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Electrochemical treatment of synthetic wastewaters containing Alphazurine A dye

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ABSTRACT

In this work, the treatment of synthetic wastewaters containing Alphazurine A (AZA) by anodic oxidation using boron doped diamond (BDD) anodes was investigated. Galvanostatic electrolyses of AZA synthetic wastewaters have led to the complete decolourization and COD removal at different operating conditions (initial pollutant concentration and agitation rate) and experimental parameters (temperature and current density). The influence of these parameters was investigated in order to find the best conditions for COD and colour removal. According to the experimental results obtained in this work, the electrochemical oxidation process is suitable for removing COD and decolourizing wastewaters containing AZA dye, due to the production of hydroxyl radicals and other oxidants on the anode surface. In general, the energy requirements for removing 95% of initial COD during galvanostatic electrolyses of AZA synthetic solutions depends mainly on the applied current density, temperature and agitation rate; it passes from 57 kWh at 30 mA cm^{-2} to 138 kWh at 90 mA cm^{-2} per kg COD removed; from 102 kWh at 25 °C to 89 kWh at 60 °C and from 141 kWh at 100 rpm to 29 kWh at 400 rpm.

1. Introduction

Synthetic dyes are extensively used in many fields of up to-date technology, such as in various branches of the textile industry [1–4], leather tanning industry [5,6], paper production [7], food technology [8,9], agricultural research [10,11], light-harvesting arrays [12], photo-electrochemical cells [13], and in hair colourings [14]. Besides, synthetic dyes have been employed for the control of the efficacy of sewage and wastewater treatment [15–17], for the determination of specific surface area of activated sludge for ground water tracing, etc. [18,19]. The chemical classes of dyes employed more frequently on industrial-scale are the azo, anthraquinone, sulfur, indigoid, triphenylmethyl (trityl), and phthalocyanine derivatives. Due to large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors [20]. The interest of water treatment containing synthetic dyes produced by industry has increased in the last years [1].

Traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants [20]. A wide range of methods has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment [1,20,21,22]. As an innovative alternative, the electrochemical processes for treating wastewater containing dyes have been proposed. The application of electrochemical technologies for wastewater treatment are benefiting from advantages such as versatility, environmental compatibility and potential cost effectiveness among others described by other authors [22,23]. Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. Therefore, the feasibility of electrochemical conversion/destruction of organic substrates in wastewater has attracted much attention since pioneering studies to the present days [24].

However, in recent years, several scientific groups have investigated the application of electrochemical oxidation alternatives for removing dyes from water using different anodes, as recently reviewed in detail by Martínez-Huitle and Brillas [25]; in particular, using diamond anodes [25,26]. These 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. In fact, it has been demonstrated that many biorefractory compounds

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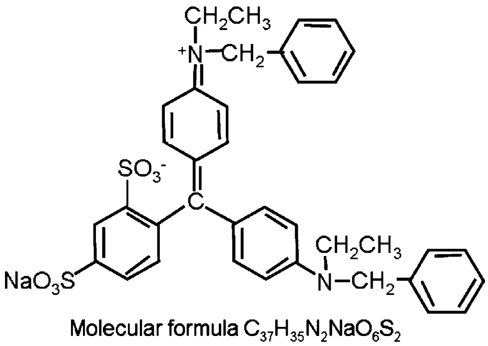

Fig. 1. Molecular formula and chemical structure of AZA dye.

and industrial wastes, including dyes, are completely mineralized with high current efficiencies [24,26].

Despite an extensive literature concerning of the application of electrochemical technologies for removing dyes from water [25], there are, to the best of our knowledge, no reports concerning Alphazurine A dye elimination by anodic oxidation.

The present paper thus describes the study of the electrochemical oxidation of wastewater containing triarylmethane dye such as Alphazurine A (AZA), using boron doped diamond anode. This complex molecule with high molecular weight, many aromatic rings and different substituted groups, as it can be seen in Fig. 1; the structural characteristics of AZA make very difficult the treatment of wastewaters containing this model dye by traditional processes. The influence of the main operating parameters, such as current density, agitation rate, and temperature, on the COD and colour removals, was investigated in order to identify optimal experimental conditions which gives high current efficiency and needs low energy requirements.

