Anodic oxidation of textile dyehouse effluents on boron-doped diamond electrode

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ABSTRACT

The electrochemical oxidation of textile effluents over a boron-doped diamond anode was investigated in the present study. Experiments were conducted with a multi-component synthetic solution containing seventeen dyes and other auxiliary inorganics, as well as an actual effluent from a textile dyeing process. The effect of varying operating parameters, such as current density (4–$50\,mA/cm^2$), electrolyte concentration (0.1–$0.5\,M\;HClO_4$), initial solution pH (1–12.3) and temperature (22–$43\,°C$), on process efficiency was investigated following changes in total organic carbon (TOC), chemical oxygen demand (COD) and color. Complete decolorization accompanied by significant mineralization (up to 85% depending on the conditions) could be achieved after 180 min of treatment. Performance was improved at higher electrolyte concentrations and lower pH values, while the effect of temperature was marginal. Energy consumption per unit mass of COD removed was favored at lower current densities, since energy was unnecessarily wasted to side reactions at higher densities.

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1. Introduction

The increasing public concern regarding the environmental contamination that arises from hazardous pollutants present in a wide variety of industrial effluents has brought about stricter legislation and lower disposal limits. Although no precise data are available in literature on total world production of dyes, the textile industry releases several million tons annually [1]. The amount of water used as solvent is the main concern since, according to EIPPCB (European Integrated Pollution Prevention and Control Bureau) estimates, over 2×10^5 tons of salty effluents are being discharged in the environment every year [2].

Several different activities are involved in the dyeing process, such as pre-treatment, dyeing, printing and finishing of the textile material. These activities are all energy and water consuming, as well as highly polluting. Typically, the dyeing process of 1 kg of cotton fabric requires 150 L of water, 0.6 kg of salts and 0.04 kg of dyes, but a majority of various other inorganic constituents (i.e. NaOH, H_2O_2, etc.) and auxiliary organic chemicals (i.e. detergents, softening, dispersing and fixing agents) are also involved [3]. During the dyeing process, about 20–25% of the initial dye content is lost and ends up in the waste stream of the industrial plant [4]. The presence of dyes in the waste effluents constitutes an important problem not only in regards to the aesthetic aspect of the receiving water bodies, but also because their presence interferes with the oxygen solubility and the photosynthetic activity of the aquatic flora, thus altering the biological cycles [5,6].

Several methods including biological oxidation, coagulation–flocculation and adsorption have extensively been investigated for the treatment of textile effluents and although they exhibit certain advantages, they cannot achieve complete decontamination typically due to the large variability in the composition of the effluent [7,8]. As environmental legislation becomes more stringent, the need for efficient and low cost treatment technologies is evident. In this context, advanced oxidation processes, such as ozonation [9], photocatalysis [10,11] and electrochemical oxidation have been evaluated for the destruction of synthetic and, to a lesser extent, actual textile effluents [1,12]. Electrochemical treatment has attracted a great deal of attention recently as it presents several advantages, such as versatility, energy efficiency, ease of operation and cost effectiveness [3,5,13].

The current efficiency of electrochemical oxidation depends strongly on the anode material. In this context, various types of anodes have been tested as a means to improve the effectiveness of oxidation and current efficiency, such as graphite [14], Pt [15], TiO_2 [16], IrO_2 [17], PbO_2 [18] and several Ti-based alloys [19] in the presence of a supporting electrolyte. In a previous study of our group, the treatability of both synthetic and actual textile effluents over a Ti–Ta–Pt–Ir anode was tested regarding the effect of various operating conditions on the efficiency of the electrochemical process [3]. In recent years, however, the boron-doped diamond (BDD) [19,20] has emerged as a very promising anodic material. It

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Table 1
Characterization of effluents used in this study.

