Use of conductive diamond photo-electrochemical oxidation for the removal of pesticide glyphosate

Humberto Rubí-Juárez¹, Salvador Cotillas², Cristina Sáez², Pablo Cañizares², Carlos
Barrera-Díaz¹, Manuel A. Rodrigo^{2*}

¹ Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón
intersección Paseo Tolloca S/N, C.P. 50120, Toluca, Estado de México, México

² Chemical Engineering Department, Faculty of Chemical Sciences and Technologies,
University of Castilla-La Mancha, Edificio Enrique Costa Novella. Campus
Universitario s/n, 13005 Ciudad Real, Spain

Abstract

In this work, the depletion of a commercial formulation of the pesticide glyphosate (RoundUp) using photolysis, electrolysis and photo-electrolysis with diamond anodes was studied. Results show that single photolysis is an inefficient technology for the removal of the pesticide; however, when coupled with electrolysis the removal yield significantly improves. The use of a combined process (photo-electrolysis) leads to the generation of higher concentrations of free radicals from the photo-activation of the oxidants electrogenerated. A major finding is that the supporting electrolyte plays a key role on the removal of glyphosate due to the generation of different oxidant species. Such species (peroxocarbonates, peroxosulfates and hypochlorite) also contribute to the depletion of the pesticide. Furthermore, the removal of glyphosate is clearly influenced by the current density because of the strong relationship between this parameter and the oxidants produced on the anode surface.

Keywords: diamond anode, electrolysis, photo-electrolysis, pesticide, glyphosate.

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26 *Corresponding author e-mail: manuel.rodrido@uclm.es. Tel.: +34-926-29-53-00 Ext.
27 3411; fax: +34-926-29-52-56

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29 **Highlights**

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- 31 - Single photolysis does not achieve the oxidation of glyphosate from wastewater.
- 32 - Coupling photolysis and electrolysis improves the total mineralization of
33 glyphosate.
- 34 - Free sulfate radicals play an important role in the mineralization of glyphosate
- 35 - Antagonistic effects were produced by UV light in electrolysis with carbonate and
36 chloride.

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1. Introduction.

In recent years, the use of pesticides has increased in agricultural activities, allowing a high production of different crops. These products are mainly organic compounds capable to remove the weeds. For this reason, there are a wide variety of pesticides which are used in high concentrations all around the World [1].

One of the products typically used in agriculture is glyphosate, a non-selective pesticide. It is an organophosphate compound which is commercially known as RoundUp (Monsanto) and, it presents a phosphate and an amine group in its structure as shown in Figure 1.

Figure 1. Molecule of glyphosate.

This compound, like most of the pesticides, is hazardous for the environment and the human health, and since it presents a high diffusion through the soil to groundwater, involving serious risks. Therefore, it is necessary to develop efficient processes that allow a complete removal of glyphosate present in wastewater [2]. In recent reports, different processes for the removal of this pesticide such as: photocatalytic degradation with TiO_2 [3] or ferrioxalate [4], electro-Fenton process with Mn^{2+} [5] or nanofiltration technology, have been described. [6]. However, none of them attain a complete removal of organic matter in wastewater. This point is very important for the environment since glyphosate degradation leads to the formation of aminomethylphosphonic acid (AMPA), which is more toxic and persistent than pesticide glyphosate [7]. For this reason, other alternatives should be proposed that remove not only the pesticide but also the total content of organic matter in wastewater.

In this context, conductive diamond electrochemical oxidation (CDEO) is considered as a promising technology for the treatment of wastewater [8-11]. This technique is based on the production of oxidant species from the ions contained in wastewater, which contribute to the degradation of organic matter [12, 13]. In comparing with other electrode materials, Boron Doped Diamond electrode (BDD) presents excellent electrocatalytic properties not only for the production of oxidants but also for the generation of higher concentration of hydroxyl radicals from water oxidation (Eq. 1) [14].

