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## **Diamondized carbon nanoarchitectures as electrocatalytic material for sulfate-based oxidizing species electrogeneration**

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26 **Abstract**

27 The introduction of nanotechnology seems to be an imperative factor to intensify the synergic  
28 effects of electrocatalytic materials to produce strong oxidant species or to increase the active  
29 sites on their surfaces as well as to enhance the conversion yield in a fuel cell, high-added  
30 value products, electrolytic treatment for environmental protection or the detection limit in  
31 electroanalysis. Recently, a new type of 3D-diamond electrodes was developed with boron-  
32 doped carbon nanowalls (B:CNW), which was manufactured using the microwave plasma-  
33 assisted chemical vapor deposition (CVD) process, improving the charge transfer and  
34 enhancing the electrochemical performance. The applicability of a BDD/boron-doped carbon  
35 nanowalls (BDD/B:CNW) anodes to degrade organic pollutants has been already  
36 investigated; however, no attempts at the electrosynthesis of oxidizing species using these  
37 diamond-carbon nanostructures have been reported yet. Therefore, the electrosynthesis of  
38 sulfate-based oxidizing species was studied here to answer relevant questions from both  
39 fundamental and practical point-of-view. The results demonstrated that persulfate was  
40 efficiently produced at the BDD plate, while that the ion-radical sulfate could be the most  
41 important oxidant at BDD/B:CNW anode when compared to other electrocatalytic materials,  
42 including BDD surfaces. Persulfate concentrations ranged from 3 to 6  $\mu\text{M}$ , depending on the  
43 applied current density (2.5, 5.0, and 15  $\text{mA cm}^{-2}$ ), at diamond electrodes. A dye-model  
44 pollutant - methyl orange (MO) was degraded below the limit of detection within 45 min  
45 using BDD/B:CNW when *in-situ* sulfate-based oxidizing species were electrogenerated.  
46 These kinds of 3D-diamond-carbon nanostructures are thus promising as novel  
47 electrocatalyst for various catalytic applications in the environmental and energy fields.

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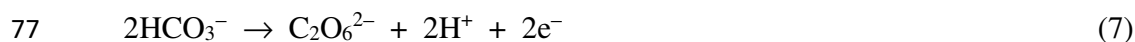
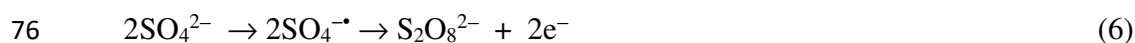
49 *Keywords:* boron-doped diamond electrode, sulfate-based oxidizing species, diamond-  
50 carbon nanoarchitectures, electrocatalyst, electrogeneration.

## 51 1. Introduction

52 The scientific community has shown a preference to apply EO as an environment-friendly  
53 electrochemical process because of its uncomplicatedness and acceptance among the  
54 electrochemical advanced oxidation processes (EAOPs), in terms of electrolytic technology,  
55 amenability, environmental compatibility, automation, no reagents use, renewable energies-  
56 driven and in-situ production of higher concentration of oxidants [1]. In the last decades, EO  
57 has competently demonstrated its effectiveness to mineralize different organic compounds in  
58 a great variety of water matrices or wastewaters [2]. Nevertheless, the extension of  
59 mineralization/degradation of these pollutants and their concentration as well as the type of  
60 the electrogenerated oxidants strongly depends on the operating parameters and the nature of  
61 the anode electrocatalytic material [3,4].

62 Various electrodes have been used in EO, like Ir-, Pt-, Ru-, Ti-, Pb- and Sn- oxide-based  
63 anodes as well as synthetic diamond films [5,6]. However, boron-doped diamond (BDD)  
64 anodes are considered the most effective electrocatalytic materials for  
65 degrading/mineralizing refractory/priority pollutants and waterborne agents [1,2,7–9]. It is  
66 due to their effective *in-situ* production of oxidizing agents, at higher concentrations, mainly  
67 reactive oxygen species (ROS) (Eq. (1)-(5)) [9]. Also, peroxodisulfate ( $S_2O_8^{2-}$ ),  
68 peroxodicarbonate ( $C_2O_6^{2-}$ ) and peroxodiphosphate ( $P_2O_8^{4-}$ ) can be electrochemically  
69 formed with ROS from the oxidation of sulfate or bisulfate by Eq. (6), bicarbonate by Eq. (7)  
70 and phosphate by Eq. (8) at the BDD surface [10,11].





79 As already scientifically stated, the effective electrosynthesis of oxidizing species requires  
80 an electrode with a large surface area, high electrocatalytic activities, long-term stability, as  
81 well as a low cost of materials [5,12]. Thus, the introduction of nanoarchitectures seems to  
82 be an essential factor to intensify the synergic effects of electrocatalytic materials to produce  
83 strong oxidant species or to increase the active sites on their surfaces [13]. Novel  
84 nanostructured materials can exhibit better electrochemical properties than their bulk  
85 counterparts with a specific pore dimension distribution and well-defined structure-  
86 morphology, maximizing the exposed-surface area and minimizing the mass transport  
87 phenomena [14–16]. Thus, the advances in the preparation of highly sophisticated  
88 electrocatalytic nanomaterials may lead to further improvements in the mineralization of  
89 organic pollutants as well as the electrosynthesis of oxidants, making them suitable for smart  
90 water solutions [17]. These technologies will play a key role in achieving the Sustainable  
91 Development Goal 6 (SDG6) since these represent a substantial opportunity if their  
92 implementation is carried out to guarantee sustainability and increase competence in water  
93 management (to treat and distribute water for human use) [18].

94 Recently, a versatile electrode was discovered, called the “3D-nanostructured BDD/B:CNW”  
95 anode. This 3D-diamondized-carbon nanostructure possesses extraordinary electrochemical  
96 properties (e.g., peculiar morphology, specific surface area and the larger extends of exposed



97 edges with a greater number of functional groups and chemisorbed heteroatoms, in particular,  
98 oxygen), allowing a higher reactivity of the carbonaceous nanostructure for environmental,  
99 fuel and sensors applications, compared to 2D-BDD electrode [19–21]. However, no  
100 information concerning the effectiveness of this 3D-nanostructured BDD/B:CNW anode to  
101 electrogeneration oxidants has been reported yet. Thus, for the first time, the electrosynthesis  
102 of sulfate-based oxidants species has been studied by using a 3D-nanoarchitected  
103 BDD/B:CNW anode to answer relevant questions from both fundamental and practical point-  
104 of-view. An organic model compound was also chosen to prove the oxidative efficiency of  
105 *in-situ*  $S_2O_8^{2-}$  electrogeneration when compared with other electrode materials. The results  
106 are discussed considering the existing literature on nanostructured electrodes for  
107 electrocatalytic advanced oxidation processes.

108

## 109 **2. Materials and Methods**

### 110 **2.1. Materials**

111 All reagents were of analytical grade and used without further purification. The water was  
112 obtained from purified water (Milli-Q system, with resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$  at 25 °C). Methyl  
113 orange (MO) purity was 95% and it was used as received.

114

### 115 **2.2. Synthesis and characterization of BDD/B:CNW**

116 BDD and BDD/BCNW were synthesized using the MWPECVD system (SEKI Technotron  
117 AX5400S, Japan). Thin films were grown on niobium substrates for a total of 5 h, resulting  
118 in 3  $\mu\text{m}$  of thickness. The detailed parameters of the thin film synthesis can be found  
119 elsewhere, for BDD [ref1] and for the BDD:BCNW in Pierpaoli et al [ref2, ref3] ~~BCNW in~~  
120 ~~Siuздak et al. [22], Dettlaff et al. [23], and Sobaszek et al. [24]~~ . The surface characteristics

121 of the BDD/B:CNW was carried out using a Hitachi model TM 3000 top microscope with a  
122 high sensitivity semiconductor backscattered electron detector to obtain scanning electron  
123 microscopy (SEM) images, using a significant magnification and operating at 15 kV voltage  
124 acceleration with a tungsten filament. The SEM images were taken under a vacuum at  
125 controlled temperatures and the energy dispersive X-ray (EDS) spectrum was obtained to  
126 analyze the concentrations of the elements in the diamond-carbon nanostructures. Raman  
127 spectra were recorded in the 50–3200  $\text{cm}^{-1}$  range, upon excitation by a 532 nm laser; the  
128 spectral resolution was equal to 2.9  $\text{cm}^{-1}$ , in the range of 50–2000  $\text{cm}^{-1}$  and 2.4  $\text{cm}^{-1}$  in the  
129 range of 2000–3200  $\text{cm}^{-1}$  with an integration time of 5 s (20 averages), with a diffraction  
130 grating of 300 lines/ $\text{mm}^2$ .

