

On the way to raise the Technology Readiness Level of diamond electrolysis

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Abstract

During the last decades, hundreds of scientific papers have focused on the use of anodes consisting of conductive diamond coatings, pointing out their outstanding capacity for the mineralization of organic pollutants contained in wastewater. Most of the works consists of the evaluation of the removal of different types of organics, with concentrations ranging from few micrograms up to several grams per liter, in different matrixes, from synthetic solutions containing large concentrations of sulfate or chloride to real wastewater. However, the technology readiness level has been stagnant in the lab at levels 4-5 and, because of the promising of the results published, there is a need to raise it up to values which indicate the full-scale applicability. In this review, two of the main challenges that should be overcome to reach higher levels are reviewed. The first is the improvement in the formulation of the doped diamond coatings targeting to be tailored for dedicated applications. Its significance is explained in terms of the high influence of these anodic surfaces on the efficiencies of the degradation of complex anthropogenic organics and, overall, on the efficient production of oxidants, that extend the oxidation of pollutants from the nearness of the anode surface to the bulk of the wastewater during electrolysis. The second is the improvement in the design of the electrochemical cell that integrates the diamond anode, trying to take advantage of the outstanding properties of diamond not only by improving the mass transport rates but also by optimizing the

combination of its very efficient oxidation paths with other non-electrochemical oxidation mechanisms.

Keywords

Tailoring; diamond; electrochemical cell; process integration

Highlights

- There is a need to increase TRL for electrolysis of wastewater with diamond anode
- Tailoring of the formulation of diamond and cell design are interesting paths to raise TRL
- Tailoring of diamond coatings influences on the in-situ production of oxidants during the electrolysis of wastewater
- Mass transport enhancements and efficient combination with other technologies attained with improved cell designs.

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1. Diamond coatings: necessity of a breakthrough material at the turn of the century.

Electrodes consisting of coatings of conductive diamond became an important revolution in the field of the electrochemical treatment of wastewater at the turn of the 20th century [1-4]. Before their production, platinum, graphitic carbon, and different formulations, including metal oxides, were occasionally tested for the removal of organics in wastewater, with varying efficiencies [5-9]. In the case of the graphitic electrodes, the electrochemical combustion of the electrode was the main observation, especially when operation conditions during testing changed from the low technology readiness level (TRL) studies in which voltametric characterizations were carried out up to bulk electrolysis. Application of large cell voltages damaged these electrodes and made their real application impossible. In the case of the platinum, better results were obtained but the cost of the material made not feasible its use in large scale applications, even using coatings of platinum on different supports like titanium. Soft oxidation was also a very important handicap with the formation of many intermediates and even polymers during the oxidation of many different types of aromatic organics. The coatings based on mixtures of metal oxides were found to be more promising, but it was found significant differences in their performance depending on the different contents in metal oxides and a huge influence of the supporting electrolyte on the efficiency of the degradation of organics contained in wastewater. Presence of ruthenium oxides was found to promote the formation of chlorine oxidants in the bulk, and this fact increases the efficiency in the conversion of organics, but formation of chlorinated hydrocarbons, usually more hazardous than the parent compounds and formation of polymers (also found typically with the use of platinum), especially when oxidizing aromatic species, were important handicaps difficult to be overcome [8]. It was observed that the use of tin and lead oxides obtained higher efficiencies than that of ruthenium and iridium, although stability of the

coatings was found to be a major handicap for the development of the technology [1, 10-15]. Thus, presence of lead or tin species in the electrolyzed wastewater was found to be a key disadvantage, difficult to be overcome [16, 17]. Currently, a great deal of effort is being made to retake this topic.

In contrast, diamond coating appeared as a very promising material with properties that were dreamed by electrochemists time ago [18]:

- large electrochemical window, meaning low interaction with the supporting electrolyte up to the limit of the oxidation/reduction of water,
- robustness, meaning low changes in surface after prolonged application and
- high efficiency in the degradation of organics, meaning that only diffusion control affects to the efficiency of the system and that in operating with high loads of organics, efficiencies close to 100% were the rule.

Diamond is not a good electric-conductivity material. In fact, it is a well-known insulating material. However, in being doped with different types of atoms its electric conductivity increases importantly and its application to the electrochemical treatment of wastewater becomes feasible. Among the different doping atoms, boron has become the reference, opposite to what it seemed at the turn of the century in which nitrogen and fluorine doping were also found to be attractive. A breakthrough point regarding the application of diamond to the electrochemical removal of organics contained in wastewater was the confirmation of the formation and the active role of hydroxyl radicals [19] with these electrodes because of two reasons [20-24]:

- It allowed to include electrochemical oxidation among the selected club of the “advanced oxidation technologies”, that were one of the most significant topics of research in the beginning of the century. In fact, together with other technologies

based on the electrochemical production of hydrogen peroxide, it constituted a very interesting subcategory: the electrochemical advanced oxidation processes, in which hundreds of publications have been made in the last years.

