Comparative Electrochemical Degradation of the Acid Yellow 49 Dye Using Boron-Doped Diamond, β-PbO₂, and DSA® Anodes in a Flow Reactor

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Received: 28 October 2014 / Accepted: 30 November 2014 / Published: 16 December 2014

The electrodegradation of the Acid Yellow 49 dye (100 mg L⁻¹ in 0.1 mol L⁻¹ Na₂SO₄) was investigated using boron-doped diamond (BDD), Ti-Pt/β-PbO₂, and Ti/RuO₂-TiO₂ (DSA®) anodes. Galvanostatic electrolyses (5, 15 or 30 mA cm⁻²) were carried out in an electrochemical flow system, with a filter-press reactor. Best performances were attained with the BDD anode and worst with the DSA® anode. The dye solution was adequately decolorized using an electrical charge per unit volume of dye solution (Q_{apl}) slightly higher than 0.60 A h L⁻¹, applied with the BDD anode at a current density of only 5 mA cm⁻². At this current density, COD and TOC abatements of 37% and 20% were attained with Q_{apl} values of only 0.60 and 1.20 A h L⁻¹, respectively; this indicates the feasibility of abating the organic load of the dye solution by simply increasing the value of Q_{apl}.

Keywords: BDD anode; RuO₂-TiO₂ anode; electrochemical degradation of wastewater; CI 18640 dye; electrooxidation of dyes.

1. INTRODUCTION

One of the consequences of the significant growth of the world population and ensuing industrial activity is the contamination of water bodies by different pollutants. The textile industry, in particular, generates large volumes of wastewaters, which commonly are deeply colored, present high organic load and chemical oxygen demand (COD) values, varying pH and toxicity, large number of particles in suspension, as well as recalcitrant compounds [1-3]. Moreover, most textile dyes are large molecules (formed by a combination of aromatic rings connected by different chromophores) that often are resistant to various degradation methods. Hence, many methodologies are being investigated for the removal/degradation of dyes, such as: microbiological [4-6], photocatalytic [7,8], adsorption
biosorption [11], radiolysis [12], ultrasonication [13], microbial fuel cells [14], as well as electrochemical [15,16] methods. In the last case, our laboratory has made several contributions, alone [17-23] or in collaboration with other laboratories [24,25].

As pointed out by Rajeshwar et al. [26], electrochemical methods present several attractive characteristics, such as: versatility, energy efficiency, amenability to automation, environmental compatibility, and cost effectiveness. Additionally, contrary to what happens with many methodologies, complete oxidation (mineralization) of organic compounds can be attained when using properly tuned electrochemical methods [27]. As extensively reviewed by Panizza and Cerisola [28], electrooxidation of organics may be carried out by direct or indirect electrolysis. In the former instance, the organics oxidation occurs by electron exchange directly with the anode surface, whereas in the latter case this electron exchange is mediated by electrogenerated oxidant species, for instance active chlorine species. Different anode materials have been employed, comparatively or not, in the electrooxidation of different organics, such as dyes [17-25,29-37], endocrine disruptors [38,39], pesticides [40,41], and pharmaceuticals [42,43].

As noted by Kapalka et al. [44], electrochemical mineralization reactions involve oxygen transfer from water to organic species while using electrical energy, with the active participation of hydroxyl radicals (•OH). The chemical reactivity of these radicals toward the oxidation of the organic species is strongly dependent on the anode material (M) used, because the strength of the •OH–M interaction varies significantly with the nature of M. The weaker this interaction, the more reactive •OH becomes toward organics oxidation (and less reactive toward the oxygen evolution reaction). Hence, anode materials may be classified from low to high oxidation power as the strength of the •OH–M interaction varies from high to low. Thus, boron-doped diamond (BDD) electrodes are classified as high oxidation power anodes and oxide electrodes such as RuO$_2$-TiO$_2$ or IrO$_2$-Ta$_2$O$_5$ (known as dimensionally stable anodes – DSA® [45]) are labeled as low oxidation power anodes [44]. Comparatively, β-PbO$_2$ electrodes may be classified as medium oxidation power anodes [18,20].