### 131 **2.3. Electrochemical measurements**

132 Experiments were carried out in a conventional three-electrode system in Pyrex material  
133 with a capacity of 10 mL, and measurements were performed between 0.0 and +1.8 V at 10  
134  $\text{mV s}^{-1}$  for quasi-steady polarization curves in 0.05 M of  $\text{Na}_2\text{SO}_4$ . BDD and BDD/B:CNW  
135 anodes have significant areas in  $\text{cm}^2$ , however, an exposed geometric area of ca. 0.075  $\text{cm}^2$   
136 was used as the working electrode for electrochemical measurements, while this area was  
137 increased for bulk electrolysis (see next subsection). A platinum wire and an Ag/AgCl (3 M)  
138 were employed as the auxiliary and reference electrodes, respectively. The electroactive  
139 surface area ( $A_{\text{real}}$ ) and the differential capacitance ( $C_{\text{DL}}$ ) were experimentally estimated [25–  
140 27], according to Eq. 1. To do that, a potential range was selected, for BDD and BDD/B:CNW  
141 electrodes, where a non-Faradaic current response is registered. This range was  $\approx 0.2$  V  
142 potential window centered on the open-circuit potential of the system. Then, cyclic  
143 voltammetry (CV) measurements were conducted in static solution by sweeping the potential



144 across the non-Faradaic region and back at 9 different scan rates (0.02, 0.04, 0.06, 0.08, 0.10,  
145 0.12, 0.14, 0.16, 0.18 and 0.20 V s<sup>-1</sup>) at 25±1°C in 0.05 M of Na<sub>2</sub>SO<sub>4</sub>. For each measurement,  
146 five voltammetric profiles were recorded, and the last curve was always selected to be used for  
147 plotting the graphics in this work.

$$148 \quad A_{\text{real}} = \frac{C_{\text{DL}}}{C^*} = \frac{\mu\text{F}}{\frac{\mu\text{F}}{\text{real cm}^2}} = \text{cm}^2 \quad (1)$$

149 In Eq. 1, C<sub>DL</sub> is the differential capacitance of the electrode-electrolyte interface and C\* is  
150 approximately 60 μF (real cm<sup>2</sup>)<sup>-1</sup> which is a reference value for porous materials, regardless of  
151 its composition [25,27]. Experiments were performed with an Autolab  
152 potentiostat/galvanostat model PGSTAT302N.

153

#### 154 **2.4. Spectrophotometric analysis**

155 For UV-vis spectrophotometric measurements to determine the production of persulfate, a  
156 Shimadzu spectrophotometer model 1800 was employed by using *in-situ* chemical oxidation  
157 (ISCO) method [28,29], operating from 190 to 800 nm. A single quartz cuvette was used  
158 with an optical path of 1 cm. It is important to remark that persulfate generation can be  
159 followed by ISCO method without H<sub>2</sub>O<sub>2</sub> interference because the analysis of absorption  
160 spectra of a yellow color solution resulting from the reaction of persulfate and iodide in the  
161 presence of sodium bicarbonate reveals a clear absorbance spectrum at 352 nm.

162

#### 163 **2.5. Electrochemical determination of methyl orange concentration**

164 Electroanalytical measurements were carried out in a conventional three-electrode system in  
165 Pyrex material with a capacity of 25 mL for determining MO concentrations by differential  
166 pulse voltammetry (DPV) analysis. BDD anode (silicon substrate, 500 ppm of boron doping,



167 2-3  $\mu\text{m}$  of thickness), with an exposed geometric area of  $0.28\text{ cm}^2$ , was used as the working  
168 electrode, while a platinum wire and Ag/AgCl (KCl 3 M) were employed as the auxiliary  
169 and reference electrodes, respectively. DPV experiments were performed with an Autolab  
170 PGSTAT 320N model to establish an analytical curve by measuring different concentrations  
171 of MO in 0.05 M  $\text{Na}_2\text{SO}_4$ . Other details of the procedure are as follows: equilibration time,  
172 5 s; modulation time, 0.05 s; interval time, 0.5 s; initial potential, 0 V; end potential, +1.8 V;  
173 step potential, 25 mV; and modulation amplitude, 100 mV. For determining MO  
174 concentration at each predetermined time during EO tests, the samples were spiked with a  
175 known quantity of a standard solution, and the standard addition method was implemented.

176

## 177 **2.6. Bulk experiments**

178 Experiments were carried out using a bulk electrochemical cell under stirring agitation which  
179 consisted of several electrodes (anodes such as BDD plate, BDD/B:CNW, TiPt, Pb/PbO<sub>2</sub>,  
180 Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> and Ti as cathode, respectively) of 1.5 cm of diameter (geometrical  
181 area  $\approx 7.07\text{ cm}^2$ ). Electrolysis of 50 mL of a synthetic solution containing 0.05 M  $\text{Na}_2\text{SO}_4$  as  
182 the supporting electrolyte was performed by applying 2.5, 10, and 15  $\text{mA cm}^{-2}$  for 150 min  
183 to prepare sulfate-based oxidizing species. Sulfate concentration was chosen based on the  
184 existing literature to produce a significant concentration of persulfate [29,30]. During all  
185 experiments, samples of the sulfate-based oxidizing solutions were collected at the end of the  
186 electrolysis, and subsequently, these were analyzed by the ISCO-spectrophotometric method,  
187 determining the final sulfate-based oxidants concentration produced. For the EO of an  
188 organic target compound, 25 mL of 0.05 M of  $\text{Na}_2\text{SO}_4$  containing  $10\text{ mg L}^{-1}$  of MO were  
189 electrochemically treated by mixing with magnetic stirring for 40 min and aliquots were

190 withdrawn at predetermined times to determine chemical oxygen demand (COD) and the  
191 concentration of the target pollutant by the electroanalytic procedure. COD levels were  
192 measured by using pre-dosed reagents (HANNA® vials) in 2 mL samples. Samples for COD  
193 determination were digested in a thermal reactor (HANNA instrument) at 150°C for 2 h.  
194 Subsequently, the samples initial and final, for all oxidation tests, were analyzed on a  
195 spectrophotometer (Hanna HI 83099), at 25°C.

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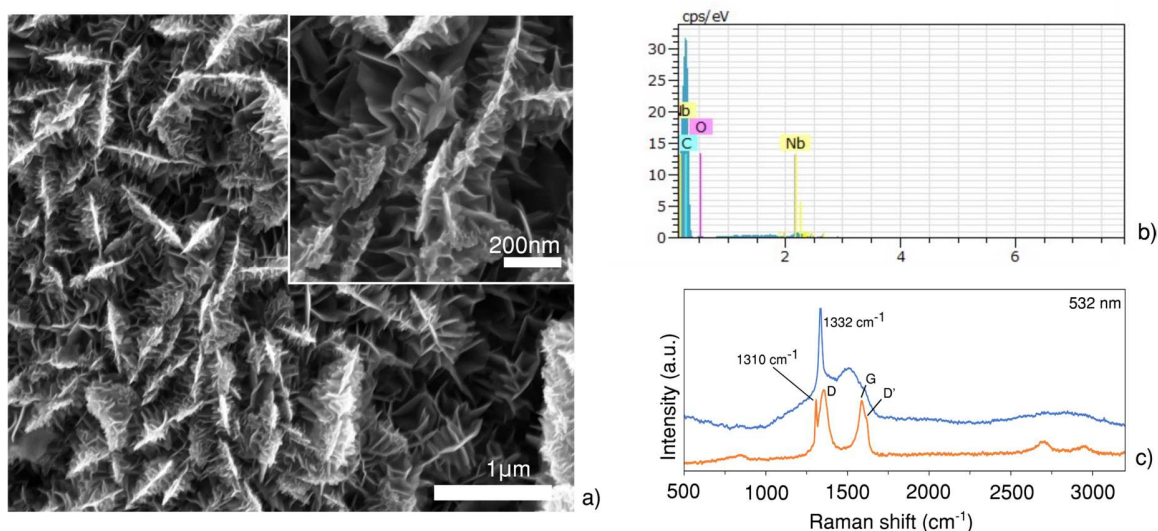
### 197 **3. Results and Discussion**

#### 198 **3.1. Characterization of diamond electrode**

199 The BDD/B:CNW electrode morphology presents microscale valleys with a diameter of a  
200 few micrometers, as observed in the SEM images (Fig. 1a). As previously reported [13,14,31]  
201 and confirmed by SEM images; on the one hand, carbon grows vertically in form of multi-  
202 layer graphene walls covered by diamond clusters. Microcavities having an opening in the  
203 range between tens and hundreds of nanometres are formed between the nanowall boundaries  
204 (Fig. 1a). On the other hand, “nano-flaps” also grow perpendicularly as secondary  
205 protuberances to the surface of the nanowalls due to the process of synthesis [13,14,31].  
206 Meanwhile, EDS spectrum evidence that the concentrations of the elements in the diamond-  
207 carbon nanostructures are preferentially carbon and oxygen, confirming the BDD/B:CNW  
208 composition (Fig. 1b).

209 In this context, the CVD process developed by Bogdanowicz’s group [14] is an innovative  
210 approach to obtaining a carbon nanostructure with concave and convex curvatures in a simple  
211 way [13,14,31]. Thus, it was possible to understand that the electrode surface and their  
212 composition, as well as the density of electronic states of electrode materials [XXX], could  
213 influence during the production of oxidant species. From the Raman spectra (Fig. 1c), the

214 intense peak at  $1332\text{ cm}^{-1}$  sharply observed for the BDD sample is assigned to  $\text{sp}^3$ -  
 215 hybridized carbon, which decreases in intensity and downshift to  $1310\text{ cm}^{-1}$  for the  
 216 BDD:BCNW sample, which is typical for typical for heavily boron-doped diamond [ref],  
 217 since the diborane concentration inside the reactor increases as well. Moreover, it is possible  
 218 to observe the G-band at around  $1580\text{ cm}^{-1}$ , arising from the presence of graphitic material  
 219 (i.e.,  $\text{sp}^2\text{-C}$ ), and the D-band which indicates defects in graphitic structures. Finally, D' is  
 220 another second-order Raman band, appearing as a shoulder peak of the G band, originating  
 221 from a second-order Raman scattering at the K point, involving one iTO phonon and one  
 222 defect state [ref].



