

Ecotoxicity Measurements of Degraded Textile Dye by Electrochemical Process Using Boron-Doped Diamond Electrodes

F.L.Migliorini^a, V. Vasconcelos^b, S.A. Alves^b, M.R.V. Lanza^b, M.R. Baldan^a and N.G. Ferreira^a

^aInstituto Nacional de Pesquisas Espaciais, São José dos Campos, Brasil.

^bInstituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil.

This work presents aspects related to production, characterization and application of boron-doped diamond (BDD) films deposited on Titanium (Ti) substrate at two different doping levels. The electrooxidation of the Brilliant Green dye is studied considering the influence of the film doping levels. The electrochemical degradation results were investigated by spectroscopic techniques UV/VIS analysis, Total Organic Carbon (TOC), High Performance Liquid Chromatography (HPLC) and toxicity against the Gram-negative bioluminescent marine bacterium *Vibrio fischeri* analysis. The BDD electrode with the higher doping level showed the better efficiency. On the other hand, the lower doped electrode showed the lower toxicity level for the degraded solutions.

Introduction

A serious global problem is the water wastage. This fact have been aggravated by the excessive use of water for many industrial and agricultural activities. In the coming decades the availability of clean water tends to be quite a challenge, considering that the fresh water reserves are limited and must be protected [1]. The planet Earth has about 75% of its surface covered by water, 97.5% of this percentage is present in the oceans and seas, the remaining 2.5% is approximately 1% fit for human consumption [2]. Thus, nowadays the toxic effluent treatments have been extensively discussed and explored. Much of the wastewater is discharged into rivers and streams causing catastrophic changes in water quality. The textile sector contributes significantly for this contamination due to its generates large volumes of toxic effluents in the worldwide. From the need to reduce the impacts of various organic pollutants present in these effluents, there is great interest in developing efficient methods for the degradation of different classes of substances. These methods aim to reduce the chemical complexity of the molecules, as well as the levels of generated waste [3-5]. In this sense, there is growing interest in the application of Advanced Oxidation Processes (AOP) for the degradation of toxic effluents, especially when it is necessary additional treatments to remove specific pollutants or to increase the efficiency of the system [6]. POA oxidation are processes which generate hydroxyl radicals (OH•), which are species highly oxidizing in sufficient quantities to cause the mineralization of organic matter to carbon dioxide, water and inorganic ions. Different methods for the generation of these radicals have been proposed. Among them, electrochemical methods emerged as a promising alternative for such purposes as they allow the transformation of certain

organic compounds in biodegradable substances or lead to the formation of $\text{CO}_2 + \text{H}_2\text{O}$. However, a major challenge is the development of anode materials, which should provide efficiency in the mineralization of organic matter. Anodes containing Doped Diamond film with boron (DDB) are being increasingly studied for the treatment of wastewater containing organic compounds, since they have high efficiency compared to other types of electrodes. In this way, we discussed the production, characterization and application of BDD films to Brilliant Green dye electrochemical degradation pointing out the ecotoxicity measurements.

Experimental Procedure

Preparation and Characterization of BDD/Ti Electrodes

These BDD/Ti electrodes were obtained by Hot Filament Chemical Vapor Deposition (HFCVD) technique. The BDD/Ti electrodes with the dimension of (2,5 x 2,5) cm^2 were prepared from H_2 (99%) and CH_4 (1%) gaseous mixture kept constant in the main gas line. The temperature and the pressure inside chamber reactor were kept at 650 °C and at 40 Torr, respectively. The sample was grown for 24 h. The doping control was obtained from an additional H_2 gas flux passing through a bubbler containing a solution of B_2O_3 dissolved in CH_3OH with the B/C ratio of 2.000 and 15.000 ppm. This additional hydrogen flow into the reactor was controlled by a rotameter which was maintained at 40 sccm (standard centimeter cubic per minute). This doping level corresponds to 10^{19} and 10^{20} cm^{-3} , respectively, evaluated by Mott Schottky Plot measurements (not shown). The top view SEM images of BDD/Ti films were obtained from a Jeol equipment JSM-5310. The quality of BDD/Ti films were analyzed from Micro-Raman spectra recorded by a Renishaw microscope system 2000 in backscattering configuration. The diamond patterns in addition to hydrides and titanium carbides phases were monitored by grazing incident X-ray diffraction (GIXRD) using a Philips X'Pert diffractometer.

