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.

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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
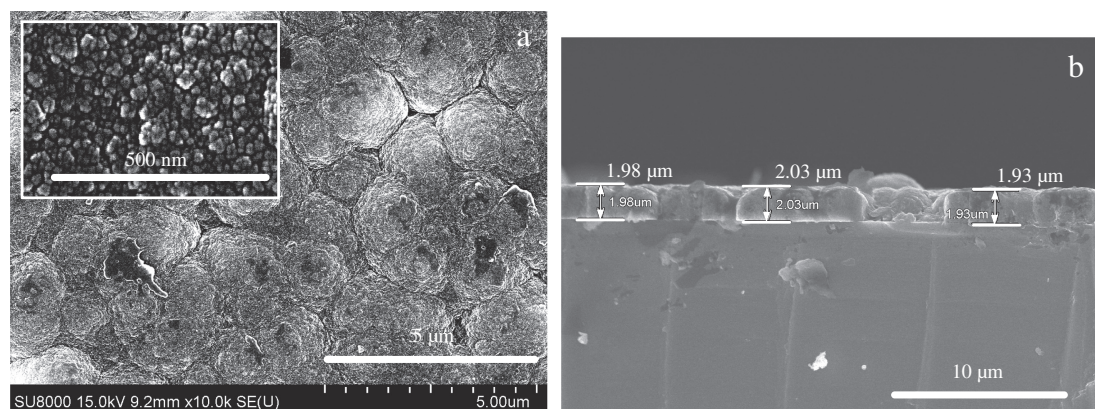
Fig. 1 – Field emission scanning electron microscopy (FESEM) micrograph of (a) top view and (b) cross section of boron-doped nanocrystalline diamond (BD-NCD) film.

(0.49) compared to cathodically polarized one (0.29) suggests that greater portions of the sp^2 carbon was eliminated from the surface during anodic polarization, most likely oxidized to CO_2 (Duo et al., 2004). Repeating the polarization to three times (Fig. 2c and d inset) gave better surface properties for cathodically polarized BD-NCD, while the anodic polarized one only needed one polarization to achieve similar result. The CV i-E curves as shown in Fig. 3 confirm these results, where the Faradaic currents were decreased after polariza-tion. As a result, the polarized BD-NCD electrode gave lower background current and wider working potential window (around 3 V) with higher oxygen evolution potential. Based on these results, from this point forward polarization was carried out anodically, once.

2.3. Effect of chemical cleaning and anodic polarization on surface hydrophilicity

The surface of diamond thin film grown *via* CVD is initially hydrogen-terminated and hydrophobic in nature as shown by the high contact angle in Fig. 4a. After chemically cleaned with both acid and organic solvent (Fig. 4b and c), a slight decrease of hydrophobicity was observed. The hydrophobicity of the film was significantly decreased after the chemically cleaned electrodes were sequentially polarized (Fig. 4d and e), suggesting a partial oxidation of the surface: diminution of C–H termination ratio and the formation of C–O terminations (Girard et al., 2007). Meanwhile, the direct polarization without prior chemical cleaning (Fig. 4f) did not significantly
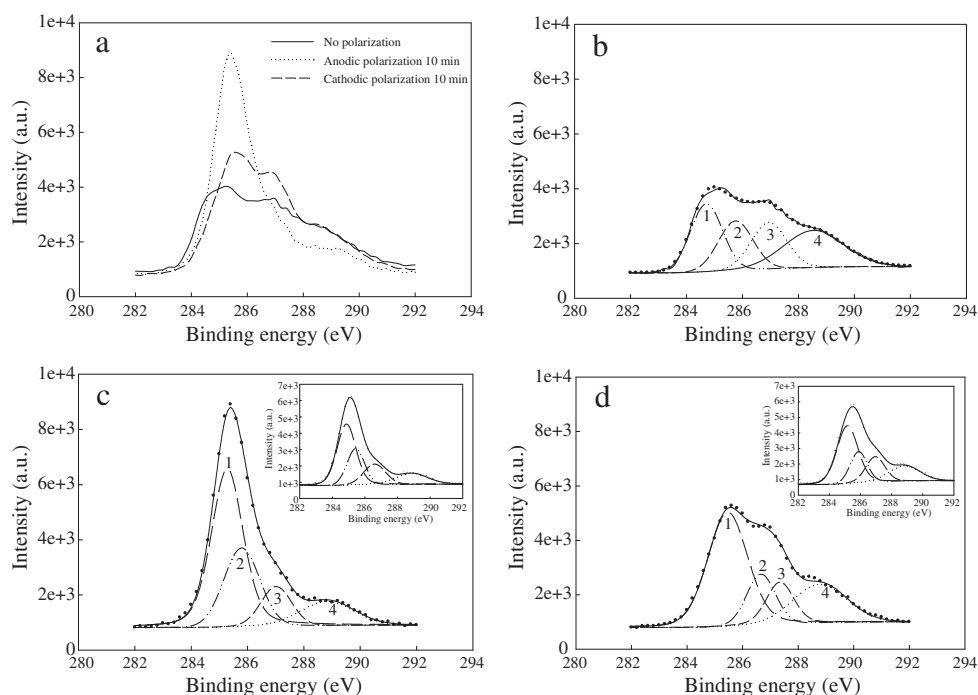

