

Review Article

A Brief Review on Environmental Application of Boron Doped Diamond Electrodes as a New Way for Electrochemical Incineration of Synthetic Dyes

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The present study was stimulated by an authoritative review on decontamination of wastewaters containing synthetic organic dyes by electrochemical methods published in Martínez-Huitl and Brillas (2009). As reviewed by the authors, there have been significant efforts on investigating the decontamination of wastewaters containing synthetic dyes by electrochemical methods, and currently, more studies are being published. A high number of electrodes have been tested in this method, including boron doped diamond (BDD) anodes. In this context, many papers have demonstrated that the use of a BDD thin film in electrochemical oxidation provides total mineralization with high current efficiency of different organics in real wastewaters. And this synthetic material deposited on several supports has been recently applied to dyestuff treatment. Although, in the last two years, more reports have been published treating electrochemically synthetic dyes wastewaters using BDD, there are few reports on the use of electrooxidation processes to degrade real textile effluents. The aim of this paper is to summarize and discuss the most important and recent results available in the literature about the application of BDD electrodes for removing azo dyes in synthetic and real wastewaters.

1. Introduction

Azo dyes are used in a wide variety of industrial processes such as, food production, cosmetics, and pharmaceuticals manufacturing and paper printing. Therefore, these dyes are frequently found in industrial wastewater effluents and are a principal cause of pollution around the world [1]. The release of colored effluents into the environment is undesirable, not only for aesthetic reasons but also because many azo dyes and their degradation byproducts are toxic to aquatic life and mutagenic to humans [2]. The effluents from the textile industry are frequently characterized by high alkalinity, biological oxygen demand, chemical oxygen demand, and total dissolved solids in addition to high

dye concentrations (>1000 ppm). The synthetic origin and complex aromatic structures of dyes make them stable and difficult to biodegrade.

Dyes are classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes), and nonionic (disperse dyes). The chromophores in ionic and nonionic dyes mostly consist of azo groups or anthraquinone types [3]. In this context, azo dye compounds constitute about one-half of the dyes that are used in the textile industry [4]. The chemical structure of this group of compounds is characterized by the presence of the azo group ($-N=N-$) chromophore, associated with aromatic systems and other groups, such as hydroxyls ($-OH$) and sulfonic groups ($-SO_3H$) [5]. The azo group can be present one or more times in the molecular structure of the

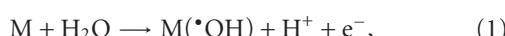
compound. Additionally, another environmental problem with respect to the use of azo dyes in the textile industry is the consumption of large amounts of potable water. In many countries where potable water is scarce, this high consumption of water has become undesirable, and wastewater recycling has been recommended in order to decrease the water requirements [2].

To avoid azo dye accumulation in aquatic systems, different methods are being developed to carry out the elimination of these compounds from wastewater. These include biological and physicochemical methods such as flocculation combined with flotation, membrane filtration, coagulation, ion exchange, irradiation, and katox treatment method [3, 6]. However, these methods are generally unsuccessful in color removal, expensive, and less adaptable to a wide range of dye wastewaters.

In recent years, electrochemical technologies have caused great interest because they offer effective means to solve environmental problems related to industrial processes [7, 8] such as wastewater contamination. The highest advantage of these methods is their environmental compatibility. Their principal reagent is the electron, which is an inherently clean species whose energy can be carefully controlled by means of an applied potential, thus avoiding parallel reactions. In traditional chemistry, secondary reactions often result in subproducts which sometimes increase removal costs [8–10].

The principal electrochemical methods are the following:

- (a) *direct electrochemical oxidation*, where the organic compound degradation occurs directly over the anode through the adsorbed $\cdot\text{OH}$, or chemisorbed active oxygen in the anode surface (often called “anodic oxidation, direct oxidation or electrochemical incineration”), by means of the following general equation [10–12]:



where the pollutants are first adsorbed on the anode surface (M) and then destroyed by the anodic electron transfer reaction,

- (b) *indirect electrochemical oxidation*, where the organic compounds are treated in the bulk solution by means of species generated in the electrode, such as $\cdot\text{OH}$ (by means of the Fenton reaction), Cl_2 , hypochlorite, peroxodisulfate, and ozone, as the most common electrochemically generated oxidants [6, 13].

In recent decades, several electrodes have been evaluated to rank anode material in terms of high stability, high activity toward organic oxidation, and cost. The types of electrodes tested included graphite, platinum, IrO_2 , RuO_2 , SnO_2 , PbO_2 , Ti/Pt , $\text{Ti}/\text{Pt}-\text{Ir}$, Ti/PbO_2 , $\text{Ti}/\text{PdO}-\text{Co}_3\text{O}_4$, and $\text{Ti}/\text{RhO}_x-\text{TiO}_2$, Ti coated with oxides of Ru/Ir/Ta [14, 15], BDD thin films, and others.

In this context, several groups have proposed the use of BDD as anode material. The electrochemical behavior of such BDD thin films deposited on different substrates (Si, Ti, Nb, or Pt) has also been studied with the aim of

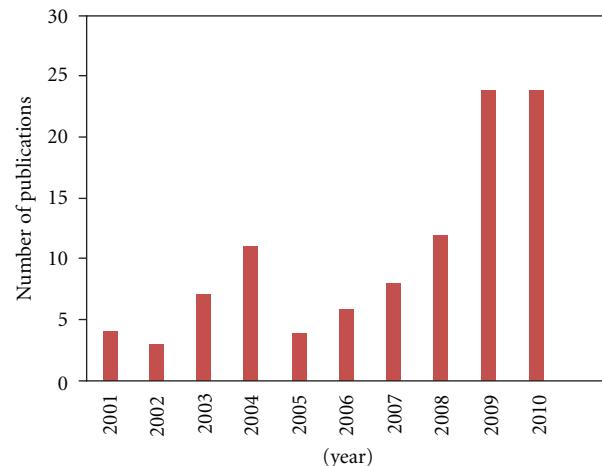


FIGURE 1: Tendency in the number of publications versus year for wastewater treatment using BDD anodes.

developing applications for the electrochemical oxidation of different organic compounds for wastewater treatment, as reviewed by Martinez-Huitle and Brillas [16], there have been significant efforts made in investigating the decontamination of wastewaters containing synthetic dyes by electrochemical methods, using especially BDD anodes. Although more reports involving electrochemical treatment of synthetic dye wastewater have been published in the last two years, there are few reports on the use of this process to degrade real textile effluents. The aim of this paper is to present the recent progress in electrochemical treatment by anodic oxidation of synthetic dye wastewaters and real effluents using BDD electrodes, focusing on the elimination of azo dyes.

2. BDD Anodes for Wastewater Treatment Applications

In the last 10 years, the boron-doped diamond anode has been an attractive material for numerous environmental applications. Figure 1 illustrates the tendency to use this kind electrode for the degradation of different refractory or priority pollutants in wastewater. Although relatively few articles were published between 2001 and 2005, the amount of articles involving BBD electrodes increased considerably between 2006 and 2010 (by means of Scopus).

2.1. Hydroxyl Radical ($\text{BDD}(\cdot\text{OH})$) Generation. Considerable $\cdot\text{OH}$ amounts may be electrogenerated on BDD anodes. These radicals, due to their weak interaction with the BDD film, present high reactivity towards organics (Rx 2–4); these processes have been efficiently used in wastewater treatment [10, 17] as follows:



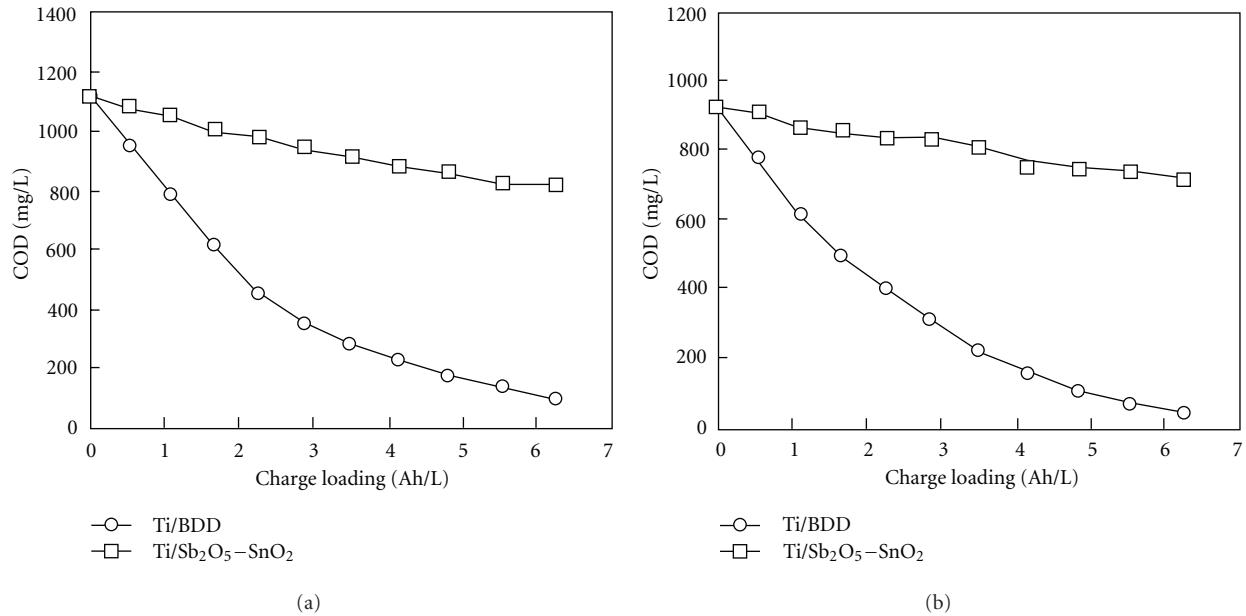
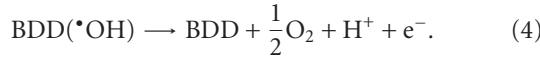


FIGURE 2: COD decay for comparison of Ti/BDD versus Ti/Sb₂O₅-SnO₂ for incineration (a) Orange II and (b) Reactive red HE-3B at current density 200 A/cm² and T = 30°C [19].

