



Influence of mediated processes on the removal of Rhodamine with conductive-diamond electrochemical oxidation



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ABSTRACT

The influence of the mediated oxidation on the removal of Rhodamine B (xanthene dye) solutions with conductive-diamond electrochemical oxidation (CDEO) is studied. To do this, four different supporting electrolytes have been used: Na₂SO₄, HClO₄, H₃PO₄ and NaCl. Total removal of organic pollutants is attained with CDEO regardless of the supporting electrolyte media used, although media clearly influences on efficiency and rate of the processes. Sulfate and phosphate media show a similar behavior, whereas electrolysis in perchlorate media behaves surprisingly better than chloride media. Current density is playing an important role. In all cases, CDEO follows a first order kinetic (linear trend in semi logarithmic plot) and kinetic constants are generally much greater than expected according to a single mass transfer electrolytic model. This is not the expected result for a direct electrochemical oxidation process and it indicates the importance of mediated electrochemical processes in the removal of Rhodamine B. The harsh oxidation conditions of CDEO lead to the formation of less reaction intermediates than other technologies. The presence of short chain aliphatic acids is discarded, and the intermediates (aromatic acids) formed during the initial stages of the process are rapidly mineralized to carbon dioxide. In chloride media, chlorinated intermediates are also formed by the action of hypochlorite.

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1. Introduction

The treatment of textile effluents has given much attention in the last years because the discharge of highly pigmented synthetic dyes to the ecosystem causes significant damage to aquatic and human lives [1]. Conventional technologies are inefficient to remove these organics due to the high water solubility of dyes (in the case of using coagulation and precipitation) [2], and to the typical pH and salt concentration of dye effluents (in the case of using biological methods) [3]. In this point, Advanced Oxidation Processes appear as a good alternative for the treatment of synthetic dyes effluents. Among them, Fenton oxidation [4,5], photocatalysis [6,7], sonochemical degradation [8,9] and electrochemical technologies [10–17] have been widely studied in literature for the treatment of a great variety of dyes. In general, these technologies are able to attain very good results in terms of decolorization due to the rapid cleavage of chromophore group of the dye molecule [16]. However, mineralization efficiency shows a marked influence of

the oxidative capacity of each degradation technology. Generally, aromatic and aliphatic acids are the main intermediates detected during dye degradation process, although their maximum concentration depends on the conditions used in each case. In this point, recent works have shown that electrochemical oxidation, and in particular conductive-diamond electrochemical oxidation (CDEO), can be successfully applied with high organic removal rates and without important operational limitations [12,18–23]. The harsh oxidation conditions attained with CDEO are explained in terms of the oxidation mechanisms involved in the process. In this way, it is well documented that during CDEO a noteworthy production of hydroxyl radicals in the nearness of diamond surfaces takes place. These radicals are fully available for oxidizing reactions but their lifetime is very short and not enough to let them diffuse to the bulk solution [23]. Thus, the action of these radicals is limited to the short region close to the electrode surface where they are produced, and the kinetic of these processes is usually controlled by mass transport. Additionally, it is well documented the availability of CDEO to produce inorganic oxidants, which are difficult or even impossible to be produced with other different anodic materials, from the oxidation of supporting electrolyte [24–26]. In fact, some works have also been focused on the electrochemical synthesis with

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diamond anodes of powerful oxidants [27] such as persulfates [28], perphosphates [24], perchlorates [29,30] and hypochlorite [25,31]. Thus, besides direct electrooxidation on the surface and oxidation by means of hydroxyl radicals in a region close to the electrode surface, the oxidation mediated by other oxidants electrogenerated on the diamond surface from the electrolyte salts should be taken into account, as it seems to increase the global oxidation efficiency [19,32–34].

The dye under consideration is Rhodamine B (RhB). It is widely used in textiles, leathers and food stuffs with high water solubility [7,35]. Thus, this work focuses on the CDEO of synthetic Rhodamine B (selected as model of xanthene dyes with very good stability) solutions in different supporting media in order to increase the understanding of the role of mediated oxidation on the degradation process.