- Mineralization, that is the conversion of organics into carbon dioxide, was found to be the most favored oxidation mechanisms, avoiding formation of chlorinated organics and polymers, that was found as a major handicap in using other types of materials as anode during the electrochemical treatment of wastewater.

2. Challenges for diamond coatings in the treatment of wastewater for the next years

Major challenges in the development of the technology were related to the price of the electrodes, the applicability of different pollutants and to the enhancement in the properties of the coatings and they focused the scientific discussion for two decades. Initially, it was assumed that the coating composition had a low influence on the performance. This was found to be not true, and many studies demonstrated that parameters like the sp^3/sp^2 ratios, the boron content and, even, the supporting material for the coating were of extreme importance, either for the oxidation of organics [25, 26] or even for the production of oxidants [27]. Regarding this later point, worth to highlight that the outstanding properties of diamond coatings make that the most important and exciting environmental application is not the oxidation of organics but the formation of oxidants, which during the treatment of wastewater is directly related to most significant contribution in terms of degradation of organic pollutants. The extreme electrochemical window makes possible what it is not efficient with other electrodes: the formation of radicals such as the sulfate, phosphate, carbonate, or nitrate and this leads to a very important “new electrochemistry” with importance in both:

- the treatment of organics, because these radicals lead to the formation of many oxidants that can extend the oxidation from the Nernst layer, where the OH radicals are present and further react with organics [28], to the bulk of the wastewater and transform the electrochemical cell from a surface heterogeneous reactor (typically diffusion controlled) to a more efficient volumetric homogeneous reactor.
- the production of species of interest to be used in different applications after convenient storage. Among them, worth to highlight peroxospecies like peroxosulfate, peroxocarbonate, peroxophosphate and other species like ozone.

Currently, after hundreds of papers in which different organic pollutants at different concentrations and with different matrixes have been tested and described, there is still one important point to be overcome in the electrochemical degradation of organics with diamond electrodes: to raise the technology readiness level [29], that is to go further from the lab to the real full-scale application. Here, there are two main handicaps to be overcome:

- The complete understanding of how the diamond material can affect to the oxidation of different organics and to the production of oxidant species. It is needed to develop tailored coatings for each particular application with good properties for degrading a particular species or to promote the formation of oxidants in the wastewater that undergoes electrochemical treatment.
- The development of new electrochemical cells capable to enhance mass transfer. Diamond coatings can attain very high efficiencies and, in order to improve them, it is required to improve mass transfer in the electrochemical cell or to develop cells in which the synergistic combination of different technologies (such as application of ultrasounds or light irradiation) can increase the efficiency of the processes. Even to

combine the anodic and the cathodic processes for the promotion of harsher oxidation conditions.

The most recent progress in both approaches is going to be reviewed in the two following sections of this work, that it is aimed to clarify which is the state of the art in the cell design for applications in which diamond coatings are to be used and which is the state of the art in the knowledge about how the formulation of the diamond coating may affect to the performance of different types of oxidation, trying to go further in the tailoring of the diamond use.

3. The diamond-tailoring challenge

One of the main challenges regarding the synthesis of BDD diamond electrodes is the developing of tailored coatings, looking for an improvement in the oxidant generation and/or the pollutants degradation. Some crucial characteristics in the performance of the BDD electrodes are their composition and the crystallinity. Recent studies have centered in the study of nanocrystalline coatings against the traditional micro crystallinity, the optimum boron doping level, the substrate nature employed in the synthesis or the ratio of diamond to graphitic carbon forms (sp^3/sp^2 ratio). However, there is not a systematic study evaluating all these characteristics, being secondary their evaluation in most cases, despite researchers recognize the extreme importance of the characteristics of diamond on the results that can be attained. A selection of the most significant contributions, made in the last years, and showing how the different parameters related to the BDD diamond structure and composition affects to wastewater treatment, are summarized in Table 1.

