^{13}\)

Figure 4 shows that the glyphosate can be attacked by reactive species \((^{\cdot}\text{OH} \text{ and NO}^{\cdot}\) of Glidarc humid air

<table>
<thead>
<tr>
<th>[Fe(^{2+})] / (mmol L(^{-1}))</th>
<th>Rate constant k / min(^{-1})</th>
<th>Correlation coefficient R(^2)</th>
<th>Standard error on rate constant</th>
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</thead>
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<tr>
<td>0.00</td>
<td>(1.39 \times 10^{-2})</td>
<td>0.989</td>
<td>(9.96 \times 10^{-4})</td>
</tr>
<tr>
<td>0.02</td>
<td>(5.98 \times 10^{-2})</td>
<td>0.995</td>
<td>(5.22 \times 10^{-4})</td>
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<tr>
<td>0.05</td>
<td>(6.26 \times 10^{-2})</td>
<td>0.970</td>
<td>(0.11 \times 10^{-4})</td>
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<td>0.10</td>
<td>(7.14 \times 10^{-2})</td>
<td>0.987</td>
<td>(9.17 \times 10^{-4})</td>
</tr>
<tr>
<td>0.20</td>
<td>(6.51 \times 10^{-2})</td>
<td>0.963</td>
<td>(0.14 \times 10^{-4})</td>
</tr>
</tbody>
</table>

**Figure 10.** A proposed pathway of glyphosate degradation by Glidarc humid air plasma.
plasma leading to the formation of \( \text{PO}_4^{3-} \). This formation can be explained by the breakage of \( \text{C–P} \) and \( \text{O–H} \) bonds in the phosphate group of the substrate. The abstraction of hydrogen follows radical mechanism and radical \( \cdot \text{H} \) formed is ionized and contributed to acidify the aqueous medium (Figure 10). First order kinetic model is in agreement with the experimental data of the orthophosphates released. The rate-limiting factors are the concentrations of the plasma active species (depends on the energy provided to the discharge) at the reaction zone and the concentration of the substrate.\(^{33,34} \) The level-off after 30 min corresponds to a drastic decrease in the effective contact between the plasma and the glyphosate, when the volume of organic phase becomes too low to cover the entire liquid surface and thus to maintain an efficient interface. The orthophosphate production rate decreases and tends to zero. Kinetics of formation of orthophosphates in each time interval (Figure 4) showed that the mechanism of their formation by degradation of glyphosate is a multi-step with overall first order.\(^{35} \)

The initial pH and the initial concentration of glyphosate also influenced the rate of formation of orthophosphates by degradation by humid air plasma. As shown in Figure 5, the degradation of glyphosate is more efficient for low values of initial pH. Glyphosate is an amphoteric compound; the basic form of glyphosate quickly undergoes degradation by plasma than the acid form (Figure 10). This pH dependence of glyphosate degradation can also be attributed to the speciation of \( \cdot \text{OH} \) and \( \text{NO} \) radical, since there are more efficient in acidic medium.\(^{29} \) Oxidising degradation reactions of organic compounds often involve protons; thus, the kinetic rate very often depends on the acidity of the medium. Furthermore, the pH values govern the relative amount of \( \cdot \text{O}_2 + \text{HO}_2^* \), which is also precursor of \( \text{H}_2\text{O}_2 \) formation and leads to more \( \cdot \text{OH} \). Besides previous works using plasma for degradation of organic compounds,\(^{35,36} \) reported that, the increasing of initial pH decreases the rate constant. This observation is attributed to the fact that \( \cdot \text{OH}, \text{HO}_2^* \) and \( \text{H}_2\text{O}_2 \) have higher oxidation effect in acidic medium.\(^{37} \)

