



Electrochemical degradation of a real textile effluent using boron-doped diamond or β -PbO₂ as anode

José M. Aquino, Gabriel F. Pereira, Romeu C. Rocha-Filho*, Nerilso Bocchi, Sonia R. Biaggio

Departamento de Química, Universidade Federal de São Carlos, C. P. 676, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 21 January 2011

Received in revised form 13 June 2011

Accepted 14 June 2011

Available online 13 July 2011

Keywords:

Wastewater electrochemical treatment

Textile wastewater remediation

Dye electrooxidation

Chloride mediated oxidation

Diamond film detachment

ABSTRACT

Constant current electrolyses are carried out in a filter-press reactor using a boron-doped diamond (Nb/BDD) or a Ti-Pt/ β -PbO₂ anode, varying current density (j) and temperature. The degradation of the real textile effluent is followed by its decolorization and chemical oxygen demand (COD) abatement. The effect of adding NaCl (1.5 g L⁻¹) on the degradation of the effluent is also investigated. The Nb/BDD anode yields much higher decolorization (attaining the DFZ limit) and COD-abatement rates than the Ti-Pt/ β -PbO₂ anode, at any experimental condition. The best conditions are $j = 5$ mA cm⁻² and 55 °C, for the system's optimized hydrodynamic conditions. The addition of chloride ions significantly increases the decolorization rate; thus a decrease of more than 90% of the effluent relative absorbance is attained using an applied electric charge per unit volume of the electrolyzed effluent (Q_{ap}) of only about 2 kAh m⁻³. Practically total abatement of the effluent COD is attained with the Nb/BDD anode using a Q_{ap} value of only 7 kAh m⁻³, with an energy consumption of about 30 kWh m⁻³. This result allows to conclude that the Nb/BDD electrode might be an excellent option for the remediation of textile effluents.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The contamination of water sources is one of the major problems of the 21st century, as water is becoming a scarce natural resource. Conventional treatment plants are not capable of completely removing all pollutants, such as dyes, antibiotics, and pesticides. Among polluting effluents, the textile ones are characterized by intense color and high organic load, as well as pH and temperature oscillations. The color is originated by un-reacted dyestuff, mainly synthetic dyes that commonly are very recalcitrant and non-biodegradable chemicals. These pollutants might cause severe problems to human health and aquatic life [1]. Thus, new methodologies need to be used to treat those contaminants before disposal, in order to obey increasingly rigid environmental regulations [2]. The most common ways to treat dye-containing wastewaters are: (i) chemical, (ii) physico-chemical, (iii) electrochemical, and (iv) advanced oxidation processes [3,4]. Among these methods, electrochemical ones have the advantage of removing the pollutants without the necessity of additional chemicals. Despite their easy implementation and the high removal rates commonly attained, the use of electric energy is the main drawback of electrochemical processes; however, the development and improvement of new anode materials tend to minimize costs associated with

energy use. As recently reviewed by Martínez-Huitle and Brillas [4], there has been a significant effort on investigating the decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. Nevertheless, there are few reports on the use of electrooxidation processes to degrade real textile effluents (for instance, Chatzisyseon et al. [5], Sakalis et al. [6], Koparal et al. [7], and Malpass et al. [8,9]).

In conventional electrooxidation processes, contaminants can be removed by (i) direct oxidation, in which the pollutant is oxidized by electron transfer directly to the anode material, or (ii) indirect oxidation, in which the electron transfer is mediated by an oxidant species [10,11]. The indirect process involves the electrogeneration of oxidants at the anode, such as the hydroxyl radical (\bullet OH) from water discharge. According to the extent of the interaction between the hydroxyl radical and anode materials, they are classified from high to low oxidation power anodes [12]. Contaminants may also be oxidized by other oxidants, such as (i) active chlorine (Cl₂, HClO, and ClO⁻), (ii) S₂O₈²⁻, and (iii) P₂O₈⁴⁻, when chloride, sulfate, and phosphate containing solutions are electrolyzed, respectively [13]. Furthermore, anode material and electrolysis conditions play an important role on the oxidant speciation and amount [14–18].

Boron-doped diamond (BDD) is an electrode material that has been largely used in the electrochemical degradation of pollutants [4,11,17–22], the electrochemical determination of organic compounds [23,24], and water disinfection [25]. The wide application of BDD is due to its high chemical and physical stabilities, high

* Corresponding author. Tel.: +55 16 3351 8078; fax: +55 16 3351 8350.
E-mail address: romeu@dq.ufscar.br (R.C. Rocha-Filho).

oxidation power, low adsorption properties, and a large window for the discharge of water [12]. Thus, considerable amounts of hydroxyl radicals may be electrogenerated on BDD anodes; these radicals, due to their weak interaction with the BDD film, present a high reactivity towards organic compounds such as the dyes contained in textile effluents. The high oxidation power of BDD anodes coupled with the knowledge of a system's hydrodynamic conditions may lead to a high rate of pollutant removal, with good current efficiencies [15]. The main drawbacks of BDD anodes are their cost and the restricted number of adequate and inexpensive substrates for the deposition of the thin diamond layer; on a Ti substrate, cracks may appear and lead to BDD film detachment [26].

Lead dioxide (PbO₂), a medium to high oxidation power anode, is an alternative anode material due to its fabrication easiness and low cost. The electrochemical performance and stability of the PbO₂ film are related to substrate preparation and electrodeposition conditions, as well as to the organic and inorganic doping species that might be used [27–29]. New methodologies have led to improved adhesion of the PbO₂ film onto the substrate [30], and also to an oxidation power of the PbO₂ anode comparable to that of the DDB anode [29]; however the most used substrate is still the Ti–Pt [18,27,28,31]. Comminellis and Chen [26] point the possible release of Pb²⁺ ions, especially in basic solutions, as the main drawback of PbO₂ anodes; in many instances, a short lifetime might be another important drawback.

In the present study the electrochemical degradation of a real textile effluent is comparatively investigated using BDD and β-PbO₂ anodes, in the presence or absence of chloride ions, with optimization of the system's hydrodynamic conditions so as to minimize energy consumption. For such, the corresponding performances in the degradation of the effluent were analyzed through two parameters: decolorization and removal of the chemical oxygen demand (COD) of the effluent.