2. Materials and methods

2.1. Chemicals and dye solution

Ultrapure water was obtained by Simplicity water purification system. Chemicals were of the highest quality commercially available, and were used without further purification. Na_2SO_4 and H_2SO_4 were purchased from Fluka. The dyestuff solution was prepared dissolving different amounts of AZA in distilled wastewater containing 0.5 M Na_2SO_4.

2.2. Electrodes

Boron doped diamond (BDD) thin-film electrode was supplied by Adamant Technologies (Neuchatel, Switzerland). It was synthesized by hot filament chemical vapor deposition technique (HF CVD) on single crystal p-type Si⟨1 0 0⟩ wafers (1–3 mΩ 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 μm h^{-1}. The obtained diamond film had 1 μm thickness, with 10–30 mΩ cm resistivity.

2.3. Electrooxidation experiments

Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 300 mL. The experiments of AZA oxidation were performed under galvanostatic conditions using a Tacussel model PJT24-1 (24V–1A) potentiostat/galvanostat. BDD was used as the anode, and zirconium as the cathode. Both electrodes were square, each with 10 cm^2 geometrical area. Reagent grade chemicals and three fold distilled water were used throughout the work. The temperature of the electrolyte was controlled using a water thermostat. Experiments were performed at 25 °C for studying the role of applied current density (30, 60 and 90 mA cm^{-2}); furthermore, the effect of the temperature was investigated, carrying out experiments in the range from 25 to 60 °C, under a current density of 60 mA cm^{-2}.

2.4. Analytical methods

Colour removal was monitored by measuring absorbance decrease, using a Hach Model DR/4000 V UV–vis spectrophotometer. Solution COD data were obtained with the same spectrophotometer after digestion of samples in a Merck Model TR-300 thermoreactor. Current efficiency (CE) for anodic oxidation of AZA was estimated from COD values, using the following relationship [24]:

$$\%\mathrm{CE} = FV\left(\frac{[\mathrm{COD}_0 - \mathrm{COD}_t]}{8I\Delta t}\right) \times 100 \qquad (1)$$

where COD_0 and COD_t are chemical oxygen demands at times $t = 0$ (initial) and t (reaction time) 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 $equiv.^{-1}$).

The energy consumption for the removal of 1 kg of COD was estimated and expressed in kWh. The average cell voltage, during the electrolysis, is taken for calculating the energy consumption, as follows [24]:

$$\text{Energy consumption} = \left(\frac{[[tVA/Sv]/1 \times 10^3]}{\Delta\mathrm{COD}/1 \times 10^6}\right) \qquad (2)$$

where t is the time of electrolysis (h); V and A are the average cell voltage and the electrolysis current, respectively; Sv is the sample volume (dm^3), and ΔCOD is the difference in COD (in g O_2 dm^{-3}).

3. Results and discussion

3.1. Colour removal

The visible spectrum of AZA reported in the inset of Fig. 2, shows maximum absorption in the range of visible light ($\lambda = 637$ nm) which is in accordance with the blue colour of AZA solutions. Thus, the measurement of the colour removal was obtained using a UV/vis spectrophotometer at 637 nm. Fig. 2 shows the decrease with time of the absorbance band at 637 nm and COD during galvanostatic electrolysis of AZA synthetic wastewaters containing 500 mg L^{-1} of

