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Laís G Vernasqui, Alexsandro J dos Santos, Guilherme V Fortunato, Matheus S Kronka, Haruna L Barazorda-Ccahuana, et al.. Highly porous seeding-free boron-doped ultrananocrystalline diamond used as high-performance anode for electrochemical removal of carbaryl from water. *Chemosphere*, 2022, 305, pp.135497. 10.1016/j.chemosphere.2022.135497 . hal-03790508

HAL Id: hal-03790508

<https://hal.sorbonne-universite.fr/hal-03790508>

Submitted on 28 Sep 2022

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1 **Highly porous seeding-free boron-doped ultrananocrystalline diamond used**
2 **as high-performance anode for electrochemical removal of carbaryl from water**

3
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26 **Abstract**

27 Boron-doped diamond (BDD) electrodes are regarded as the most promising catalytic materials that are
28 highly efficient and suitable for application in advanced electrochemical oxidation processes targeted at the
29 removal of recalcitrant contaminants in different water matrices. Improving the synthesis of these electrodes
30 through the enhancement of their morphology, structure and stability has become the goal of the material
31 scientists. The present work reports the use of an ultranano-diamond electrode with a highly porous structure
32 (B-UNCD_{ws}/TDNT/Ti) for the treatment of water containing carbaryl. The application of the proposed
33 electrode at current density of 75 mA cm⁻² led to the complete removal of the pollutant (carbaryl) from the
34 synthetic medium in 30 min of electrolysis with an electric energy per order of 4.01 kWh m⁻³ order⁻¹. The
35 results obtained from the time-course analysis of the carboxylic acids and nitrogen-based ions present in the
36 solution showed that the concentrations of nitrogen-based ions were within the established maximum levels
37 for human consumption. Under optimal operating conditions, the proposed electrode was successfully
38 employed for the complete removal of carbaryl in real water. Thus, the findings of this study show that the
39 unique, easy-to-prepare BDD-based electrode proposed in this study is a highly efficient tool which has
40 excellent application potential for the removal of recalcitrant pollutants in water.

41

42

43 *Keywords:* Recalcitrant pollutants; Water treatment; Advanced oxidation processes; Electrochemical
44 technologies; Boron-doped diamond synthesis.

45

1. Introduction

Anodic oxidation (AO) is one of the major electrochemically-driven technologies which have been widely applied for the remediation of recalcitrant organic substances - including dyes, personal care and pharmaceutical products, and pesticides, usually present in water bodies (Sirés and Brillas, 2012; Sirés et al., 2014; Baddouh et al., 2018; Garcia-Segura et al., 2018b; Martínez-Huitle and Panizza, 2018; dos Santos et al., 2021b;). AO is considered an environmentally friendly technique as the process does not require the use of chemicals and oxidants are electrogenerated *in situ*. Several studies have shown that the electrocatalytic properties of the anode material are among the main factors that determine the efficiency of the AO process (Panizza and Cerisola, 2009; Sirés et al., 2014; Moreira et al., 2017; dos Santos et al., 2019, 2021a). In this context, boron-doped diamond (BDD) anode is regarded as the best material for application in AO due to its excellent properties including high stability, inert surface, and large O₂ overpotential window (Kapałka et al., 2009). The large O₂ overpotential window of BDD anode helps generate a huge amount of oxidant species such as physisorbed hydroxyl radicals (M([•]OH), Eq. (1) which can attack organic pollutants (R) non-selectively, turning them into non-hazardous products or even leading them to complete combustion, as shown in Eq. (2) below (do Vale Júnior et al., 2019; Brillas, 2021; Karim et al., 2021; Mostafa et al., 2021).



The properties of BDD can be enhanced considerably by varying the concentration of boron, film thickness, and sp²/sp³ ratio, as well as the electrode morphology and porosity (Baluchová et al., 2019; Mei et al., 2019). As pointed out in the literature, one can promote the contact between the electrolyte and the electrode by increasing the electrochemical surface area through the adjustment of the film porosity from macro to nanoporous depending on both the porosity of the substrate and specific post-growth treatment on the diamond surface. So far, a number of studies reported in the literature have employed the seeding substrate pre-treatment mechanism to boost the diamond growth through the application of the chemical vapor deposition technique (Wei et al., 2009; Szunerits et al., 2015; Yang et al., 2016). This pre-treatment mechanism involves the use of diamond powder to improve diamond growth since diamond is unable to grow naturally on non-diamond substrates. Due to the fast deposition kinetics, this seeding substrate pre-treatment procedure, which boosts the diamond growth, favors the formation of agglomerated structures; on the other hand, the fast deposition

74 kinetics makes it harder to obtain structures with nano or ultranano-porosity which are more suitable and
75 efficient for improving the efficiency of the AO process (May and Mankelevich, 2008; Luong et al., 2009;
76 Macpherson, 2015).

77 As an alternative to the typical BDD synthesis method, in a previous study (Vernasqui et al., 2022), our
78 research group proposed the use of an innovative boron-doped ultrananocrystalline diamond grown on titanium
79 dioxide nanotube without the seeding substrate pre-treatment procedure (B-UNCD_{ws}/TDNT/Ti). The use of
80 titanium dioxide nanotubes (TDNT) allows spontaneous diamond growth under slower deposition kinetics
81 compared to the seeding process, and this enables one to have higher control of deposition and the ability to
82 produce extremely thin films, in addition to maintaining the porosity of the substrate material. This approach
83 represents a major step forward in the synthesis of BDD and helps explore the unique properties of BDD when
84 it comes to the treatment of recalcitrant pollutants. Thus, this study evaluates the efficiency of the innovative
85 B-UNCD_{ws}/TDNT/Ti electrode when applied for the removal of carbaryl (CBR) pesticide in both synthetic
86 and real media under the AO process. Carbaryl is a broad-spectrum N-methyl carbamate insecticide applied
87 worldwide for the control of pests during the production of crops (cotton, corn, soybean, nut, fruits, and
88 vegetables) and for the protection of lawns, home gardens and other ornamental plants (Koshlukova and Reed,
89 2014).

90 CBR ranks second among the insecticides that are commonly detected in surface water (Nair et al., 2022).
91 CBR can dissolve in water, migrate through soil, and find its way into groundwater, contaminating it (Wu et
92 al., 2019). People are mostly exposed to CBR through the intake of food and water or other liquids. Depending
93 on the individual and the dose of CBR ingested into the body, the person may experience a variety of symptoms
94 which range from weakness to reduced heart and lung function. In view of that, it is essentially important to
95 develop techniques that are capable of removing this type of contaminant from food and water so as to prevent
96 excessive human exposure to this pollutant and the occurrence of severe health problems in humans. To
97 analyze the efficiency and viability of the proposed anode in terms of CBR degradation, different current
98 densities were tested, and the best operating conditions were applied for the analysis of real drinking water
99 with a view to evaluating the potential of the technique in real applications. The presence of different oxidants
100 in the system was evaluated using scavenger compounds. Energetic figures of merit were calculated, and the
101 evolution of intermediates produced during the treatment process was also thoroughly monitored. For

102 comparison purposes, the study also provides comprehensive data related to the physical and electroanalytical
103 characterization of the proposed B-UNCD_{ws}/TDNT/Ti anode.
104

105 **2. Materials and methods**

106 *2.1 Chemical reagents*

107 Carbaryl (CBR) pesticide (99 % purity, Sigma-Aldrich) was used as a model pollutant. Analytical grade
108 potassium sulfate – acquired from Neon, was used as supporting electrolyte; methanol (MeOH) and *tert*-
109 butanol (TBH), both acquired from Sigma Aldrich, were used as scavengers; and acetonitrile – obtained from
110 Merck, was used as mobile phase for the conduct of high-performance liquid chromatography (HPLC)
111 analysis. All reagents were used directly without extra purification. Ultrapure water from a Millipore Milli-Q
112 system (electric resistivity >18 M Ω cm at 25 °C) was used to prepare the aqueous solutions.

