Removal of herbicide glyphosate by conductive-diamond electrochemical oxidation

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Abstract

This work focuses on the removal of herbicide glyphosate by electrolysis with boron doped diamond anodes. Both the electrolysis of the pure reagent and that of a commercial dispersion (RoundUp) are evaluated. Results show that it is possible to attain a complete mineralization of this herbicide and point out the key role of the supporting electrolyte in the efficiency of the process. This role is explained in terms of the electrogeneration of oxidants. The electrolysis of glyphosate also leads to the release of phosphate and nitrate anions. Further electrochemical and chemical reactivity explains the occurrence of ammonium and other nitrogen species in the electrolyte during the process. Regarding the influence of the type of herbicide (chemical or commercial), competitive reactions have been observed between the electrolysis of herbicide and surfactant, which help to explain the lower efficiency observed in the degradation of RoundUp. Regarding the influence of the operation current density, the process is found to be more efficient at low current densities but at these conditions it is not possible to attain the complete mineralization of pollutant.

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26 **Keywords:** diamond anode, electrolysis, herbicide, glyphosate.

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31 **Highlights**

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- 33 - Glyphosate can be removed from wastewater by electrolysis with diamond
- 34 anodes.
- 35 - PO_4^{3-} , NO_3^- and CO_2 are the main final products of the oxidation of glyphosate.
- 36 - Oxidants electrogenerated have an important effect on glyphosate degradation.
- 37 - A complete mineralization of organic matter is obtained at 100 mA cm^{-2} in Cl
- 38 media.

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1. Introduction.

Nowadays, there is an increasing use of pesticides in agriculture, with outstanding benefits in terms of increases in crops production and hence in economy. However, these products are extremely hazardous to human health and, therefore, its occurrence in soils or even in groundwater or surface water should be prevented. One of the herbicides most commonly used around the World for different crops is glyphosate [1], an organophosphate and non-selective herbicide which is commonly known as RoundUp (Monsanto). It was classified as low toxicity compound by the Environmental Protection Agency (EPA) and the World Health Organization (WHO) at the beginning of nineties [2]. However, in 2015, the WHO has affirmed that glyphosate can promote cancer in humans [3]. For this reason, it is necessary to develop novel and clean technologies that attains the removal of this pesticide from soils and water. Over the last decade, several authors have studied different processes for the removal of glyphosate from wastewater; indeed most of the studies were focused on the evaluation of Advanced Oxidation Processes (AOPs). In this sense, Chen and Liu [4] evaluated the photocatalytic degradation of glyphosate using TiO_2 as photocatalyst. They studied the influence of different parameters on the process and concluded that the best conditions to obtain a higher removal of glyphosate are a TiO_2 concentration of 6.0 g l^{-1} , a long time of illumination and the addition of Fe^{3+} , Cu^{2+} , H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ or KBrO_3 . At the same time, Chen et al. [5] assessed the removal of glyphosate by photocatalysis with a ferrioxalate system. They irradiated light at 365 nm with a 250 W metal halide lamp. The efficiency of glyphosate removal increased with decreasing the concentration of herbicide and Fe^{3+} /oxalate ratios. Likewise, pH values between 3.5 and 5.0 favored the orthophosphate release, up to around 60 % and, therefore, the removal of glyphosate. Later, Balci et al. [6], studied an electro-Fenton process modified with Mn^{2+} and other

metals as catalysts. Carbon felt and Pt were used as cathode and anodes, respectively. With this combined system, they achieved a complete removal of glyphosate from wastewater using current intensities higher than 100 mA. Another electrochemical process was developed by Aquino et al. [7]. This process consisted of an electrochemical oxidation with different Dimensionally Stable Anodes (DSA[®]) anodes. They studied the influence of the pH, the herbicide concentration and the supporting electrolyte (Na₂SO₄ and NaCl) using DSA anodes based on RuO₂ and IrO₂. The removal of glyphosate was attained at 30 mA cm⁻² after 4 h of electrolysis. More recently, Hu et al. [8] carried out the adsorption of glyphosate over alum sludge in dewatered and liquid forms. This study concluded that alum sludge has a high adsorption capacity of 85.9 and 113.6 mg g⁻¹ for dewatered and liquid forms, respectively. Finally, Saitúa et al. [9] assessed the applicability of nanofiltration at pilot plant for the treatment of synthetic and natural waters polluted with glyphosate (48 mg dm⁻³). In this research, toxicity analyses were carried out using fish to evaluate the process efficiency. They obtained a glyphosate rejection of about 80 %.

