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Applicability of diamond electrode/anode to the electrochemical treatment of a real textile effluent

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ABSTRACT

In this work, a real effluent discharged by Brazilian textile industry, has been electrochemically treated using boron doped diamond (BDD) anode for removing chemical oxygen demand (COD) and colour. Preliminary experiments were performed under real discharged effluent conditions (pH and conductivity) in order to verify the applicability of this treatment process. However, a partial elimination of COD and colour effluent were achieved, depending on applied current density (20, 40 and 60 mA cm⁻²), respectively. Therefore, different set of experiments were carried out where an amount Na₂SO₄ was added in the real effluent; then, COD of textile effluent was satisfactorily reduced by employing different operational conditions (current density, temperature, Na₂SO₄ concentration, flow rate), reducing the time of depuration and consequently, the costs, confirming the potential efficiency of this textile effluent treatment.

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1. Introduction

Textile industry produces large quantities of wastewater during the washing and dyeing process, which contain large quantities of dye, and are disposed together with the textile effluent. The pollution potential of textile dyes and intermediates compounds was first raised due to its toxicity and carcinogenicity that can cause damage to human health and environment. It should be mentioned that colouration in water courses affects water transparency and gas solubility [1,2].

Thus, the development of treatment technologies suitable for the removal of colour and reduction of toxicity of textile effluents is important. For the removal of dyes from wastewater a wide range of techniques have been developed and proposed [1–11]. However, the most useful industrial treatment is bioremediation technology because it can be performed on site, at lower cost, with limited inconveniences, minimal environmental impact, it eliminates the waste permanently and it can be used in conjunction with methods of physical and chemical treatments [5]. But, this process requires long times and specific treatment conditions and in addition, heavy metals, radio nucleotides, complex molecules, biorefractory and some chlorinated compounds are not suitable for bioremediation [6].

In this context, electrochemical technologies have caused great interest because they offer effective means to solve environmental problems related to industrial processes [12–15]. These techniques have been investigated for decolourisation and degrading dyes from aqueous solutions (dyes solutions, synthetic and actual wastewaters) by several scientific groups and a wide variety of electrode materials have been suggested, such as graphite, platinum, IrO₂, RuO₂, SnO₂, PbO₂, Ti/Pt, Ti/Pt–Ir, Ti/PbO₂, Ti/PdO–Co₃O₄ and Ti/RhO_x–TiO₂, Ti coated with oxides of Ru/Ir/Ta and BDD thin films [2]. However, electrochemical oxidation of organics to CO₂ occurs with a significant rate and efficiency only using anodes with high oxygen evolution overpotential such as PbO₂ and BDD [16].

Using these anodes, at high potential, highly reactive ·OH are generated on their surface by water discharge, thus leading to overall combustion of organic compounds [12–14,16]:



Furthermore, this technology would have generally public acceptance, which makes the treatment using anodes with high oxygen evolution overpotential promising alternative to replace or complement the conventional treatments

Although more reports involving electrochemical treatment of dye wastewaters have been published in the last 5 years, there are few reports concerning to the use of this process using BDD

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anodes to degrade real textile effluents [17–23]. For this reason, the purpose of the present study was to evaluate the applicability of electrochemical oxidation process using diamond electrode as alternative depuration (decolourisation and detoxification) treatment of textile effluent obtained from a Brazilian textile industry. The influence of the main operating parameters, such as current density, temperature, flow conditions and addition salts, on the COD and colour removal were investigated, in order to identify the electrochemical conditions which give high current efficiency with low energy requirements for attaining Brazilian legal requirements [24].

2. Materials and methods

2.1. Textile dye effluent characteristics

The effluent sample was collected from outlet discharged effluent in a Brazilian textile industry situated in Natal (Northeast of Brazil). It was mainly composed of dyes, amylum and different additives. In order to remove the suspended solids that influence the electrochemical process, the effluent was subjected to a filtration pre-treatment using a 170 mesh. After filtration, the effluent contained a high concentration of COD (650 mg dm⁻³) and Hazen Units (1204 HU) [25]. Its conductivity was 2.70 mS cm⁻¹ and the pH was around 10.2. It is worth noting that these conditions were determined from the effluent, as discharged after textile colouration process; without any physical–chemical treatment.