113 *2.2 B-UNCD_{ws}/TDNT/Ti synthesis and characterization*

114 The synthesis of the B-UNCD_{ws}/TDNT/Ti electrode was performed under a two-step approach. The first
115 step involved obtaining anodized TDNTs and the second step involved the deposition of diamond through the
116 application of the hot filament chemical vapor deposition (HFCVD) technique as described by (Vernasqui et
117 al., 2022). A commercial microcrystalline BDD thin film doped on a silicon substrate (acquired from NeoCoat)
118 were employed for comparison purposes. The synthesized anode material (B-UNCD_{ws}/TDNT/Ti) was
119 analyzed by field emission gun scanning electron microscopy (FEG-SEM, TESCAN Mira 3), Raman
120 scattering spectroscopy - using 514.5 nm line of argon ion-laser (Lab- RAMHR evolution from Horiba
121 Scientific), and X-ray diffraction (XDR – PANanalytical model X'Pert Pro MPD diffractometer with CuK α
122 radiation). Cyclic voltammetry (CV), linear scan voltammetry (LSV), and electrochemical impedance
123 spectroscopy (EIS) measurements were performed using N₂-saturated H₂SO₄ or K₂SO₄ solutions with the aid of
124 an Autolab PGSTAT128N potentiostat/galvanostat equipped with FRA2.X module. The electrochemical
125 assays were carried out in a three-electrode electrochemical cell which consisted of the following: B-
126 UNCD_{ws}/TDNT/Ti, Pt plate (Degussa) and Ag/AgCl (~3.0 M KCl, Analyser Co.) used as working, counter,
127 and reference electrodes, respectively. The specific capacitance values were determined by the double-layer
128 capacitance (C_{dl}) method as described in (McCrory et al., 2013). The LSV analyses were performed in a
129 potential window ranging from 0 to 3.0 V *vs.* Ag/AgCl at scan rate of 20 mV s⁻¹. The impedance analyses were
130 conducted at 2.3 V *vs.* Ag/AgCl, with potential perturbation of 25 mV (rms) and frequency range of 10 mHz
131 to 100 kHz. The EIS data were analyzed using an electric equivalent circuit (EEQC) with the aid of the Nova®

132 2.1.4 software. Water contact angle measurements were performed using Attension Theta Flex tensiometer by
133 pouring water droplets (of 5 μL) on the B-UNCD_{WS}/TDNT/Ti electrode.

134 2.3 Anodic oxidation experimental setup and analytical techniques

135 The electrochemical treatment of CBR in 50 mM K_2SO_4 , at $\text{pH} = 7.0$, was carried out in a 250 mL lab-scale
136 glass reactor operated at 400 rpm magnetic stirring rate, at 25 °C. The anode/cathode pair employed for the
137 conduct of the experiments was as follows: B-UNCD_{WS}/TDNT/Ti (geometric area of 2.0 cm^2) – as anode, and
138 a platinum wire – as cathode. The electrodes were positioned vertically with 1.0 cm distance between them.
139 All experiments were performed at constant current density (j) using a power supply from MINIPA (MPL-
140 3305). Prior to the conduct of each experiment, the electrodes were cleaned using a 50 mM K_2SO_4 solution at
141 $j=100 \text{ mA cm}^{-2}$ for 20 min. The drinking water used in the experiments was obtained from the water treatment
142 plant in the city of Bariri, São Paulo State, Brazil – the effluent was stored at 4 °C. Table 1 shows the physical
143 chemical characterization of the real effluent. At predetermined periods of time (0, 5, 10, 15, 20, 30, 40, 50
144 and 60 min), the samples were collected, filtered, and injected into the Shimadzu High-Performance Liquid
145 Chromatograph (HPLC) for the analysis of the rate/degree of carbaryl removal. A C18 column (250×4.6, 5
146 μm) was used for the HPLC analysis, and the mobile phase employed consisted of a mixture of
147 water/acetonitrile (ratio 60:40) applied at a flow rate of 1.0 mL min^{-1} . The electric energy per order (EE/O), a
148 figure of merit established by the IUPAC (Lanzarini-Lopes et al., 2017), was estimated based on Eq. (3) in
149 order to determine the economic viability of the AO process.

$$150 \quad EE/O = (\text{kWh m}^{-3} \text{order}^{-1}) = \frac{E_{\text{cell}} I t}{V_s \log(c_0/c_f)} \quad (3)$$

151 where E_{cell} is the cell potential (V), I is the current intensity (A), t is the experiment time (s), V_s is the solution
152 volume (L), and c_0 and c_f correspond to the initial and final concentrations of CBR (Garcia-Segura et al., 2018).

153 The mineralization of the pollutant was evaluated by the Total Organic Carbon (TOC) technique using the
154 Shimadzu VCPN TOC equipment. Carboxylic acids and nitrogenous species were detected using the Metrohm
155 Ion Chromatography system, as described by (dos Santos et al., 2021a).

156

157 **Table 1.** Physical-chemical characterization of the drinking water employed in the experiments.

Physical Characteristics	Values
pH	7.50
Conductivity (uS cm ⁻¹)	129.7
Total organic carbon (mg C L ⁻¹)	0.45
Chemical Characteristics	Values (mg L⁻¹)
Ammonia (NH ₄ ⁺)	0.134
Calcium (Ca ²⁺)	12.79
Magnesium (Mg ²⁺)	2.94
Potassium (K ⁺)	1.23
Sodium (Na ⁺)	4.47
Chloride (Cl ⁻)	3.31
Nitrate (NO ₃ ⁻)	0.72
Sulfate (SO ₄ ²⁻)	1.55