Nevertheless, most of the processes described above do not allow to attain a complete removal of the organic matter in wastewater and, therefore, it is necessary to look for other technologies that allow not only remove the herbicide but also other organic products from its degradation, reaching a total mineralization of the organic matter. One of the most promising technologies for the treatment of wastewater polluted with organics are the electrochemically assisted oxidation [6, 10-13] and in particular conductive-diamond electrochemical oxidation (CDEO) [14, 15]. It is a well-known electrochemical advanced oxidation technology with very promising results which overcome results obtained by electrolysis with other anode materials [16-18]. This technology has been proven efficient in the removal of different organic pollutants such

as hormones [19, 20], antibiotics [21, 22], β -blockers [23, 24], etc. Likewise, CDEO has been successfully tested in the removal of different pesticides [25-28] mainly due to that higher concentrations of hydroxyl radicals are generated by water oxidation over anode surface. These radicals present a higher oxidation capacity and can react with the organics present in wastewater, favoring its complete mineralization.

CDEO is considered a robust technology and, for that reason, it has been checked for other wastewater treatments such as the disinfection of actual effluents from wastewater treatment plants (WWTP) [29-31] or the treatment of landfill leachate [32, 33]. The advantages of CDEO in comparing to other conventional treatments are [34-36]:

- The main reagent is the electron.
- Many processes occur in the same electrochemical cell.
- Soft operation conditions, mainly room temperature and atmospheric pressure.
- The addition of chemicals is not required.

However, the main drawback of this technology is the mass transfer limitations from the organic pollutant to the anode surface and, in order to overcome this limitation, the effect of mediated oxidation by oxidants produced from oxidation of the salts contained in wastewater has demonstrated to be capable to excel this constraint [18].

With this background, the main aim of the present work is to evaluate the application of CDEO for the removal of glyphosate in wastewater. The influence of the current density ($10\text{-}100\text{ mA cm}^{-2}$) and the supporting electrolyte (Na_2CO_3 ; Na_2SO_4 ; NaCl) has been studied because they seem to present a clear influence in the kinetic process and the process efficiency [37].

2. Material and methods.

2.1. Chemicals.

Glyphosate (pure), sodium carbonate, sodium sulfate, sodium chloride (Sigma-Aldrich, Spain) were analytical grade and used as received. RoundUp (industrial glyphosate) was provided by Fercampo (Ciudad Real, Spain), a specialized herbicide shop which sell the product for the industry. Acetonitrile HPLC grade, 2,6-pyridinedicarboxylic acid and nitric acid (Sigma-Aldrich, Spain) were used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity: 18.2MΩcm at 25°C) was used to prepare all solutions.

2.2. Analytical techniques.

Prior to each analysis, all samples were filtered with 0.22 μm nylon filters Scharlau provided by Scharlab. The removal of glyphosate was followed by total organic carbon (TOC). In addition, two of the final products of complete glyphosate oxidation are phosphate and nitrate (Eq. 1). For this reason, the concentration of phosphate and nitrate were measured by ion chromatography, as indirect measures of glyphosate degradation.