2.2. Anodic oxidation experiments

Bulk electrochemical oxidations in batch under steady conditions were conducted using an undivided electrolytic flow cell under galvanostatic conditions, similar to electrochemical system already reported in other works [16,26]. The textile effluent was stored in a thermostated glass reservoir of 1 dm³ and it was recirculated through the electrolytic cell by means of a centrifugal pump working in the flow range 200–400 dm³ h⁻¹. The cell contained a BDD electrode as anode and a 54.7 cm² Ti plate as cathode. BDD anode was circular with a diameter of 10 cm, but with an effective area of 54.7 cm² and with one side only exposed to the solution. The interelectrode distance was 1 cm. BDD electrode was supplied by Adamant Technologies (Switzerland) and it was synthesised as described in previous works [26] maintaining the quality parameters (single-crystal with a thickness of 1 μm (±5%) and a resistivity of 15 mΩ cm (±30%) with a boron concentration of 5000 ppm, *p*-silicon wafers (1–3 mΩ cm and 1 mm thick)). In order to stabilize its surface (hydrophilic nature) and to obtain reproducible results, the BDD electrode was pre-treated at 25 °C by anodic polarisation in 1 M HClO₄ at 10 mA cm⁻² for 30 min [16].

The anodic oxidation experiments of real textile effluent were performed under galvanostatic conditions using a MINIPA 3015 power supply. Experiments were performed at 25 °C for studying the role of applied current density ($j = 20, 40$ and 60 mA cm⁻²), while the temperature effect (25, 40 and 60 °C) was studied under a current density of 40 mA cm⁻². The temperature of the electrolyte was controlled using a jacket- thermostat.

2.3. Depuration monitoring methods

Colour removal was monitored by measuring absorbance decrease; using a UV 1800 Shimadzu spectrophotometer. Experimentally, decolourisation process was determined by the expression [2]:

$$\text{Relative absorbance} = \frac{[ABS_t]}{ABS_0} \quad (3)$$

where ABS_t correspond to the absorbance, at the maximum visible wavelength of the wastewater, at time t and ABS_0 is its initial absorbance. Hazen Units (UH) is a industrial parameter to determine the effluent colour conditions for discharging procedure after treatment and these were determined using a Hach Model DR/2500 spectrophotometer calibrated with a method 8025 (Pt–Co units) [25]. pH variation was measured using a Methrom pH metre. Decontamination of real effluent was monitored from the abatement of their COD. Values were obtained, using a HANNA HI 83099 spectrophotometer after digestion of samples in a HANNA thermo-reactor, in order to estimate the Total Current efficiency (TCE, in.%) for anodic oxidation of textile effluent, using the following relationship:

$$\%TCE = FV \left(\frac{[COD_0 - COD_t]}{8I\Delta t} \right) \times 100 \quad (4)$$

where COD_0 and COD_t are chemical oxygen demands at times $t = 0$ (initial) and t (time t) in g O₂ dm⁻³, respectively; I the current (A), F the Faraday constant (96,487 C mol⁻¹), V the electrolyte volume (dm³), 8 is the oxygen equivalent mass (g eq.⁻¹) and Δt is the electrolysis time, allowing for a global determination of the overall efficiency of the process.

Additionally, the limiting current can be estimated from the value of COD using the Eq. (3) for anodic oxidation of a real wastewater, as indicated by Panizza and Cerisola [16].

$$I_{\text{lim}}(t) = 4FAk_m \text{COD}(t) \quad (5)$$

where $I_{\text{lim}(t)}$ is the limiting current (A) at a given time t , 4 the number of exchanged electrons, A the electrode area (m²), F the Faraday's constant, k_m the average mass transport coefficient in the electrochemical reactor (m s⁻¹) and $COD(t)$ the chemical oxygen demand (mol O₂ m⁻³) at a given time t .