CDEO has been tested for the treatment of different industrial wastewater [15-17] and the removal of several types of pollutants, such as: antibiotics, hormones, among others [18-23]. Recently, due to the outstanding results obtained in the treatment of these types of wastewater, CDEO has been used for disinfection processes, reaching high efficiencies [24-27]. Nevertheless, the main drawback of this technology is the mass transfer limitations from pollutants contained in wastewater to the anode surface. In order to overcome this limitation, new research is required to improve the efficiencies attain by single CDEO in new treatment alternatives [28]. In this way, the irradiation of UV light has shown a great influence in the CDEO performance for the removal of organics [29-32]. This technology combined with CDEO allows to generate higher concentrations of free radicals from the photo-activation of the oxidants electrogenerated [33]. These new species significantly contribute to the degradation of organic matter in wastewater, improving the efficiencies of CDEO. The coupling of both techniques can be named as conductive diamond photo-electrochemical oxidation (CDPEO).

The main aim of this work is to evaluate the synergistic/antagonistic effects resulted of coupling CDEO and UV light irradiation for the removal of the pesticide glyphosate. Because of their great relevance in the production of oxidants, the influence of the

supporting electrolyte and that the current density applied are also studied in the search of a better understanding of the performance of photoelectrochemical processes with diamond anodes.

2. Material and methods.

2.1. Chemicals.

Sodium carbonate, sodium sulfate and sodium chloride (Sigma-Aldrich, Spain) were analytical grade and used as received. RoundUp (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: 18.2 MΩcm at 25°C) was used to prepare all solutions.

2.2. Experimental setup.

Electrolyses were carried out in a single compartment electrochemical cell. Circular boron doped diamond (BDD) plates (Adamant Technologies, Switzerland) with a geometric area of 78 cm² was used as anode and stainless steel (SS) as cathode. The last one consists of a grid, in order to allow the light to pass through the electrochemical cell. Likewise, one of the cell covers was made of quartz. The inter-electrode gap between both electrodes was 9 mm. A low pressure Hg vapor UV lamp VL-215MC (Vilber Lourmat), $\lambda = 254$ nm, intensity of 930 $\mu\text{W}/\text{cm}^2$ and energy 4.89 eV irradiated 4 W directly to the quartz cover. A Delta Electronika ES030-10 power supply (0-30V, 0-10A) provided the electric current. Wastewater was stored in a glass tank (1 dm³).

Synthetic wastewater was prepared with 100 mg dm⁻³ of pesticide and 3,000 mg dm⁻³ of supporting electrolyte. All experiments (0.6 dm³) were carried out under galvanostatic conditions, natural pH and discontinuous mode. Samples (0.02 dm³) were collected in the

glass tank and the oxidants compounds (peroxocarbonate, peroxosulfate and hypochlorite) were measured immediately.

The influence of the nature of the supporting electrolyte (Na_2CO_3 , Na_2SO_4 , NaCl) and the current density ($10\text{--}100\text{ mA cm}^{-2}$) were studied on the electrochemical removal of the pesticide.

2.3. Analytical procedures.

The removal of glyphosate was followed by total organic carbon (TOC) and two of the final products of its complete degradation (phosphate and nitrate) (Eq. 2). These ionic species were determined 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 [34, 35]. 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 Kolthoff & Carr (1953) [36] and Standard methods [37]. pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+.