2. Experimental

2.1. Chemicals

All chemicals, including Pb(NO₃)₂ (a.r., Acros), sodium lauryl sulfate, SLS (99%, Fisher Scientific), H₂PtCl₆ (99.9%, Aldrich), HCl (36.5%, Mallinckrodt), H₂SO₄ (98%, Mallinckrodt), NaCl (a.r., JT Baker), and Na₂SO₄ (a.r., Qhemis), were used as received. Distilled and deionized water (Millipore Milli-Q system, ρ ≥ 18.2 MΩ cm) was used for the preparation of all solutions.

2.2. Electrodes

The β-PbO₂ films were electrodeposited on a platinized Ti substrate using a conventional electrochemical cell, with a calomel reference electrode and two AISI-304 stainless steel plates as counter electrodes. The procedures involving the Ti substrate platinization and the β-PbO₂ film preparation are fully described in a previous work [32]; hereinafter, this electrode will be referred to as Ti–Pt/β-PbO₂.

The BDD anodes were Diachem[®] electrodes, produced by Condias (Germany) by a chemical vapor deposition process. The diamond layer was deposited onto a niobium substrate, with a boron doping level in the range 2000–4500 ppm; hereinafter, this electrode will be referred to as Nb/BDD.

2.3. Textile effluent

A local dye house (from a carpet and rug industry) provided the textile effluent, which was sampled at the entrance reservoir of the industry's biological treatment station. This effluent originates from the different dyeing units, thus being a complex

Table 1

Physico-chemical characteristics of the real textile effluent (values in parentheses refer to the filtered effluent).

Parameter	Numerical value
pH	7.11 (7.55)
Conductivity/μS cm ⁻¹	273 (254)
Total solids/mg L ⁻¹	558
Volatile solids/mg L ⁻¹	378
Turbidity/NTU	172 (14.7)
DFZ ^a (λ = 436 nm)/m ⁻¹	(27.3)
COD/mg L ⁻¹	729 (300)

^a Spectral absorption coefficient, determined according to the DIN-38404/1 standard.

mixture of dyes and additives whose exact composition is unknown and dependent on the production schedule. Nevertheless, Table 1 shows the as-received characteristics of this industrial effluent, which was characterized by an intense dark yellow color and the presence of a high amount of fibers. Thus, before the electrochemical degradation experiments, the effluent was filtered two times with conventional filtering paper. Furthermore, due to the low conductivity of the effluent, Na₂SO₄ was added until a 0.1 mol L⁻¹ concentration was reached.

2.4. Electrochemical degradation experiments and analyses

All electrochemical experiments were carried out using samples of the same collected effluent, in order to avoid compositional and concentration variations. These experiments were carried in a one-compartment filter-press reactor containing the Nb/BDD or Ti–Pt/β-PbO₂ anode; two AISI-304 stainless steel plates were used as counter electrodes to the Nb/BDD anode, while two nickel plates were used as counter electrodes to the Ti–Pt/β-PbO₂ anode. The Nb/BDD anode exposed area was 5.2 cm × 6.3 cm (each face), while the Ti–Pt/β-PbO₂ anode exposed area was 3.1 cm × 1.9 cm (each face). Details on the experimental setup and the electrochemical filter-press reactor are reported elsewhere [32]. In order to determine the best experimental conditions for the electrochemical degradation of the textile effluent, the following parameters were investigated: electric current density (*j*) and temperature (25 °C and 55 °C). Other parameters were kept fixed: effluent volume (0.40 L) and flow rate (360 L h⁻¹).

Values for *j* were chosen taking into account the limiting current density (*j*_{lim}) of the electrochemical system, which was obtained according to the procedure described by Cañizares et al. [33]. First, the mass transport coefficient (*k*_m) was obtained using the following equation:

$$k_m = \frac{I_{lim}}{nFAC_B} \quad (1)$$

where *I*_{lim} is the limiting current, *n* the number of electrons involved in the oxidation of K₄[Fe(CN)₆] to K₃[Fe(CN)₆], *F* the Faraday constant, *A* the anode area, and *C*_B the bulk concentration of K₄[Fe(CN)₆]. The values obtained for the mass transport coefficient were 2.9 × 10⁻⁵ m s⁻¹ for the Nb/BDD anode and 8.6 × 10⁻⁵ m s⁻¹ for the Ti–Pt/β-PbO₂ anode. Then, the current densities were chosen using this other equation [12]:

$$j_{lim}(t) = 4Fk_mCOD(t) \quad (2)$$

where *j*_{lim}(*t*) is the limiting current density and *COD*(*t*) the chemical oxygen demand of the effluent at a given time *t*. Considering that *COD*(0) = 300 mg L⁻¹, the investigated values of *j* for the electrochemical experiments were 5, 10, and 20 mA cm⁻² for the Nb/BDD anode, and 15, 30, and 45 mA cm⁻² for the Ti–Pt/β-PbO₂ anode. The lower values of current density (5 and 15 mA cm⁻²) are related to charge-transfer control and the others to mass-transfer control.

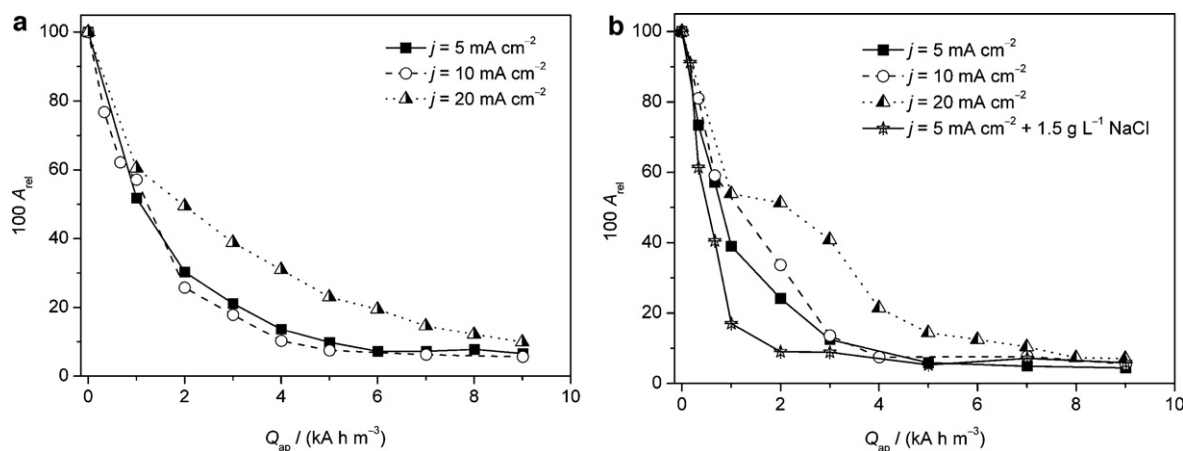


Fig. 1. Relative absorbance (at 400 nm), A_{rel} , as a function of the applied electric charge per unit volume of the effluent, Q_{ap} , for the electrochemical degradation of the real textile effluent with the Nb/BDD anode: (a) 25 °C and (b) 55 °C.