Table 1. Influence of the diamond formulation on its performance in electrochemical oxidation of wastewater

Variables of the study	Experimental conditions	Main results	Reference
[B]/[C] ratio: 1000, 2000 and 10000 ppm	<p>Cell system:</p> <p>Si/BDD anodes (crystalite 5-10 nm) using Microwave Plasma Assisted Chemical Vapor Deposition.</p> <p>Film thickness: 2 μm.</p> <p>Stainless steel cathode.</p> <p>Ag/AgCl (0.1 M KCl) as reference electrode.</p> <p>Surface area: 4 cm^2.</p> <p>Electrochemical oxidation:</p> <p>Dye rubin F-2B: 20 mg L^{-1}.</p> <p>Current density: 2.5 and 5 mA cm^{-2}.</p> <p>Electrolyte: 0.05 M Na_2SO_4 or 0.12 M NaCl.</p>	<p>The highest [B]/[C] ratio produced an electrode with smaller average grain size and higher content of sp^2 phase. The dye degradation was the highest using the [B]/[C] ratio of 10000 ppm and NaCl as electrolyte, achieving a complete removal of dye absorbance using less than 0.1 Ah L^{-1} of charge passed, whereas the 2000 ppm anode only produced a reduction of 75 % of dye absorbance.</p>	Bogdanowicz et al. 2013 [30]
[B]/[C] ratio: 500, 5000 and 10000 ppm	<p>Cell system:</p> <p>Si/BDD anodes (crystalite 5-10 nm) using Microwave Plasma Assisted Chemical Vapor Deposition.</p> <p>Film thickness: 2 μm.</p> <p>Tantalum plate cathode.</p> <p>Ag/AgCl (0.1 M KCl) as reference electrode.</p> <p>Surface area: 10 cm^2.</p> <p>Electrochemical oxidation:</p> <p>Landfill leachates: diluted 1:1 (real wastewater).</p> <p>Current density: 12.5, 25 and 50 mA cm^{-2}.</p>	<p>The average grain size was 1 μm for the 500 and 5000 ppm anodes, and smaller in the 10000 ppm electrode (0.5 μm).</p> <p>Landfill leachates contained high COD and N-NH_4^+ concentrations. The boron doping level did not influence in the COD removal. However, the BOD_{20} conversion (20-day biochemical oxygen demand) increased from 48% using the 5000 ppm anode to 78 % for the 500 ppm one.</p>	Fudala-Ksiazek et al. 2018 [31]
[B]/[C] ratio: 100, 200, 1300, 2500 and 8000 ppm	<p>Cell system:</p> <p>Commercial Si/BDD (Adamant Technologies)</p> <p>Film thickness: 1-2 μm.</p> <p>Stainless steel cathode.</p> <p>Surface area: 4 cm^2.</p>	<p>The five anodes used were able to achieve a high Penicillin G removal (> 90 %). However, the electrodes with lower doping level (100 and 200 ppm) presented higher COD and TOC conversions (80-90 % and ≈ 50 %, respectively).</p>	Gonzaga et al. 2020 [32]

<p>[B]/[C] ratio: 1000, 10000, 20000 and 30000 ppm</p> <p>Surface termination (C–H or C–O)</p>	<p>Electrochemical oxidation:</p> <p>Penicillin G in synthetic urine: 50 mg L⁻¹. Current density: 30 mA cm⁻².</p>	<p>respectively) and obtained higher reduction in the hazardousness of the effluent (from 96 % of <i>Vibrio fischeri</i> inhibition of the initial sample to less than 15 % using the 100 and 200 ppm anodes).</p>	<p>Kuang et al. 2020 [33]</p>
<p>[B]/[C] ratio: 100, 200, 1300, 2500 and 8000 ppm</p>	<p>Cell system:</p> <p>Si/BDD anodes using a Microwave Plasma-Assisted Chemical Vapor Deposition Pt plate as cathode. Ag/AgCl (0.1 M KCl) as reference electrode. Surface area: 9.62 cm².</p> <p>Electrochemical reduction:</p> <p>NaNO₃: 0.01 M. Linear sweep voltammetry measurements at 100 mV s⁻¹.</p>	<p>The hydrogen termination favors the adsorption of nitrate in the electrode surface, and consequently, its reduction. The highest electrochemical reduction of nitrate (85 %) was obtained with the electrode with a ratio [B]/[C] of 10000 ppm, acting the 1000 ppm one as a semiconductor with poor conductivity and inhibiting the reduction of nitrate and the higher boron doped electrodes.</p>	<p>Santos et al. 2020 [34]</p>
<p>[B]/[C] ratio: 500 and 10000 ppm</p>	<p>Cell system:</p> <p>Commercial BDD (Admant Technologies) Film thickness: 1–2 μm. Stainless steel cathode. Surface area: 4 cm².</p> <p>Electrochemical oxidation:</p> <p>Clopyralid: 100 mg L⁻¹. Current density: 30 mA cm⁻². Electrolyte: 0.021 M Na₂SO₄ or 0.063 M NaCl.</p>	<p>Although none of the anodes studied were able to degrade the clopyralid after 8 h of treatment, the best results in terms of clopyralid and DOC removal (88.6 and 85 %, respectively) were obtained with the [B]/[C] ratio of 200 ppm. The low boron doped anodes favored the mineralization and reduced the formation of intermediates, achieving effluents more biodegradable, increasing the BOD₅/COD from 8 to 55-60 % after treatment.</p>	<p>Pierpaoli et al. 2021 [35]</p>