The energy consumption per volume of treated effluent was estimated and expressed in kWh m⁻³. The average cell voltage during the electrolysis (cell voltage is reasonably constant with just some minor oscillations, for this reason is calculated the average cell voltage), is taken for calculating the energy consumption by expression [2]:

$$\text{Energy consumption} = \left(\frac{\Delta E_c \times I \times t}{1000 \times V} \right) \quad (6)$$

where t is the time of electrolysis (h); ΔE_c (V) and I (A) are the average cell voltage and the electrolysis current, respectively; and V is the sample volume (m³).

3. Results and discussion

3.1. Preliminary electrochemical experiments of a real textile effluent

As it was evidenced by other authors [13–23,26,27], BDD has great oxidation ability to remove organic pollutants, requiring shorter electrolysis time to reach overall mineralisation, thus leading to remarkably higher current efficiency and relative energy consumptions. For this reason, the good removal efficiencies suggest the possibility of using electrochemical oxidation as treatment technology for treating real textile effluents [17–23].

In this context, an effluent of an actual Brazilian textile industry was employed to assess the efficiency on electrochemical treatment using diamond electrodes as an alternative for removing organic matter and colour. As shown in Fig. 1, the decrease of the absorbance, as a function of time, was achieved during galvanostatic electrolysis of real textile effluent (1 dm³) after 12 h by applying different current densities under real discharged effluent conditions (see Section 2). However, the Brazilian regulations for colour removal [24], i.e. 300 HU, were completely attained at 40 and 60 mA cm⁻², after 6 and 4 h, respectively; as showed in inset

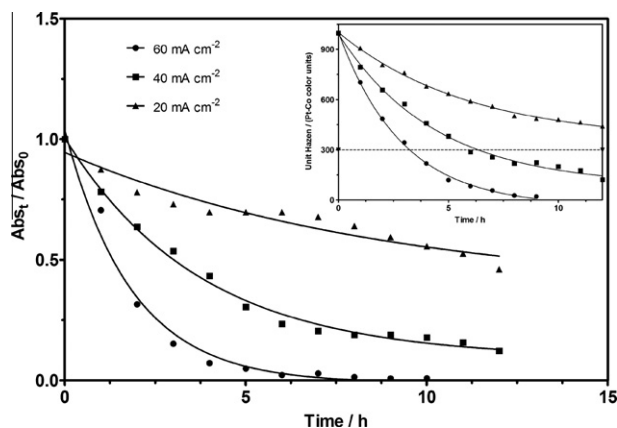


Fig. 1. Electrochemical decolourisation process of a real textile effluent (effluent as obtained), as a function of time, by applying different current densities (20, 40 and 60 mA cm⁻²) at 25 °C and flow rate of 250 dm³ h⁻¹. Inset: Decrease of HU, as a function of time, at different applied current densities. Dashed line indicates the Brazilian limit regulation in HU to discharge the effluent.

of Fig. 1. Whereas at 20 mA cm⁻² of current density, no more than partial colour removal was achieved (i.e. ≈50%, 400 HU) after 12 h of electrolysis.

Furthermore, the COD results clearly indicate that the highest removal rate is achieved at 40 and 60 mA cm⁻², see Fig. 2, because of there is a greater charge passing into the cell that favours the electrogeneration of more hydroxyl radicals produced on BDD surface (Eq. (1)). Despite the complete COD decay occurs under last conditions, long times are required for complete removal, 19 and 17 h, respectively. In contrast, incomplete COD removal was achieved by applying 20 mA cm⁻² after 23 h (Fig. 2). These results clearly indicate that, as observed during colour removal, the low conductivity and organic matter dissolved in the effluent complicate the depuration treatment. Consequently, increasing current density and time treatment, a higher charge consumed for complete mineralisation is needed because during the electrochemical process a relative greater amount of ·OH wasted in parasite non-oxidising reactions such as oxygen evolution. It is confirmed from the current efficiencies (TCE, in.%) obtained for each current density applied (inset Fig. 2) under these conditions, ranging from 23% to 14%.