2.4. Synergy coefficient.

The synergy coefficient (%) was used to evaluate the effect of coupling photolysis and electrolysis processes. It can be calculated by the removal of TOC for the different processes studied (photolysis, electrolysis, and photo-electrolysis) (Eq. 3).

$$\text{Synergy coefficient} = \frac{\Delta\text{TOC}_{\text{photo-electrolysis}} - \Delta\text{TOC}_{\text{photolysis}} - \Delta\text{TOC}_{\text{electrolysis}}}{\Delta\text{TOC}_{\text{photolysis}} + \Delta\text{TOC}_{\text{electrolysis}}} \cdot 100 \quad [3]$$

3. Results and discussion.

Figure 2 compares the evolution of TOC concentration during the photolysis, electrolysis and photo-electrolysis of synthetic wastewater polluted with 100 mg dm⁻³ of the pesticide glyphosate (RoundUp) at two different current densities: 10 mA cm⁻² (for which hydroxyl radicals role is not expected) and 100 mA cm⁻² (in which hydroxyl radical can be the key to explain the reactivity of the system) [38]. Sodium carbonate, sodium sulfate and sodium chloride were used as supporting electrolytes in order to evaluate their role in the electrolysis of the pesticide.

No significant changes are observed during single UV irradiation process, which suggests that single photolysis is not a proper technology for the removal of glyphosate. Even, the small variations of TOC concentration may be related to the accuracy of the analytical equipment, more than a treatment outcome, because not a clear decreasing trend is observed. On the other hand, TOC decreases with the operation time during single

electrolysis and photo-electrolysis, regardless the current density applied. However, within the reaction time scheduled, it is only possible to attain a complete mineralization of organic matter during photo-electrolysis in sulfate media at 100 mA cm⁻². This fact indicates that the supporting electrolyte and the current density have a great influence on the removal of the pesticide. The formation of hydroxyl radicals (favored at 100 mA cm⁻²) also contributes to the mineralization process of organic matter. The differences observed between electrolytes may be mainly related to the formation of different oxidant species and differences can be explained in terms of their different properties (in particular, their oxidation capability) [39, 40]. Likewise, UV light irradiation seems to have a significant effect on the mineralization process, this outcome becomes more important when working at higher current densities.

To shed light on the removal of glyphosate by electrolysis and photo-electrolysis processes, Figure 3 shows the efficiency (η) of TOC removal for both technologies at the two current densities studied and with different supporting electrolytes. This parameter can be easily calculated from the ratio between the variation of the TOC concentration and the applied electric charge (Ah dm⁻³) (Eq. 4) for an arbitrary reaction period (for which an applied electric charge Q_i is passed).

$$\eta = \frac{TOC_0 - TOC_{Q_i}}{Q_i} \quad [4]$$

In this work, for the experiments carried out at 10 mA cm⁻², an electric charge (Q_i) of 1.0 Ah dm⁻³ has been selected whereas 10.0 Ah dm⁻³ has been the charge used for the processes at 100 mA cm⁻². Both charge values correspond to the same operation time (30 minutes).

Figure 2. TOC decay as function of the operation time during the UV irradiation, electrolysis and photo-electrolysis of synthetic wastewater containing 100 mg dm^{-3} of pesticide and $3,000 \text{ mg dm}^{-3}$ of supporting electrolyte Na_2CO_3 , Na_2SO_4 and NaCl . Black points: electrolysis; grey points: photolysis; white points: photo-electrolysis. ($\blacksquare, \blacksquare, \square$) Na_2CO_3 ; ($\blacktriangle, \triangle, \Delta$) Na_2SO_4 ; ($\bullet, \bullet, \circ$) NaCl ; $\text{UV}_{254 \text{ nm}}$: 4 W; a) j : 10 mA cm^{-2} ; b) j : 100 mA cm^{-2} .

Figure 3. Mineralization efficiency reached with an initial concentration of 100 mg dm⁻³ of glyphosate by electrolysis and photo-electrolysis. White bars (j: 10 mA cm⁻²; Q: 1 Ah dm⁻³); black bars (j: 100 mA cm⁻²; Q: 10 Ah dm⁻³).

