



# The effect of the $sp^3/sp^2$ carbon ratio on the electrochemical oxidation of 2,4-D with p-Si BDD anodes



F.L. Souza<sup>a</sup>, C. Saéz<sup>b</sup>, M.R.V. Lanza<sup>a</sup>, P. Cañizares<sup>b</sup>, M.A. Rodrigo<sup>b,\*</sup>

<sup>a</sup> Instituto de Química de São Carlos, Universidade de São Paulo, P.O. Box 780, CEP 13560-970 São Carlos, SP, Brazil

<sup>b</sup> Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

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## ABSTRACT

Boron-doped diamond films on silicon substrates (p-Si BDD) with different  $sp^3/sp^2$  carbon ratios are systematically varied in electrodes used to oxidize 2,4-dichlorophenoxyacetic acid (2,4-D) in synthetic wastewater containing chlorides. 2,4-D is completely mineralized during the electrolysis. A higher  $sp^3/sp^2$  ratio in the anode results in a more rapid and efficient oxidative removal of 2,4-D. Chlorinated compounds such as 4-chlororesorcinol, 2-chlorophenol, and 2,4-dichlorophenol form as intermediates during the oxidative treatment. Although these compounds are completely depleted during the electrolysis, their maximum observed concentrations decrease as the  $sp^3$  content increases in the anode. On the contrary, higher maximum concentrations are observed for non-chlorinated intermediates, especially hydroquinone, and there is a greater formation of chlorates and perchlorates in chloride-containing solutions as the  $sp^3$  content increases in the anode.

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## 1. Introduction

Electro-oxidation with diamond anodes carried out at the laboratory or bench scale has been demonstrated to be a very effective treatment for the removal of various types of organic pollutants typically resilient to removal by other technologies, such as dyes, pharmaceuticals, phthalates and pesticides [1]. In this context, compared with carbonaceous, platinum and metal oxide electrodes, conductive diamond-coated electrodes exhibit exemplary properties such as high overpotential for water electrolysis, excellent chemical and electrochemical stability, satisfactory conductivity and the ability to generate various powerful oxidants depending on the wastewater composition and the operational conditions [2,3]. These excellent properties are attributed to the production and weak adsorption of hydroxyl radicals  $HO^\bullet$  [4], which results in a low electrochemical activity of the oxygen evolution reaction and, consequently, in a high chemical reactivity for the oxidation of organics [5]. However, the intensive study of the applications of diamonds in environmental remediation [6–8], few studies have assessed the properties of the diamond coating in terms of the remediation process performance. Thus, many important features are known to influence the efficiency of

diamond electrode performance, such as the doping type and level, morphological features, non-diamond impurity content, crystallographic orientation, and surface group functionalities (H, O, F, etc.), and one of the most significant is certainly the  $sp^3/sp^2$  ratio.

Diamond is an extremely hard crystalline form of carbon, with each carbon atom tetrahedrally bonded to four other  $sp^3$  hybridized carbons. By doping the deposited diamond film grown by chemical vapor deposition (CVD) with impurities such as boron, nitrogen, or fluoride, the wide gap of diamond (5.5 eV) can be reduced, producing a semiconductor material. According to the literature, the most interesting doping agent is boron. In the synthetic boron-doped diamond (BDD), boron acts as an electron acceptor due to an electron deficiency in its external shell imparting p-type semiconducting properties. The effect of boron doping has been studied by many authors. An interesting contribution from Bogdanowicz [9] involved the impact of the [B]/[C] ratio (boron/carbon ratio) in a Si/BDD electrode on the efficiency of the electrochemical oxidation of the reactive dye Rubin F-2B 9. Electrodes with [B]/[C] = 10,000 attained a higher electroactivity than those with [B]/[C] = 2000, and the former electrodes were much more efficient in the degradation of the dye. These differences were explained in terms of the surface microstructure of the diamond films and the relatively low surface resistivity. These results also suggest that a higher boron concentration might contribute to the enhancement of electric forces responsible for the electro-generation of oxidants. Similar

\* Corresponding author. Fax: +34 926295256.

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

conclusions were drawn from the study of the dye reactive orange (RO) 16 [10]. This work demonstrated that the diamond electrodes doped with the greatest amount of boron exhibited the highest performance for similar contents of non-diamond carbon. The presence of graphite in the sample with a higher boron percentage may be hidden beneath by the other nearby band features. However, a small volume of randomly distributed non-diamond carbon atoms may form different conduction routes that contribute to the performance of this electrode.

These results illustrate the significance of not only the boron content but also the  $sp^2$  carbon content in electrolytic performance. It is important to consider that diamond coatings are synthesized under conditions in which graphite synthesis is competitive, and non-diamond components may also be incorporated into their structure. Studies have demonstrated that these aggregates can be associated with amorphous regions that contain  $sp^2$  graphite domains. Cominellis's group intensively studied the electron transfer kinetics of composite diamond ( $sp^3$ )–graphite ( $sp^2$ ) electrodes in various works [11–13] [14–17]. Their results demonstrated that the graphite particles deposited on the electrode surface promote this outer-sphere reaction by acting as charge transfer mediators between the redox couple and the electrode surface. Consequently, the decrease in electrode activity after anodic polarization may be explained by the corrosion of the graphitic ( $sp^2$ ) active species initially present on the electrode surface. After these pioneering studies, Enache [18] showed that the diamond electrode background current and the working potential window are influenced by the electroactivity of these non-diamond carbon impurities, and Migliorini [19] demonstrated the influence of methane addition to the gas phase for different doping levels on BDD films grown on titanium substrates. The  $sp^2$  phase increased with  $CH_4$  addition for all films studied. For highly doped films, this diamond grain decrease favored  $sp^2$  carbon incorporation at the diamond grain boundaries. Regarding the same topic, Guinea et al. also studied the effect of the  $sp^3/sp^2$  ratio [20] in the degradation of enrofloxacin, demonstrating that this ratio has a crucial effect on the efficiency of the degradation; tailoring new electrodes for special applications could be a topic of a great interest in the development of environmental electrochemistry. Similar results were obtained by de Araujo [21] in a recent study in which the influence of the  $sp^3/sp^2$  ratio on the degradation of rhodamine B (RhB) was assessed. Electrolysis performed by diamonds with a lower content of  $sp^3$  carbon led to less abrupt oxidation curves, favoring the electrochemical conversion of RhB. In the presence of higher contents of diamond carbon, total organic carbon (TOC) decayed more rapidly, and a sort of electrochemical combustion may be justified.

