



## Activation by light irradiation of oxidants electrochemically generated during Rhodamine B elimination



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### ABSTRACT

In this work, the role of chloro-species generated during the electrolysis of Rhodamine B (RhB) solutions containing chloride and perchlorate salts as supporting electrolytes was studied. Likewise, the effect of light irradiation in the activation of the oxidants is also evaluated. To do this, essays of electrolysis, photoelectrolysis, and chemical oxidation in the presence of light with the oxidant generated electrochemically were carried out. Results showed that RhB was effectively oxidized by electro-irradiated techniques. Color removal is faster than chemical oxygen demand (COD) and total organic carbon (TOC) removal, due to the rapid attack of chromophore group of the molecule. In general, light irradiation has a positive effect during the electrolysis of RhB at high current densities. In chloride media, light irradiation seems to favor the decomposition of hypochlorite produced. The effect of light irradiation is explained in terms of the activation of oxidants in the bulk of the electrolytic treatment by production of highly efficient radicals. Results of chemical oxidation essays may indicate that UV light irradiation has not a clear catalytic influence out of an electrolytic environment. The findings presented in this communication are described and discussed in the light of the existing literature.

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### 1. Introduction

In the recent years, the electrochemical treatment of dyes has demanded a special attention, focused mainly on the comparison of different anode materials, for example: Pt, PbO<sub>2</sub>, Ti/Pt, Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub>, and BDD anodes [1–4] or combination of different electrochemical technologies to remove dyes [1,5–11] (anodic oxidation with other processes such as oxidants production, ultraviolet light (UV) irradiation, ultrasound (US) irradiation, electro-Fenton (EF), photoelectro-Fenton (PEF) and so on).

The electrochemical treatment by direct or indirect approaches [10], is based on the elimination of pollutants directly on the anode surface or/and, via production of •OH [9–16] or additional oxidants [17–24], such as chlorine, (per)bromate, persulfate, ozone, hydrogen peroxide, percarbonate, and others, directly on-site using only water, salt, and electrical energy.

Nevertheless, the reactivity of many of the raw oxidants produced in electrochemical oxidation (EO) with organics is not very high and some sort of activation is often required to obtain a clear improvement of the process [10]. The formation of these highly reactive species (activated oxidants) from the oxidants contained in the wastewater is possible

by three different modes [10]: (i) chemical activation, (ii) activation by light irradiation and (iii) activation by ultrasound (US) irradiation.

In the first case, it involves the combination of the oxidant produced electrochemically with another species (not necessary an oxidant), which leads to the production of a third, very reactive species. This is the case of the well-known Fenton processes [9]. UV light irradiation promotes the formation of highly active species [25]. This irradiation can be applied naturally (solar driven) or artificially (using UV lamps). Then, the photoactivation (or light-assisted decomposition) of electrochemically generate reactive species, such as H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>, is attained [26–29]. Finally, US irradiation consists in the promotion of ultrasonic cavitation behavior [30]. This phenomenon takes place in a very short moment and space, increasing temperature and pressure [31]. After that, it can produce significant changes in chemical composition of the hot spot, and consequently promote the formation of new radical species and components, and so, it can increase the reactivity of the system [32].

Therefore, the aim of this work is to study the light irradiation activation of oxidants electrochemically generated at BDD anode when NaCl or HClO<sub>4</sub> are used as supporting electrolytes. Treatment of synthetic solutions containing RhB was performed in order to establish the mechanisms involved and their effect on the efficiency. It is important to mention that, RhB is widely used in textiles, leathers, and food stuffs with high water solubility [32,33], and for this reason, it was chosen as model organic pollutant.

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## 2. Material and methods

### 2.1. Chemicals

The chemical reagents used in this study were of high purity. RhB (98%) was supplied by Aldrich. Solution of  $7.04 \times 10^{-3}$  M NaCl or  $7.04 \times 10^{-3}$  M HClO<sub>4</sub> were prepared and after that, these electrolytes were used for preparing a solution of RhB with concentration of  $2.09 \times 10^{-4}$  M, for each experiment. All aqueous solutions were prepared using Milli-Q water.

### 2.2. Analytical procedures

Color removal was monitored by UV–visible technique using a UV-1603 spectrophotometer Model Shimadzu, at a wavelength of 550 nm. Chemical oxygen demand (COD) was performed by using pre-dosage vials with 2 mL of sample. For the analysis of total organic carbon (TOC), it was necessary for a minimum volume of 10 mL of each one of the samples to be analyzed. These analyzes were carried out in a TOC analyzer Multi N/C and the results obtained through the Analytikjena program. RhB samples before and after the treatments were collected and transferred to vials own high-resolution liquid chromatography (HPLC), injecting 50  $\mu$ L of each sample for analysis in Agilent 1100 HPLC (flow of 0.200 mL/min). Two columns were used for the analysis of intermediates generated during degradation of RhB. The mobile phases used for analyzing aromatics and aliphatic acids by HPLC technique were 0.9 ml of 98% formic acid in 1 dm<sup>3</sup> of water and a mixture of acetonitrile and water (1:1), respectively.