This behaviour is frequently characteristic of electrolysis under mass transport control when the electrolysis is performed applying

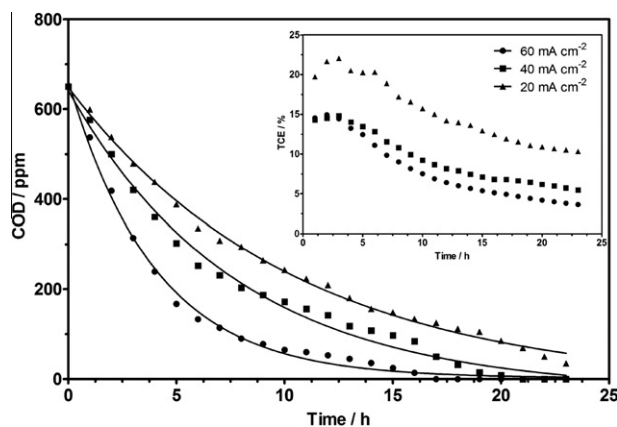


Fig. 2. Influence of applied current on the evolution of COD and TCE (inset), as a function of time, during electrochemical treatment of actual textile effluent (as discharged) on BDD anode at different current densities. Conditions: $T = 25$ °C and flow rate of 250 dm³ h⁻¹.

a current higher than the limiting one, as already indicated by other authors [16,27]. For a recirculation rate of 250 dm³ h⁻¹ the mass transfer coefficient was 2.5×10^{-5} m s⁻¹ and the limiting current results in a value of 1.07 A, according Eq. (5). This current is relatively low than all the currents applied in this work (1.1–3.3 A), suggesting that the oxidation in these conditions could be occurring under mass transport control. These assumptions, treating a real effluent, are in agreement with the studies recently published by Panizza and Cerisola [16] during the anodic oxidation of a real carwash wastewater.

Although the applicability of this treatment seems feasible, long times would be required to complete decolourisation and organic matter removal (more than 18 h, see Fig. 2). However, as confirmed by other authors [16,27,28], the colour and COD can be completely removed by electrochemical oxidation with BDD anode generating effective oxidant species (chlorine, hydrogen peroxide, perphosphates, and peroxodisulphates) on its surface. For this reason, new set of experiments was performed to favour the production of reactive oxidant species, plus hydroxyl radicals.

3.2. Electrochemical decolourisation of a real textile effluent adding Na₂SO₄

Electrooxidation experiments were performed in order to further achieve complete colour elimination. Firstly, an amount of Na₂SO₄ (5 g dm⁻³) was dissolved in the real effluent. After that, a number of electrolysis-experiments were carried out by applying different values of current density (20, 40 and 60 mA cm⁻² at 25 °C), as investigated under original discharged effluent conditions. It is important to remark that after addition of Na₂SO₄, pH value decreases from 10.2 to 9.1.

As it can be observed from Fig. 3, when Na₂SO₄ was added in the effluent, colour removal rate was significantly increased, achieving different values of efficiency (95%, 100% and 100% of colour removal after 12 h, 8 h and 4 h of electrolysis, for 20, 40 and 60 mA cm⁻², respectively). Under these experimental conditions, the Brazilian regulations concerning to the colour removal (low than 300 HU) were attained, in all cases (data not showed). These findings were achieved due to the increase in the conductivity of real effluent when Na₂SO₄ was added, favouring the electrogeneration of peroxodisulphates on BDD surface. In fact, electrolysis BDD anodes in aqueous media, containing sulphate ions, generates peroxodisulphate (Eq. (7)) [16,27,28].

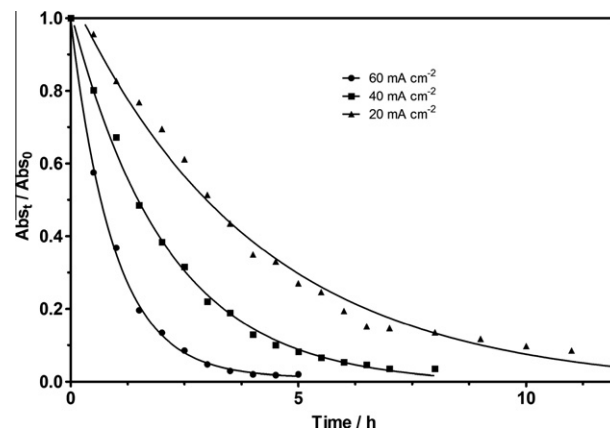


Fig. 3. Colour removal of a real effluent, as a function of time, applying different current densities using BDD anode. Experimental conditions: $T = 25$ °C, 5 g dm⁻³ of Na₂SO₄ and flow rate = 250 dm³ h⁻¹.