Property	Synthetic effluent	Actual effluent
Total dye content (mg/L)	361[a]	Nd
Auxiliary organic chemicals (mg/L)	0	Nd
Na_2SO_4 (mg/L)	5500	Nd
Na_2CO_3 (mg/L)	440	Nd
NaOH (mg/L)	110	Nd
COD (mg O_2/L)	300	470
TOC (mg C/L)	82	120
Suspended solids (mg/L)	0	68
Conductivity (mS/cm)	8.4	7.2
pH	11.2	8.8
Cu_{total} (mg Cu/L)	0	0.065
Cr_{total} (mg Cr/L)	0	0.03
Fe_{total} (mg Fe/L)	0	0.103

Nd: not determined.
[a] The contribution of each dye is given in reference [3].

possesses several advantageous properties such as an extremely wide potential window for water discharge, robust oxidation capacity, corrosion stability in very aggressive media, an inert surface with low adsorption and resistance to corrosion. Using this anode at high potential, highly reactive $HO^\bullet$ radicals generated on its surface lead to combustion of the organic compounds R [20–23]:

$$H_2O \rightarrow HO^\bullet + H^+ + e^- \tag{1}$$

$$R + HO^\bullet \rightarrow CO_2 + H_2O \tag{2}$$

The present study aims to assess the feasibility of an electrochemical BDD system for the treatment of both synthetic and actual textile effluents. The influence of various process parameters such as applied current density, electrolyte concentration, temperature and pH on the efficiency of the process has been investigated for the treatment of the synthetic textile effluent. Optimal operating conditions were then employed for the treatment of the real effluent. Process efficiency has been evaluated in terms of color removal, chemical oxygen demand (COD) reduction, mineralization and energy consumption.

2. Materials and methods

2.1. Textile effluent characterization

The synthetic textile effluent used in the present study is a mixture of seventeen commercial dyes with a total dye concentration of 361 mg/L. All of the dyes were kindly provided by Epilektos SA, a textile manufacturing industry located in central Greece. In order to simulate the actual effluent, appropriate amounts of inorganic salts (e.g. Na_2SO_4 and Na_2CO_3) and NaOH were also added. The contribution of each dye to the total dye content was determined according to information provided by the textile manufacturer and is given in previous work [3]. The resulting synthetic wastewater has an intense blue–black color and is highly alkaline.

The actual textile effluent was also provided by Epilektos SA. The effluent has a light grey–blue color, low content of suspended solids, alkaline pH and a COD content (after filtration with 1.2 μm GF/C, Whatman) of 470 mg O_2/L. The dye composition and chemical characteristics of the simulated and real effluents are given in Table 1.

2.2. Electrochemical experiments

All experiments were performed in a batch type, laboratory scale electrochemical reactor. This single-compartment cell comprised a BDD anode with an active working area of 15 cm^2 and a zirconium cathode enclosed in a porous porcelain pot, while a magnetic

bar provided continuous stirring. The actual wastewater was filtered (1.2 μm GF/C, Whatman) prior to each run in order to remove any suspended particles present. In a typical run, the effluent was mixed with the appropriate amount of $HClO_4$, the current intensity was then set to the desired value and the voltage was automatically regulated to match the current value. $HClO_4$ was chosen as the supporting electrolyte because no oxidizing species liable to react with organics are generated as occurs in the case of Cl^- and SO_4^{2-} media (i.e. production of Cl_2 and $S_2O_8^{2-}$, respectively) [24]. In all cases, the treated volume was 0.12 L. All runs were carried out at constant temperature regulated by a water jacket installed around the reactor. Appropriate dilutions of 10 M NaOH solution were used for pH adjustment.

2.3. Analytical procedures

Effluent mineralization was assessed following the decay of dissolved total organic carbon (TOC) on a TOC analyzer (5050A, Shimadzu) and COD according to the dichromate method [25].

The extent of decolorization that had occurred during the electrochemical oxidation was monitored on a Hach-Lange D5000 UV–vis spectrophotometer by scanning the sample absorbance in the 200–800 nm band. Changes in effluent pH and conductivity after electrolytic treatment were determined with a Crison GLP 21 pH meter and a Toledo conductivity meter, respectively.

2.4. Determination of limiting current and energy consumption

The limiting current density for the electrochemical incineration of the wastewater can be related to the initial COD_0 (mol O_2/m^3) as follows [26]:

$$j_{lim} = 4Fk_mCOD_0 \tag{3}$$

where j_{lim} is the limiting current density (A/m^2), F is the Faraday constant (96,487 C/mol) and k_m is the average mass transport coefficient in the electrochemical cell equal to 1.72×10^{-5} m/s [23].

Depending on the applied current density, two different operating regimes can be identified. First, when the applied current density is lower than the limiting value, electrolysis is under current control with high current efficiency and the COD decreases linearly with time. Second, when the applied current density is higher than the limiting value, electrolysis is under mass transport control with lower current efficiency and the COD decreases exponentially with time [26].

