

## A COMPARISON OF ELECTRODEPOSITED Ti/ $\beta$ -PbO<sub>2</sub> AND Ti-Pt/ $\beta$ -PbO<sub>2</sub> ANODES IN THE ELECTROCHEMICAL DEGRADATION OF THE DIRECT YELLOW 86 DYE<sup>#</sup>

José M. Aquino, Kallyni Irikura, Romeu C. Rocha-Filho\*, Nerilso Bocchi and Sonia R. Biaggio

Departamento de Química, Universidade Federal de São Carlos, CP 676, 13560-970 São Carlos – SP, Brasil

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The electrochemical performance of electrodeposited Ti/ $\beta$ -PbO<sub>2</sub> and Ti-Pt/ $\beta$ -PbO<sub>2</sub> anodes was galvanostatically evaluated (batch mode, 50 mA cm<sup>-2</sup>) to degrade the Direct Yellow 86 dye (100 or 200 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + 1.5 g L<sup>-1</sup> NaCl), investigating the effect of pH and temperature. Similar results were obtained for both electrodes and the best conditions for removal of color and chemical oxygen demand are pH 7 and 40 °C, when 90% decolorization is attained by passing a charge of only ~0.13 A h L<sup>-1</sup> and total mineralization is achieved with expenditure of ~5 kW h m<sup>-3</sup>.

Keywords: PbO<sub>2</sub> anode; electrochemical degradation of wastewater; indirect oxidation.

### INTRODUCTION

Different technologies for the treatment of textile wastewater have been extensively studied due to its harmful impact on the environment and also to increasingly rigid environmental regulations.<sup>1,2</sup> Textile wastewater is characterized mainly by its intense color and high organic load, due to non-reacted dyestuff. Synthetic dye molecules are by design chemically stable and thus can remain in the environment for long periods,<sup>3</sup> eventually causing severe aquatic<sup>4</sup> and health problems.<sup>5</sup> Hence the need to use and implement methods to remove these pollutants from textile wastewater before they are discharged.

Biological, physicochemical, and chemical methods are commonly used technologies for textile wastewater treatment, despite innumerable limitations considering pollutant abatement.<sup>1,2,6,7</sup> Electrochemical methods have been extensively used for wastewater decontamination since they offer an environmentally friendly way of removing toxic inorganic or organic species via redox reactions.<sup>8-17</sup> These methods may be a good option for textile wastewater treatment, since they are easy to implement, versatile, and can lead to high organic and color removals;<sup>6</sup> their main drawbacks regard the use of electrical energy and the poor current efficiencies attained at low pollutant concentrations.<sup>15,16</sup> However, the use of adequate anode materials, coupled with optimized operation conditions, tend to minimize these problems.

The electrochemical oxidation of pollutants can occur in two ways: directly, when the organic pollutant is oxidized by electron transfer directly to the electrode, or indirectly, when this electron transfer is mediated by some electroactive species (an oxidant generated at the anode).<sup>16</sup> The most common electrogenerated oxidants in indirect oxidation processes are: the hydroxyl radical ( $\bullet$ OH), from the oxidation of water;<sup>16,17</sup> Cl<sub>2</sub>, HOCl, and OCl<sup>-</sup> (frequently referred to as active chlorine), from the oxidation of chloride ions;<sup>16,18</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, from the oxidation of sulfate ions.<sup>16,19</sup>

According to the nature of the interaction between the hydroxyl radical and anode materials, Kapalka *et al.*<sup>20</sup> classified them from high (boron-doped diamond – BDD) to low (dimensionally stable anodes – DSA) oxidation power anodes; in this classification, lead dioxide (PbO<sub>2</sub>) is a medium oxidation power anode. The electro-

chemical oxidation mediated by active chlorine is commonly used with medium to low oxidation power anodes in order to increase the pollutant oxidation rate and the process current efficiency.<sup>21</sup> Indeed, it has been shown that oxidation rates comparable to those on BDD anodes are obtained when using PbO<sub>2</sub> or DSA (medium or low oxidation power) anodes in the presence of chloride ions.<sup>6,14,18</sup> When using active chlorine, it might be essential to have the solution pH under control in order to improve the pollutant removal efficiency, since pH dictates the predominant chlorine species in the electrolyzed solution.<sup>22</sup> Thus, different pH conditions were reported as the best ones for color and organic removals.<sup>6,18,23</sup> The possible formation of undesirable chloro-organic derivatives is a known drawback of electrooxidation processes in chloride-containing solutions, although very few papers have actually reported these compounds.<sup>24</sup> Undesirable inorganic compounds, such as ClO<sub>4</sub><sup>-</sup> ions, which are mainly formed in electrooxidations using BDD anodes, also represent serious health problems.<sup>25</sup>