These powerful oxidising agents can oxidise organic materials by a chemical reaction whose rate increases with the amount of sulphate ions in solution or/and temperature [28–30].

3.3. COD removal by electrochemical treatment

COD decay was also monitored by applying 20, 40 and 60 mA cm⁻² of current density when an amount of 5 g of Na₂SO₄ were dissolved in a 1 dm³ of the effluent. Fig. 4 shows the influence of the current density on the COD decay during the electrochemical oxidation of the real textile wastewater on BDD anode, as a function of time, at 25 °C.

Results clearly indicate that the complete COD removal is achieved, in all cases; because these conditions favour the electro-generation of more hydroxyl radicals [31] and peroxodisulphates [28–30] on BDD surface. It is important to mention that, treatment time, in the presence of 1 g dm⁻³ Na₂SO₄ (Fig. 4), was reduced respect to the time employed to eliminate COD completely at real discharged conditions (Fig. 2). On the other hand, an increase on current efficiency was observed (inset on Fig. 4) because the electro-generation of peroxodisulphates avoid mass transport limitations and also the secondary reaction of oxygen evolution.

3.4. Effect of Na₂SO₄ dissolved in the effluent

Fig. 5 shows the influence of Na₂SO₄ concentration (in g dm⁻³) as a function of the time and current efficiency (inset) values during galvanostatic electrolysis of real textile wastewaters by applying 20 mA cm⁻² of applied current density.

As can be observed, the COD removal was poor in absence of Na₂SO₄ in solution (Fig. 5). However, COD removal rate increases significantly when the amount of Na₂SO₄ was increased in solution. But, no relevant efficiencies were achieved when the Na₂SO₄ concentration was increased from 5 to 20 g (inset in Fig. 5). 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; employing similar electrolysis-times to achieve complete COD abatement. Then, from industrial point of view, only an amount of 5 g of Na₂SO₄ can be added to the effluent to favour the complete removal of dissolved organic matter.

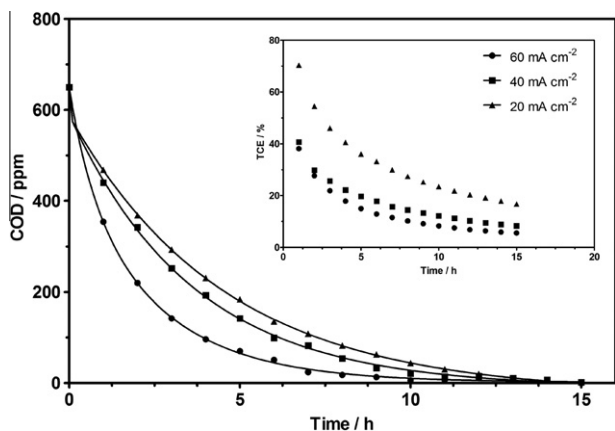


Fig. 4. Influence of applied current on the evolution of COD and TCE (inset), as a function of time, during electrochemical treatment of actual textile using BDD anode. Experimental conditions: $T = 25\text{ }^{\circ}\text{C}$, 5 g dm^{-3} of Na₂SO₄ and flow rate = $250\text{ dm}^3\text{ h}^{-1}$.

