



Removal of herbicide glyphosate by conductive-diamond electrochemical oxidation



Humberto Rubí-Juárez^a, Salvador Cotillas^b, Cristina Sáez^b, Pablo Cañizares^b, Carlos Barrera-Díaz^a, Manuel A. Rodrigo^{b,*}

^a Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón intersección Paseo Tollocan S/N, C.P. 50120 Toluca, Estado de México, Mexico

^b 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

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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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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 TiO₂ 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 TiO₂ concentration of 6.0 g l⁻¹, a long time of illumination and the addition of Fe³⁺, Cu²⁺, H₂O₂, K₂S₂O₈ or KBrO₃. 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 Fe³⁺/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 Mn²⁺ 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 Neto and de Andrade [7]. This process consisted of an electrochemical oxidation with different Dimensionally Stable Anodes (DSA[®]) anodes. They studied the

* Corresponding author.

E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

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 as 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 (10–100 mA cm⁻²) and the supporting electrolyte (Na₂CO₃; Na₂SO₄; 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

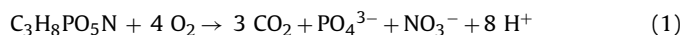
2.1. Chemicals

Glyphosate (pure), sodium carbonate, sodium sulfate, sodium chloride (Sigma-Aldrich, Spain) were analytical grade and used as received. RoundUp (industrial glyphosate) was provided by Fer-

campo (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. 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 930Compact 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 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 As₂O₃ in 2 M NaOH [38,39]. 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 Standard methods [40] and Kolthoff and 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 cm², boron concentration of 500 mg dm⁻³, a thickness of 2.62 μm, sp³/sp² 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 (0–30 V, 0–10 A). Wastewater was stored in a glass tank (1 dm³).

Synthetic wastewater consisted of a solution containing 100 mg dm⁻³ of herbicide and 3000 mg dm⁻³ of supporting electrolyte (Na₂CO₃, Na₂SO₄, NaCl). All experiments (0.6 dm³) 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 dm³. The oxidants compounds (peroxocarbonate, peroxosulfate and hypochlorite) were measured immediately.

The current density applied ranged from 10 to 100 mA cm⁻². Prior to use in galvanostatic electrolysis assays, the electrodes were cleaned for 10 min in a 5000 mg dm⁻³ Na₂SO₄ solution at pH 2 and 300 A m⁻² to remove any kind of impurity from its surface.

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