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 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. 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.

Keywords: Electrolysis, photoelectrolysis, chloride, Rhodamine B, diamond electrode.

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, PbO₂, Ti/Pt, Ti/Ru_{0.3}Ti_{0.7}O₂ 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_2O_2 or O_3 , 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_4 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.

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 7.04×10^{-3} M NaCl or 7.04×10^{-3} M HClO_4 were prepared and after that, these electrolytes were used for preparing a solution of RhB with concentration of 2.09×10^{-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 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 μ 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 dm³ 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 disc electrode and stainless steel as anode and cathode, respectively (each with 78 cm² of geometrical area). Experiments were carried out at 25°C by applying a current density (j) of 15 or 90 mA cm⁻² using a power supply to treat a 1 dm³ 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 NaClO₄ at 90 mA cm⁻² for 480 minutes. 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 $930 \mu\text{W}/\text{cm}^2$ and energy 4.43-6.20 eV (15 watts)) 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

Figure 1 compares the removal of color (Fig. 1a) and COD (Fig. 1b) from wastewater containing RhB in HClO_4 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 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 (Figures 1a and 1b) [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 (equation 1) or oxygen (equation 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. 3 and 4) [9,16]. This can help to explain the small improvements observed during the color decay in RhB elimination during photoelectrolysis (Fig. 1a) [34].

However, the concentration of hydroxyl radicals produced seem not be enough to remove organic matter dissolved in solution (Fig. 1b) during photoelectrolysis, or actually, the irradiation seems to favor the decomposition of oxidant species [27,34], decreasing the photo-electrochemical treatment efficiency respect to the electrolysis with BDD anode.

Figure 2 compares the removal of color (Fig. 2a) and COD (Fig. 2b) from wastewater containing RhB in NaCl as supporting media by single photolysis, electrolysis and photoelectrolysis. As it can be observed, in absence of current, the removal of color (Fig. 2a, squares) and COD (Fig. 2b, squares) is almost nil. However, in chloride media

when current is applied, the depletion of RhB molecule is almost instantaneous (very rapid removal of color (Fig. 2a, triangles and circles)), mainly in the electrolysis carried out at 90 mA cm⁻² (Fig. 2a, circles). In all cases, the COD decreases slower than absorbance (Fig. 2b) but significantly faster than the trend observed in the electrolysis carried out in perchloric media (Figure 1b).

Main differences between the treatment of wastes containing perchloric acid or chlorides derived from the oxidants produced [22,35]. In chloride media, it is expected the formation of hypochlorite and hypochloric acid (eqs. 5 and 6) whose role in the treatment of a great variety of wastewaters has been tested in literature [3,20-23,35]. Moreover, in the case of using diamond electrodes the formation of other chloro-species such as chlorite, chlorate and perchlorate is also expected depending on the operation conditions (eqs. 7 to 9) [21,35,36]. Nevertheless, at the light of the obtained results (Figs. 2a and 2b), active chlorine species seem to attack very rapidly RhB molecule to form chlorinated intermediates which are slowly degraded.

Moreover, the role of mediated oxidation seems to be more relevant at 15 mA cm⁻² than at 90 mA cm⁻². The high COD removal obtained in the electrolysis carried out at 15 mA cm⁻² can be attributed to an interaction between hydroxyl radicals and Cl⁻ to form different active chlorine species on BDD surface [20,22,35], improving the elimination of RhB and the by-products formed. Conversely, at 90 mA cm⁻², the formation of

refractory species by chlorination may be favored, and consequently, a slower decay of organic matter is attained (Fig. 2b).

Meanwhile, the use of light irradiation does not seem to contribute COD removal of electrolytic system (Fig. 2b, see blue curves of triangles and circles), being its effect very negative in the electrolysis carried out at 15 mA cm⁻². In this case, light irradiation effect on electrolysis should be focused on the decomposition of hypochlorite [28,29] to form hydroxyl and chlorine radicals as the main products resulting of the light assisted degradation of hypochlorite (eqs. 10 and 11).

Figure 3 shows the changes in the mineralization of the organic load (in terms of TOC removal) during the photolysis, electrolysis and photoelectrolysis of RhB solutions in perchloric acid (Fig. 3a) and chloride media (Fig. 3b). As it was observed, mineralization rates obtained in the essays carried out in perchloric media (Fig. 3a) are consistent with absorbance and COD changes shown in Figure 1. However, in this case, light irradiation favors mineralization process, mainly during the initial stages of the process when 90 mA cm⁻² were applied using BDD anode. Conversely to COD removal assumptions, the light irradiation favors the activation of oxidants to more stable species [25], favoring RhB mineralization. Probably, the measurements related to COD (Fig. 1b) were affected by the chemical reaction between dichromate with H₂O₂ produced at BDD anode, hiding significantly the effect of irradiation, when it was used.