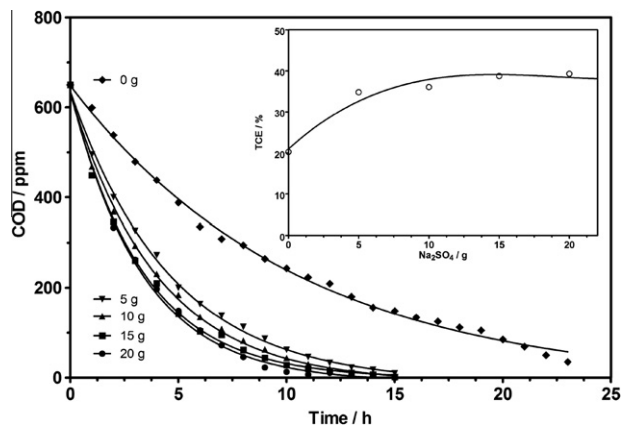


Fig. 5. Influence of Na₂SO₄ concentration on the evolution of COD and %TCE (inset), as a function of time, during electrochemical treatment of actual textile effluent on BDD anode by applying 20 mA cm^{-2} of applied current density. Conditions: $T = 25\text{ }^{\circ}\text{C}$, flow rate = $250\text{ dm}^3\text{ h}^{-1}$.

3.5. Influence of temperature

The treatment of the actual textile effluent was also carried out at 60 °C by applying current densities of 20, 40 and 60 mA cm⁻². The latter temperature was selected, because it mimics the real temperature of the effluent discharged by the textile industry (60 °C). It was observed (Fig. 6) that changes in temperature have a strong influence on oxidation rate at all current densities and varying the temperature from 25 to 60 °C; since the COD removal after 9 or 10 h of treatment was 100% at 60 °C. As reported in literature [16,27], this behaviour was principally attributed not to an increase of the activity of the anodes (due to an increase of temperature) but to an increase of the indirect reaction of organics with electrogenerated oxidising agents from electrolyte oxidation.

In fact, as mentioned above, peroxodisulphates can be formed in solutions containing sulphates, especially at higher temperatures (60 °C), as already demonstrated by other authors [2,16,28], during electrolysis with BDD electrodes. These reagents are very powerful oxidants and can oxidise organic matter leading to an increase in colour removal rates and COD decay. Complete decolourisation (data not showed) and COD removal rates (Fig. 6) noticeably increased when the temperature was increased. Under these conditions, a modest increase on TCE was also achieved respect to the temperature of 25 °C.

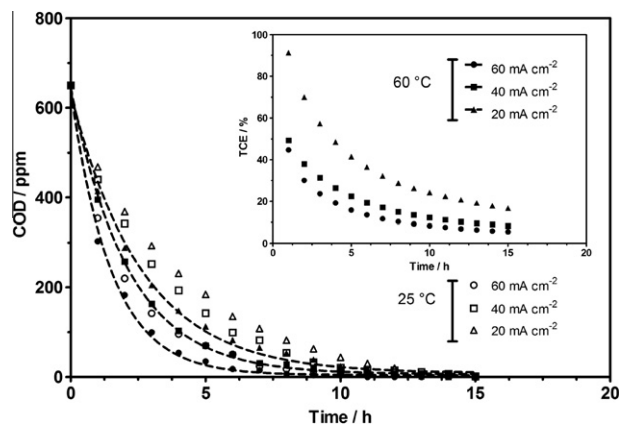


Fig. 6. Comparison of the influence of temperature on the evolution of COD, as a function of time and %TCE (inset) during oxidation of actual textile effluent on BDD anode. Conditions: 40 mA cm^{-2} of current density; 5 g of Na₂SO₄ and flow rate = $250\text{ dm}^3\text{ h}^{-1}$.

3.6. Effect of the flow rate

In order to verify the important role of mass transfer on the electrochemical treatment of real textile effluent, the influence of flow rate during BDD-anodic oxidation was studied varying the flow rate. Experiments were performed at four rates, in the range of 200–400 dm³ h⁻¹. Fig. 7 shows the flow rate effect on the COD removal as a function of the time, during galvanostatic electrolysis by applying 40 mA cm⁻² of current density. As can be seen, the total COD removal was achieved under different flow rates. It appears that the hydrodynamic conditions affect the rate of COD removal because this behaviour is due to that sulphates present in solution produce a chemical oxidant and therefore these avoid the problems due to mass transport.

