Review

Boron Doped Diamond Electrode for the Wastewater Treatment

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Os estudos sobre eletroquímica do diamante iniciaram-se há mais de quinze anos, com o primeiro artigo publicado nessa área, por Pleskov. Depois disso, pesquisas começaram no Japão, Estados Unidos, França, Suíssa e outros países, sendo que nos últimos anos o número de publicações aumentou consideravelmente. Filmes de diamante têm sido o objeto de aplicações e pesquisa fundamental em eletroquímica, abrindo um novo campo conhecido como eletroquímica de eletrodos de diamante. Aqui, nós apresentamos uma breve história e o processo de síntese de filme de diamante. O principal objetivo deste trabalho é resumir os resultados mais importantes em oxidação eletroquímica, usando-se eletrodos de diamante.

Electrochemical studies of diamond were started more than fifteen years ago with the first paper on diamond electrochemistry published by Pleskov. After that, work started in Japan, United States of America, France, Switzerland and other countries. Over the last few years, the number of publications has increased considerably. Diamond films have been the subject of applications and fundamental research in electrochemistry, opening up a new branch known as the electrochemistry of diamond electrodes. Here, we first present a brief history and the process of diamond film synthesis. The principal objective of this work is to summarize the most important results in the electrochemical oxidation using diamond electrodes.

Keywords: electrochemical oxidation, diamond electrode, pollutants, efficiency, wastewater treatment

1. Introduction

Since the first paper about the electrochemistry of boron doped polycrystalline diamond published by Pleskov *et al.*[1] in 1987, the boron-doped diamond (BDD) thin films are found to be particularly attractive for electrolysis and electroanalytical applications due to their outstanding properties, which are significantly different from those of other conventional electrodes, e.g. glassy carbon or platinum electrode.[2] In addition to innate properties of diamond, such as high thermal conductivity, high hardness and chemical inertness, the attractive features of conductive BDD include a wide electrochemical potential window in aqueous and non-aqueous media, very low capacitance and extreme electrochemical stability.[2,3]

Diamond exhibits very high overpotentials for the chemical species following the inner-sphere mechanism because of the inertness of the surface for adsorption.[4] This is the reason it exhibits high overpotentials for the oxygen and hydrogen evolution resulting in a wide electrochemical potential window. While this helps in the electroanalysis of a wide variety of chemical species, the inactiveness of diamond electrode for certain species such as glucose[5,6] and H_2O_2 necessitates the modification of the diamond electrode with catalysts to activate it. For example, Duo and co-workers[7,8] showed that the deposition of small amounts of IrO_x clusters on the diamond surface dramatically enhances both the oxygen evolution reaction and the oxidation of organics in the potential region of water decomposition. Chemically modified electrodes have shown advantages over conventional electrodes.

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In previous results, electrochemistry of BDD and its advantages compared to conventional electrodes have been reported for electrochemical oxidation of several important chemical species. The electrochemical oxidation method has been proposed for the destruction and/or the conversion of mixed waste, when the wastewater contains refractory organic pollutants or toxic substances. The principal aim of the wastewater treatment is complete oxidation of organics to CO_2 or the conversion of toxic organics to biocompatible compounds.[9-12]

Several studies have been completed, with the goal of developing applications in the electrochemical oxidation of organics for wastewater treatment. Comninellis and co-workers[13-15] have found that the electrochemical oxidation of most organics in aqueous media occurs only at high potentials, with a concomitant evolution of O_2; in addition, the nature of the anodic material strongly influences the process selectivity and efficiency. Hence, a model for the anodic oxidation of organics in acidic media, including competition with oxygen evolution, has been proposed.[13-15] In this model, the electrochemical and chemical reactivity of the adsorbed hydroxyl radicals are explained, underlining the important role of the nature of the anode material. Depending on the interactions between hydroxyl radicals and the electrode surface, anodes can be distinguished as "active" or "non-active" materials.[14-16] Among the particular characteristics of BDD, its chemical inertness is well recognized; for this reason, this material is considered an ideal "non-active" electrode on which organics oxidation and oxygen evolution take place through the formation of weakly adsorbed and very reactive hydroxyl radicals.