The chromatography system was a Metrohm 930 Compact IC Flex coupled to a conductivity detector. The column Metrosep A Supp 7 was used to determine the anions (PO_4^{3-} and NO_3^-). Furthermore, a column Metrosep A Supp 4 was used to analyze the cations, mainly ammonium (NH_4^+). The mobile phase consisted of 85:15 v/v 3.6 mM Na_2CO_3 /acetonitrile for the determination of anions with a flow rate of 0.8 ml min⁻¹. A solution of 1.7 mM HNO_3 and 1.7 mM 2,6-pyridinedicarboxylic acid was used as mobile phase for the determination of cations with a flow rate of 0.9 ml min⁻¹. The temperature of the oven was 45 and 30°C for the determination of anions and cations, respectively. The volume injection was 20 μl. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.

Hypochlorite was analyzed by titration with 0.001 M As_2O_3 in 2 M NaOH [38, 39]. The pretreatment of the samples consists of the addition of $2 \cdot 10^{-3} \text{ dm}^3$ of 2 M NaOH to $10 \cdot 10^{-3} \text{ dm}^3$ of the sample in order to increase the pH. Percarbonate and persulfate were determined iodometrically according to Standard methods [40] and Kolthoff & Carr [41], respectively. pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+.

2.3. Electrochemical cell.

Electrolyses were carried out in a single compartment electrochemical flow cell. Boron doped diamond (BDD) (Adamant Technologies, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of 78 cm^2 , boron concentration of 500 mg dm^{-3} , a thickness of $2.62 \text{ }\mu\text{m}$, sp^3/sp^2 ratio of 206 and p-Si as support. The electrode gap between anode and cathode was 3 mm. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). Wastewater was stored in a glass tank (1 dm^3).

Synthetic wastewater consisted of a solution containing 100 mg dm^{-3} of herbicide and $3,000 \text{ mg dm}^{-3}$ of supporting electrolyte (Na_2CO_3 , Na_2SO_4 , NaCl). All experiments (0.6 dm^3) were carried out under galvanostatic conditions, natural pH and discontinuous mode. At this mode of operation, the production of oxidant species is cumulative and it is related to the total Q (Ah dm^{-3}) applied at a given moment. The samples were collected in the glass tank and the sample volume was 0.02 dm^3 . The oxidants compounds (peroxocarbonate, peroxosulfate and hypochlorite) were measured immediately.

The current density applied ranged from $10\text{--}100 \text{ mA cm}^{-2}$. Prior to use in galvanostatic electrolysis assays, the electrodes were cleaned for 10 min in a $5000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$ solution at pH 2 and 300 A m^{-2} to remove any kind of impurity from its surface.

3. Results and discussion.

Figure 1 shows changes in TOC concentration during the electrolysis of synthetic wastewater polluted with 100 mg dm^{-3} of the herbicide glyphosate (pure and industrial) and different electrolytes media (sodium carbonate, sodium sulfate and sodium chloride). The differences observed in the initial TOC concentration between pure and industrial (RoundUp) herbicide is due to the presence of a surfactant in the last one.

As it can be observed, TOC concentration decreases with the applied electric charge, reaching lower final values at higher current densities. However, the process efficiency is lower when the current density increases because of the diffusion control of the herbicide removal rate and the higher concentration of hydroxyl radicals which are used in other reactions [42]. For example, at an electric charge of about 6.0 Ah dm^{-3} , TOC removal was 79 % at a current density of 10 mA cm^{-2} whereas a 56 % was attained at 100 mA cm^{-2} , both in chloride media during the electrolysis of pure glyphosate.

On the other hand, the supporting electrolyte has a great influence, being the removal of glyphosate more efficient in chloride media, regardless the current density applied. Likewise, TOC depletion is less efficient during the electrolysis in carbonate media, and it is not possible to attain the complete mineralization of the organic matter even at higher current densities. Finally, the process in sulfate media shows a higher removal than that obtained during the electrolysis with carbonate, as supporting electrolyte. In addition, the process efficiency is lower if the results are compared to the process in chloride media (pure glyphosate; j : 100 mA cm^{-2} ; Q : 58.9 Ah dm^{-3} ; final $\text{TOC}_{\text{Na}_2\text{CO}_3}$: 10.45 mg dm^{-3} ; final $\text{TOC}_{\text{Na}_2\text{SO}_4}$: 3.09 mg dm^{-3} ; final TOC_{NaCl} : 0.00 mg dm^{-3}). This behavior can be related to the formation of different oxidants during the electrolysis in the different electrolytes.