2. Materials and methods

2.1. Chemicals

RhB was supplied by Sigma–Aldrich Laborchemikalien GmbH (Steinheim, Germany). Anhydrous sodium sulfate, sodium chloride, perchloric acid and phosphoric acid, used as supporting electrolytes, were analytical grade purchased from Fluka. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system, with resistivity > 18 MΩ cm at 25 °C. Sulfuric acid and sodium hydroxide used to adjust the solution pH were analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Analytical procedures

The Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer to estimate the mineralization grade ($[(\text{TOC}_0 - \text{TOC}_t)/(\text{TOC}_0)]$ where TOC_0 is the initial value and TOC_t is the measurement at different times during electrolysis). Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively. The concentrations of the compounds were quantified by HPLC (Agilent 1100 series). The detection wavelength used to detect dye was 248 nm. The column temperature was 25 °C. Volume injection was set to 50 μL. The analytical column used was Phenomenex Gemini 5 μm C18. The mobile phases were 0.9 mL of 98% formic acid in Milli-Q water for analyzing intermediates. Samples extracted from electrolyzed solutions were filtered with 0.20 μm Nylon filters before analysis. Moreover, the acids intermediates formed during the experiments were detected with a detection wavelength of 190 nm.

Chemical oxygen demand (COD) was performed by using pre-dosage vials with 2 mL of sample containing with mercury salts to eliminate the chloride interference up to 2000 mg dm⁻³.

Samples of electrolytes were extracted into non-aqueous medium (2 mL of CCl₄ HPLC grade with 20 μL of electrolysis sample) and were subjected to GC–MS analysis using GC-FOCUS and MS-ISQ Thermo Scientific to identify the intermediates following the conditions: GC: Varian column VF5 ms with a composition of 5% de fenil-arylene and 95% de dimetilpolisiloxane. Temperature program: 40 °C – 5 min; 12 °C/min – 100 °C; 10 °C/min – 200 °C and 10 °C/min – 270 °C – 5 min. Injector: 220 °C. Mode: Splitless. Gas flow: 0.8 mL/min. MS: Transfer line: 270 °C; ions source temperature: 220 °C, Mass range: 40–500 m/z. Injection: 1 μL.

2.3. Electrochemical cells

Electrolyses were carried out in a single compartment electrochemical flow cell working under a batch-operation mode

[32]. Conductive–Diamond Electrodes (p-Si–boron-doped diamond) were used as anode and a stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm² and an electrode gap of 9 mm. Boron-doped diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si <1 0 0> wafers (0.1 Ω cm, Siltronix).

2.4. Experimental procedures

Bench-scale electrolyses of 1000 cm³ of wastewater were carried out under galvanostatic conditions. The current density employed ranged from 15 to 120 mA cm⁻². The cell voltage did not vary during electrolysis, indicating that conductive-diamond layers did not undergo appreciable deterioration or passivation phenomena. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 10 min in a 0.035 M Na₂SO₄ solution at 15 mA cm⁻² to remove any kind of impurity from its surface.

The wastewater consisting of 100 mg dm⁻³ of Rhodamine B (initial TOC ≈ 71 mg dm⁻³ and initial COD = 210 mg dm⁻³) and different electrolytes (Na₂SO₄, HClO₄, H₃PO₄ and NaCl with similar concentration of 1000 mg dm⁻³) was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 21.4 dm³ h⁻¹). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point (25 °C).

3. Results and discussion

Fig. 1 shows the progress of the mineralization during electrolyses at two large current densities (60 and 120 mA cm⁻²) of synthetic wastewater consisting of aqueous solutions containing 100 mg dm⁻³ of RhB (≈ 71 mg dm⁻³ of initial TOC) and different electrolytes (Na₂SO₄, HClO₄, H₃PO₄ and NaCl). As it can be observed, total removal of organic pollutants can be attained with CDEO regardless of the supporting electrolyte media used, although media clearly influences on efficiency and rate of the processes, and current density is playing an important role. This is interesting because it confirms that CDEO is robust enough to deplete pollution but it also informs about the occurrence of different mechanisms of oxidation that should be related with the supporting media. Thus, although chloride media could be expected to show the best results because of the well-known production of chlorine (and then of hypochlorite and hypochloric acid), it attains the worst results and, in fact, it is the only case in which the complete mineralization is not attained for a current charge applied of 100 Ah dm⁻³. This behavior can be attributed to an interaction between hydroxyl radicals and Cl⁻ (chloride acts as scavenger of •OH) to form different active chlorine species on BDD surface [25,30,36] with this non-active material and to the formation of refractory species by chlorination. At the same time, the chloride concentration in the solution can also promote the importance of Cl₂ production at BDD surface, decreasing the Cl⁻, and consequently, the production of active chlorine species.

A very interesting observation is the effect of current density in the perchlorate test that shifts towards faster mineralization at higher current densities. Initially, it is strange because in that media no oxidants production is expected and perchlorate is not a good oxidant at room temperature so, it is not expected to participate in the oxidation. However, higher concentration of hydroxyl radicals are produced under these experimental conditions as well as it can be related to the nature of the hydroxyl radicals produced at different non-active anodes, as already proposed by Bejan and

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