

Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation

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Received 15 February 2007; received in revised form 7 August 2007; accepted 8 August 2007

Available online 12 August 2007

Abstract

Electrochemical oxidation of synthetic wastewater containing acid blue 22 on a boron-doped diamond electrode (BDD) was studied, using cyclic voltammetry and bulk electrolysis. The influence of current density, dye concentration, flow rate, and temperature was investigated, in order to find the best conditions for COD and colour removal. It was found that, during oxidation, a polymeric film, causing BDD deactivation, was formed in the potential region of water stability, and that it was removed by anodic polarisation at high potentials in the region of O₂ evolution. Bulk electrolysis results showed that the electrochemical process was suitable for completely removing COD and effectively decolourising wastewaters, due to the production of hydroxyl radicals on the diamond surface. In particular, under optimal experimental conditions of flow rates (i.e. 300 dm³ h⁻¹) and current density (i.e. 20 mA cm⁻²), 97% of COD was removed in 12 h electrolysis, with 70 kWh m⁻³ energy consumption. © 2007 Elsevier B.V. All rights reserved.

Keywords: Boron-doped diamond anode; Electrochemical oxidation; Decolourisation; Dyes

1. Introduction

Effluents from textile and paper industries contain large quantities of organic compounds, inorganic salts, and reactive dyes. The release of coloured wastewater in the environment is a considerable source of non-aesthetic pollution and eutrophication. Therefore, proper treatment of these wastewaters has drawn increasing attention.

Commonly employed methods for colour removal are: adsorption [1], coagulation [2], chemical oxidation with ozone [3] or Fenton's reagent [4], and advanced oxidation processes [5,6]. However, these processes are quite expensive and involve several operational problems. For these reasons, there has been increasing interest in the use of new methods such as electrochemical oxidation [7,8].

Many studies have been carried out on electrochemical treatment of organic compounds, and several anode materials have been tested. However, several of them have been shown to rapidly lose efficacy due to surface fouling (glassy carbon [9]), while others have only selectively oxidized pollutants, without

their complete incineration (Ti/IrO₂, Pt [10]). Complete mineralization of organics to CO₂ has only been obtained using high oxygen overvoltage anodes, such as SnO₂ [11–13], PbO₂ [13–17] and boron-doped diamond [18], since, during high potential electrolysis, these electrodes produce hydroxyl radicals from the water discharge on their surfaces. With regard to these electrodes, common drawbacks of SnO₂ and PbO₂ are a short service-life [19] and the release of toxic ions, while BDD anodes have good chemical and electrochemical stability even in strong aggressive media, long life, and a wide potential window for water discharge. Thus, they are promising anodes for industrial-scale wastewater treatment. Indeed, it has been demonstrated that many biorefractory compounds such as phenols [20,21], chlorophenols [15,22,23], pesticides [24,25], and industrial wastes [26] can be completely mineralised with high current efficiency, even close to 100%, using BDD anodes.

The aim of this work was to study electrochemical oxidation of a wastewater model containing reactive dye, using a boron-doped diamond anode. Acid blue 22 was chosen as a model dye, because it is a commercially common triarylmethane dye, containing many aromatic rings and sulphonic groups, making its treatment with traditional processes difficult. The impact of the main operating parameters, such as current density, flow rate,

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and temperature, affecting COD and colour removal, was investigated, in order to identify optimal experimental conditions.

2. Experimental

The dyestuff solution was prepared dissolving different amounts of acid blue 22 ($C_{32}H_{25}N_3O_9S_3Na_2$) in distilled wastewater in 0.5 M Na_2SO_4 . The molecular structure of the acid blue 22 is illustrated in Fig. 1.

The boron-doped diamond (BDD) thin-film electrode was supplied by CSEM (Switzerland). It was synthesised by hot filament chemical vapour deposition technique (HF CVD) on single crystal p-type Si (100) wafers (1–3 m Ω cm, Siltronix).

The filament temperature ranged from 2440 to 2560 °C, while the substrate temperature was 830 °C. The reactive gas was methane in excess dihydrogen (1% CH_4 in H_2). The dopant gas was trimethylboron with 3 mg dm $^{-3}$ concentration. The gas mixture was supplied to the reaction chamber at a flow rate of 5 dm 3 min $^{-1}$, with a diamond layer growth rate of 0.24 μ m h $^{-1}$.