Figure 1. Influence of the current density on the TOC decay as function of the applied electric charge and the operation time during the electrochemical oxidation containing 100 mg dm⁻³ of herbicide and Na₂CO₃, Na₂SO₄ and NaCl as supporting electrolyte. Full points: industrial glyphosate; empty points: pure glyphosate. (■, □) Na₂CO₃; (▲, △) Na₂SO₄; (●, ○) NaCl; a) j : 10 mA cm⁻²; b) j : 100 mA cm⁻².

Regarding the influence of the nature of the herbicide (pure and industrial), no significant differences were observed during the process, being the removal of

glyphosate more efficient in chloride media for both compounds, regardless the current density applied.

Glyphosate presents a phosphate group, which is placed in the end of the molecule, and, therefore, it indicates that it would be possible to separate it easily. In literature, a mechanism for glyphosate degradation by electrolysis has been proposed, showing the formation of phosphate as final product (Figure 2) [7]. For this reason, the evolution of TOC together with the phosphorous concentration can provide a great deal of information about the degradation of herbicide [4, 5, 43, 44]. The total phosphorous release contained in 100 mg dm⁻³ of glyphosate would lead to 18.31 mg dm⁻³. Figure 3 shows the evolution of phosphate anion during the electrolysis of glyphosate in different electrolyte media and current densities.

Figure 2. Mechanism for glyphosate degradation by electrolysis [7].

Figure 3. Influence of the current density on the phosphorous release as function of the applied electric charge and the operation time during the electrochemical oxidation containing 100 mg dm⁻³ of herbicide and Na₂CO₃, Na₂SO₄ and NaCl as supporting electrolyte. Full points: industrial glyphosate; empty points: pure glyphosate. (■,□) Na₂CO₃; (▲,Δ) Na₂SO₄; (●,○) NaCl; a) j: 10 mA cm⁻²; b) j: 100 mA cm⁻².

Phosphate concentration increases with the applied electric charge until reach final values of about 18 mg P dm⁻³. This fact indicates that all phosphorous contained in

glyphosate has been released. No significant differences were found between the pure and industrial herbicide. However, different behaviors can be seen depending on the supporting electrolyte. In chloride media, the phosphate release is very efficient during the electrolysis, reaching the maximum value (around 18 mg dm⁻³) at operation times lower than 15 minutes. Furthermore, the process is more efficient at low current densities, as previously observed on the evolution of TOC concentration, and, therefore, the applied electric charge necessary to attain the maximum concentration is lower (j: 10 mA cm⁻²; Q: 0.38 Ah dm⁻³; j: 100 mA cm⁻²; Q: 1.17 Ah dm⁻³). Regarding the evolution of phosphate in carbonate and sulfate media, a higher efficiency can be observed when the first one is used as supporting electrolyte at low current density. This behavior can be related to the rapid breaking of the P-C bond, which can take place by the attack of peroxocarbonates electrochemically generated (Eq. 2). Nevertheless, the process in both media (Na₂CO₃ and Na₂SO₄) is less efficient compared to the results obtained in chloride media.

The lower phosphate release rate in carbonate and sulfate media seems to be directly related to the mineralization of the organic matter, which is not too efficient. This behavior can be due to the amine group of the molecule (N-H) keeps the carbons in its structure. However, inorganic nitrogen could be released during the electrolysis and, for that reason, an analysis of the main nitrogen species was carried out. Figure 4 shows the evolution of inorganic nitrogen anions (NO₂⁻ and NO₃⁻) with the applied electric charge and the operation time at different current densities. The maximum concentration of inorganic nitrogen that can be released from 100 mg dm⁻³ of glyphosate is about 8 mg dm⁻³.