The performance of each anode in the textile effluent degradation was analyzed through the extent of decolorization and COD removal of the textile effluent. In order to compare these performances, the same total value of electric charge per unit volume of the electrolyzed effluent (Q_{ap}) was applied in all the experiments (9 kA h m^{-3}). Absorbance (A) and COD measurements were done on 2.5 mL samples of electrolyzed effluent, collected after each 1 kA h m^{-3} of Q_{ap} was applied. The effluent absorbance was determined from 190 nm to 820 nm in a UV-vis spectrophotometer (HP8452 diode array detector). After the absorbance determination, the COD of each sample was determined. For such, they were digested for 2 h at 150 °C; then, after reaching ambient temperature, their absorbance was read at 620 nm with a Hach DR/2010 model spectrophotometer [34]. Additionally, the decolorization efficiency was evaluated by determining the spectral absorption coefficient (DFZ, at $\lambda = 436 \text{ nm}$; DIN-38404/1 standard) of the textile effluent at the end of each electrolysis.

3. Results and discussion

First of all, it should be noted that in some experiments without chloride addition to the effluent, when the lowest current (5 mA cm^{-2}) was applied there was some deactivation of the Nb/BDD anode, that is, the COD value of the effluent would not decrease any further. That behavior is probably related to organic adsorption onto the anode surface, thus forming an adsorbed film. In these cases, the Nb/BDD anode was readily reactivated by the following pre-treatment: application of 50 mA cm^{-2} during 30 min in H_2SO_4 0.5 mol L^{-1} . Nevertheless, the data presented hereinafter involve experiments that did not present this deactivation.

The electrochemical degradation of the textile effluent using either the Nb/BDD or the Ti-Pt/ β -PbO₂ anode led to decolorization of the effluent and decrease in its COD as the electrolyses progressed. In order to quantify the decolorization, the absorbance of the effluent (at 400 nm, at which maximum absorbance is obtained) after a given value of Q_{ap} (a given time t) was compared to that for $Q_{ap} = 0$, resulting in a relative absorbance value, $A_{rel} = A_t/A_0$. A relative COD value was similarly obtained: $COD_{rel} = COD_t/COD_0$.

3.1. Decolorization of the textile effluent

Fig. 1 shows the variation of A_{rel} as a function of Q_{ap} for the different electrolyses carried out with the Nb/BDD anode, at 25 °C and 55 °C. Clearly, the best conditions for color removal are attained at the lower current densities, when the amount of oxygen evolved at the anode is less significant; hence, a higher fraction of Q_{ap} is

related to the decolorization of the textile effluent. Under these conditions, A_{rel} becomes less than 10% for a minimum value of Q_{ap} of about 5 kA h m^{-3} , at 25 °C. On the other hand, for any current density, the higher temperature enhances the decolorization rate due to the increased oxidation power of the hydroxyl radicals (compare Fig. 1b to Fig. 1a). Thus, the condition $j = 5 \text{ mA cm}^{-2}$ at 55 °C is considered the best one for the decolorization of the effluent due to the lower energy consumption and higher current efficiency involved, as it will be discussed below. In order to investigate a possible further increase in the rate of the decolorization process, an additional experiment was carried out at 5 mA cm^{-2} and 55 °C with 1.5 g L^{-1} NaCl added to the textile effluent. As it can be seen in Fig. 1b, the addition of NaCl to the effluent caused an increase in its decolorization rate, due to the electrogeneration of active chlorine [17]; now A_{rel} becomes less than 10% for a minimum value of Q_{ap} of only about 2 kA h m^{-3} .

Fig. 2 shows the variation of the relative absorbance as a function of Q_{ap} for the different electrolyses of the textile effluent carried out with the Ti-Pt/ β -PbO₂ anode. Again, the best conditions for the decolorization of the effluent were the lower current density (in this case, 15 mA cm^{-2}) and the higher temperature (55 °C); however, the rate of decolorization attained is much lower in comparison to the one attained with the Nb/BDD anode. The higher oxidation power of the Nb/BDD anode clearly prevails, yielding a greater decolorization capacity. An additional experiment was also carried out in the presence of 1.5 g L^{-1} NaCl, at 15 mA cm^{-2} and 55 °C. As it can be seen in Fig. 2b, the addition of NaCl caused again an increase in the rate of the decolorization process; however, now the value of A_{rel} becomes less than 10% only for a minimum value of Q_{ap} of about 5 kA h m^{-3} , which is 2.5 times the one necessary using the Nb/BDD anode. It should be noted that, after the end of each experiment, the surface of the Ti-Pt/ β -PbO₂ anode presented a brown color, due to the formation of an adsorbed film [35], which could contribute to the lower decolorization efficiency presented by this anode. Moreover, the better efficiency in the presence of NaCl could be also attributed to the diminishment of the degree of formation of this film due to active chlorine (in this case the surface of the Ti-Pt/ β -PbO₂ anode presented a lighter brown color).

It is not easy to compare the results here reported on decolorization with those obtained by other authors who reported on electrooxidation processes to degrade real textile effluents, especially because each effluent was different. Chatzisyneon et al. [5], using a titanium (grade II/VII) anode covered by a thin film of tantalum, platinum and iridium alloy, attained 98% decolorization of the real textile effluent within 10–15 min, regardless of the applied current. From their best data (use of 5 A for 10 min, 8 L of effluent),

