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Electrochemical removal of Reactive Black 5 azo dye using non-commercial boron-doped diamond film anodes

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ABSTRACT

Although various processes for the removal of Reactive Black 5 (RB5) dye from textile wastewater have been studied, the degradation pathway of RB5 on boron-doped diamond (BDD) films has not been elucidated. We here report the efficient electro-oxidation of RB5 in aqueous solution using BDD/Ti electrodes and we propose a degradation route based on intermediates and byproducts identified by high performance liquid chromatography-mass spectrometry. BDD films doped with 5000 or 15,000 ppm of B were grown on Ti plates using the hot filament chemical vapor technique to produce electrodes E1 and E2, respectively. Films were evaluated by scanning electron microscopy, X-ray diffraction and Raman spectroscopy before and after several hours of electrolysis and were shown to be of high quality and stability. Total removal of color from RB5 solution was achieved with either electrode by electrolysis at low current density (50 mA cm^{-2}). Total mineralization of the dye solution could be attained with electrode E2 at an applied current density of 100 mA cm^{-2}. Under these conditions, 91% of the chromatographic area associated with RB5 (monitored at 311 nm) was removed, thereby verifying cleavage of the aromatic rings of the dye. Furthermore decolorization of RB5 followed pseudo zero-order kinetics with both electrodes and the apparent rate constant was higher with electrode E2. The results obtained indicate that BDD/Ti is a promising material for the electro-degradation of RB5 since aromatic rings and chromophoric groups were ruptured during electrolysis to generate aliphatic compounds, such as oxalic acid, that can be easily converted into CO_2.

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1. Introduction

The homobifunctional dye Reactive Black 5 (RB5) (Fig. 1) is a member of a class of azo dyes in which the aromatic substituents (R, R') of the chromophoric group R-N=N-R' typically bear functional elements such as -OH and -SO_3H [1]. Although RB5 is used widely in textile dying [2], the vinyl sulfone moieties of the molecule are hydrolyzed during processing to 2-hydroxyethylsulfone groups that do not fix onto cellulose fibers. The hydrolyzed form is, therefore, easily discarded to wastewater [3], a situation that can cause environmental problems since RB5 is considered a recalcitrant compound [4]. It is noteworthy that the EC_{50} value of the non-hydrolyzed form of RB5 against the bioluminescent bacterium *Vibrio fischeri* is 27.59 ± 4.01 mg L^{-1} while that of the hydrolyzed form is 11.49 ± 3.68 mg L^{-1} [5]. Furthermore, it is hydrolyzed RB5 that is usually found in textile wastewater and this form of the dye is considered to be a weak genotoxin [5].

Unfortunately, the processes normally employed in sewage treatment plants are not able to degrade many of the dyes present in industrial effluents [6–8]. In this context, electro-oxidation has been proposed as a promising alternative method for the removal of pollutants from wastewater, especially those with high anionic content [9,10]. The efficiency of electro-oxidation depends on a number of parameters, including the characteristics of the electrode [11]. Currently, boron-doped diamond (BDD) is considered one of the best electrode materials for the electro-oxidation of organic pollutants [12] since it offers a number of advantages such as high chemical and physical stability, high oxidative power, low

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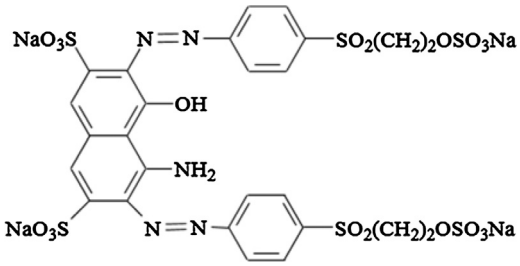

Fig. 1. Structure of Reactive Black 5 dye (RB5).

level of adsorption and a wide window for the discharge of water [13,14].

Anodic polarization of BDD films generates hydroxyl radicals ($^{\bullet}OH$) through the oxidation of water molecules adjacent to the electrode surface [15].

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \quad (1)$$

Because of the low adsorption ability of $^{\bullet}OH$ on BDD in the absence of organic compounds, the $^{\bullet}OH$ thus generated can react with each other to form H_2O_2. However, in the presence of organic matter, the radicals act as strong oxidizing agents to yield water, CO_2 and other oxidation products [15].

$$BDD(^{\bullet}OH) + \text{organic compounds} \rightarrow BDD + \text{oxidized products} + H^+ + e^- \quad (2)$$

Moreover, depending on the nature of the supporting electrolyte, other weaker oxidizing agents, including $S_2O_8^{2-}$ formed by the oxidation of SO_4^{2-} and HSO_4^- ions, can be generated on the BDD surface and such species may also take part in oxidation reactions [16,17].