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250 **Figure 4.** Influence of the current density on the nitrogen anions release as function of
 251 the applied electric charge and the operation time during the electrochemical oxidation
 252 containing 100 mg dm^{-3} of herbicide and Na_2CO_3 , Na_2SO_4 and NaCl as supporting
 253 electrolyte. Black/red points: $\text{NO}_3^-/\text{NO}_2^-$ industrial glyphosate; white/blue points: NO_3^-
 254 $/\text{NO}_2^-$ pure glyphosate. (■) Na_2CO_3 ; (▲) Na_2SO_4 ; (●) NaCl ; a) j : 10 mA cm^{-2} ; b) j : 100
 255 mA cm^{-2} .

As it can be observed, nitrate increases with the applied electric charge being its concentration higher during the electrolysis of industrial glyphosate, regardless the current density applied. This behavior is due to the presence of nitrogen in the surfactant contained in this herbicide, which suggests that the electrochemical oxidation of the surfactant can take place together with the removal of glyphosate. Overall, nitrate concentration is higher during the electrolysis in chloride media at low current densities. This fact is related to the higher electrochemical production of oxidants species, which attack the organic pollutant, favoring the nitrogen release. Specifically, the production of hypochlorite can take place by the electro-oxidation of chlorides (Eqs 3-4). Likewise, BDD anodes present excellent catalytic properties to form hydroxyl radicals from water oxidation (Eq. 5). These radicals can react with electrogenerated hypochlorite favoring the formation of chlorine compounds in high oxidation (chlorate and perchlorate) during the electrolysis of organics in chloride media (Eqs. 6-8) [45]. These species have a strong oxidizing power and, therefore, they contribute to the removal of pollutants.

On the other hand, the lower formation rate of nitrates in sulfate media can be due to a lower concentration of oxidants in wastewater or the formation of other organonitrogenated compounds (TOC concentration is not complete removed). Likewise, a similar behavior was observed during the electrolysis of pure glyphosate in

carbonate media at 10 mA cm⁻² (Figure 4a). On the contrary, the concentration of nitrates increases with the applied electric charge in these media (carbonate and sulfate) when working at 100 mA cm⁻². This behavior is related to a higher concentration of peroxocarbonates (Eq. 2) and peroxosulfates (Eq. 9) electrochemically generated in synthetic wastewater. These results are in agreement with previous researches of our group, in which it is demonstrated that the production of peroxosulfates and peroxocarbonates is clearly influenced by the current density.

At this point, it is important to highlight the trend observed in nitrate concentration during the electrolysis at higher current densities. As previously commented, there is an initial increase of nitrates by the attack of the electrogenerated oxidants to the herbicide. However, its concentration decreases at higher applied electric charges as shown in Figure 4b. This fact is related to the electrochemical reduction of nitrates on the cathode surface, favoring the production of ammonium (Eqs. 10-11) [46].

In addition, the presence of nitrites was observed during the electrolysis in chloride and carbonate media at higher current densities. This species presents a typical characteristic behavior as intermediate compound in the evolution of nitrogen. Nitrites can lead to the formation of nitrates by its chemical oxidation (Eqs. 12-13) and, therefore, the production of ammonium can be favored by the nitrates electroreduction.

Figure 5 shows changes in ammonium concentration during the electrolysis of synthetic wastewater polluted with 100 mg dm^{-3} of the herbicide glyphosate (pure and industrial) and different electrolytes media (sodium carbonate, sodium sulfate and sodium chloride).

As it can be observed, ammonium increases with the applied electric charge, being its concentration slightly higher when working at 100 mA cm^{-2} . This behavior is related to the higher concentration of nitrates at higher current densities. However, significant differences were observed depending on the electrolyte used. In this context, the concentration of ammonium was almost zero during the electrolysis in chloride media, which is due to the potential reaction between ammonium and the electrogenerated hypochlorite, favoring the production of chloramines (Eqs. 14-16) [47].

