

# Electrochemical oxidation of Acid Yellow 1 using diamond anode

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**Abstract** The electrochemical oxidation of a synthetic wastewater containing Acid Yellow 1 on boron-doped diamond was investigated. The influence of applied current (0.5–3 A), dye concentration (1–3 g L<sup>-1</sup>), temperature (25–40 °C) and flow-rate (75–300 L h<sup>-1</sup>) on colour removal and current efficiency was evaluated. It was demonstrated that the complete decolourization and COD removal were achieved in any experimental conditions indicating that the electrochemical oxidation on BDD electrodes is a suitable method for treatment of wastewaters polluted with synthetic dyes. In particular it was found that the decay of Acid Yellow 1 follows a pseudo-first-order kinetic and the oxidation rate was favoured by increasing current and flow-rate, while it was almost unaffected by solution temperature.

**Keywords** Boron-doped diamond anode · Electrochemical oxidation · Decolourisation · Dyes

## 1 Introduction

Large amounts of coloured wastewaters are produced annually world-wide, not only by textile industries but

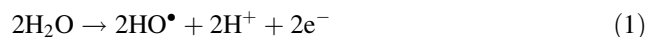
also by other industrial operations such as printing, coffee absorption, yeast preparation and edible oil refinery [1]. Even if the wastewaters contain low concentration of dye, they present strong colour and turbidity and their discharge is particularly troublesome because of its negative visual impact. Decolouration of effluents is a well-known technical problem and therefore the research is devoted to find an effective treatment capable of solving this problem.

Physical and chemical methods such as coagulation [2, 3], electro-coagulation [4–6], flocculation [7], adsorption [8], Fenton's process [9, 10], ozonation [11, 12] and combined processes [13, 14] have demonstrated to be effective, however, some of these methods present important drawbacks as sludge problems, high investment, elevated operational costs, or pollution problems from residual compounds.

As an alternative, electrochemical oxidation appears to be a promising method to solve the environmental problems caused by discharge of dye effluents [15–22].

Many electrode materials have been tested for electrochemical treatment of dye solutions, including Iridium or Ruthenium oxide [23–25], PbO<sub>2</sub> [26, 27], Pt [19, 28] SnO<sub>2</sub> [29] but high current efficiency, even about 100%, was obtained only using boron-doped diamond (BDD) anode [30–34].

In fact, using BDD, which presents an extremely high overpotential for oxygen evolution and an inert surface with low adsorption properties, the organic compounds are incinerated to CO<sub>2</sub> by electrogenerated hydroxyl radicals from water discharge [35]:



The aim of this work was to study the electrochemical oxidation of a synthetic dye solution containing Acid

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Yellow 1, using boron doped diamond anodes. Acid Yellow 1 (AY1), a nitro dye, has been selected as a model compound because it is widely used as a direct dye in drugs, cosmetics, and medical devices, but its degradation is still little studied [36]. The influence of the main operating parameters, such as current density, flow-rate, dye concentration and temperature on COD decay and colour removal has been investigated.

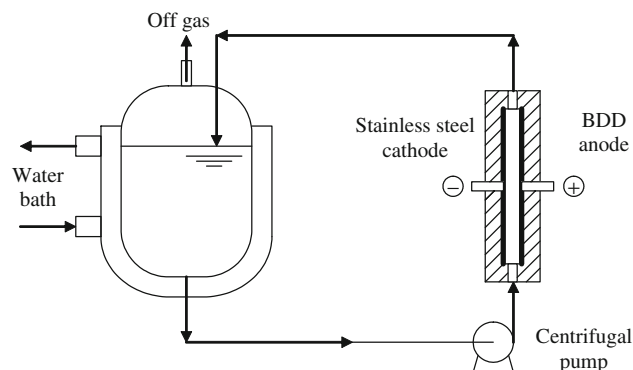
## 2 Experimental

The dyestuff solution was prepared dissolving different amounts of AY1 ( $C_{10}H_4N_2Na_2O_8S$ ) in distilled wastewater in 0.5 M  $HClO_4$ . The chemical structure and other characteristics of AY1 are shown in Table 1.  $HClO_4$  was chosen as supporting electrolyte, because it does not generate some oxidizing species liable to react with organics, as occurs using  $Cl^-$  medium (i.e. generation of  $Cl_2$ ) or  $SO_4^{2-}$  medium (i.e. production of  $S_2O_8^{2-}$ ). All reagents were analytical grade supplied by Carlo Erba Reagents.