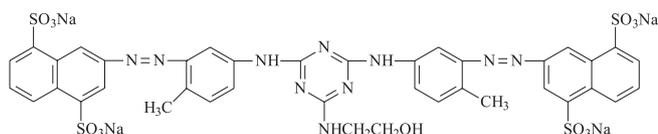
PbO<sub>2</sub> film anodes are interesting materials for the electrochemical degradation of pollutants due to their medium to high oxidation power, easiness of preparation, and low cost.<sup>12-14,23</sup> The PbO<sub>2</sub> film electrochemical performance and stabilization are influenced by the presence of doping species,<sup>12,13,26</sup> electrodeposition conditions,<sup>26,27</sup> and substrate preparation. The main concern when using PbO<sub>2</sub> anodes is the possible release of toxic Pb<sup>2+</sup> ions and problems related to the adherence of the oxide film to the substrate that reduce the lifetime of the anodes. Titanium substrates covered with platinum (Ti-Pt) are well known to lead to good stability of the PbO<sub>2</sub> films,<sup>12</sup> with low levels of Pb<sup>2+</sup> ions released into solution;<sup>28</sup> however the extensive use of platinum is not economically feasible. Thus, many PbO<sub>2</sub> anodes prepared directly on the Ti substrate have been reported, with previous substrate pretreatment or modification: sandblasting followed by etching in concentrated hydrochloric acid;<sup>29</sup> polishing with 320-grit paper strips, etching in boiling 20% hydrochloric acid for 1 h followed by deposition of a SnO<sub>2</sub>-Sb coating;<sup>30</sup> and etching in boiling 1.6 mol L<sup>-1</sup> oxalic acid for 2 h.<sup>27</sup> The presence of fluorine ions<sup>31</sup> or surfactants<sup>32</sup> in the electrodeposition bath can contribute to a more stable oxide film due to the diminishment of the amount of oxygen evolution, which could cause cracks in the oxide surface leading to scaling. Furthermore, these species can improve the PbO<sub>2</sub> film adherence<sup>21</sup> and its crystallinity.<sup>31</sup>

Studies on the degradation of the diazo dye Direct Yellow 86 – DY 86 (CAS number 50925-42-3 and C.I. number 29325 – Figure 1) are

\*e-mail: romeu@ufscar.br

<sup>#</sup> It is with great pleasure that we dedicate this article in honor of “brother Hans”, to whom SBQ owes much.

quite rare. Shen and Wang<sup>33</sup> reported on its decomposition by a UV/H<sub>2</sub>O<sub>2</sub> process in continuous annular photoreactors. Hsueh *et al.*<sup>34</sup> reported on its decolorization by *Aeromonas hydrophila*, comparatively to other dyes in order to study the effect of chemical structure. On the other hand, Kuo *et al.*<sup>35</sup> reported studies on the possible removal of the DY 86 dye from solution using carbon nanotubes. As far as we are aware, no study on the degradation of this dye by electrochemical methods has been reported.



**Figure 1.** Chemical structure of the Direct Yellow 86 dye (C<sub>39</sub>H<sub>30</sub>N<sub>10</sub>O<sub>13</sub>S<sub>4</sub>Na<sub>4</sub>)

In our laboratory, the electrochemical degradation of textile dyes has been investigated previously using doped and undoped  $\beta$ -PbO<sub>2</sub> anodes, in the absence or presence of chloride ions, but these electrodes were always electrodeposited onto Ti-Pt substrates.<sup>12,14,23</sup> Thus, the aim of the present paper is to produce and characterize undoped Ti/ $\beta$ -PbO<sub>2</sub> and Ti-Pt/ $\beta$ -PbO<sub>2</sub> anodes, as well as comparatively evaluate their performances in the electrochemical degradation of the DY 86 dye in the presence of chloride ions. For such, the evolution of the color and chemical oxygen demand (*COD*) of solutions of this dye is followed with time of electrolysis.

## EXPERIMENTAL

### Chemicals

All chemicals, including Pb(NO<sub>3</sub>)<sub>2</sub> (a.r., Acros), sodium lauryl sulfate, SLS (99%, Fisher Scientific), H<sub>2</sub>PtCl<sub>6</sub> (99.9%, Aldrich), HCl (36.5%, Mallinckrodt), HNO<sub>3</sub> (69-70%, Mallinckrodt), NaCl (a.r., JT Baker), Na<sub>2</sub>SO<sub>4</sub> (a.r., Qhemis), and DY 86 (Quimanyl), were used as received. Doubly deionized water (Millipore Milli-Q system,  $\rho \geq 18.2$  M $\Omega$  cm) was used for the preparation of all solutions.