	<p>Stainless steel mesh cathode. Ag/AgCl (0.1 M KCl) as reference electrode. Surface area: 10.5 cm².</p> <p>Electrochemical oxidation: PFOA and PFOS: 0.1 mg L⁻¹ in phosphate buffer or in landfill leachates. Current density: 25–75 mA cm⁻².</p>	<p>efficiencies of 80 and 78 % for PFOA and PFOS at 75 mA cm⁻²; being lower than 50 % at 25 mA cm⁻². Furthermore, the anode with lower doping level ([B]/[C] ratio of 500 ppm) presented higher activity in the COD and NH₄⁺ removal (50 and 25 %, respectively).</p>	
Niobium and silicon substrates	<p>Cell system: Commercial Si/BDD (NeoCoat). Commercial Nb/BDD (METAKEM). Ti disc plate cathode. Surface area: 63.5 cm².</p> <p>Electrochemical oxidation: Acid Violet 7: 200 mg L⁻¹. Current density: 15–60 mA cm⁻². Electrolyte: 0.05 M Na₂SO₄.</p>	<p>Faster Acid Violet 7 degradation was obtained with Nb/BDD anode at a current density of 60 mA cm⁻². Moreover, lower energy consumption and lower cost were obtained with Nb/BDD anode at 15 mA cm⁻². Nevertheless, similar results were achieved in terms of COD removal for both anodes.</p>	Brito et al. 2018 [36]
Niobium, silicon, and tantalum substrates	<p>Cell system: Commercial BDD (Adamant Technologies) over different substrates (Niobium, silicon, and tantalum) [B]/[C] ratio: 2500 ppm Film thickness: 6–8 μm. Surface area: 78 cm².</p> <p>Electrochemical oxidation: Current density: 30–150 mA cm⁻². Electrolyte: 1M NaCl or 1M H₂SO₄.</p>	<p>During the electrolysis of chloride, the BDD supported on Ta presents the higher conversion to hypochlorite (> 95 %) at 150 mA cm⁻², due to the higher amount of hydroxyl radicals generating, followed by Nb and Si (85 and 66 %, respectively). However, the production of persulfate follows the inverse trend, being the Si support the most active (11 % of conversion against 9 and 6 % for Nb and Ta, respectively).</p>	Moraleda et al. 2019 [37]
Silicon and tantalum substrates	<p>Cell system: Commercial Si/BDD and Ta/BDD (Adamant Technologies) [B]/[C]: 2500 ppm</p>	<p>Ta/BDD promoted the oxidation of cobalt (II) to cobalt (III) in acid pH at 100 mA cm⁻² (90 % of conversion), whereas the Si/BDD did not produce</p>	Escalona-Durán et al. 2021 [38]

	<p>Film thickness: 6–7 μm. Stainless steel cathode. Surface area: 78.6 cm^2.</p> <p>Electrochemical oxidation:</p> <p>Cobalt (II): 0.59 mg L^{-1} Current density: 100 mA cm^{-2}. Electrolyte: 1 M H_2SO_4.</p> <p>Cell system:</p> <p>Commercial Si/BDD: Microcrystalline BDD coating on silicon (Adamant Technologies). Commercial Nb/BDD: Nanocrystalline BDD coating on niobium (Advanced Diamond Technologies). Film thickness: 2–3 μm. Stainless steel and Tungsten cathodes. Surface area: 70 cm^2.</p> <p>Electrochemical oxidation:</p> <p>Perfluorooctanoic acid: 100 mg L^{-1}. Current density: 1–5 mA cm^{-2}. Electrolyte: 0.035 M Na_2SO_4.</p> <p>Cell system:</p> <p>Si/BDD using Microwave Plasma Assisted Chemical Vapor Deposition Ti/Diamond fibers: nanocrystalline BDD coating using Microwave Plasma Assisted Chemical Vapor Deposition over carbon fibers sputtered on a titanium layer. Pt-wire cathode. Surface area: 0.196 cm^2.</p> <p>Electrochemical oxidation:</p>	<p>any transformation in the cobalt (II), remaining almost inalterable. Voltametric studies revealed that the direct electrolysis is the main route for the cobalt (III) formation.</p>	
Coating crystallinity		<p>The use of anodes with microcrystalline coating produced a complete removal of the pollutant, whereas the nanocrystalline anode only achieved 21–87% using the higher current density. This fact produced an increase in the energy consumption from 1.4 kWh m^{-3} for microcrystalline anodes to 52.4 kWh m^{-3} for nanocrystalline one.</p>	Gomez-Ruiz et al. 2019 [39]
Coating crystallinity		<p>The diamond fiber anode was able to degrade completely methyl orange in 180 min whereas the microcrystalline anode achieved less than 50% degradation at the same time. Moreover, the diamond fiber anode removed phenol or tetracycline until obtained effluents with concentrations below their limit of detection.</p>	Jian et al. 2021 [40]