From Figure 3, it can be observed that the electrolytic process yields a higher pollutant removal efficiency when the current density applied is high. This is quite interesting since this is not the expected behavior [41-43], because typically in electrolysis with diamond anodes, low concentration of organics (such as the one used in the synthetic wastes studied in this work) leads to mass transport controlled processes, for which the higher the current density applied, the lower is the resulting efficiency [41]. This unexpected behavior has to be explained in terms of the mediated oxidation mechanisms, promoted during the electrolysis with diamond anodes, with the formation of different oxidants from ions contained in wastewater matrix [22]. Indeed, we have previously reported, the production of peroxocompounds from anions such as phosphate, sulfate and carbonate and the production of oxochlorinated anions from chloride (Eqs. 5 to 10), and their effect on organics contained in wastewater [32].

215 This mediated oxidation mechanism can help to explain the large differences observed in
 216 the electrolysis of pesticide in the presence of carbonate and sulfate and the very small
 217 differences observed in the case of chloride. In the first case, peroxosulfates and
 218 peroxocarbonates production is known to be improved by the action of hydroxyl radicals
 219 (Eqs. 11 to 20), which are promoted at very high current densities (because of the also
 220 associated anodic potential) [44], while in the latter case, occurrence of hydroxyl radicals
 221 implies the formation of undesired perchlorates [45], which are kinetically inefficient in
 222 the oxidation of pesticide at room temperature, in addition to have a negative impact in
 223 environment and human health.

234 Regarding the influence of light irradiation two important observations have to be pointed
 235 out. As in non-irradiated processes, electro-irradiated processes are more efficient at
 236 higher current densities and, obviously, the promoted anodic production of oxidants at
 237 higher current densities can also explain this improvement. However, light irradiation
 238 does not always improve the efficiency as compared to the non-irradiated processes and
 239 a clear difference in the efficiency can be observed between the low and the high current
 240 densities tests. While for high current densities, light irradiation always leads to a higher
 241 efficiency, in the electrolysis at low current densities, differences are smaller or even
 242 negative (as happen in the case of carbonates) (Figure 2).

243 Light irradiation is known to produce the decomposition of peroxocompounds with the
 244 subsequent formation of more powerful radicals (Eqs. 21 to 23) [46]. Because the
 245 production of these species is higher at higher current densities, the promotion observed
 246 operating at 100 mA cm⁻² is clearly justified [31]. It is important to take into account that
 247 oxidation capacity of radicals is several folds over that shown by the non-radical species
 248 [47]. In addition, in the case of electrolysis in chloride media, light irradiation is known
 249 to produce the formation of chlorine radicals from hypochlorite. This radical improves
 250 the oxidation reaction rate, as well as prevent the further oxidation of gaseous chlorine
 251 (and hence of hypochlorite) to chlorates and perchlorates, as pointed out in equations 21
 252 to 23 [48].

In order to clarify the electrochemical production of oxidants and its role on the removal of glyphosate, Figure 4 compares the time-course of the concentration of percarbonate, persulfate and hypochlorite electrochemically generated during CDEO and CDPEO at the two different current densities studied. In order to obtain comparable results, these concentrations are expressed in terms of oxygen-equivalent concentration, by considering only the number of electrons exchanged by each mole of oxidant produced. The reduction of each mole of oxygen during oxidation processes needs for 4 electrons, while the production of carbonate, sulfate and hypochlorite, only 2.

Figure 4. Influence of the current density on electrogenerated oxidants as function of the operation time during the electrochemical (CDEO) and photo-electrochemical (CDPEO) oxidation of synthetic wastewater containing 100 mg dm⁻³ of herbicide and Na₂CO₃, Na₂SO₄ and NaCl as supporting electrolyte. Full points: CDEO; empty points: CDPEO. (■,□) C₂O₆²⁻; (▲,Δ) S₂O₈²⁻; (●,○) ClO⁻; a) j: 10 mA cm⁻²; b) j: 100 mA cm⁻².