Based on a literature review, this article summarizes and discusses the recent results available in the literature concerning the application of diamond electrode in electrochemical processes for water treatment. Also a brief introduction about the electrochemical characteristics and other properties of this electrode are presented.

2. Synthesis of Diamond

As diamond is the densest allotrope of carbon, at high pressure diamond should be the most stable form of the solid carbon. This reasoning was the basis for the high-pressure high-temperature (HPHT) growth techniques that have been used in commercial synthesis for the last 30 years. Much effort has been spent during the 60's and 70's to investigate diamond growth at low pressures. Diamond synthesis was successfully achieved by Chemical Vapor Deposition (CVD) techniques at low pressures.[17] Early CVD of diamond was carried out by thermal decomposition of carbon-containing gases such as CH_4 and $CO^{18,19}$ at gas

temperatures between 600 and 1200 °C. The typical deposition conditions were: methane concentration of 1% in hydrogen, substrate temperature of 700-1000°C, filament temperature approximately of 2000 °C, total gas pressure of 13–133 mbar, and reaction time of 3 h. The diamond growth rates are in the order of 0.1 to near 1000 mm h^{-1},[20] demonstrating the good prospect of diamond films for some industrial applications. The conductivity of diamond can be improved significantly by doping with boron. Boron doping is usually achieved by adding B_2H_6,[21,22] or $B(OCH_3)_3$,[23,24] to the gas stream, or placing boron powder near the edges of the substrate prior to insertion into the CVD chamber.[25] Since the late 70's and early 80's when CVD was established as an economical, relatively fast and easy process for producing diamond and it has been considered in different reviews and articles.[26-28]

3. Electrochemistry of Diamond

The first paper on the electrochemistry of boron doped polycrystalline diamond was published by Pleskov *et al.* in 1987.[1] The demonstration of the possibility of performing electrochemistry on polycrystalline diamond resulted in considerable interest in electrodes fabricated from this new material. Three advantages of diamond electrodes were identified. First, it was demonstrated that diamond electrodes have a large potential window in aqueous solution with low background currents.[29-59] Second, it was shown that electrodes formed from polycrystalline diamond possess physical properties similar to those of bulk diamond,[60-64] including: hardness, low environmental impact, high hole mobility, high thermal conductivity and excellent resistance to radiation damage. Third, the surface is stable and there is little evidence of degradation of electrochemical activity with time[40,43,65] These characteristics of diamond electrodes have been employed in a number of applications.

The quality of conducting diamond films is usually investigated by recording the background cyclic voltammetric *j-E* curves of the electrodes. In fact, the magnitude of the background current, the working potential window and the features of the curves are sensitive to the presence of non-diamond carbon impurities.[66-68] In general, high quality diamond film has a flat, featureless voltammetric response in the potential range between -0.3 and 1.2 V *vs.* SHE, with a background current 10 times lower than polished glassy carbon.[7,51,69] Non-diamond surface impurities are more active than diamond and cause a higher background current. The increased surface charge density is evident from a larger double-layer charging current.[69] Acidic washing, oxygen plasma and other techniques will oxidize the sp^2 carbon and eliminate impurities from the

diamond surface without any change in morphology or damage to the microstructure. Cyclic voltammetry can detect sp^2 impurities and their removal with a higher sensitivity than Raman Spectroscopy.[69]

Another important property of high-quality diamond is the wide potential window between hydrogen and oxygen evolution. A total region of around four volts is available within which rather low background currents are recorded.[29-33] With its combination of a low background current, an extremely high overvoltage for oxygen and hydrogen evolution, and an extremely high stability, diamond is a suitable material for some industrial applications.