The obtained diamond film had 1 μ m thickness, with 10–30 m Ω cm resistivity. In order to stabilise the electrode surface and obtain reproducible results, the diamond electrode was pre-treated by anodic polarisation in 1 M $HClO_4$ at 10 mA cm $^{-2}$ for 30 min. Following this treatment the surface became hydrophilic.

Cyclic voltammetry was carried out at 25 °C in a conventional three-electrode cell with 100 mV s $^{-1}$ scan rate, using a computer controlled EG&G potentiostat, M 273 model. BDD has been used as working electrode, a saturated calomel electrode (SCE) as reference, and Pt wire as counter electrode. The exposed apparent area of the working electrodes was 1 cm 2 . Bulk oxidations were performed in a one-compartment electrolytic flow cell under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. BDD was used as the anode, and stainless steel as the cathode. Both electrodes were square, each with 25 cm 2 geometrical area and 0.5 cm inter-electrode gap. The solution was stored in a 300 ml thermo-regulated glass tank and

circulated through an electrochemical reactor by a centrifugal pump with different flow rates in the range of 100–300 dm 3 h $^{-1}$.

Colour removal was monitored by measuring absorbance decrease, using a spectrophotometer (Perkin-Elmer Lambda 2). Solution COD was measured during electrolysis using a Dr. Lange LASA50 system.

Current efficiency (CE) for anodic oxidation of methyl red was calculated from COD values, using the following relationship:

$$CE(\%) = \frac{COD_0 - COD_t}{8It} FV100 \quad (1)$$

where COD_0 and COD_t are chemical oxygen demands at times $t=0$ (initial) and t (in g O_2 dm $^{-3}$), respectively, I the current (A), F the Faraday constant (96,487 C mol $^{-1}$), V the electrolyte volume (dm 3), and 8 is the oxygen equivalent mass (g equiv. $^{-1}$).

3. Results and discussion

3.1. Cyclic voltammetry

In order to select the correct potential region for electrolysis, some current/potential curves were recorded at 100 mV s $^{-1}$ scan rate.

Fig. 2 shows the consecutive cyclic voltammograms obtained for BDD in contact with wastewater containing acid blue 22. In the first scan, a shoulder at about 1.0 V versus SCE, and a well defined peak at about 1.6 V versus SCE, corresponding to acid blue 22 oxidation, can be observed. As the number of cycles increased, the anodic current peak decreased until steady state was reached. This decrease in electrode activity was caused by the deposition of polymeric adhesive products on the electrode surface. A similar behaviour has been observed for the oxidation of other aromatic compounds [15,21,27].

However, the polymeric film was removed by treatment with the same solution at $E = 2.5$ V versus SCE, and the BDD surface

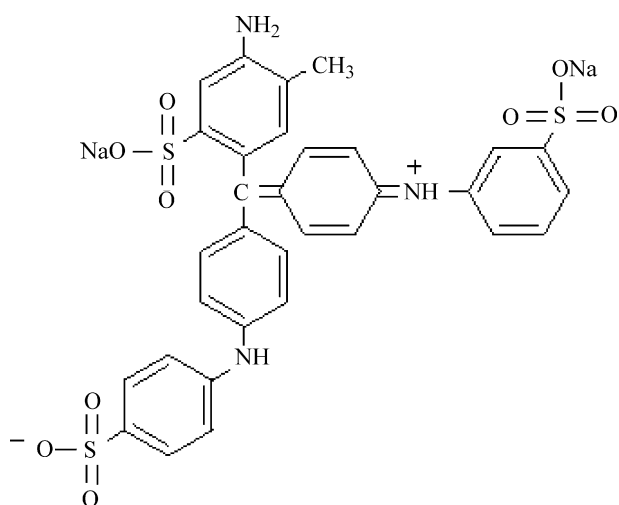


Fig. 1. The molecular structure of the acid blue 22.