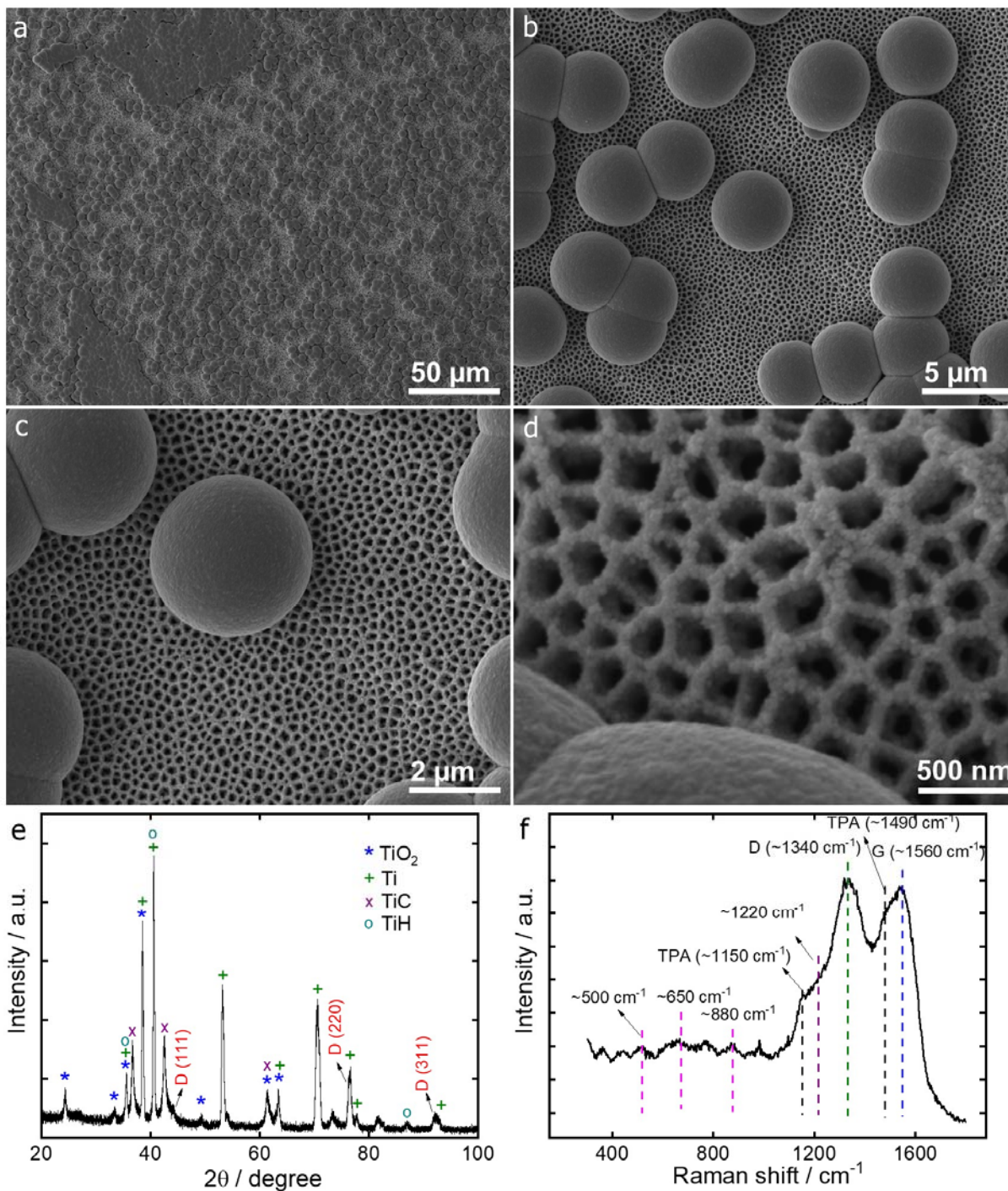
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159 **3. Results and discussion**

160 *3.1. Morphological, physical, and electrochemical characterizations of the B-UNCD_{WS}/TDNT/Ti*

161 Figure 1(a-d) shows the remarkable homogeneous morphology of the UNCD_{WS}/TDNT/Ti with different
 162 growth planes obtained after chemical vapor deposition on TDNT in different magnifications. As can be
 163 observed, the entire surface of the electrode is covered by a thin layer, and one will notice the presence of a
 164 diamond film in the pore walls which helps maintain the porosity of the electrode surface. Furthermore, one
 165 can see clusters of ballas diamond which are distributed on the sample surface. In the XRD analysis (Fig. 1e),
 166 the crystalline peaks observed were identified as TiO₂, TiC, TiH, and Ti –based on the Inorganic Crystal
 167 Structure Database (ICSD: 9658, 044494, 044747, and 076144, respectively). The diamond peaks (111), (220),
 168 and (311) present in $2\theta = 44.1^\circ$, 76.3° , and 91.9° can be found convoluted with other peaks (Ownby et al.,
 169 1992). The (220) preferential orientation in the diffractogram is related to the high nucleation process which
 170 is enhanced by the TiC – derived from the formation of TiO₂ on the TDNT substrate, present on the electrode
 171 surface (Vernasqui et al., 2022). Fig. 1f shows the Raman spectra obtained at the standard 514 nm wavelength.
 172 As expected, the sample exhibited a typical ultranano-diamond behavior, with signal bands attributed to the
 173 formation of trans-poly-acetylene at around 1,150 and 1,490 cm⁻¹ and a band at around 1,220 cm⁻¹ which is
 174 attributed to the inclusion of boron in the diamond lattice, in addition to the usual G band (1,560 cm⁻¹, attributed
 175 to E_{2g} vibration). The diamond peak typically located at 1,332 cm⁻² for microcrystalline films is completely
 176 hidden in the sample by the D band attributed to amorphous sp² bonds, which is usually expected for these

177 films. In addition, one will observe the presence of three other peaks at around 500, 650, and 880 cm^{-1} linked
 178 to B dimers vibrations (Mermoux et al., 2002; Crisci et al., 2008; dos Santos et al., 2022).

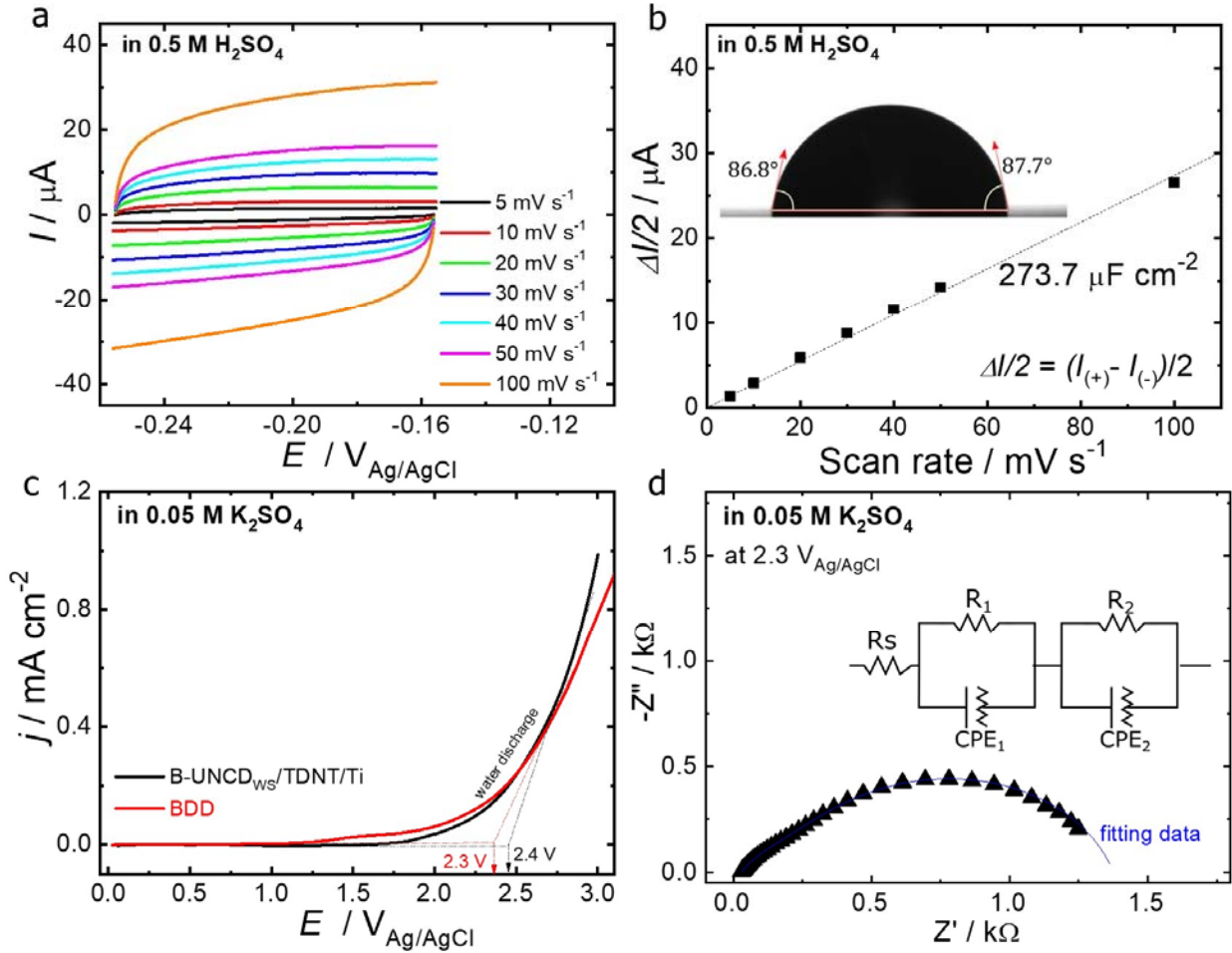


179
 180 **Fig 1.** Physical characterization of the B-UNCD_{ws}/TDNT/Ti electrode. (a-d) Representative FEG-SEM
 181 images, (e) XRD pattern, and (f) Raman spectra.