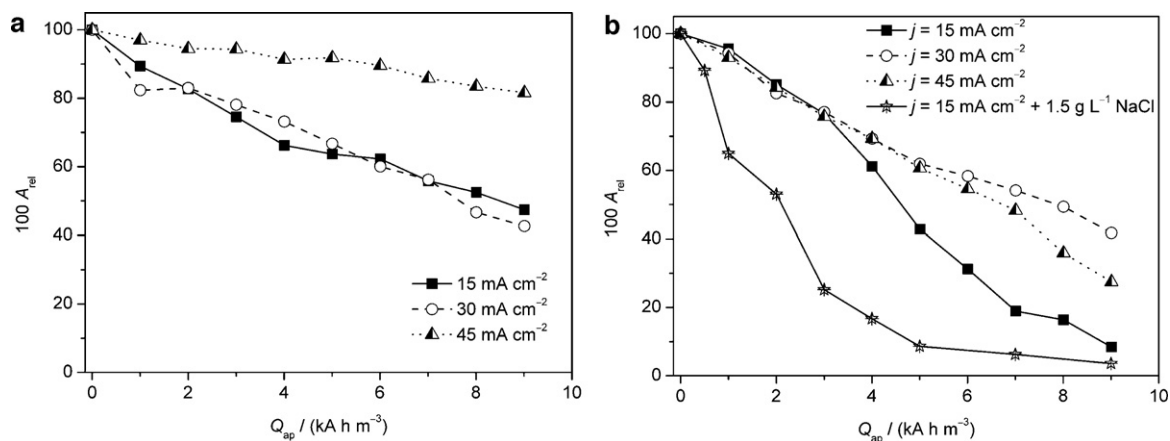


Fig. 2. Relative absorbance (at 400 nm), A_{rel} , as a function of the applied electric charge per unit volume of the effluent, Q_{ap} , for the electrooxidation of the real textile effluent on the Ti-Pt/ β -PbO₂ anode: (a) 25 °C and (b) 55 °C.

one infers that a charge of only 0.38 kC L^{-1} was used, which is much lower than the one used in our best case (5.8 kC L^{-1}); however, they added NaCl to the effluent so as to have a minimum concentration of 10 g L^{-1} , while we used only 1.5 g L^{-1} . From the data reported by Sakalis et al. [6], one may infer that a charge of about 6.4 kC L^{-1} was used to attain 90% decolorization of the textile effluent (0.5 L; no NaCl added, since the initial concentration of Cl^- in the effluent was 40 mg L^{-1}) using a Nb/BDD anode; a lower degree of decolorization was attained with a Ti/Pt anode. On the other hand, Malpass et al. [9] report that about 90% decolorization was attained only when NaCl (5.85 g L^{-1}) was added to the textile effluent (0.25 L), independently of the composition of the DSA anode used; from their best data, one may infer that a charge of about 16 kC L^{-1} was used. From all these results, it becomes clear that decolorization by electrooxidation is facilitated by the addition of Cl^- ions to the real effluent; in other words, degradation of the chromophore of the dyes is more easily attained in the presence of active chlorine [17]. Similar conclusions have been reached previously for the degradation of different dyes—see, for example, Andrade et al. [18] or Aquino et al. [32,36,37]. In fact, Malpass et al. [8] showed that complete decolorization of the textile effluent could be attained by the direct addition of OCl^- ions at a concentration of $\sim 0.50 \text{ g L}^{-1}$.

The decolorization efficiency may be evaluated through the DFZ value ($\lambda = 436 \text{ nm}$) of the textile effluent at the end of an electrolysis. The obtained results (reported in Tables SI-1 and SI-2 in the supplementary data) allow to conclude that the DFZ values were always below the limit (7 m^{-1}) at the end of electrolyses carried out with the Nb/BDD anode. In the case of the Ti-Pt/ β -PbO₂ anode, which showed a lesser decolorization capacity, DFZ values below the limit were obtained only at the end of the experiments carried out at 15 mA cm^{-2} and 55 °C.

3.2. Removal of the chemical oxygen demand

Fig. 3 shows the variation of COD_{rel} as a function of Q_{ap} for the experiments using the Nb/BDD anode. Similarly to the decolorization, the best conditions for the COD removal were the lower current density (5 mA cm^{-2}) and the higher temperature (55 °C): a 90% COD decrease was reached after a value of Q_{ap} of only 2 kA h m^{-3} , and total removal was attained for a Q_{ap} value of 7 kA h m^{-3} . These results are in agreement with the decolorization ones. However, total COD abatement was not accomplished in the experiments carried out at 25 °C—see Fig. 3a (a COD decrease of about 90% was attained after a value of Q_{ap} of about 4 kA h m^{-3} , but did not decrease thereafter). The effluent seems to have some recalcitrant compounds (or degradation products) that are not

oxidized at 25 °C. On the other hand, complete COD abatement was accomplished at 55 °C, due to the higher oxidation power of the electrogenerated oxidants. However, the additional experiment carried out at 5 mA cm^{-2} and 55 °C in the presence of 1.5 g L^{-1} NaCl had an unexpected outcome: no improvement of the COD removal. In fact, for intermediate charges the COD removal rate was slightly lower than for the experiment without chloride addition, while at the end of the electrolysis comparable COD removal rates were obtained. The effect of chloride on the electrooxidation of organics with BDD is not clear: Costa et al. [38] or Wu et al. [39] reported an improvement of the COD removal rate in the presence of chloride ions, while Cabeza et al. [40] did not. That behavior seems to be related to the current density, hydrodynamic conditions, electrolyte pH during electrolysis, and chloride ion concentration, as interestingly shown by Anglada et al. [41]. The lack of improvement of the COD removal rate is probably due to the higher oxidation states of electrogenerated chloro species leading to chlorites, chlorates and possibly perchlorates [40,42]. These inorganic compounds are not effective in the oxidation of organics [42] and can lead to a low surface concentration of hydroxyl radicals available to organics oxidation [17]. Alkaline pH also favors the formation of chlorate on BDD, as observed by Anglada et al. [41]. As the final pH during the experiment with NaCl added to the textile effluent was slightly alkaline (8.4), the possible generation of that inorganic compound coupled with the diminishment of active chlorine concentration is likely to have occurred. These characteristics could have resulted in the lack of improvement of the COD removal rate. Moreover, the contrasting effect of chloride ions on the color and COD removals indicates that the electrogenerated active chlorine species are quite selective for the oxidation of the chromophore of the dyes.

