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Electrodegradation of Azo Dyes Using the Oxide $BaPb_{0.9}Sb_{0.1}O_{3-\delta}$ as Anode Material

M.J. Pacheco,[a] **M.L.F. Ciríaco,**[a] **A. Lopes,**[a,*] **I.C. Gonçalves,**[a]
M.R. Nunes,[b] **M.I. Pereira**[b]

[a]*Dep. of Chemistry, University of Beira Interior, 6201-001 Covilhã, Portugal*
[b]*Dep. of Chemistry and Biochemistry, CITECMAT, FCUL, 1749-016 Lisboa, Portugal*

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Abstract

The electrochemical oxidation of four different azo dyes, C.I. Acid Orange 7 (AO7), C. I. Direct Red 254 (DR254), C. I. Direct Red 80 (DR80) and Yellow Gold Sandolan (YGS), was performed using as anode material an oxide with a perovskite like structure, $BaPb_{0.9}Sb_{0.1}O_{3-\delta}$. Bulk electrolysis was studied using Na_2SO_4 as electrolyte, at a current density of 5 mA cm^{-2}.

UV-Visible absorbance measurements, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and High Performance Liquid Chromatography (HPLC) analysis were performed, in order to follow the colour and COD removals and the mineralization index.

The obtained results show an almost complete colour removal for the solutions containing AO7, DR254 or DR80, after 24 h essay. For these dyes, after 96 h electrodegradation experiment, COD removals between 30 and 70 % and TOC removals ranging from 15 to 40 % were obtained. However, for the experimental conditions used, the electrodegradation of YGS was not possible.

Keywords: C. I. Acid Orange 7, C. I. Direct Red 80, C. I. Direct Red 254, Yellow Gold Sandolan, azo dyes, electrochemical degradation, perovskite.

Introduction

The colour and organic load removals from the effluents of textile and paper industries are, nowadays, a priority. In particular, dyes released to the environment by these effluents present a serious problem that has to be solved [1-3]. Therefore, when biologic methods to treat the effluents fail or generate

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[*] Corresponding author. E-mail address: analopes@ubi.pt

muthagenic and carcinogenic dye metabolites, an alternative or sequential process must be performed. The use of electrochemical degradation techniques, as a tertiary treatment, can be a solution for the pollution problem, leading to the mineralization of the recalcitrant and hazardous compounds [4-11].

The choice of the material to be used as anode in electrodegradation essays is very important, and aspects concerning its efficiency, chemical and mechanical stability in working conditions and its durability, are fundamental subjects that have to be studied. Besides this important request, its cost is also a determining aspect for its applicability, being the main reason why noble metals are being replaced by lower cost materials, namely by metallic oxides presenting conductor electric behaviour.

Metallic oxides that present perovskite like structure, ABO_3, can be used for some technological applications, namely as anode materials [12, 13]. Several perovskites were already applied as material for electrocatalysis in O_2 and Cl_2 evolution, since they possess electrochemical stability in basic solutions, suitable electric conductivity and wide potential window [14, 15]. These characteristics can make them potentially good materials to be used as anodes for the oxidation of organic compounds.

In the present work, the study is focused on the electrochemical degradation of several azo dyes using as anode material an oxide with a perovskite like structure, $BaPb_{0.9}Sb_{0.1}O_{3-\delta}$.

Experimental details

Electrodes preparation

The $BaPb_{0.9}Sb_{0.1}O_{3-\delta}$ powder samples were prepared by conventional solid-state reaction [16]. Stoichiometric amounts of $BaCO_3$, PbO_2 and Sb_2O_3 were mixed and ground in an agate mortar and heated at 1123 K in a tubular furnace for 48 h; intermediate regrinding was carried out. The formation of single phase was ascertained by X-ray powder diffraction studies recorded using a Philips X-ray diffractometer PW 1730 with automatic data acquisition (APD Philips v3.5B). The operating conditions were 40 mA and 30 kV, using Cu kα radiation (λ= 0.15406 nm).