Condition Monitoring and Degradation of Dye Brilliant Green

The electrochemical degradation of Brilliant Green dye solution supplied by Aldrich (~96% m/m) was performed in a polypropylene home-made single cell with capacity of 0.45 L. The BDD/Ti working electrode (~ 4.15 cm^2 of the geometric area) was located at the bottom of the cell. A platinum screen, 2 cm in diameter, was used as a counter electrode and a commercial Ag/AgCl electrode (3.0 mol L^{-1} KCl solutions) was used as the reference electrode. All the degradation assays were performed at 25 °C and at constant stirring. The electrooxidation experiments were performed at current density of 100 mA cm^{-2} using 100 mg L^{-1} of the Brilliant Green dye and K_2SO_4 0.1 mol L^{-1} , in a total treatment time of 300 min. All electrochemical measurements were carried out using a potentiostat/galvanostat AUTOLAB model PGSTAT 302 (Eco Chimie) coupled with a BRTS-10A current booster, controlled by the GPES software.

Instrumentation and analytical conditions

Concentration analyses of Brilliant Green dye were carried out with high pressure liquid chromatography (HPLC) Shimadzu 20A with UV/Visivel detector SPD-20A. The stationary fase used was a reverse fase columnm (C_{18} Varian Pursuit 5 250x4.6 mm) while the mobile fase was the ammonium acetate/methanol with proportion of

70:30 with flow of 0.8 mL min^{-1} for wavelength of the 249 nm at 40°C . The ion chromatograph Pro 850 Metrohm was used to detect and to quantify the inorganic ions formed during the electrolysis. A column A Supp 5 with mobile phase of $3.2 \times 10^{-3} \text{ mol L}^{-1}$ of sodium carbonate and $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of sodium bicarbonate (J.T Baker) was used with flow of 0.7 mL min^{-1} and a conductivity detector. The Total Organic Carbon (TOC-VCPN Shimadzu) technique was employed to determine the removed organic material. The UV-Vis spectra were recorded in Varian Cary 50 Scan spectrometer in the range from 300 to 600 nm. The maximum absorption used to calculate the concentration by UV/Vis was at wavelength of 426 nm. In this study, toxicity against the Gram-negative bioluminescent marine bacterium *Vibrio fischeri* (NRRL B-11177- BLX-104 Lyo 5) analysis and the activation solutions were obtained from Biolum LYO[®] test kit. A solution of NaCl 2% in pH 7 was used as control solution in the system. The electrolysis samples were prepared at conductivity of 50 mS cm^{-1} , pH 6 to 8.5 prior to the analysis. Starting from the sample's concentration, eight consecutive dilutions were prepared and the bioluminescence (at 490 nm) of the assay mixture containing the bacterium was determined after 15 min of incubation. The luminescence was measured using a LUMIStherm automatic incubation block (LUMIStox 300 DR LANGE, GERMANY) according to technical requirements of DIN 38412 L34 and L341.

Results and discussion

Morphological and Structural Characterization of Diamond Electrode

Top view SEM images of the diamond films deposited on the Ti substrates are depicted in Fig. 1, which corresponds to a general view of the both surface morphologies electrodes. These electrodes differ from each other by their morphology and boron content. The images in Fig. 1 show that the BDD grew with a continuous and uniform surface morphology, characterized by well-shaped microcrystalline grains with sharp facets and crystallographic orientation varying between $\langle 111 \rangle$ and $\langle 200 \rangle$.