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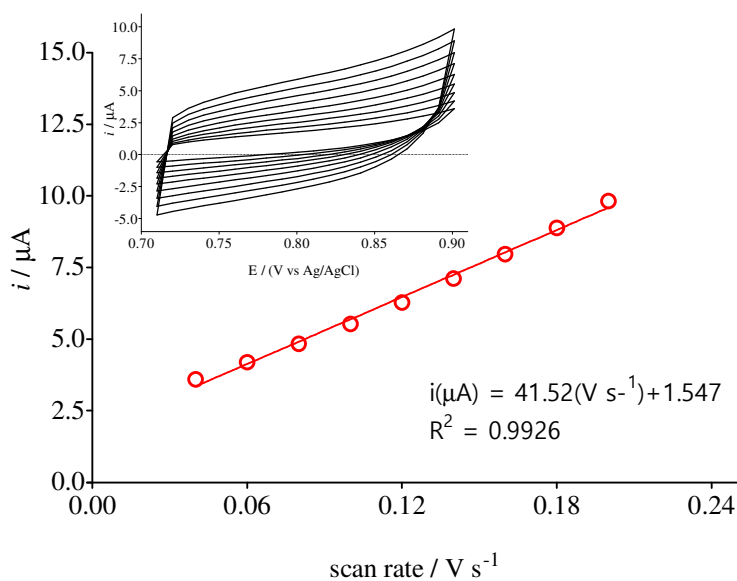
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225 **Fig. 1.** (a) SEM images of the BDD/BCNW grown on Nb, (b) EDS spectrum, confirming the  
 226 composition of BDD/BCNW electrode: C (94.42 wt.%, 97.40 at.%), O (2.90 wt.%, 2.25 at.%)  
 227 and Nb (2.68 wt.%, 0.36 at.%). And (c) Raman spectra for the BDD and BDD:BCNW  
 228 samples.

229

230 **3.2. Electrochemical measurements**

231 CV curves in a non-faradaic potential range were recorded at different scan rates (0.04, 0.06,  
 232 0.08, 0.10, 0.12, 0.14, 0.16, 0.18 and 0.20  $\text{V s}^{-1}$ ) to estimate the electro-active surface of BDD  
 233 and BDD/B:CNW electrodes. By plotting the current, which was measured in the middle of  
 234 the double-layer region and recorded at different scan rates, versus the scan rate (e.g.:  
 235 BDD/B:CNW, Fig. 2); a straight line was obtained, which allowed determining the double  
 236 layer capacitance values for these electrocatalytic materials (Insets in Fig. 2). Then, by using  
 237 the Eq. (1), the geometric area of the electrodes ( $\approx 0.075 \text{ cm}^2$ ) and the  $C_{\text{DL}}$  values obtained  
 238 ( $5.40 \mu\text{F}$  and  $41.52 \mu\text{F}$  for BDD and BDD/B:CNW, respectively); the real surface areas were  
 239 estimated, obtaining  $0.216 \text{ cm}^2$  and  $0.692 \text{ cm}^2$  for BDD and BDD/B:CNW, respectively. It  
 240 is important to remark that, based on existing literature data [26], reference values ( $C^*$ ) for  
 241 compact and porous materials should be considered to estimate the electroactive surface area,  
 242 regardless of its composition. Then,  $60 \mu\text{F (real cm}^2)^{-1}$  was the reference value for  
 243 BDD/B:CNW, while,  $25 \mu\text{F (real cm}^2)^{-1}$  for BDD plate due to the most homogeneous surface  
 244 [26,27,32].



245

246 **Fig. 2.** Cyclic voltammetric (CV) analysis (from 0.04 to 0.20 V s<sup>-1</sup>) to estimate the  
247 capacitance for BDD/B:CNW electrode in 0.05 M of Na<sub>2</sub>SO<sub>4</sub> by plotting the current values  
248 in the double-layer regions as a function of scan rate. Inset: double-layer capacitance  
249 measurements by using CV technique at different scan rates.

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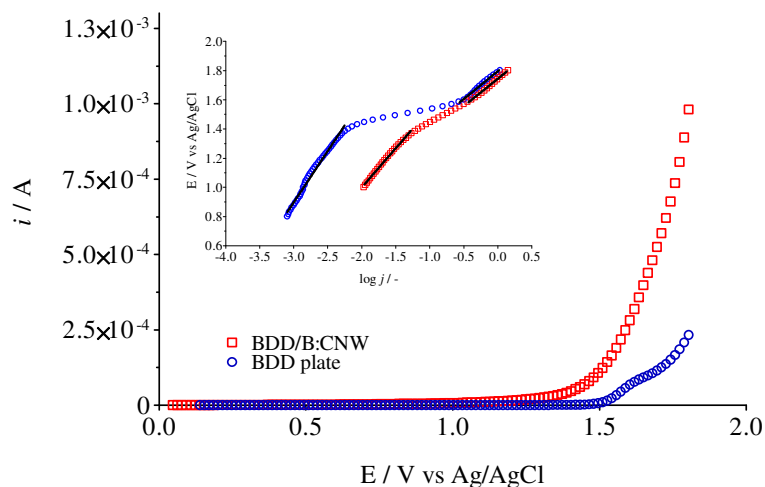
251 Although there are several methods to experimentally determine the real surface area such as  
252 hydrogen adsorption, double layer capacitance, surface oxide reduction, underpotential  
253 deposition of metals, and adsorbed carbon monoxide stripping [27]; for the case of BDD  
254 electrodes, some approaches could be efficiently applied. However, the double-layer  
255 capacitance method allows to obtain accurate surface measurements, avoiding significant  
256 surface changes due to the oxygen/hydrogen evolution, formation/reduction of oxides, and  
257 modification of carbon materials [27,32,33]. The double-layer capacitance also allows  
258 measuring the total surface area accessible to the solution, and it is not destructive [27]. In  
259 fact, in this case, the real electrode areas are superior to the geometrical value; it could be  
260 due to the character of diamond surfaces, allowing for proper contact of the solution with all  
261 active sites and consequently, a significant increase in the real area was achieved respect to  
262 0.075 cm<sup>2</sup>.

263 For BDD/B:CNW electrode, an increase in the porous properties of the material was achieved  
264 due to the 3D nanostructures (see SEM images, Fig. 1) [20,21,24]; for this reason, an increase  
265 in the solution contact (solution diffusion between/into the porous) could be expected [14].  
266 Meanwhile, this behavior is reduced in the BDD plate due to the homogeneous surface. In  
267 this context, the roughness factor ( $RF = A_{\text{real}}/A_{\text{geometric}}$ ) was also determined for BDD and

268 BDD/B:CNW electrodes, considering the geometric surface and the estimated electroactive  
269 area for each one of the electrodes, achieving values of about 2.88 and 9.22, respectively.  
270 From these results, it is possible to deduce that, the new type of 3D-diamond electrodes with  
271 boron-doped carbon nanowalls (B:CNW) increased its roughness by about 3.2-folds in  
272 comparison to the BDD plate surface [14,15,21,34,35]. This result evidenced that, the  
273 roughness controls the contact of the active sites with the solution and thus, increasing its  
274 active area [14,21].

275 On the other hand, it is important to characterize the potential window and anodic  
276 oxygen evolution reaction by electrochemical measurements at both carbon materials. Fig. 3  
277 shows the polarization curves registered at BDD and BDD/B:CNW anodes in a sulfate  
278 solution. A slight variation in the potential window is achieved, evidencing an important  
279 change in the potential of the oxygen evolution reaction (OER). This behavior is mainly  
280 associated with the different carbon constituents on the BDD surfaces as well as the  
281 electrochemical decomposition of the supporting electrolyte [30,36,37]. Linear polarization  
282 curves for BDD/B:CNW electrode showed that the potential for the OER was shifted to a less  
283 positive potential ( $\approx 1.43$  V vs Ag/AgCl). Based on previous works [36,38], it was  
284 demonstrated that graphite electrode presents lower oxygen overpotential than BDD  
285 electrodes, similar to the behavior achieved at BDD/B:CNW. Conversely, BDD plate showed  
286 to be a poor electrocatalyst for OER, shifting this reaction to more positive potentials (Fig.  
287 3).





288

289 **Fig. 3.** Polarization curves registered at BDD and BDD/B:CNW electrodes in 0.05 M of  
 290  $\text{Na}_2\text{SO}_4$ . Inset: data in terms of Tafel plots at lower and higher overpotential regions from the  
 291 potential of hydroxyl radicals' formation.