As observed in figure 4, the production of peroxocarbonates is the less efficient and it does not show a great influence on the current density applied, reaching final values lower than 1 mmol O₂. In addition, the concentration of this oxidant species is slightly lower during CDPEO which may be related to the production of free carbonate radicals by light decomposition of peroxocarbonates (Eq. 21). A similar behavior was observed in the production of peroxosulfates during CDEO and CDPEO. The concentration of S₂O₈²⁻ was higher when compared to peroxocarbonate and, the differences between both processes (CDEO and CDPEO) are more remarkable. In this context, the final concentration of peroxosulfate during CDEO was 1.10 and 5.42 mmole O₂, whereas 0.49 and 1.10 mmole O₂ were obtained during CDPEO, both for 10 and 100 mA cm⁻² respectively. Therefore, the production of free sulfate radicals (Eq. 22) is more efficient at higher current densities and this behavior can be explained in terms of a higher production of peroxosulfate, favoring the total removal of the organic matter in wastewater (Figure 2b). Regarding the production of oxidants in chloride media, no significant differences were observed in the generation of hypochlorite at low current densities (Figure 4a) between CDEO and CDPEO, reaching a final value of around 25 mmole O₂ in both processes. However, a different behavior was observed during the process in chloride media at 100 mA cm⁻² (Figure 4b). In this case, hypochlorite follows a characteristic trend as reaction intermediate: there is an initial increase followed by a decrease. Furthermore, its

concentration was almost nil at the end of both processes (CDEO and CDPEO), which indicates that this species is oxidized to other chlorinated compounds in higher oxidation state (i.e. chlorate and perchlorate). Likewise, it is important to mention that hypochlorite concentration is depleted faster in CDPEO than in CDEO (t_{CDPEO} : 90 min; t_{CDEO} : 180 min) and this fact may be related to the potential production of free chlorine radicals during CDPEO (Eq. 23) that prevents formation of perchlorates.

The supporting electrolyte has a great influence on the removal efficiencies since different oxidants are produced, this can be observed in Figures 3 and 4. Clearly photo-activated persulfate plays a key role in the removal of glyphosate during CDPEO, in spite of the higher concentration of chlorine oxidants produced in the reaction media.

The oxidation of glyphosate leads to phosphorous release (Figure 1). Therefore, the increase in phosphorous concentration is directly related to the removal of glyphosate [3, 4, 49, 50]. In this context, Figure 5 shows the evolution of phosphate during photolysis, electrolysis and photo-electrolysis processes in different media and current densities. The maximum theoretical concentration that can be released from 100 mg dm^{-3} of glyphosate is $18.31 \text{ mg P dm}^{-3}$.

As it can be observed, phosphorous concentration was nil during the 3 h-long tests, indicating that glyphosate may be refractory to single UV irradiation. However, phosphate anion increases during electrolysis and photo-electrolysis, reaching a final value around 18 mg dm^{-3} . This fact indicates that there is an efficient phosphorous release during CDEO and CDPEO. The differences observed are related to the nature of the supporting electrolyte and the current density.

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313 **Figure 5.** Phosphorous release as function of the operation time during the UV irradiation,
 314 electrochemical (CDEO) and photo-electrochemical (CDPEO) oxidation of synthetic
 315 wastewater containing 100 mg dm⁻³ of pesticide and Na₂CO₃, Na₂SO₄ and NaCl as
 316 supporting electrolyte. Black points: CDEO; grey points: photolysis; white points:
 317 CDPEO. (■, ■, □) Na₂CO₃; (▲, ▲, △) Na₂SO₄; (●, ●, ○) NaCl; a) j : 10 mA cm⁻²; b) j : 100
 318 mA cm⁻².