Fig. 4 shows the variation of COD_{rel} as a function of Q_{ap} for the experiments using the Ti-Pt/ β -PbO₂ anode. The COD decay is favored at the lower current density (15 mA cm^{-2}) and the higher temperature (55 °C), which is in agreement with the decolorization and COD results using the Nb/BDD anode; however the efficiency of the Ti-Pt/ β -PbO₂ anode is much inferior in comparison to that of the Nb/BDD anode, due to the higher oxidation power of the latter. The additional experiment carried out with 1.5 g L^{-1} NaCl added to the effluent at the best conditions for color and COD removals (15 mA cm^{-2} and 55 °C) yielded an improvement in the COD removal rate in comparison to the experiment without chloride addition, as observed in the literature for other anode materials [8]. That behavior is different from the one observed for the Nb/BDD anode in the presence of chloride ions, being a consequence of the lower oxidation power of the Ti-Pt/ β -PbO₂ anode in comparison

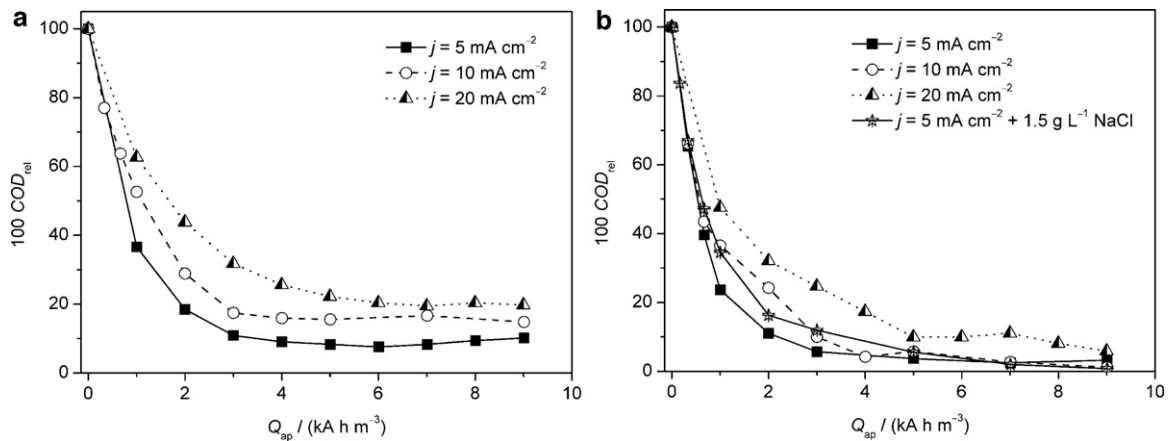


Fig. 3. Relative chemical oxygen demand, COD_{rel} , as a function of the applied electric charge per unit volume of the effluent, Q_{ap} , for the electrooxidation of the real textile effluent on the Nb/BDD anode: (a) 25 °C and (b) 55 °C.

to the Nb/BDD one, at which chloro species are more easily oxidized to higher oxidation states. Thus, the active chlorine formed with the Ti–Pt/ β -PbO₂ anode is mainly used for the oxidation of the organic matter, particularly of the chromophore of the dyes as attested by the higher decolorization rates attained. The high values of Q_{ap} required for COD abatement of the textile effluent in comparison to those of synthetic dye solutions [18,32,37,38] might be due to the great variety and complexity of organic compounds present in the effluent.

3.3. Instantaneous current efficiency and energy consumption

The instantaneous current efficiency (ϵ_{inst}) for the electrochemical degradation of the textile effluent may be obtained by:

$$\epsilon_{inst} = \frac{(COD_{t+\Delta t} - COD_t)FV}{8I\Delta t} \quad (3)$$

where COD_t and $COD_{t+\Delta t}$ are the COD values at time t and $t + \Delta t$, respectively, and V is the volume of the electrolyzed effluent.

Fig. 5 shows the variation of ϵ_{inst} as a function of Q_{ap} for the best COD removal experiments (55 °C) with the Nb/BDD and Ti–Pt/ β -PbO₂ anodes—for the other conditions, see Fig. SI-1 in the supplementary data. Only the Nb/BDD anode yielded ϵ_{inst} values close to 1.0 in the beginning of the experiments, when the electrooxidation is under charge-transfer control (this was also true for $j = 10 \text{ mA cm}^{-2}$ —see Fig. SI-1a in the supplementary data); however as the electrolysis progresses, the COD decreases and the

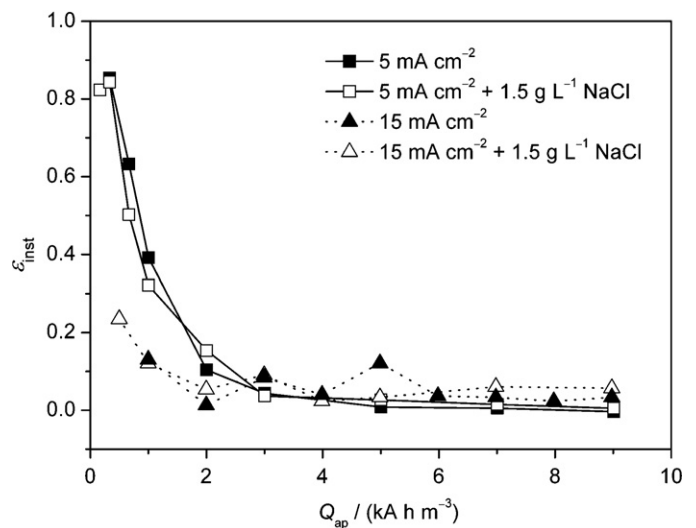


Fig. 5. Instantaneous current efficiency, ϵ_{inst} , as a function of the applied electric charge per unit volume of the effluent, Q_{ap} , for the best COD removal experiments (55 °C) with the Nb/BDD (solid lines) and the Ti–Pt/ β -PbO₂ anodes (dotted lines).

process changes to being under mass-transfer control, with the consequent diminishment of the ϵ_{inst} values due to the increasingly significant oxygen evolution reaction (OER). Very similar results

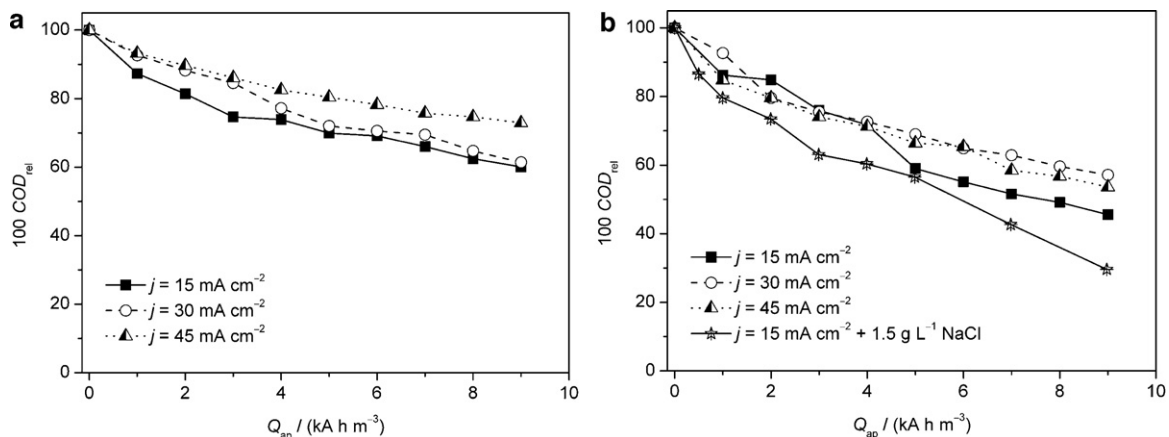


Fig. 4. Relative chemical oxygen demand, COD_{rel} , as a function of the applied electric charge per unit volume of the effluent, Q_{ap} , for the electrooxidation of the real textile effluent on the Ti–Pt/ β -PbO₂ anode: (a) 25 °C and (b) 55 °C.