Previous works have demonstrated that electrode characteristics and the relation between the conductivity of the BDD film and the level of impurities present is important to attain higher electrode efficiencies in electrochemical applications. These are not the only factors affecting the performance of electrolysis with diamonds; the diamond's properties also influence the production of oxidants [22,23], in which the thickness of the coating was found to play a very important role.

However, further is necessary to clarify this point, and the present work assessed the performance of Si/BDD with different  $sp^3$ - $sp^2$  ratios in the electrolytic removal of a model pesticide from water. Synthetic wastewater containing solutions of the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) and sodium chloride were used. The influence of the  $sp^3/sp^2$  ratio on pesticide removal and chloride oxidation was evaluated during the electrolysis. Pesticide remediation is a major environmental issue [24,25,26]. Typically, these substances exhibit bio-recalcitrant properties and high toxicity and persist in the environment. In addition, they can be easily transported by several mechanisms and may therefore

contaminate groundwater by leaching through the soil and surface water through runoff. The herbicide 2,4-D is the most commonly used acidic phenoxy herbicide in agriculture, forestry, and lawn care and is used to a lesser extent in parks, golf courses, and gardening. 2,4-D is highly water-soluble (i.e., 900 mg/L at 25 °C) and can be detected in surface water and ground water even long after its use [27]. Conventional methods for wastewater treatment such as coagulation or biological treatment are unsatisfactory or ineffective in the removal of 2,4-D from wastewater. For this reason, many technologies are currently being studied and developed to efficiently destroy this pollutant, and electrolysis with BDD is among the most promising.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals, including sodium sulfate and sodium chloride from Fluka (Spain) and 2,4-D, hydroquinone, 1,4-benzoquinone, 4-chlororesorcinol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol from Sigma-Aldrich (Spain) were of analytical grade and used as received. HPLC-grade acetonitrile (Sigma-Aldrich, Spain) was used as the mobile phase. Double-deionized water (Millipore Milli-Q system, resistivity = 18.2 M $\Omega$  cm at 25 °C) was used to prepare all solutions.

### 2.2. Experimental setup

All electrolytic tests were carried out in a single-compartment electrochemical flow cell. Boron-doped diamond electrodes supplied and characterized by Adamant Technologies (Switzerland) synthesized the monocrystalline p-type Si substrate (thickness 2 mm, resistivity 100 m $\Omega$  cm) with a diamond coating of 2–3  $\mu$ m by the hot filament chemical vapor deposition technique (HF CVD). The diamond quality and the boron level were analyzed by micro-Raman scattering spectroscopy [28], and the certificate of analysis was signed by the testing engineer (reference number: 24,026); the electrodes used as the anode all had a boron concentration of 500 ppm and had the following distinct  $sp^3/sp^2$  ratios: BDD<sub>1</sub> = 165, BDD<sub>2</sub> = 176, BDD<sub>3</sub> = 206, BDD<sub>4</sub> = 225, BDD<sub>5</sub> = 262 and BDD<sub>6</sub> = 323. A BDD electrode with an  $sp^3$ - $sp^2$  ratio of 176 was used as the cathode. Both electrodes were circular (100 mm diameter), covering a geometric area of 70 cm<sup>2</sup>. The BDD electrode was polarized for 10 min in a 1 M Na<sub>2</sub>SO<sub>4</sub> solution at 15 mA cm<sup>-2</sup> prior to the electrolysis assays.

Galvanostatic electrolysis was carried using 0.6 dm<sup>3</sup> of a solution containing 100 mg dm<sup>-3</sup> 2,4-D at natural pH (3.5). Aqueous sodium chloride (0.05 M) was used as the supporting electrolyte. The solution was recirculated between the cell and an auxiliary tank at a constant flow rate (26.4 dm<sup>3</sup> h<sup>-1</sup>) to favor mixing conditions, gas stripping and temperature regulation. A heat exchanger coupled with a controlled thermostatic bath was used to maintain the temperature at 25 °C.

### 2.3. Analysis procedures and methods

All samples taken from the electrolyzed solutions were filtered through Whatman<sup>®</sup> nylon membrane filters (0.45  $\mu$ m) before analysis. Measurements of pH were carried out with an InoLab WTW pH meter. The decay of the herbicide and the evolution of its aromatic products were followed by reversed-phase chromatography and measurements of TOC and chemical oxygen demand (COD). The chromatography system was an Agilent 1100 series coupled a UV detector. A Phenomenex Gemini 5  $\mu$ m C18 analytical column was used. The mobile phase consisted of 60 % acetonitrile/40 % water with 2 % acetic acid (flow rate of 0.4 cm<sup>3</sup> min<sup>-1</sup>). The UV

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