Coating crystallinity	<p>Methyl orange, phenol or tetracycline: 10–50 mg L⁻¹. Voltage: 2.5 V. Electrolyte: 0.1 M Na₂SO₄.</p> <p>Cell system:</p> <p>Ti/BDD microcrystalline anodes using Microwave Plasma Assisted Chemical Vapor Deposition. Ti/BDD nanocrystalline anodes using Microwave Plasma Assisted Chemical Vapor Deposition. Stainless steel cathode. Surface area: 5 cm².</p> <p>Electrochemical oxidation:</p> <p>Ciprofloxacin: 15 mg L⁻¹. Current density: 10–80 mA cm⁻². Electrolyte: 0.05 M Na₂SO₄.</p>	Nanocrystalline BDD anode presented higher efficiency in the degradation of ciprofloxacin at 80 mA cm ⁻² than the microcrystalline one, achieving complete removal in 20 and 60 min, respectively. Moreover, the nanocrystalline BDD obtained higher TOC conversion (60 %) and mineralization current efficiency (4%) than microcrystalline anode (40 % of TOC removal and 2 % of efficiency).	Dos Santos et al. 2022 [41]
Sp ³ /sp ² ratio	<p>Cell system:</p> <p>Commercial BDD (Adamant Technologies) with sp³/sp² ratio of 175 and 329 Film thickness: 2–3 μm. Stainless steel cathode. Surface area: 0.4 cm².</p> <p>Electrochemical oxidation:</p> <p>1-Butyl-3-methylimidazolium chloride: 100 mg L⁻¹. Current density: 25–100 mA cm⁻². Electrolyte: 0.1 M Na₂SO₄.</p>	A higher sp ³ /sp ² ratio produced a higher 1-Butyl-3-methylimidazolium degradation at 50 mA cm ⁻² (95% for the anode with 175 sp ³ /sp ² ratio and 90 % for the 329 sp ³ /sp ² ratio one) and higher mineralization (75 vs 65 %) due to a more intense hydroxyl radicals' generation. Moreover, the lowest concentration of chlorate and perchlorate were obtained at the highest current density studied, although the final effluent present higher phytotoxicity than the initial one.	Marcionilio et al. 2020 [42]

From these contributions it can be drawn several of the main highlights on the influence of the formulation of the diamond on the removal of organics:

- Ratio [B]/[C]. Different authors have been studied the influence of the boron doping in the removal efficiency of pollutants of different nature in water. Doping levels between 100 and 30000 ppm have been evaluated, obtaining as main results that the use of a low boron doping level favored the anodic oxidation of organic pollutants in water [32, 34, 35] and the cathodic reduction of nitrates [33]. For example, Gonzaga et al. (2020) [32] evaluated the degradation of Penicillin G in urine, being the TOC removal reducing from 50% to 32% when the boron doping level increased from 100 ppm to 8000 ppm. Nevertheless, the use of a very low boron content can produce that the electrode works as a semiconductor, reducing the conductivity, and consequently, the degradation. On the other hand, Fudala-Ksiazek et al. (2018) [31] studied the mean grain size obtained in Si/BDD with different boron doping using the Microwave Plasma Assisted Chemical Vapor Deposition method. As can be seen in Figure 1A, they observed that when the [B]/[C] ratio increase from a doping level of 500 to 10000 ppm, the crystallites reduced their mean size in the anode synthesis (from 1 to 0.5 μm).
- Substrate of the electrode. Most studies focused on the performance of BDD electrodes employed silicon substrate. However, recent studies have been demonstrating that the use of alternatives support can favor the formation of different radicals. Moraleda et al. (2019) [37] showed that the use of BDD/Ta anodes presented a higher activity in the generation of hydroxyl radicals than the Si or Nb substrates. This high generation of radicals favored the transformation of chloride into hypochlorite, and later to chlorate and perchlorate. For example, Ta/BDD achieved a hypochlorite conversion of more than 95 % of a synthetic

solution of 1 M of NaCl at 150 mA cm^{-2} , whereas the BDD/Si and BDD/Ni reached 66 and 85 % of hypochlorite conversion, respectively. However, using H_2SO_4 as electrolyte, BDD/Ta anodes presented the lower persulfate generation (6% of 1 M H_2SO_4 conversion at 150 mA cm^{-2}), being the silicon one the most active in the sulfate transformation (11 % at the same conditions). This fact is again related to the high hydroxyl amount produced with Ta substrate. This radical reacted with persulfate reducing the oxidant amount produced in the process. Similar results were obtained by Brito et al. 2018 [36] comparing Nb and Si substrates in the degradation of the Acid Violet 7 dye. They evidenced that BDD/Nb produced a faster degradation of the dye (almost complete color removal in less than 30 min at 60 mA cm^{-2} , whereas the Si one needed 90 min at the same conditions). However, in terms of COD removal, after 120 min, similar results were obtained (85 and 83 % conversion at 60 mA cm^{-2} using Si/BDD and Ni/BDD, respectively). The authors explain this behavior due to the higher amount of sulfates and persulfates produced by the Si/BDD anode, respect to the Ni/BDD.