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. The filament temperature ranged from 2,440 to 2,560 °C, while the substrate temperature was 830 °C. The reactive gas was methane in excess of hydrogen (1%  $CH_4$  in  $H_2$ ). The dopant gas was trimethylboron with 3 mg  $L^{-1}$  concentration.

The obtained diamond film had 1  $\mu m$  thickness. In order to stabilize 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.

Bulk oxidations were performed in a one-compartment electrolytic flow cell under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. BDD was used as



**Fig. 1** Detail of the experimental setup for the anodic oxidation of Acid Yellow 1

the anode, and stainless steel as the cathode. Both electrodes were square, each with 50  $cm^2$  geometrical area and 1 cm inter-electrode gap. The solution was stored in a 0.4 L thermo-regulated glass tank and circulated through an electrochemical reactor by a centrifugal pump with different flow rates in the range of 75–300  $L h^{-1}$  (Fig. 1).

A JascoV-570 UV/VIS spectrophotometer using silica cells of path length 1 cm was used for the determination of AY1 concentration and the total amount of aromatics. A Lambert-Beer diagram was established to correlate the absorbance at 380 nm to AY1 concentration and the absorbance at 254 nm to the concentration of aromatics [37]. Solution COD was measured during electrolysis using a Dr. Lange LASA50 system.

Instantaneous Current Efficiency (ICE) for anodic oxidation was calculated from COD values, using the following relationship [38]:

$$ICE (\%) = \frac{(COD_t - COD_{t+\Delta t})}{8 \cdot I \cdot \Delta t} F \cdot V \cdot 100 \quad (2)$$

where  $COD_t$  and  $COD_{t+\Delta t}$  are chemical oxygen demands at times  $t$  and  $t + \Delta t$  (in  $g_{O_2} L^{-1}$ ) respectively,  $I$  is the current (A),  $F$  is the Faraday constant ( $96,487 C mol^{-1}$ ),  $V$  is the electrolyte volume (L), and 8 is the oxygen equivalent mass ( $g eq^{-1}$ ).

The specific energy consumption ( $E_{sp}$ ), expressed in  $kWh m^{-3}$  was calculated using the relationship:

$$E_{sp} = \frac{I \cdot t \cdot V_c}{V} \quad (3)$$

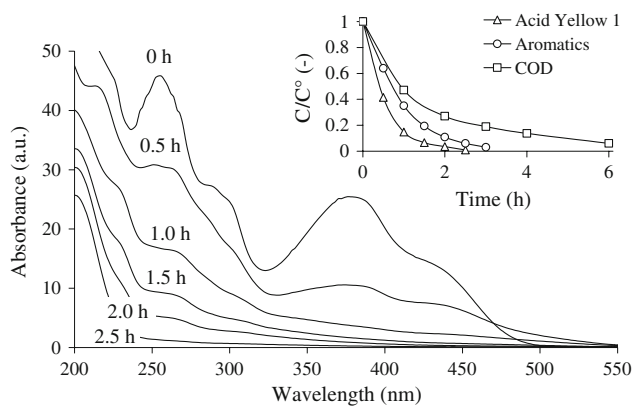
where  $I$  is the current (A),  $t$  is the electrolysis time (h),  $V_c$  is the cell potential (V) and  $V$  is the electrolyte volume (L).