According to the literature, reaction (3) is in competition with the side reaction of free •OH discharge to O₂ without any participation of BDD surface, following the next reaction:



However, many authors have reported that during incineration process of BDD anodes at high potentials, a great number of organic pollutants are completely mineralized by the reaction with electrogenerated free •OH species [18]. In this context, some papers have reported (period from 2003 to 2010) the incineration of a great number of synthetic azo dyes by reaction with electrogenerated •OH species over BDD anode.

2.2. Electrochemical Treatment of Synthetic Dye Solutions. The study of the treatment of synthetic dyes using BDD anodes started in 2003, when Chen and coworkers [19] tested the mineralization of Orange II and Reactive red HE-3B. They proposed the comparison of physicochemical and electrochemical properties for two different electrodes, Ti/BDD and Ti/Sb₂O₅-SnO₂, using a thermostatic reactor controlled with a water bath. They evaluated the efficiency for mineralization of 750 mg/L of Orange II and 1500 mg/L of Reactive red HE-3B in each electrode, measuring the chemical oxygen demand (COD) decay using a supporting electrolyte, 2 g/L of Na₂SO₄. It was observed that the rate of COD decay considerably increased when the Ti/BDD electrode was used. Figure 2(a) shows that the decay of Orange II at the Ti/BDD anode was 91%, and this removal efficiency was higher than that obtained at the Ti/Sb₂O₅-SnO₂ anode (26%). In the case of Reactive red HE-3B, Figure 2(b) shows that the performance of COD abatement was very similar.

The Ti/BDD electrode achieved about 95% removal, whereas Ti/Sb₂O₅-SnO₂ only 22%. In light of these results, Ti/BDD anodes are much more efficient than those composed of Ti/Sb₂O₅-SnO₂.

After that, this application motivated other researchers to investigate the use of BDD anodes for removing dyes from synthetic wastewaters, such as the degradation of the azo dye Eriochrome Black T (EBT) by Cañizares et al. [20]. Figure 3 shows the abatement of 100 mg/dm³ of EBT where TOC 70% and COD 90%, after that 20 Ah dm⁻³ was applied. When 1813 mg/dm³ has been treated, both TOC and COD decreased considerably after 80 Ah dm⁻³, achieving closely 100% of degradation. During the BDD oxidation of EBT molecules, a great variety of intermediates (changes in the COD) was observed, attaining complete incineration at the final electrolysis time. Sakalis et al. [21] compared the use of two different anodes: platinized titanium (Pt/Ti) and Niobium/synthetic diamond (Nb/D), in order to improve the electrochemical incineration of synthetic samples containing four reactive azo dyes. Different experimental conditions were evaluated, such as supporting electrolyte, concentration of electrolyte, effect of applied potential, pH, and temperature. Under the optimum electrochemical conditions, complete elimination of dyes was achieved, using both electrodes Pt/Ti and Nb/D. However, the use of Nb/D anodes showed the best performances on removal efficiency for the most important parameters such as biochemical oxygen demand (BOD₅), COD, and TOC.

The influence of the anode on the electrochemical oxidation of methylene blue (MB) was evaluated by Panizza et al. [22]. Direct electrolysis using boron-doped diamond and the indirect electrolysis mediated by active chlorine electrogenerated on a TiRuO₂ oxide anode, was compared for

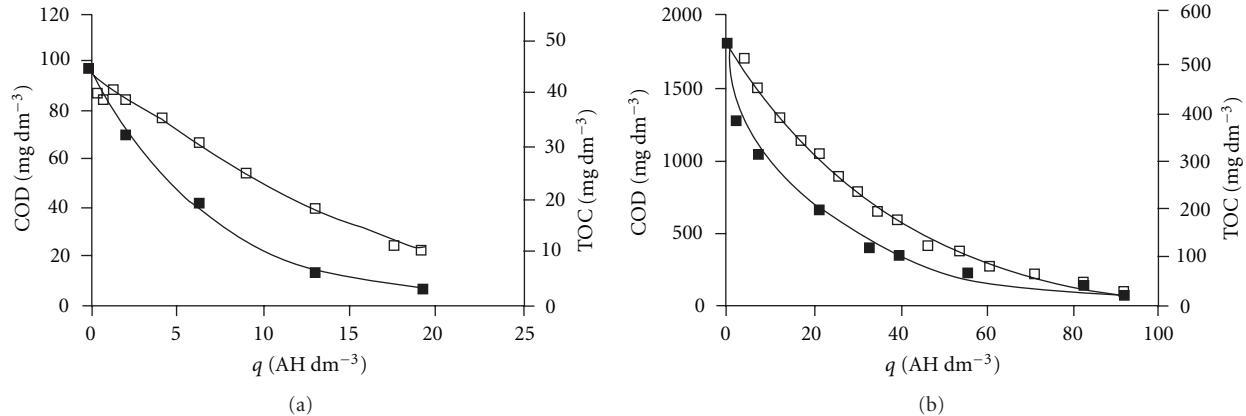


FIGURE 3: Changes in the COD (■) and in the TOC (□) with the current charge passed during electrolyses of EBT-polluted synthetic wastes. Operation conditions: current density, 300 A·m $^{-2}$; $T = 25^\circ\text{C}$. Waste composition: sodium sulfate Na₂SO₄, 5000 mg·dm $^{-3}$; natural pH. COD₀: (a) 100 and (b) 1813 mg·dm $^{-3}$ O₂ [20].

removing MB. The study was carried out on COD and color removal efficiencies as a function of time, for each type of electrochemical processes. Figure 4 shows the comparison of COD abatement and color removal for both processes (direct and indirect electrolysis). As can be observed, the graph shows interesting results, because indirect electrolysis facilitates faster mineralization and decolorization of the solution. The authors attributed this behavior to the strong bleaching properties of active chlorine, and the efficiency of direct electrolysis is limited by the mass transport of pollutants to the anode surface in solutions containing low concentrations of organics.

Based on the literature results reported by Panizza and Cerisola, the ability to remove organic pollutants, like azo dyes, is more evident when diamond electrodes are used. These assertions were confirmed when the electrocatalytic properties of different materials are compared; the anodic oxidation of methyl red was studied comparing the electrocatalytic properties of Ti–Ru–Sn ternary oxide, platinum, lead dioxide, and boron-doped diamond anodes. The results of the study demonstrated a different reactivity of electrogenerated hydroxyl radicals for each electrode, limiting the removal efficiency of methyl red removal and COD abatement.

The authors speculate that on BDD, which is well known to have weak adsorption properties due to its inert surface, hydroxyl radicals are very weakly adsorbed and consequently they are very reactive toward organics oxidation. On the contrary, lead dioxide is hydrated and hydroxyl radicals are expected to be more strongly adsorbed on its surface and consequently less reactive. For these reasons, TiRuSnO₂ and Pt anodes, which are good electrocatalysts for the oxygen evolution reaction due to their low oxygen evolution overpotential, showed poor elimination efficiencies. Contrarily PbO₂ and BDD anodes, with high oxygen evolution overpotential making those poor electrocatalysts for the oxygen evolution reaction, had higher rates of COD and color removals. The same behavior was observed when Panizza and Cerisola [23] compared the electrocatalytic

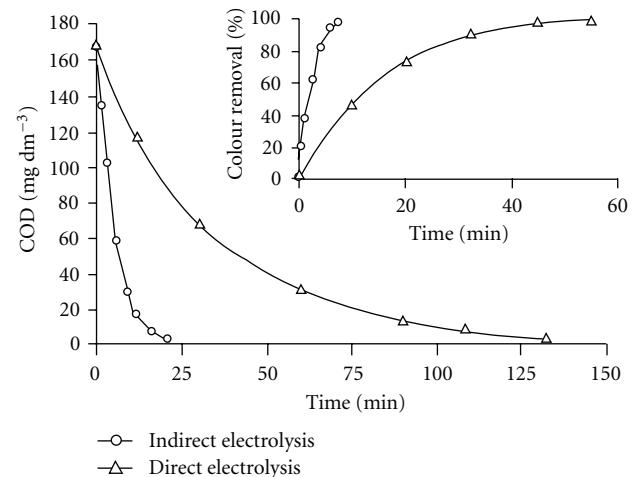


FIGURE 4: Comparison of the COD evolution and colour removal (inset) during the direct and mediated electrolysis of the methylene blue. Indirect electrolysis: Cl⁻ concentration = 1.2 g dm $^{-3}$; $i = 60 \text{ mA cm}^{-2}$; flow rate: 180 dm $^3 \text{ h}^{-1}$; $T = 40^\circ\text{C}$. Direct electrolysis: $i = 20 \text{ mA cm}^{-2}$; flow rate: 180 dm $^3 \text{ h}^{-1}$, $T = 40^\circ\text{C}$ [22].

properties between lead dioxide (PbO₂) and BDD anodes for the electrochemical incineration of methyl red, using an electrolytic flow cell with parallel plate electrodes. Results indicated that, for all of the applied currents, the COD decreased to zero, after 8 hours of treatment using a PbO₂ anode. Whereas, the COD decreased to zero with all applied currents after 4 h of treatment using a BDD anode, resulting in complete mineralization of the dye by means of the electrogenerated ·OH radicals. The influence of the current density on the COD and CE during the electrochemical oxidation of methyl red at the BDD anode is shown in Figure 5.