182

183 Fig. 2a shows the capacitive features of the surface of the B-UNCD_{WS}/TDNT/Ti electrode which was
184 evaluated in N₂-saturated 50mM H₂SO₄ solution. The CVs recorded at different scan rates in the double layer
185 region (centered at the open circuit potential) point to the capacitive effect of the electrode. Based on the plot
186 of average peak current *versus* scan rate in Fig. 2b, the B-UNCD_{WS}/TDNT/Ti electrode recorded specific
187 capacitance of ca. 274 $\mu\text{F cm}^{-2}$; this value is higher than the specific capacitance value obtained for micro and
188 nanocrystalline diamond films (115 $\mu\text{F cm}^{-2}$, on average) previously reported in the literature (dos Santos et
189 al., 2022). The high specific capacitance values obtained for the electrode reflect the existence of high surface
190 roughness and high active surface area, which provides the electrolyte solution access to the electrode surface
191 (Frackowiak and Béguin, 2001; Siuzdak et al., 2015). The inset of Fig. 2b shows the hydrophobicity/wettability
192 of the surface of the B-UNCD_{WS}/TDNT/Ti electrode; this was evaluated using the water contact angle
193 measurement procedure. A water contact angle of ca. 87° shows that the B-UNCD_{WS}/TDNT/Ti material is a
194 reasonably wettable substrate. A surface with intermediate wettability can provide the electrolyte solution easy
195 access to the electrode surface and facilitated mass transport of gaseous species formed on the electrode surface
196 which, when combined together, lead to the improvement of the electrolysis efficiency efficiency (Almeida et
197 al., 2008; Watanabe et al., 2010). Linear scan voltammetry (LSV) measurements were recorded in N₂-saturated
198 50 mM K₂SO₄ solution, as shown in Fig. 2c. As can be observed, the B-UNCD_{WS}/TDNT/Ti electrode exhibited
199 an onset potential for water discharge at 2.45 V *vs.* Ag/AgCl; this value is slightly higher than the values
200 previously reported for diamond films with different morphologies (dos Santos et al., 2022) and for commercial
201 microcrystalline BDD thin film - which exhibited an onset potential of 2.35 V *vs.* Ag/AgCl. Onset potential
202 values for water discharge greater than 1.23 V *vs.* SHE (ca. 1.03 V *vs.* Ag/AgCl) are expected to favor the
203 generation of reactive oxygen species (i.e. •OH) rather than oxygen evolution during the electrolysis process
204 (Kapałka et al., 2007). The seeding-free production of diamond allows the formation of highly porous
205 ultranano-structures - which are in line with the surface characteristics of the substrate used, favoring the
206 formation of extremely thin diamond films. In fact, this behavior is observed in the B-UNCD_{WS}/TDNT/Ti
207 electrode, since an extremely thin-porous diamond film covering the TDNT gives rise to relatively lower
208 current densities for water discharge compared to the current densities typically presented by micro- and nano-
209 diamonds (dos Santos et al., 2022) .

210



211

212 **Fig 2.** Electrochemical characterization of the B-UNCD_{ws}/TDNT/Ti electrode. (a) Cyclic voltammograms
 213 obtained from the application of N₂-saturated 0.5 M H₂SO₄ as supporting electrolyte at different scan rates. (b)
 214 $\Delta I/2$ vs. scan rate plot; inset: water contact angle measurement. (c) LSV curves for B-UNCD_{ws}/TDNT/Ti and
 215 commercial BDD electrodes obtained in N₂-saturated 0.05 M K₂SO₄ (employed as supporting electrolyte) and
 216 scan rate of 20 mV s⁻¹. The scan started at 0 V vs. Ag/AgCl. (d) Complex-impedance plane representation;
 217 inset: simulated electric equivalent circuit (EEQC).

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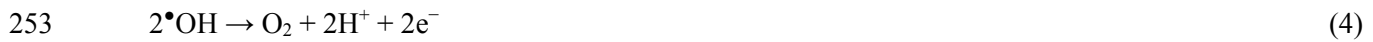
219 Fig. 2d shows the complex-impedance plot obtained for the B-UNCD_{ws}/TDNT/Ti electrode in N₂-
 220 saturated 50 mM K₂SO₄ close to the water discharge onset potential. The EIS response revealed the capacitive-
 221 resistive character of the ultranano-diamond electrode, which is characterized by two structural layers linked
 222 to the presence of TDNT/Ti. The simulated electric equivalent circuit (EEQC) can be represented by a
 223 resistance related to the electrolyte and two RQ components, where both are connected in series (Ennaceri et
 224 al., 2020) (R(RQ)(RQ) circuit, c.f. inset of Fig. 2d). The first RQ component is associated with large porous

225 spherical ultranano-diamond structures; these structures consist of a charge transfer resistance and a constant
226 phase element (CPE) which is linked to the double layer capacitance (Almeida et al., 2008). The second RQ
227 component, which exhibits a more resistive character, is linked to porous TDNT which is finely coated by
228 ultranano-diamond film probably with some exposed TDNT dots (Ennaceri et al., 2020). The results obtained
229 from the physical and electrochemical characterization analyses show that the B-UNCD_{ws}/TDNT/Ti electrode
230 has outstanding physical-chemical properties, and this makes it highly suitable for application in
231 electrocatalytic water technologies as will be discussed in the next section.