Three classes of electrochemical applications may be identified: *i*) Synthesis of chemicals; *ii*) Electro-analysis and *iii*) Destruction of pollutants. The diamond surface is not favorable for adsorption, so that electrochemical processes that involve adsorbed intermediates (H_2, O_2 and X_2 evolution) are hindered on diamond. They will require very high overpotential in order to proceed at an appreciable rate. The wide potential window without electrolyte decomposition and the high stability of diamond allow electrochemical reactions to be carried out at potentials otherwise difficult to reach. Direct synthetic reactions have been carried out, such as the production of ammonia, chlorine, Ag^{2+} and peroxodisulfate.[70-74] Diamond has been tested in the oxidation of many organic compounds for wastewater treatment, and an extremely high current efficiency was obtained.[75-78] The low background currents on diamond lead to an improved signal-to-background ratio as compared with glassy carbon.[79,80] Negligible adsorption phenomena have been found on diamond surfaces for a wide range of compounds.[51] After partial surface fouling, the response of electrodes could be restored by simple electrochemical oxidation without modifying the morphological properties of the polycrystalline film.[76,78]

3.1. Inner sphere reactions at diamond electrodes

The BDD electrodes are characterized by very slow kinetics of inner-sphere reactions such as O_2 evolution. In fact, very high overpotentials are required for these kind of processes. The very weak bond between the diamond surface and active intermediates (hydroxyl radicals) is the cause of the slow kinetics of this kind of a reaction. However, the weakly bonded hydroxyl radicals are chemically extremely active, and at potentials close to oxygen evolution, the oxidation of organics results in a complete combustion incineration of the organic species. In this potential region, all fouling effects are avoided and a very high current efficiency is obtained.

3.2. The oxygen evolution reaction and organic oxidation on 'non-active' and 'active' electrodes[81]

It has been found that, frequently, electrochemical oxidation of certain organics in aqueous media occurs, without any loss of electrochemical activity, only at high potential values, with concomitant evolution of oxygen.[3,9,10,12,82] Furthermore, it has been found that the nature of the electrode material strongly influences both the selectivity and the efficiency of the process.[13,14,83,84] In order to interpret these observations, a comprehensive model has been proposed.[13,14,83,84] This model allows two different cases to be distinguished: 'non-active' and 'active' anodes. The first step in all cases is the discharge of water molecules to hydroxyl radicals:

$$M + H_2O \rightarrow M \ (^{\bullet}OH) + H^+ + e^- \qquad (1)$$
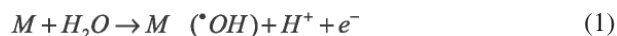
Where M designates an active site at the anode surface.

The electrochemical and chemical activity of hydroxyl radicals strongly depends on the nature of the electrode material used. With 'non-active' electrodes there is a weak interaction between electrode M and hydroxyl radicals ($^{\bullet}OH$). In this case the oxidation of organics is controlled by hydroxyl radicals:

$$M \ (^{\bullet}OH) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad (2)$$
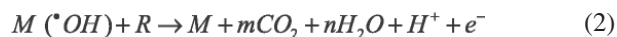
This reaction occurs in competition with oxygen evolution by hydroxyl radical discharge, which occurs without any participation of the anode surface:

$$M(^{\bullet}OH) \rightarrow M + \frac{1}{2}O_2 + H^+ + e^- \qquad (3)$$
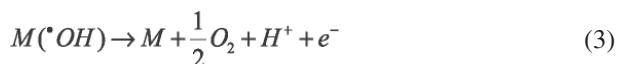
With 'active' electrodes there is a strong interaction between electrode M and hydroxyl radicals ($^{\bullet}OH$). In this case the hydroxyl radicals may interact with the anode, with a possible transfer of oxygen from the hydroxyl radicals to the anode surface and the formation of so-called higher oxide (reaction 4 with M = IrO_2).

$$M(^{\bullet}OH) \rightarrow MO + H^+ + e^- \qquad (4)$$

The surface redox couple MO/M can act as a mediator in the partial (selective) oxidation of organics (reaction 5 with M = IrO_2).

$$MO + R \rightarrow M + RO \qquad (5)$$

This reaction occurs in competition with oxygen evolution due to chemical decomposition of the higher oxide (reaction 6 with M=IrO_2).