292

293 Meanwhile, additional effects could be observed when the analysis of the Tafel plots  
 294 is executed.  $E/\log j$  plots at both BDD electrodes are shown in the inset of Fig. 3, considering  
 295 the real surface area for each one of them. As can be observed, the Tafel plots change their  
 296 slope according to the lower overpotential region ( $<1.6$  V) or high overpotential region  
 297 ( $>1.62$  V). At BDD/B:CNW, the OER seems to be the main process than that registered at  
 298 BDD plate. However, no unique slope can be attributed to the Tafel plots at both BDD  
 299 electrodes due to the complex set of the electrochemical reactions taking place involving  
 300 most probably the OER and persulfate production. Tafel slopes about  $0.6117$  V decade $^{-1}$  and  
 301  $0.5363$  V decade $^{-1}$  for BDD plate and BDD/B:CNW electrode were estimated, respectively,  
 302 at lower overpotential region. Meanwhile,  $0.3810$  V decade $^{-1}$  and  $0.3740$  V decade $^{-1}$  in the



303 high overpotential region were obtained for BDD plate and BDD/B:CNW electrodes,  
 304 respectively. Two distinct linearity regions can be attributed to the electrochemical reactions  
 305 on the Nernst layer at BDD surface, associated with the sulfate ions in solution and water  
 306 discharge, which are transformed to persulfate and hydroxyl radicals ( $\cdot\text{OH}$ ) as well as oxygen,  
 307 respectively [39,40]. From Tafel plots data as well as the current and potentials (inset of Fig.  
 308 3), it is possible to infer that an important electrochemical reaction at the lower overpotential  
 309 region is attained at both diamond electrodes, which could be associated with the specific  
 310 interaction of sulfate ions with each one of the carbon surfaces [37,40,41].

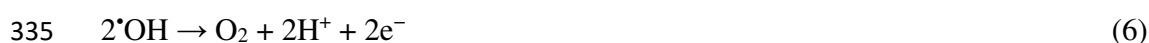
311 Based on the existing literature [3,4,8], in the case of diamond electrodes, the  
 312 mechanisms followed depend strongly on (i) extension of the oxidation of  $\text{SO}_4^{2-}$  ions at the  
 313 diamond surface, via direct electron transfer, to produce persulfate (Eq. 2), (ii) the production  
 314 of  $\cdot\text{OH}$  at anode surface in the reaction cage (Eq. 1), (iii) the interaction of  $\cdot\text{OH}$  with  $\text{SO}_4^{2-}$   
 315 ions, in the Nernst layer, to favor the production of  $\text{SO}_4^{\cdot-}$  (principal intermediate) and  
 316 subsequently, persulfate (Eq. 3), as well as, in some cases, the association between the  $\text{sp}^2$ -  
 317 impurities on its surface and the adsorption of  $\text{SO}_4^{2-}$  ions on these active sites to also form  
 318  $\text{SO}_4^{\cdot-}$  and then, producing persulfate (Eqs. 4 and 5),



323 In the case of the BDD plate, the electrochemical reactions, which occurs at the lower  
 324 overpotential region ( $<1.6$  V), a more strong interaction is attained than that at BDD/B:CNW.



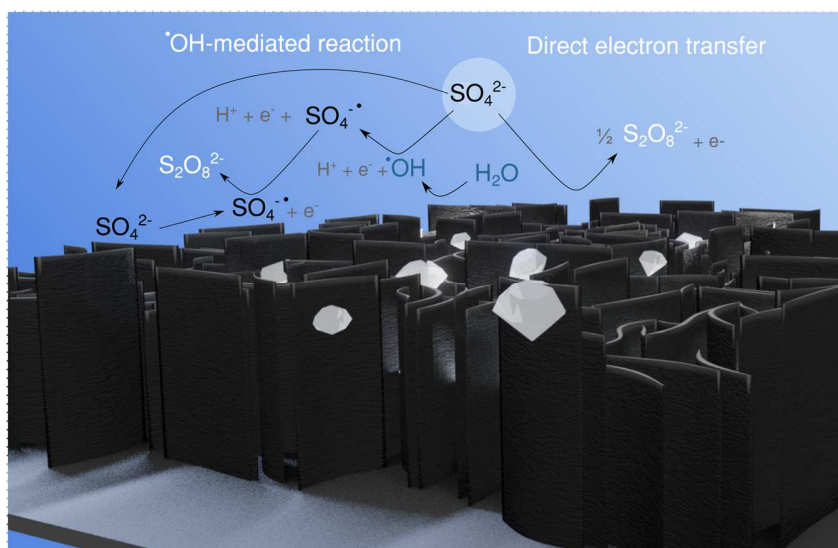
325 The Tafel slope is higher than the other one ( $0.6117 \text{ V decade}^{-1}$  and  $0.5363 \text{ V decade}^{-1}$ , for  
326 plate BDD and BDD/B:CNW electrode, respectively). These behaviors appear to be  
327 associated to the production of  $\text{S}_2\text{O}_8^{2-}$  or  $\text{SO}_4^{\bullet-}$  at BDD surface [41], evidencing that, a direct  
328 electron transfer is attained at BDD plate, in the former. While a fast-adsorptive interaction  
329 of  $\text{SO}_4^{2-}$  ions on B:CNW-active sites ( $\text{sp}^2$ -configuration) is achieved to form  $\text{SO}_4^{\bullet-}$  at  
330 BDD/B:CNW electrode (Eq. 8) [36]. Afterward, at both electrodes, similar surface-layer-  
331 based approaches are accomplished at a higher overpotential region ( $>1.6 \text{ V}$ ), which are  
332 related to the production of  $\bullet\text{OH}$  (Eq. 1) and  $\text{O}_2$  (Eq. 6) as well as the formation of sulfate-  
333 based oxidizing species (such as  $\text{SO}_4^{\bullet-}$  (Eq. 3) or  $\text{S}_2\text{O}_8^{2-}$  (Eq. 3 and 7)) by the participation  
334 of free heterogeneous  $\bullet\text{OH}$  (Eq. 3).



337 It is important to remark that, the surface-layer-based processes are achieved closer  
338 to the electrode surface, in the Nernst layer (from Armstrong to nanometers), which mainly  
339 depend on the diffusion distance of the free heterogeneous  $\bullet\text{OH}$ , the thickness of the diffusion  
340 layer, the convection (agitation and flow rate) and the diffusion coefficient of  $\text{SO}_4^{2-}$  ions in  
341 the solution [8]. However, the limiting steps to produce  $\text{S}_2\text{O}_8^{2-}$  could be regarded as the  
342 diffusion of sulfate in the diffusion layer to react with the free heterogeneous  $\bullet\text{OH}$  (Eq. 3) as  
343 well as the subsequent reactions at BDD ( $\text{SO}_4^{\bullet-}$ )-sites on diamond surface (Eq. 5).

344 For this reason, it is necessary to control the current density to stabilize the  $\text{S}_2\text{O}_8^{2-}$   
345 electrogenerated, determining the extension of the production of  $\text{S}_2\text{O}_8^{2-}$  at both electrodes.





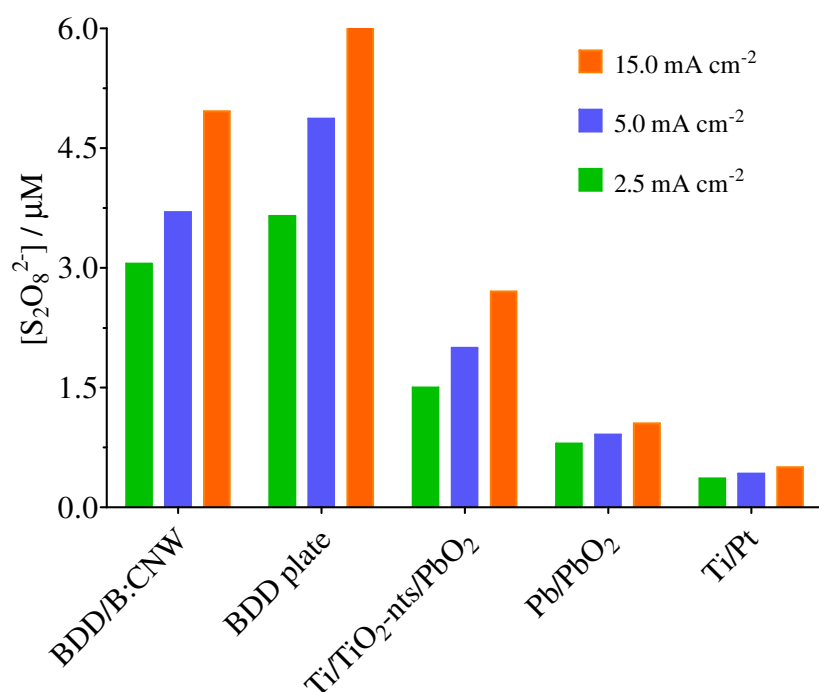
346

347 Fig xx – Schematic representation of the persulfate reaction pathway on the  
 348 BDD/BCNW electrode

349

### 350 3.3. Electrochemical production of persulfate

351 By applying different current densities (2.5, 5.0 and 15.0 mA cm<sup>-2</sup>) at 25 °C, the  
 352 S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration produced at both electrodes was determined by ISCO method (Fig. 4).  
 353 Based on the existing literature, the maximum S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration is achieved between 120  
 354 and 150 min of electrolysis (inset in Fig. 4), then, the final persulfate concentration was  
 355 plotted for all electrocatalytic materials at different applied current densities (Figure 4).



356

357 **Fig. 4.** Electrochemically persulfate generated at different anode materials. Batch cell with  
 358 50 mL of 0.05 M Na<sub>2</sub>SO<sub>4</sub> at 25°C.