On the other hand, mineralization results obtained during photolysis and photoelectrolysis (Fig. 3b) at NaCl by applying 90 mA cm⁻² are also consistent with absorbance and COD depletions shown in Figure 2. In this point, it is important to notice the results obtained during electrolysis and photoelectrolysis carried out at 15

mA cm⁻² using BDD anode. Under this condition, the electrolysis of RhB solution is very rapid, and color (Fig. 2a), COD (Fig. 2b) and even TOC (Fig. 3b) suffer a fast decrease during the first stages of the electrolysis. However, when light is irradiated to this system an abrupt decrease of mineralization rate is obtained [34]. This very low mineralization may confirm the formation of refractory species by chlorination of RhB molecule, if compared to color and COD removal. As stated before, the differences observed at 15 mA cm⁻² in presence and absence of light irradiation may be related to the decomposition of the oxidants (mainly hypochlorite) involved in the oxidation process [28,29].

To check the role of mediated oxidation in the overall EO process and the activation of electrogenerated oxidants by means of light irradiation, several chemical oxidation essays have been carried out in absence and presence of light irradiation. Figures 4 to 6 show the COD (Fig. 4), TOC (Fig. 5) and absorbance (Fig. 6) variations, in terms of the percentage variance (%Δ(normalized measurement)), during the chemical oxidation of RhB solutions with the oxidant solution produced by electrolysis of perchloric acid and sodium chloride solutions.

When the solutions of oxidants produced electrolytically are added to a wastewater containing RhB, electrogenerated oxidants interact chemically with RhB and organic intermediates generated in the bulk. However, no clear influence of light irradiation can be drawn. In fact, no significant mineralization was attained in all chemical essays (Fig. 5). Taking into account that, the negative values obtained in TOC removals may be related to the accuracy of the analytical techniques. Regarding the COD removal (Fig. 4), oxidants electrogenerated in chloride (without irradiation) seem to be more effective and this can be related to the better interaction between RhB molecules and hypochlorite electrochemically generated. However, in both supporting media, a

negative influence of light irradiation in COD removal can be drawn (Fig. 4, blue squares, full and clear, respectively). Regarding RhB depletion (Fig. 6), the higher the oxidant dose the higher the RhB elimination. Moreover, in this case, oxidants from during electrolysis of perchloric solutions seems to be relatively more effective (full squares, blue and black, respectively; in Fig. 6) than those obtained in chloride solutions electrolysis. It can be because in HClO_4 medium, electrochemically generated oxidant species could be converted to hydroxyl radicals (such H_2O_2 or O_3 (equations 3 and 4)) via irradiation; attacking the chromophore dye group, and consequently, eliminating rapidly RhB from solution. It is just the opposite trend observed in electrochemical essays. The diffuse effect of light irradiation may indicate that UV light irradiation has not a clear catalytic influence out of an electrolytic environment. In fact, the different behavior observed in chemical and electrochemical essays suggests that oxidants play a different role in the electrolysis of organics than that expected according to their chemical reactivity [34]. It may be due to simultaneous processes that occur in the electrochemical cell [35].

Figure 7 shows the specific efficiency (ηq), in terms of mineralization and oxidation of organic matter, of the electrolysis and photoelectrolysis in chloride and perchlorate media at different operation conditions. This parameter can be easily calculated from the slope of the semilogarithmic plot $\ln(\text{concentration})$ vs. q (eqs. 12) [37], where K_L is the mass transfer coefficient, A is the electrode area, k_{mediated} the kinetic constant of mediated oxidation and V the reaction volume) because in a discontinuous electrochemical cell, like the one used in this study, it is directly and simultaneously related to the efficiency of the process.

$$\ln\left(\frac{[C]_{\text{bulk}}}{[C]_{\text{bulk}_0}}\right) = \frac{K_L \cdot A + k_{\text{mediated}} \cdot V}{I} q = \eta q \quad (12)$$

As it can be observed, efficiency decreases as the applied current density increases (Fig. 7). Initially, this can be explained in terms of a diffusion control of the oxidation rate. The decrease in the efficiency for the largest current density assessed, in terms of oxidation and mineralization, is smaller than expected, mainly in perchloric media, and this can be due to an additional effect of mediated electro-oxidation processes (by means of k_{mediated}). In chloride media, the efficiency for RhB oxidation is higher than mineralization because RhB decay can be attained by fragmentation of chromophore group while mineralization requires a sequence of oxidation reactions with more electric current requirements [22,35]. Regarding the UV light irradiation, its effect is very negative in the electrolysis carried out at the lowest current density, but at 90 mA cm^{-2} a very slight improvement of the specific efficiency is attained [34,37].