Figure 5. Influence of the current density on the nitrogen cations release as function of the applied electric charge and the operation time during the electrochemical oxidation containing 100 mg dm^{-3} of herbicide and Na_2CO_3 , Na_2SO_4 and NaCl as supporting electrolyte. Full points: industrial glyphosate; empty points: pure glyphosate. ($\blacksquare, \square$) Na_2CO_3 ; ($\blacktriangle, \triangle$) Na_2SO_4 ; ($\bullet, \circ$) NaCl ; a) j : 10 mA cm^{-2} ; b) j : 100 mA cm^{-2} .

325 On the other hand, the ammonium concentration shows an intermediate characteristic
 326 behavior when working in carbonate media at low current densities. There is an initial
 327 increase by the nitrates electroreduction followed by a decrease. This is due to the
 328 stripping process which takes place because the pH during this electrolysis was around
 329 11 and, therefore, the production of ammonia was favored (Eq. 11). At higher current
 330 densities, the concentration of ammonium increases with the applied electric charge
 331 during the process in carbonate media. This fact may be related to a higher
 332 concentration of oxidants, which favor the nitrogen release and, therefore, the
 333 subsequent formation of nitrates and ammonium. Likewise, the concentration of
 334 ammonium is higher during the treatment of industrial glyphosate, which shows that the
 335 nitrogen contained in the surfactant is being released. A similar behavior was observed
 336 during the process in sulfate media where the ammonium concentration increases with
 337 the applied electric charge. In this case, the attack of persulfate to the organic pollutant
 338 seems to play a key role in the nitrogen concentration. Thus, the ammonium
 339 concentration is higher in this experiment in comparison to the results obtained when
 340 using carbonate as supporting electrolyte. This is due to peroxosulfate, which presents a
 341 higher oxidizing power than peroxocarbonate. Furthermore, ammonium concentration is
 342 higher during the electrolysis of pure glyphosate because there are no competitive
 343 reactions for the formation of peroxosulfate.

344 Figure 6 shows the changes in cell voltage and conductivity with the applied electric
 345 charge at different current densities during the electrolysis of synthetic wastewater
 346 polluted with 100 mg dm⁻³ of glyphosate.

Figure 6. Influence of the current density on the cell voltage and conductivity as function of the applied electric charge and the operation time during the electrochemical oxidation containing 100 mg dm⁻³ of herbicide and Na₂CO₃, Na₂SO₄ and NaCl as supporting electrolyte. Black/red points: conductivity/cell voltage industrial glyphosate; white/blue points: conductivity/cell voltage pure glyphosate. (■) Na₂CO₃; (▲) Na₂SO₄; (●) NaCl; a) j: 10 mA cm⁻²; b) j: 100 mA cm⁻².

The cell voltage slightly decreases with the applied electric charge for all the experiments carried out. This behavior is directly related to the changes in the

conductivity, which increase around 10-30 % during the process. These changes can be due to the electrochemical oxidation of the herbicide and the subsequent release of ions (P and N) to wastewater. Likewise, the formation of intermediates products or other oxidants, from the electrolysis of the supporting electrolyte, together with water electrolysis may contribute to increase the conductivity in wastewater. In this context, higher changes were observed in conductivity when using chloride as supporting electrolyte (10 mA cm⁻²: +28 %; 100 mA cm⁻²: +21 %) and they can be related to the fastest release of N and P ions and a higher production of oxidants from chloride electrooxidation.

Furthermore, the decrease observed in the cell voltage is directly related to the energy consumption and, therefore, a decrease in the cell voltage leads to a decrease in the energy required to carry out the process. Thus, the process costs could be significantly reduced.

Finally, to verify the presence of oxidants in wastewater and its role (previously commented) in the removal of glyphosate by electrochemical oxidation with diamond anodes, an analysis of the main electrogenerated oxidants species was carried out. Specifically, the concentration of hypochlorite, peroxocarbonate and peroxosulfate was monitored. Figure 7 shows the results of these analyses.