359 As can be observed, an increase in the concentration of persulfate was attained when  
 360 the applied current density was increased (Fig. 4). For BDD plate, a significant enhancement  
 361 in the production of persulfate was attained concerning those achieved at BDD/B:CNW  
 362 electrode. This behavior is related to the favored mechanism to electrogenerated persulfate  
 363 [8]. According to the Tafel plot analysis, a stronger interaction is attained at a lower  
 364 overpotential region (<1.6 V) which indicated that the electrochemical production of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>  
 365 via direct electron transfer could be attained at BDD plate [3,8]. Meanwhile, at higher  
 366 potentials, the production of •OH radicals favors an enhancement of the persulfate  
 367 concentration [29]. Conversely, at BDD/B:CNW anode, the production of persulfate depends

368 on the formation of  $\text{SO}_4^{\cdot-}$  at BDD surface (which seems to be the main intermediate), and the  
369 subsequent surface-layer-based reactions of  $\text{SO}_4^{\cdot-}$  [10,37,42,42]. In this sense, the results  
370 related to the quantification of persulfate concentration indicated that the extension of the  
371 persulfate mechanism depends on the nature of the electrode and the  $j$  (which is directly  
372 associated with the cell potential). In fact, at lower  $j$ , the increase in the persulfate  
373 concentration is less significant than those achieved when higher  $j$ . For example, at BDD  
374 plate, from 2.5 to 5.0  $\text{mA cm}^{-2}$ , the persulfate concentration increases by 1.33-folds, while  
375 from 5.0 to 15.0  $\text{mA cm}^{-2}$ , it increases by 1.64-folds. Similar behavior is observed at  
376 BDD/B:CNW anode, where increases of about 1.21-folds and 1.34-folds were estimated,  
377 passing from 2.5 to 5.0  $\text{mA cm}^{-2}$ , and from 5.0 to 15.0  $\text{mA cm}^{-2}$ , respectively. However, there  
378 are significant differences in the persulfate concentrations electrochemically generated.

379 Another feature that should be indicated is that a successive intensification on the  $j$   
380 could favor an increase in the production of  $\cdot\text{OH}$  radicals as well as an increase in the oxygen  
381 evolution reaction [43–45]. In the former, these can react with the  $\text{SO}_4^{2-}$  ions in the diffusion  
382 layer to form  $\text{SO}_4^{\cdot-}$  (Eq. 3); and subsequently, produce  $\text{S}_2\text{O}_8^{2-}$  [42,46]. Meanwhile, when  $j$   
383 increases significantly, these can be also wasted favoring the production of  $\text{O}_2$  (Eq. 6), in the  
384 latter. These assertions are in agreement with the behavior reported by Pires *et al.* using BDD  
385 electrode [36], by applying  $j$  values higher than 15  $\text{mA cm}^{-2}$ . On the contrary, at  
386 BDD/B:CNW anode, more active BDD ( $\text{SO}_4^{\cdot-}$ )-sites on the diamond surface can be formed  
387 by increasing the  $j$  values (Eq. 3), favoring an increase in the production of persulfate via  
388 Eqs. (4) and (5).

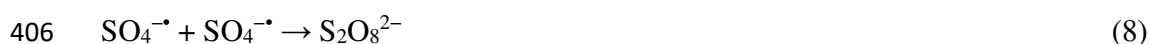
389 To understand the fundamentals of the mechanism related to the nature of  
390 electrocatalytic material, the electrogeneration of persulfate at diamond electrodes was also



391 compared to TiPt, Pb/PbO<sub>2</sub> and Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>. As can be observed at Fig. 4, it is  
392 evident that S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is efficiently produced at both diamond electrodes, by applying different  
393 *j*, with respect to the other anodic materials. This enhancement in the persulfate  
394 electrosynthesis is due to the mechanisms associated with the anodic surfaces used as well  
395 as the extension of each one of them.

396 Primarily, it is important to remark that no similar production of •OH radicals, via  
397 water discharge, is attained at all electrocatalytic materials due to their active and non-active  
398 nature. Then, following this statement [1,35], higher production of •OH radicals implies  
399 higher production of persulfate. For example, Ti/Pt produced lower concentrations of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>  
400 (0.36, 0.42 and 0.5 μM at 2.5, 5.0 and 15.0 mA cm<sup>-2</sup>, respectively) because lower  
401 electrogeneration of •OH radicals was reached at its surface, limiting the electrosynthesis  
402 mechanism via the participation of free heterogeneous •OH Eqs. (3), (7) and (8).

403 Conversely, at the diamond electrode (e.g.: BDD plate), the efficient production of  
404 •OH radicals is attained, favoring the generation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (such as 3.65, 4.87 and 7.98 μM  
405 at 2.5, 5.0 and 15.0 mA cm<sup>-2</sup>, respectively) via the formation of SO<sub>4</sub><sup>•-</sup>.



407 Secondly, the formation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> via direct electron transfer and/or via (SO<sub>4</sub><sup>•-</sup>)-active  
408 sites on the electrode surfaces depends on the interaction of SO<sub>4</sub><sup>2-</sup> ions and the  
409 electrocatalytic activity of each anode. In this frame, although the extension of the  
410 mechanisms is not completely clear, it seems that the electrogeneration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, via direct  
411 oxidation of SO<sub>4</sub><sup>2-</sup>, is attained at Ti/Pt surface, as the main approach, confirming that a



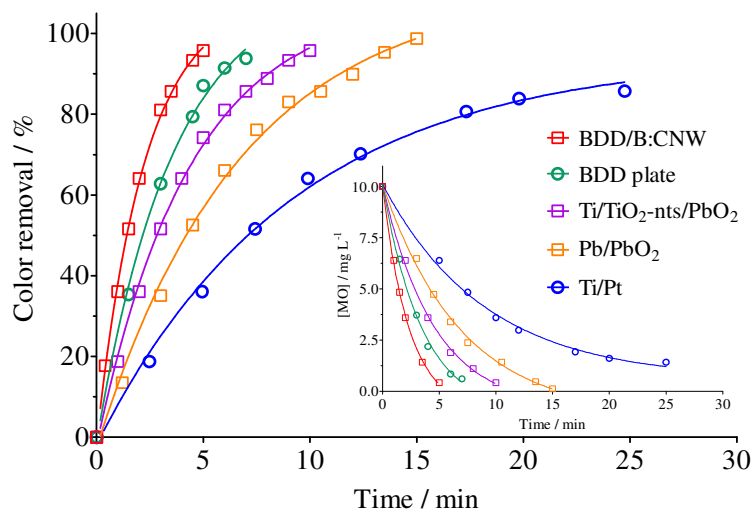
412 complex set of electrochemical and chemical reactions can be attained at non-active anodes  
413 and consequently, improving the electrosynthesis yield of  $S_2O_8^{2-}$  concentration.

414

### 415 **3.4. Electrochemical oxidation of a target organic compound**

416 To evaluate the performance of the persulfate electrochemically generated at diamond  
417 surfaces and the other materials, oxidation in-situ experiments were carried out. Solutions of  
418 25 mL of 0.05 M of  $Na_2SO_4$  containing 10 mg  $L^{-1}$  of MO were electrochemically treated by  
419 applying 15 mA  $cm^{-2}$ , mixing with magnetic stirring during 40 min and aliquots were  
420 withdrawn at predetermined times to determine the color removal, COD decay, and the  
421 concentration of the target pollutant by an electroanalytic procedure. As can be observed in  
422 Fig. 5, EO process with BDD/B:CNW anode removed more than 95% of solution color in 5  
423 min of electrolysis. Meanwhile, 93.8%, 95.7%, 98.6% and 85.8% were removed in 7, 10, 15  
424 and 25 min at BDD plate, Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>, Pb/PbO<sub>2</sub> and TiPt, respectively.  
425 According to the spectrophotometric measurements, the intensity of the visible band at 465  
426 nm continuously diminished until it disappears as a function of time during the galvanostatic  
427 electrolysis, leading to complete solution discoloration, in all cases. However, the absorbance  
428 changes were reasonably rapid at BDD/B:CNW, BDD plate, Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> and  
429 Pb/PbO<sub>2</sub> anodes, indicating that the fragmentation of the MO chromophore group is rapidly  
430 attained [29], promoting the elimination of color's solution and after that, the formation of  
431 many other intermediates.





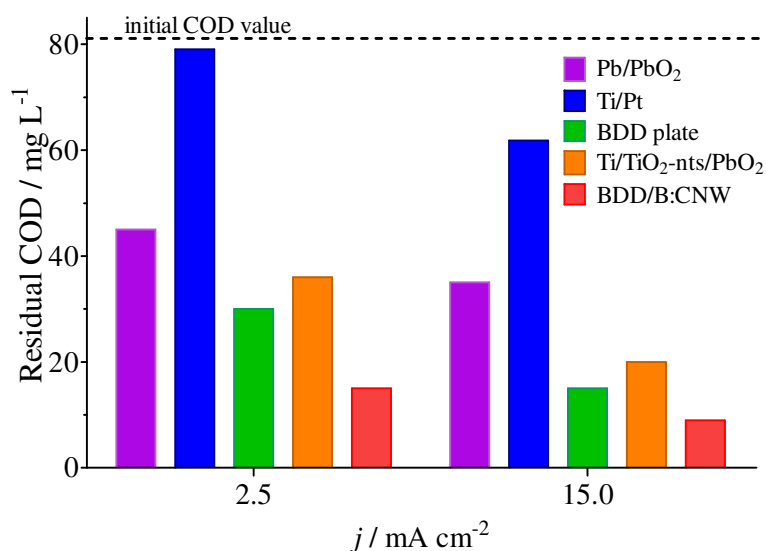
432

433 **Fig. 5.** Color removal effectiveness, as a function of time, at different anodic materials  
 434 electrogenerating *in-situ* sulfate-based oxidizing species by applying  $15 \text{ mA cm}^{-2}$  at  $25^\circ\text{C}$ .  
 435 Inset: MO concentration decay, as a function of time, under similar experimental conditions.