- Coating crystallinity. Regarding the size of the coating crystallinity of the BDD anodes, nanocrystalline and microcrystalline BDD coatings have been investigated. Recently, dos Santos et al. (2022) [41] compared the electrochemical degradation of ciprofloxacin with nano- and microcrystalline BDD. As can be seen in Figure 1B, the microcrystalline BDD presented a surface with microcrystalline grains randomly oriented, whereas the nanocrystalline BDD presents a surface with small grains forming small agglomerates. In this study, they obtained a higher pseudo-first order degradation rate constant of the antibiotic with nanocrystalline coating (0.1991 min^{-1}) than with the

microcrystalline one (0.0759 min^{-1}) using the same current density (80 mA cm^{-1}). Regarding the mineralization degree, nanocrystalline BDD achieved a TOC removal of 62.3 % whereas microcrystalline BDD achieved a 43.5 %. Considering these results, nanocrystalline coating favored the antibiotic degradation due to its physicochemical properties, such as the surface roughness produced by the boron content or the higher specific capacitance and lower charge transfer resistance. Jian et al. (2021) [40] also obtained better results using nanocrystalline BDD than microcrystalline BDD in the degradation of organic pollutants from wastewater. In this case, the nanocrystals of BDD were deposited in the external surface of carbon fibers, obtaining diamond fibers. These diamond fibers present a higher activity than traditional microcrystalline BDD, achieving complete removal of different pollutants in less than 180 min. Opposite results were obtained by Gomez-Ruiz et al. (2019) [39]. In this study, microcrystalline BDD supported on Si presented a first-order kinetic in the PFOAs removal 50 times higher than the obtained by the nanocrystalline BDD supported on Ni. In this case, it is important to remark that the BDD anodes were commercial using different supports, so the comparison of the crystalline size should be carried out using the same material.

- Sp^3/sp^2 ratio. Finally, regarding the sp^3/sp^2 ratio, different authors observed that an increase in the [B]/[C] ratio produced an increase in the graphitic carbon form [1,2]. Specifically, Fudala-Ksiazek et al. (2018) [31] found that an increase of this ratio produced a higher BPA and BOD_{20} degradation in landfill leachates, but a decrease of this ratio produced a higher removal efficiency of N-NH_4^+ . Similar results have been obtained by Marcionilio et al. (2020) [42] using BDD with sp^3/sp^2 ratios of 175 and 329, obtaining more efficient process when the ratio increased, due to a high oxidative action and a reduction in the generation of

chlorate and perchlorate formation and almost complete mineralization at 100 mA cm⁻².