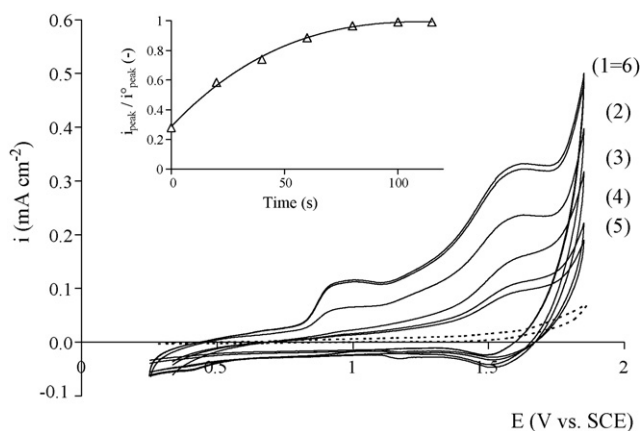
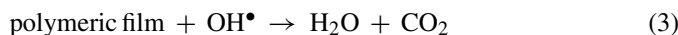


Fig. 2. Consecutive cyclic voltammograms of BDD for a solution of acid blue 22 at a 0.3 mM concentration: consecutive cycles 1, 2, 3, 4 and 5. Curve 6 after reactivation at +2.5 V vs. SCE for 100 s. Dotted line: background curve in 0.5 M Na_2SO_4 . The trend of the normalised current peak (i_{peak}/i_{peak}^0 , where i_{peak}^0 is the current peak during the first scan), during reactivation at 2.5 V vs. SCE is shown in the inset.

could be regenerated. Indeed, it has been demonstrated [28] that water oxidation on BDD involves the formation of hydroxyl radicals that oxidise the polymeric film on its surface:



When polarisation time exceeded 100 s, the acid blue 22 voltammogram resumed the shape of the first cycle, thus indicating complete electrode surface reactivation (Fig. 2, curve 6). The trend of the normalised current peak ($i_{\text{peak}}/i_{\text{peak}}^0$, where i_{peak}^0 is the current peak during the first scan) as a function of polarisation time at 2.5 V versus SCE, is illustrated in Fig. 2 inset.

After establishing that acid blue 22 oxidation can only be performed without electrode fouling in the potential region of water discharge, electrolyses were carried out at current densities equal or higher than 20 mA cm^{-2} , that correspond to an anode potential in this region. Anodic oxidation of the dye solution was performed under different experimental conditions, in order to find the best operating settings.

3.2. Current density effect

Current density impact on COD and current efficiency during acid blue 22 electrochemical oxidation are shown in Fig. 3.

As can be observed, total COD removal is obtained under all conditions, indicating complete dye mineralization by means of its reaction with electrogenerated OH^\bullet radicals (Eq. (2)). However, oxidation with OH^\bullet radicals is not the only oxidation mechanism occurring on conductive-diamond anodes. Indeed [29,30], some peroxodisulphates have been demonstrated to develop in solutions containing sulphates, during electrolysis with BDD electrodes (reaction (4)):



These reagents are known to be very powerful oxidants and to oxidise organic matter, increasing COD and colour removal rate.

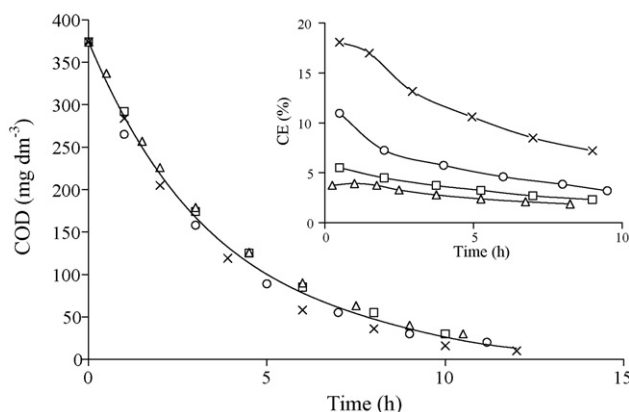


Fig. 3. Influence of the current density on the evolution of the COD and current efficiency (inset) as a function of time during the electrolysis solution of acid blue 22 at a 0.3 mM concentration on the boron-doped diamond anode. $T = 25^\circ\text{C}$; flow rate: $300 \text{ dm}^3 \text{ h}^{-1}$; current density: (x) 20 mA cm^{-2} ; (o) 40 mA cm^{-2} ; (□) 60 mA cm^{-2} ; (Δ) 80 mA cm^{-2} .