The specific energy consumption (E_c) in kWh/kg COD removed is determined according to the following equation [21]:

$$E_c = \frac{UIt/60}{(COD_0 - COD)V} \tag{4}$$

where U is the mean applied voltage (V), I is the current (A), t is the treatment time (min), V is the liquid volume (L), and COD_0 and COD are the COD values (g O_2/L) at times 0 and t.

3. Results and discussion

3.1. Effect of current density

The degradation of the organic pollutants in an electrochemical system occurs through two different mechanisms: (a) direct anodic oxidation, where the pollutants are adsorbed onto the anode surface and then destroyed through electron transfer reactions, and (b) indirect oxidation, where electrochemically generated oxidants (i.e. hydroxyl radicals, chlorine, hydrogen peroxide, hypochlorite, ozone and peroxodisulfate) oxidize the pollutants in the liquid bulk. The latter mechanism is dominant in the degradation of organics
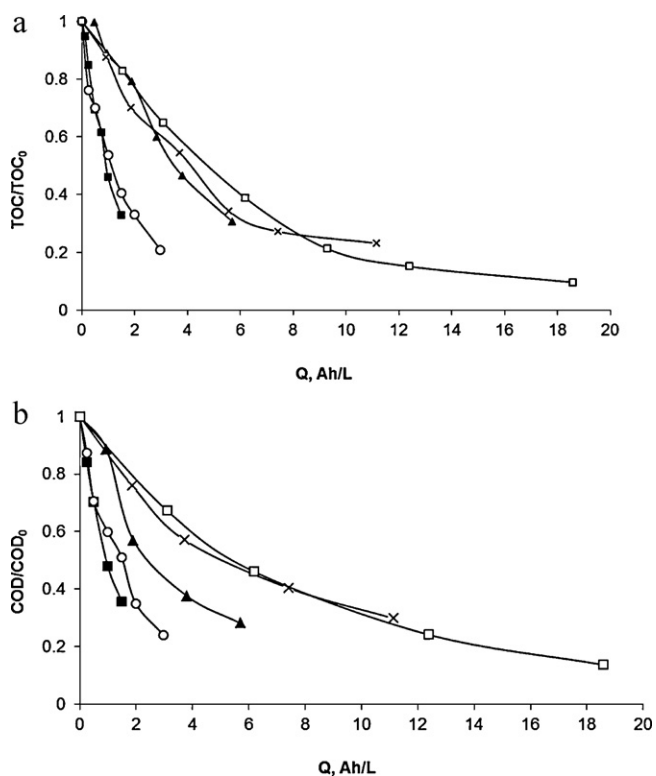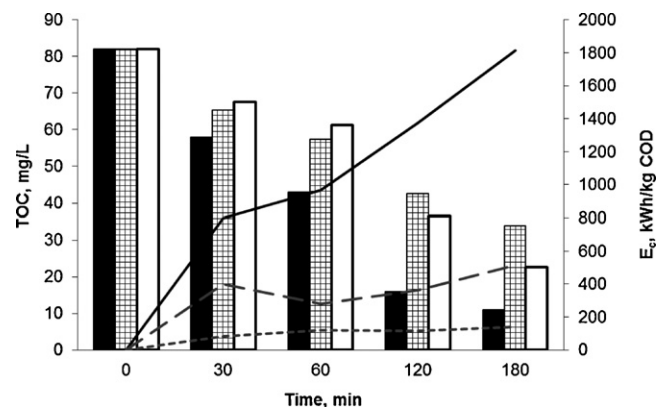
Fig. 1. Effect of current density on (a) TOC and (b) COD abatement during the electrochemical oxidation of synthetic textile effluent: (■) 4 mA/cm^2; (○) 8 mA/cm^2; (▲) 15 mA/cm^2; (×) 30 mA/cm^2; (□) 50 mA/cm^2. [HClO$_4$] = 0.5 M; pH 1; T = 22 °C.