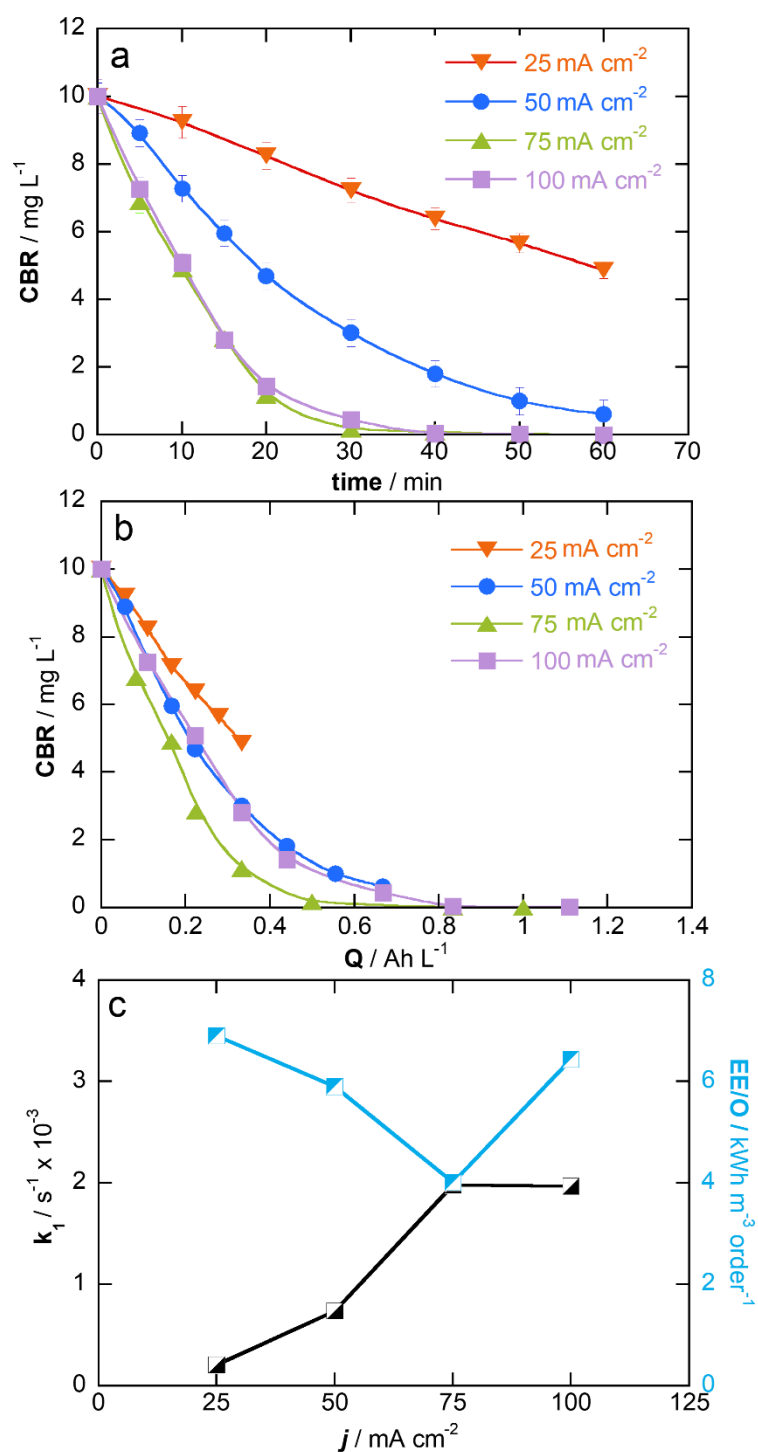
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233 3.2. Electrochemical treatment of CBR using the B-UNCD_{ws}/TDNT/Ti anode.

234 In electrochemical advanced oxidative processes (EAOPs), current density (j) is an essentially important
235 electrokinetic parameter; this parameter controls the quantity of electrons circulating in the system, and
236 consequently, the amount of $\bullet\text{OH}$ that can be generated. Bearing that in mind, the efficiency of the B-
237 UNCD_{ws}/TDNT/Ti anode was assessed based on the application of different current densities for the treatment
238 of 10 mg L⁻¹ of carbaryl (CBR) in 50 mM K₂SO₄ (used as supporting electrolyte) at pH = 7.0. Looking at the
239 results shown in Fig. 3a, one will observe that the application of the B-UNCD_{ws}/TDNT/Ti anode effectively
240 resulted in CBR degradation irrespective of the current density applied. Interestingly though, after 30 min of
241 treatment, there were changes in the degradation pattern. The following degradation rates (in decreasing order)
242 were obtained under the application of different current densities: 75 mA cm⁻² (99.9 %) > 100 mA cm⁻² (97.5
243 %) > 50 mA cm⁻² (69.9 %) > 25 mA cm⁻² (27.8 %). An approximately 9-fold increase was observed in CBR
244 degradation from the current density of 25 to 75 mA cm⁻² over time; this was certainly due to the increase in
245 the amount of $\bullet\text{OH}$ generated in the electrolysis (Eq. (1)). However, the two highest applied current densities
246 (75 and 100 mA cm⁻²) exhibited a quite similar behavior in terms of CBR removal; this behavior can be
247 attributed to the presence of parasitic/non-oxidative reactions. Indeed, the occurrence of parasitic reactions is
248 favored by the increase in current density due to the competition between $\bullet\text{OH}$ with O₂ evolution (Eq. (4)).
249 Another point worth mentioning is that due to its non-selective character, $\bullet\text{OH}$ can react with each other
250 (dimerization reaction), producing hydrogen peroxide (H₂O₂), which is a weaker oxidant compared to $\bullet\text{OH}$ –
251 see reaction 5 below (Brillas et al., 2010; Srivastava et al., 2021). Both reactions 4 and 5 decrease the oxidative
252 power of the system once they consume $\bullet\text{OH}$.



255 From the viewpoint of the applied charge, the pattern of CBR degradation shown in Fig. 3b is quite similar
256 to that observed in Fig. 3a. At 0.33 Ah L^{-1} , the final CBR concentrations obtained from the application of
257 current densities of 25, 50, 100 and 75 mA cm^{-2} were 4.87, 3.01, 2.81, 1.16 mg L^{-1} , respectively. In fact, the
258 optimal j value that promoted a complete removal of CBR was 75 mA cm^{-2} , with charge consumption of 0.50
259 Ah L^{-1} ; for comparison purposes, the application of the current density of 100 mA cm^{-2} requires charge
260 consumption of 0.84 Ah L^{-1} to obtain a complete removal of CBR. Taking a closer look at the relationship
261 between the pseudo-first-order kinetics constant (k_1) and EE/O (Fig. 3c), one will observe that when k_1
262 increases, EE/O decreases – see the following results obtained at different current densities: 25 mA cm^{-2}
263 ($2.1 \times 10^{-4} \text{ s}^{-1}$, $R^2 = 0.994$; $6.90 \text{ kWh m}^{-3} \text{ order}^{-1}$), 50 mA cm^{-2} ($7.4 \times 10^{-4} \text{ s}^{-1}$, $R^2 = 0.991$; $5.87 \text{ kWh m}^{-3} \text{ order}^{-1}$),
264 100 mA cm^{-2} ($1.8 \times 10^{-3} \text{ s}^{-1}$, $R^2 = 0.983$; $6.44 \text{ kWh m}^{-3} \text{ order}^{-1}$) and 75 mA cm^{-2} ($1.9 \times 10^{-3} \text{ s}^{-1}$, $R^2 = 0.987$; 4.01
265 $\text{kWh m}^{-3} \text{ order}^{-1}$). These results clearly show that high j values are required for the effective degradation of
266 CBR; in essence, this finding shows that there is a mass transfer mechanism controlled by diffusion in which
267 the porosity plays a fundamental role by increasing the anode effective surface and favoring the pollutants-
268 oxidant contact. The supply of energy above $j = 75 \text{ mA cm}^{-2}$ does not translate into better performance and
269 greater cost-effectiveness of the process, as observed in Figs. 3a-c. In fact, the application of current densities
270 above 75 mA cm^{-2} may fuel the occurrence of non-oxidizing reactions as previously discussed; in contrast, the
271 application of current densities below 75 mA cm^{-2} may cause resistance in the system probably due to the low
272 level of boron on the anode surface. Thus, the current density of 75 mA cm^{-2} was selected for the conduct of
273 further experiments.