$$MO \rightarrow \frac{1}{2}O_2 \qquad (6)$$

3.3. The oxygen evolution reaction and the oxidation of organic substances on 'non-active' diamond electrodes

Diamond electrodes have been defined as 'non-active' electrodes. In fact, they do not provide any catalytically active site for the adsorption of reactants and/or products in aqueous media. Intermediates such as hydroxyl radicals produced by water decomposition at 'non-active' anodes (reaction 1) are considered to be involved in the oxidation of organics in aqueous media. These intermediates are responsible for the electrochemical combustion of the organic compounds (reaction 5). The electrochemical activity (overpotential for oxygen evolution) and the chemical reactivity of adsorbed hydroxyl radicals (rate of oxidation of the organic substances by electrogenerated hydroxyl radicals) are strongly related to the strength of interaction between anode (M) and hydroxyl radicals ($^{\bullet}$OH). As a general rule, the weaker the M-OH$^{\bullet}$ interaction, the lower will be the anode's activity toward oxygen evolution (high overvoltage anodes), and the higher its reactivity for the oxidation of organics (fast chemical reaction). At high anodic potentials close to the potential of water decomposition, the activity of BDD electrodes is considerably enhanced, and there is no evidence of a loss of electrode activity.[71,75,76,78,85] In the case of aromatic compounds, it has been found that the polymeric film formed in the region of water stability can be destroyed by subjecting the electrode to high anodic potentials (E > 2.3 V *vs.* SHE) in the region of O_2 evolution. This treatment can restore the electrode's activity. In fact, the applied potential is located in the region of water discharge at BDD electrodes, and this involves the production of reactive intermediates (hydroxyl radicals, OH$^{\bullet}$) which oxidize the polymeric film on the anode surface.

A model has been developed[13,14,77,83,84] to describe the combustion of organics (R) on BDD anodes. It assumes that both the oxidation of organics and the oxygen evolution reaction take place exclusively through mediation by hydroxyl radicals, *i.e.* the electrode itself does not exhibit any 'active' character. This assumption simplifies the general mechanism presented above according to reactions 1 to 6, so that a reaction scheme involving three different reactions is obtained with M = BDD.
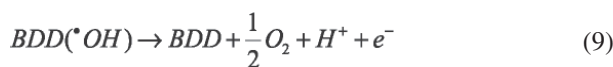
The first reaction is the electrochemical discharge of water leading to hydroxyl radical formation (reaction 1).

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \qquad (7)$$
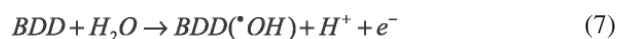
These hydroxyl radicals are then consumed by two competing reactions: *i*) combustion of organics (reaction 2):

$$BDD(^{\bullet}OH) + R \rightarrow BDD + mCO_2 + nH_2O + H^+ + e^- \qquad (8)$$

and *ii*) oxygen evolution (reaction 3):

$$BDD(^{\bullet}OH) \rightarrow BDD + \frac{1}{2}O_2 + H^+ + e^- \qquad (9)$$

Molecular oxygen very probably also participates in the combustion of organics according to the following reaction scheme:

1) Formation of organic radicals, R*, by a dehydrogenation mechanism:

$$RH + BDD(^{\bullet}OH) \rightarrow R* + H_2O + BDD \qquad (10)$$

2) Reaction of the organic radical with dioxygen

$$R* + O_2 \rightarrow ROO* \qquad (11)$$

3) Further abstraction of a hydrogen atom with the formation of an organic hydroperoxide (ROOH):

$$ROO* + R'H \rightarrow ROOH + R'* \qquad (12)$$

Since the organic hydroperoxides are relatively unstable, decomposition of such intermediates often leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These scission reactions continue rapidly until the organic substance has been completely transformed to CO_2 and H_2O. A kinetic model can be developed for this reaction scheme by making the following further assumptions: *i*) adsorption of the organic compounds at the electrode surface is negligible; *ii*) the overall rate of electrochemical combustion of organics (involving hydroxyl radicals and the formation of hydroperoxide) is a fast reaction and is controlled by mass transport of organics to the anode surface.