Fig. 2. Effect of current density on TOC removal (bars – left Y-axis) and energy consumption (lines – right Y-axis) during the electrochemical oxidation of synthetic textile effluent: (black bar, dotted line) 8 mA/cm^2; (grid bar, dashed line) 15 mA/cm^2; (white bar, solid line) 50 mA/cm^2. [HClO$_4$] = 0.5 M; pH 1; T = 22 °C.

on a BDD anode, where water discharge (Eq. (1)) leads to the formation of HO• near the anode surface and, consequently, to the mineralization of the organic matter (Eq. (2)) [27].

The effect of current density on TOC and COD abatement was investigated for values below (i.e. 4 mA/cm^2) and over (i.e. 8, 15, 30 and 50 mA/cm^2) the limiting current of 6.2 mA/cm^2 which was computed according to Eq. (3). The results are shown in Fig. 1. As seen, higher charges are required to obtain the same removal efficiency at increased current densities. The best efficiency is achieved at 4–8 mA/cm^2 since, compared to other current densities, higher degrees of mineralization are obtained at significantly lower electrical charges; this could be ascribed to the fact that current densities of 4–8 mA/cm^2 are close to the limiting current density where high efficiencies are expected [27,28].

Taking into consideration that electrochemical treatment is an energy consuming process accompanied by potentially high operating costs, its efficiency was also evaluated in terms of energy consumption. Fig. 2 shows temporal changes of TOC, as well as the energy consumption at three different current densities (i.e. 8, 15 and 50 mA/cm^2). E_c is significantly lower at milder current densities and does not undergo considerable increase even after prolonged treatment, with cumulative values (i.e. after 180 min) between 140 and 516 kWh/kg COD removed at 8 and 15 mA/cm^2, respectively. This is not the case at the higher current density (i.e. 50 mA/cm^2) where mineralization proceeds slightly faster than at 15 mA/cm^2 but with particularly high consumption of electrical energy (i.e. 1813 kWh/kg COD). It is observed that at prolonged treatment times (i.e. over 50% mineralization) the increase in E_c is more pronounced at high current density values, presumably due to the enhancement of the side reaction of oxygen evolution. Similar results are given in Table 2, which shows energy requirements alongside the respective specific cost to achieve 50% mineralization at various current densities. For instance, increasing current density from 8 to 15 mA/cm^2 causes a 3-fold increase in E_c (i.e. from

115 to 364 kWh/kg COD) and, consequently, in specific cost (i.e. from 8 to 25 €/kg COD). This is also the case at even higher current densities, since part of the energy is wasted to side reactions other than those contributing to COD decrease. With this in mind, all subsequent experiments were performed at 8 mA/cm^2 current density.

3.2. Effect of electrolyte concentration

Fig. 3 shows the effect of electrolyte concentration on performance at 8 mA/cm^2. Increasing HClO$_4$ concentration from 0.25 to 0.5 M does not exert a strong influence on TOC or COD removal (i.e. 65–75% removal occurs after 180 min in either case); however, decreasing the electrolyte concentration to 0.1 M brings about 20% reduction in process efficiency (i.e. from 70 to 50% after 180 min). Although the use of HClO$_4$ at increased concentrations does not induce the generation of additional oxidants, it enhances effluent conductivity and, consequently, electron transfer [29]. The voltage during the reaction decreased from 15 to 10 V when the electrolyte concentration increased from 0.1 to 0.5 M, respectively (data not shown). This means that adding more electrolyte results in lower energy consumption (i.e. 110 instead of 317 kWh/kg COD) for the same TOC or COD removal (i.e. 50 ± 2%).

3.3. Effect of initial pH

It is well known that the influence of pH strongly depends on the nature of the investigated organics. In this respect, experiments were also performed at near-neutral (i.e. pH 6.6) and alkaline (i.e. pH 12.3) conditions and the results are shown in Fig. 4, alongside with data at acidic conditions (i.e. pH 1).

Table 2
Energy consumption and specific cost for 50% mineralization at different current density values. Numbers in brackets correspond to the treatment time (min) required to achieve 50% mineralization.