### $\beta$ -PbO<sub>2</sub> film preparation on Ti and Ti-Pt substrates

Firstly, 3.1 cm  $\times$  2.7 cm (each face) Ti plates were sandblasted followed by cleaning with 2-propanol in an ultrasonic bath for 20 min. The procedure involving the Ti substrate platinization is fully described in a previous work.<sup>12</sup>  $\beta$ -PbO<sub>2</sub> films were electrodeposited on the Ti and Ti-Pt substrates in a conventional electrochemical cell, using a calomel reference electrode and two AISI-304 stainless steel plates as counter electrodes. The deposition bath was composed of 0.1 mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub>, 1.0 g L<sup>-1</sup> SLS for the Ti substrate or 0.5 g L<sup>-1</sup> SLS for the Ti-Pt substrate, in 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>. The electrolysis was carried out at 65 °C for the time necessary to obtain a 50 mg cm<sup>-2</sup> PbO<sub>2</sub> film, assuming 100% faradaic efficiency. The applied current density (*j*) in the electrodeposition was 5 or 20 mA cm<sup>-2</sup> for the Ti or Ti-Pt substrate, respectively. As soon as the electrodeposition was finished, the electrodes were transferred to and maintained in a vessel containing deionized water initially at 65 °C, until ambient temperature was reached.

### Electrodes characterization

X-ray diffraction measurements were carried in order to characterize the phases of the PbO<sub>2</sub> film; the analysis was a 2 $\theta$ - $\theta$  (where  $\theta$  is the diffraction angle), with a continuous sweeping rate equal to 1° min<sup>-1</sup>, ranging from 20° to 80°. The morphology of the  $\beta$ -PbO<sub>2</sub> grains was examined by scanning electron microscopy (SEM).

The electrochemical behavior of the electrodes in a 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution was analyzed by cyclic voltammetry. Additionally, an accelerated test of the Ti/ $\beta$ -PbO<sub>2</sub> (3.88 cm<sup>2</sup>) and Ti-Pt/ $\beta$ -PbO<sub>2</sub> (3.68 cm<sup>2</sup>) anodes was carried out galvanostatically (150 mA cm<sup>-2</sup>) for 12 h at 40 °C, also in a 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. For such, a conventional electrochemical cell was used with a saturated calomel reference electrode and two AISI-304 stainless steel plates as counter electrodes; the H<sub>2</sub>SO<sub>4</sub> solution (100 mL) was continuously stirred. Samples of the solution were collected at the end of the accelerated test, for Pb detection in a flame atomic absorption spectrometer (FAAS); the anodes were also analyzed for mass loss.

### Electrochemical degradation of the DY 86 dye

The experiments on the electrochemical degradation of the DY 86 dye were carried out in a stirred cell (600 mL beaker) with turbulent promoters attached to the wall, a PbO<sub>2</sub> anode, a calomel reference electrode, and two AISI-304 stainless steel plates as counter electrodes. The experiments were carried out galvanostatically in the batch mode, using 400 mL of a 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution containing 100 or 200 mg L<sup>-1</sup> DY 86; the NaCl concentration was fixed at 1.5 g L<sup>-1</sup>. Considering that in previous works on the degradation of dyes<sup>23</sup> we found that optimal conditions for *COD* removal were attained at a high current density, its value was fixed at 50 mA cm<sup>-2</sup>. The investigated variables were pH (3, 7, and 11) and temperature (10, 25 and 40 °C).

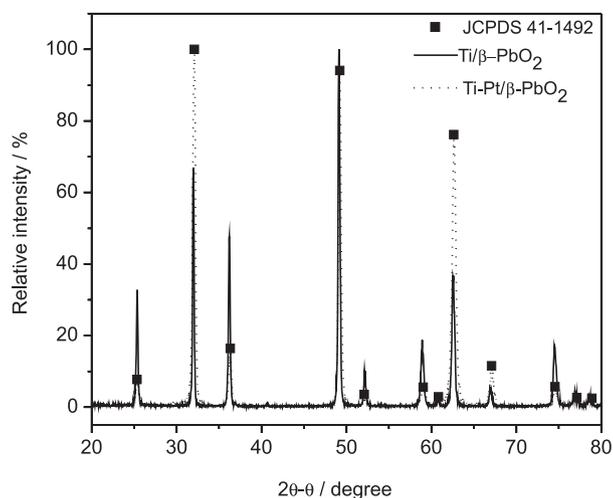
### Analyses

The evolution of the color and *COD* of the DY 86 solutions was followed with time of electrolysis. The dye decolorization was monitored at certain time intervals by sampling of 3 mL of the solution (initial dye concentration of 100 mg L<sup>-1</sup>). The solution color was analyzed from 200 to 800 nm in a UV-vis spectrophotometer (HP 8452 diode array detector). The charge per unit volume of the electrolyzed solution required for 90% decolorization (*Q*<sup>90</sup>) was used to establish the best operation conditions for color removal. Then, using these best operation conditions, the *COD* removal experiments were carried out by electrolyzing a 200 mg L<sup>-1</sup> DY 86 solution. The *COD* measurements were done with commercial reagents (Hach) using 2 mL samples of the electrolyzed solution, which were further oxidized by digestion at 150 °C for 2 h. Then, the absorbance of each sample was read in a Hach DR/890 model spectrophotometer.