## 3 Results and discussion

Figure 2 shows the changes in the UV-Visible spectra obtained during the electrolysis of 1  $g L^{-1}$  of AY1 applying a current of 1 A. UV-Visible spectrum shows an

**Table 1** Physicochemical properties of Acid Yellow 1

Chemical name	2-Naphthalenesulfonic acid
Chemical formula	$C_{10}H_4N_2Na_2O_8S$
Chemical structure	
Molecular weight	358.19 $g mol^{-1}$
Colour index	10,316



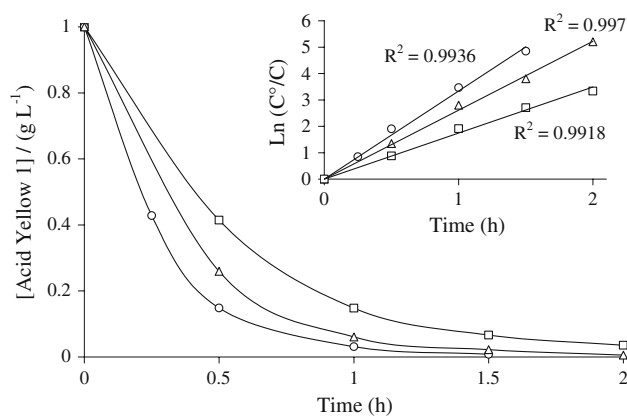
**Fig. 2** Evolution of UV-vis spectra with time during electrolysis of Acid Yellow 1. Conditions: [AY1]: 1 g L<sup>-1</sup>; I = 1 A; T = 25 °C; flow-rate = 300 L h<sup>-1</sup>. Inset: evolution of the normalised concentration of Acid Yellow 1, aromatics and COD

absorption maximum within the range of visible light (wavelength = 380 nm) and a strong sharp peak in the ultraviolet region for benzenoid and/or quinoid absorption (wavelength = 274 nm). During electrolysis, both the peaks decreased until disappearance, meaning complete solution decolourisation and aromatic removal after about 3 h of electrolysis. Onset of Fig. 2 shows the variation of the normalised absorbance, i.e. ratio absorbance/initial absorbance at these two wavelengths and normalised COD. As it can be observed, the intensity of bands at 380 nm decreases more rapidly than the absorption band at 274 nm and COD. This fact indicated that the AY1 oxidation process could start with the breakage of the nitro group (discoloration of the solution), continue with the cleavage of the aromatic ring (removal of band at 274 nm) to form aliphatic intermediates that are finally mineralized to carbon dioxide.

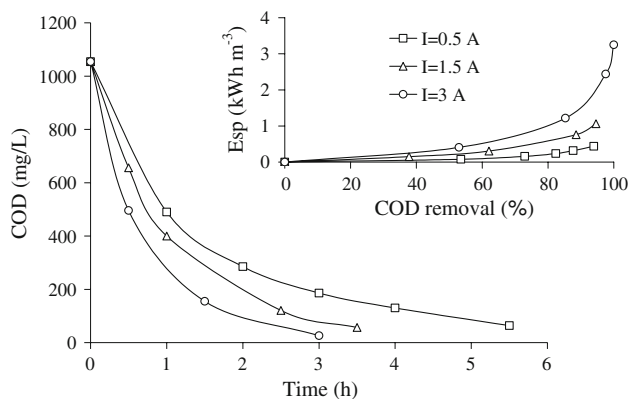
The effect of several operational parameters including applied current, initial dye concentration, flow rate and temperature on COD and colour removal was studied during the electrochemical treatment of AY1 using BDD electrodes.

The removal of AY1 during the electrolyses at different current densities is reported in Fig. 3. The decay of AY1 (Fig. 3, inset) could be very satisfactorily described by a pseudo-first-order kinetics with specific rate constants of  $4.84 \times 10^{-4}$ ,  $7.26 \times 10^{-4}$  and  $9.28 \times 10^{-4} \text{ s}^{-1}$  for electrolysis at 0.5, 1.5 and 3 A, respectively. The pseudo first-order reaction can be attributed to the fact that in galvanostatic conditions a stationary concentration of OH<sup>•</sup> radicals is reached. The oxidation rate increases with rising current because there is a greater charge passing into the cell that favours the electrogeneration of more HO<sup>•</sup> from reaction (1).