274 **Fig 3.** Effect of current density on the degradation of CBR concentration relative to (a) electrolysis time
 275 and (b) applied charge. (c) Pseudo-first order kinetic decay of CBR and electrical energy per order versus
 276 current density. Operating conditions: 10 mg L⁻¹ of CBR; 50 mM of K₂SO₄ (used as supporting electrolyte) at
 277 pH = 7.0.

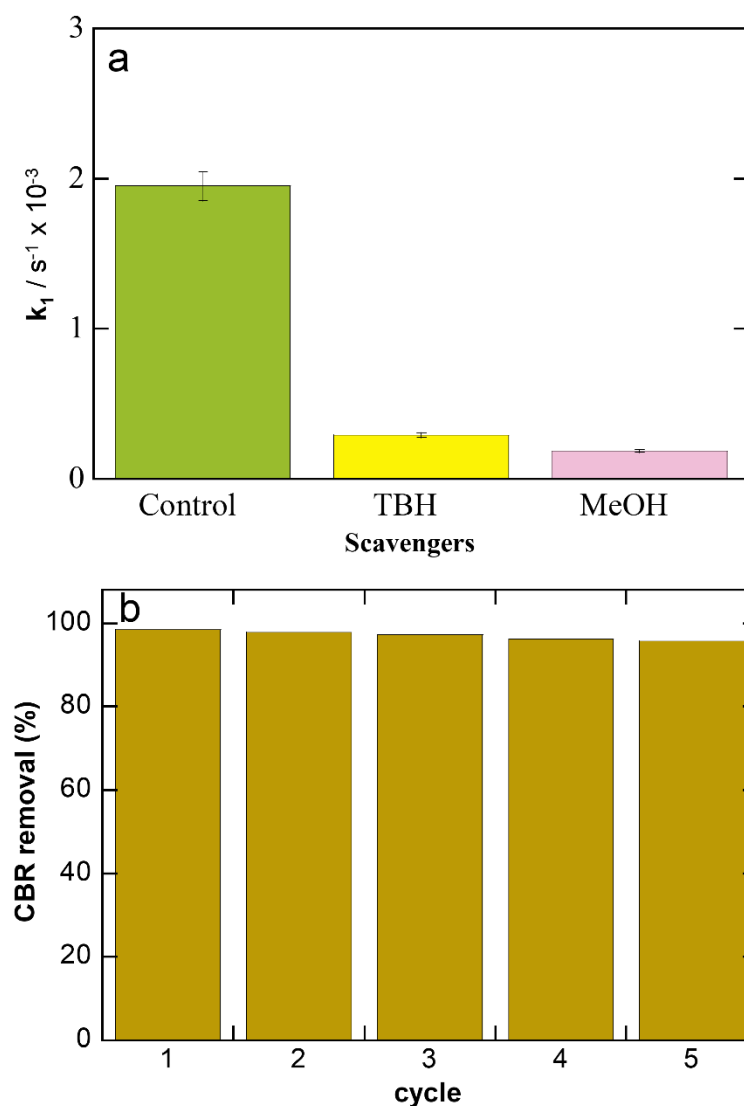
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279 The AO process allows the in-situ generation of radical species. To gain a meaningful understanding
280 regarding the contribution of these radical species in the degradation of CBR, TBH was used to scavenge $\bullet\text{OH}$,
281 while MeOH was used to scavenge $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$. Different pollutant:scavenger ratios (1:50, 1:100, 1:200,
282 1:400) were used to find the optimal testing concentration. The k_1 values obtained for CBR removal were found
283 to be influenced by the presence of scavengers up to the ratio 1:200; the values then remained constant at
284 higher concentrations – after 1:200 (data not shown). So, when the ratio of 1:200 was employed, the application
285 of the TBH and MeOH scavengers led to a reduction in the k_1 value from $1.9 \times 10^{-3} \text{ s}^{-1}$ to $2.9 \times 10^{-4} \text{ s}^{-1}$ and 1.8×10^{-4}
286 s^{-1} (Fig. 4a), respectively. A careful analysis of these results showed that $\bullet\text{OH}$ - the main oxidant, represented
287 84.7% of the results ($= 100 \times (k_{1,\text{control}} - k_{1,\text{TBH}})/k_{1,\text{control}}$), while $\text{SO}_4^{\bullet-}$ represented only 5.8% ($(k_{1,\text{TBH}} -$
288 $k_{1,\text{MeOH}})/k_{1,\text{control}}$), and the rest accounted for 9.5%. It should be noted that $\text{SO}_4^{\bullet-}$ can be electrogenerated through
289 direct oxidation via one-electron of sulfate - see Eq. (6). The remaining 9.5% can be attributed to non-radical
290 oxidation which is associated with the direct oxidation of the pollutant and persulfate activation - both
291 phenomena occurring on the anode surface (Song et al., 2018).



293 The stability of the *B-UNCD_{WS}/TDNT/Ti* electrode for longer operation periods was evaluated using five
294 consecutive fed-batch tests of 60 min duration. During all the tests, the operating conditions were kept
295 unchanged. As can be seen in Fig. 4b, the carbaryl removal rate was practically the same (around 100%) for
296 the first five tests; this result points to the efficient performance and long-term stability of the *B-*
297 *UNCD_{WS}/TDNT/Ti* electrode applied for the degradation of recalcitrant compounds in water.

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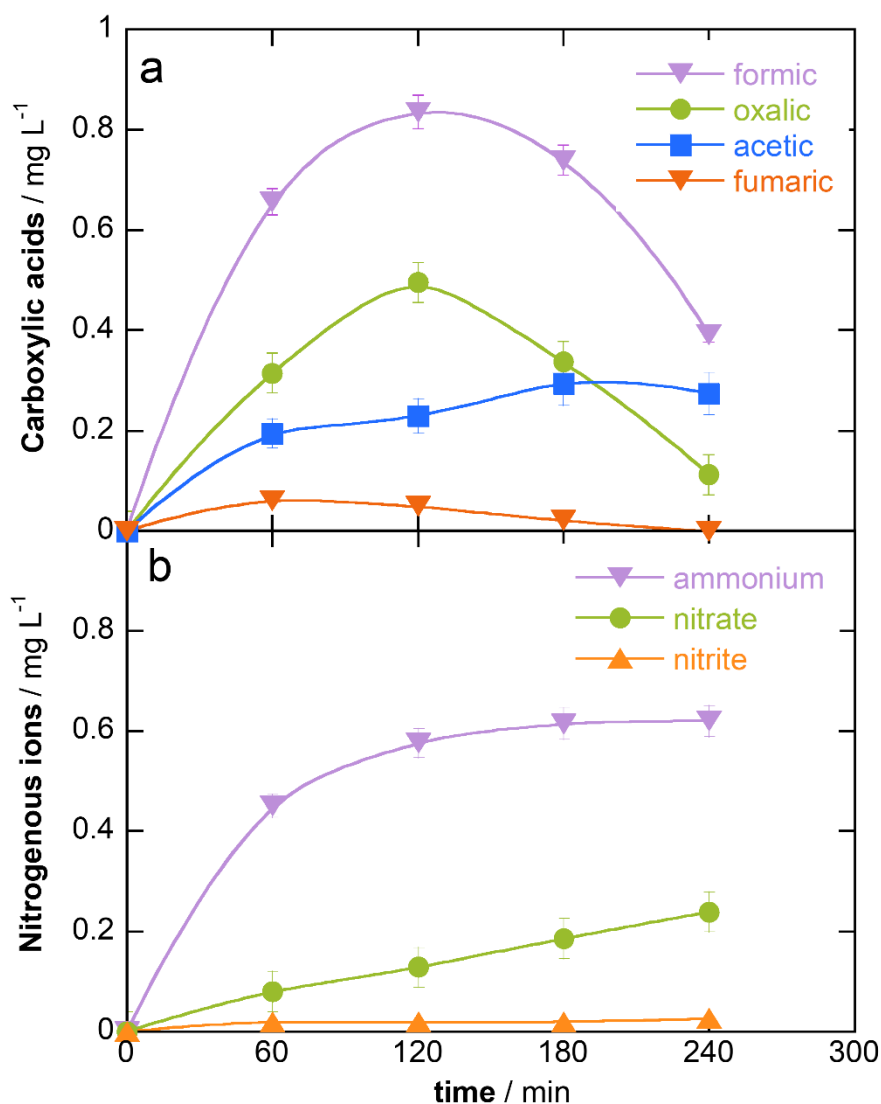