Acid Yellow 49 (AY49 – see Figure 1) is a brilliant yellow azo dye extensively used in the dyeing of wool, silk, and polyamide fiber, or wool blended fabrics (also used in leather coloring). Nevertheless, as far as we could ascertain, so far no investigation on its degradation has been reported; only studies on its removal by adsorption using the clay mineral sepiolite [46], char from pyrolysis/gasification of sewage sludge [47], or fungi (Cunninghamellaelegans) [48] have been reported. Hence, in this article, for the first time in the literature, we report results on the electrooxidative degradation of the AY49 dye, which was comparatively carried out using BDD, Ti-Pt/β-PbO$_2$, and Ti/RuO$_2$-TiO$_2$ (hereinafter simply referred to as β-PbO$_2$ and DSA®, respectively) anodes in an electrochemical flow system, with a filter-press reactor, at different current densities. The degradation of the AY49 dye was monitored by UV/vis spectrophotometry and determinations of chemical oxygen demand and total organic carbon content.
2. EXPERIMENTAL

2.1. Materials

All chemicals were used as received: AY49 (Quimanil) and Na\textsubscript{2}SO\textsubscript{4} (p.a. Qhemis). Solutions were prepared using deionized water ($\rho \geq 18.2$ M$\Omega$ cm) from a Millipore 221 Milli-Q system. The$\beta$-PbO\textsubscript{2} electrode was produced in our laboratory according to a previously described procedure [19,24]. The BDD electrode (BDD film deposited on a niobium substrate; boron doping level in the range 2000 – 4500 ppm) was acquired from Condias GMbH Conductive Diamond Products (Itzehoe, Germany), whereas the DSA\textsuperscript{®} electrode was provided by De Nora do Brasil (Sorocaba, Brazil). The exposed geometric areas of these electrodes were 14.6, 15.0, and 18.6 cm$^2$, respectively.

2.2. Electrochemical degradation of the AY49 dye

The electrochemical degradation experiments were carried out in a flow electrochemical system, with a filter-press reactor, described in detail by Aquino et al. [19]. Before each degradation experiment, the flow electrochemical system was thoroughly rinsed with deionized water, followed by a 10 min anodic pre-conditioning of the working electrode (to oxidize possible organic contaminants that might have become adsorbed during the previous electrolysis) using a 0.1 mol L$^{-1}$ Na\textsubscript{2}SO\textsubscript{4} solution (supporting electrolyte) and the same current density of the degradation experiment itself. The investigated current density values were 5, 15, and 30 mA cm$^{-2}$, whereas all other parameters were kept constant: volumetric flow ($q_v = 7.0$ L min$^{-1}$), temperature ($\theta = 25$ °C), and solution volume ($V = 0.5$ L).

During the AY49 degradation electrolyses, the solution was sampled at specific times to monitor its decolorization and degrees of oxidation (chemical oxygen demand – COD) and mineralization (total organic carbon content – TOC). UV-vis spectra were obtained using a Hewlett Packard (model 8453) spectrophotometer, in the range of 190 – 820 nm, with the maximum adsorption for the AY49 dye occurring at 400 nm due to its azo chromophore. The decolorization efficiency was evaluated using the spectral absorption coefficient: $DFZ = [A(\lambda) / l]$, where $A(\lambda)$ is the absorbance at $\lambda = 436$ nm and $l$ the measuring cuvette thickness, in mm [method B, in reference 49]. Additionally, COD determinations were carried out by dichromate oxidation, using a Hach (model DRB 200)
digestor and a Hach (model DR/2010) spectrophotometer, whereas COT determinations were done using a Sievers Innovox Laboratory TOC Analyzer from GE Analytical Instruments.

