



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



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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.

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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 Fig. 1.

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 TiO₂ [3] or ferrioxalate [4], electro-Fenton process with Mn²⁺ [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

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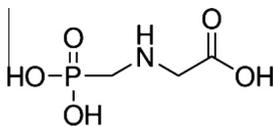


Fig. 1. Molecule of glyphosate.

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 photoelectrochemical 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 M Ω cm at 25 °C) was used to prepare all solutions.

2.2. Experimental setup

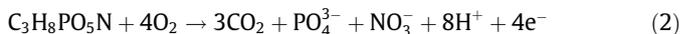
Electrolyses were carried out in a single compartment electrochemical cell. Circular boron doped diamond (BDD) plates (Adamant Technologies, Switzerland) with a geometric area of 78 cm² was used as anode and stainless steel (SS) as cathode. The last one consists of a grid, in order to allow the light 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 μ W/cm² and energy 4.89 eV irradiated 4 W directly to the quartz cover. A Delta Electronika ES030-10 power supply (0–30 V, 0–10 A) 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 3000 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 (Na₂CO₃, Na₂SO₄, NaCl) and the current density (10–100 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 (PO₄³⁻ and NO₃⁻). Furthermore, a column Metrosep A Supp 4 was used to analyze the cations, mainly ammonium (NH₄⁺). The mobile phase consisted of 85:15 v/v 3.6 mM Na₂CO₃/acetonitrile for the determination of anions with a flow rate of 0.8 ml min⁻¹. A solution of 1.7 mM HNO₃ 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 μ l. 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 As₂O₃ in 2 M NaOH [34,35]. The pretreatment of the samples consists of the addition of 2 · 10⁻³ dm³ of 2 M NaOH to 10 · 10⁻³ dm³ of the sample in order to increase the pH. Percarbonate and persulfate were determined iodometrically according to Kolthoff & Carr [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

Fig. 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

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