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Decontamination of real textile industrial effluent by strong oxidant species electrogenerated on diamond electrode: Viability and disadvantages of this electrochemical technology

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ABSTRACT

In a previous work [1], the treatment of dye solutions containing Remazol Red BR (RRB) and Novacron Blue C-D (NB) by anodic oxidation using boron doped diamond anode (BDD) demonstrated that the electrochemical treatment is an efficient alternative for removing color and chemical oxygen demand (COD) and this technology can be used for depuration of real effluents. More recently, these assumptions have been confirmed by oxidizing electrochemically a real textile effluent using BDD anode [2]. Then, as a further development of the research carried out in these previous studies [1,2], in the present work, it has been considered appropriate to extend the investigation to the anodic oxidation, using BDD anode, of a specific real effluent discharged by Brazilian textile industry, adding Na₂SO₄ or NaCl salts in order to verify the applicability of this treatment producing in situ strong oxidant species (peroxodisulfates or active chlorine, respectively).

In this study, we also attempt to discuss critical evidence about the viability of peroxodisulfates or active chlorine. Results obtained in this research clearly demonstrated that the effect of the electrogenerated strong oxidant species, peroxodisulfates or active chlorine, depends on electrocatalytic mechanism followed on BDD surface, improving the color and COD removal. However, there is a limit of NaCl for treating real effluents avoiding the formation of organochloride compounds; and it is a subject of critical importance, from the environmental point of view, to apply this alternative treatment.

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1. Introduction

In the last years, many research groups have demonstrated that boron-doped diamond (BDD) anodes allow complete mineralizations up to near 100% of current efficiency (because it has several technologically important characteristics including an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high O_2 evolution overvoltage) of a large number of organic pollutants, such as carboxylic acids, benzoic acid, cyanides, cresols, herbicides, drugs, naphthol, phenolic compounds, polyhydroxybenzenes, polyacrylates, surfactants, etc.; as summarized and discussed by authoritative reviews [3–7].

A considerable number of laboratories have also investigated the applicability of BDD anodes for the electrochemical treatment of

wastewaters and the number of related publications has increased rapidly [6]. Among them, the electrochemical treatment of aqueous wastes containing dyes (dyes solutions, synthetic and actual wastewaters) have created great interest [8] because BDD anode has been defined as non-active electrode, since it is expected that it do not provide any catalytically active site for the adsorption of reactants and/or products in aqueous media [6]. Hydroxyl radical (BDD(•OH)) formed from water discharge on its surface from reaction: $H_2O \rightarrow •OH + e^- + H^+$, is then considered the responsible species for the electrochemical combustion of organic pollutants, although slower reactions with other reactive oxygen species (H_2O_2 and O_3) and electrogenerated oxidants (active chlorine, peroxodisulphate, peroxodicarbonate or peroxodiphosphate) are also feasible [3,5–7].

Taking into consideration the above information, many electrochemical studies for depuration of wastewaters containing dyes (dyes solutions, synthetic and real textile effluents) have been performed for studying the influence of chloride, sulphate and phosphate in the depuration rate process using BDD anodes

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[3,8–14]. However, no attempts have been published concerning to the electrochemical treatment of real textile effluent, comparing the efficiency of the strong oxidant species produced in situ and their disadvantages. For these reasons, this research aims to test the performance of electrochemical treatment process using BDD anodes as an alternative to treat a real textile effluent in order to reduce dye-contamination and strong color, comparing the influence of the strong oxidant species electrogenerated on its surface (peroxodisulfates or active chlorine) and getting more attention on the intermediates produced during degradation to determine its environmental viability.

2. Materials and methods

2.1. Real effluent characteristics

The effluent sample was mainly composed of Remazol Red BR (RRB), Novacron Blue C-D (NB), amylum and different additives (specific textile coloration process involving NB and RRB; two dyes widely used in a Northeast Brazilian Textile industry [1]). This effluent contained a high concentration of COD (1018 mg dm⁻³) and Hazen Units (7504 HU). Its conductivity was 5.90 mS cm⁻¹ and pH was around 12.4. It is worth noting that these conditions were determined from the effluent without any physical–chemical treatment (effluent directly obtained after textile coloration process).