The behavior of phosphorous release, in carbonate media, is similar at 10 mA cm^{-2} , regardless the irradiation of UV light. In both cases (CDEO and CDPEO), there is an initial increase until reach a maximum value, from which it remains constant. Small differences in the final concentration can be due to an initial concentration of glyphosate lower than 100 mg dm^{-3} in synthetic wastewater. Nonetheless, these results are in agreement with TOC depletion in carbonate media, where no significant changes were observed between CDEO and CDPEO at these conditions (Figure 2a). On the other hand, phosphorous release follows a similar behavior in comparison to the removal of organic matter during CDEO and CDPEO with carbonate at 100 mA cm^{-2} . However, as expected, CDPEO is more efficient for phosphate release because the attack of free carbonate radicals is more aggressive than percarbonate (Figure 5b). These results highlight that both, percarbonate and carbonate radical, are suitable to attack the P-C bond.

Regarding chloride media, phosphorous release is very low when working at 10 mA cm^{-2} and using UV light irradiation (t: 180 min; P_{CDEO} : 16.60 mg dm^{-3} ; P_{CDPEO} : 5.74 mg dm^{-3}). This fact seems to indicate that free chlorine radical could be less efficient than hypochlorite for the removal of glyphosate (Figure 5a). On the contrary, no significant changes were found between CDEO and CDPEO at 100 mA cm^{-2} (t: 180 min; P_{CDEO} : 17.85 mg dm^{-3} ; P_{CDPEO} : 17.67 mg dm^{-3}). This behavior can be related to a higher concentration of oxidants in wastewater, favoring phosphorous release.

Sulfate media has been found to be the most appropriate electrolyte for the removal of organic matter from glyphosate and, for this reason, it is not surprising that phosphate release becomes also the fastest in this media. In addition, phosphorus release is more efficient during CDPEO, regardless the current density applied (Figure 5). This fact is due to the attack of sulfate radicals produced from the photo-activation of electrogenerated peroxosulfate (Eq. 22). Nevertheless, the maximum concentration of

phosphate that can be released is attained during single CDEO at the current densities studied. In this case, the main species responsible of phosphate release is expected to be electrochemically generated peroxosulfate.

Even though phosphorous release is very efficient during CDEO and CDPEO at different current densities, it is not possible to attain the complete mineralization of organic matter when working with carbonate or chloride as supporting electrolyte. This fact can be related to the amine group of the molecule (N-H) chemically bond to carbon. Initially, it is expected than nitrogen could be released during the process and therefore, the main nitrogen species were monitored. Figure 6 shows the concentration of nitrogen released during CDEO and CDPEO at 10 mA cm^{-2} . In this case, the maximum nitrogen concentration that can be released from 100 mg dm^{-3} of glyphosate is about 8 mg dm^{-3} .

The concentration of nitrates increases as the reaction progresses during both processes (CDEO and CDPEO) as shown in Figure 6. However, different behaviors can be seen depending on the supporting electrolyte used. Nitrates increase with the operation time until reaching a final value of about $6.40 \text{ mg N dm}^{-3}$ when using carbonate as supporting electrolyte during CDEO. Likewise, its concentration follows a similar trend during CDPEO, being the maximum concentration achieved $5.31 \text{ mg N dm}^{-3}$. At this point, it is important to bear in mind the effect of UV light irradiation on nitrogen speciation. The lower nitrate concentration can be also related to the photon absorption of UV, favoring the production of nitrite or nitrite radical (Eqs. 24-25) [51, 52].

In this context, the concentration of nitrite slightly increases with the operation time. This highlights the interaction between nitrates and UV light irradiation during the process.

Figure 6. Nitrogen release as function of the operation time during the electrochemical (CDEO) and photo-electrochemical (CDPEO) oxidation of synthetic wastewater containing 100 mg dm⁻³ of pesticide. a) Anions; black/red points: NO₃⁻/NO₂⁻ CDEO; white/blue points: NO₃⁻/NO₂⁻ CDPEO. b) Cations; black points: NH₄⁺ CDEO; white points: NH₄⁺ CDPEO. (■) Na₂CO₃; (▲) Na₂SO₄; (●) NaCl; j: 10 mA cm⁻².