436 In fact, when MO concentration was followed during the EO tests, it gradually  
 437 decreased and it was dependent on the nature of the material used. Again, non-active anodes  
 438 were more efficient to remove MO from the solution (inset in Fig. 5), following an efficacy  
 439 order as BDD/B:CNW > BDD plate > Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> > Pb/PbO<sub>2</sub> > Ti/Pt. Only Ti/Pt  
 440 anode was less efficient, achieving 85% of removal from the MO initial concentration.  
 441 Analyzing the results obtained, BDD/B:CNW seems to be the most efficient anodic material  
 442 for the elimination of organic compounds from aqueous solution via  $\text{SO}_4^{2-}/\text{SO}_4^{\cdot-}/\text{S}_2\text{O}_8^{2-}$   
 443 system in concomitance with free heterogeneous  $\cdot\text{OH}$ . However, the elimination of color and  
 444 MO is not an indicator of the effective removal of organic matter. Therefore, COD removal  
 445 was evaluated, at the end of the electrolysis time (40 min), by applying low and high  $j$  values



446 (2.5 and 15 mA cm<sup>-2</sup>). As observed in Fig. 6, different residual values of COD were  
 447 determined indicating that the organic matter was oxidized in all cases.



448

449 **Fig. 6.** Residual COD values, as a function of  $j$  (2.5 and 15.0 mA cm<sup>-2</sup>), after 40 min of  
 450 electrolysis at different anodic materials in EO tests at 25°C.

451

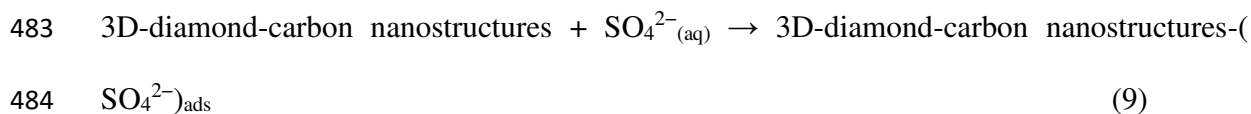
452 On the one hand, residual COD concentrations in solution of about 15.1 and 9.0 mg  
 453 L<sup>-1</sup> were determined at 2.5 and 15 mA cm<sup>-2</sup> with BDD/B:CNW anode corresponding to  
 454 81.80% and 89.15% of COD removals, considering 83.0 mg L<sup>-1</sup> as initial COD. On the other  
 455 hand, lower COD removals (4.76% and 25.51% at 2.5 and 15 mA cm<sup>-2</sup>, respectively) were  
 456 achieved using Ti/Pt, as electrocatalytic material, that still represents a significant amount of  
 457 dissolved organic matter in solution. Based on these results, it is clear that the elimination of  
 458 organic matter occurred by the reactions attained in the reaction cage as surface-layer-based  
 459 approaches via SO<sub>4</sub><sup>•-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and free heterogeneous <sup>•</sup>OH. But, the intensification of the



460 process is attained when a synergic effect is reached via the participation of all oxidant  
461 species, which depends on the extension of the electrogeneration of each one of the oxidants,  
462 mainly at non-active anodes.

463 The results obtained at diamond electrodes, such as the real surface area, Tafel plots,  
464 persulfate production, and electrochemical degradation, evidenced that the concentration of  
465  $\text{SO}_4^{\bullet-}$ ,  $\text{S}_2\text{O}_8^{2-}$  and free heterogeneous  $\bullet\text{OH}$  could be different, under the experimental  
466 conditions exposed here. This hypothesis is mainly related to the efficacy to produce  
467 persulfate, discoloration level, and MO decay as well as COD removal comparing both BDD  
468 plate and BDD/B:CNW anodes. In the former, all parameters were efficiently achieved and  
469 superior to BDD/B:CNW anode. Meanwhile, COD was significantly removed from synthetic  
470 effluent at BDD/B:CNW anode than the other electrodes. This behavior could be associated  
471 with the electrochemical generation of prior species that reacts in Nernst layer with the  
472 organic compound before generating  $\text{S}_2\text{O}_8^{2-}$ . According to the literature [8,29],  $\text{SO}_4^{\bullet-}$  radicals  
473 are the potential candidate, as already experimental [41] and theoretically [47] established;  
474 in the case of diamond electrodes, the formation of BDD-( $\text{SO}_4^{\bullet-}$ ) sites is a pre-requisite step  
475 to produce  $\text{S}_2\text{O}_8^{2-}$  by recombining two  $\text{SO}_4^{\bullet-}$  species (Eq. (13)). However, as already proved  
476 by electrochemical measurements, this behavior is strongly dependent on the carbon  $\text{sp}^2$ -  
477 impurities content on the BDD surface. Graphitic  $\text{sp}^2$  carbon act as the adsorption site for  
478 sulfate-based species (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ) at the diamond electrode, favoring the generation  
479 of  $\text{SO}_4^{\bullet-}$ , thus producing  $\text{S}_2\text{O}_8^{2-}$ . In the case of BDD/B:CNW electrode, its surface was  
480 meaningly enlarged due to the 3D-diamond-carbon nanostructures. These nanostructures  
481 (nano-flaps, nanowalls, as well as microcavities and micro-valleys) contain a key quantity of  
482 hot-spot active sites, which could participate as adsorption sulfate-based species.





486 In this context, the formation of active-( $\text{SO}_4^{\cdot-}$ ) sites is mainly attained at BDD/B:CNW (Eq.  
487 9), producing higher concentrations of  $\text{SO}_4^{\cdot-}$  at its surface when compared to the production  
488 of free heterogeneous  $\cdot\text{OH}$ . Although similar oxidation-reduction potentials are registered  
489 between  $\text{SO}_4^{\cdot-}$  (2.5–3.1 V vs. NHE) and  $\cdot\text{OH}$  (2.74 V vs. NHE), different extinction lifetimes  
490 are attained in solution, 30–40  $\mu\text{s}$  for  $\text{SO}_4^{\cdot-}$  and less than 1  $\mu\text{s}$  for  $\cdot\text{OH}$  [8], which allows to  
491 substantially improve the  $\text{SO}_4^{\cdot-}$  mass transfer performances and subsequently, its contact  
492 chance and effectiveness with the pollutants in solution, as *surface-layer-* or as *volume-*  
493 *solution-* oxidation approaches [3,8,9,29,48]. Additionally, a wide pH window (from 2.0 to  
494 8.0), due to the pH adjustment, can be used to favor the efficacy of the  $\text{SO}_4^{\cdot-}$  with the organic  
495 pollutants. Consequently, BDD/B:CNW produces a higher concentration of  $\text{SO}_4^{\cdot-}$  that, which  
496 is available at active sites on its surface with a substantial lifetime, enhances the organic  
497 matter removal (see Fig. 6) concerning other electrodes, mainly BDD plate.

498

## 499 **Conclusions**

500 In summary, we can conclude that,

- 501 (i) BDD/B:CNW electrode is constituted by 3D-diamond-carbon nanostructures  
502 which increase significantly its electroactive surface area, as confirmed by the  
503 double layer capacitance determination obtaining an expansion of about 3.2-  
504 folds respect to the area of a BDD plate.

505 (ii) The roughness factor indicated that the 3D-nanomaterial increased its porous  
506 properties which were also confirmed by SEM images for BDD/B:CNW  
507 surface.

508 (iii) In both diamond materials, electrochemical measurements have indicated that  
509 the complex set of the electrochemical reactions takes at lower and higher  
510 over potential regions. However, it mainly seems that the persulfate  
511 electrosynthesis depends on the stability/reactivity of  $\cdot\text{OH}$  and diamond  
512 surface active sites to favor the production of  $\text{SO}_4^{\cdot-}$ . In the case of BDD plate,  
513 it produces rapidly  $\text{SO}_4^{\cdot-}$ , via reaction between  $\cdot\text{OH}$  and  $\text{SO}_4^{2-}$ , which form  
514  $\text{S}_2\text{O}_8^{2-}$ , but it is a less reactive oxidizing species. Meanwhile,  $\text{SO}_4^{\cdot-}$  species  
515 are adsorbed at sp<sup>2</sup>-active sites at BDD/B:CNW favoring their participation  
516 in the oxidation of MO.

517 (iv) In the case of  $\text{PbO}_2$ -based electrodes, indirect oxidation of  $\text{SO}_4^{2-}$  via  
518 heterogeneous free  $\cdot\text{OH}$  can be hypothesized where a possible formation of the  
519 active-( $\text{SO}_4^{\cdot-}$ ) sites can be also feasible at  $\alpha$ -  $\text{PbO}_2$  or  $\beta$ -  $\text{PbO}_2$  sites, which  
520 should be still completely elucidated.

521 These conclusions open a new landscape associated with the real mechanism to  
522 produce sulfate-based oxidizing species at BDD anodes as well as the electrochemical  
523 generation of these oxidants at other non-active and active anodes.