The influence of different operational conditions (such as initial dye concentration, Na₂SO₄ concentration as supporting electrolyte, current density, flow rate, and initial pH) during azo dye degradation has received great attention by

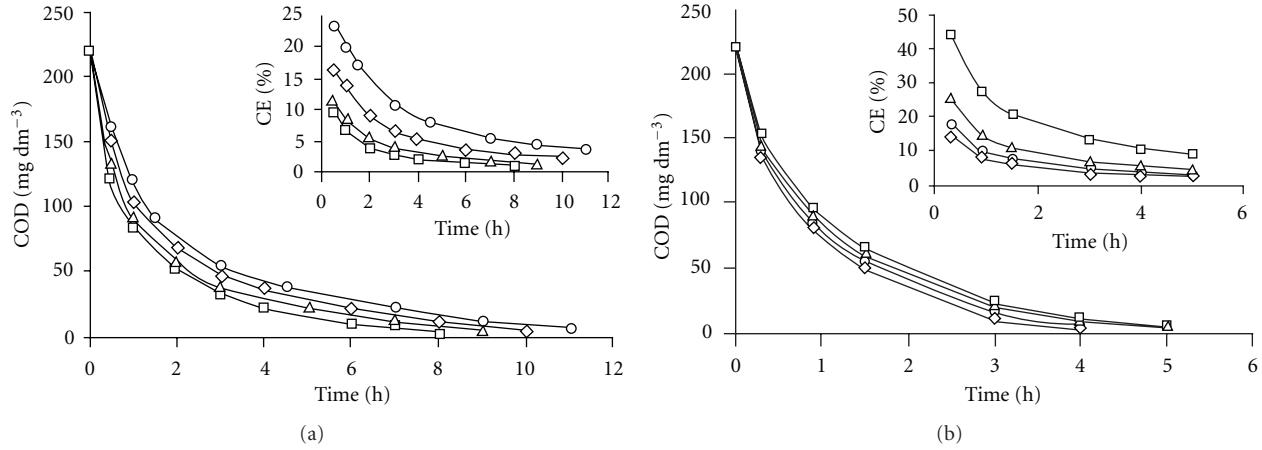


FIGURE 5: Influence of the applied current on the evolution of the COD and current efficiency (inset) as a function of time during the electrolysis of methyl red on the (a) PbO_2 and (b) BDD anodes, respectively. Flow rate = $180 \text{ dm}^3 \text{ h}^{-1}$; pH = 3; applied current = (○) 0.5, (◊) 1, (△) 1.5, (□) 2 A [23].

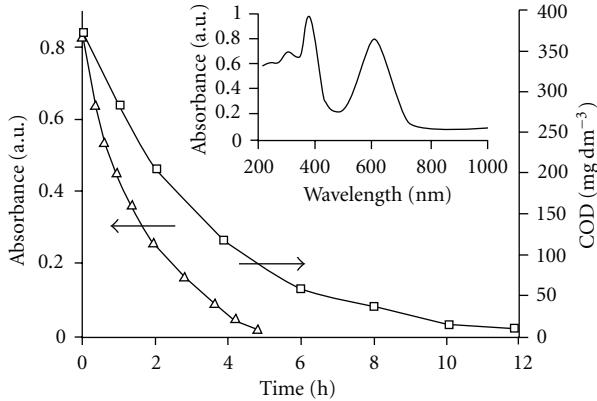


FIGURE 6: Trend of absorbance band at 594 nm (Δ) and COD (\square) during the anodic oxidation solution of acid blue 22 at a 0.3 mM concentration on the BDD electrode at $i = 20 \text{ mA cm}^{-2}$, flow rate = $300 \text{ dm}^3 \text{ h}^{-1}$, $T = 25^\circ\text{C}$. UV spectrum of the acid blue 22 is shown in the inset [24].

several authors (Panizza and Cerisola [24], Bensalah et al. [25], Koparal et al. [26], Carvalho et al. [27], and Saez et al. [28]).

For example, Panizza and Cerisola evaluated the electrochemical oxidation of synthetic wastewater containing acid blue 22 dye using a BDD electrode [24]. This study investigated the influence of certain variables such as current density, dye concentration, flow rate, and temperature on the abatement of COD and color. Figure 6 presents an interesting comparison between color removal and COD abatement for 0.3 mM of acid blue 22 by applying 20 mA cm^{-2} current density. Complete solution decolorisation after about 4 h of electrolysis was achieved, while 7 h was necessary to complete COD elimination, indicating that acid blue 22 was oxidized initially to colorless intermediates and then to carbon dioxide. Figure 7 compares energy consumption (kWh m^{-3}) for COD and color removal of acid blue 22 at a 0.3 mM concentration during electrochemical oxidation

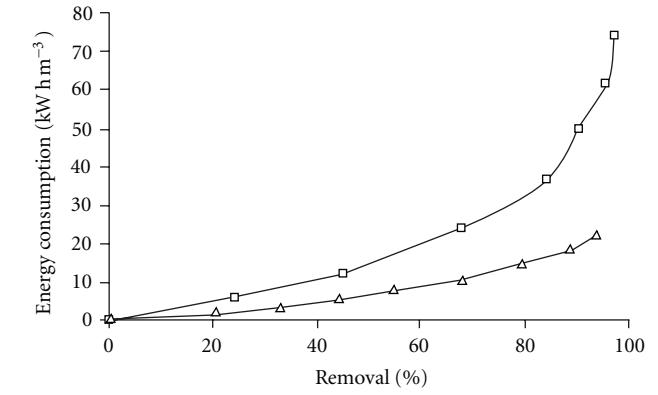


FIGURE 7: Evolution of the specific energy consumption against the removal of COD (\square) and color (\triangle) during the anodic oxidation of acid blue 22. Acid blue 22 concentration: 0.3 mmol; current density 20 mA cm^{-2} ; flow rate $300 \text{ dm}^3 \text{ h}^{-1}$; $T = 25^\circ\text{C}$ [24].

using a BDD anode. The result is very important from an economic point of view because the energy consumption increased almost linearly with color removal but had a sharp increase with COD removal. On the other hand, Bensalah et al. [25] investigated the treatment of synthetic wastewaters containing Alphazurine A (AZA) by anodic oxidation using BDD anodes, monitoring COD and color removal under different operational conditions. According to the experimental results obtained in this work, the electrochemical oxidation process is suitable for removing COD and decolorizing wastewaters containing AZA dye, due to the production of hydroxyl radicals and other oxidants on the anode surface. Whereas, the energy requirements for removing 95% of initial COD during galvanostatic electrolyses of AZA synthetic solutions depends mainly on the applied current density, temperature and agitation rate; it passes from 57 kWh at 30 mA cm^{-2} to 138 kWh at 90 mA cm^{-2} per kg COD removed; from 102 kWh at 25°C to 89 kWh at

TABLE 1: Percentage of color removal and COD decay obtained for the electrochemical oxidation treatment with BDD anodes of selected synthetic dyes solutions under optimized conditions at ambient temperature or 25°C.

Dye	Solution	Electrolytic system	$j^a/\text{mA cm}^{-2}$	Color removal/%	COD decay/%	Ref.
<i>Si/BDD</i> 3,4,5-trihydroxybenzoic acid)	1000 mg dm ⁻³ in HClO ₄	A one-compartment electrolytic flow cell with parallel plate electrodes.	20–60	100	100	[43]
Remazol Brilliant Blue	50 mg dm ⁻³ RBBR, 0.05 M Na ₂ SO ₄ and 0.01 M NaCl with an initial pH of 5.8 and conductivity 8.5 ms cm ⁻¹	Batch mode in a 100-mL single-compartment cell with a boron-doped diamond anode of geometric area 5 cm ² .	20–40	99	98	[29]
Acid Yellow 1	1000 mg dm ⁻³ in 0.5 M HClO ₄	A one-compartment electrolytic flow cell with a BDD of 50 cm ² . A two compartments Thermostated cell under different current densities, temperatures, and COT concentration.	0.5–1.5 ^b	100	100	[30]
O-toluidine	1×10^{-4} – 1×10^{-3} M ^c	thermojacketed BTT reactor was used with BDD Raschig's rings. In a 150 mL, one-compartment electrolytic cell with a BDD of 4 cm ² .	20–100	— ^d	70–90	[33]
Basic Blue 3	1000 mg dm ⁻³	In an one-compartment filter-press flow cell.	0.5–0.875	99	87	[34]
Crystal violet	33–600 mg dm ⁻³	Batch recirculation reactor containing one-compartment cell equipped with boron-doped diamond anode and Pt cathode.	2.5–15	100	80–95	[44]
Acid Black 210	500 mg dm ⁻³	Electrolytic cell with a single compartment without diaphragm with Ti/BDD (1.5 cm ²) anode and Ti/RuO ₂ –TiO ₂ –SnO ₂ (9 cm ²) cathode.	25–100	100	80–97	[35]
<i>Nb/BDD</i> Orange II	50 mg dm ⁻³ in the presence of different supporting electrolytes, 200 mL in each run	1.29–7.68	80–98	80–95	[31]	
<i>Ti/BDD</i> Alizarin Red S	0.278 mM ^c	40	100	100	[41]	

^a Applied current density, ^b potential, ^cmolar concentration, ^dnot determined.

60°C and from 141 kWh at 100 rpm to 29 kWh at 400 rpm. Based on results reported by several authors (Panizza and Cerisola [24], Bensalah et al. [25], Koparal et al. [26], Carvalho et al. [27] and Saez et al. [28]), the electrochemical technique is economically suitable for waste pre-treatment to remove color. However, although complete COD removal is technically feasible, its high-energy cost makes this technique unsuitable for a refining process.

Nevertheless, the application of electrochemical technologies for decolorization and degradation of azo dyes has been investigated and reported by several scientific groups, as recently reviewed in details by Martínez-Huitel and Brillas [16]. However, since this review was published, new results have been published and more statements have been established. The destruction by EO with BDD of dyes such as Remazol Brilliant Blue Reactive [29], Acid Yellow 1 [30], Orange II [31], Reactive Orange 16

[32], O-Toluidine [33], Basic Blue 3 [34], acid black 210 [35], Trichloroethylene [36], methylene blue [37], 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid (A1), 5-amino-2-methoxybenzenesulfonic acid (A2), 2,4-dihydroxyaniline hydrochloride (A3) and benzene-1,4-diamine (A4) [38], methyl orange [39], Reactive brilliant red X-3B [40], Alizarin Red S [41], Aniline (AN) and Ortanic (OA), Metanilic (MA) and Sulfanilic (SA) acids [42], Gallic acid [43] and Crystal Violet [44], has been studied. In these studies the influence of pH, dye content, temperature, supporting electrolyte, cathode material, current density, and anode potential was investigated for optimizing degradation conditions. Many of these authors also estimated the color removal, current efficiency and decay in COD and/or TOC, which mainly depended on the above parameters. Data are collected in Table 1, and the most relevant papers will be discussed and commented below.