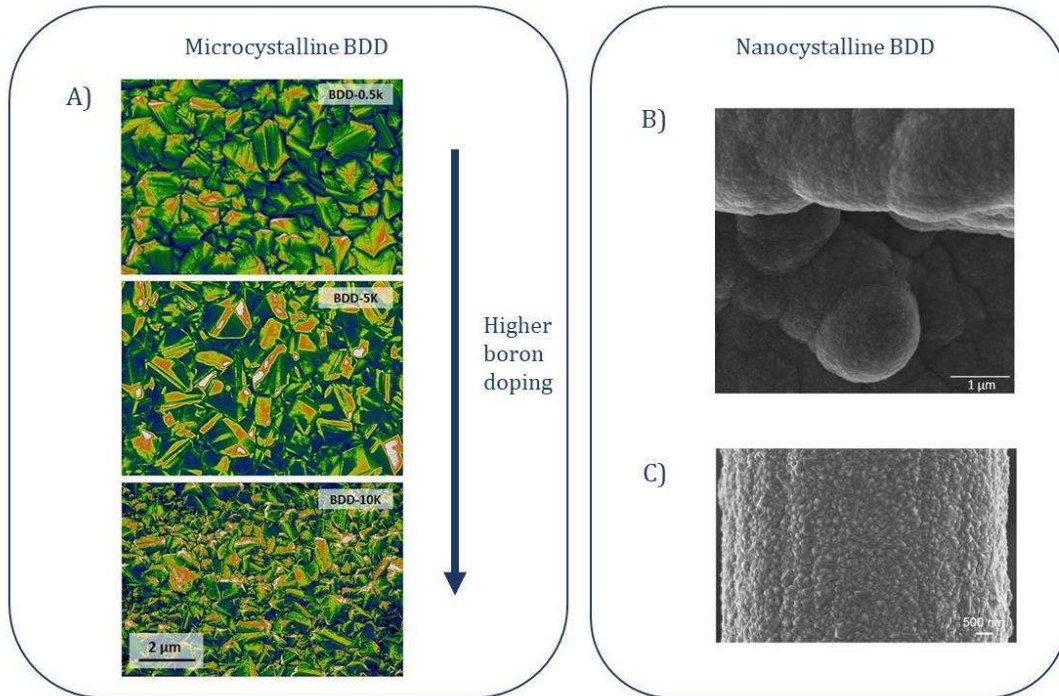


Figure 1. A) SEM images of different [B]/[C] ratio microcrystalline BDD anodes [31], B) field emission gun-scanning electron microscopy (FEG-SEM) of nanocrystalline BDD anode [41] and C) field emission scanning electron microscopy (FESEM) image of diamond fiber anodes [40]. Reproduced with the permission of Fudala-Ksiazek et al. (2018), Jian et al. (2021) and dos Santos et al. (2022).

From the results presented in this work, can be establish the following statements in order to design a BDD anode for the degradation of organic pollutants in wastewater: i) a low [B]/[C] ratio favors the mineralization of the organic pollutants, ii) the support material can influence the anode behavior, being one or other substrate more adequate for the formation of different radical species, iii) nanocrystalline BDD produced, in general, higher organic matter degradation, and iv) higher sp^3/sp^2 ratios favors the mineralization of the wastewater.

4. The challenge of developing cells adapted for diamond anodes.

Traditionally, electrode structure, composition and behavior had focused way more research efforts than the study and improvement of the electrochemical reactor [43,44]. However, to successfully scale-up any advanced oxidation process containing BDD electrodes it is necessary to fully understand the reactor role [45-48]. Both hydrodynamic and electric properties are fundamental to achieve a good electrochemical result. Walsh et al. depicted with a high level of detail all the parameters that are put into stake when a reactor is designed [49]. They also claimed that good feedback between simulation, designing and testing is mandatory to have good results. In this regard, the intimate relationship between design, flow simulation and 3D printing manufacture will play a fundamental role in the upcoming years [50-56]. Improving mass transport is crucial to achieve less energy consumption during the electrochemical decontamination of a water stream, moreover if the conductivity of the effluent is low. This problem may be faced with the above mentioned CFD-3D printing approach or directly using existing reactor architectures and adding it to the BDD technology. Moreover, different techniques like those coming from the application of processes based on sonoelectrochemistry or photoelectrochemistry can be coupled to electrochemical remediation using BDD electrodes and these combinations can be considered as a good way to upgrade the reactor performance. Most of the innovation in the BDD reactor field can be addressed to one of the approaches named in the upper lines and that can be summarized and described as follows:

- A. Modification of the traditional electrochemical reactor with other techniques like photo-electrochemistry or sono-electrochemistry. For instance, Brillas et al achieved important results in the Fenton technology by coupling the

photoelectrochemical generation highly oxidant species along with the positive effect of UV radiation in the degradation of contaminants [57].

- B. Combination of different types of reactors to achieve an upgrade in the hydrodynamic and electrical capacities. In this sense, Pérez et al. successfully combined a microfluidic reactor with a flow-through configuration giving a massive energy saving in water treatment of low conductive effluents [58,59]. A narrow interelectrode gap of 400 μm and a superior mass transfer coefficient of $1.45 \cdot 10^{-5} \text{ms}^{-1}$ led to a 6 to 15 times less energy consumption than a regular flow-through system.
- C. Achieving a polymer electrolyte membrane assembly (PEM) configuration with BDD electrodes. PEM configuration allows a zero-gap between electrodes and then an easy way to work with low conductive environments to decrease as much as possible ohmic drop. Isidro et al. used and compared different commercial cells (CabECO® and Mikrozon®) using PEM configuration with BDD electrodes [60,61]. They found that they were able to disinfect water preventing the formation of hazardous side-products like chlorates and perchlorates.
- D. Designing the reactor according to a Computational Fluid Dynamic (CFD) model and simulation followed by Computer Aided Design (CAD) of the optimized reactor parameters and elements. A complete CFD model may help, not only to optimize our reactor but also to establish a mathematical model to recreate and scale-up other similar processes [62]. With an effective iteration between design and CFD simulation, the reactor can be fast produced by 3D printing technology. This fast feedback to the designed reactor can evaluate the proposed CFD model and allow a rapid iteration and optimization of the design. A good workflow in all

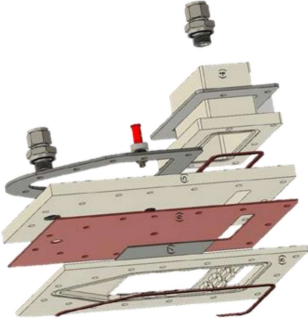
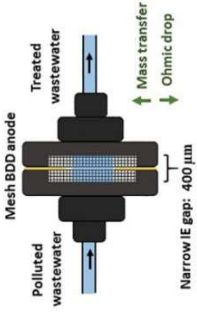
three stages (CFD-CAD-3D printing) is a powerful tool that allow a rapid and solid scale-up of any electrochemical process.