524

525

526

527

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## 539 **5. References**

- 540 [1] C.A. Martínez-Huitle, M. Panizza, Electrochemical oxidation of organic pollutants  
541 for wastewater treatment, *Curr. Opin. Electrochem.* 11 (2018) 62–71.  
542 <https://doi.org/10.1016/j.coelec.2018.07.010>.
- 543 [2] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, C.A. Martinez-Huitle,  
544 M.A. Rodrigo, I. Sire, O. Scialdone, Single and Coupled Electrochemical Processes  
545 and Reactors for the Abatement of Organic Water Pollutants: A Critical Review,  
546 *Chem. Rev.* 115 (2015) 13362–13407. <https://doi.org/10.1021/acs.chemrev.5b00361>.
- 547 [3] S.O. Ganiyu, C.A. Martínez-Huitle, M.A. Oturan, Electrochemical advanced  
548 oxidation processes for wastewater treatment: Advances in formation and detection  
549 of reactive species and mechanisms, *Curr. Opin. Electrochem.* 27 (2021).  
550 <https://doi.org/10.1016/j.coelec.2020.100678>.
- 551 [4] S.O. Ganiyu, E.V. dos Santos, C.A. Martínez-Huitle, S.R. Waldvogel, Opportunities

- 552 and challenges of thin-film boron-doped diamond electrochemistry for valuable  
553 resources recovery from waste: Organic, inorganic, and volatile  
554 product electrosynthesis, *Curr. Opin. Electrochem.* (2021) 100903.  
555 <https://doi.org/10.1016/J.COELEC.2021.100903>.
- 556 [5] G.R. Salazar-Banda, G.D.O.S. Santos, I.M. Duarte Gonzaga, A.R. Dória, K.I.  
557 Barrios Eguiluz, *Developments in electrode materials for wastewater treatment,*  
558 *Curr. Opin. Electrochem.* 26 (2021). <https://doi.org/10.1016/j.coelec.2020.100663>.
- 559 [6] D. Clematis, M. Panizza, *Application of boron-doped diamond electrodes for*  
560 *electrochemical oxidation of real wastewaters,* *Curr. Opin. Electrochem.* (2021)  
561 100844. <https://doi.org/10.1016/J.COELEC.2021.100844>.
- 562 [7] P.V. Nidheesh, M. Zhou, M.A. Oturan, *An overview on the removal of synthetic*  
563 *dyes from water by electrochemical advanced oxidation processes,* *Chemosphere.*  
564 197 (2018) 210–227. <https://doi.org/10.1016/j.chemosphere.2017.12.195>.
- 565 [8] G. Divyapriya, P. V. Nidheesh, *Electrochemically generated sulfate radicals by*  
566 *boron doped diamond and its environmental applications,* *Curr. Opin. Solid State*  
567 *Mater. Sci.* 25 (2021) 100921. <https://doi.org/10.1016/J.COSSMS.2021.100921>.
- 568 [9] C.A. Martínez-Huitle, E. Brillas, *A critical review over the electrochemical*  
569 *disinfection of bacteria in synthetic and real wastewaters using a boron-doped*  
570 *diamond anode,* *Curr. Opin. Solid State Mater. Sci.* 25 (2021) 100926.  
571 <https://doi.org/10.1016/j.cossms.2021.100926>.
- 572 [10] K. Groenen Serrano, *A critical review on the electrochemical production and use of*  
573 *peroxo-compounds,* *Curr. Opin. Electrochem.* 27 (2021) 100679.  
574 <https://doi.org/10.1016/j.coelec.2020.100679>.
- 575 [11] A.S. Mora, S.T. McBeath, C.A. Cid, M.R. Hoffmann, N.J.D. Graham, *Diamond*

- 576 electrode facilitated electrosynthesis of water and wastewater treatment oxidants,  
577 *Curr. Opin. Electrochem.* 32 (2022) 100899.  
578 <https://doi.org/10.1016/J.COEELEC.2021.100899>.
- 579 [12] G.R. Pointer Malpass, A. de Jesus Motheo, Recent advances on the use of active  
580 anodes in environmental electrochemistry, *Curr. Opin. Electrochem.* (2021) 100689.  
581 <https://doi.org/10.1016/j.coelec.2021.100689>.
- 582 [13] X. Du, M.A. Oturan, M. Zhou, N. Belkessa, P. Su, J. Cai, C. Trelu, E. Mousset,  
583 Nanostructured electrodes for electrocatalytic advanced oxidation processes: From  
584 materials preparation to mechanisms understanding and wastewater treatment  
585 applications, *Appl. Catal. B Environ.* 296 (2021) 120332.  
586 <https://doi.org/10.1016/J.APCATB.2021.120332>.
- 587 [14] M. Pierpaoli, P. Jakobczyk, M. Sawczak, A. Łuczkiwicz, S. Fudala-Książek, R.  
588 Bogdanowicz, Carbon nanoarchitectures as high-performance electrodes for the  
589 electrochemical oxidation of landfill leachate, *J. Hazard. Mater.* 401 (2021) 123407.  
590 <https://doi.org/10.1016/J.JHAZMAT.2020.123407>.
- 591 [15] M. Pierpaoli, M. Szopińska, B.K. Wilk, M. Sobaszek, A. Łuczkiwicz, R.  
592 Bogdanowicz, S. Fudala-Książek, Electrochemical oxidation of PFOA and PFOS in  
593 landfill leachates at low and highly boron-doped diamond electrodes, *J. Hazard.*  
594 *Mater.* 403 (2021). <https://doi.org/10.1016/j.jhazmat.2020.123606>.
- 595 [16] S. Dutta, A. Bhaumik, K.C.W. Wu, Hierarchically porous carbon derived from  
596 polymers and biomass: effect of interconnected pores on energy applications, *Energy*  
597 *Environ. Sci.* 7 (2014) 3574–3592. <https://doi.org/10.1039/C4EE01075B>.
- 598 [17] B.K. Mishra, S. Chakraborty, P. Kumar, C. Saraswat, Sustainable Solutions for  
599 Urban Water Security, 93 (2020). <https://doi.org/10.1007/978-3-030-53110-2>.

- 600 [18] B. Van der Bruggen, Sustainable implementation of innovative technologies for  
601 water purification, *Nat. Rev. Chem.* 2021 54. 5 (2021) 217–218.  
602 <https://doi.org/10.1038/s41570-021-00264-7>.
- 603 [19] M. Pierpaoli, A. Dettlaff, M. Szopińska, K. Karpienko, M. Wróbel, A. Łuczkiwicz,  
604 S. Fudala-Książek, R. Bogdanowicz, Simultaneous opto-electrochemical monitoring  
605 of carbamazepine and its electro-oxidation by-products in wastewater, *J. Hazard.*  
606 *Mater.* 419 (2021). <https://doi.org/10.1016/j.jhazmat.2021.126509>.
- 607 [20] R. Bogdanowicz, Functionalized nanodiamonds as a perspective green carbo-catalyst  
608 for removal of emerging organic pollutants, *Curr. Opin. Solid State Mater. Sci.* 26  
609 (2022) 100991. <https://doi.org/10.1016/J.COSSMS.2022.100991>.
- 610 [21] R. Bogdanowicz, J. Ryl, Structural and electrochemical heterogeneities of boron-  
611 doped diamond surfaces, *Curr. Opin. Electrochem.* 31 (2022) 100876.  
612 <https://doi.org/10.1016/J.COELEC.2021.100876>.
- 613 [22] K. Siuzdak, M. Ficek, M. Sobaszek, J. Ryl, M. Gnyba, P. Niedziałkowski, N.  
614 Malinowska, J. Karczewski, R. Bogdanowicz, Boron-Enhanced Growth of Micron-  
615 Scale Carbon-Based Nanowalls: A Route toward High Rates of Electrochemical  
616 Biosensing, *ACS Appl. Mater. Interfaces.* 9 (2017) 12982–12992.  
617 [https://doi.org/10.1021/ACSAMI.6B16860/SUPPL\\_FILE/AM6B16860\\_SI\\_001.PD](https://doi.org/10.1021/ACSAMI.6B16860/SUPPL_FILE/AM6B16860_SI_001.PDF)  
618 F.
- 619 [23] A. Dettlaff, P. Jakóbczyk, M. Ficek, B. Wilk, M. Szala, J. Wojtas, T. Ossowski, R.  
620 Bogdanowicz, Electrochemical determination of nitroaromatic explosives at boron-  
621 doped diamond/graphene nanowall electrodes: 2,4,6-trinitrotoluene and 2,4,6-  
622 trinitroanisole in liquid effluents, *J. Hazard. Mater.* 387 (2020) 121672.  
623 <https://doi.org/10.1016/J.JHAZMAT.2019.121672>.