The electrochemical oxidation of aniline (AN) and ortanilic (OA), metanilic (MA), and sulfanilic (SA) acids (dyes precursors) was studied by Santos et al. [42] using a BDD electrode. Model solutions of the different amines with concentrations of 200 mg L^{-1} in $0.035 \text{ M Na}_2\text{SO}_4$ were oxidized using a batch cell by applying 200 and 300 A m^{-2} . Results showed a good elimination of the persistent pollutants, with COD and TOC removals always higher: AN: 91% and 90%, OA: 75% and 82%, MA: 88% and 87%, and SA: 85% and 79% (for 200 and 300 A m^{-2} , resp.). The combustion efficiencies, calculated for the first hour of the runs, for the 300 A m^{-2} assays, were the following: AN: 0.93, OA: 0.28, MA: 0.82, and SA: 0.83, indicating the efficiency of the BDD anode for removing these dyes precursors. For all the amines studied, after 6 h degradation, only oxalic and maleic acids were identified by HPLC. Additionally, analysis performed to the content of different forms of nitrogen in solution led to the conclusion that, in the case of the sulfonated amines, the amino group was mainly eliminated in the form of ammonia, since AMN content increases while TKN decreases.

Another study evaluated the electrochemical oxidation of several dyes precursors [38], such as 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid (A1), 5-amino-2-methoxybenzenesulfonic acid (A2), 2,4-dihydroxyaniline hydrochloride (A3), and benzene-1,4-diamine (A4), using a BDD electrode as the anode. Tests were run at room temperature with model solutions of the different amines at concentrations of 200 ppm , using $0.035 \text{ M Na}_2\text{SO}_4$ aqueous solutions as electrolytes, in a batch cell with recirculation at different current densities (200 and 300 A m^{-2}).

From the results obtained by these authors, the anodic oxidation of four dyes precursors, using a BDD anode, showed high COD and TOC removals (see Figure 8). For the assays run with the first two compounds, after 4 h , no amine was detected by HPLC. For the tests with the other two compounds, small amounts of the amines were still present at the end of the assay, and higher combustion efficiencies were observed. Apparently, a high initial amine removal rate leads to a lower degree of mineralization. Additionally, the substituent has an effect on the rate of degradation mainly due to its contribution to the molar volume, since diffusivity and, consequently, mass transfer coefficient decrease with its increase. The anodic oxidation of 2,4-dihydroxyaniline hydrochloride and benzene-1,4-diamine was the only instance where hydroquinone and maleic acid were identified as metabolites, after a 6 h run. These particular oxidations also produced higher combustion efficiencies. It seems that the early formation of oxalic acid reduces the ability to obtain mineralization. On the other hand, the formation of other intermediates, like hydroquinone, may lead to an easier complete combustion of the organic matter. Analysis performed to different forms of nitrogen content led to the conclusion that the amino group is mainly eliminated in the form of ammonia, since AN content increases while TKN decreases during the anodic oxidation.

Zhou and Särkkä [39] compared the electrochemical degradation of methyl orange on the mixed metal oxide

(MMO) and BDD electrodes. The effect of several parameters such as current density, pH, electrolyte types, and initial dye concentration were investigated in terms of decolorization. COD and TOC removals, as well as energy consumption, were estimated. The degradation on two electrodes presented different trends in operative parameters. High current density enhanced the decolorization on both electrodes, but the promotion on MMO was not as significant as that on the BDD electrode, which led to a sharp increase of specific energy consumption, as shown in Figure 9. The decolorization of MMO performed better at acidic conditions for two electrodes, but the dependence of pH on BDD was not as obvious as that on MMO electrodes.

The presence of NaCl favored the indirect oxidation of active chlorines on MMO electrodes, which greatly improved the decolorization rate. High initial concentration enhanced general current efficiency (GCE) although the COD and TOC removal efficiency was decreased. The GCE on BDD was much higher than that on MMO, indicating that it was much more efficient. The BDD electrode yielded high combustion efficiency, while on MMO is greatly improved in the presence of NaCl .

Due to the applicability of mediated oxidation using DSA or BDD anodes, other groups have focused attention on this electrochemical process, evaluating different operating conditions. For example, the electrochemical degradation of chloride-mediated and chloride-free dye wastewaters (a synthetic solution containing high concentration methylene blue (MB), with 1000 mg L^{-1}), was investigated by Wu and coworkers [37]. In chloride-free wastewater, the electrochemical degradation efficiency of dye on BDD electrode was much higher than that on DSA, with a COD removal of 100% and 26% for BDD and DSA, respectively. In chloride-mediated dye wastewater, COD removal was faster than that in chloride-free wastewater on both BDD and DSA electrodes with COD removal efficiencies higher than 95%, whereas the rate of COD removal on DSA was faster than that on BDD electrode. The investigation indicated that DSA is more suitable than BDD electrode in degradation of dye wastewaters containing chloride in terms of energy and time saving. However, for chloride-free dye wastewaters, BDD electrode is more appropriate, in regards to environmental protection, because of its ability to achieve complete mineralization. These assumptions are confirmed by the results reported in Figure 10.

As shown by several authors [16] and Wu et al. [37], the high chlorine evolution potential in Cl^- -mediated wastewater may cause difficulty in the formation of active chlorine from wastewater and decrease the rate of electrochemical degradation of organic compounds, leading to a slower electrochemical degradation process on BDD. The lower chlorine evolution potential of 1.0 V on the DSA probably makes the formation of active chlorine on DSA surface much easier, so that the oxidation rate of MB on DSA is much higher than that on BDD due to the strong oxidative property of active chlorine. As the electrolysis takes place, the concentration of chloride in electrolyte decreases gradually, and the amount of active chlorine on the electrode surface

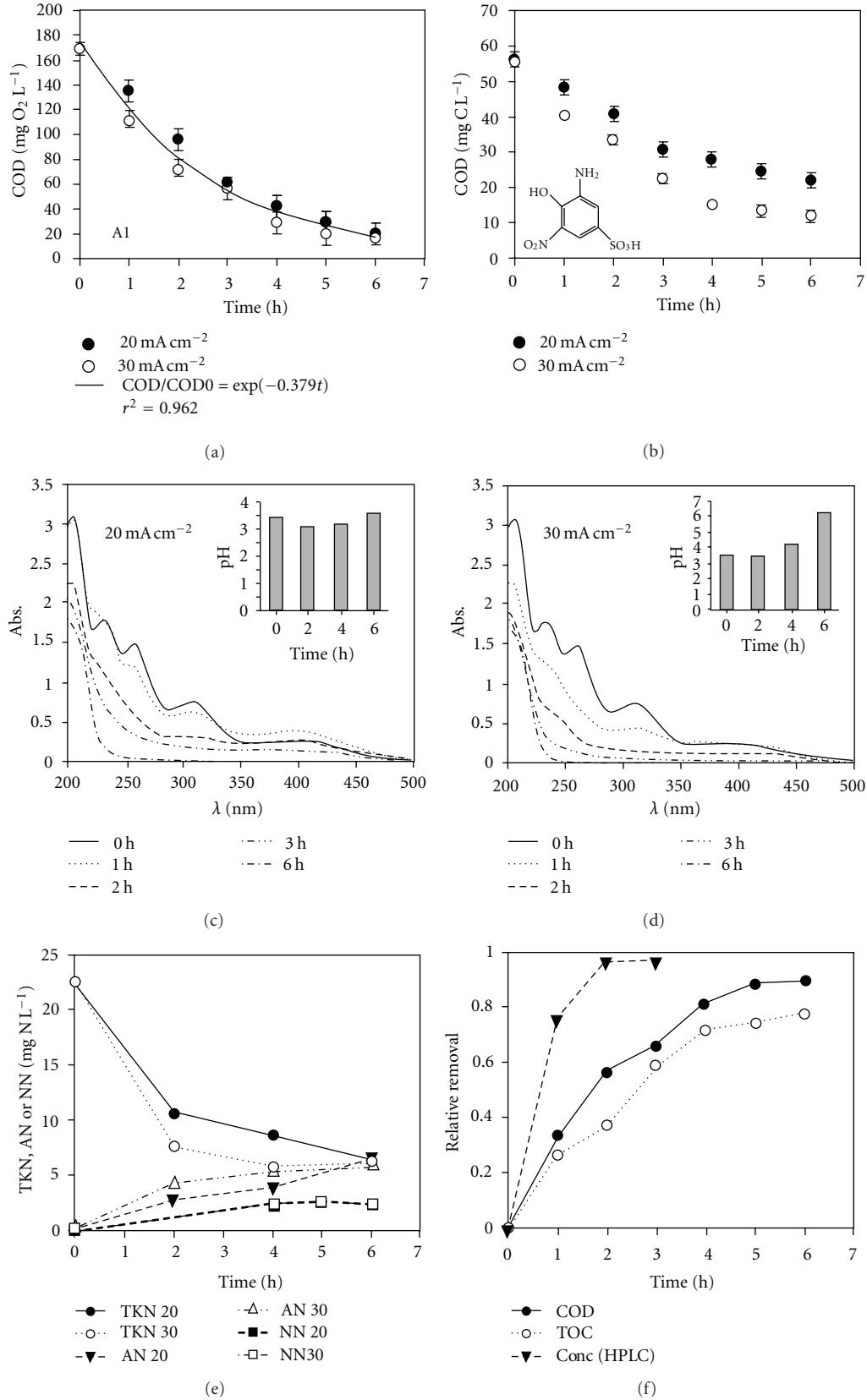


FIGURE 8: Variations of COD (a), TOC (b), absorbance and pH (c, d), TKN, AN and NN (e) and relative removals of COD, TOC and concentration (f) versus time observed during the degradation assays of the amine A1, with an initial concentration of 200 mg L^{-1} , performed with a BDD anode (8 cm^2). Cathode: stainless steel (8 cm^2); current density: 20 and 30 mA cm^{-2} ; electrolyte $0.035 \text{ M Na}_2\text{SO}_4$ aqueous solution [38].