## RESULTS AND DISCUSSION

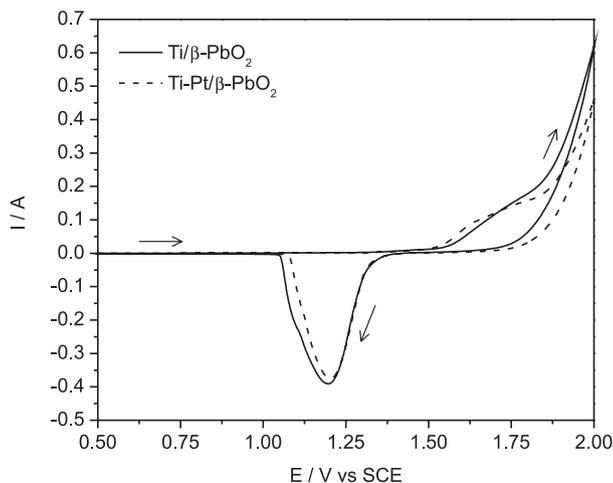
### Electrodes characterization

Figure 2 shows the X-ray diffraction spectra for the Ti/ $\beta$ -PbO<sub>2</sub> and Ti-Pt/ $\beta$ -PbO<sub>2</sub> anodes. By comparing the obtained phase angles corresponding to the different diffraction lines with those indexed according to the JCPDS 41-1492 card, it was possible to conclude that both PbO<sub>2</sub> films are present as the tetragonal  $\beta$ -phase; no peaks for the  $\alpha$ -phase were detected in the spectra. Furthermore, the SEM images (Figure 1S, supplementary materials) revealed the typical pyramidal grains of the PbO<sub>2</sub>  $\beta$ -phase. The oxide film of the Ti/ $\beta$ -PbO<sub>2</sub> anode (Figure 1Sa) is made up of larger grains because its electrodeposition rate was slower (applied current density of 5 mA cm<sup>-2</sup>), a procedure that should also have led to a reduced number of defects in the film. These characteristics are most probably the reason why the oxide film of the Ti/ $\beta$ -PbO<sub>2</sub> anode presents some peaks of higher intensity in the diffraction spectrum (Figure 2).



**Figure 2.** X-ray diffraction spectra for the  $\beta$ - $\text{PbO}_2$  films on the Ti and Ti-Pt substrates

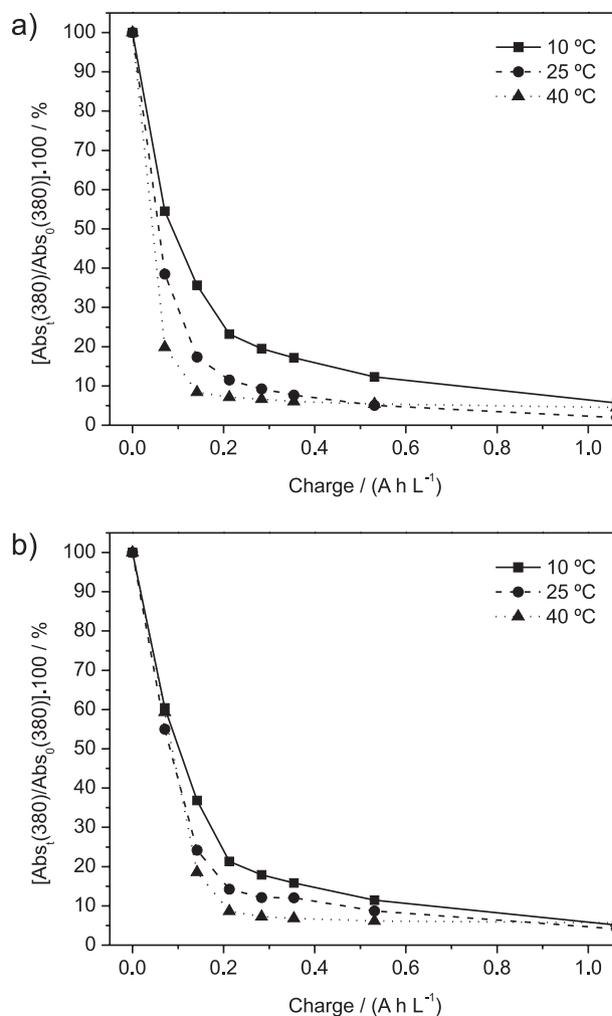
The cyclic voltammograms (2<sup>nd</sup> cycle) of the two anodes in a 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (Figure 3) show an anodic response starting above 1.5 V, before oxygen evolution, and a cathodic response below 1.4 V. These cathodic and anodic responses correspond to the conversion  $\text{PbO}_2 \rightarrow \text{PbSO}_4$  and the reverse conversion  $\text{PbSO}_4 \rightarrow \text{PbO}_2$ , respectively, as previously discussed by Feng and Johnson,<sup>36</sup> for instance. No significant potential or current difference is observed in these voltammograms, except for the fact that the oxygen evolution reaction starts at a somewhat lower potential on the Ti/ $\beta$ - $\text{PbO}_2$  anode.