The performance of a BDD electrode is related to the quality of the film and the adhesion of the film to the substrate. These parameters, along with the morphology, microstructure, stability and resistivity of the film, are influenced by the doping level. Well-faceted films are obtained when boron levels are low, but the resistivity of the film drops drastically with increased doping. On the other hand, the amounts of impurities such as graphite are increased in highly doped films, and adhesion of the film to the Ti plate becomes more difficult [18]. Nevertheless, studies addressing the influence of film doping level on efficiency in the electro-oxidation of organic compounds are sparse [19–21].

RB5 has been chosen as a model organic pollutant by a number of researchers, and details are available concerning degradation of the dye by electro-assisted Fenton and Fenton-like oxidation [4,22–25], photo-electrochemical [26,27] and electro-coagulation [28] processes, electrochemical reduction [29–32], and electrochemical oxidation with Ti/SnO_2-Sb-Pt [3], Pt [33], graphite [34] and Pt/Ti [35] electrodes. However, very few studies have focused on the application of BDD as electrodic material for the removal of RB5. For example, Iglesias et al. [22] investigated the removal of RB5 by the electro-Fenton process using a BDD anode and graphite sheet cathode and reported that 97.2% of color was removed after 90 min of electrolysis at 5 V applied potential. Additionally, electro-oxidation of RB5 (100 mg L^{-1} in 0.02 mol L^{-1} Na_2SO_4) in a bipolar trickle tower reactor (recirculated batch mode at 100 mL min^{-1} flow rate) with BDD/Nb electrodes in the form of Raschig rings afforded 97% color removal, 29.3% mineralization and a reduction in initial toxicity [36].

Further studies are still required in order to elucidate completely the influence of electrochemical techniques on water matrices and degradation products. One important issue concerns the degradation pathways of organic pollutants, with particular emphasis on the identification of degradation intermediates or byproducts, to ensure that the treated wastewater is safe for discharge into the environment [37]. However, the degradation pathway depends critically on the formation of $^{\bullet}OH$, a process that is regulated by the electrodic material employed [38]. To the best of our knowledge, the degradation pathway of RB5 on a BDD anode has yet to be elucidated and the intermediates or byproducts of the process identified.

This paper addresses the electro-oxidation of RB5 using BDD/Ti electrodes with different levels of boron doping, and proposes a route of degradation of the dye based on intermediates and byproducts identified by high performance liquid chromatography-mass spectrometry (HPLC–MS). The efficiency of the degradation process was evaluated by monitoring color removal, decay in dye concentration and decrease in total organic carbon (TOC), and by assessing current efficiency and energy consumption.

2. Experimental

2.1. Materials

Acetonitrile was purchased from Panreac, H_2SO_4 was from J.T. Baker, K_2SO_4 was from Labsynth and RB5 dye (55% pure) was from Sigma–Aldrich. All reagents were used without further purification. Aqueous solutions were prepared with purified water (18.2 MΩ cm^{-1} resistivity) from a Millipore Milli-Q water purification system.

2.2. Preparation and characterization of BDD electrodes

BDD films were grown on Ti substrates using the hot filament chemical vapor deposition (HFCVD) technique. The deposition of diamond on Ti is strongly influenced by stresses between film and substrate that arise from extrinsic and intrinsic factors. For this reason, some form of pre-treatment must be applied to the substrate surface in order to decrease the stress and increase the rate of nucleation [39–41]. In the present study, Ti electrodes (25 × 25 × 5 mm) were subjected to air abrasion with glass beads, since the mechanical incisions so induced effectively increase the surface area and roughness of the substrate and improve the mechanical anchoring of the film.

BDD/Ti electrodes were prepared using a mixture of H_2 (99%) and CH_4 (1%), the composition of which was kept constant in the main gas line to the reactor chamber. The doping agent was supplied via an additional H_2 line that passed through a bubbler containing B_2O_3 dissolved in methanol with a B/C ratio of 5000 ppm for the formation of electrode E1 and 15,000 ppm for electrode E2. The temperature and pressure inside the reactor chamber were maintained at 923 K and 5.3 kPa, respectively, and the films were grown over a total deposition time of 24 h. Top view scanning electron microscope (SEM) images of the BDD films were obtained with a Jeol model JSM-5310 instrument. The X-ray diffraction (XRD) patterns of diamond together with those of the Ti hydride (TiH) and carbide (TiC) phases were monitored by grazing incident XRD using a Philips X'Pert diffractometer with CuKα radiation (λ = 1.54 Å) and θ–2θ scans from 30° to 80° for all samples. BDD film quality was assessed from Micro-Raman spectra recorded on a Renishaw system 2000 microscope operated in the backscattering configuration.

2.3. Electrochemical degradation of RB5

Electrochemical reactions were carried out in a laboratory-constructed one-compartment polypropylene cell (volumetric capacity 0.45 L) equipped with a BDD/Ti working electrode, a Pt counter-electrode and a commercial reference electrode (Ag/AgCl in 3 mol L^{-1} KCl). The cell was connected to a Metrohm Autolab PGSTAT 302 potentiostat/galvanostat coupled with a model BRTS

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