3. RESULTS AND DISCUSSION

The efficiency of the electrochemical degradation of the AY49 dye was first evaluated through its decolorization. For such, the decay of the absorbance of the dye solution at the maximum absorbance wavelength (400 nm) was monitored as the electrolysis progressed. Figure 2 shows spectra obtained throughout specific electrolyses carried out at \( j = 30 \text{ mA cm}^{-2} \) for each anode material (see figure legend). From these spectra, it is clear that the absorption band centered around 400 nm decreases as each electrolysis advances, the same being true for the UV bands that are related to aromatic transitions (\( \pi \rightarrow \pi^* \)); however, this decrease is much less marked when the DSA® anode is used. From these spectra, values of the relative absorbance at \( \lambda = 400 \text{ nm} \) may be calculated as a function of time \( (A_{rel} = A_t / A_{r0}) \). Hence, Figure 3 shows plots of \( A_{rel} \) as a function of the applied electric charge per unit volume of the electrolyzed solution \( (Q_{apl}) \), for electrolyses carried out at \( j = 5, 15, \) and \( 30 \text{ mA cm}^{-2} \) using the different anode materials. In all cases, there is a gradual decolorization \( (A_{rel} \) decreases) of the AY49 dye solution, but significantly higher decolorization rates are attained with the \( \beta \)-PbO\(_2\) and, foremost, BDD anodes than with the DSA® anode. When \( j = 15 \text{ mA cm}^{-2} \) is used (Fig. 3b), about 99% decolorization is attained with the BDD anode, whereas comparable decolorization degrees are attained with the BDD and \( \beta \)-PbO\(_2\) anodes only for \( j = 30 \text{ mA cm}^{-2} \), as it has been reported before for the case of the Reactive Blue 19 dye [24]; actually, at this current density (see Fig. 3c) the decolorization performance attained with these electrodes is quite similar. On the other hand, analogously to results previously reported for the electrochemical degradation of other dyes [23,50], the decolorization performance attained with the DSA® anode is much worse, at most about 60% of those attained with the other anodes. From these results, the importance of using higher oxidation power anodes becomes clear, since they present superior electrooxidation performances, here materialized as higher decolorization rates.

Taking into account the decolorization degrees attained with the three anodes (shown in Fig. 3), it is possible to assess their performances to attain 50% decolorization of the AY49 dye solution by comparing the respective values of \( Q_{apl} \) needed in each case (referred as \( Q^{50} \)). From these values (listed in Table 1 for the different anodes at the three current densities investigated), it is clear that the best performances (lower \( Q^{50} \) value) are always attained with the BDD anode, which has the highest oxidation power [44]. In fact, a \( Q^{50} \) value of only 0.09 A h L\(^{-1}\) is needed when using the BDD anode at the lowest current density investigated \( (j = 5 \text{ mA cm}^{-2}) \), whereas a twofold or sixfold \( Q^{50} \) value is needed when the \( \beta \)-PbO\(_2\) or DSA® anode is used. From analyses of the \( Q^{50} \) values listed in Table 1, one may also infer that the difference in performance between the BDD and \( \beta \)-PbO\(_2\) anodes becomes smaller as the current density is increased. Nevertheless, from the point of view of energy use, it is much better to operate at the lowest current density, when the performance of the BDD anode is significantly better.
Figure 2. UV-vis absorption spectra (190 – 820 nm) for solution samples collected at different times during electrolyses ($i = 30$ mA cm$^{-2}$) of a 100 mg L$^{-1}$ AY49 solution in aqueous 0.1 mol L$^{-1}$ Na$_2$SO$_4$ using the DSA® (a), β-PbO$_2$ (b), and BDD (c) anodes. Other experimental parameters in these electrolyses: $q_V = 7.0$ L min$^{-1}$, $\theta = 25$ °C, and $V = 0.5$ L.
Figure 3. Relative absorbance (at $\lambda = 400$ nm), $A_{rel}$, as a function of the applied electric charge per unit volume of the AY49 dye solution, $Q_{apl}$, for the electrochemical degradation of a 100 mg L$^{-1}$ AY49 solution in aqueous 0.1 mol L$^{-1}$ Na$_2$SO$_4$ using different anodes (indicated in the figures) at the current densities of 5 (a), 15 (b), and 30 (c) mA cm$^{-2}$. Other experimental parameters in these electrolyses: $q_v = 7.0$ L min$^{-1}$, $\theta = 25^\circ$C, and $V = 0.5$ L.
Assuming pseudo-first order kinetics for the decolorization process of the AY49 dye, the following equation can be used to obtain the values of the apparent decolorization rate constant \( k_{ap} \) for the electrolyses with the different anodes (data presented in Fig. 3):

\[
\ln \frac{A_t}{A_{t=0}} = \ln A_{rel} = -k_{ap}t
\]

As can be inferred from the \( k_{ap} \) values presented in Table 2, there is mainly an increase in the decolorization rate constants as the current density increases. Furthermore, for the BDD and DSA\(^{®}\) anodes the values of the rate constants are the same for the higher current densities, an indication that the latter are higher than the respective limiting current density for these anodes.