4. BDD Electrode for Wastewater Treatment

The boron-doped diamond film electrode represents an attractive anode material for the degradation of refractory or priority pollutants such as ammonia, cyanide, phenol, chlorophenols, aniline, various dyes, surfactants, alcohols and many other compounds.[16,86-121] Unlike PbO_2, SnO_2 and TiO_2, the BDD thin films deposited on Si, Ta, Nb and W by CVD have shown excellent electrochemical stability.[24] However, the application of BDD electrodes for wastewater

treatment has been mostly studied with Si-supported devices, in spite of the difficulties related to their industrial application, due to the fragility and the relatively low conductivity of the Si substrate. On the other hand, large-scale usage of Nb/BDD, Ta/BDD and W/BDD electrodes is impossible due to the unacceptably high costs of Nb, Ta and W substrates. On the contrary, titanium possesses all required features to be a good substrate material; Ti/BDD has been used for the destruction of several pollutants, like dyes,[122,123] carboxylic acids[123] and phenol.[123] Carey *et al.* patented the use of diamond films as anodes for organic pollutants oxidation.[104] Also Comninellis and coworkers investigated the anodic oxidation of various pollutants with Si/BDD electrodes, as well as the mechanism by which the organic substrates are oxidized at this electrode surface through the formation of a film of hydroxyl radicals at the Si/BDD surface, which may represent a 'reaction cage' for the process.[24,75,76,85,92,96-100,103,106,120] Related results have been summarized in Table 1. The CE obtained is very high, ranging from 33.4 to more than 95%, depending on pollutant characteristics and oxidation conditions. The work by Beck *et al.*[124] also reports results obtained by Fryda *et al.*[24], comparing the Si/BDD with Ti/SnO_2, Ta/PbO_2 and Pt for the oxidation of phenol. At a charge loading of 20 Ah L^{-1}, the total organic carbon (TOC) was reduced from an initial value of 1500 to about 50 mg L^{-1} at Si/BDD, and to about 300, 650 and 950 mg L^{-1} at Ti/SnO_2, Ta/PbO_2 and Pt, respectively.

On the other hand, some articles report that during oxidation of organic compounds, such as phenol, diuron, 3,4-dichloroaniline and triazines, the crucial point to obtain high yields is the rate of mass transfer of the reactant towards the electrode surface.[93-95] Thus, they developed an impinging cell to obtain high mass transfer coefficients. With this cell, at a current density of 15 mA cm^{-2}, a faradic yield of 100% was achieved, up to the almost complete disappearance of the organic load.[93-95]

Some papers have also compared the behavior of BDD with other electrodes, such as SnO_2, PbO_2, IrO_2, for the oxidation of organic pollutants. Chen *et al.* reported that the current efficiency obtained with Ti/BDD in oxidizing acetic acid, maleic acid, phenol, and dyes was 1.6–4.3-times higher than that obtained with the typical Ti/Sb_2O_5–SnO_2 electrode.[123] Other have demonstrated that Si/BDD electrodes are able to achieve faster oxidation and better incineration efficiency than PbO_2 in the treatment of naphthol,[107,108] 4-chlorophenol[85] and chloranilic acid.[88] In contrast, the incineration of oxalic acids,[86] which require a strong adsorption of the organic on the electrode surface, is lower than on PbO_2, but is higher than on Pt, Au and IrO_2 anodes.

The diamond electrodes have been also used as cathode materials for the electrochemical reduction of nitrate ions dissolved in high concentrations in effluents.[125-128]. Levy-Clement *et al.*[126] found that at applied potentials between -1.5 and -1.7 V vs. SCE the amount of NO_3^- reduced is a constant 10% and that it is mainly transformed into gaseous products, then it increases to 29% at -2V with almost equal parts of nitrite and nitrogenous gas formed, without the production of ammonium.

Another aspect to be taken into consideration is the production of powerful oxidants, like the peroxo-disulphate;[129,130] these species can participate in the oxidation of the organic substrates, allowing higher efficiencies.