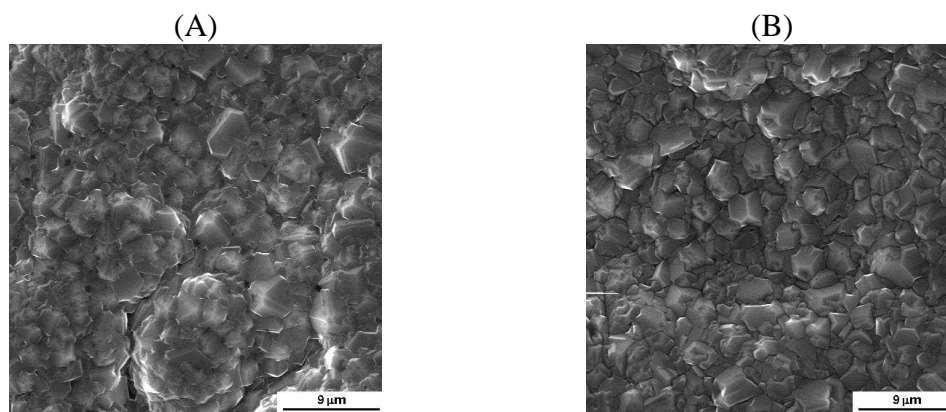


Figure 1: Scanning electron micrographs (SEM) of diamond films grown on titanium substrate with (A) 2000 ppm and (B) 15000 ppm.

The Raman scattering spectra were registered to investigate the composition and the quality of BDD/Ti films and are presented in Fig. 2 (A). Visible Raman spectroscopy confirmed the good quality of the BDD films by the presence of the narrow band at 1332 cm^{-1} characteristic to the diamond signature [7]. This peak decreased in intensity due to boron incorporation in diamond films. The effect of boron

doping is reflected in the spectral features. There is the appearance of the two bands located at 500 cm^{-1} and at 1220 cm^{-1} attributed to B-B vibrations and B-C vibrations, respectively. X-ray diffraction results are shown in Fig. 2 (B). The patterns were collected in the incidence angle of 1° over the range from 30° to 80° . For this geometry, the grazing incident X-ray diffraction (GIXRD), the oblique angle to the penetration depth of the X-rays is largely reduced, facilitating the identification of different phases present in the BDD films. X-ray diffraction showed diamond diffraction planes corresponding to the (111) and (220) diamond diffraction, respectively assuring the material crystallinity. It was identified carbides (TiC) and hydrides (TiH) patterns in the films/substrate interface.

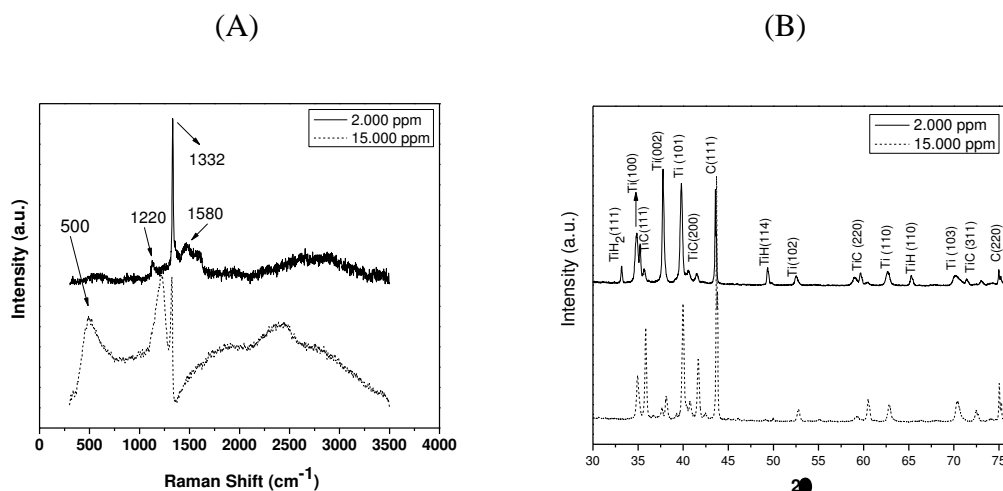


Figure 2: (A) Raman Spectra of diamond films grown with the B/C ratio of 2.000 and 15.000 ppm. (B) X-ray diffraction of diamond films grown with the B/C ratio of 2.000 and 15.000 ppm.

