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Electrochemical decolorization of dye wastewater by surface-activated boron-doped nanocrystalline diamond electrode

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ABSTRACT

Complex organics contained in dye wastewater are difficult to degrade and often require electrochemical advanced oxidation processes (EAOPs) to treat it. Surface activation of the electrode used in such treatment is an important factor determining the success of the process. The performance of boron-doped nanocrystalline diamond (BD-NCD) film electrode for decolorization of Acid Yellow (AY-36) azo dye with respect to the surface activation by electrochemical polarization was studied. Anodic polarization found to be more suitable as electrode pretreatment compared to cathodic one. After anodic polarization, the originally H-terminated surface of BD-NCD was changed into O-terminated, making it more hydrophilic. Due to the oxidation of surface functional groups and some portion of sp^2 carbon in the BD-NCD film during anodic polarization, the electrode was successfully being activated showing lower background current, wider potential window and considerably less surface activity compared to the non-polarized one. Consequently, electrooxidation (EO) capability of the anodically-polarized BD-NCD to degrade AY-36 dye was significantly enhanced, capable of nearly total decolorization and chemical oxygen demand (COD) removal even after several times of re-using. The BD-NCD film electrode favored acidic condition for the dye degradation; and the presence of chloride ion in the solution was found to be more advantageous than sulfate active species.

Introduction

Boron-doped diamond (BDD) film is a very prominent material receiving many interests in environmental application particularly to be used as electrode to degrade different refractory pollutants in wastewater *via* electrooxidation (EO). The most important properties of this electrode are large potential window, low adsorption, high corrosion stability in very aggressive media, high efficiency in oxidation processes, and also low double-layer capacitance and background current (Martínez-Huitle and Alfaro, 2008).

Wastewater EO using BDD electrode that has been extensively studied is of dyes (Peralta-Hernández et al., 2012). Azo dye, characterized by the presence of one or more azo bonds (NN) in their structure, is one of the most commonly used type of dyes represents 50% of dye production worldwide (Sleiman et al., 2007). Unfortunately, 15% of the dyes used during the industrial process are released in wastewater (Santos et al.,

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2008). Color caused by dyestuffs contained in the wastewater is posing high negative impact and frequently become main target of wastewater treatment (Diogo et al., 2011).

In wastewater treatment by EO, the quality and properties of the electrode used is an essential factor. An electrode is termed as "active" when it is exhibiting low background current and rapid rate reaction kinetic (Swain, 2007). Surface termination on the conductive diamond electrode by electrochemical methods (water reduction to produce H-terminations or oxidation for O-terminations) is quite popular (Salazar-Banda et al., 2006). Especially for diamond electrode, anodic polarization as surface pretreatment is considered as the simplest activation method (Duo et al., 2004), and evidently results in an improvement in reproducibility of the electrode response (Rao and Fujishima, 2000). Oxygen is more electronegative than carbon compared to hydrogen; therefore surface termination with oxygen induces a surface dipole that will increase the electron affinity (Vidhya et al., 2007). After cathodic polarization, an enhanced electrochemical activity was reported when measuring electron transfer reaction of several redox couples (Suffredini et al., 2004).

However, the study of electrode pretreatment effects on its properties has not been frequently correlated to its application for pollutant destruction. Contrary to electroanalytical application, surface treatment/modification of diamond electrode for water treatment application is even considered unnecessary (Kraft, 2007). The objective of this study was to investigate the enhancement of the boron doped nanocrystalline diamond (BD-NCD) film electrode performance in degrading organic dye wastewater, simulated with Acid Yellow (AY-36) dye, with respect to the electrochemical polarization pretreatment applied. The effect of other important parameters such as pH and active species present in the solution was also studied.

1. Material and methods

The preparation of BD-NCD film electrode by hot filament chemical vapor deposition (HFCVD) has been reported elsewhere (Juang et al., 2013). The surface properties of BD-NCD film were evaluated by field emission scanning electron microscopy (FESEM) images (Hitachi SU8010, Japan) and X-ray photoelectron spectroscopy (XPS) spectra (PHI Quantera, USA).