Similar behaviour was also obtained for COD removal (Fig. 4), that is the COD removal increases with rising



**Fig. 3** Effect of applied current on the evolution of Acid Yellow 1 concentration during the electrolysis with BDD anode. Conditions: [AY1]: 1 g L<sup>-1</sup>; T = 25 °C; flow-rate = 300 L h<sup>-1</sup>; I = (□) 0.5 A; (Δ) 1.5 A; (○) 3 A. The inset presents the corresponding kinetic analysis assuming a pseudo first-order reaction



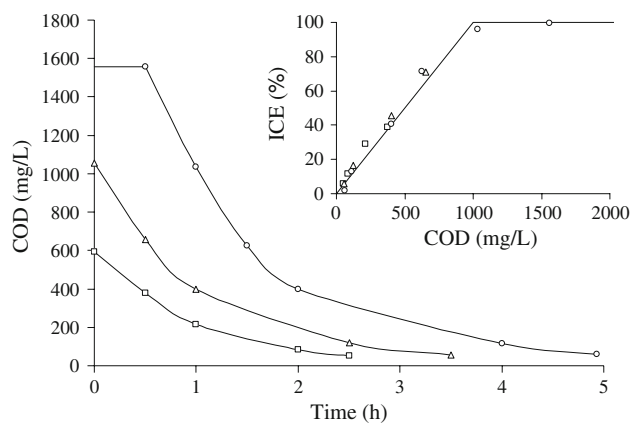
**Fig. 4** Effect of applied current on the evolution of COD during the electrolysis with BDD anode. Conditions: [AY1]: 1 g L<sup>-1</sup>; T = 25 °C; flow-rate = 300 L h<sup>-1</sup>; I = (□) 0.5 A; (Δ) 1.5 A; (○) 3 A. The inset presents the specific energy consumption (E<sub>sp</sub>) as a function of COD removal

current. However, increasing applied current resulted in a lower current efficiency and higher cell voltage and, consequently, in increasing energy consumption (Fig. 4, inset).

In order to optimize the oxidation rate and the energy consumption, the successive experiments were performed applying a current of 1.5 A.

Figure 5 shows the effect of the initial dye concentration on COD and ICE evolution during electrolysis at 25 °C by applying a current of 1.5 A. Overall COD removal is achieved in all the cases and the time for complete oxidation increased with dye concentration as expected from the presence of a greater amount of organic in the solution.

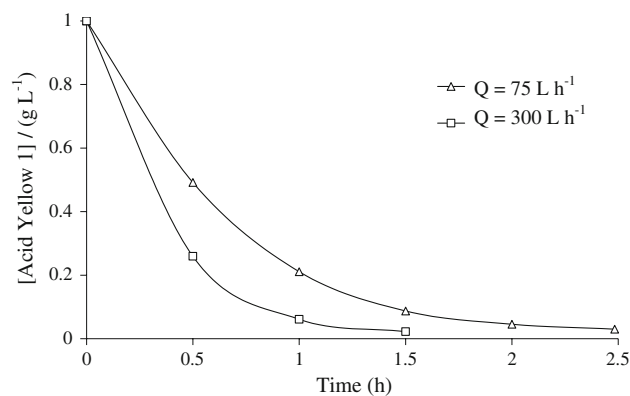
However it is interesting to observe that at high initial concentration, at the beginning of the electrolysis the COD decreased linearly with specific charge and ICE remained about 100% (Fig. 5, inset). This indicates that the electrolysis was performed at a current below the limiting one



**Fig. 5** Influence of initial AY1 concentration on COD evolution during electrolysis with BDD anode. Conditions:  $I = 1.5$  A;  $T = 25$  °C; flow-rate =  $300$  L h<sup>-1</sup>; [AY1]: (□)  $1$  g L<sup>-1</sup>; (Δ)  $2$  g L<sup>-1</sup>; (○)  $3$  g L<sup>-1</sup>. Inset: variation of ICE with COD

and under these conditions the oxidation of AY1 is controlled by the rate at which electrons are delivered at the anode. On the contrary, at low concentration, ICE decreases linearly to zero with COD, meaning that the oxidation was carried out at current density higher than the limiting one and the process was under mass-transport control. Under these conditions, characteristic of electrolysis of solutions with low values of COD [39, 40], the process is controlled by the rate at which organic molecules are transported from the bulk liquid to the electrode surface.