2.2. Electro-oxidation experiments

Bulk oxidations were carried out in an undivided electrochemical cell, the reaction compartment having a capacity of 0.5 L. The anodic oxidation experiments of real textile effluent were performed under galvanostatic conditions using a VERSTAT3galvanostat (Princeton Applied Research). BDD anode (synthesized as described in Ref. [15]) was supplied by Adamant Technologies (Neuchatel, Switzerland). BDD was used as the anode, and titanium as the cathode. Both electrodes were square, each with 10 cm² geometrical area. Experiments were performed at 25 °C for studying the role of salts dissolved in the effluent by applying current densities (*j*) of 20, 40 and 60 mA cm⁻², while the temperature effect (25, 40 and 60 °C) was studied under current densities of 40 and 60 mA cm⁻². The temperature of the electrolyte was controlled using a water thermostat.

2.3. Analytical methods

Color removal was monitored by measuring absorbance decrease; using a UV 1800 Shimadzu spectrophotometer. Experimentally, decolorization process was determined by the expressions (1) and (2) reported in the first part of this work [1]. Hazen Units (HU) were determined using a spectrophotometer (Hach Model DR/2500) calibrated with a method 8025 (Pt-Co units) [16]. pH variation was measured using a Methrom pH meter. Decontamination of real effluent was monitored from the abatement of their COD. Values were obtained, using a HANNA HI 83099 spectrophotometer after digestion of samples in a HANNA thermo-reactor. The energy consumption was estimated considering the volume of effluent treated (kWh m⁻³). The average cell voltage during the electrolysis is taken into consideration for calculating the energy consumption by expression reported in previous works [1,2]. The production of strong oxidants peroxodisulfates and active chlorine were confirmed for some experiments using the I_2/I^- titration and the N,N-diethyl-p-phenylenediamine (DPD) colorimetric methods, respectively [17,18].



Fig. 1. Electrochemical decolorisation process of a real effluent, as a function of time, applying different current densities values at $25 \,^{\circ}$ C (curve a: 60 mA cm⁻², effluent as obtained; curve b: 20 mA cm⁻², 5 g of Na₂SO₄; curve c: 40 mA cm⁻², 5 g of Na₂SO₄ and curve d: 60 mA cm⁻², 5 g of Na₂SO₄). Inset: photographs showing color removal.

3. Results and discussion

3.1. Electrochemical treatment of a real textile effluent un-additional salts (as obtained from industry)

In the first part of this work [1], we have studied the application of the electrochemical oxidation of synthetic dye wastewaters (Remazol Red BR (RRB) and Novacron Blue C-D (NB)) using a BDD anode. This anode evidenced its great oxidation ability to remove the dissolved organic pollutants, requiring shorter electrolysis time to reach overall mineralization, leading higher current efficiencies and lower specific energy consumptions.

The good removal efficiencies suggest the possibility for using electrochemical oxidation as technology for treating real textile effluents. In fact, this anode has been previously used to treat electrochemically textile effluents [2,14,19]. However, each effluent was different, for this reason, it is not easy to compare the results. Then, a specific effluent of an actual Brazilian textile industry was employed to assess the efficiency on electrochemical treatment (using BDD anodes) as an alternative for removing organic matter and color.

As shown in Fig. 1 (curve a), the decrease of the absorbance, as a function of time, during galvanostatic electrolysis of real textile effluent (0.5 L) was monitored for the period of 12 h by applying 60 mA cm^{-2} of current density under original discharged effluent conditions ($T=25^{\circ}$). However, the Brazilian regulations [20] for color removal were not attained under these circumstances. No more than partial color removal was achieved ($\approx 21\%$ (5940 HU, see photos)), due to the low conductivity of the effluent and higher organic pollutant concentrations dissolved in the effluent (NB, RRB amylum and different additives), which increases the decolorisation time required for complete elimination. On the other hand, COD was partially removed, decaying from 1018 mg dm⁻³ to 890 mg dm⁻³, approximately 12.6%.

The effect of temperature was also studied, at 60 °C by applying $60 \text{ mA} \text{ cm}^{-2}$, mimicking the real temperature utilized to discharge effluents by the textile industry. It was observed that increasing the effluent temperature from 25 °C to 60 °C, the COD abatement remains very similar. This can be justified because the effects are expected to be merely due to hydroxyl radicals generated at the electrode surface, and changes of temperature affect incineration rate through the electrochemical water oxidation together with the parasite reactions consuming OH radicals.

Although the applicability of this treatment seems feasible, long time would be required to complete decolorisation and organic Download English Version:

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