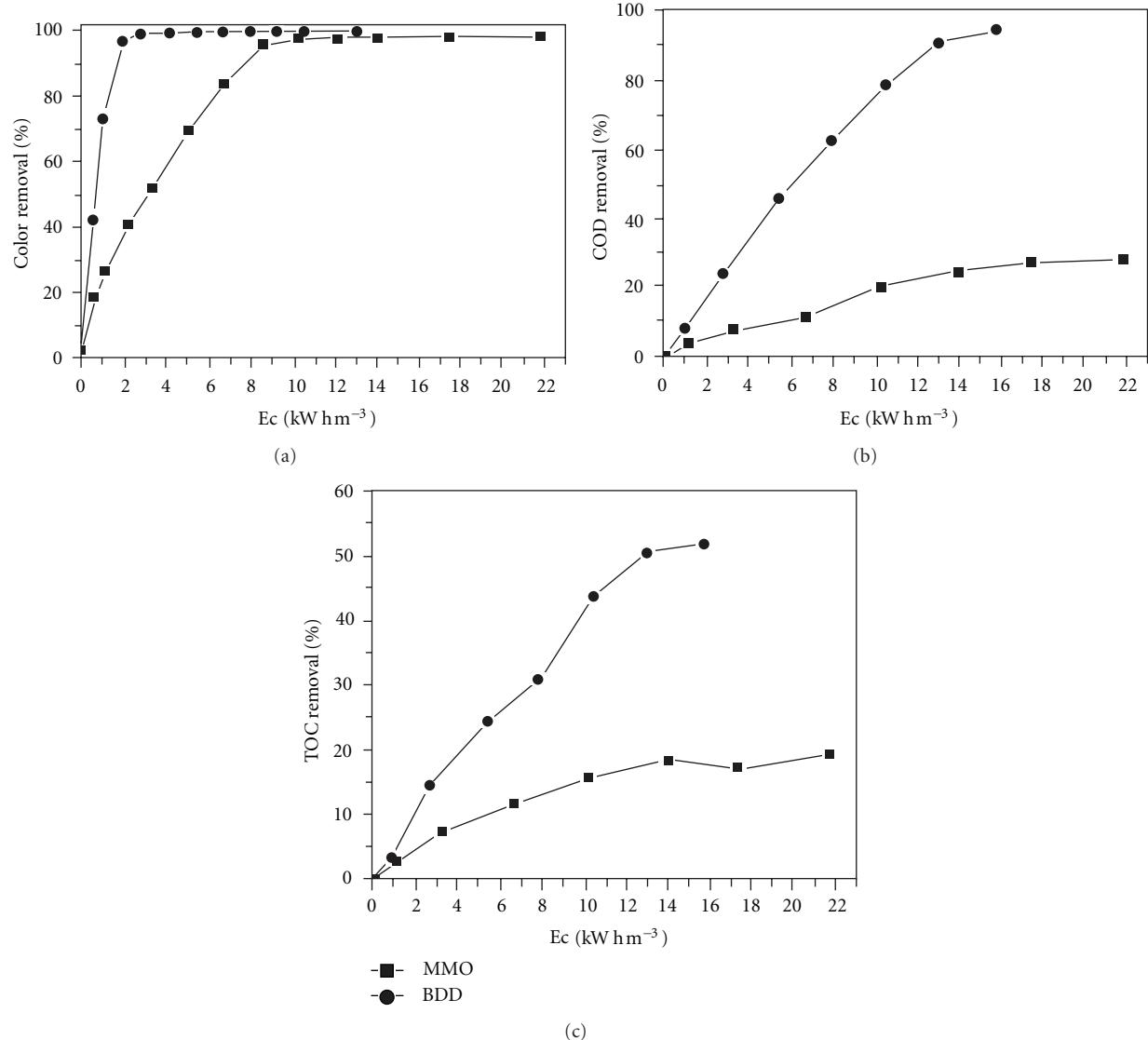


FIGURE 9: The removal of color, COD, and TOC on two electrodes. Conditions: electrolyte: Na_2SO_4 0.1 M + NaCl 0.05 M; pH 3; MO 200 mg L^{-1} ; current density: 50 mA cm^{-2} . Reprinted with permission of Separation and Purification Technology [39].

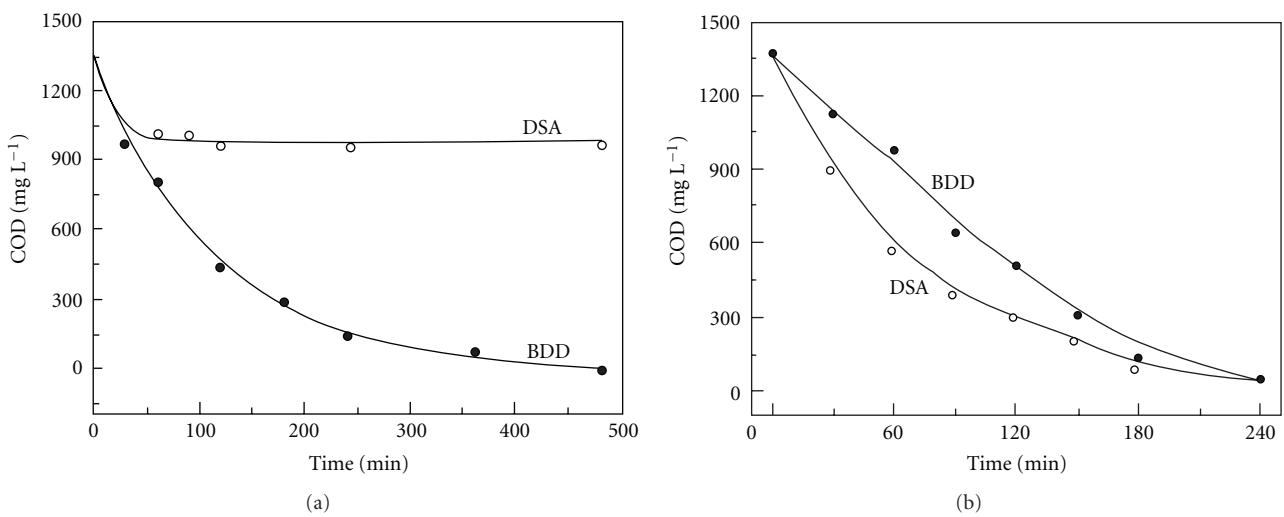


FIGURE 10: COD (a) in MB degradation in chloride-free wastewater and COD (b) in MB degradation in chloride-mediated wastewater [37].

decreases, so that the rate of electrochemical decontamination of wastewater is lowered. However, this electrochemical treatment of chloride-containing wastewater will introduce strong toxic halogen compounds and requires a second step to remove this chlorinated organic compound (e.g., by adsorption on activated carbon, coupled/integrated methods [45], or emerging technologies [16]).

Therefore, new electrochemical processes are being studied. For example, photocatalysis on nanosized TiO_2 and electrocatalysis on BDD electrode, two advanced oxidation processes (AOPs) in the field of wastewater treatment, were combined into one batch reactor by Zhang and coworkers [40]. Reactive brilliant red X-3B dye was used as a model compound to study the combinatory effect between photocatalysis and electrocatalysis. The aim of this study was to confirm that the oxidants produced on BDD anodes such as hydrogen peroxide, ozone, and peroxydisulfate could raise the quantum efficiency of photocatalytic processes. Initially, the performances of the separate processes in the elimination of X-3B were compared and different reaction systems of the same size were employed to study the performance in X-3B decolorization, listed as (1) BDD alone; (2) BDD with UV light, without TiO_2 ; (3) TiO_2 photocatalysis with UV light; (4) BDD + UV + TiO_2 ; (5) BDD + UV + TiO_2 + aeration. The air rate was set to 5.0 L/h by a small magnetic air pump.

The experimental conditions were set as follows: initial concentration of X-3B (C_0) 50 mg/L; current density 25.2 mA/cm²; pH 2.72 (adjusted with 1.0 M H_2SO_4). The time for removing color completely was studied for each reaction system, and the results were illustrated in Figures 11(a) and 11(b). It can be deduced that photocatalysis coupled with electrocatalysis in one reactor will degrade pollutants faster than either process alone. The results obtained show some interesting phenomena, commonly called synergistic effect. Both BDD electrode and TiO_2 film produces $\cdot\text{OH}$ on their surfaces, and a portion of them may react directly with X-3B. As have been well established by the literature, oxidation of pollutants at the BDD anode occur under mass transfer control mainly in a thin liquid film near the electrode surface, where the concentration of $\cdot\text{OH}$ is very high. Similar phenomenon also exists in photocatalytic systems. But the adding of salts (SO_4^{2-}) can trap part of these $\cdot\text{OH}$ to form peroxides and diffuse into the whole solution to allow full contact with X-3B. Then $\cdot\text{OH}$ are set “free” by activating these mixture of oxidants (H_2O_2 , $\text{S}_2\text{O}_8^{2-}$) with UV light, thus promotes the performance as well as the generation of more $\cdot\text{OH}$ on the surfaces of both BDD electrode and TiO_2 film. These experimental results revealed the suitability of the combination of the two oxidation processes for accelerating the removal of dye pollutants from solution.

Other scientific groups are studying the preparation of new electrocatalytic materials with similar characteristics of BDD anodes in order to decrease the cost of treatment and increase removal efficiency. In this context, interesting results have been reported by Andrade and Tasso [46] who studied the performances of the Ti-Pt/ β -PbO₂ and BDD electrodes in the electrooxidation of simulated wastewaters containing 85 mg L⁻¹ of the Reactive Orange 16 dye using

a filter-press reactor. The electrolyses were carried out at the flow rate of 7 L min⁻¹, at different current densities (10–70 mA cm⁻²), and in the absence or the presence of chloride ions (10–70 mM NaCl). In the absence of NaCl, total decolorisation of the simulated dye wastewater was attained independently of the electrode used. However, according to the results reported by the authors, the performance of the BDD electrode was better than that of the Ti-Pt/ β -PbO₂ electrode; the total decolorizations were achieved by applying only 1.0 Ah L⁻¹ and 2.0 Ah L⁻¹, respectively. In the presence of NaCl, with the electrogeneration of active chlorine, the times needed for total color removal were markedly decreased; the addition of 50 mM Cl⁻ or 35 mM Cl⁻ (for Ti-Pt/ β -PbO₂ or BDD, resp.) to the supporting electrolyte led to a 90% decrease of these times (at 50 mA cm⁻²). On the other hand, total mineralization of the dye in the presence of NaCl was attained only when using the BDD electrode (for 1.0 Ah L⁻¹); for the Ti-Pt/ β -PbO₂ electrode, a maximum mineralization of 85% was attained (for 2.0 Ah L⁻¹). For total decolorization of the simulated dye wastewater, the energy consumption per unit mass of dye oxidized was only 4.4 kWh kg⁻¹ or 1.9 kWh kg⁻¹ using the Ti-Pt/ β -PbO₂ or BDD electrode, respectively. Clearly the BDD electrode proved to be the best anode for the electrooxidative degradation of the dye, either in the presence or the absence of chloride ions. In the absence of chloride, this high performance is due to the fact that the electrogenerated hydroxyl radicals are weakly adsorbed on the BDD because of its inertness; consequently, they are very reactive towards the dye oxidation. On the Ti-Pt/ β -PbO₂ surface, the hydroxyl radicals are more strongly adsorbed, thus being less reactive. Whereas, the addition of chloride to the simulated dye wastewater had a very marked effect on the dye degradation; the time needed for total decolorization of the dye decreased by 90%. This increased performance is most probably related to the weak chlorohydroxyl adsorption strength on the BDD surface, as it is the case with the hydroxyl radical.