The initial concentration of target molecules plays an important role in the treatment of waste water by Glidarc discharge since the final application is in the industries where the effluents are relatively concentrated. It comes out from Figure 6 that the orthophosphate release is more efficient for concentrated solutions. This is due to the fact that with concentrated solutions, the probability of collision between primary (\( \cdot \text{OH}, \text{NO}^* \)) and secondary (\( \text{H}_2\text{O}_2, \text{NO}_2 \)) active species and molecules of glyphosate at the reaction interface is more important.\(^{35} \) The effective surface between the plasma and glyphosate is low for dilute solutions\(^{33} \) and the rate of degradation is earlier governed by diffusion process comparatively to more concentrated solutions that the reaction rate is for a relative long time controlled by \( \cdot \text{OH}.\(^{38} \) It could therefore be suggested that higher rate of degradation occurred for higher initial concentrations contrary to results obtained in previous works.\(^{39} \) However, after 90 min of exposure, almost the same rate of orthophosphates is produced both for dilute and concentrated solutions of glyphosate.

When glyphosate solution is mixed with ferrous ions and exposed to Glidarc plasma flame, the rate of degradation increases due to \( \text{H}_2\text{O}_2 \) consumption by \( \text{Fe}^{2+} \) to form \( \cdot \text{OH} \) radicals leading to increase the rate of degradation of glyphosate.\(^{40} \) The Gliding arc plasma in humid air/Fenton mechanism that accompanies the above suggestions is:

\[
\begin{align*}
\text{H}^* + \text{O}_2 & \rightarrow \text{HO}^* \\
\text{HO}^* + \text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}^*_2 + \text{NO}^*_2 & \rightarrow \text{NO}_2 + \text{OH}^* \\
\text{OH}^* + \text{OH}^* & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^* + \text{OH}^* \\
\text{Fe}^{2+} + \text{OH}^* & \rightarrow \text{Fe}^{3+} + \text{OH}^* \\
\text{RH} + \text{OH}^* & \rightarrow \text{R}^* + \text{H}_2\text{O} \rightarrow \text{products} \\
\text{H}_2\text{O}_2 + \text{OH}^* & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
\text{Fe}^{3+} + \text{HO}_2^* & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \\
\text{H}^* + \text{O}_2 & \rightarrow \text{HO}^* \\
\text{HO}^*_2 + \text{NO}^*_2 & \rightarrow \text{NO}_2 + \text{OH}^* \\
\text{OH}^* + \text{OH}^* & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^* \\
\text{RH} + \text{OH}^* & \rightarrow \text{R}^* + \text{H}_2\text{O} \rightarrow \text{products} \\
\text{H}_2\text{O}_2 + \text{OH}^* & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
\text{Fe}^{3+} + \text{HO}_2^* & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \\
\end{align*}
\]

Although Abdelmalek et al.\(^{40} \) in their previous work found that the catalytic activity of ferrous ions is probably negligible in humid air plasma because of eventual oxidation by nitrites, which parasites their reaction with hydrogen peroxide to form \( \cdot \text{OH} \), our study showed that the catalytic effect of \( \text{Fe}^{2+} \) was not negligible in the case of degradation of glyphosate. This may be due to the presence in the medium of \( \text{PO}_4^{3-} \) ions, which can probably hinder the reaction of nitrites with ferrous ions by electron acceptor limitation. An excess of catalyst reduces the mass transfer and therefore the kinetics of degradation likewise. Figure 7 showed that the production of \( \text{PO}_4^{3-} \) increases with an increase \( \text{Fe}^{2+} \) concentration. Its proofs that ferrous ions can sufficiently utilize the residual hydrogen peroxide generated by plasma to produce a larger amount of the reactive, non-selective radicals \( \cdot \text{OH} \) (equation 9 to equation 18), which rapidly mineralize glyphosate and produce orthophosphates.\(^{41} \) However, an excess of \( \text{Fe}^{2+} \) scavenged \( \cdot \text{OH} \) radicals and slowed the degradation of glyphosate as described by nonoxidizing reaction (equation 16).\(^{41,42} \)