3.7. Energy consumption and cost estimation

Comparison between the trend of energy consumption (kWh dm⁻³) as a function of COD removal, at different applied current densities (20, 40 and 60 mA cm⁻²) and experimental conditions (real discharged conditions and Na₂SO₄ dissolved in the effluent) is presented in Fig. 8. As can be observed, BDD consumed less energy when an amount of Na₂SO₄ was added in the effluent than that consumed under real discharged effluent conditions. In fact, in the presence of Na₂SO₄ less time is necessary for COD removal and also the cell potential is low (4.1 V). These results point out the high performance BDD-anodic oxidation for treating textile wastewaters. However, this electrochemical process can be a feasible pre-treatment method as a previous step to biological depuration or it could be coupled with other wastewater treatments (e.g.: UV irradiation, Fenton, adsorption) reducing significantly the cost and time treatment.

4. Concluding remarks

On basis of the results obtained for anodic oxidation of a dye-stuff effluent, the electrochemical technology can be suitable as an alternative for pre-treatment of textile real effluents under the real discharge conditions employed by the Brazilian textile industry (COD, pH = 10 and temp = 60 °C) for complete COD and colour removal.

However, if an amount of Na₂SO₄ is added, the efficiency of the process can be strongly improved. It is important to mention that in the Brazilian textile industry, complete COD and colour removal are attained after 5 or 6 days of biological depuration together with a subsequent physical–chemical treatment (under specific pH and temperature conditions). Conversely, COD and colour were

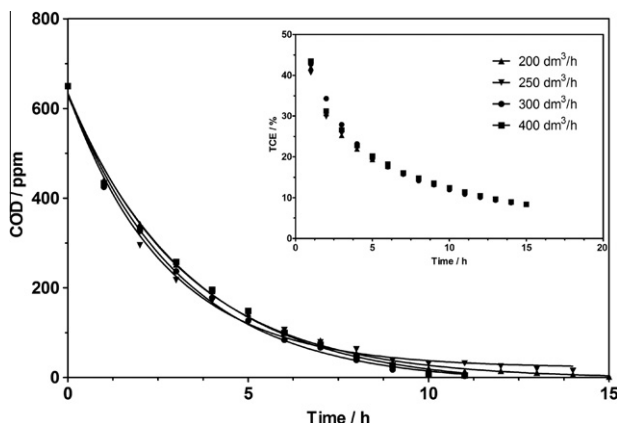


Fig. 7. Influence of flow rate on the evolution of COD, as a function of time and %TCE (inset) during oxidation of actual textile effluent on BDD anode. Conditions: 40 mA cm⁻² of current density; 5 g of Na₂SO₄ and T = 25 °C.

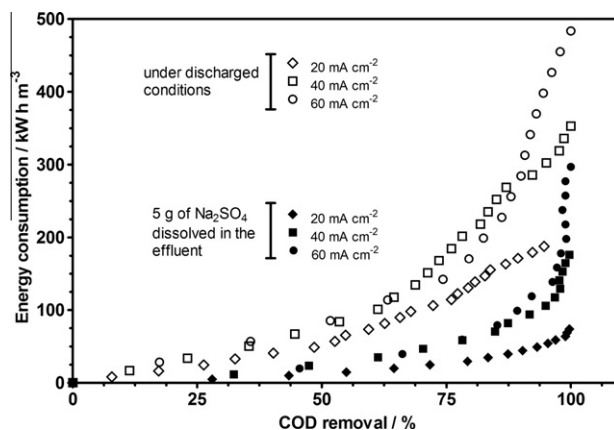


Fig. 8. Energy consumption of the electrochemical process, as a function of COD removal and effluent conditions, during oxidation of actual textile effluent on BDD anode by applying different current densities.

efficiently reduced after 15 h of electrochemical process, attaining Brazilian legal requirements and maintaining the same discharged conditions with the addition of a small amount of Na₂SO₄; in consequence, the time treatment was reduced and costs, confirming the potential efficiency of this dyestuff treatment.