Current density (mA/cm^2)	Energy consumption (kWh/kg COD)	[a]Specific Cost (€/kg COD)
50	967 (60)	68
30	563 (60)	39
15	364 (120)	25
8	115 (120)	8
4	41 (120)	3

[a] Based on the mean value of electricity for industrial use in Greece, i.e. 0.07 €/kWh.
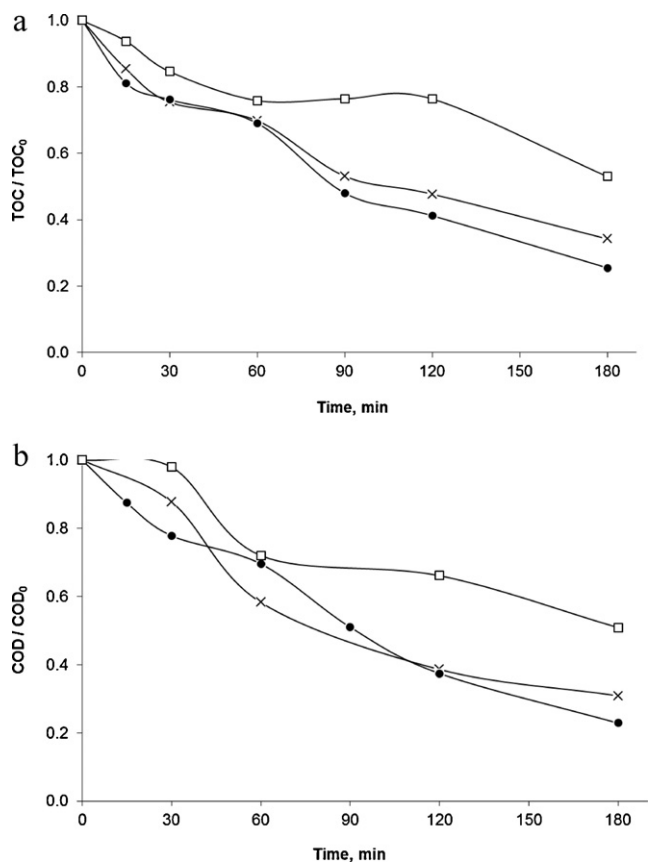
Fig. 3. Effect of $HClO_4$ concentration on (a) TOC and (b) COD abatement during the electrochemical oxidation of synthetic textile effluent: (□) 0.1 M; (×) 0.25 M; (●) 0.5 M. Current density = 8 mA/cm^2; pH 1; T = 22 °C.

Degradation is clearly favored at acidic conditions where about 60% and 52% COD and TOC removal, respectively occurs after 120 min of reaction; the respective values are about 53% and 40% at pH 6.6 and 40% at pH 12.3. This effect may be due to the extensive oxidation and/or chemical modification (under alkaline conditions) of the electrode surface, which suggests a change in the surface properties. It should be noted here that a thorough evaluation of the pH effect on performance is not possible given the complexity of the synthetic effluent which contains seventeen dyes with different chemical structures and properties, and consequently different reactivities. Moreover and since the solution was not buffered at
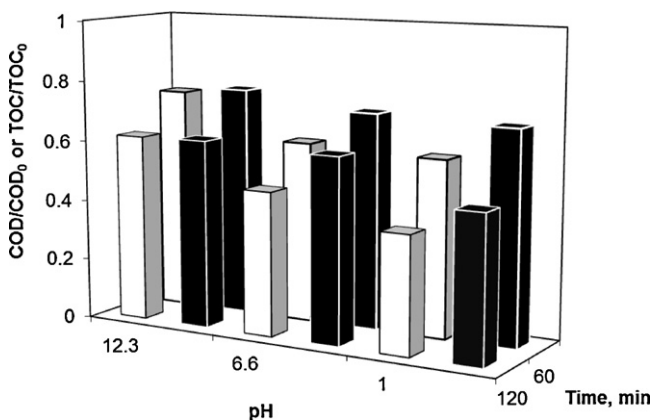

Fig. 4. Effect of initial pH on TOC (black bars) and COD (white bars) abatement during the electrochemical oxidation of synthetic textile effluent. Current density = 8 mA/cm^2; [$HClO_4$] = 0.25 M; T = 22 °C.
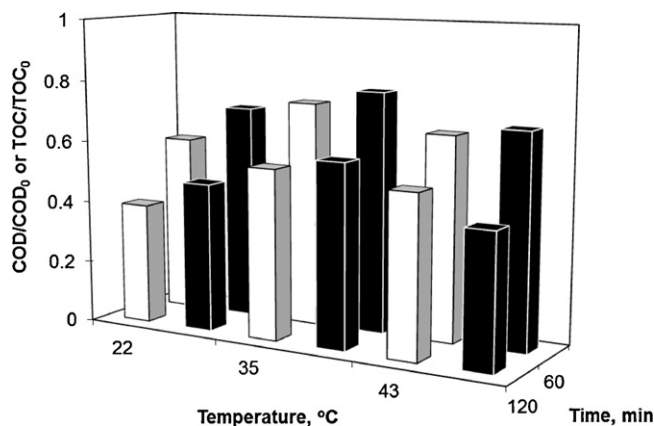