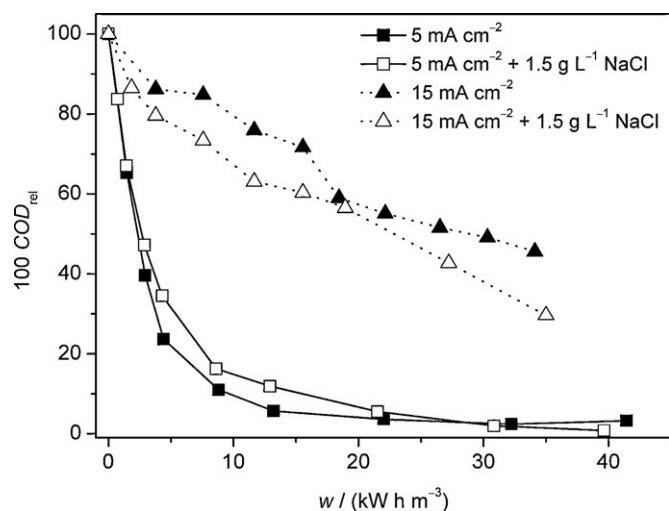


Fig. 6. Electric energy consumption per unit volume of the effluent, w , as a function of the relative chemical oxygen demand, COD_{rel} , for the best conditions ($55\text{ }^{\circ}\text{C}$) for electrooxidation of the real textile effluent on the Nb/BDD (solid lines) and Ti–Pt/ β -PbO₂ (dotted lines) anodes.

were obtained when chloride ions were added to the effluent. For $j = 20\text{ mA cm}^{-2}$, lower ε_{inst} values were obtained due to the significant increase of the OER—see Fig. SI-1a in the supplementary data. On the other hand, even for the best experiments with the Ti–Pt/ β -PbO₂ anode, the ε_{inst} values remained very low throughout, starting at 0.15 and rapidly decreasing towards zero. When chloride ions were added to the effluent, the initial ε_{inst} value increased to 0.24 due to the indirect oxidation mediated by the chloro species. Clearly, in comparison to the Nb/BDD anode, the Ti–Pt/ β -PbO₂ anode is not effective in the electrooxidation of the textile effluent, due to the low values of ε_{inst} —see Fig. SI-1b in the supplementary data; this means that almost all of the supplied charge is being wasted in side reactions. It should be noted that the experiments carried out at $25\text{ }^{\circ}\text{C}$ (see Fig. SI-1b in the supplementary data) showed even smaller ε_{inst} values than the ones at $55\text{ }^{\circ}\text{C}$, which could be related to the lower oxidation power of the hydroxyl radicals at that temperature.

The electric energy consumption per unit volume of electrolyzed effluent (w), at different times during electrolyses, may be obtained by:

$$w = \frac{Ult}{V} \quad (4)$$

where U is the cell potential, and I the electric current applied.

Fig. 6 shows the variation of w as a function of COD_{rel} for the best conditions for COD removal using the Nb/BDD and Ti–Pt/ β -PbO₂ anodes—for the other conditions, see Fig. SI-2 in the supplementary data. In the case of the Nb/BDD anode, the value of w required for almost complete degradation of the textile effluent is about 30 kW h m^{-3} , in the absence or presence of chloride ions added to the effluent. On the other hand, the use of the Ti–Pt/ β -PbO₂ anode would require a much higher value of w to attain the complete degradation of the textile effluent, due to the poor current efficiency of this anode. The addition of NaCl to the effluent leads to an improvement in the value of w , but still quite far from the one attained with the Nb/BDD anode.

Similarly to the case of decolorization, it is not easy to compare the results here reported on COD abatement and the corresponding energy consumption with those obtained by other authors. Chatzisyseon et al. [5], using a titanium (grade II/VII) anode covered by a thin film of tantalum, platinum and iridium alloy, attained

COD decays of about 40% (pH 6 or 9.5) and 60% (pH 3), applying 20 A for 180 min, with 40 g L^{-1} NaCl added to the real textile effluent. From the values of energy consumption reported by the authors, one may infer a w value of about 80 kW h m^{-3} for the experiment at pH 9.5 for a COD decay of only 40%; clearly the performance of the anode material used is very poor, as the current efficiency is only 5.5%. On the other hand, Sakalis et al. [6] reported that the COD of a real effluent could be reduced from 150 mg L^{-1} to 10 mg L^{-1} , in 30 min of electrolysis, using a Nb/BDD anode at an applied potential of 18 V. From their data, one may infer a w value of about 36 kW h m^{-3} , which coincidentally is similar to the w value obtained in this work using the same type of anode. From these results and those here reported, it becomes clear that COD abatement by electrooxidation is more efficiently attained using BDD anodes. A similar conclusion was reached by Andrade et al. [18], who compared the performance of Si/BDD and Ti–Pt/ β -PbO₂ anodes in the degradation of the Reactive Orange 16 dye.

3.4. On the stability of the anodes

The Ti–Pt/ β -PbO₂ anode was stable during all the experiments, and no loss of the PbO₂ film or deactivation of the anode was noticed. The specific determination of Pb in the electrolyte was not carried out; however, Ciriaco et al. [31], which used a Ti–Pt/ β -PbO₂ anode prepared according to the methodology adopted in our laboratory [27,28] to degrade Ibuprofen, did not detect Pb (by atomic absorption spectroscopy—AAS) in electrolyte samples collected at the end of their degradation assays (except for one sample—0.22 ppm, which was just above their AAS detection limit—0.2 ppm). Additional evidence on the good stability of this electrode was previously obtained in our laboratory, by a service life test [27].