**Figure 3.** Cyclic voltammograms (2<sup>nd</sup> cycle) of the Ti/ $\beta$ - $\text{PbO}_2$  and Ti-Pt/ $\beta$ - $\text{PbO}_2$  anodes in a naturally aerated 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, at 25 °C.  $v = 10 \text{ mV s}^{-1}$

### Electrochemical degradation of the DY 86 dye: decolorization

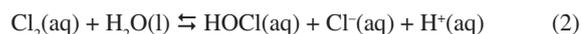
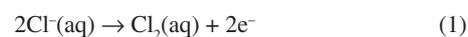
As it was previously shown,<sup>6,14,18</sup> when Cl<sup>-</sup> ions are added to the solution the rate of dye decolorization is increased significantly. Figure 4 shows for the two anodes how the relative absorbance (at 380 nm) of the dye solution (100 mg L<sup>-1</sup> DY 86) changed as a function of the electric charge passed through the electrochemical cell per unit volume of solution, at pH 7 for the three temperatures investigated; similar decay curves were obtained at pH 3 and 11 (Figures 2S and 3S, supplementary materials). From these results one can see that the decolorization is significantly favored as the temperature is increased, independently of which anode was used; the best results



**Figure 4.** Relative absorbance (at 380 nm) as a function of the applied electric charge for the decolorization of a 100 mg L<sup>-1</sup> DY 86 solution (400 mL) at pH 7, at different temperatures (indicated in the figures): a) Ti/ $\beta$ - $\text{PbO}_2$  anode; b) Ti-Pt/ $\beta$ - $\text{PbO}_2$  anode.  $j = 50 \text{ mA cm}^{-2}$

were obtained at 40 °C, for pH 3 and 7. Table 1 shows the results obtained for  $Q^{90}$ , kinetic constants, apparent activation energy, cell potential, and energy consumption per unit volume of the solution associated to  $Q^{90}$ . The best operation conditions (lowest values of  $Q^{90}$  and energy consumption) for the decolorization were attained for pH 7 at 40 °C (Table 1). At this pH value, for the Ti/ $\beta$ - $\text{PbO}_2$  anode, when the temperature is lowered from 40 to 25 or 10 °C, the value of  $Q^{90}$  increases twofold or more than fivefold, respectively. On the other hand, when at 40 °C the pH is decreased from 7 to 3, the value of  $Q^{90}$  increases by about 40%; however, if the pH is increased from 7 to 11, the value of  $Q^{90}$  increases more than sixfold. Similar but not as marked variations are found for the Ti-Pt/ $\beta$ - $\text{PbO}_2$  anode. Clearly, the best conditions for inactivation of the chromophore of the DY 86 dye by electrolysis with Cl<sup>-</sup> ions added to the solution are pH 7 and temperature of 40 °C.

As extensively discussed by Cheng and Kelsall,<sup>22</sup> when solutions containing Cl<sup>-</sup> ions are electrolyzed the generated chlorine gas is hydrolyzed and disproportionates, forming hypochlorous acid (HClO):



**Table 1.** Electric charge required for 90% decolorization ( $Q^{90}$ ), apparent kinetic constant ( $k_{ap}$ ), activation energy ( $E_a$ ), cell potential ( $E$ ), and energy consumption per unit volume of the electrolyzed solution associated to  $Q^{90}$  ( $EC$ ) for the galvanostatic electrolytic decolorization of a 100 mg L<sup>-1</sup> DY 86 solution (400 mL) under different pH and temperature conditions, for the two PbO<sub>2</sub> anodes.  $j = 50$  mA cm<sup>-2</sup>; supporting electrolyte: 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + 1.5 g L<sup>-1</sup> NaCl