In particular cases, for high organic concentrations and low current densities, the chemical oxygen demand (COD) decreased linearly and the Instantaneous Current Efficiency (ICE) remained about 100%, indicating a kinetically controlled process. While for low organic concentrations or high current densities, the COD decreased exponentially and the ICE began to fall due to the mass-transport limitation and the side reactions of oxygen evolution. For example, the trend of the COD and ICE was obtained by Panizza *et al.*[76] during the electrochemical oxidation of 2-naphthol. In order to describe these results these authors developed a comprehensive kinetic model that allowed them to predict the trend of the COD and current efficiency for the electrochemical combustion of the organic with BDD electrodes and to estimate the energy consumption during the process.[76,77,110]

Other applications of BDD for the destruction and/or determination of organic pollutants were obtained by Avaca and co-workers[105,131-139] where the comparison between the BDD and other anodic materials have permitted use of alternative techniques during the oxidation of the organic pollutants. The BDD electrode is the best choice for several electroanalysis studies, as demonstrated by the electrochemical oxidation of 4-nitrophenol in 0.1 mol L^{-1} BR buffer electrolyte.[131]

A comparison between the analysis performance of a hanging mercury drop electrode (HMDE) and a BDD electrode for the quantification of 4-nitrophenol (4-NP) in spiked pure and natural waters was reported.[132] The square wave voltammetry was chosen as the electroanalysis technique. For the reduction process, the quantification limits varied between 5.7 and 66.0 µg L^{-1} for the HMDE and between 14.1 and 61.3 µg L^{-1} for the BDD electrode for water samples with increasing degree of contamination. The oxidation of 4-NP on BDD was also used for analysis purposes and the quantification limits in this case varied from 9.4 to 53.1 µg L^{-1}. Also this material was used for determining

Table 1. Anodic oxidation of organic compounds by BDD electrode. Abbreviations: COD= Chemical Oxygen Demand, T= Temperature, [ ]=concentration, J= Current density, I=intensity, E=potential; Efficiency was expressed in ICE (Instantaneous current efficiency), ACE (Apparent current efficiency), EOI (Electrochemical oxidation index), CE (current efficiency), GCE (General current efficiency) and Percentage