The perovskite electrode discs were prepared by pressing the powders into a 1.3 cm^2 geometric area pellet, which was sinterized at synthesis temperature, for 12 hours. The ohmic contacts were done gluing a silver disc (with a welded copper wire) to the pellet with a silver epoxy resin. This device was mounted in a glass tube with an epoxy resin (Fig.1).

Cyclic voltammetric studies

Cyclic voltammetric (CV) experiments were run, in aqueous solutions containing 5 g L^{-1} Na_2SO_4, in the absence and in the presence of 350 mg L^{-1} of the respective dye, deaerated with bubbling N_2. These studies were carried out in a three electrode cell using an Ag/AgCl reference electrode, a Pt disc counter electrode and a perovskite pellet working electrode. The cell was connected to a potenciostat/galvanostat Voltalab, 40 model PGZ301. The curves were recorded in the potential region from –0.5 to 2.5 V, at a potential sweep rate of 100 mV s^{-1}.

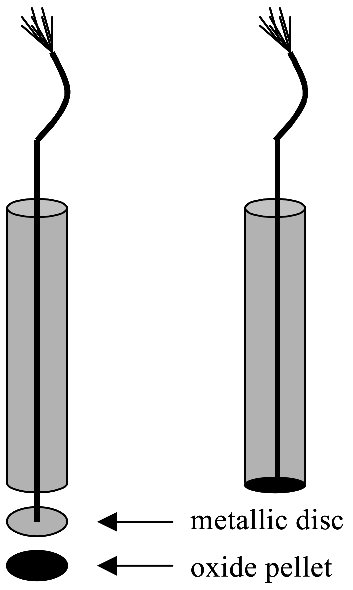


Figure 1. Working electrode preparation.

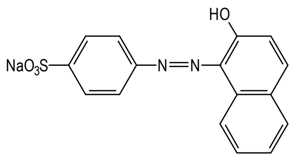
Electrodegradation experiments

The electrochemical treatments were performed in a one-compartment cell using a power source (GW, Lab DC power supply, Model: GPS-3030D). The perovskite electrode disc was used as anode and a platinum foil, with 2 cm^2 geometric area, as cathode. The applied current density was 5 mA cm^{-2} and the experiments duration was 96 hours.

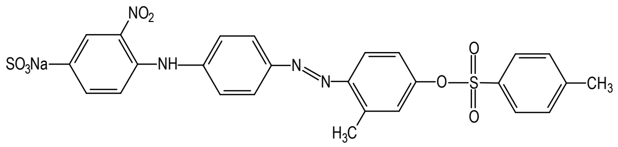
As the effluents from textile and paper industries usually present high sulphate content, sodium sulphate with a concentration of 5 g L^{-1} was chosen as electrolyte. The dyes used (Fig.2) were C.I. Acid Orange 7 (P.A., +85%, Aldrich), Yellow Gold Sandolan MF-RL SGR (64 %, Clariant), both monosulphonated azo dyes, C.I. Direct Red 254 (Fastusol Rot 50L, BASF), a diazo dye, and C.I. Direct Red 80 (P.A., +70%, Ciba Geigy) a poliazo dye, with initial concentrations of 350 mg L^{-1} and a solution volume of 125 mL.

During the degradation tests, dye concentration was followed by spectrophotometry, using a UNICAM Heλios-α UV/VIS spectrophotometer. A dye free cell was used as control.

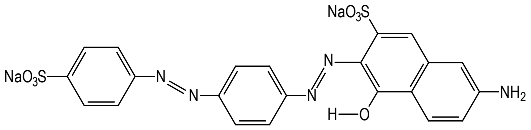
The trend of oxidation was monitored by Chemical Oxygen Demand (COD) determinations, according to standard procedures (American Public Health Association, 1995) [17], and the Total Organic Carbon (TOC) content was also measured (Shimadzu TOC analyzer, model TOC-VCPH/CPN) in order to follow the mineralization index of the organic compounds, defined as TOC/COD ratio.