Conditions	Ti/ $\beta$ -PbO <sub>2</sub>					Ti-Pt/ $\beta$ -PbO <sub>2</sub>				
	$Q^{90}$ / A h L <sup>-1</sup>	$k_{ap}$ / mol <sup>-1</sup> L min <sup>-1</sup>	$E_a$ / kJ mol <sup>-1</sup>	$E^*$ / V	$EC^{**}$ / kW h m <sup>-3</sup>	$Q^{90}$ / A h L <sup>-1</sup>	$k_{ap}$ / mol <sup>-1</sup> L min <sup>-1</sup>	$E_a$ / kJ mol <sup>-1</sup>	$E^*$ / V	$EC^{**}$ / kW h m <sup>-3</sup>
pH 3, 10 °C	0.433	0.330	26.5	4.41	1.91	0.695	0.261	29.9	3.91	2.72
pH 3, 25 °C	0.440	0.602		4.01	1.76	0.517	0.326		3.39	1.75
pH 3, 40 °C	0.176	0.969		3.20	0.56	0.171	0.896		3.23	0.55
pH 7, 10 °C	0.717	0.273	28.1	4.09	2.93	0.391	0.312	24.8	4.09	1.60
pH 7, 25 °C	0.258	0.684		4.00	1.03	0.320	0.443		3.65	1.17
pH 7, 40 °C	0.126	0.847		3.42	0.43	0.130	0.863		3.06	0.40
pH 11, 10 °C	1.605	0.021	32.5	4.16	6.68	0.813	0.035	29.7	4.01	3.26
pH 11, 25 °C	0.869	0.091		4.33	3.76	0.499	0.074		3.35	1.67
pH 11, 40 °C	0.908	0.077		3.03	2.75	0.463	0.117		3.05	1.41

\* Average cell potential (vs. SCE). \*\* Considering 90% decolorization.

For pH < 3.3, Cl<sub>2</sub> is the predominant species in solution, becoming the only species in solution for pH ≤ 1. For pH > 3, reaction 2 becomes irreversible, and HClO is the predominant species in the pH range 3.4 to 7.5. As the pH increases, HClO deprotonates:



For pH ≥ 7.6, the hypochlorite ion (ClO<sup>-</sup>) becomes the predominant species; for pH ≥ 10, ClO<sup>-</sup> is the only chlorine species in solution. Hence, the best conditions for decolorization of the DY 86 dye (pH 7) occur when the HClO and ClO<sup>-</sup> species are the oxidants present in solution, approximately in the proportion 2:1,<sup>22</sup> whereas the worst conditions occur when the ClO<sup>-</sup> species is the sole oxidant present in solution (pH 11).

High temperatures favor the mediated oxidation probably due to the increasing power of the electrogenerated oxidants. That behavior is in agreement with the higher values of the apparent second-order kinetic constants for reactions at 40 °C (Table 1). A second-order model was chosen because it better fits the experimental data ( $R > 0.95$ ). The apparent activation energies have similar values and do not seem to depend on the solution pH; their high values indicate that the DY 86 dye decolorization is highly temperature sensitive,<sup>37</sup> as the data in Table 1 clearly show. Moreover, the results here presented are in agreement with the ones of Szpyrkowicz and Radaelli,<sup>37</sup> who also reported a second-order kinetic behavior as well as a temperature dependence for the decolorization of an azo dye, as in the present work.

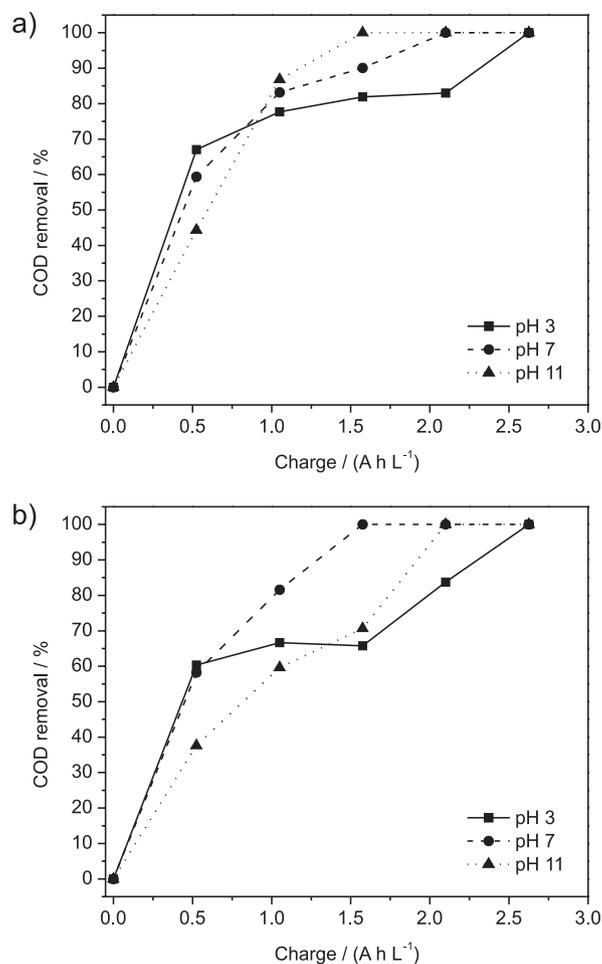
Recently we reported on the electrochemical degradation of the dyes Reactive Red 141 and Acid Blue 62 (100 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>) on Ti-Pt/ $\beta$ -PbO<sub>2</sub> anodes.<sup>23</sup> For the Reactive Red 141 dye, the best conditions for decolorization occur at very low pH values, at temperatures greater than 25 °C, with at least ~1.4 g L<sup>-1</sup> NaCl added to the solution. In the case of the Acid Blue 62 dye, these conditions are pH 4, at temperatures equal or lower than 25 °C, with 1.0 – 2.0 g L<sup>-1</sup> NaCl added to the solution. Based on these results and the ones here reported, clearly the necessary NaCl concentration is about 1.5 g L<sup>-1</sup> NaCl, but the pH and temperature vary with the dye being degraded.