Anode	Pollutant	Current density, intensity or potential	Efficiency (ICE, EOI, ACE, %)	Removal efficiency	Comment	Intermediates	Ref.
BDD	Isopropanol	30 mA cm⁻²	85%	90%	1 mol L⁻¹ H₂SO₄, transport limitations	acetic, oxalic, formic acids	98
BDD	Herbicides	I=100-450 mA	ACE=8-12%	40% (1 h), 70-90% (3 h)	pH=3, 0.5 mol L⁻¹ H₂SO₄, [Herbicide]=100 mg L⁻¹	4-Chlorophenol, 4-Chloro-o-cresol, maleic and oxalic acids	99
BDD	Maleic, formic and oxalic acids	30 mA cm⁻²	ICE=0.2-0.8 depending carboxylic acid and [ ]	90%	H₂SO₄/Na₂SO₄, pH=2, T=20°C	CO₂	117
BDD	Phenol	15-60 mA cm⁻²	100-50% (5Ah L⁻¹ passed) and >50% (after 5Ah L⁻¹ passed)		[phenol]=from 350 to 1500 mg L⁻¹, T=25°C	Hydroquinone, benzoquinone, maleic, fumaric and oxalic acids	119
BDD	Phenol	5 mA cm⁻²	ICE= 0.5	90%	HClO₄ 1 mol L⁻¹, T=25°C, [phenol]=20 mmol L⁻¹	Hydroquinone, benzoquinone, catechol, maleic, fumaric and oxalic acids	103
BDD	Phenol	300 A cm⁻²	33%, CE	90%	HClO₄ 1 mol L⁻¹, T=25°C, [phenol]=20 mmol L⁻¹, pH=2, charge loading 4.5 Ah L⁻¹	Hydroquinone, benzoquinone, catechol, maleic, fumaric and oxalic acids	103
BDD	Carboxylic acids (acetic)	30 mA cm⁻²	90% (acetic)	98%	1 mol L⁻¹ H₂SO₄, T=30°C	oxalic acid and CO₂	75
BDD	Carboxylic acids (formic)	30 mA cm⁻²	90% (formic)	100%	1 mol L⁻¹ H₂SO₄, T=30°C	CO₂	75
BDD	Carboxylic acids (oxalic)	30 mA cm⁻²	70% (oxalic)	90%	1 mol L⁻¹ H₂SO₄, T=30°C	CO₂	75
BDD	Polyacrylates	0.1-0.3 A dm⁻²	37-100%	99%	HClO₄ 1 mol L⁻¹, T=30-60°C	Hydroquinone, benzoquinone, catechol, maleic, fumaric and oxalic acids	120
BDD	2-naphthol	15-60 mA cm⁻²	ICE=100% (8Ah L⁻¹)	90%	[naphthol]=2-9 mmol L⁻¹ [ ]=100-500 mg L⁻¹	polimerization and CO₂	76
BDD	Phenolic compounds	153-510 mA cm⁻²		90%	Re number= 3500-15000	Hydroquinone, benzoquinone, maleic, aliphatic acids	94
BDD	Chloranilic acid	6.3-50 mA cm⁻²	GCE=0.7-0.4	90%	H₂SO₄ T=25-60°C	Hydroquinone, ketomalonic and oxalic acid	88
BDD	Multicomponent mixtures (phenol, phenyl-methanol, 1-phenyl-ethanol and m-cresol)	100-300 A cm⁻²	near 100%	COD removal from 5000 to 300	Na₂CO₃ 0.1 mol L⁻¹ supporting electrolyte, pH=7.0 using H₂SO₄ 5% v/v		91
BDD	Pentachlorophenol	E=0.9 V	96%, CE	80%, [PCP] removal	buffer pH=5.5, [PCP]=5.0x10⁻⁵ mol L⁻¹	2, 3, 4, 5, 6 - pentachloro - 4 - pentachloro-phenoxy- 2, 5- cyclohexadienone, p-chloranil, hydroquinone	105
BDD	Pentachlorophenol	E=2.0 V	90%, CE	86%, [PCP] removal	buffer pH=5.5, [PCP]=5.0x10⁻⁵ mol L⁻¹	2, 3, 4, 5, 6 - pentachloro - 4 - pentachloro-phenoxy- 2, 5- cyclohexadienone, p-chloranil, hydroquinone	105
BDD	Pentachlorophenol	E=3.0 V		95%, [PCP] removal	buffer pH=5.5, [PCP]=5.0x10⁻⁵ mol L⁻¹	2, 3, 4, 5, 6 - pentachloro - 4 - pentachloro-phenoxy- 2, 5- cyclohexadienone, p-chloranil, hydroquinone	105
BDD	Benzoic acid	I=1.5 A	ICE=100% initial times	90%, COD	0.5 mol L⁻¹ HClO₄, [BA]=different concentrations	Salicylic acid, 2, 5-dihydroxybenzoic acid and hydroquinone	110
BDD	Benzoic acid	I=1.5 A	ICE=100% initial times	90%, COD	0.5 mol L⁻¹ HClO₄, [BA]=different concentrations	Salicylic acid, 2, 5-dihydroxybenzoic acid and hydroquinone	110
BDD	Polyhydroxybenzenes	15-60 mA cm⁻²	ICE=100% from 4000-2000 COD concentrations, and decrease ICE from 1800 to 100 COD concentrations	90%, COD	T=15-60°C, initial concentration 1.1-36 mmol L⁻¹, pH=2 and 12, transport limitations	aliphatic compounds	113
BDD	Kodak 6 first developer	1000 A cm⁻²		73%, COD	Initial COD=32500 mg L⁻¹, Vol=30 mL, I=0.31 A, electrolysis time 6.25 h		104
BDD	Kodak E6 color developer	1000 A cm⁻²		80%, COD	Initial COD=19050 mg L⁻¹, Vol=30 mL, I=0.31 A, electrolysis time 4.75 h		104
BDD	Phenol solution	1000 A cm⁻²		94%, COD	Initial COD=3570 mg L⁻¹, Vol=60 mL, I=0.31 A, electrolysis time 18 h		104
BDD	Hydroquinone solution	500 A cm⁻²		97%, COD	Initial COD=23530 mg L⁻¹, Vol=60 mL, I=0.15 A, electrolysis time 38 h		104
BDD	CN⁻	360 A cm⁻²	41%, CE	95%, [CN-] removal	1 mol L⁻¹KOH		24
BDD	isopropanol	300 A cm⁻²	>95%	<90%, conversion	[isopropanol]= 0.17 mol L⁻¹	CO₂	92
BDD/Electro-Fenton	Herbicides	I=100-450 mA	ACE=8-12%	60%(1h), 80-99%(3h)	pH=3, 0.5 mol L⁻¹ H₂SO₄, [Herbicide]=100 mg L⁻¹	4-Chlorophenol, 4-Chloro-o-cresol, maleic and oxalic acids	99
Ti/BDD	Dyes	100 A m⁻²	70-90%	80-97%, COD	T=30°C, Vol=25 mL, initial dyes concentration =1000mg L⁻¹ initial pH 4.70-6.7	Some polymeric products in the Monozol T-blue HFG oxidation	122
Ti/BDD	Acetic acid	200 A m⁻²	64%, CE	97%, COD(After 5.53 Ah L⁻¹)	Vol=30 mL, Na₂SO₄ (2000 mg L⁻¹), T=30°C	CO₂	123
Ti/BDD	Maleic acid	200 A m⁻²	61%, CE	96%, COD(After 6.43 Ah L⁻¹)	Vol=30 mL, Na₂SO₄ (2000 mg L⁻¹), T=30°C	CO₂	123
Ti/BDD	Phenol	100 A m⁻²	78.5%, CE	97%, COD(After 4.85 Ah L⁻¹)	Vol=30 mL, Na₂SO₄ (2000 mg L⁻¹), T=30°C	CO₂	123
Ti/BDD	Orange II	200 A m⁻²	54.9%, CE	91%, COD(After 6.25 Ah L⁻¹)	Vol=30 mL, Na₂SO₄ (2000 mg L⁻¹), T=30°C	Various pollutants	123
Ti/BDD	Reactive RedHE-3B	200 A m⁻²	46.9%, CE	95%, COD(After 6.25 Ah L⁻¹)	Vol=30 mL, Na₂SO₄ (2000 mg L⁻¹), T=30°C	Various pollutants	123