It can also be observed that the oxidation rate (i.e. dCOD/dt) is not affected by the applied current. However, an increase in current density results into a decrease in current efficiency (Fig. 3, inset) due to increased side reactions in oxygen evolution (Eq. (5)):



The exponential COD decrease and CE values well below 100% indicate that oxidation was carried out at a current density higher than the stoichiometrically required minimum to oxidise wastewater organic content, and that the process was under mass-transport control. Under these conditions, that are typical of electrolysis of low COD solutions [31,32], oxidation is controlled by the rate at which organic molecules are carried from the bulk liquid to the electrode surface, rather than by the rate at which electrons are delivered to the anode.

In order to improve current efficiency and reduce the charge required for complete oxidation, electrolysis could have been performed at a lower current density, below the limiting one. However, this is not practically feasible, because it corresponds to an anode potential in the region of water stability, where acid blue 22 oxidation produces a polymeric adhesive film that decreases electrode activity, as demonstrated by voltammetric measurements.

3.3. Colour removal

Colour removal during electrolysis was also monitored with spectrophotometry.

UV spectra of acid blue 22, reported in Fig. 4 (inset), show maximum absorption in the range of visible light (wavelength = 594 nm) and a strong, sharp peak in the ultraviolet region for benzenoid and quinoid absorption (wavelength = 376 nm). During electrolysis of a solution of acid blue 22 at a 0.3 mM concentration at 20 mA cm^{-2} , the peak in the visible region decreased until disappearance, meaning complete solution decolourisation after about 4 h of electrolysis. Furthermore, a faster decrease in the absorption band at 594 nm, when

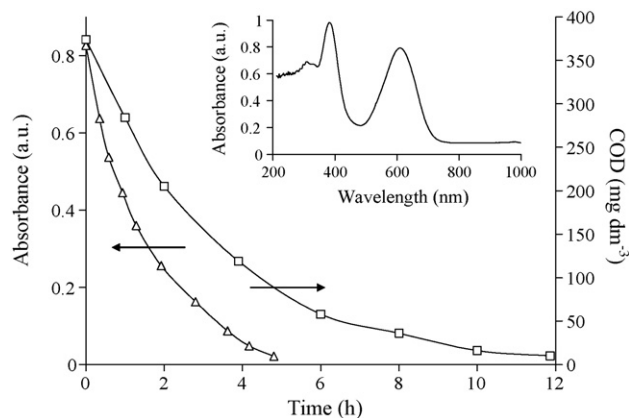


Fig. 4. Trend of absorbance band at 594 nm (Δ) and COD (□) during the anodic oxidation solution of acid blue 22 at a 0.3 mM concentration on the BDD electrode at $i = 20 \text{ mA cm}^{-2}$, flow rate = $300 \text{ dm}^3 \text{ h}^{-1}$, $T = 25^\circ\text{C}$. UV spectrum of the acid blue 22 is shown in the inset.

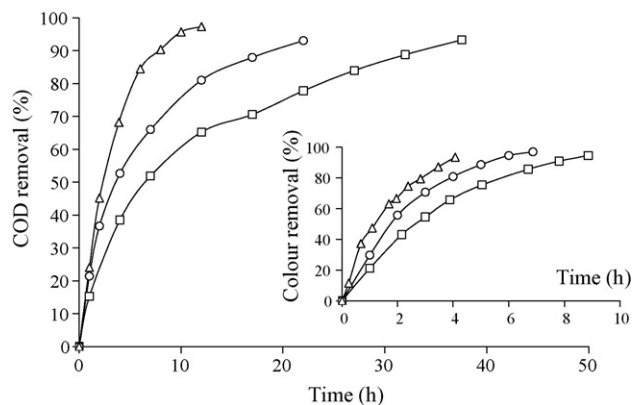


Fig. 5. Influence of the flow rate on the COD and colour (inset) removal as a function of time during the electrolyses of acid blue 22 at a 0.3 mM concentration on the boron-doped diamond anode. Current density: 20 mA cm^{-2} ; $T = 30^\circ\text{C}$; flow rate: (\square) $100 \text{ dm}^3 \text{ h}^{-1}$; (\circ) $180 \text{ dm}^3 \text{ h}^{-1}$; (\triangle) $300 \text{ dm}^3 \text{ h}^{-1}$.

compared to COD removal, indicated that acid blue 22 was oxidised initially to colourless intermediates, and then to carbon dioxide (Fig. 4).