Fig. 2 – (a) C1s spectra of BD-NCD film before and after anodic and cathodic polarization, and the deconvolution of the peaks of (b) non-polarized (c) anodically and (d) cathodically polarized BD-NCD for 10 min. 1, 2, 3 and 4 are sp^2, sp^3, alcoholic and carbonil carbon phase respectively, [●] is fitted peaks' sum. (Inset: BD-NCD polarized for three times (30 min)).
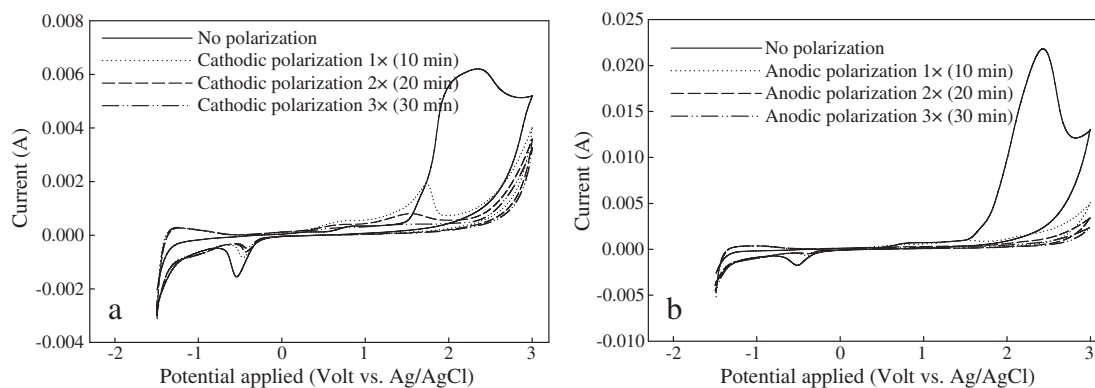
Fig. 3 – Background CV *i-E* curve of BD-NCD in 0.1 mol/L Na$_2$SO$_4$ electrolyte, 0.01 V/s scan rate after (a) cathodic (b) anodic polarization.

change the contact angle from the original. These results show that to maximize the effect, an extra chemical cleaning is necessarily performed prior to the polarization.

Hydrophilic property of the film will ensure maximum contact between wastewater in which organic dye contained with the BD-NCD surface, increasing the electroactivity of the electrode towards soluble pollutants. Also to be noted, that the success of electrochemical advanced oxidation processes (EAOPs) for decolorization and organic degradation here relies on the extent of •OH production *via* water discharge on the surface of BD-NCD film, thus hydrophilicity of the electrode surface plays important role. A study also suggests that exposing BDD electrode to anodic potential increases hydrophilicity and promotes adsorptive properties (Wadhawan et al., 2001). Even though the nature of highly reactive free •OH produced on the surface of BDD is still debated among authors, some have suggested that oxidation reactions are restricted only within an adsorbed film adjacent to the electrode surface (Radjenovic and Sedlak, 2015).