It is worth to mention that despite all four approaches are very different from the technological point of view, they merge into the same improvements to the processes they are applied: high current efficiency, low energy consumption. These aspects are fundamental to be used in relevant operating conditions and are the target of many companies which aims to provide a reliable technology with real applications. For instance, the company CONDIAS GmbH (Germany) has successfully made different commercial BDD cells that have been tested in real conditions [63,64], each one of them are designed and optimized for different applications and shows the path to put economical efforts into an electrochemical BDD reactor design.

Finally, Table 2 summarizes recent works that aim to focus their research on the reactor upgrade. New features introduced to the reactor technology are pointed out along with the improvements obtained. In the same way, it is important to correlate the approach used to improve the reactor and the TRL reached. Using this information, two clear conclusions can be drawn:

- Reactor improving has a huge impact in the electrochemical process, equal or even more than the electrode nature in terms of energy consumption and undesired side-products.
- TRL level shows that more efforts must be done to push the reactor design to commercial or near-commercial results.

Table 2. Different features introduced to electrochemical BDD reactors. Processes and the main results obtained are briefly described, along with the TRL level and the approach followed in terms of the classification introduced in this work. Miniaturized figures of ref [62], [58], [63], [64] and [67] (Reproduced with permission) are included to a better understanding of the approach used.

New features introduced	Process	Main results	TRL	Approach	Ref
Electrode connection Pre-chamber and turbulence promoter	Electrogeneration of Fe(IV)	Superior current efficiency	4	D 	[62]
Microfluidic/Flow-through configuration	Low conductive wastewater treatment	Low interelectrode gap. 6 times low energy consumption	2	B 3D Flow-through 	[58]

Microfluidic/Flow-through configuration	Soil washing effluent treatment	Low ohmic drop in low conductive solution 6-15 times lower energy consumption compared to commercial cell	4	B	[59]
Perforated Multi-anode flow-through cell	Water disinfection	Contaminants efficiently transported to anode surface Less side-oxidation products	9	C,D	[63]
Miniaturized reactor with removable cartridge	Ozone generation	Low power consumption Adaptable to many household applications	9	C,D	[64]
Jet aerator with no compressor	Electro-fenton. Generation of H ₂ O ₂	Low ohmic drop Fast generation of H ₂ O ₂ at 98% FE.	3	B	[65]
Downflow bubble column reactor	Degradation of Phenol	Better absorption of generated O ₂ /O ₃ Contact time of bubbles increased	3	B	[66]

<p>Double anode reactor with UV irradiation in electrodes and bulk</p>	<p>Soil washing effluent</p>	<p>Easy scale-up solution Lower toxicity of effluent Low charge passed (down to 5 Ah L⁻¹)</p>	<p>3</p>	<p>A</p> 	<p>[67]</p>
<p>Continuous flow reactor with different number of electrodes tested (28 vs 14). CFD study</p>	<p>Mineralization of chlorinated hydrocarbons</p>	<p>Minimization of dead flow areas Mathematical model obtained to scale up the process</p>	<p>4</p>	<p>D</p>	<p>[68]</p>
<p>Scalable approach through optimized configuration</p>	<p>Synthesis of graphene oxide</p>	<p>Better conversion, structure and conductivity of GO Cost-effective production</p>	<p>3</p>	<p>D</p>	<p>[69]</p>

5. Conclusions and outlook

From this work the following conclusions and perspective remarks can be highlighted:

- There is a need to increase the technology readiness level of the electrochemical oxidation of wastewater with diamond anodes. After hundreds of papers published, the TRL still remains low and there are several paths that are still unexplored, and they are claiming for further work. The most important are the tailoring in the electrode formulation and the electrochemical cell design.
- Tailoring of diamond electrodes have been investigated to improve the efficiency of anodic oxidation processes, pointing out that not only the composition of the coating but also the support in which it is deposited are worth to be studied. It is especially important to promote the formation of oxidant from salts contained in the wastewater matrix.
- Despite diamond anodes exhibit outstanding characteristics, there is still room for improvements and this gap is related to the design of electrochemical cells that improve mass transfer or that allow to merge different oxidation processes improving the overall performance.

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