Electrochemical degradation of the Brilliant Green dye with BDD/Ti electrodes

UV/VIS analysis and TOC Measurements

To evaluate the electrodes efficiencies an important parameter is the color removal during the degradation process of the species. The Brilliant Green dye presents two bands of absorption in the visible spectrum ($\sim 320\text{ nm}$ and $\sim 426\text{ nm}$, respectively). The green hue of this dye is attributed to the presence of secondary absorption band at 426 nm associated with the azo group and absorption around 320 nm may be associated with the transitions of the aromatic rings. Figure 2 shows the absorption spectra for the electrodes with different doping levels for the Brilliant Green dye solution electrolyzed at current density of 100 mA cm^{-2} .

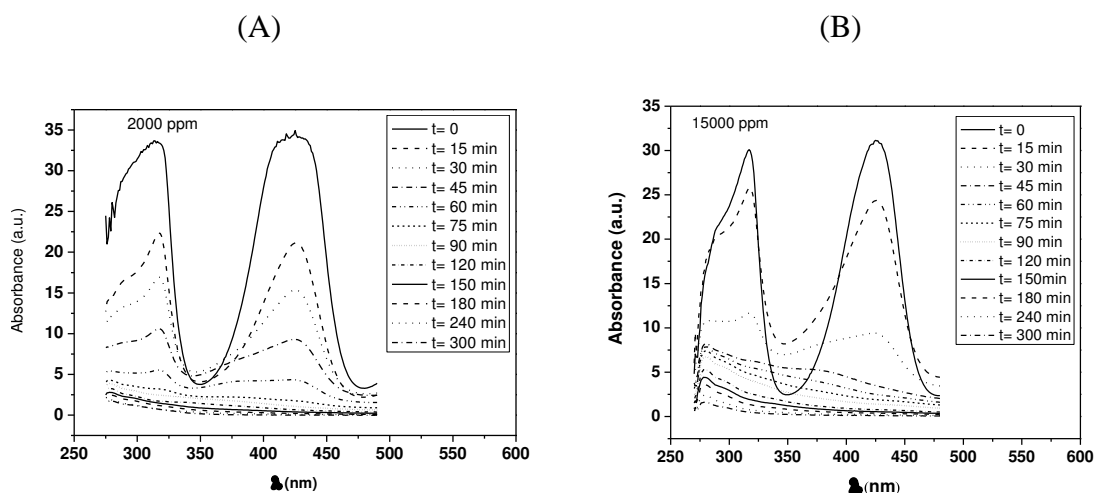


Figure 3: Absorption spectra for the Brilliant Green dye at 100 mAcm^{-2} with the diamond films grown on titanium substrate with different doping levels: (A) 2000 ppm and (B) 15000 ppm.

For both electrodes, it is possible to observe an extreme reduction in the intensities of the two azo-dye absorbance bands as a function of the electrolysis time. Afterwards degradation time of 150 min these two bands are totally vanished using the higher doped BDD whereas they are vanished after 240 min using the lower doped electrode. This behavior shows the great efficiency of the electrochemical treatment for the color reduction by using BDD/Ti electrodes. It is interesting to highlight that both electrodes were efficient in the rupture of the azo group in the aromatic bonds of the azo-dye molecule, but with greater efficiency for electrode with the B/C ratio of 15.000 ppm. Total organic carbon (TOC) results confirmed the higher efficiency for the organic matter reduction when the electrode of 15.000 ppm was used compared to that for electrode of 2.000 ppm. They presented 72% and 57% of TOC elimination, respectively.