3.4. Effect of recirculation flow rate

In order to further investigate the effects of operating parameters on acid blue 22 oxidation on BDD, electrolyses were performed at different flow rates, in the range of $100\text{--}300 \text{ dm}^3 \text{ h}^{-1}$. As can be seen from Fig. 5, COD trend and colour removal were strongly affected by hydrodynamic conditions. In particular, complete decolourisation was promoted by a high flow rate, indicating that oxidation on BDD is a mass-transfer controlled process. Similar results were also obtained by Polcaro et al. [32] during oxidation of phenolic compounds on a boron-doped diamond electrode.

3.5. Effect of dye concentration

Fig. 6 shows changes in COD over time, during electrolyses of synthetic wastes polluted with initially different acid blue 22

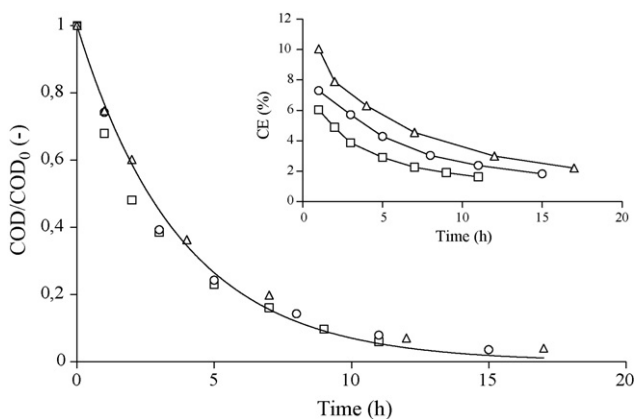


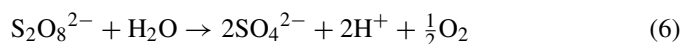
Fig. 6. Influence of the initial acid blue 22 concentration on the ratio COD/COD_0 and current efficiency (inset) during the electrolyses of acid blue 22 on the boron-doped diamond anode. Current density: 40 mA cm^{-2} ; $T = 25^\circ\text{C}$; flow rate: $300 \text{ dm}^3 \text{ h}^{-1}$; acid blue 22 concentration: (\square) 0.1 mM ; (\circ) 0.2 mM ; (\triangle) 0.3 mM .

concentrations. It can be observed, that trends of COD/COD_0 ratio coincide, and similar specific energy values are required to achieve complete waste mineralization. This indicates that both oxidation rate and process efficiency are directly proportional to organic matter concentration. The inset of Fig. 6 shows changes in current efficiency obtained in the same electrolysis essays. As can be observed, for high pollutant concentrations, maximum efficiencies are obtained during initial process phases, with subsequent constant efficiency loss during the experiment. This behaviour is characteristic of discontinuous electrochemical oxidation of wastewaters with conductive-diamond anodes. It is usually explained in terms of mass transfer limitations, assuming that the main mechanism involved in electrochemical oxidation on conductive diamond anodes is a direct or a hydroxyl-radical mediated electrochemical oxidation process [33,34].

3.6. Effect of temperature

Temperature impact on COD changes during acid blue 22 incineration was determined by applying 20 mA cm^{-2} current density, as shown in Fig. 7. As can be seen, temperature increase led to a less efficient process.

Temperature has little impact on electrochemical oxidation with OH^\bullet radicals. Thus, the influence of this parameter must be interpreted in terms of the effect by mediated electroreagents (e.g. peroxodisulphates). Normally, an increase in temperature leads to increases in mediated oxidation rates due to their chemical nature. However, at high temperature, peroxodisulfates are also chemically decomposed into oxygen:



Thus, an increase in temperature accelerates both the oxidation rate of organics with peroxodisulfate (positive effects), and also peroxodisulfate decomposition (negative effects). Which of the two processes prevails, depends on organic pollutant temperature and nature. As can be seen in Fig. 7, temperature increase from 25 to 60°C during acid blue 22 oxidation mostly favours the negative effect of peroxodisulfate decomposition.