Regarding the reaction rates (Fig. 8), these can be easily calculated from the slope of the semi-logarithmic plot $\log(\text{concentration})$ vs. time. The changes in the kinetics constants are very different of that of the specific efficiencies, in spite it is worth to consider that values of kinetic rates constant are strongly related to previous specific efficiencies. In this point it is important to notice the negative effect of light irradiation in the oxidation of RhB and mineralization during the electrolysis at 15 mA cm^{-2} , which can be related to the decomposition of hypochlorite electrogenerated. The effect of current density is the typical for a mass transfer controlled process with a significant contribution of mediated EO [37]: the higher the current density, the higher the production of mediated active species and hence the higher the kinetic constant.

4. Conclusions

From this work the following conclusions can be drawn:

- RhB is rapidly degraded using electrolysis with diamond electrodes, but although media clearly influences on efficiency and rate of the processes; current density is playing an important role.
- Light irradiation effects are greater at high current densities. A relevant negative effect is attained during photoelectrolysis in chloride media and low current density. This is related to the desactivation of hypochlorite massively generated under this operating condition.
- RhB is oxidized chemically by the oxidants electrolytically produced during the electrolysis of a chloride or perchlorate solution in the same conditions used for the electrolysis of wastewater. But, light irradiation has not a clear catalytic influence out of an electrolytic environment.

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6. References

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Figure Captions.

Figure 1. (a) Color and (b) COD removal progress during the photolysis, electrolysis and photoelectrolysis of solutions containing RhB in HClO_4 by applying $j = 0 \text{ mA cm}^{-2}$ at (■) no UV irradiation, (■) UV irradiation; $j = 15 \text{ mA cm}^{-2}$ at (▲) no UV irradiation, (▲) UV irradiation and $j = 90 \text{ mA cm}^{-2}$ at (●) no UV irradiation, (●) UV irradiation.

Figure 2. (a) Color and (b) COD removal progress during the photolysis, electrolysis and photoelectrolysis of solutions containing RhB in NaCl by applying $j = 0 \text{ mA cm}^{-2}$ at (■) no UV irradiation, (■) UV irradiation; $j = 15 \text{ mA cm}^{-2}$ at (▲) no UV irradiation, (▲) UV irradiation and $j = 90 \text{ mA cm}^{-2}$ at (●) no UV irradiation, (●) UV irradiation.

Figure 3. Mineralization behaviour during the photolysis, electrolysis and photoelectrolysis of solutions containing RhB in HClO_4 (a) and NaCl (b) under different conditions: $j = 0 \text{ mA cm}^{-2}$ at (■) no UV irradiation, (■) UV irradiation; $j = 15 \text{ mA cm}^{-2}$ at (▲) no UV irradiation, (▲) UV irradiation and $j = 90 \text{ mA cm}^{-2}$ at (●) no UV irradiation, (●) UV irradiation.

Figure 4. Variation in the percentage of normalized COD as a function of oxidant dose in solution produced by the electrolyses of HClO_4 and NaCl , during the chemical oxidation of RhB: HClO_4 : (■) no UV irradiation, (■) UV irradiation. NaCl : (■) no UV irradiation, (■) UV irradiation.

Figure 5. Variation in the percentage of normalized TOC as a function of oxidant dose in solution produced by the electrolyses of HClO_4 and NaCl , during the chemical oxidation of RhB: HClO_4 : (■) no UV irradiation, (■) UV irradiation. NaCl : (■) no UV irradiation, (■) UV irradiation.

Figure 6. Variation on the percentage of normalized RhB concentration as a function of oxidant dose in solution produced by the electrolyses of HClO_4 and NaCl , during the

chemical oxidation of RhB. HClO₄: (■) no UV irradiation, (■) UV irradiation. NaCl: (□) no UV irradiation, (□) UV irradiation.

Figure 7. Specific efficiency (ηq) in the oxidation and mineralization of RhB solutions by electrolysis and photoelectrolysis in NaCl and HClO₄ at different operation conditions. NaCl: (□) RhB oxidation, (■) mineralization; HClO₄: (□) RhB oxidation, (■) mineralization.

Figure 8. Kinetic constants in the oxidation and mineralization of RhB solutions by electrolysis and photoelectrolysis in NaCl and HClO₄ at different operation conditions. NaCl: (□) RhB oxidation, (■) mineralization; HClO₄: (□) RhB oxidation, (■) mineralization.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8