Regarding nitrogen speciation in chloride media, nitrates concentration is higher during CDEO. Once again, it can be related to the effect of UV light on nitrogen species during CDPEO (Eqs. 24-25). Therefore, this fact suggests a rapid promotion of nitrogen anions to nitrogen radicals in this media (Cl) during CDPEO because the presence of nitrite anion was discarded.

On the other hand, nitrate concentration follows a different trend, in comparison to the results in carbonate and chloride media, when using sulfate as supporting electrolyte. There is an initial increase with the operation time followed by a decrease. Likewise, the maximum concentration of nitrate released was lower in sulfate media. This fact can be related to the production of free radicals by the irradiation of UV light (Eq. 25). However, nitrogen released as nitrate was higher during CDPEO (2.21 vs. 0.77 mg N dm⁻³). At this point, it is important to highlight that nitrate decay can be due to its electroreduction on the cathode, favoring the production of ammonium (Eqs. 26-27) [53].

This species was also monitored during the process (Figure 6b) and, as it can be observed, ammonium increases with the operation time during the process in carbonate and sulfate media. Its generation is clearly influenced by the supporting electrolyte used. In this context, ammonium follows a characteristic trend of an intermediate compound during the process in carbonate media. In this case, a stripping process can take place due to the alkaline conditions in wastewater (pH ≈ 11), favoring the production of ammonium ions (Eq. 27). Therefore, ammonium concentration decreases at the end of the process.

Likewise, the concentration of this species is lower when using UV light irradiation, which indicates that the formation of free nitrogen radicals is favored (Eq. 25).

Regarding the ammonium concentration in sulfate media, it increases with the operation time. However, this species is higher during CDPEO when comparing the results obtained in CDEO. This behavior explains the marked decrease observed in nitrate concentration.

Finally, ammonium concentration was practically nil during CDEO and CDPEO in chloride media. This fact is related to the potential reaction between ammonium and hypochlorite (previously electrogenerated, Eqs. 8-10). As result, inorganic chloramines are formed in wastewater (Eqs. 28-30) [53].

Figure 7 focusses on the evolution of nitrogen compounds during CDEO and CDPEO at 100 mA cm⁻². As it can be observed, nitrates increase with the operation time during both processes. The maximum concentration of this species is attained during CDEO in carbonate media (6.40 mg N dm⁻³). This value is similar than that obtained during the process in carbonate media at 10 mA cm⁻² (Figure 6a). However, the generation of nitrates is more efficient at low current densities, which may be related to mass transfer limitations (previously commented). Likewise, the presence of nitrites was observed at higher current densities in carbonate media. This species follows a characteristic trend of an intermediate compound which suggests that nitrites are being oxidized to nitrates (Eqs. 31-32).

Figure 7. Nitrogen release as function of the operation time during the electrochemical (CDEO) and photo-electrochemical (CDPEO) oxidation of synthetic wastewater containing 100 mg dm⁻³ of pesticide. a) Anions; black/red points: NO₃⁻/NO₂⁻ CDEO; white/blue points: NO₃⁻/NO₂⁻ CDPEO. b) Cations; black points: NH₄⁺ CDEO; white points: NH₄⁺ CDPEO. (■) Na₂CO₃; (▲) Na₂SO₄; (●) NaCl; j: 100 mA cm⁻².

[31]

On the other hand, nitrate and nitrite follow the same trend during CDPEO at 100 mA cm⁻², being the concentration of nitrates higher. As it can be observed, both species decrease at the end of the process (Figure 7). This behavior suggests that the production of nitrite radicals is favored when working at higher current densities (Eq. 25). Likewise, the decrease observed in nitrites concentration can also be related to the photo-chemical reaction between this species and UV light, producing nitric oxide radicals (Eq. 33) [51, 52].