1.1. Electrochemical polarization

Electrochemical polarization was done by applying 3 V (anodic) and −1.5 V (cathodic) of DC current for 10 min, in a single cell three-electrode system by positioning BD-NCD as working electrode. The polarization is repeated twice (20 min) or three times (30 min) when mentioned so. The counter and reference electrodes were Pt rod (Metrohm, Switzerland) and Ag/AgCl in 3 mol/L KCl (Metrohm, Switzerland), respectively. A 0.1 mol/L Na_2SO_4 was used as the electrolyte. This experiment was performed using manually controlled potensiotat/galvanostat Autolab PG Stat 302N (Metrohm, Switzerland). Cyclic voltammetry (CV) was performed using the same system run by Nova software version 1.10 with a scan rate of 10 mV/sec. N_2 gas was purged into the solution for deoxygenation for 10 min before every experiment. Chemical cleaning was carried out by immersing the electrodes in concentrated nitric acid and/or isopropyl alcohol for 10 min.

1.2. Dye wastewater decolorization

EO of AY-36 dye was conducted by bulk electrolysis experiment in a single cell (150 mL) two-electrode system under constant stirring. Unless stated otherwise, the experiments were carried out using 20 mg/L AY-36 (in 15 mmol/L KCl) for 2 hr at controlled current of 10 mA/cm^2 with initial pH of 3 (adjusted with H_2SO_4). BD-NCD and Pt plate with surface areas of 2 cm^2 were applied as anode and cathode, respectively. Periodical sampling was performed and samples were analyzed for the chemical oxygen demand (COD) concentration (Hach DR/4000 Spectrophotometer, USA) and Ultraviolet/Visible absorbance (Hitachi U3010 Spectrophotometer, Japan). For the effect of sulfate and chloride ions, 20 mg/L AY-36 was dissolved in Na_2SO_4 0.15 mmol/L (pH adjusted to 3 with H_2SO_4) and KCl 0.15 mmol/L (pH adjusted to 3 with $HClO_4$), respectively.

2. Results and discussion

2.1. Surface morphology of BD-NCD film

Thermally assisted diamond growth by HFCVD has been one of the most favorable techniques since early 1980s (Yehoda, 2002). Fig. 1 shows FESEM image of the BD-NCD fabricated *via* HFCVD in present study. A nodular surface morphology without faceting suggests a ballas (ball-like) structure of diamond film (Fig. 1a), composed of agglomerates of small grains (inset). This kind of diamond film is frequently termed as cauliflower-like structure and is typical of NCD films (Braga et al., 2009). The ballas structure is due to the spherullitic growth of the crystal when a relatively low density of primary nucleation and a high rate secondary nucleation occur (Kulisch and Popov, 2006). Fig. 1b shows that the film was 2 μm thick and no evidence of columnar growth, also typical of NCD (May et al., 2008). The additional morphology information and Raman spectra of this film are reported elsewhere (Nurhayati et al., 2015).

2.2. Effect of polarization on surface properties and electrochemical activities

The alteration of surface properties of the film after polarization was examined by high resolution XPS spectra of C1s, as shown in Fig. 2. The electrochemical treatments imposed to the electrodes obviously affect the XPS spectra characteristics (Fig. 2a). Deconvolution of these curves using Lorentzian–Gaussian fitting procedure reveals the carbon phase in the film as shown in Fig. 2b–d. These figures show four peaks assigned as sp^2 and sp^3 carbon, and adventitious carbon of alcoholic and carbonyl functional group (Azevedo et al., 2009) denoted as peaks 1, 2, 3 and 4, respectively. Generally, the Csp^2 and Csp^3 peaks are located approximately at 284.3–284.6 and 285.0–286.0 eV, respectively (Murugaraj et al., 2012; Teng et al., 2010). Peaks 3 and 4 are decreased after polarization, suggesting that the surface functional groups were oxidized/reduced, with anodic polarization proved to be more effective. The higher sp^3/sp^2 area ratio of anodically polarized BD-NCD