2.3. Electrochemical Treatment of Real Wastewaters Polluted with Dyes.

Few papers have demonstrated that the use of a BDD thin film in EO provides total mineralization with high current efficiency of real textile wastewaters [16]. However, more studies have been published in the last three years.

Chatzisymeon et al. [47], using a titanium (grade II/VII) anode covered by a thin film of tantalum, platinum, and iridium alloy, attained 98% decolorization within 10–15 min, regardless of the applied current. From their best data (use of 5 A for 10 min, 8 L of effluent), one infers that only 0.38 kC L⁻¹ was used, which is much lower than the value used in our best case (5.8 kC L⁻¹); however, they added NaCl to the effluent to have a minimum concentration of 10 g L⁻¹ while we used only 1.5 g L⁻¹.

Fytianos et al. [48] compared the use of two different anodes: platinized titanium (Pt/Ti) and Nb/BDD, in order to improve the electrochemical incineration of synthetic samples containing four reactive azo dyes and real wastewater. They compare their treatment through biochemical oxygen

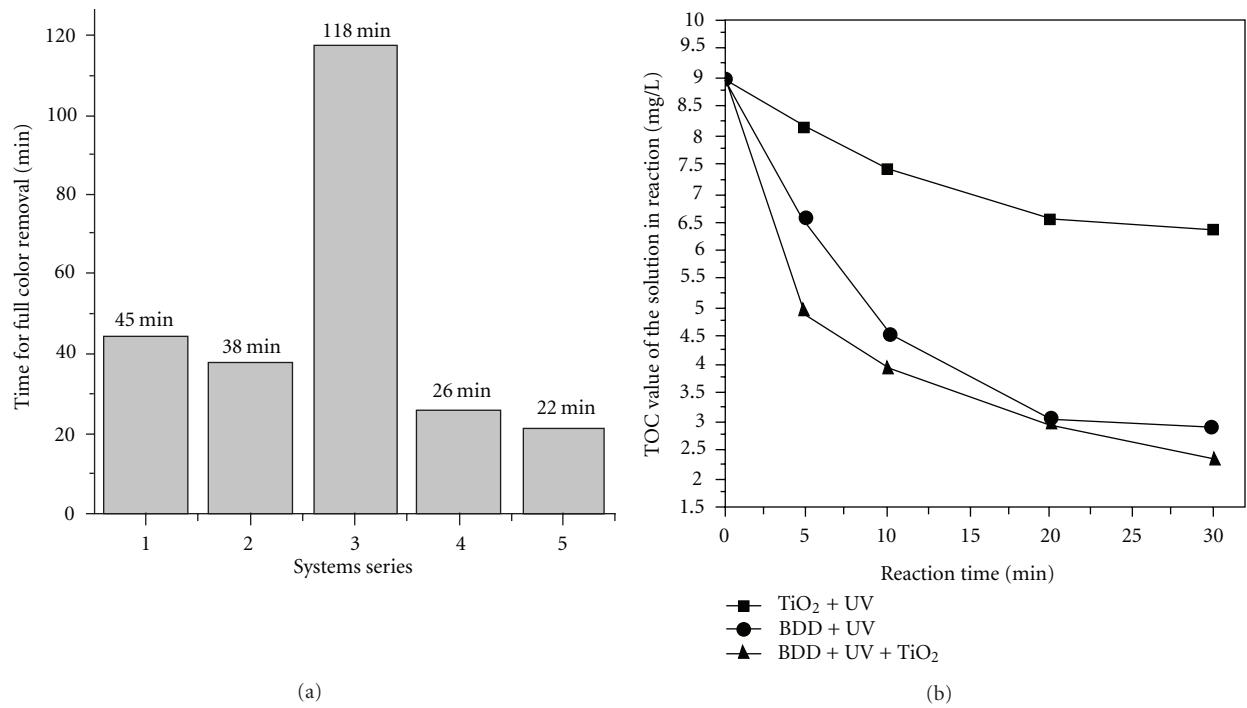


FIGURE 11: (a) Comparison on degradation performance of different reaction systems and (b) TOC decay with reference to electrolysis time for the mineralization of X-3B with three different systems (C_0 : 50 mg/L, I_{appl} = 25.2 mA/cm², pH 2.72) [40].

TABLE 2: Initial and final values of the most important environmental parameters of electrochemically treated wastewater under optimal conditions [48].

Environmental parameter	Initial wastewater	Electrochemically treated wastewater	
		Pt/Ti	Nb/D
pH	9	8	8
% Dye removal (436 nm)	—	67.3	81.2
% Dye removal (526 nm)	—	82.4	89.1
% Dye removal (620 nm)	—	80.3	89.5
Chlorides (mg/L)	224	174	112
Hypochlorites (mg/L)	—	0.2	82.4
BOD ₅ (mg/L)	149	25	75
COD (mg/L)	150	70	10
COD/BOD ₅	1	2.8	0.13
TOC (mg/L)	164	100	78
Temperature (°C)	25	28	40.5

Time of treatment: 30 min.

demand (BOD₅), COD, TOC, energy consumption, and efficiency of the anodes. In this context, the authors evaluated

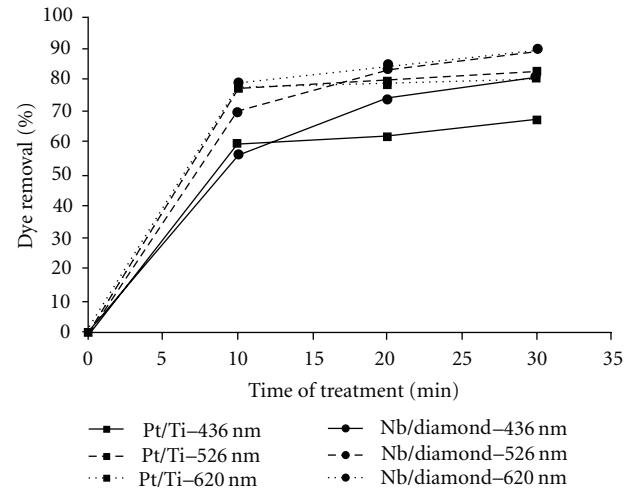


FIGURE 12: Decoloration efficiency of Nb/D and Pt/Ti, treating real wastewater. Applied potential: 18 V; time of treatment: 30 min [48].

different experimental conditions such as type and concentration of supporting electrolyte, effect of applied potential, pH, and temperature. Table 2 shows initial and final values of the most important environmental parameters of electrochemically treated wastewater under optimal conditions using both Pt/Ti and Nb/BDD electrodes. As can be seen, the use of Nb/BDD anode increased the efficiency removal for the most important parameters such as BOD₅, COD, TOC, and dye removal. An interesting result was shown in Figure 12, where the authors present the comparison of Pt/Ti and Nb/BDD electrodes, to treat real wastewater,

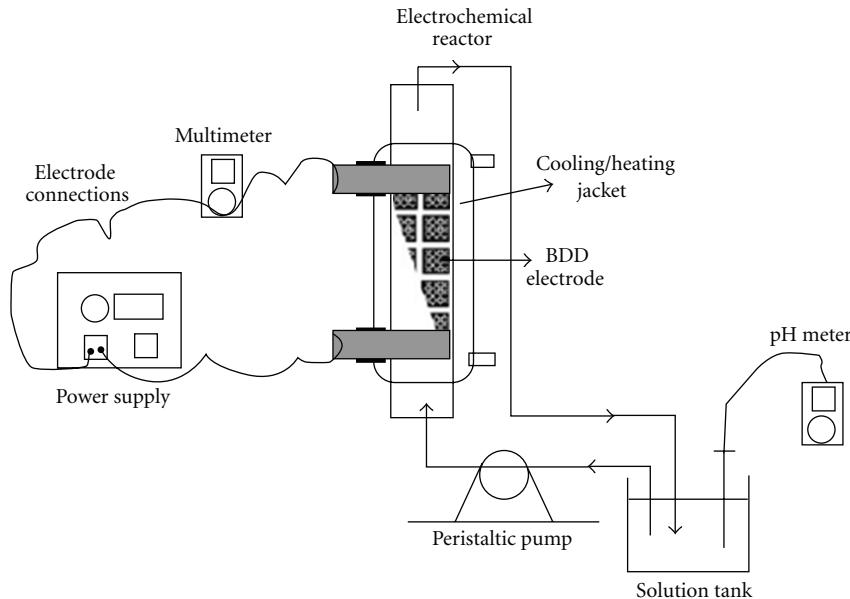


FIGURE 13: Experimental setup used in the studies for the degradation of Basic Red 29 (BR29) [26].

without any further addition of electrolytes. These results clearly indicated that after 30 min treatment, the rate of decoloration for the two anodes was very similar. However, the Nb/BDD achieved a higher decoloration removal (85–90%), resulting in practically colorless final wastewater.