#### Electrochemical degradation of the DY 86 dye: COD removal

Previously,<sup>14</sup> when the performance of a Ti-Pt/ $\beta$ -PbO<sub>2</sub> anode was compared to that of a boron-doped diamond (BDD) anode in the degradation of the Reactive Orange 16 dye (85 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>), we showed that when Cl<sup>-</sup> ions are added to the solution the extent of dye degradation using the Ti-Pt/ $\beta$ -PbO<sub>2</sub> anode was increased

significantly, but not enough to lead to total mineralization (only 80% COD removal, compared to 100% for the BDD anode at a lower value of the applied electric charge).

Figure 5 shows for the two anodes how the COD removal percentage of the dye solution (200 mg L<sup>-1</sup> DY 86) changed as a function of the electric charge passed through the electrochemical cell per unit volume



**Figure 5.** Percentage of COD removal as a function of the applied electric charge for the degradation of a 200 mg L<sup>-1</sup> DY 86 solution (400 mL) at different pH values (indicated in the figures): a) Ti/ $\beta$ -PbO<sub>2</sub> anode; b) Ti-Pt/ $\beta$ -PbO<sub>2</sub> anode.  $j = 50$  mA cm<sup>-2</sup> and  $\theta = 40$  °C

**Table 2.** Apparent kinetic constant ( $k_{ap}$ ), cell potential ( $E$ ), and energy consumption per unit volume of the electrolyzed solution ( $EC$ ), for the galvanostatic electrolytic COD removal of a 200 mg L<sup>-1</sup> DY 86 solution (400 mL) at 40 °C and different pH values, for the two PbO<sub>2</sub> anodes.  $j = 50$  mA cm<sup>-2</sup>; supporting electrolyte: 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + 1.5 g L<sup>-1</sup> NaCl

Condition	Ti/β-PbO <sub>2</sub>			Ti-Pt/β-PbO <sub>2</sub>		
	$k_{ap} / (10^{-2} \text{ min}^{-1})$	$E^* / \text{V}$	$EC^{**} / \text{kW h m}^{-3}$	$k_{ap} / 10^{-2} \text{ min}^{-1}$	$E^* / \text{V}$	$EC^{**} / \text{kW h m}^{-3}$
pH 3	2.76	2.81	7.39	2.52	2.53	6.65
pH 7	5.21	2.73	5.73	5.63	2.77	4.36
pH 11	6.75	2.82	4.44	2.74	2.64	5.55

\*Average cell potential (vs. SCE). \*\*Considering 100% of COD removal.

of solution, for three different values of pH, at 40 °C; this temperature was chosen because it led to better decolorization results. By analyzing Figure 5 one can conclude that both anodes are capable of mineralizing the DY 86 dye, independently of the solution pH; however, clearly the degradation is faster in neutral (pH 7) or basic (pH 11) solution, when lower values of the applied electric charge are necessary to attain total mineralization. Although the OCl<sup>-</sup> species has a lower oxidation potential than the Cl<sub>2</sub> or HClO ones, its concentration might be higher because it is an ionic species (the other two are gaseous); this might explain why high COD removal rates are also attained for pH 11 solutions. Nevertheless, looking at the degradation process from the point of view of removing both color and COD, clearly the best operation conditions are pH 7 and 40 °C. Table 2 shows the values of the kinetic constants of the fitting of an apparent first-order model ( $R > 0.91$ ), cell potential, and energy consumption per unit volume of the electrolyzed solution to attain complete mineralization. As expected from the results presented before, the lowest values of energy consumption were also obtained for the neutral and basic solutions.