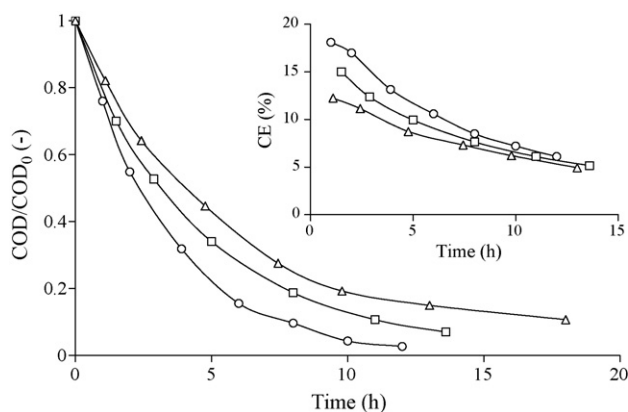


Fig. 7. Influence of the temperature on the evolution of the ratio COD/COD_0 and ICE (inset) as a function of time during the electrolyses of acid blue 22 on the boron-doped diamond anode. Acid blue 22 concentration: 0.3 mmol ; current density: 20 mA cm^{-2} ; flow rate: $300 \text{ dm}^3 \text{ h}^{-1}$; temperature: (\circ) $T = 25^\circ\text{C}$; (\square) $T = 40^\circ\text{C}$; (\triangle) $T = 60^\circ\text{C}$.

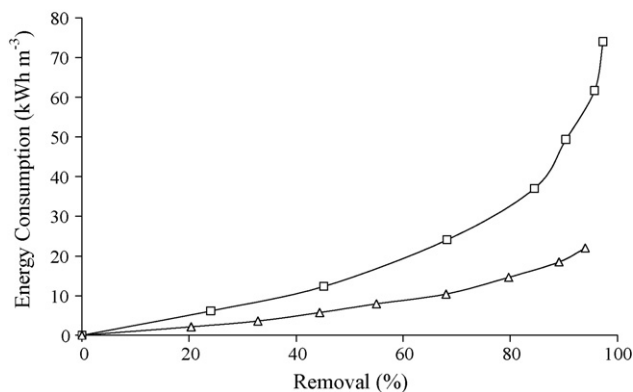


Fig. 8. Evolution of the specific energy consumption against the removal of COD (□) and colour (△) during the anodic oxidation of acid blue 22. Acid blue 22 concentration: 0.3 mmol; current density: 20 mA cm⁻²; flow rate: 300 dm³ h⁻¹; T=25 °C.

To confirm that temperature impact on oxidation rate is related to the nature of organic pollutants, some papers report that COD removal increased with temperature [27,29,33], while others that COD removal decreased with temperature [35,36].

3.7. Energy consumption

Finally, Fig. 8 compares energy consumption (kWh m⁻³) for COD and colour removal during electrochemical oxidation of a solution of acid blue 22 at a 0.3 mM concentration.

Energy consumption increased almost linearly with colour removal, whereas it had a sharp increase with COD removal. This means that this technique is economically suitable for waste pre-treatment to remove colour. Further, although complete COD removal is technically feasible, its high-energy cost makes this technique unsuitable for a refining process.

4. Conclusion

Electrochemical treatment of a synthetic solution containing acid blue 22 dye was investigated using a BDD electrode. The influence of current density, recirculation flow rate, initial dye concentration, and temperature on COD and colour removal was analysed and the following conclusions can be drawn:

- A polymeric film, which caused electrode fouling, developed during oxidation in the potential region of water stability, which could be removed by high-potential anodic polarisation in the region of O₂ evolution.
- Complete COD and colour removal was obtained within the investigated range regardless of current density, flow rate, temperature, and initial dye concentration, due to the formation of hydroxyl radicals from the water discharge.
- The oxidation rate was significantly affected by electrolyte flow rate and dye concentration, meaning that oxidation was under mass-transport control.
- High temperatures improve chemical decomposition of electrogenerated peroxodisulphate, thus decreasing the global oxidation rate.

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