Koparal et al. [26] has demonstrated that the electrochemical incineration of Basic Red 29 (BR29) treatment in a bipolar trickle tower (BTT) reactor by using Raschig's ring-shaped BDD electrodes is an originally setup to this goal. The experimental electrochemical reactor is illustrated in Figure 13. The effects of some important parameters such as initial dye concentration, Na_2SO_4 concentration as supporting electrolyte, current density, flow rate, and initial pH on the removal efficiency were studied. From the results by Koparal et al. [26], the initial COD of real effluent was 566.45 mg/L and decreased gradually to a final value of 52.38 mg/L after 8 h of treatment. A decrease in COD of nearly 91% was achieved with an energy consumption of 1.4 kW h/g COD removed. Usually, the toxicity assays for electrochemistry treatments are not performed. However, microtox bioassay tests were performed in this study to assess the textile wastewater treated in the electrochemical reactor in a given time intervals including the time zero. A toxicity result was given as relative toxicity index (RTI), Figure 14. Initial toxicity values showed that wastewater was highly toxic. According to the result, this method was found to be successful for dye and COD removal, indicating that it is also successful for toxicity reduction. As can be seen toxicity reduction was also achieved by using electrochemical oxidation, however, the toxicity was decreased to a lesser extent for textile wastewater.

Interesting research about the electrochemical oxidation of the biotic degradation products of the textile dye C.I. Acid Orange 7 (AO7) was achieved using a BDD electrode by Carvalho and collaborators [27]. They have proposed the use of real effluent obtained from anaerobic sludge

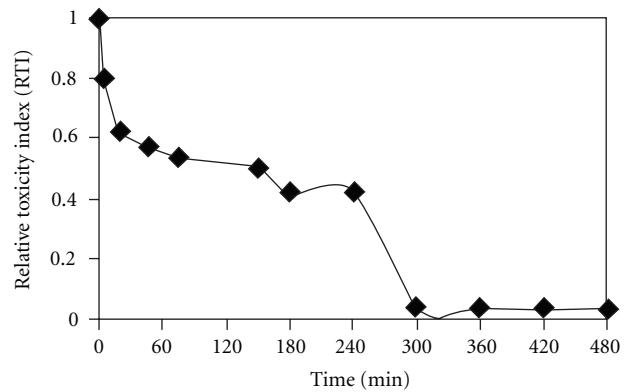


FIGURE 14: Variation of toxicity with time in the textile wastewater ($i = 1 \text{ mA/cm}^2$, $Q = 36.3 \text{ mL/min}$) [26].

blanket (UASB) reactors operating under mesophilic or thermophilic conditions. The electrolysis was studied using two supporting electrolytes: NaCl and Na_2SO_4 . The influences of some important variables such as initial metabolite concentration and current density on the electrodegradation rates of the biotic products were analyzed. Table 3 summarizes the results of the removal of COD, TOC, absorbance at 486 nm (AO7) and 250 nm (Arom) and relative current efficiency obtained after the electrochemical degradation of the effluents from the UASB reactors. Results have shown that under thermophilic conditions and 20 mA cm^{-2} of applied current density, it is possible to obtain higher removal efficiency of COD (90%) and TOC (30%) and diminished absorbance: Abs_{286} (100%) and Abs_{250} (90%). These data have demonstrated that BDD anodes could be an important tool for treating real effluents without the use of other chemical reagents or long time periods.

TABLE 3: Removals of COD and TOC, Absorbance at 468 nm (AO7) and 250 nm (Arom), and relative current efficiency obtained after the electrochemical degradation of the effluents from the UASB reactors [27].

Current density/mA cm ⁻²	Electrolyte	10			20			
		N	S	C	N	S	C	
<i>Mesophilic</i>								
% Removal								
COD		45	52	67	72	84	72	
TOC		41	21	19	31	31	24	
Abs ₄₈₆		66	77	90	89	100	100	
Abs ₂₅₀		73	70	75	85	86	81	
EC/EC _{N20}		0.31	0.19	0.19	1	0.57	0.52	
<i>Thermophilic</i>								
% Removal								
COD		54	52	63	83	67	90	
TOC		30	29	24	31	31	30	
Abs ₄₈₆		72	43	100	81	81	100	
Abs ₂₅₀		69	65	77	81	78	91	
EC/EC _{N20}		0.32	0.24	0.20	1	0.58	0.51	

N: no added electrolyte, S: sulphate, C: chloride, 10, 20: current densities of 10 and 20 mA cm⁻², EC: energy consumption, EC/EC_{N20}: relative efficiencies values are calculated with respect to the assay with no added electrolyte at 20 mA cm⁻².

On the other hand, Malpass et al. [49] report that about 90% decolorization was attained only when NaCl (5.85 g L⁻¹) was added to the real textile effluent (0.25 L), independently of the composition of the DSA anode used; from their data, one may infer that about 16 kC L⁻¹ was used. From all these results, it becomes clear that decolorization by electrooxidation is facilitated by the addition of Cl⁻ ions to the real textile effluent. In other researches, degradation of dye chromophores is more easily attained in the presence of active chlorine. In fact, Malpass et al. [50] showed that complete real textile effluent decolorization could be attained by the direct addition of OCl⁻ ions at a concentration of ~0.50 g L⁻¹.

Most relevant applications of anodic oxidation for treating real effluents have been published [51–58]. The electrochemical treatment of acrylic fiber-manufacturing, biorefractory wastewater, simulated ground water containing MTBE and BTEX, tannery wastewater, olive pomace leachate, biologically pretreated dye wastewater, biologically pretreated coking wastewater, and ink effluents are some examples of the applicability of this technology using BDD anodes.

Diamadopoulos and coworkers [58] studied the effluent treatment from flexographic printing by precipitation/coagulation and electrochemical oxidation over BDD electrodes. Precipitation with 3 g/L of lime led to complete removal of effluent turbidity (initial value of about 410 NTU) but only about 20% decrease in chemical oxygen demand (COD) (initial value of about 1,900 mg/L). In addition, higher lime dosages (up to 15 g/L) had no

effect on separation. Preliminary electrochemical oxidation experiments in the presence of sulphuric acid as supporting electrolyte showed that treatment performance (in terms of COD removal and decrease in sample absorbance at 300 nm) increased with increasing applied current, being more efficient at shorter treatment times and lower currents with efficiency reaching 30%. Following lime precipitation, the effluent was electrochemically oxidized at alkaline conditions for 360 min yielding 64% absorbance reduction and 50% COD removal (this corresponds to 60% overall COD removal for the combined process). Finally, they attributed the slightly low electrochemical treatment performance to limestone deposition and fouling of electrodes and other electrochemical reactor components, as evidenced by the gradual drop in conductivity/current throughout the operation.

In another case, the electrochemical treatment of acrylic fiber-manufacturing wastewater (AFMW) with BDD electrode was investigated by Zhang et al. [51]. A factorial design methodology was employed to evaluate the statistically important operating variables of treatment time (1–2 h), flow rate (400–600 mL/min), current intensity (0.50–1.00 A), and initial COD load (362–723 mg/L) on the treatment efficiency. The latter was assessed in terms of COD and ammonia-nitrogen (NH₃-N) removal. The results clearly demonstrated the suitability of the BDD technology for COD removal, as well as the unique behavior in removing NH₃-N. However, they performed a comparison electrochemical treatment between DSA and BDD anodes in order to understand both behaviors. These results showed great potential of the BDD technology to be an effective option for treating AFW, due to the efficient reduction of COD, energy consumption and treatment time in respect to the DSA anode, as shown in Figure 15. The excellent performance of the BDD technology might be attributed to the presence of free hydroxyl radicals generated on nonactive BDD electrode, as well as the chloride-free nature of AFW.

A practical application of electrochemical oxidation in biorefractory wastewater treatment was performed by Zhu et al. [52]. In this study, the performance of a smaller BDD anode (24 cm²) system in a continuous mode of electrochemical oxidation of phenol-simulated wastewater was first investigated. The performance was described by the response surface methodology (RSM). Next, the RSM was extended to examine the scale-up feasibility of BDD anode systems with similar configurations. They demonstrated that both COD degradation efficiency and specific energy consumption could be expected at the same level even as the system was enlarged over 100 times, which implied that BDD anode system could be successfully scaled up through controlling the same retention time, current density, initial COD, and conductivity conditions. Based on this study, a larger BDD anode (2904 cm²) system was constructed, and systematic measurements were made on its performance in the electrochemical oxidation of phenol-simulated wastewater. Under optimum conditions, the larger BDD anode system easily reduced the COD of phenol simulated wastewater from 633 mg L⁻¹ to 145 mg L⁻¹ (<150 mg L⁻¹, National Discharge Standard of China) during 80 min with specific energy

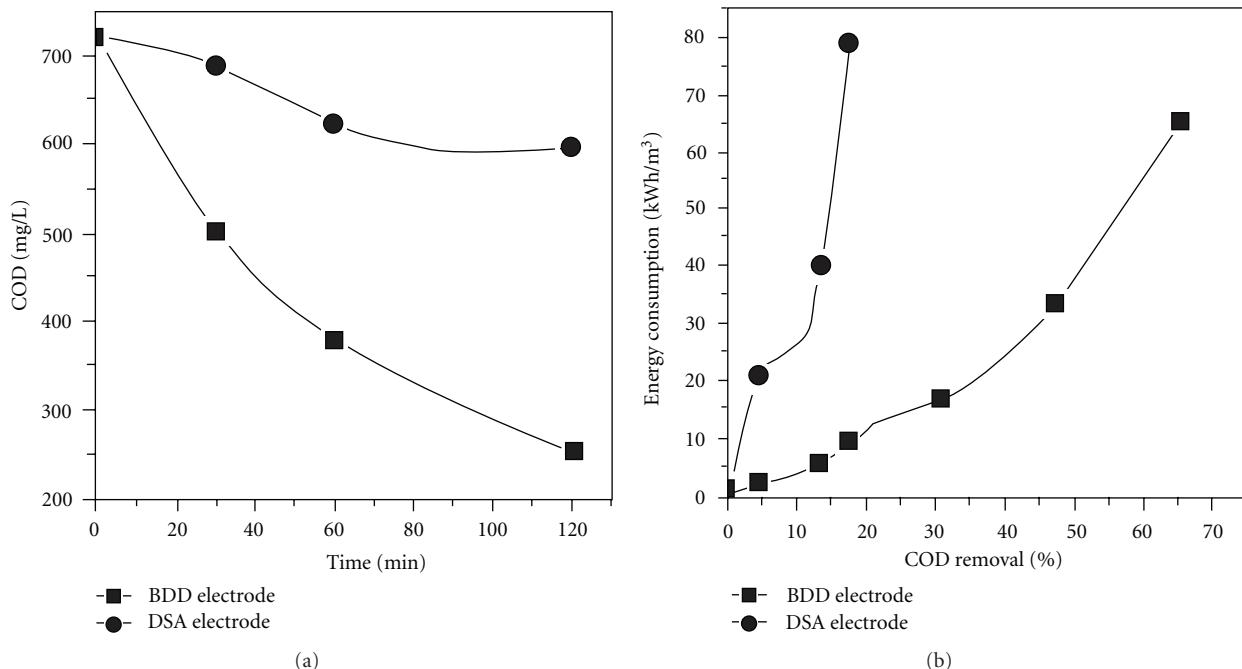


FIGURE 15: (a) Comparison of the evolution of COD during electrochemical treatment; (b) evolution of the specific energy consumption against COD removal during electrochemical treatment of acrylic fiber wastewater on DSA and BDD electrode. Conditions: applied current: 0.50 A, flow rate: 400 mL/min, $T = 45 \pm 1^\circ\text{C}$ [51].

consumption of only 31 kWh kg COD⁻¹. These engineering results can motivate other research groups to employ BDD anodes to scale up this electrochemical process.