2.4. AY-36 dye degradation capability of BD-NCD

Fig. 5 shows a significant improvement of the BD-NCD performance in decolorization and COD removal after polarization, as an obvious consequence of the phenomena described in

previous sections. When the BD-NCD was used as-is (only deionized water cleaning), the decolorization (90%) and COD removal (40%) were generally slightly decreased every time the electrode was re-used (Fig. 5a), indicating that fouling was building up. On the other hand, the polarized electrode showed consistent efficiency with almost total decolorization and COD removal (Fig. 5b). This result suggests that anodic polarization would reactivate the BD-NCD surface after prior-use. As for the decreased performance on the fourth cycle of polarized electrode, it is essential to be noted that we observed film detachment after the fourth polarization treatment. Therefore, this decrease was not caused by the electrode fouling, but rather as a result of the decrease in surface area of the active film due to as mentioned film detachment after prolonged exposure to electricity. The COD concentrations in some cases were increased before eventually decreased, indicating the formation of intermediates, as confirmed in Fig. 6.

Fig. 6 shows one main peak in the visible light region and several peaks in the UV region. Inset figure shows the relative intensity variations of these peaks with times. The intensities of the UV peaks of non-polarized BD-NCD (Fig. 6a) were higher than polarized one (Fig. 6b) indicating the formation of phenol (280 nm), benzene (256 nm) and carboxyl (230 nm) as intermediates which were further degraded at a longer operation time. Regarding AY-36 degradation, Sleiman et al. (2007)
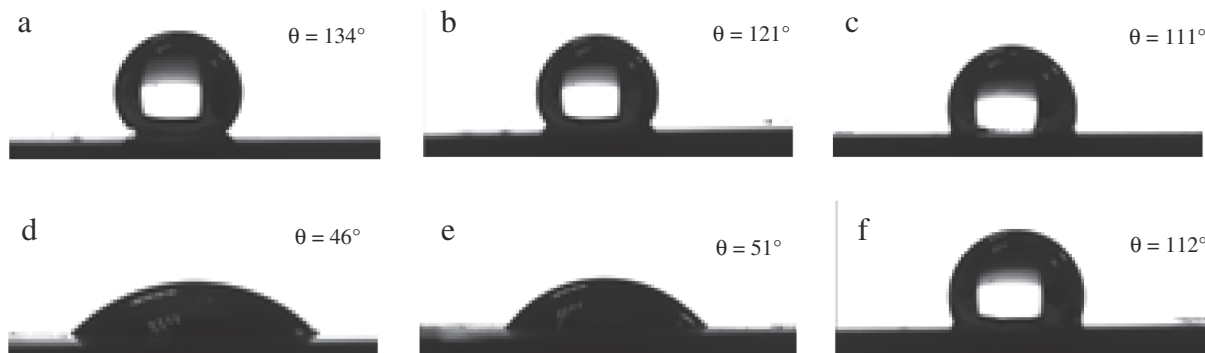

Fig. 4 – Water contact angle of BD-NCD film (a) as grown, and after chemically cleaned with (b) propanol followed with nitric acid (c) nitric acid followed with propanol (d) propanol and nitric acid followed by polarization (e) nitric acid and propanol followed by polarization, and (f) after polarization without prior chemical cleaning.
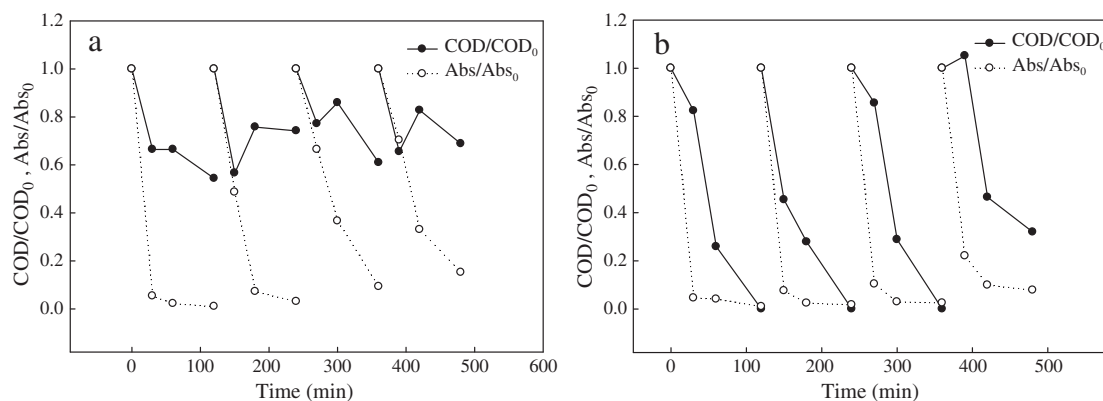
Fig. 5 – Degradation of and color in lifecycle test of BD-NCD (a) without polarization, rinsed with DI water before every cycle (b) with polarization, re-polarized before every cycle. DI: deionized.