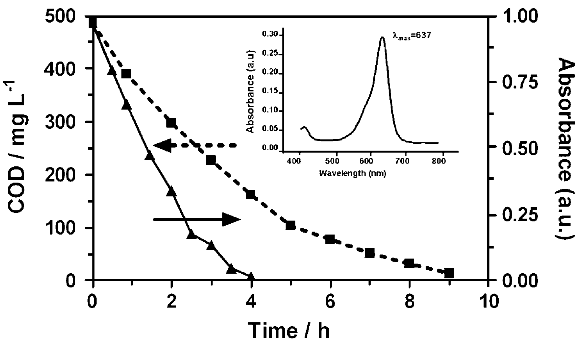

Fig. 2. Evolution with time of absorbance band at 637 nm and COD during BDD-anodic oxidation of AZA. Inset: visible spectrum of the AZA. Operating conditions: COD_0 = 500 mg L^{-1}, electrolyte: 0.5 M Na_2SO_4, current density j = 60 mA cm^{-2}, temperature T = 25 °C, agitation rate: 300 rpm.

COD by applying 60 mA cm^{-2} of current density. As can be observed, both parameters (absorbance and COD) were satisfactorily reduced during the treatment. The intensity of the visible band decreases continuously until its disappearance after about 4 h of electrolysis leading to complete solution decolourization. At this electrolysis-time, only 60% of the initial COD was removed. Furthermore, the changes in absorbance are more rapid than those observed for COD, indicating that during the first stages of the treatment, there are mechanisms that involve the oxidation of the dye to other more simple organics. The oxidation of this complex molecule AZA can lead to the formation of many intermediates (with rapid decrease in the absorbance at 637 nm) by elimination of chromophore groups prior to the formation of aliphatic carboxylic acids and carbon dioxide (that justifies the changes in the COD values).

3.2. Influence on applied current density

Fig. 3 presents the influence of the applied current density on the decay of COD (Fig. 3A) and the variation of current efficiency (Fig. 3B) during electrochemical oxidation of synthetic waste of AZA containing 500 mg L^{-1} of COD. As can be observed, the complete removal of COD was achieved, independently of the applied current density. It indicates the complete dye elimination by means of its reaction with electrogenerated OH$^\bullet$ radicals [27,28]. On the contrary, it seems that the current efficiency depends mainly on the applied current density (Fig. 3B) and high current efficiencies were obtained (especially at the beginning of electrolyses) only for the lowest current density (j = 30 mA cm^{-2}). The increase of applied current density reduces visibly the efficiency of the electrochemical process. This behavior suggests that the oxidation of AZA could be carried out by both direct electrooxidation and mediated oxidation (hydroxyl radicals and other strong oxidants electrogenerated from the oxidation of the supporting electrolyte). It appears that the mediated oxidation by the electrogenerated reagents from the anodic oxidation of supporting electrolyte plays important role in the efficiency of the electrochemical process. It has been suggested [29–31] that, at BDD electrodes, the $^\bullet$OH radicals formed by water oxidation (Eq. (3)) can be either electrochemically oxidized to dioxygen (Eq. (4)) or contribute to the complete oxidation of the organic compounds, in this case, dyes (Eq. (5)):