HPLC Qualitative Detection and Ecotoxicity Tests

The aromatic intermediates produced during each electrochemical treatment containing Brilliant Green dye were detected by high performance liquid chromatography (HPLC) using a wavelength of 254 nm. The appearance of chromatographic signal at 254 nm is related to the π - π^* transition of the conjugated systems, such as aromatic compounds that make up the solution of the Brilliant Green dye. From HPLC results it was possible to observe that for both electrodes the formation of other peaks occurred with lower retention time, which implies the presence of more polar compounds characteristics of the dye study. Comparing the results we can observe the same trend for both electrodes, but the electrode with the B/C ratio of 15.000 ppm showed a lower amount of peaks in addition to lower retention time compared to those for electrode of 2.000 ppm, which would imply in the presence of more polar compounds that present small aromatic chains. This reduction in the aromaticity of Brilliant Green dye solution led to the possible formation of compounds of aliphatic chain. From an environmental standpoint these compounds are very important because they tend to be biodegradable.

In order to evaluate the toxicity at 100 mg L⁻¹ of the Brilliant Green dye, an exposure time of 15 min was selected. The ecotoxicity tests showed the higher efficiency for the 2.000 ppm electrode (Table 1). The results showed that for the film with a doping level of 2.000 ppm the toxicity decreased in approximately 96%, while for the film of 15.000 ppm it was 31%. This result can be associated to the high conductivity of the 15.000 ppm electrode that may improve the secondary reactions generated through the supporting electrolyte. In this sense, the high generation of peroxodisulfate ions from these secondary reactions provides this high toxicity in the degraded solutions [8]. This behavior was also observed in the ecotoxicity measurements using only the supporting electrolyte. In similar way, such species could be responsible for increasing the medium toxicity. According to the literature [8] coexisting salts can affect the toxicity tests and exhibit a very strong stimulating effect on the accurate toxicity test, mainly at lower exposure times. Hence, these results suggest that the Brilliant Green dye is a toxic compound. However, after the electrolysis, using the two electrodes BDD, a considerable decrease was observed in the toxicity of these solutions containing this compound.

Table 1: Toxicity against the Gram-negative marine bioluminescent bacterium *Vibrio fischeri* of an electrolyte containing a dye before and after electrochemical treatment

Sample	Relative toxicity (%) ^a
Original solution (dye)	100
Solution after treatment (2.000 ppm)	3,34
Solution after treatment (15.000 ppm)	69,92

^a Relative toxicity calculated as: [(initial EC 50 /final EC 50)x100].

Conclusion

The electrode with higher doping level showed better efficiency to reduce the aromaticity, the dye color, and the TOC for the degraded solutions. However, the ecotoxicity tests showed the higher efficiency for the 2.000 ppm electrode. This result can be associated to the high conductivity of the 15.000 ppm electrode that may improve the secondary reactions generated through the supporting electrolyte. In this sense, the high generation of peroxodisulfate ions from these secondary reactions provides this high toxicity in the degraded solutions when 15.000 ppm electrode is used.

Acknowledgments

The authors gratefully acknowledge the financial support provided by FAPESP (2010/18462-2), CNPq and CAPES.

References

1. A. Lahkimi, M.A. Oturan, N. Oturan, M. Chaouch, Environmental chemistry letters, 5, 35-39, (2007).
2. M.T. Gassi, <http://qnesc.s bq.org.br/online/cadernos/01/aguas.pdf>. 16 de setembro de 2014.
3. M. Panizza, G. Cerisola, *Electrochim. Acta*, 51, 191, (2005).
4. M. Panizza, L. Ouattara, E. Baranova, C. Comninellis, *Electrochem. Commun.* 5, 365, (2003).
5. E. Brillas, M. A. Baños, M. Skoumal, P. L. Cabot, J. A. Garrido, R. M. Rodríguez, *Chemosphere*, 68, 199, (2007).
6. M. Panizza, G. Cerisola, Journal of Electroanalytical Chemistry, 638, 236-240, (2010).
7. May, P. W.; Ludlow, W. J.; Hannaway, M.; Heard, P. J.; Smith, J. A.; Rosser, K. N. Diamond and Related Materials 17, 105-11 (2008).
8. P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Journal of Applied Electrochemistry, 39, 2143-2149, (2009).