proposed that phenol, benzene and carboxyl are final intermediates before finally mineralized to CO_2 and water, and are products of oxidation of initial intermediates such as benzene sulfonic acid, hydroxyl-diphenyl amine, diphenylamine and hydroquinone.

The decline of 434 nm peak of polarized and non-polarized electrodes was faster than other peaks and was not significantly different between both, suggesting that color removal, as the NN of the AY-36 dye was broken, was relatively easier to achieve than the breaking of the aromatic rings. The latter may require several steps and longer reaction time. Nevertheless, oxidation mechanism seems to be dependent on the nature of the dye (Saez et al., 2007).

BDD film is known as a material possessing the highest oxygen evolution potential and has been favored to be applied as electrode in electrochemical process for water treatment (Särkkä et al., 2015). In recent practical application, most researchers in this field use commercially available BDD either for solely EO process or combine it with other EAOP techniques (Ruiz et al., 2011) to degrade refractory organics with satisfactory results. Even though anodic oxidation process is preferred due to the maturity of this technology (Radjenovic and Sedlak, 2015) application of BDD for reductive

process is also receiving attention (Cruz-González et al., 2010). Table 1 presents the current application of BDD film to degrade various kinds of organic pollutants and compared to the results achieved in present work.

2.5. Effect of active species and pH

Other than hydroxyl radicals formation on the BD-NCD film surface (Eq. (1)) (Marselli et al., 2003), peroxodisulfate and soluble chlorine can also be generated according to Eqs. (2) and (3) if the solution contains sulfate or chloride ion, respectively (Brillas and Martinez-Huitle, 2009). It is beneficial to have either one or both of them in the solution to assist the EO because hydroxyl radicals can only exist at a very close proximity to the surface of electrodes (physically adsorbed) and in a very short time, while the other two active species can exist in the bulk solution for relatively longer time. Thus, having other active species in the solution will synergistically improve the oxidation process. While •OH is a very strong oxidant offering mineralization (Eq. (4)), soluble chlorine and peroxodisulfate or other secondary oxidants are less strong and provide partial oxidation of organics (R) resulting in intermediate (R*) formation (Eq. (5)) that need progressive oxidation processes to be further degraded. Due to
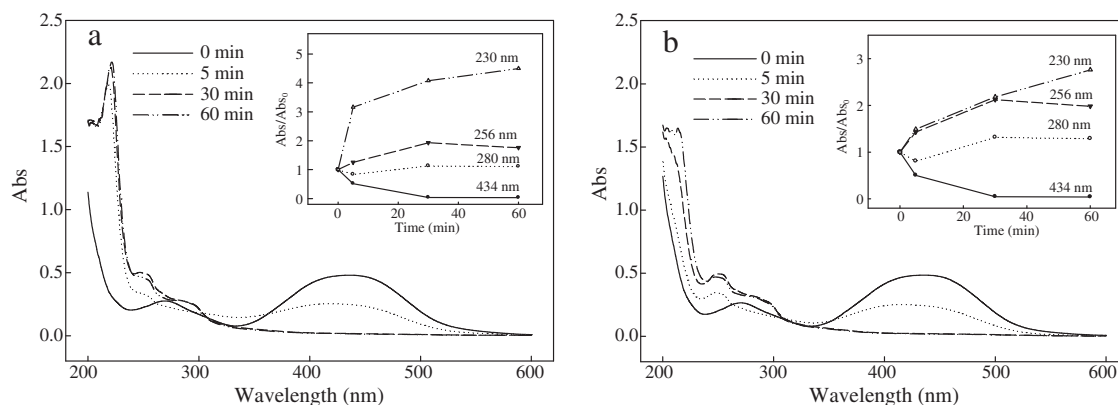

Fig. 6 – UV/Visible spectra of Acid Yellow (AY-36) during 1 hr electrolysis with BD-NCD (a) without polarization (b) anodically polarized. Inset: the relative absorbance of AY-36 (434 nm), phenol (280 nm), benzene (256 nm) and carboxyl (230 nm) through time. UV: ultraviolet.