As mentioned above, the electrochemical degradation of the dye Acid Blue 62 (100 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + 1.5 g L<sup>-1</sup> NaCl) using a Ti-Pt/β-PbO<sub>2</sub> anode was previously studied in our laboratory.<sup>23</sup> For this dye, the best conditions for COD removal are pH 11, at 45 °C. Based on these results and the ones here reported, clearly better degradation results are obtained at a higher temperature.

### Accelerated tests

Tables 1 and 2 show that the electrolyses carried out with the Ti/β-PbO<sub>2</sub> anode needed a somewhat higher value of cell potential than when the Ti-Pt/β-PbO<sub>2</sub> anode was used; this suggests that some passivation of the Ti substrate occurred during the PbO<sub>2</sub> film electrodeposition to obtain the Ti/β-PbO<sub>2</sub> anode.

After the accelerated tests of the anodes (150 mA cm<sup>-2</sup>, for 12 h in a 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 40 °C), a mass loss of 0.9% was detected for the Ti/β-PbO<sub>2</sub> anode, whereas no significant mass loss was found for the Ti-Pt/β-PbO<sub>2</sub> anode. However, when the used H<sub>2</sub>SO<sub>4</sub> solutions were tested, Pb<sup>2+</sup> contents of 3.5 and 1.9 ppm were found for the Ti/β-PbO<sub>2</sub> and Ti-Pt/β-PbO<sub>2</sub> anodes, respectively. Finally, it should be mentioned that after the 12 h test, scaling of the oxide film was detected on the Ti/β-PbO<sub>2</sub> anode; nevertheless, no sign at all of film detachment was detected after the electrochemical degradation experiments. From these results one can conclude that the β-PbO<sub>2</sub> film on the Ti-Pt/β-PbO<sub>2</sub> anode is stabler than the one on the Ti/β-PbO<sub>2</sub> anode; hence, the electrodeposition of the oxide directly on the Ti substrate needs to be further investigated so as to further increase the stability of the oxide film and minimize the passivation of the substrate.

### CONCLUSIONS

The electrodeposition of the β-PbO<sub>2</sub> phase on a titanium substrate

was successfully accomplished, with no alpha phase present; however, the cell potentials attained when this Ti/β-PbO<sub>2</sub> anode was used (somewhat higher than those attained when a Ti-Pt/β-PbO<sub>2</sub> anode was used) for the electrolysis of the DY 86 dye indicate that the Ti substrate was partly passivated during the electrodeposition of the β-PbO<sub>2</sub> film. Additionally, the results of the accelerated tests indicate that the Ti/β-PbO<sub>2</sub> anode is not as stable as the Ti-Pt/β-PbO<sub>2</sub> anode; hence, further investigations need to be carried out on the electrodeposition of the β-PbO<sub>2</sub> directly on Ti in order to further improve the stability of the Ti/β-PbO<sub>2</sub> anode.

Despite the above highlighted differences in the stability of the two anodes, their performances in the color or COD removal of the DY 86 dye solution did not present any significant difference. The best conditions for decolorization of the DY 86 dye (100 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, 400 mL) in the presence of Cl<sup>-</sup> ions (1.5 g L<sup>-1</sup>) using any of the anodes are pH 7 and 40 °C; under these conditions, 90% decolorization is attained passing an electric charge per unit volume of the electrolyzed solution of only about 0.13 A h L<sup>-1</sup>. On the other hand, using any of the anodes at 40 °C, the mineralization of the dye (200 mg L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + 1.5 g L<sup>-1</sup> NaCl, 400 mL) is faster if the solution is neutral (pH 7) or basic (pH 11), when lower values of applied charge are necessary to attain total mineralization; under these conditions, total mineralization is attained with an energy consumption per unit volume of the electrolyzed solution of around 5 kW h m<sup>-3</sup>. Consequently, from the point of view of removing both color and COD, clearly the best operation conditions are pH 7 and 40 °C, when the HClO and ClO<sup>-</sup> species are the oxidants present in solution, approximately in the proportion 2:1.

Finally, the very low values of electric charge needed to attain 90% decolorization and the low values of energy consumption to attain complete mineralization, per unit volume of dye solution, indicate the feasibility of applying the electrochemical process to degrade the DY 86 dye using β-PbO<sub>2</sub> anodes in the presence of chloride ions added to the solution.

### SUPPLEMENTARY MATERIAL

Three figures are available as supplementary material: SEM micrographs of the β-PbO<sub>2</sub> films (Figure 1S); relative absorbance as a function of the applied electric charge for the decolorization of a DY 86 solution at pH 3 (Figure 2S) and at pH 11 (Figure 3S), at different temperatures, using Ti/β-PbO<sub>2</sub> and Ti-Pt/β-PbO<sub>2</sub> anodes. These figures can be downloaded as a PDF file from <http://quimicanova.sbgq.org.br>.

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