Fig. 5. Effect of temperature on TOC (black bars) and COD (white bars) abatement during the electrochemical oxidation of synthetic textile effluent. Current density = 8 mA/cm^2; [$HClO_4$] = 0.25 M; pH 1.

the working pH value, the latter progressively decreased during the reaction presumably due to the formation of oxidized by-products (this was more pronounced for the runs performed at near-neutral and alkaline conditions); in this respect, changes in solution pH over time may also affect reactivity.

3.4. Effect of temperature

Fig. 5 shows the evolution of TOC and COD as a function of electrolysis time and reaction temperature (i.e. 22, 35 and 43 °C). Although removal appears to be slightly enhanced at ambient temperature, the effect is marginal and this is in good agreement with previous studies [24]. In this respect, operation at inherent temperature should be preferred in order to avoid extra treatment costs associated with increased temperatures.

3.5. Effect of matrix

In order to assess the treatability of actual textile effluents, an additional run was performed at the optimal conditions determined from runs with the synthetic effluent, i.e. 8 mA/cm^2 of current density, 0.25 M of electrolyte, acidic conditions and inherent temperature. The results, alongside data from the corresponding run with the synthetic effluent, are shown in Fig. 6. TOC profiles are nearly common for both types of effluent with removal reaching about 70% after 180 min of treatment. A somewhat different behavior is observed for COD where partial oxidation of the
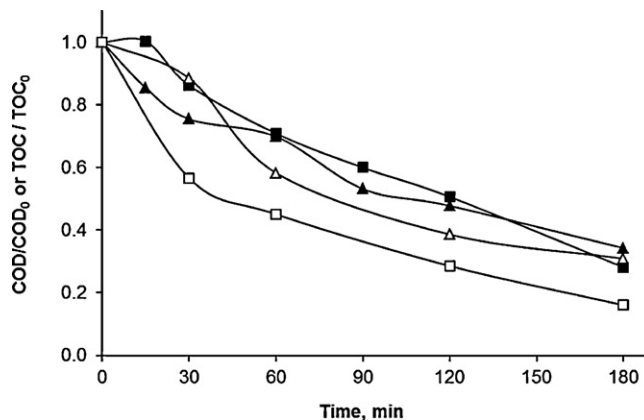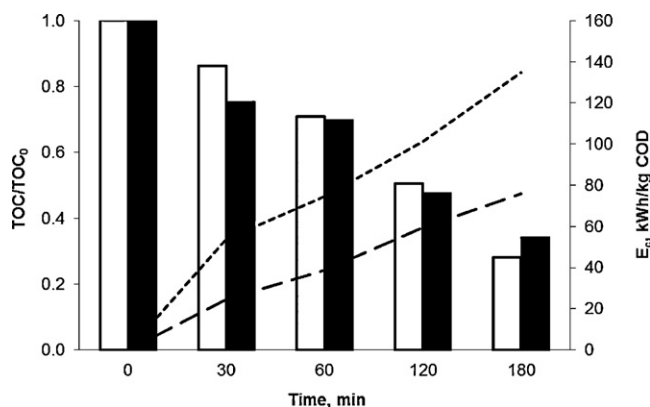

Fig. 6. TOC (closed symbols) and COD (open symbols) abatement during the electrochemical oxidation of (▲, △) synthetic and (■, □) actual textile effluents. Current density = 8 mA/cm^2; [$HClO_4$] = 0.25 M; pH 1; T = 22 °C.

Fig. 7. TOC removal (bars – left Y-axis) and energy consumption (lines – right Y-axis) during the electrochemical oxidation of (black bar, dotted line) synthetic and (white bar, dashed line) actual textile effluent. Current density = 8 mA/cm^2; [HClO$_4$] = 0.25 M; pH 1; T = 22 °C.