On the other hand, despite the Nb/BDD anode having presented a much better performance in the degradation of the real textile effluent, as discussed above, this electrode presented instability problems during the studies whose results are here reported. During some experiments with the Nb/BDD anode, localized detachments of the diamond film from the niobium substrate occurred throughout the electrode area (photos of the surface of two Nb/BDD electrodes with such damage can be seen in Fig. SI-3 in the supplementary data). These detachments occurred when the Nb/BDD anode was used in electrolyses of the real textile effluent at $55\text{ }^{\circ}\text{C}$ with NaCl addition. This problem is similar to what was noticed before for BDD deposited on titanium substrates, when cracks may appear and cause the detachment of the diamond film [19]. Most authors do not report any problem with their BDD anodes; however, their substrate is most commonly p-type Si [18,20–22,31,38–42]. The localized detachments of the diamond film on the Nb/BDD anode may be caused by minute defects in the diamond film, which lead to oxide growth on the underlying niobium substrate (passivation films are easily formed on Nb, as discussed, for instance, by Biaggio et al. [43]) and consequent detachment of the diamond film. Fortunately, the COD abatement performance of the Nb/BDD anode is just as good in the presence as in the absence of NaCl in the effluent.

4. Conclusions

The results of an investigation of the electrochemical degradation of a real textile effluent using an Nb/BDD or Ti–Pt/ β -PbO₂ anode have been presented, in the absence and presence of chloride ions, for the system's optimized hydrodynamic conditions. The Nb/BDD anode yielded much higher decolorization and COD removal rates than the ones obtained with the Ti–Pt/ β -PbO₂ anode, at any experimental condition. The best conditions were

attained applying a current density of 5 mA cm^{-2} , at 55°C , without NaCl addition, when the electrochemical process is under charge-transfer control and the Nb/BDD anode is stable. Moreover, for the Nb/BDD anode, at the end of each electrolysis the DFZ value was always below the limit.

The rate of decolorization of the real textile effluent was increased in the presence of chloride ions (1.5 g L^{-1} NaCl). Thus, using the Nb/BDD anode the relative absorbance of the effluent could be reduced to less than 10% using an applied electric charge per unit volume of the electrolyzed effluent of only about 2 kA h m^{-3} . This higher decolorization rate has been accounted for by the greater ability of active chlorine to degrade the chromophore of the dyes present in the effluent.

On the other hand, the COD removal rate was not increased when NaCl was added to the real textile effluent. Nevertheless, practically total COD removal was attained with the Nb/BDD anode using an applied electric charge per unit volume of the electrolyzed effluent of only 7 kA h m^{-3} , with an energy consumption of about 30 kWh m^{-3} . This result, which has been accounted for by the high oxidation power of the hydroxyl radicals electrogenerated at the surface of the Nb/BDD anode, allows to conclude that the Nb/BDD anode could be an excellent option for the remediation of textile effluents, specially if its cost is diminished.

Finally, if one's goal is simply the decolorization of a textile effluent, the Ti–Pt/ β -PbO₂ anode might still be an adequate choice, especially if one takes into account the cost of BDD anodes and the possible instability of diamond films in the presence of chloride ions.

Acknowledgements

Financial support and scholarships from the Brazilian funding agency CNPq (National Council for Scientific and Technological Development) are gratefully acknowledged. Professors Antonio A. Mozeto, Pedro S. Fadini, and Alzir A. Batista (DQ-UFSCar) are also gratefully acknowledged for granting access to different apparatuses.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.06.039.