299 **Fig 4.** (a) Effect of the application of different scavengers on the pseudo-first order kinetic decay of CBR.
 300 (b) Effect of the B-UNCD_{WS}/TDNT/Ti electrode on CRB removal over 5 cycles of electrolysis. Operating
 301 conditions: 10 mg L⁻¹ of CBR; 50 mM of K₂SO₄ at pH = 7.0 (employed as supporting electrolyte).

302

303 Although complete CBR degradation was obtained, the environmental problem has still not yet to be
 304 addressed. In certain treatment processes, the final by-products obtained after the treatment are found to be
 305 more persistent than the original pollutant. In view of that, a thorough analysis was performed to study the
 306 mineralization process ($\approx 95\%$ - data not shown) and identify/quantify the final by-products generated after
 307 the pollutant treatment process. Fig 5a shows the time-course of the evolution of the concentration of short
 308 linear carboxylic acids derived from the opening of the naphthalene group present in the CBR. The results
 309 obtained from the mineralization analysis pointed to the presence of a mixture of oxalic, fumaric, formic, and

310 acetic acids, with maximum concentrations of 0.496 mg L⁻¹ (120 min), 0.061 mg L⁻¹ (60 min), 0.835 mg L⁻¹
311 (120 min) and 0.295 mg L⁻¹ (180 min), respectively, which were partially converted to CO₂, with the exception
312 of the fumaric acid which was completely mineralized. In addition, an analysis was also performed in order to
313 study the evolution of nitrogenous ions – see the results obtained in Fig. 5b. Looking at the results shown in
314 Fig 5b, one will observe that the initial amount of nitrogen in the CBR (0.649 mg L⁻¹) was mostly converted
315 to ammonia (0.62 mg L⁻¹ - 74.30%), followed by nitrate (0.23 mg L⁻¹ - 8.32%) and nitrite (0.026 mg L⁻¹ -
316 1.23%). The remaining 16.15% of the total mass was probably related to volatile N-products, as reported in
317 previous studies (Çelebi et al., 2015; Oriol et al., 2021). Depending on their concentration levels, the exposure
318 to nitrate, nitrite, and ammonia ions may pose serious risks to human health. However, it is worth mentioning
319 that the remaining concentrations of nitrate and nitrite after the electrochemical treatment were found to be
320 below the maximum contamination level (MCL) stipulated for drinking water according to the US
321 Environmental Protection Agency (EPA): 10.0 and 1.0 mg N L⁻¹, respectively. According to the same agency,
322 there is no legally established MCL for ammonia.



324 **Fig 5.** Time course of the evolution of (a) short linear carboxylic acids and (b) nitrogenous species
 325 during the treatment of 10 mg L⁻¹ of CBR in 50 mM K₂SO₄, with pH = 7.0 (employed as supporting
 326 electrolyte), and $j = 75 \text{ mA cm}^{-2}$.

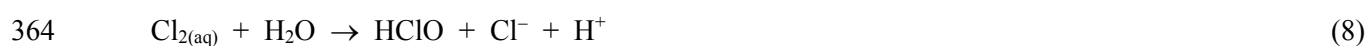
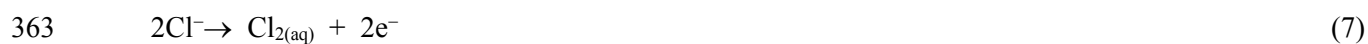
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328 3.3. Electrochemical treatment of CBR in real medium

329 Clearly, the experiments conducted using ultrapure water helped us understand the degree of efficiency of
 330 the treatment process applied in this study and its mechanism of operation for the removal of CBR in synthetic
 331 medium. However, conducting experiments in synthetic aqueous medium alone is not sufficient for us to have
 332 a more realistic understanding of the treatment process and the impact of the presence of other compounds
 333 (i.e., inorganic ions, natural organic matter) on the pollutant degradation. Thus, based on the satisfactory results
 334 obtained from the experiments conducted using synthetic medium, we evaluated the efficiency of the *B*-

335 *UNCDWS/TDNT/Ti* anode when applied for the treatment of real effluents. The analysis was conducted using
336 the optimal current density of 75 mA cm^{-2} in real drinking water spiked with different concentrations of CBR
337 ($5.0 - 20 \text{ mg L}^{-1}$). As can be observed in Fig. 6, irrespective of the initial concentration of CBR, there was a
338 sharp decrease in the pollutant concentration in the first 15 min of reaction; thereafter, the decrease in the
339 pollutant concentration took a more gradual pattern. The initial concentration of CBR is a parameter of interest
340 since it provides one with fundamental information regarding the range of pollutant concentration that can be
341 efficiently treated in reasonable periods of time. For instance, in 30 min of treatment, the pollutant removal
342 rates obtained were 99.8 %, 93.5 % and 89.4% for the initial concentrations of 5.0, 10, and 20 mg L^{-1} ,
343 respectively.

344 The analysis of real water samples shows the presence of other compounds besides the pollutant and the
345 electrolyte, and this can positively or negatively affect the removal of the contaminant. A comparison of the
346 results obtained from the experiments conducted using real effluent with the results obtained from the
347 experiments conducted using synthetic medium under the same operating conditions showed that the span of
348 time required to obtain a complete removal of the pollutant was 1.2 times higher in the real effluent than in the
349 synthetic medium (with a reduction of k_1 from $1.9 \times 10^{-3} \text{ s}^{-1}$ to 1.6×10^{-3} for the experiment in real effluent and
350 in synthetic medium, respectively). The presence of natural organic matter in the real medium (Table 1)
351 competes for the electrogenerated oxidants, undermining the efficiency of the process. On the other hand, the
352 presence of chloride in real medium allows the electrogeneration of active chlorine species ($\text{Cl}_{2(\text{aq})}$ – Eq. (7);
353 HClO – Eq. (8); OCl^- – Eq. (9)), which may enhance the performance of the system. Generally, these species
354 are generated at the following pH levels: $\text{pH} \leq 3$ ($\text{Cl}_{2(\text{aq})}$), pH range 3-8 (HClO), and $\text{pH} > 8$ (ClO^-). Thus, the
355 oxidation of organic matter mediated by active chlorine species is found to be stronger in acidic than in alkaline
356 media due to the higher standard potential of $\text{Cl}_{2(\text{aq})}$ ($E^\circ = 1.36 \text{ vs SHE}$) and HClO ($E^\circ = 1.49 \text{ vs SHE}$) compared
357 to that of ClO^- ($E^\circ = 0.89 \text{ vs SHE}$) (Burgos-Castillo et al., 2018; Garcia-Segura et al., 2018b). However, it
358 seems that the presence of chlorine species in the medium did not have such a significant impact on CBR
359 removal; this was probably because of the low initial concentration of chloride, which was not enough to
360 induce the electrogeneration of high amount of active chlorine species. It is interesting to note that at the end
361 of the experiment, no chloro oxyanions, such as chlorate and perchlorate, were detected in the solution; this is
362 evidently reassuring because these species are carcinogenic.