$$H_2O \rightarrow {}^\bullet OH + H^+ + e \tag{3}$$

$$^\bullet OH \rightarrow \frac{1}{2}O_2 + H^+ + e \tag{4}$$

$$\text{dyes} \xrightarrow{^\bullet OH} CO_2 + H_2O \tag{5}$$

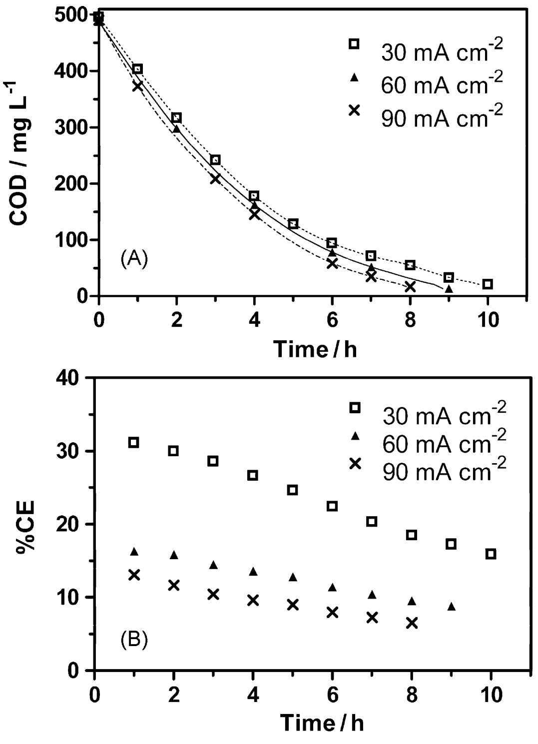

Fig. 3. Influence of applied current density on the evolution with time of (A) COD and (B) current efficiency (%CE) during BDD-anodic oxidation of AZA. Operating conditions: COD$_0$ = 500 mg L^{-1}, electrolyte: 0.5 M Na$_2$SO$_4$, temperature T = 25 °C, agitation rate: 300 rpm.

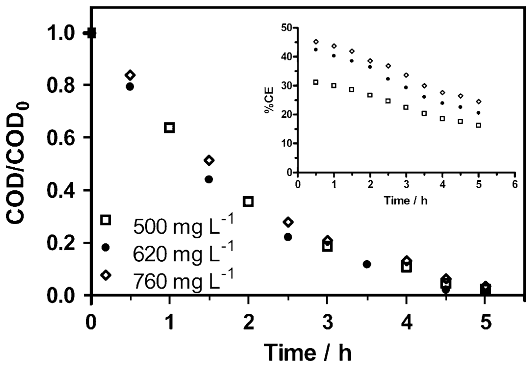

Fig. 4. Influence of AZA initial concentration on the evolution with time of normalized COD during BDD-anodic oxidation of AZA. Operating conditions: electrolyte: 0.5 M Na$_2$SO$_4$, current density j = 30 mA cm^{-2}, temperature T = 25 °C, agitation rate: 300 rpm.

On the other hand, other oxidants can be formed at the diamond surface ($H_2S_2O_8$, O_3) [32,33] and participate in the oxidation of the dye, in the proximity of the electrode surface and/or in the bulk of the electrolyte. Peroxodisulfates have been demonstrated to be formed in solutions containing sulfates [32,33], during electrolysis with BDD electrodes (Eq. (6)):

$$2SO_4{}^{2-} \rightarrow S_2O_8{}^{2-} + 2e^- \tag{6}$$

These reagents are known to be very powerful oxidants and can oxidize organic matter leading to an increase in COD and colour removal rates [25].

In the case of the oxidation of AZA, it can also be observed that, the oxidation rate is not affected by the applied current density. The COD decays and CE values increase, remaining under 100%. This indicates that, for the fluid-dynamics and current density conditions used in this work, the oxidation of AZA was also carried out at a current density higher than the minimum stoichiometrically required for oxidizing wastewater organic content. This outcome is in agreement with the data reported by Panizza and Cerisola [27,28]. Under these conditions, that are used for electrolyses of low COD solutions, the oxidation is controlled by the rate at which organic molecules are carried from the bulk liquid to the electrode surface (in the initial stages), rather than by the rate at which electrons are delivered to the anode. After, in the final stages, the electrochemical oxidation of the dye is controlled by mass transport.

3.3. Influence of dye concentration

Fig. 4 shows the influence of initial COD concentration (in mg L^{-1}) as a function of the time and current efficiency (inset) values during galvanostatic electrolyses of AZA synthetic wastewaters under 30 mA cm^{-2} of applied current density. As can be observed, the trends of normalized COD are moderately overlapped and same electrolysis-times are required to achieve complete COD abatement. This indicates that the oxidation rate and process

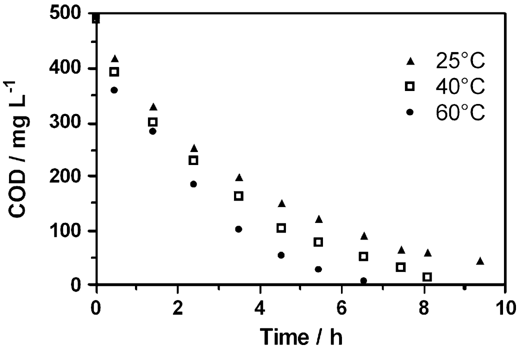

Fig. 5. Influence of temperature on the evolution with time of COD during BDD-anodic oxidation of AZA. Operating conditions: $COD_0 = 500\ mg\ L^{-1}$, electrolyte: 0.5 M Na_2SO_4, current density $j = 30\ mA\ cm^{-2}$, agitation rate: 300 rpm.