Table 1 – Performances of boron-doped diamond (BDD) film electrode for various wastewater treatments by different electrochemical advanced oxidation processes (EAOPs) in recent application.

BDD electrode	Pollutant	Process	Condition	Performance	Ref.
Commercial BDD electrode by Metakem GmbH™, Germany	Aqueous paracetamol and diclofenac solution	Electrooxidation (EO) and electro-Fenton (EF)	Current density of 6.25 mA/cm²	50% and 80% mineralization for EO and EF respectively	(García-Montoya et al., 2015)
Commercial BDD thin film on Nb substrate by CONDIAS GmbH	Landfill leachates	Anodic oxidation (AO) and electro-Fenton (EF)	Current density of 20.83 mA/cm²[a]	~90% and ~83% dissolved TOC removal for EF and AO respectively[a]	(Oturan et al., 2015)
BDD film on Ti substrate grown by HFCVD	Reactive Black 5 azo dye	Electrooxidation	Current density of 50 mA/cm²	100% color removal and ~40% TOC removal	(Vasconcelos et al., 2015)
Commercial BDD film (5 µm-thick) on Nb substrate by CONDIAS GmbH	Anti-inflammatory drug diclofenac	Sonoelectrochemical degradation	Constant voltage of 7.2 V	90% degradation with pseudo first order kinetics with a rate constant of 0.505/min	(Finkbeiner et al., 2015)
Commercial BDD thin-film electrode by NeoCoat (La-Chaux-de-Fonds, Switzerland)	Mixture of food color additives (E122, E124 and E129)	Electro-Fenton (EF) and UVA photoelectro-Fenton (PEF)	Current density of 33.3 mA/cm²	Total color removal for both processes and 83% and 99% DOC removal for EF and PEF respectively	(Brillas, 2015)
BDD (2 µm-thick, nanocrystalline) on Ti substrate grown by HFCVD	Metanil Yellow AY 36 azo dye	Electrooxidation	Current density of 10 mA/cm²	Almost total decolorization and COD removal	This work

HFCVD: hot filament chemical vapor deposition; TOC: Total organic carbon; UVA: Ultraviolet A.
[a] Calculated value.

the high reactivity of the physically adsorbed •OH, Eq. (4) can only occur on the surface of the electrode while degradation by Eq. (5) can possibly occur in the bulk solution.

$$M(H_2O) \rightarrow M(\bullet OH)_{ads} + H^+ + e^- \tag{1}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \tag{3}$$

$$M(\bullet OH)_{ads} + R \rightarrow M + CO_2 + H_2O + inorganic\ ions \tag{4}$$

$$Secondary\ oxidants + R \rightarrow R^* \rightarrow CO_2 + H_2O + inorganic\ ions \tag{5}$$
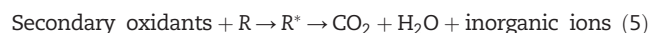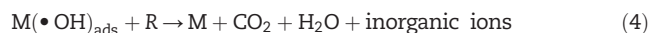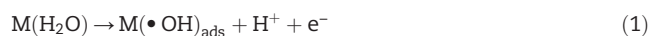
Fig. 7a shows that incorporating chloride in the dye solution was more advantageous in AY-36 decolorization compared to sulfate which is in agreement with other studies on azo dye EO using BDD (Bogdanowicz et al., 2013). Nevertheless, this is in contrast with Murugananthan et al.'s investigation on oxidation of atenolol under the presence of NaCl, Na_2SO_4 and $NaNO_3$. They found that BDD was more effective under the presence of Na_2SO_4 (Murugananthan et al., 2011). The risk of production of some toxic chloro-organics and electrogeneration of chlorine-oxygen byproducts such as ClO_2^-, ClO_3^- and ClO_4^- (Brillas and Martinez-Huitle, 2009), can be prevented by setting the pH to acidic (below pH 4). Coincidentally, Fig. 7b shows that acidic condition (pH 3) was relatively favorable in this study. Different researchers reported different pH effects though; some favored high pH (Martínez-Huitle and Alfaro, 2008), while some showed no pH dependence (Palma-Goyes et al., 2010). These suggest that the effect of pH and the role of active chlorine in EO are circumstantial and depend on other factors involved such as the type of pollutants, the electrode used, and the current density applied.