References

- G.A.R. Oliveira, E.R.A. Ferraz, F.M.D. Chequer, M.D. Grando, J.P.F. Angeli, M.S. Tsuboy, J.C. Marcarini, M.S. Mantovani, M.E. Osugi, T.M. Lizier, M.V.B. Zanon, D.P. Oliveira, Chlorination treatment of aqueous samples reduces, but does not eliminate, the mutagenic effect of the azo dyes Disperse Red 1, Disperse Red 13 and Disperse Orange 1, *Mutat. Res./Genet. Toxicol. Environ. Mutagen.* 703 (2010) 200–208.
- C. Hessel, C. Allegre, M. Maisseu, F. Charbit, P. Moulin, Guidelines and legislation for dye house effluents, *J. Environ. Manage.* 83 (2007) 171–180.
- S. Mondal, Methods of dye removal from dye house effluent—an overview, *Environ. Eng. Sci.* 25 (2008) 383–396.
- C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, *Appl. Catal. B87* (2009) 105–145.
- E. Chatzisyneon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Electrochemical treatment of textile dyes and dyehouse effluents, *J. Hazard. Mater.* B137 (2006) 998–1007.
- A. Sakalis, K. Fytianos, U. Nickel, A. Voulgaropoulos, A comparative study of platinumised titanium and niobe/synthetic diamond as anodes in the electrochemical treatment of textile wastewater, *Chem. Eng. J.* 119 (2006) 127–133.
- A.S. Kopal, Y. Yavuz, C. Gürel, U.B. Ögütveren, Electrochemical degradation and toxicity reduction of C.I. Basic Red 29 solution and textile wastewater by using diamond anode, *J. Hazard. Mater.* 145 (2007) 100–108.
- G.R.P. Malpass, D.W. Miwa, D.A. Mortari, S.A.S. Machado, A.J. Motheo, Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration, *Water Res.* 41 (2007) 2969–2977.
- G.R.P. Malpass, D.W. Miwa, S.A.S. Machado, A.J. Motheo, Decolorisation of real textile waste using electrochemical techniques: effect of electrode composition, *J. Hazard. Mater.* 156 (2008) 170–177.
- C.A. Martínez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.* 109 (2009) 6541–6569.
- A. Kapalka, G. Fóti, C. Comninellis, Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment, *J. Appl. Electrochem.* 38 (2008) 7–16.
- P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Synthesis of novel oxidants by electrochemical technology, *J. Appl. Electrochem.* 39 (2009) 2143–2149.
- C.Y. Cheng, G.H. Kelsall, Models of hypochlorite production in electrochemical reactors with plate and porous anodes, *J. Appl. Electrochem.* 37 (2007) 1203–1217.
- M. Panizza, A. Kapalka, C. Comninellis, Oxidation of organic pollutants on BDD anodes using modulated current electrolysis, *Electrochim. Acta* 53 (2008) 2289–2295.
- O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl, *Water Res.* 43 (2009) 2260–2272.
- A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, J.R. Ruiz, Electrochemical treatment of waters containing BDD anodes: kinetics of the reactions involving chlorides, *J. Appl. Electrochem.* 39 (2009) 2083–2092.
- L.S. Andrade, T.T. Tasso, D.L. Silva, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, On the performances of lead dioxide and boron-doped diamond electrodes in the anodic oxidation of simulated wastewater containing the Reactive Orange 16 dye, *Electrochim. Acta* 54 (2009) 2024–2030.
- M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, *Electrochim. Acta* 51 (2005) 191–199.
- E. Hmani, S.C. Elaoud, Y. Samet, R. Abdelhédi, Electrochemical degradation of waters containing O-Toluidine on PbO₂ and BDD anodes, *J. Hazard. Mater.* 170 (2009) 928–933.
- M. Murugananthan, S.S. Latha, G.B. Raju, S. Yoshihara, Anodic oxidation of ketoprofen—an anti-inflammatory drug using boron doped diamond and platinum electrodes, *J. Hazard. Mater.* 180 (2010) 753–758.
- M.J. Pacheco, V. Santos, L. Ciriaco, A. Lopes, Electrochemical degradation of aromatic amines on BDD electrodes, *J. Hazard. Mater.* 186 (2011) 1033–1041.
- K. Pecková, J. Musilová, J. Barek, Boron-doped diamond film electrodes—new tool for voltammetric determination of organic compounds, *Crit. Rev. Anal. Chem.* 39 (2009) 148–172.
- R.A. Medeiros, B.C. Lourenço, R.C. Rocha-Filho, O. Fatibello, A simple FIA system for the simultaneous determination of phenolic antioxidants with multiple pulse amperometric detection at a boron-doped diamond electrode, *Anal. Chem.* 82 (2010) 8658–8663.
- V. Schmalz, T. Dittmar, D. Haaken, E. Worch, Electrochemical disinfection of biologically treated wastewater from small treatment systems by using boron-doped diamond (BDD) electrodes—contribution for direct reuse of domestic wastewater, *Water Res.* 43 (2009) 5260–5266.
- C. Comninellis, G. Chen, Importance of the electrode material in the electrochemical treatment of wastewater containing organic pollutants, in: C. Comninellis, G. Chen (Eds.), *Electrochemistry for the Environment*, Springer, New York, 2010, pp. 25–54.
- L.S. Andrade, L.A.M. Ruotolo, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, J. Iniesta, V. García-García, V. Montiel, On the performance of Fe and Fe,F doped Ti–Pt/PbO₂ electrodes in the electrooxidation of the Blue Reactive 19 dye in simulated textile wastewater, *Chemosphere* 66 (2007) 2035–2043.
- L.S. Andrade, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, J. Iniesta, V. García-García, V. Montiel, Degradation of phenol using Co- and Co,F-doped PbO₂ anodes in electrochemical filter-press cells, *J. Hazard. Mater.* 153 (2008) 252–260.
- G. Zhao, Y. Zhang, Y. Lei, B. Lv, J. Gao, Y. Zhang, D. Li, Fabrication and electrochemical treatment application of a novel lead dioxide anode with superhydrophobic surfaces, high oxygen evolution potential, and oxidation capability, *Environ. Sci. Technol.* 44 (2010) 1754–1759.
- I. Sirés, C.T.J. Low, C. Ponce-de-León, F.C. Walsh, The deposition of nanostructured β -PbO₂ coatings from aqueous methanesulfonic acid for the electrochemical oxidation of organic pollutants, *Electrochem. Commun.* 12 (2010) 70–74.
- L. Ciriaco, C. Anjo, J. Correia, M.J. Pacheco, A. Lopes, Electrochemical degradation of Ibuprofen on Ti/Pt/PbO₂ and Si/BDD electrodes, *Electrochim. Acta* 54 (2009) 1464–1472.
- J.M. Aquino, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Electrochemical degradation of the Reactive Red 141 dye on a β -PbO₂ anode assessed by the response surface methodology, *J. Braz. Chem. Soc.* 21 (2010) 324–330.
- P. Cañizares, J. García-Gómez, I.F. Marcos, M.A. Rodrigo, J. Lobato, Measurement of mass-transfer coefficients by an electrochemical technique, *J. Chem. Educ.* 83 (2006) 1204–1207.
- A.D. Eaton, L.S. Cleesceri, A.E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, 19th ed., United Book Press, Baltimore, 1995, part 5000.
- M. Panizza, G. Cerisola, Electrocatalytic materials for the electrochemical oxidation of synthetic dyes, *Appl. Catal. B* 75 (2007) 95–101.

- [36] J.M. Aquino, K. Irikura, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, A comparison of electrodeposited Ti/ β -PbO₂ and Ti-Pt/ β -PbO₂ anodes in the electrochemical degradation of the Direct Yellow 86 dye, *Quím. Nova* 33 (2010) 2124–2129.
- [37] J.M. Aquino, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Electrochemical degradation of the Acid Blue 62 dye on a β -PbO₂ anode assessed by the response surface methodology, *J. Appl. Electrochem.* 40 (2010) 1751–1757.
- [38] C.R. Costa, F. Montilla, E. Morallón, P. Olivi, Electrochemical oxidation of acid black 210 dye on the boron-doped diamond electrode in the presence of phosphate ions: effect of current density, pH, and chloride ions, *Electrochim. Acta* 54 (2010) 7048–7055.
- [39] M. Wu, G. Zhao, M. Li, L. Liu, D. Li, Applicability of boron-doped diamond electrode to the degradation of chloride-mediated and chloride-free wastewaters, *J. Hazard. Mater.* 163 (2009) 26–31.
- [40] A. Cabeza, A.M. Urriaga, I. Ortiz, Electrochemical treatment of landfill leachates using a boron-doped diamond anode, *Ind. Eng. Chem. Res.* 46 (2007) 1439–1446.
- [41] A. Anglada, A. Urriaga, I. Ortiz, Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped diamond anodes, *Environ. Sci. Technol.* 43 (2009) 2035–2040.
- [42] P. Cañizares, L. Martínez, R. Paz, C. Sáez, J. Lobato, M.A. Rodrigo, Treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes, *J. Chem. Technol. Biotechnol.* 81 (2006) 1331–1337.
- [43] S.R. Biaggio, N. Bocchi, R.C. Rocha-Filho, F.E. Varela, Electrochemical characterisation of thin passive films on Nb electrodes in H₃PO₄ solutions, *J. Braz. Chem. Soc.* 8 (1997) 615–620.