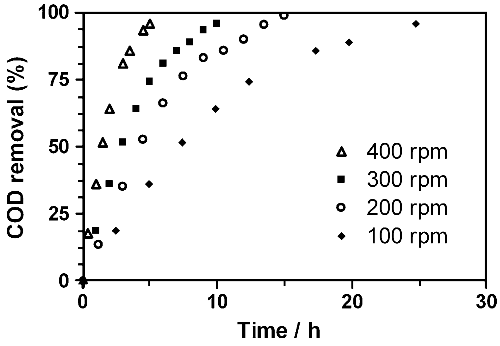

Fig. 6. Influence of the agitation rate on the evolution with time of COD removal time during BDD-anodic oxidation of AZA. Operating conditions: $COD_0 = 500\ mg\ L^{-1}$, electrolyte: 0.5 M Na_2SO_4, current density $j = 30\ mA\ cm^{-2}$, temperature $T = 25\ °C$.

efficiency are directly proportional to organic matter concentration. This outcome is in agreement with the data reported by Panizza and Cerisola [27,28]. It can also be seen, that maximum efficiencies were obtained for the initial stages of the process (high COD concentrations), and after given a decrease in the current efficiencies, continuously down to very low COD values. This is usually explained in terms of mass transfer limitations assuming that both direct oxidation and mediated oxidation on the BDD surface by hydroxyl radicals and other electrogenerated oxidants from the supporting electrolyte (peroxodisulfates) contribute in the electrochemical process. This behavior has been suggested by other authors, as recently reviewed and described in detail by Martínez-Huitle and Brillas [25].

3.4. *Effect of temperature*

Fig. 5 shows the influence of temperature on the COD decay as function of time by applying $30\ mA\ cm^{-2}$ of current density. As can be seen, total COD removal was achieved in all cases. It seems that the temperature has a modest impact on the kinetics of the electrochemical oxidation of AZA because the rate of COD removal was slightly increased by increasing the temperature. The increase of temperature from 25 to 60 °C decreases the electrolysis-time required for the total removal from 8 to 6.5 h. A change in the temperature has slight influence on the electrooxidation with hydroxyl radicals. But, this can be explained by the increase on the chemical reactions rates, especially accelerates the oxidation rate of organics with electrogenerated oxidants from the oxidation of sulfates at BDD anodes (e.g.: peroxodisulfates). However, at high temperatures, thermal decomposition of peroxodisulfates could be taken place. As a result, negligible increase in the oxidation rate was observed in the oxidation of AZA by increasing the temperature, in agreement with results reported by other authors [31–35].

3.5. *Effect of the agitation rate*

In order to verify the important role of mass transfer on the electrochemical treatment of AZA synthetic solutions, the influence of agitation rate during BDD-anodic oxidation of AZA was studied varying the magnetic stirrer rate. Experiments were performed at four rates, in the range of 100–400 rpm. Fig. 6 shows the agitation rate effect on the COD removal as a function of the time, during galvanostatic electrolyses of AZA synthetic wastewaters containing $500\ mg\ L^{-1}$ of COD by applying $30\ mA\ cm^{-2}$ of current density. As can be seen, the almost total COD removal was obtained under different agitation rates. It appears that the hydrodynamic conditions strongly affect the rate of COD removal. High magnetic stirrer rates led to more rapid and high efficient electrochemical process which confirms the suggestion previously mentioned concerning the mass transfer limitations in the range of concentration tested in our work and under the current density conditions. Similar results were also obtained by Panizza and Cerisola [27,28] during the oxidation of synthetic dyes waters on BDD anodes.