In order to verify the influence of the hydrodynamic conditions on the oxidation of AY1, several electrolyses were performed at different recirculation flow rates, and the results are reported in Fig. 6. The increase of the flow-rate from  $75$  to  $300$  L h<sup>-1</sup> enabled a faster removal of AY1, since the mineralisation time decreased from  $2.5$  to  $1.5$  h.



**Fig. 6** Effect of the recirculation flow-rate on the evolution of Acid Yellow 1 concentration during the electrolysis with BDD anode. Conditions: [AY1]:  $1$  g L<sup>-1</sup>;  $T = 25$  °C;  $I = 1.5$  A; flow-rate = (Δ)  $75$  L h<sup>-1</sup>; (□)  $300$  L h<sup>-1</sup>

These results confirm that the oxidation of solutions containing low concentration of dyes is under mass-transport control.

The oxidation of AY1 was also carried out at different temperatures by strictly thermostating the system, applying a current of  $1.5$  A and with a flow-rate of  $300$  L h<sup>-1</sup>.

Several authors reported that an increase in temperature favours organic oxidation [25, 41] but they attributed this behaviour not to an increase in the activity of the BDD anode but to an increase in the indirect reaction in organics with electrogenerated oxidising agents from electrolyte oxidation.

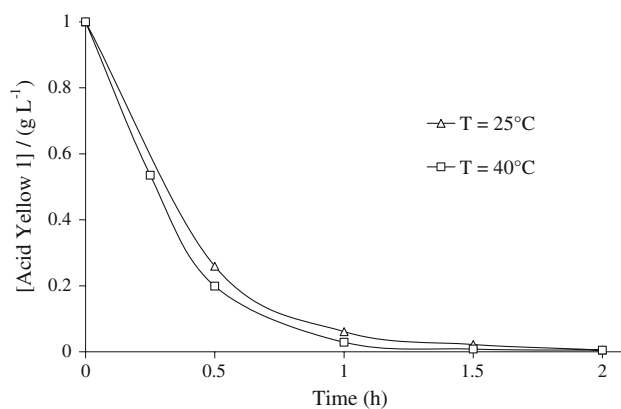
In fact, electrolysis with diamond anodes in media containing chloride, sulphate or phosphate ions generates chlorine (Eq. 4), peroxodisulfate (Eq. 5), and peroxodiphosphate (Eq. 6).



These powerful oxidizing agents can oxidize organic materials by a chemical reaction whose rate increases with temperature, following the Arrhenius law.

However, in a medium that cannot generate oxidizing species, such as HClO<sub>4</sub>, higher temperatures do not yield to a significant increase of the oxidation rate during the electrochemical incineration process (Fig. 7). This result is in agreement with other studies reported in literature for the oxidation of naphthol [42].

The small difference between the results obtained at the two temperatures is only due to an increase of the diffusion rate with rising temperature due to the decrease of the medium viscosity.



**Fig. 7** Effect of the temperature on the evolution of Acid Yellow 1 concentration during the electrolysis with BDD anode. Conditions: [AY1]:  $1$  g L<sup>-1</sup>;  $I = 1.5$  A; flow-rate =  $300$  L h<sup>-1</sup>;  $T =$  (Δ)  $25$  °C; (□)  $40$  °C

## 4 Conclusions

Electrochemical oxidation using a BDD anode has been successfully applied to treat a synthetic wastewater containing Acid Yellow 1. The experimental results showed that:

- the almost total colour and COD removal was obtained, within the range studied, regardless of the experimental conditions, due to the formation of hydroxyl radicals from the water discharge;
- the oxidation of AY1 followed two different trends: at low initial AY1 concentrations, the process was under mass transport control, and the removal of AY1 was well described by a pseudo-first order kinetic; while, for high dye concentration, COD, and so AY1 concentration, decreased linearly with the time, meaning that the oxidation was controlled by charge transfer and it could be described by a zero-order kinetic expression.
- the removal rate of AY1 increases with applied current and flow rate, while it is almost unaffected by solution temperature.

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