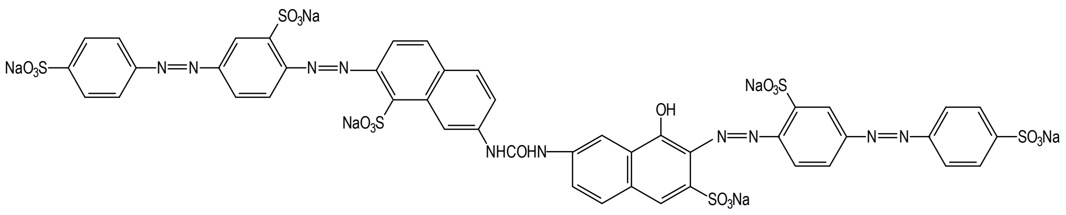
C.I. Acid Orange 7



Yellow Gold Sandolan



C.I. Direct Red 254



C.I. Direct Red 80

Figure 2. Chemical structures of the dyes Acid Orange 7, Yellow Gold Sandolan, Direct Red 254 and Direct Red 80.

All the essays were replicate, and COD and TOC values presented are the average of the results obtained in the different runs.

Both dye and metabolite concentrations were followed by HPLC in a Spectra-Physics (Germany) system equipped with a gradient pump, a reversed-phase column RP-18 (i.d. 4.6 mm, length 250 mm, stationary phase particle size 10 μm) and a UV (Diode-Array) detector at 240 nm. The eluents consisted of a phosphate buffer solution (0.70 g/L NaH_2PO_4 and 0.58 g L^{-1} $NH_4(H_2PO_4)$ (A) and methanol (B). The linear gradient elution ranged from A/B (85/15) to A/B (20/80) in 45 minutes with a flow rate of 1 mL min^{-1} and 20 μL injection volume. The eluents and the samples were previously filtered. The identification of the azo dyes was achieved by comparison of retention times to those of the respective standards.

Results and discussion

Fig. 3 presents cyclic voltammograms recorded, between the hydrogen and oxygen evolution potentials, in sodium sulphate solutions, in the presence and absence of the studied dyes. In the absence of dyes, the curves present a shoulder, just before oxygen evolution, which was assigned to the oxidation of the sulphate to the persulphate, in solution, on the basis of the calculated equilibrium potential for this process at pH=7 (1.724 V vs. Ag/AgCl) [18]. In the presence of dyes, similar patterns were observed; no extra oxidation or reduction peaks were recorded, within the same potential window, indicating that no other redox processes occur in this potential range.

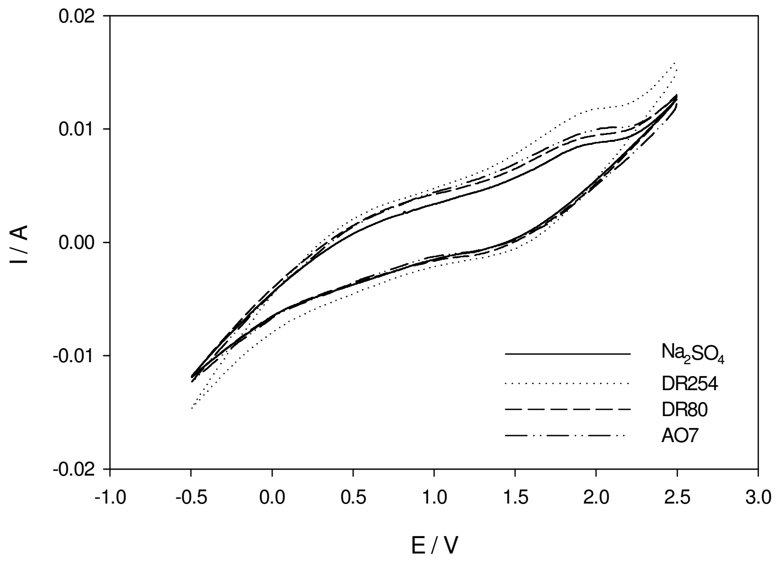


Figure 3. Cyclic voltammograms for the systems $BaPb_{0.9}Sb_{0.1}O_3$ / Na_2SO_4 (5 g L^{-1}) and $BaPb_{0.9}Sb_{0.1}O_3$ / Na_2SO_4 (5 g L^{-1}) + dye (0.35 g L^{-1}). Sweep rate 100 mV s^{-1}; working electrode geometric area 1.3 cm^2.