In present work, the experiments to investigate the effect of pH used KCl as supporting electrolyte which mean under all pH condition chloride ions were provided while the experiments to study the effect of active species were performed under acidic condition (pH 3). Scialdone et al. (2009) investigated the performance of BDD electrode in oxalic acid EO under acidic and basic condition using H_2SO_4 as supporting electrode in the presence or absence of active chlorine species. They found that adding NaCl in the solution in acidic condition will increase degradation performance while in basic condition it gave the opposite effect. In the chloride ions' presence, oxidation of organics is possibly facilitated by more than one active chlorine species other than soluble Cl_2, such as HCLO and ClO^-, depending on the pH of the solution. At acidic condition with pH up to 3 Cl_2 predominate while HClO and ClO^- in the pH range of 3–8 and higher than 8, respectively (Salazar et al., 2014). Additionally, the order of chlorine species with decreasing standard potential is: HClO (E_0 = 1.49 V vs. SHE) > Cl_2 (E_0 = 1.36 V vs. SHE) > ClO^- (E_0 = 0.89 V vs. SHE) (Brillas and Martinez-Huitle, 2009), therefore it can be expected that EO of dye to occur faster in acidic condition. The poor decolorization performance in basic condition is possibly caused by the formation of inactive hydroperoxide which act as •OH scavenger (Murugananthan et al., 2011). Moreover, in Na_2SO_4 solution the dominant oxidant is •OH while in NaCl electrolyte •OH and active chlorine species both take part in EO process (Bogdanowicz et al., 2013; Scialdone et al., 2009).
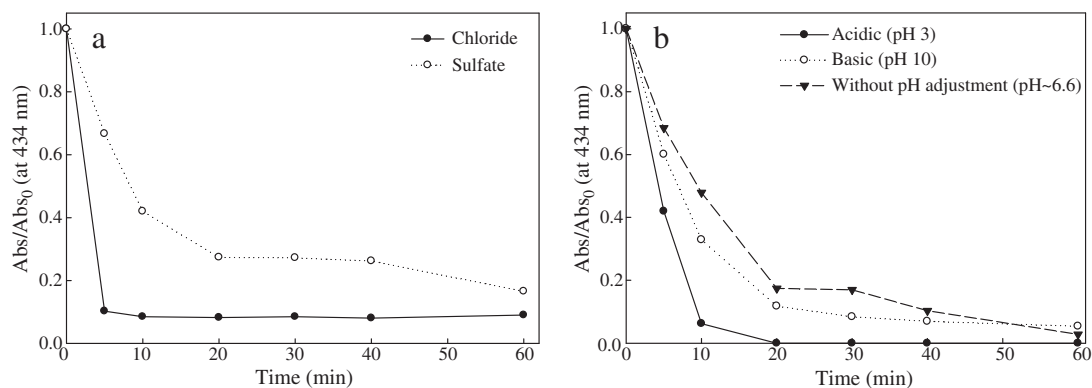
Fig. 7 – Effect of (a) active species present in the solution (supporting electrolyte: 0.15 mmol/L Na$_2$SO$_4$ pH 3 by H$_2$SO$_4$, and 0.15 mmol/L KCl pH 3 by HClO$_4$) and (b) pH (supporting electrolyte: 0.15 mmol/L KCl, acid and basic adjustment by H$_2$SO$_4$ and NaOH respectively) on AY-36 decolorization.

3. Conclusion

The effect of electrochemical polarization on BD-NCD film electrode fabricated via HFCVD was investigated. Via anodic polarization, the originally H-terminated surface of BD-NCD film is changed into O-terminated, increasing its hydrophilicity. This treatment also act as surface cleaning and activation process result in a wider potential window, higher oxygen evolution potential and more stable background current. Consequently, the capability of anodically polarized BD-NCD to degrade AY-36 dye is greatly enhanced. The AY-36 EO by BD-NCD favored acidic condition with the presence of chlorine active species in the solution.

Acknowledgments

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