Fig. 8. Decolorization of synthetic textile effluent during electrochemical oxidation. Current density = 8 mA/cm^2; [HClO$_4$] = 0.25 M; pH 1; T = 22 °C.

effluent's organic content seems to be favored in the case of the actual effluent. TOC reduction corresponds exclusively to the conversion of the organic content to carbon dioxide and water (i.e. total oxidation reactions), while COD reduction may be due to both total oxidation and the conversion of organics to more oxidized reaction intermediates (i.e. partial oxidation). In this respect, (i) the complexity of the real matrix associated with the occurrence of auxiliary organic substances that may be less susceptible to complete oxidation than dyes and, (ii) the presence of various inorganic salts (e.g. NaCl) that may lead to the indirect formation of reactive species (e.g. hypochlorite) would promote partial over total oxidation reactions.

Fig. 7 shows changes in cumulative energy consumption, as well as the respective degree of mineralization for both effluents. Although mineralization is nearly identical regardless the effluent, the energy consumed is lower for the actual than the synthetic effluent. For example E_c is about 75 and 135 kWh/kg COD after 180 min of reaction for the actual and synthetic effluent, respectively; this is due to the fact that (i) the COD removal of the actual effluent is higher than that of the synthetic one (see Fig. 6), and (ii) the initial COD value of the former is 55% greater than that of the latter.
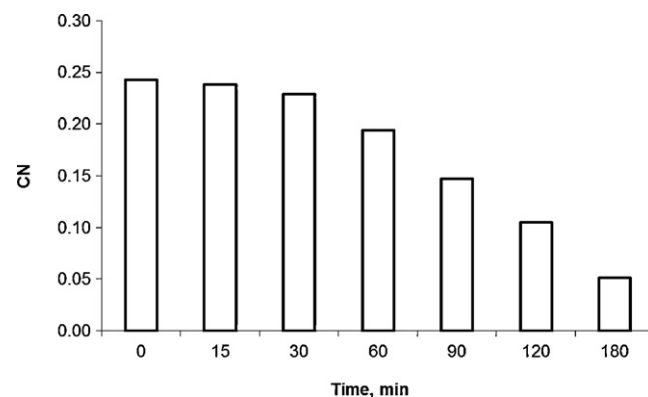
3.6. Decolorization

The degree of decolorization occurring during the electrochemical treatment of the synthetic effluent was monitored according to the color number (CN) which is defined as follows:

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \tag{5}$$

Spectral absorbance coefficients (SAC), which are defined as the ratio of the respective absorbance values over the cell thickness, were determined at 436, 525 and 620 nm. As seen in Fig. 8, CN decreases continuously upon electrochemical treatment to a value of 0.05 after 180 min, which accounts for over 80% decolorization. The synthetic effluent's color has turned from intense blue–black to pale yellow at the end of the treatment.

Due to the particularly low dye content of the actual effluent, no absorbance bands over 300 nm were detected during the spectral scanning, therefore the application of Eq. (5) in this case was not feasible. However, complete decolorization could be achieved after 180 min of reaction for the actual effluent, whose color turned from grey–blue to transparent.

4. Conclusions

The main conclusions drawn from this study can be summarized as follows:

(1) Electrochemical oxidation on BDD anode is capable of destroying the chromophore groups of the dyes used in the present study at short treatment times and relatively low energy consumption. Significant mineralization of the synthetic textile effluent ranging between 60% and 85% can be achieved under all current densities employed in the present study. Nonetheless, the choice of the operating current is decisive since high densities (e.g. 50 mA/cm^2) are likely to favor side reactions (i.e. oxygen evolution), thus decreasing efficiency and increasing energy consumption (i.e. up to 1813 kWh/kg COD). The optimal conditions for the electrochemical oxidation of the synthetic textile effluent were determined at 8 mA/cm^2 current density, strongly acidic conditions (i.e. pH 1) and 0.25 M HClO$_4$ electrolyte.
(2) Treatment performance, in terms of mineralization and COD reduction, is also affected by operating parameters such as electrolyte concentration and effluent pH. On the other hand, the effect of temperature (in the range 22–43 °C) appears to be marginal, thus allowing operation at inherent conditions.
(3) The water matrix may also affect electrochemical treatment on BDD anode, since actual effluents usually contain large concentrations of several auxiliary organics and inorganic species whose interference may affect strongly the efficiency of the process.

Acknowledgement

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