**Table 1.** Applied electric charge per unit volume of the AY49 dye solution \( (Q^{50}) \) needed to attain 50% decolorization by electrochemical degradation of a 100 mg L\(^{-1}\) AY49 solution in aqueous 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\), using different anodes and current densities \( (j) \). Other experimental parameters in these electrolyses: \( q_V = 7.0 \text{ L min}^{-1}, \theta = 25 \text{ °C}, \text{ and } V = 0.5 \text{ L} \)

<table>
<thead>
<tr>
<th>Anode</th>
<th>( j ) (mA cm(^{-2}))</th>
<th>( Q^{50} ) (A h L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSA(^{®})</td>
<td>5</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.94</td>
</tr>
<tr>
<td>( \beta)-PbO(_2)</td>
<td>5</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.55</td>
</tr>
<tr>
<td>DDB</td>
<td>5</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**Table 2.** Values of the apparent decolorization rate constant \( k_{ap} \) obtained with the three anodes at the different current densities \( (j) \) used in the electrolyses.

<table>
<thead>
<tr>
<th>( j ) (mA cm(^{-2}))</th>
<th>BDD ( k_{ap} ) ( (10^{-3} \text{ min}^{-1}) )</th>
<th>( \beta)-PbO(<em>2) ( k</em>{ap} ) ( (10^{-3} \text{ min}^{-1}) )</th>
<th>DSA(^{®}) ( k_{ap} ) ( (10^{-3} \text{ min}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>18</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>15</td>
<td>6.0</td>
</tr>
<tr>
<td>30</td>
<td>24</td>
<td>25</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Next, the decolorization efficiency attained with the different anodes at the end of the electrolyses was evaluated through the spectral absorption coefficient ($DFZ$) values at 436 nm. As can be inferred from the results shown in Table 3, lower $DFZ$ values are always attained with the BDD anode, whereas the highest values (reflecting a lesser decolorization capacity) are attained with the DSA® anode. Considering that the limiting $DFZ$ value is $7.0 \text{ m}^{-1}$ for the direct or indirect discharge of wastewater into water bodies, from the obtained results (see Table 3) we conclude that adequate decolorization degrees are attained with either the BDD or $\beta$-PbO$_2$ anode when a current density of 30 mA cm$^{-2}$ is used. However, when the current density is lowered to half that value (15 mA cm$^{-2}$), an adequate decolorization degree is attained only if the BDD anode is used. Clearly, the decolorization capacity of the BDD anode is much superior to those of the other anodes; even when a current density of only 5 mA cm$^{-2}$ is used, the $DFZ$ value attained with this anode ($7.1 \text{ m}^{-1}$) is practically the same as the limiting one. Thus, for further experiments, this current density was chosen because it means significantly lower energy consumption.

Table 3. $DFZ$ values of the AY49 dye solution after applying different electrical charges per unit volume of the solution ($Q_{apl}$) with the three anodes at different current densities ($j$)

<table>
<thead>
<tr>
<th>$j$ (mA cm$^{-2}$)</th>
<th>BDD ($DFZ$ (m$^{-1}$))</th>
<th>$\beta$-PbO$_2$ ($DFZ$ (m$^{-1}$))</th>
<th>DSA® ($DFZ$ (m$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5*</td>
<td>7.1</td>
<td>14.9</td>
<td>84.7</td>
</tr>
<tr>
<td>15**</td>
<td>2.0</td>
<td>10.1</td>
<td>78.6</td>
</tr>
<tr>
<td>30***</td>
<td>2.0</td>
<td>3.4</td>
<td>75.9</td>
</tr>
</tbody>
</table>

$Q_{apl}$: * 0.60 Ah L$^{-1}$; ** 1.35 Ah L$^{-1}$; *** 2.70 Ah L$^{-1}$.