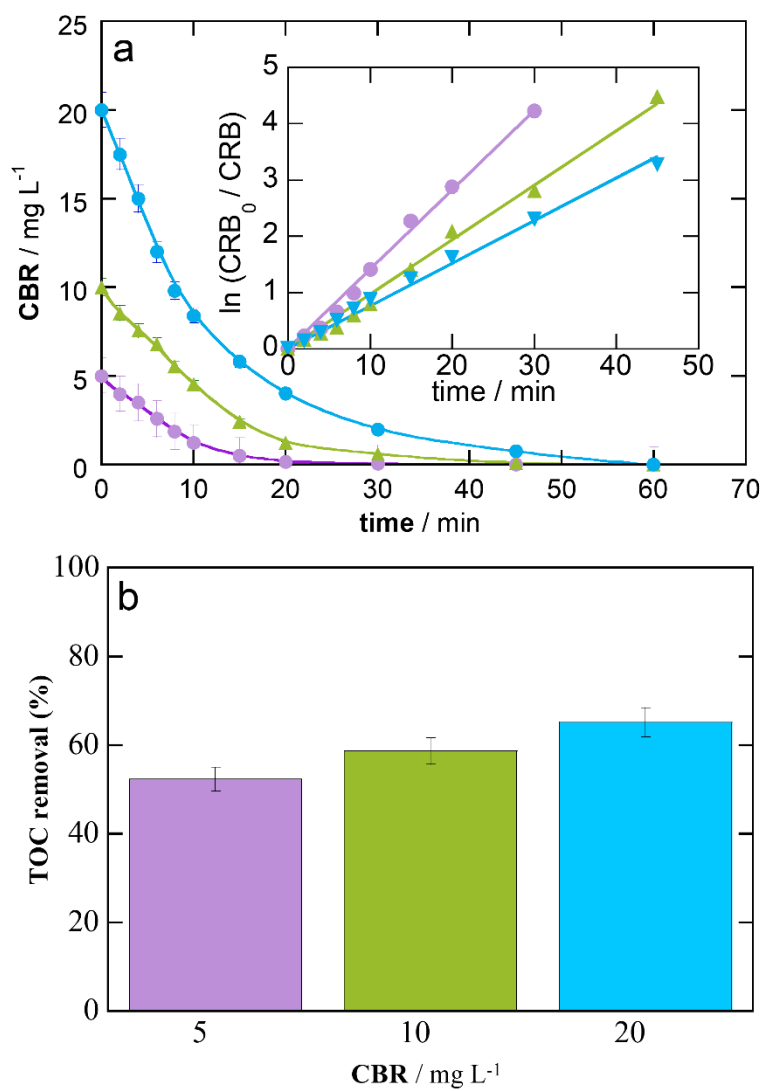


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367 With regard to the mineralization tests performed using the real effluent (Fig. 6b), the results obtained showed
368 that none of the experiments yielded 100% removal rates. In fact, at the end of the treatment, TOC removal
369 rates of 52.3, 58.7 and 65.2% were obtained for the tests conducted using 5, 10 and 20 mg L⁻¹ of CBR,
370 respectively. Increasing the concentration of CBR may lead to the generation and accumulation of a huge
371 number of intermediates and by-products, and these additional compounds compete with the pollutant
372 molecules to react with the same amount of •OH radicals, thus decreasing the removal efficiency of the process.
373 It is worth pointing out that the pattern of TOC removal was found to be entirely different from that observed
374 in CBR degradation. In the mineralization experiments, the removal efficiency was found to be higher for the
375 test with higher initial CBR concentration. The mineralization phenomenon is boosted in the presence of higher
376 organic load, diminishing the extent/magnitude of parasitic reactions. Based on the results obtained in this
377 study, it is clear that the *B-UNCD_{WS}/TDNT/Ti* electrode has proven to be highly efficient when applied for the
378 removal of different concentrations of CBR. Regarding CBR mineralization, the application of the proposed
379 electrode was found to require longer treatment times to obtain satisfactory results; still, the TOC removal
380 rates of 52.3– 65.5 % obtained in 60 min of treatment are found to be reasonable considering that this is the
381 first time the proposed electrode has been employed for CBR degradation. The encouraging results obtained
382 in this study (based on the application of the proposed electrode for CBR removal) can be most likely attained
383 when the proposed technique is applied for the treatment of other recalcitrant water pollutants.

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387 **Fig 6.** (a) Carbaryl degradation over time and (b) mineralization after 60 min treatment of real water with
 388 different CBR concentrations at current density of 75 mA cm^{-2} .

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4. Conclusions

The present work reported the synthesis of B-UNCD_{ws}/TDNT/Ti electrodes with extremely thin diamond films using an innovative methodology without seeding substrate pre-treatment and their successful application for the treatment of water containing recalcitrant compounds. The material proposed in this study was found to possess suitable electrochemical properties, including highly porous ultranano-structures, improved specific capacitance (274 $\mu\text{F cm}^{-2}$) and high onset potential for water discharge (ca. 2.4 V vs. Ag/AgCl); these properties favored the generation of reactive oxygen species during the electrolysis process. Owing to the combination of the aforementioned properties, the application of the proposed electrode at the current density of 75 mA cm⁻² contributed effectively toward the complete removal of CBR in synthetic medium in 30 min ($Q=0.5 \text{ Ah L}^{-1}$) with electric energy consumption per order of 4.01 kWh m⁻³ order⁻¹. The use of scavengers in the treatment process helped confirm that $\bullet\text{OH}$ was the main oxidant species (with effective contribution of $\approx 84.7\%$) that took part in the degradation of the pollutant. The results obtained from the analysis of the final by-products of the electrolysis pointed to the presence of carboxylic acids, including acetic, formic, fumaric and oxalic acids, but zero or minimal concentrations of these acids were detected at the end of the electrochemical treatment. The concentrations of nitrogenated species monitored over the treatment period were found to be within the maximum contamination level for drinking water; this evidently helps reduce the health risks posed by the presence of these substances in water. The results obtained from the application of the proposed electrode for the removal of CBR in real effluents were found to be satisfactory; complete degradation was obtained within 20-60 min treatment of effluents containing 5 – 20 mg L⁻¹ of CBR while TOC removal rates of 52.3– 65.5 % were obtained after 60 min of treatment. This work highlights the advantages of improving the synthesis of BDD electrode and its contribution toward enhancing the effectiveness and competitiveness of electrochemical advanced oxidation processes when applied for the degradation of recalcitrant pollutants.

416 **Acknowledgments**

417 The authors acknowledge the financial support provided by the following Brazilian research funding
418 agencies: Brazilian National Council for Scientific and Technological Development - CNPq (grant
419 #465571/2014-0 and #303943/2021-1), São Paulo Research Foundation - FAPESP (grants #2014/50945-4,
420 #2017/23464-3, #2017/10118-0, #2019/04421-7, #2019/20634-0, #2019/00592-1 and #2021/07615-7) and the
421 Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES – Finance Code 001) in support of
422 this work. Haruna L. Barazorda-Ccahuana is grateful for the financial assistance received in support of the
423 internal project UCSM 7309-CU-2020. Dr. Ana S. Fajardo is likewise grateful for the funding granted by the
424 European Union Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant
425 agreement No 843870.

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