As it can be observed, the maximum concentration of oxidants is higher when working at higher current densities. Peroxocarbonate and persulfate increase with the applied electric charge, reaching final values of around 16 and 25 mg dm⁻³, respectively for 10 mA cm⁻². Likewise, the final concentration of peroxocarbonate and peroxosulfate was 20 and 145 mg dm⁻³ when working at 100 mA cm⁻². The lower concentration of peroxocarbonate is directly related to the lower efficiency in TOC removal (Figure 1) and, therefore, in the removal of glyphosate. No significant differences were observed

381 between pure and industrial glyphosate for the production of peroxocarbonates and
 382 peroxosulfates during the electrolysis.

383

384 **Figure 7.** Influence of the current density on electrogenerated oxidants as function of
 385 the applied electric charge and the operation time during the electrochemical oxidation
 386 containing 100 mg dm^{-3} of herbicide and Na_2CO_3 , Na_2SO_4 and NaCl as supporting
 387 electrolyte. Full points: industrial glyphosate; empty points: pure glyphosate. ($\blacksquare, \square$)
 388 $\text{C}_2\text{O}_6^{2-}$; ($\blacktriangle, \triangle$) $\text{S}_2\text{O}_8^{2-}$; ($\bullet, \circ$) ClO^- ; a) $j: 10 \text{ mA cm}^{-2}$; b) $j: 100 \text{ mA cm}^{-2}$.

On the other hand, the concentration of hypochlorite is much higher than the oxidants concentration generated during the electrolysis in carbonate and sulfate media. This explains the higher efficiencies obtained in the removal of glyphosate when using chloride as supporting electrolyte. However, in this case, there are significant differences as function of the nature of the herbicide. In this context, the maximum concentration of hypochlorite was 400 and 500 mg dm⁻³ during the electrolysis of industrial and pure glyphosate at 10 mA cm⁻², respectively. This fact indicates that there are competitive reactions during the electrolysis of industrial herbicide in chloride media: the electrochemical oxidation of surfactant and supporting electrolyte (NaCl).

The maximum hypochlorite concentration is higher when working at 100 mA cm⁻² (pure glyphosate: 1,125 mg dm⁻³; industrial glyphosate: 760 mg dm⁻³) and, the trend observed is different in comparing the results at low current densities. There is an initial increase in the concentration by the electro-oxidation of chlorides followed by a decrease that could correspond to the removal of herbicide or the evolution of hypochlorite to other chlorine compounds in high oxidation state, such as chlorate and perchlorate. These compounds (chlorate and perchlorate) are very hazardous and its presence should be avoided in wastewater. At this point, it is important to highlight that different alternatives have been described for avoiding the formation of these compounds during the electrolysis: working at very low current densities or the addition of a chemical reagent capable to react with hypochlorite, favoring its reduction [31, 48]. The higher hypochlorite concentration at 100 mA cm⁻² explains the total removal of the organic matter in wastewater at applied electric charges lower than 40 Ah dm⁻³ (Figure 1b).

Finally, it is important to point out that the electrochemical production of different oxidants during the electrolysis of wastewater polluted with glyphosate follows the same electrocatalytic model as has been described in literature by Sirés et al. [14].

4. Conclusions.

From this work, the following conclusions can be drawn:

- Wastewater polluted with glyphosate can be mineralized by conductive-diamond electrochemical oxidation due to the attack of oxidants electrochemically generated during the process.
- Peroxocarbonate, peroxosulfate and hypochlorite are the main oxidants species responsible of the herbicide removal in carbonate, sulfate and chloride supporting electrolytes. The production of these oxidants is higher when working at 100 mA cm^{-2} , favoring the mineralization of organic matter. Likewise, higher concentrations of hypochlorite are generated in comparing to the production of peroxocarbonate or peroxosulfates. This is the reason why a complete mineralization is attained in chloride media. In addition, higher concentrations of hydroxyl radicals are generated when working at higher current densities (100 mA cm^{-2}) and these species also contribute to the removal of glyphosate.
- The electrolysis of industrial glyphosate (RoundUp) leads to competitive reactions between the electrolysis of herbicide, surfactant and supporting

electrolyte. Therefore, the removal of this type of commercial herbicide is less efficient than the removal of pure glyphosate.

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