Coking wastewater contains high concentrations of refractory and toxic compounds, and the water quality usually cannot meet the discharge standards after conventional biological treatment processes. For this reason, the electrochemical oxidation using BDD anode for advanced treatment of coking wastewater was investigated by Zhu et al. [59]. Under the experimental conditions (current density 20–60 mA cm⁻², pH 3–11, and temperature 20–60°C) using a BDD anode, complete mineralization of organic pollutants was almost achieved. Surplus ammonia-nitrogen (NH₃-N) was further removed thoroughly when pH was not adjusted at alkaline value. Moreover, the TOC and NH₃-N removal rates in the BDD anode cell were much greater than those in other common anode systems such as SnO₂ and PbO₂ anode cells. Also, the energy consumption of 64 kWh kg COD⁻¹ observed in the BDD anode system was only about 60% as much as those observed in SnO₂ and PbO₂ anode systems. Other results reported by these authors revealed that, in the BDD anode cell, organic pollutants were mainly degraded by reaction with free hydroxyl radicals, and electrogenerated oxidants (S₂O₈²⁻, H₂O₂, and other oxidants) played a less important role. Direct electrochemical oxidation and indirect electrochemical oxidation mediated by active chlorine can be negligible. These results showed great potential of BDD anode systems in engineering applications as a final treatment of coking wastewater.

A synthetic tannery wastewater, prepared with several compounds used by finishing tanneries, was studied in

chloride-free media [54] comparing the efficiency removal at different anode materials: Si/BDD, Ti/SnO₂-Sb, and Ti/SnO₂-Sb-Ir. The influence of pH and current density on the treatment was assessed by measuring total phenols, COD, TOC, and absorbance. Results showed that faster decrease in these parameters occurred when the Si/BDD anode was used (see Figure 16). Good results were obtained with the Ti/SnO₂-Sb anode, but its complete deactivation was reached after 4 h of electrolysis at 25 mA cm⁻², indicating that the service life of this electrode was short. The Ti/SnO₂-Sb-Ir anode is chemically and electrochemically more stable than the Ti/SnO₂-Sb anode, but it was not suitable for the electrochemical treatment under the studied conditions in this research. According to the authors, no significant changes were observed for electrolysis performed at different pH conditions with Si/BDD, and this electrode led to almost complete mineralization after 4 h of electrolysis at 100 mA cm⁻². The increase in current density resulted in faster wastewater oxidation, with lower current efficiency and higher energy consumption. Si/BDD proved to be the best electroclic material for the direct electrooxidation of tannery wastewaters.

Moreover, the results published by these authors are evidence that electrooxidation in chloride-free media is more advantageous than that carried out in chloride-containing media because it avoids formation of toxic organochloride compounds.

3. Concluding Remarks

This paper summarizes the most relevant investigations carried out on electrochemical treatment processes for

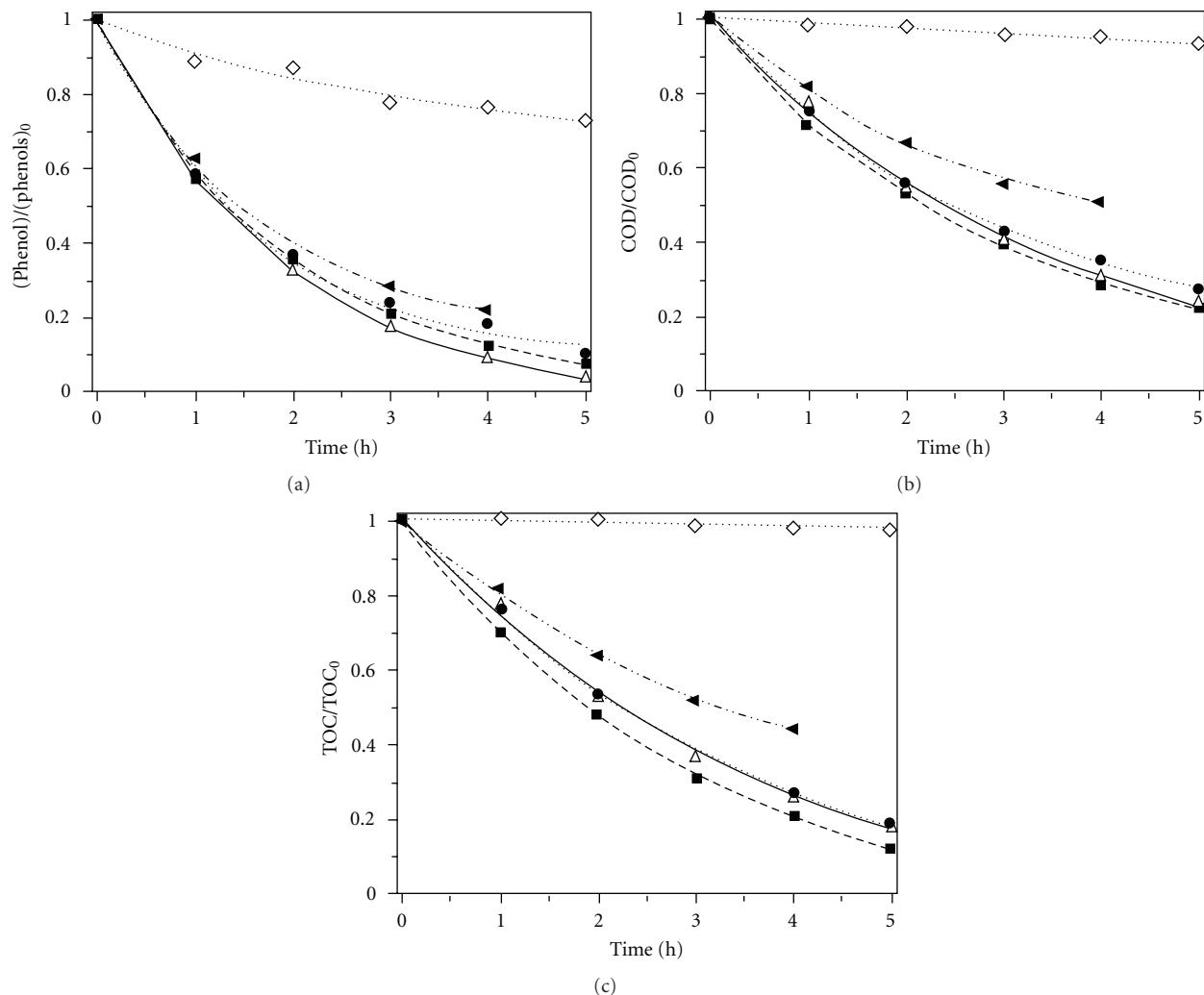


FIGURE 16: Effect of the electrodic material and pH on the electrooxidation of the synthetic tannery wastewater in $0.10 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at 25 mA cm^{-2} : (a) $(\text{phenols})/(\text{phenols})_0$, (b) COD/COD_0 , and (c) TOC/TOC_0 as a function of electrolysis time. Electrolysis conditions: (\diamond) $\text{Ti/SnO}_2\text{-Sb-Ir}$ and pH 2.4, (\blacktriangleleft) $\text{Ti/SnO}_2\text{-Sb}$ and pH 2.4, (\blacksquare) Si/BDD and pH 2.4, (\bullet) Si/BDD and pH 7.3, and (\triangle) Si/BDD and pH 12.0 [54].

oxidation of synthetic dye compounds with the use of BDD anodes. The efficiency of these electrochemical processes seems to be strongly dependent on parameters such as synthetic dye concentration, pH, applied current intensity, and supporting electrolyte, but the most important parameter is the kind of electrode material. As was mentioned, several authors tested different surfaces, such as Ti/BDD, $\text{Ti/Sb}_2\text{O}_5\text{-SnO}_2$, Pt/Ti, TiRuO_2 , and PbO_2 in order to evaluate an anode material with the best conditions with respect to high stability, high activity towards organic oxidation and low cost. However, BDD anodes always offer the most advantages regarding removal efficiency and decontamination of wastewaters. The cost of BDD application could be limited due to the price of BDD anode preparation and fragility of the required electrocatalytic materials. Additionally, electrical potentials exhibited by electrochemical oxidation processes using BDD anodes increase energy consumption, limiting the use in industrial application.

Perhaps, the key will be to use integrated methods or BDD electrochemical technologies coupled with other advanced oxidation processes.

Moreover, according to the results reported by other authors and in view of a concern for environmental protection, the advantages of BDD, high oxygen evolution potential, and low chlorine evolution potential will make it take precedence over other electrodes in the degradation of chloride-free dye wastewater. Therefore, in practical applications, the degradation of chloride-free wastewaters, especially the degradation of those in water supply and drainage system, should be performed on BDD electrodes rather than DSA for the sake of environmental protection in spite of high energy and time consumption. However, for effluents from industries and domestic sewage that contain Cl^- ions, electrochemical degradation should be carried out on DSA anodes, due to the higher energy requirements and lower removal efficiencies when using BDD anodes.

Acknowledgments

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