the pentachlorophenol in waters and these results were satisfactorily compared with those obtained on a conventional Hg electrode showing that the use of the BDD electrode is an interesting and desirable alternative for analytical detections. These latter results illustrate the advantages arising from the possibility of using an oxidation process on BDD electrodes for analytical purposes in contaminated matrixes.

Also the column of intermediates is a key point for the evaluation of data in Table 1: in fact, several metabolites are generally produced during the oxidation of the original organic substrate. Starting from an aromatic compound, hydroxylated derivatives are found as initial intermediates, but in the final stages of the oxidation process several carboxylic acids are produced, the last being usually oxalic acid. The formation of these acids increases the process time and highlights possible mass transport limitations; interestingly, some anode materials are more efficient than others for their elimination.[86]

5. Final Remarks

This paper has attempted to give an overview of the applications of BDD electrode in the wastewater treatment and the mechanisms during this process. Without doubt the BDD electrodes have showed numerous applications in the electrochemistry area of research. The most important properties of this electrode are a large potential window, lower adsorption, corrosion stability in very aggressive media, high efficiency in oxidation processes, very low double-layer capacitance and background current. All of these characteristics make this material ideal in the elimination of organics from water. Also, thanks to these properties, conducting diamond seems to be a promising electrode material and so, in the last decades, it has been studied with the goal of developing applications in three broad areas: electro-synthesis, electro-analysis and sensor technology; and water treatment, which includes the purification of wastewater and the disinfection of drinking water.

Due to the importance of BDD in the electrochemistry research; the number of articles about production and applications of this material have increased in various countries. Also other recent and relevant papers in this field have been published during this year.[140-144]

Special Dedication

Dedicated to Professor Christos Comninellis for the experimental and scientific contributions about the wastewater treatment using the Boron-Doped Diamond electrode, as well as for his articles about the electro-chemical oxidation of the organic pollutants.

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