In Fig. 4, the UV-Visible spectra for the electrodegradation of the different dyes studied are presented. For the essays with AO7, DR254 and DR80 we can observe a strong decrease of the absorvance in the visible region during the first 24 h (≥ 95 % colour removal). This is due to the break of the azo bonds that absorb in this region. Analyzing the UV zone, we can see that the absorbing bands, characteristics of the aromatic groups, also have a decrease, but not so sharp. At the 24 h spectra, we can even observe an increase in the absorbance in this region, resulting from the concentration of aromatics that augments whenever an azo bond is broken. These findings are in accordance with a degradation mechanism that has as first step the break of the azo bond, followed by the complete combustion of the resulting aromatic metabolites.

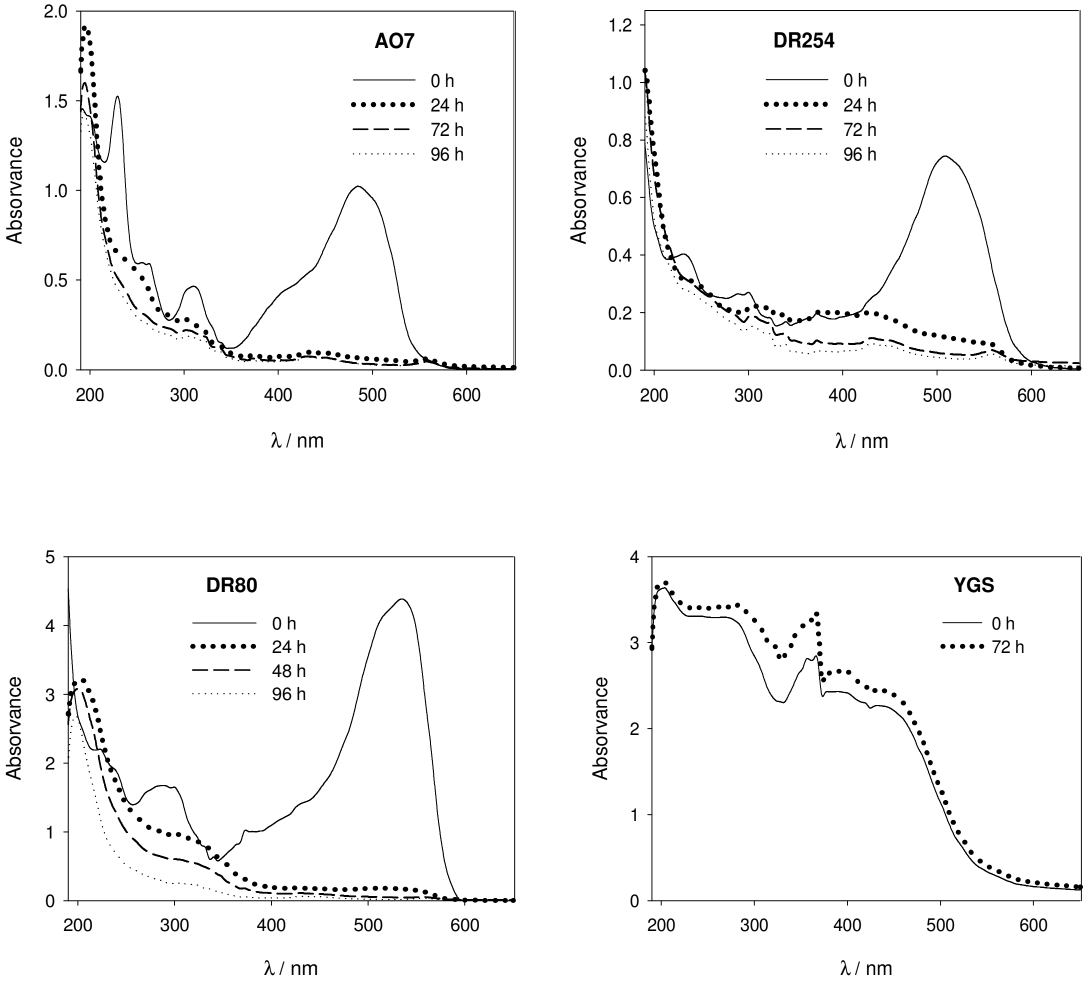


Figure 4. UV-Visible spectra of the electrochemical degradation of the dyes AO7, DR254, DR80 and YGS at different times.