References

- [1] E. Forgacs, T. Cserhati, G. Oros, *Environ. Int.* 30 (2004) 953.
- [2] C.A. Martínez-Huitle, E. Brillas, *Appl. Catal. B: Environ.* 87 (2009) 105.
- [3] G.S. Gupta, S.P. Shukla, G. Prasad, V.N. Singh, *Environ. Technol.* 13 (1992) 925.
- [4] S.P. Shukla, G.S. Gupta, *Ecotoxicol. Environ. Saf.* 24 (1992) 155.
- [5] C. Nascimento, D. de Paiva Magalhães, M. Brandão, A. Batouli Santos, M. Chame, D. Baptista, M. Nishikawa, M. da Silva, *Braz. Arch. Biol. Technol.* 54 (2011) 621.
- [6] R. Boopathy, *Bioresour. Technol.* 74 (2000) 63.
- [7] I. Kabadasil, O. Tunay, D. Orhon, *Water Sci. Technol.* 40 (1999) 261.
- [8] O. Tunay, I. Kabadasil, D. Orhon, G. Cansever, *Water Sci. Technol.* 40 (1999) 237.
- [9] T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol.* 77 (2001) 247.
- [10] G.M. Shaul, T.J. Holdsworth, C.R. Dempsey, K.A. Dostal, *Chemosphere* 22 (1991) 107.
- [11] O.J. Hao, H. Kim, P.C. Chiang, *Environ. Sci. Technol.* 30 (2000) 449.
- [12] G. Chen, *Sep. Purif. Technol.* 38 (2004) 11.
- [13] C.A. Martínez-Huitle, S. Ferro, *Chem. Soc. Rev.* 35 (2006) 1324.
- [14] M. Panizza, G. Cerisola, *Chem. Rev.* 109 (2009) 6541.
- [15] E. Brillas, I. Sires, M.A. Oturan, *Chem. Rev.* 109 (2009) 6570.
- [16] M. Panizza, G. Cerisola, *J. Electroanal. Chem.* 638 (2010) 28.
- [17] J.M. Peralta-Hernández, M. Méndez-Tovar, R. Guerra-Sánchez, C.A. Martínez-Huitle, J.L. Nava, *Int. J. Electrochem.*, 2012. <http://dx.doi.org/10.1155/2012/154316> (Article ID 154316).
- [18] E. Chatzizymeon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mazarinos, *J. Hazard. Mater.* 137 (2006) 998.
- [19] A. Sakalis, K. Fytianos, U. Nickel, A. Voulgaropoulos, *Chem. Eng. J.* 119 (2006) 127.
- [20] A.S. Kopal, Y. Yavuz, C. Gürel, Ü.B. Ögütveren, *J. Hazard. Mater.* 145 (2007) 100.
- [21] G.R.P. Malpass, D.W. Miwa, S.A.S. Machado, A.J. Motheo, *J. Hazard. Mater.* 156 (2008) 170.
- [22] G.R.P. Malpass, D.W. Miwa, D.A. Mortari, S.A.S. Machado, A.J. Motheo, *Water Res.* 41 (2007) 2969.
- [23] J.M. Aquino, G.F. Pereira, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, *J. Hazard. Mater.* 192 (2011) 1275.
- [24] Environmental Northeast Brazilian Laws: Instrução Normativa n 1 de 03/11/2004 do Instituto de Desenvolvimento e Meio Ambiente – IDEMA.
- [25] International Organization for Standardization, ISO 2211:1973, Measurement of Colour in Hazen units (Platinum–Cobalt Scale) of Liquid Chemical Products.
- [26] C.A. Martínez-Huitle, M.A. Quiroz, C. Cominellis, S. Ferro, A. De Battisti, *Electrochim. Acta* 50 (2004) 949.
- [27] N. Bensalah, M.A. Quiroz Alfaro, C.A. Martínez-Huitle, *Chem. Eng. J.* 149 (2009) 348.
- [28] M. Panizza, G. Cerisola, *J. Hazard. Mater.* 153 (2008) 83.
- [29] P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, *Ind. Eng. Chem. Res.* 45 (2006) 3468.
- [30] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, *Electrochim. Acta* 52 (2006) 325.
- [31] B. Marselli, J. García-Gómez, P.A. Michaud, M.A. Rodrigo, C. Cominellis, *J. Electrochem. Soc.* 150 (2003) D79.