Decolorization might be an important parameter, which, however, provides no information on the reduction of the organic load of the solution. Hence, the organic load of the AY49 solution was monitored through $COD$ and $TOC$ determinations for electrolyses at $j = 5 \text{ mA cm}^{-2}$. As can be seen in Fig. 4, the BDD anode yields the highest reductions in the organic load; for a $Q_{apl}$ value of 0.60 Ah L$^{-1}$, the solution $COD$ decreases by more than 35%, whereas for a $Q_{apl}$ value of 1.2 Ah L$^{-1}$, the solution $TOC$ decreases by about 20%. Comparing the results in Figs. 4a and 4b, one may infer that the rate of $TOC$ abatement is about half that of the $COD$ abatement. Once again, the DSA® anode yields the worst results, due to its low electrooxidative capacity. Comparing the decolorization (Fig. 3c) and organic abatement (Fig. 4) rates attained with the BDD anode, clearly it is much easier to decolorize the AY49 dye solution than to abate its organic load. This is certainly due to the quite complex nature of the AY49 molecule (see Fig. 1), a characteristic common to most dye molecules. Similar results have been previously reported for other dye solutions or wastewaters [17,20,31], i.e. the need to use much greater values of $Q_{apl}$ to attain a significant degree of organic load abatement than those necessary to attain an adequate degree of decolorization.
Figure 4. (a) Relative chemical oxygen demand, $\text{COD}_{\text{rel}} (=\text{COD}_t / \text{COD}_{t=0})$, and (b) relative total organic carbon content, $\text{TOC}_{\text{rel}} (=\text{TOC}_t / \text{TOC}_{t=0})$, as a function of the applied electric charge per unit volume of the AY49 dye solution, $Q_{\text{apl}}$, for the electrochemical degradation of a 100 mg L$^{-1}$ AY49 solution in aqueous 0.1 mol L$^{-1}$ Na$_2$SO$_4$ using different anodes (indicated in the figures) at a current density of 5 mA cm$^{-2}$. Other experimental parameters in these electrolyses: $q_V = 7.0$ L min$^{-1}$, $\theta = 25$ °C, and $V = 0.5$ L

4. CONCLUSIONS

The results of an investigation of the electrochemical oxidation of the AY49 dye using either a DSA®, β-PbO$_2$ or BDD anode in a flow filter-press reactor have been presented. To the best of our knowledge, this is the first report in the literature on the degradation of this specific dye by any means. We showed that solutions of this dye can be electrochemically decolorized; indeed, the color of a 100 mg L$^{-1}$ solution was adequately abated to fulfill the disposal requirements of the DIN-7887/94 standard, applying electrical charges per unit volume of dye solution ($Q_{\text{apl}}$) only slightly higher than
In general, the best performances were attained with the BDD anode and the worst with the DSA® anode. The electrochemical decolorization process followed pseudo-first order kinetics, with the best conditions (lower energy expenditure) being attained using a current density of only 5 mA cm$^{-2}$. Using this same current density, COD and TOC abatements of 37% and 20% were attained with $Q_{apl}$ values of only 0.60 and 1.20 A h L$^{-1}$, respectively; this indicates the feasibility of abating the organic load of the dye solution by simply increasing the value of $Q_{apl}$. The rate of degradation of the AY49 dye attained with the DSA®, β-PbO$_2$, and BDD anodes increases as the oxidation power of these electrodes increases, i.e. as the strength of the interaction of electrogenerated hydroxyl radicals with the electrode surface becomes weaker, rendering these radicals more active toward the oxidation of the dye molecule.

ACKNOWLEDGEMENTS

Financial support and scholarships from the Brazilian funding agencies CNPq (National Council for Scientific and Technological Development) and FAPESP (São Paulo Research Foundation – process no. 2012/13002-9) are gratefully acknowledged. The provision of the DSA® anode by De Nora do Brasil is also gratefully acknowledged. Finally, Professors Antonio A. Mozeto, Pedro S. Fadini, and Alzir A. Batista (DQ-UFSCar) are gratefully acknowledged for granting access to different apparatuses.

References