According to Panizza *et al.* [19], when using high oxygen overvoltage anodes hydroxyl radicals can be electrogenerated from water. These radicals have a very important role in the complete mineralization of the organic molecules, since the oxidation reaction can take place in bulk with increased rate, especially when the concentration of dye is low and the process at the anode would become diffusion controlled. This increase in the oxidation rate promoted by hydroxyl radicals also decreases the probability of organic molecules reaching the cathode, to be reduced there. This way, the probability of other reactions than the hydrogen evolution to happen in the cathode is very limited. This fact is corroborated by the decrease in COD verified during the degradation process.

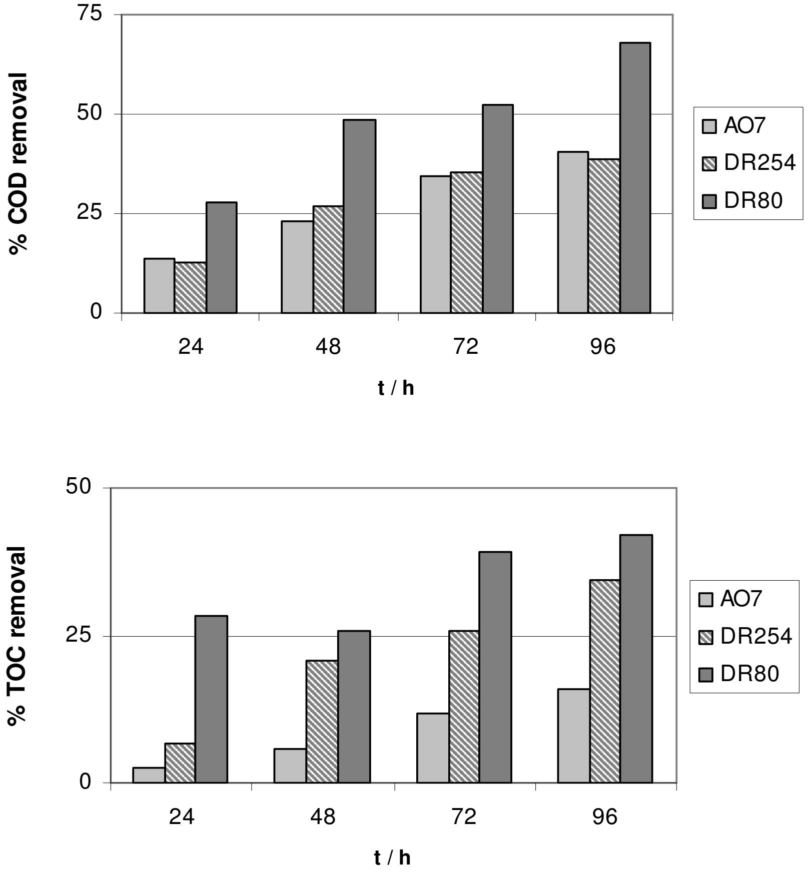


Figure 5. COD and TOC removals as a function of the essay duration for the electrochemical degradation of the dyes AO7, DR254 and DR80.

For the YGS, the UV-Visible spectra (Fig. 4) show an increase in absorbance, probably due to the solvent evaporation, thus indicating that, despite YGS being an azo dye, this electrodegradation was not well succeeded. The main dissimilarity observed during the experimental runs for this dye was the potential difference between anode and cathode, which was around 2 V for the essays with YGS and higher than 3 V for the experiments with the other dyes. In fact, the electrodegradation of this dye was already accomplished at a boron doped diamond anode, with much higher current densities [20]. Apparently, at the lower current densities used in this work, the organic compounds involved (dye and impurities) form a polymer at the electrode surface, with a resulting fouling. However, when very high current densities are used, with high overpotentials, the anode surface can be kept cleaned by the oxygen evolution, being the degradation mechanism mostly promoted by hydroxyl radicals.