- 624 [24] M. Sobaszek, K. Siuzdak, J. Ryl, M. Sawczak, S. Gupta, S.B. Carrizosa, M. Ficek,  
625 B. Dec, K. Darowicki, R. Bogdanowicz, Diamond Phase (sp<sup>3</sup>-C) Rich Boron-Doped  
626 Carbon Nanowalls (sp<sup>2</sup>-C): Physicochemical and Electrochemical Properties, J.  
627 Phys. Chem. C. 121 (2017) 20821–20833.  
628 [https://doi.org/10.1021/ACS.JPCC.7B06365/ASSET/IMAGES/MEDIUM/JP-2017-](https://doi.org/10.1021/ACS.JPCC.7B06365/ASSET/IMAGES/MEDIUM/JP-2017-063658_0016.GIF)  
629 [063658\\_0016.GIF](https://doi.org/10.1021/ACS.JPCC.7B06365/ASSET/IMAGES/MEDIUM/JP-2017-063658_0016.GIF).
- 630 [25] S. Trasatti, Electrocatalysis: understanding the success of DSA®, *Electrochim. Acta*.  
631 45 (2000) 2377–2385. [https://doi.org/10.1016/S0013-4686\(00\)00338-8](https://doi.org/10.1016/S0013-4686(00)00338-8).
- 632 [26] C. Calas-Blanchard, M. Comtat, J.L. Marty, S. Mauran, Textural characterisation of  
633 graphite matrices using electrochemical methods, *Carbon N. Y.* 41 (2003) 123–130.  
634 [https://doi.org/10.1016/S0008-6223\(02\)00269-5](https://doi.org/10.1016/S0008-6223(02)00269-5).
- 635 [27] M. Łukaszewski, Electrochemical Methods of Real Surface Area Determination of  
636 Noble Metal Electrodes – an Overview, *Int. J. Electrochem. Sci.* 11 (2016) 4442–  
637 4469. <https://doi.org/10.20964/2016.06.71>.
- 638 [28] C. Liang, C.F. Huang, N. Mohanty, R.M. Kurakalva, A rapid spectrophotometric  
639 determination of persulfate anion in ISCO, *Chemosphere.* 73 (2008) 1540–1543.  
640 <https://doi.org/10.1016/j.chemosphere.2008.08.043>.
- 641 [29] K.C.F. Araújo, K.N.O. Silva, M.K.S. Monteiro, D.R. da Silva, M.A. Quiroz, E.V.  
642 dos Santos, C.A. Martínez-Huitle, Towards Use of Persulfate Electrogenerated at  
643 Boron Doped Diamond Electrodes as Ex-Situ Oxidation Approach: Storage and  
644 Service-Life Solution Parameters, *J. Electrochem. Soc.* 169 (2022) 033506.  
645 <https://doi.org/10.1149/1945-7111/AC59F8>.
- 646 [30] G.O.S. Santos, K.I.B. Eguiluz, G.R. Salazar-Banda, C. Sáez, M.A. Rodrigo,  
647 Understanding the electrolytic generation of sulfate and chlorine oxidative species



- 648 with different boron-doped diamond anodes, *J. Electroanal. Chem.* 857 (2020)  
649 113756. <https://doi.org/10.1016/j.jelechem.2019.113756>.
- 650 [31] H. Huang, M. Yan, C. Yang, H. He, Q. Jiang, L. Yang, Z. Lu, Z. Sun, X. Xu, Y.  
651 Bando, Y. Yamauchi, Graphene Nanoarchitectonics: Recent Advances in Graphene-  
652 Based Electrocatalysts for Hydrogen Evolution Reaction, *Adv. Mater.* 31 (2019)  
653 1903415. <https://doi.org/10.1002/ADMA.201903415>.
- 654 [32] O.A. Trasatti, S. Petri, Real surface area measurements in electrochemistry, *J.*  
655 *Electroanal. Chem.* 327 (1992) 353–376.  
656 [https://doi.org/https://doi.org/10.1016/0022-0728\(92\)80162-W](https://doi.org/10.1016/0022-0728(92)80162-W).
- 657 [33] J.M. Doña Rodríguez, J.A. Herrera Melián, J. Pérez Peña, Determination of the Real  
658 Surface Area of Pt Electrodes by Hydrogen Adsorption Using Cyclic Voltammetry,  
659 *J. Chem. Educ.* 77 (2000) 1195. <https://doi.org/10.1021/ed077p1195>.
- 660 [34] R. Bogdanowicz, A. Fabiańska, L. Golunski, M. Sobaszek, M. Gnyba, J. Ryl, K.  
661 Darowicki, T. Ossowski, S.D. Janssens, K. Haenen, E.M. Siedlecka, Influence of the  
662 boron doping level on the electrochemical oxidation of the azo dyes at Si/BDD thin  
663 film electrodes, *Diam. Relat. Mater.* 39 (2013) 82–88.  
664 [https://doi.org/https://doi.org/10.1016/j.diamond.2013.08.004](https://doi.org/10.1016/j.diamond.2013.08.004).
- 665 [35] J. Ryl, L. Burczyk, A. Zielinski, M. Ficek, A. Franczak, R. Bogdanowicz, K.  
666 Darowicki, Heterogeneous oxidation of highly boron-doped diamond electrodes and  
667 its influence on the surface distribution of electrochemical activity, *Electrochim.*  
668 *Acta.* 297 (2019) 1018–1027. <https://doi.org/10.1016/J.ELECTACTA.2018.12.050>.
- 669 [36] J.P. De Paiva Barreto, K.C. De Freitas Araújo, D.M. De Araújo, C.A. Martínez-  
670 Huitle, Effect of sp<sup>3</sup>/sp<sup>2</sup> ratio on boron doped diamond films for producing  
671 persulfate, *ECS Electrochem. Lett.* 4 (2015) E9–E11.

- 672 <https://doi.org/10.1149/2.0061512eel>.
- 673 [37] T.F. Da Costa, J.E.L. Santos, D.R. da Silva, C.A. Martinez-Huitle, BDD-electrolysis  
674 of oxalic acid in diluted acidic solutions, *J. Braz. Chem. Soc.* 30 (2019) 1541–1547.  
675 <https://doi.org/10.21577/0103-5053.20190051>.
- 676 [38] P.K. Jiwanti, K. Natsui, K. Nakata, Y. Einaga, The electrochemical production of  
677 C2/C3 species from carbon dioxide on copper-modified boron-doped diamond  
678 electrodes, *Electrochim. Acta.* 266 (2018) 414–419.  
679 <https://doi.org/10.1016/j.electacta.2018.02.041>.
- 680 [39] P.A. Michaud, M. Panizza, L. Ouattara, T. Diaco, G. Foti, C. Comninellis,  
681 Electrochemical oxidation of water on synthetic boron-doped diamond thin film  
682 anodes, *J. Appl. Electrochem.* 33 (2003) 151–154.  
683 <https://doi.org/10.1023/A:1024084924058>.
- 684 [40] K. Serrano, P.A. Michaud, C. Comninellis, A. Savall, Electrochemical preparation of  
685 peroxodisulfuric acid using boron doped diamond thin film electrodes, *Electrochim.*  
686 *Acta.* 48 (2002) 431–436. [https://doi.org/https://doi.org/10.1016/S0013-](https://doi.org/https://doi.org/10.1016/S0013-4686(02)00688-6)  
687 [4686\(02\)00688-6](https://doi.org/https://doi.org/10.1016/S0013-4686(02)00688-6).
- 688 [41] K.C. de Freitas Araújo, D.R. da Silva, E.V. dos Santos, H. Varela, C.A. Martínez-  
689 Huitle, Investigation of persulfate production on BDD anode by understanding the  
690 impact of water concentration, *J. Electroanal. Chem.* 860 (2020) 113927.  
691 <https://doi.org/10.1016/j.jelechem.2020.113927>.
- 692 [42] Y.U. Shin, H.Y. Yoo, Y.Y. Ahn, M.S. Kim, K. Lee, S. Yu, C. Lee, K. Cho, H. il  
693 Kim, J. Lee, Electrochemical oxidation of organics in sulfate solutions on boron-  
694 doped diamond electrode: Multiple pathways for sulfate radical generation, *Appl.*  
695 *Catal. B Environ.* 254 (2019) 156–165.

- 696 <https://doi.org/10.1016/J.APCATB.2019.04.060>.
- 697 [43] W. Wu, Z.H. Huang, T.T. Lim, Recent development of mixed metal oxide anodes  
698 for electrochemical oxidation of organic pollutants in water, *Appl. Catal. A Gen.* 480  
699 (2014) 58–78. <https://doi.org/10.1016/J.APCATA.2014.04.035>.
- 700 [44] M.S.M. Sillanpää, Electrode materials used for electrochemical oxidation of organic  
701 compounds in wastewater, (n.d.). <https://doi.org/10.1007/s11157-017-9426-1>.
- 702 [45] M. Moradi, Y. Vasseghian, A. Khataee, M. Kobya, H. Arabzade, E.N. Dragoi,  
703 Service life and stability of electrodes applied in electrochemical advanced oxidation  
704 processes: A comprehensive review, *J. Ind. Eng. Chem.* 87 (2020) 18–39.  
705 <https://doi.org/10.1016/J.JIEC.2020.03.038>.
- 706 [46] L.W. Matzek, M.J. Tipton, A.T. Farmer, A.D. Steen, K.E. Carter, Understanding  
707 Electrochemically Activated Persulfate and Its Application to Ciprofloxacin  
708 Abatement, *Environ. Sci. Technol.* 52 (2018) 5875–5883.  
709 [https://doi.org/10.1021/ACS.EST.8B00015/SUPPL\\_FILE/ES8B00015\\_SI\\_001.PDF](https://doi.org/10.1021/ACS.EST.8B00015/SUPPL_FILE/ES8B00015_SI_001.PDF).
- 710 [47] J. Davis, J.C. Baygents, J. Farrell, Understanding Persulfate Production at Boron  
711 Doped Diamond Film Anodes, *Electrochim. Acta.* 150 (2014) 68–74.  
712 <https://doi.org/10.1016/j.electacta.2014.10.104>.
- 713 [48] K.N.O. Silva, K.C.F. Araújo, D.R. da Silva, C.A. Martínez-Huitle, E.V. dos Santos,  
714 Persulfate-soil washing: The green use of persulfate electrochemically generated  
715 with diamond electrodes for depolluting soils, *J. Electroanal. Chem.* 895 (2021)  
716 115498. <https://doi.org/10.1016/j.jelechem.2021.115498>.
- 717