Regarding the nitrogen speciation in chloride media at higher current densities, no significant concentrations of nitrites were detected during both processes. However, nitrates concentration increase with the operation time until reaching a maximum value from which its concentration decreases. This behavior has been observed in both processes (CDEO and CDPEO) and it is related to the potential generation of ammonium (Eqs. 26-27). Likewise, the decrease observed during CDPEO is also due to the formation of free radicals by UV light irradiation (Eq. 25).

The generation of nitrates was lower during both processes at higher current densities in sulfate media. In these cases, the final concentration of nitrates was lower in comparing to the results obtained in carbonate and chloride media. This behavior indicates that the production of ammonium and free nitrogen radicals is promoted when using sulfate as supporting electrolyte. In this context, ammonium concentration was higher during CDPEO in sulfate media (Figure 7b). This explains the lower efficiency in nitrates generation during the removal of glyphosate in this media.

Overall, ammonium concentration is higher when working at 100 mA cm⁻² in sulfate and carbonate media (Figure 7b). In chloride media, as previously described (Figure 6), the ammonium concentration was almost nil due to the potential formation of inorganic chloramines (Eqs. 28-30). A different behavior was only observed during CDEO at 100 mA cm⁻². In this case, the concentration of ammonium increases with the applied electric charge. This fact can be related to a higher concentration of oxidants (peroxocarbonate) in wastewater which promotes the nitrogen release and the formation of both nitrate and ammonium.

Finally, Figure 8 shows the effect of the current density and the supporting electrolyte on the synergy coefficient. It is interesting to note that antagonistic effects have been found when coupling electrolysis and UV irradiation in carbonate and chloride media at lower current densities (-4.26 and -44.26 %, respectively). On the contrary, a synergistic effect was found during the process in sulfate media (8.11 %), which indicates a clear contribution of photo-activated persulfate to the removal of glyphosate.

Figure 8. Effect of the current density and supporting electrolyte on the observed synergism/antagonism of UV irradiation on electrolysis in terms of pollutant mineralization. ■ Na₂CO₃; ■ Na₂SO₄; □ NaCl.

On the other hand, synergistic effects were found when coupling both technologies at 100 mA cm⁻², regardless the electrolyte used. However, the synergy coefficient was very low during the process in chloride media (0.57 %). This fact suggests that the oxidants electrogenerated are not efficiently used for the degradation of the pesticide. Likewise, the maximum synergy coefficient (42.89 %) has been obtained during the process in carbonate media, although it is important to remark that the complete mineralization of organic matter was not attained during CDPEO in carbonate media. Finally, the process in sulfate media shows a marked synergistic effect at higher current densities (26.40 %) and, in this case, the organic matter was completely removed (Figure 2b). This fact again points out the very significant contribution of photo-activated persulfate on the removal of glyphosate.

Conclusions.

From this work, the following conclusions can be drawn:

- Single photolysis is an inefficient technology for the complete removal of glyphosate and electrolysis requires to apply a high electric charge to attain a complete mineralization of the organic matter.
- Wastewater containing glyphosate can be mineralized by conductive-diamond photo-electrochemical oxidation.
- The electrochemical production of oxidants has a great influence in the removal of the pesticide, reaching higher concentrations at 100 mA cm⁻². Likewise, these

species are photo-activated by the irradiation UV light, favoring the formation of free radicals which also contribute to the mineralization of the organic matter.

- Synergistic effects were found when coupling UV irradiation and electrolysis in sulfate media, regardless the current density applied. However, it is only possible to attain a complete mineralization of organic matter at 100 mA cm^{-2} , where the production of free sulfate radicals is higher. In carbonate media, a clear antagonistic effect was observed during photo-electrolysis at low current densities whereas a significant synergistic effect was found at 100 mA cm^{-2} . Nonetheless, the organic matter is not completely removed in this media because the production of oxidants (percarbonate) was low. Chloride media is not a recommended electrolyte for the removal of RoundUp by photo-electrolysis due to the presence of competitive reactions between the attack of hypochlorite to the pesticide and its electrooxidation to other chlorinated compounds in higher oxidation state.

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