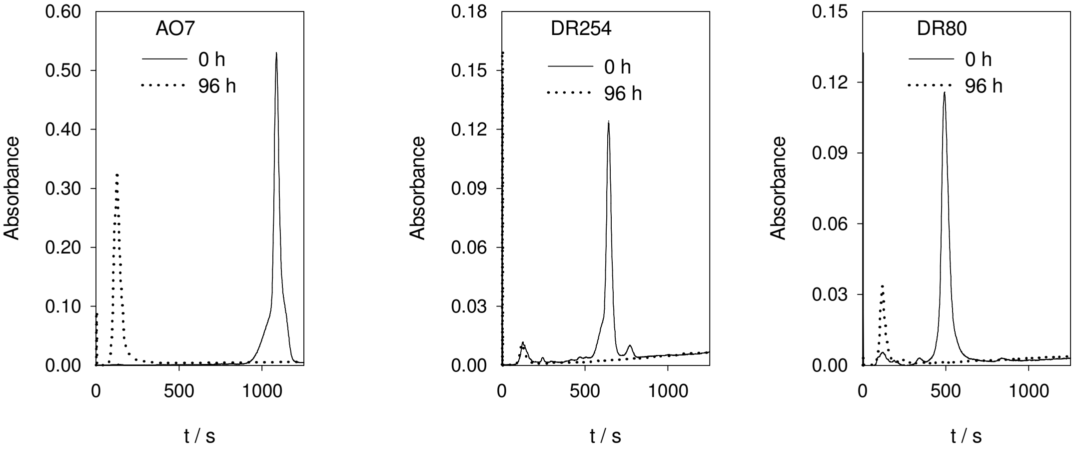


Figure 6. HPLC results for the electrochemical degradation of the dyes AO7, DR254 and DR80 at the beginning and the end of the essays.

The decrease in absorbance with time for the AO7, DR254 and DR80 degradation essays goes along with the removal of COD and TOC (Fig. 5), but in a smaller extent. This figure also shows a decrease in COD higher than the decrease in TOC, pointing to a degradation mechanism involving several intermediate species that undergo oxidation more easily than mineralization. Only for DR254, COD and TOC removals are identical (38 and 34 %, respectively). This fact can be due to the substituting groups that may slow down the oxidation reaction or speed up the mineralization mechanism. Among these dyes, DR80 is the one that experiences the fastest degradation reaction, probably due to the fact that it possesses 4 azo bonds. Therefore, once the azo bonds are broken, the resulting augment in aromatics concentration will increase the efficiency of the electrodegradation.

The HPLC results (Fig. 6) also indicate an almost complete removal of the initial dye from the solution, after 96 h essay, and the appearance of new species, with lower retention time. The peaks due to these species also display a regular decrease with time (data not shown). The final HPLC result for AO7 electrodegradation presents a signal higher than those for the oxidation of the other dyes. This fact is probably due to the lower TOC removal for AO7, meaning less mineralization and, consequently, an increased concentration in degradation metabolites.

Regarding the perovskite behavior as anode, when used with current densities up to 5 mA cm^{-2} the electrode presents a good mechanical and electrochemical stability, allowing its use for more than 240 hours with reproducible results. However, for current density of 10 mA cm^{-2} the oxygen evolution increases significantly and, after 120 hours use, some cracks in the surface can be observed.

Conclusions

The results of this study provide support for using the perovskite $BaPb_{0.9}Sb_{0.1}O_{3-\delta}$ as an anode material available for the electrodegradation of the azo dyes AO7, DR254 and DR80. For these dyes, the color removal after 24 h was higher than 95 %, corresponding to the break down of the azo bonds (-N=N-) that absorb in the visible zone. These results are in accordance with HPLC results.

COD and TOC removals are compatible with a mechanism that involves first the break of the azo bond, followed by a gradual oxidation of the metabolite species, prior to the final mineralization.

The electrochemical degradation of Yellow Gold Sandolan was not well succeeded with this oxide electrode, at the applied experimental conditions.

Acknowledgements

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