3.6. *Energy consumption estimation*

Table 1 presents the energy consumption required to remove 95% of the initial COD at different conditions. As can be observed, during the electrolyses of AZA synthetic wastewaters containing $500\ mg\ L^{-1}$ of COD, the energy consumption seems to be proportional to the applied current density. It increases from 56.84 to $137.8\ kWh\ kg^{-1}$ of COD removed when the current density passes from 30 to $90\ mA\ cm^{-2}$. The values obtained were higher than those obtained during the electrolyses for slighter pollutants proposed in the literature (range of $35–50\ kWh\ kg^{-1}$ COD removed) due to the chemical structure complexity of AZA dye. Table 1 also compares the energy consumption ($kWh\ kg^{-1}$ of COD removed) values during anodic oxidation at different temperatures. Since the process efficiency remains almost constant (Fig. 6), doubling the temperature allowed to diminish the requested treatment time. In addition, energy consumption values at different agitation rates were also reported, confirming the decrease of charge required when an increase on the hydrodynamic conditions was attained. These results point out the high performance BDD-anodic oxidation for treating synthetic dyeing wastewaters compared to other advanced oxidation processes [1,36–40]. The energy consumption makes use-

Table 1
Energy consumption ($kWh\ kg^{-1}$ of COD), calculated from Eq. (2), for 95% of COD removal during BDD-anodic oxidation of AZA for: (i) different applied current densities; (ii) temperatures; and (iii) different agitation rates. $COD_0 = 500\ mg\ L^{-1}$, electrolyte: 0.5 M Na_2SO_4.

Experimental conditions	Energy consumption ($kWh\ kg^{-1}$ of COD)
Applied current density[a] ($mA\ cm^{-2}$)	
30	56.8
60	102.6
90	137.8
Temperature[b] (°C)	
25	102.3
40	92.4
60	89.6
Agitation rate[c] (rpm)	
100	141.1
200	85.6
300	57.0
400	28.5

[a] $T = 25\ °C$, agitation rate: 300 rpm.
[b] $j = 60\ mA\ cm^{-2}$, agitation rate: 300 rpm.
[c] $j = 30\ mA\ cm^{-2}$, $T = 25\ °C$.

less BDD-anodic oxidation for elimination of COD of wastewaters polluted with dyes but it can be a feasible process for decolourizing wastewaters containing dyes as a pre-treatment process.

4. Concluding remarks

The main conclusions of this work can be summarized in the following points:

(i) BDD-anodic oxidation can be used successfully to remove completely all COD and colour from synthetic wastewaters polluted with AZA, considering the specific operating conditions (initial organic load, current density, temperature and agitation rate). It seems that the complete decolourization of the synthetic wastewaters was more rapid than the total COD removal, suggesting the formation of other intermediates prior to the formation of carboxylic acids and carbon dioxide.

(ii) The influence of current density, initial COD, temperature and agitation rate as functions of time, during galvanostatic electrolyses of AZA synthetic wastewaters, showed that the oxidation by the electrogenerated reagents from the anodic oxidation of supporting electrolyte (e.g.: OH and peroxodisulfates) plays important role in the efficiency of the electrochemical process.

(iii) COD decay as a function of time during bulk electrolyses of AZA synthetic wastewaters was significantly affected by dye concentration and agitation a rate, meaning that oxidation rate was under mass transfer control.

(iv) Energy consumption measured during galvanostatic electrolyses of AZA synthetic wastewater solutions depends largely on the applied current density but modest influence of temperature on the energy requirements was observed. A decrease on energy consumption was also observed when an increase in the agitation rate was attained.

Further experiments are in progress in order to improve the current efficiency and reduce the charge required for complete oxidation, performing experiments at a lower current density below to limit value. Also, other parameters such as pH variation, TOC and intermediates produced during electrochemical process will be studied and reported in detail in a separate paper in a near future.

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