A significant increase in TOC reduction of glyphosate solution is also observed (Figure 8). The percentage of TOC reduction reached 68.42% after 90 min of exposure to gliding arc plasma in absence of iron II ions. However, the reduction in TOC was almost zero during the first 10 min, which can be considered, as an induction period and attributed to the low concentration of oxidizing
As we can see, the mineralization is appreciable and goes in straight line with the TOC reduction measured in the case of degradation of other organic compound by gliding arc discharge in humid air.\textsuperscript{23,32,43,44} The kinetics of TOC reduction was studied and showed to be first order (Figure 8). The rate of mineralization of glyphosate when exposed to Glidarc in humid air increases with the addition of ferrous ions in the buffer aqueous medium (Figure 9) due to the increase of $\cdot$OH coming from decomposition of H$_2$O\textsuperscript{45,47} produced in the discharges and evidenced by Burlica et al.\textsuperscript{29} The TOC reduction also increases with the concentration of the catalyst. The kinetic rates of TOC reduction increased with the concentration of ferrous ions to a certain value and decreased (Table 1). This may be due to the fact that the excessive addition of ferrous ions operates negatively on glyphosate degradation. This phenomenon can be explained by the existence of parasitical reaction, which consumes $\cdot$OH radicals.\textsuperscript{46} Similar results were obtained by Souza et al. who uses the Fenton process.\textsuperscript{48} The low rate of mineralization (28% after 120 min of treatment) that they obtained may be due to the fact that they have been working with the commercial formulation.

Figures 3, 4 and 8 show that glyphosate is degraded by Glidarc plasma via C–N and C–P bonds breakage followed by a considerable reduction in TOC as reported in the previous works using advanced oxidized processes (AOPs).\textsuperscript{13,15,40} The cleavage of C–N and C–P bonds is attributed to $\cdot$OH radicals. Thus, Figure 10 proposes a probable reaction pathway of glyphosate degradation by Glidarc plasma.

As can be seen in Figure 10, the $\cdot$OH radical attacks glyphosate (step 2), which leads to the formation of a carbon centred radical $\cdot$OOC-CH$_2$-NH$_2$-CH$_2$-O-O$^\cdot$ and orthophosphates.\textsuperscript{16} The generated radical can react with molecular oxygen (step 3)\textsuperscript{49} present in the medium at high concentration to give a new radical $\cdot$OOC-CH$_2$-NH$_3^+$-CH$_2$-O-O$^\cdot$, which reacts directly with NO$^\cdot$ (step 4) and then H$_2$O (step 5) to form $\cdot$OOC-CH$_2$-NH$_3^+$, and CH$_2$O.\textsuperscript{49} Glycine may undergo decarboxylation due to the presence of $\cdot$OH (step 6) to give CO$_2$ and $\cdot$CH$_2$-NH$_3^+$ radical. $\cdot$CH$_2$-NH$_3^+$ then reacts with O$_2$ and $\cdot$OH (step 7 and 8), respectively to yield formaldehyde and NH$_2$. The formaldehyde generated in the process can be directly oxidized into formic acid by the dissolved oxygen and mineralized into CO$_2$ by combined action of $\cdot$OH and once more oxygen.\textsuperscript{30,51}

Conclusions

The aim of this work was to study the degradation of glyphosate by the gliding arc discharge. It was found that gliding arc discharge can efficiently degrade glyphosate evidenced by the formation of orthophosphates. The efficiency of orthophosphate increases with the increase of initial concentration. The degradation is more efficient in acid medium with the best pH values in the range of 3.5-6.3. The gliding arc discharge mineralizes glyphosate evidenced by a measure of the percentage of TOC reduction. The ferrous ions can catalyze the degradation of glyphosate, thus improving the efficiency of orthophosphate released and the TOC reduction. The kinetics of the release of orthophosphate by gliding arc discharge obeyed first-order rate law with kinetic constant $7.83 \times 10^{-2}$ min$^{-1}$. The kinetics of the TOC reduction was also first order with a kinetic constant $1.39 \times 10^{-2}$ min$^{-1}$. The degradation of glyphosate by gliding arc discharge was mainly done by hydroxyl radical and NO$^\cdot$ followed by the C–N and C–P cleavages.

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