### 2.3. Bulk electrolysis

Electro-oxidation experiments were carried out in a flow electrochemical cell (undivided) with a BDD disk electrode and stainless steel as anode and cathode, respectively (each with 78 cm<sup>2</sup> of geometrical area). Experiments were carried out at 25 °C by applying a current density ( $j$ ) of 15 or 90 mA cm<sup>-2</sup> using a power supply to treat a 1 dm<sup>3</sup> of solution of RhB. Each one of the experiments was stopped when lower TOC values were attained. The spectrophotometric and HPLC analyses were performed for all samples.

### 2.4. Chemical oxidation tests

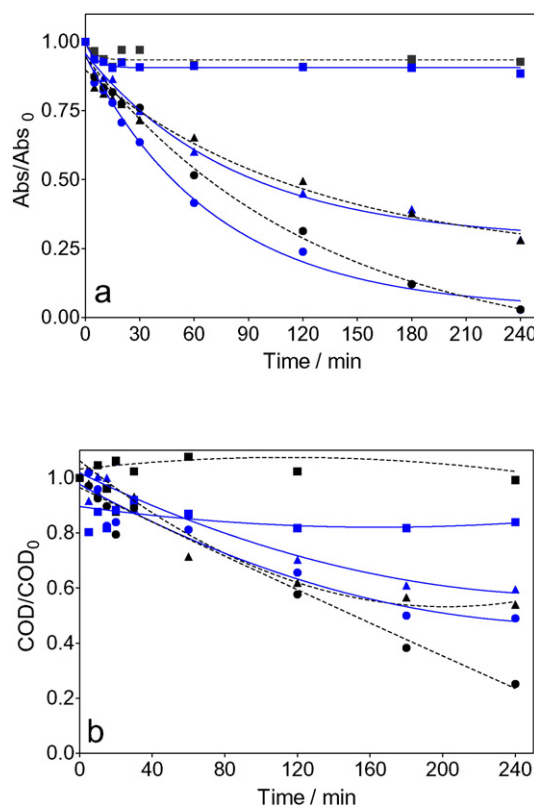
Solutions of oxidants were prepared by electrolyzing a solution of NaCl or NaClO<sub>4</sub> at 90 mA cm<sup>-2</sup> for 480 min. Then the resulting solutions were dosed to synthetic wastewater containing RhB to assess the chemical oxidation of this organic by the oxidants produced electrolytically, in absence or in presence of light irradiation.

### 2.5. Light irradiation

A UV lamp VL-215MC (Vilber Lourmat,  $\lambda = 254$  nm, intensity of 930  $\mu$ W/cm<sup>2</sup> and energy 4.43–6.20 eV (15 W)) was used to irradiate directly the quartz cover of the electrochemical cell (in the photoelectrolysis tests) or the beakers in which the chemical oxidation was carried out (in the photochemical oxidation test).

## 3. Results and discussion

Fig. 1 compares the removal of color (Fig. 1a) and COD (Fig. 1b) from wastewater containing RhB in HClO<sub>4</sub> by single photolysis, electrolysis, and photoelectrolysis. The changes observed in absorbance (about 5% in Fig. 1a (black dashed curve with black squares)) in the experiments without current and UV irradiation application may be related to the disaggregation of small colloids of RhB caused by the stirring of the solutions. As it can be observed, single photolysis only attains a very slight change in the color (about 10%, see Fig. 1a (blue squares)) and COD that



**Fig. 1.** (a) Color and (b) COD removal progress during the photolysis, electrolysis and photoelectrolysis of solutions containing RhB in HClO<sub>4</sub> by applying  $j = 0$  mA cm<sup>-2</sup> at (■) no UV irradiation, (■) UV irradiation;  $j = 15$  mA cm<sup>-2</sup> at (▲) no UV irradiation, (▲) UV irradiation and  $j = 90$  mA cm<sup>-2</sup> at (●) no UV irradiation, (●) UV irradiation.

it is negligible if compared to the results of electrolytic experiments (approximately 20% of decay, see Fig. 1b (blue squares)). The small absorbance removal observed during photolysis essays (when the solution is irradiated by UV light, without current application) can be related to the fragmentation of the chromophore group of RhB molecule by light irradiation [25,34]. Meanwhile, when an increase on the applied current is attained, removal efficiency is improved, in terms of color and COD (Fig. 1a and b) [35]. However, it is important to indicate that the irradiation of light does not contribute to improve the COD removal when current is applied (Fig. 1b (blue continuous curves with blue triangles and circles)), and it only seems to contribute to attack RhB molecule (Fig. 1a), favoring a slight decrease of absorbance respect to the tests by applying current. This observation can be related to the oxidation mechanism involved in the degradation process: direct and mediated processes carried out by oxidant electrogenerated in the system [22, 23,35]. In perchlorate media, no chlorinated-oxidants production is expected and perchlorate is not a good oxidant at room temperature so, it is not expected to participate in the oxidation [22]. However, hydroxyl radicals are produced during conductive diamond electrolysis [22] and these oxidant species are transformed into more stable oxidants by combining with other hydroxyl radicals (Eq. (1)) or oxygen (Eq. (2)) producing hydrogen peroxide or/and ozone [10].



Both ozone and hydrogen peroxide can be affected by UV light irradiation and they can regenerate the hydroxyl radical in the bulk under light irradiation (Eqs. (2) and (4)) [9,16]. This can help to explain

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