

Study of the Discoloration Rate of Rhodamine B as a Function of the Operating Parameters at Pt and BDD Electrodes

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Abstract

The chemical reaction of rhodamine B by electro-generated species using Pt and BDD electrodes was performed. The product(s) of this chemical reaction are related to the supporting electrolyte and electrolysis time. The rate of discoloration is affected by the current density, initial pH, temperature, and the nature of the supporting electrolyte. However, the initial dye concentration and the ionic strength did not show any significant effect on both electrodes. Discoloration of the dye and mineralization were not observed in presence of sulfate and nitrate with the Pt electrode, but occurred slowly with the BDD electrode. In the presence of KCl and KBr, the discoloration was very fast with both electrodes, and was accompanied with partial degradation. In the presence of KCl, the colorless rhodamine B solution turned rose after several hours of being set at rest.

Keywords: Pt and BDD electrodes, discoloration, Rhodamine B, sulfate, chloride.

Introduction

The xanthene dyes such as Eosin Y, rose Bengal, and rhodamine B have been proved to be a very useful class of luminescent and triplet forming dyes for theoretical studies and practical applications. The importance of these probes is due to their photophysical and photochemical behavior with the environment [1]. These dyes are water-soluble, and thus they can be adsorbed on all kinds of natural and synthetic fibers. They are also used to color plastics, and leather [2]. Some xanthene dyes, have been reported to be toxic to various insect species in the laboratory [3-7]. The neurotoxicity and carcinogenicity of xanthene dyes to humans and animals have also been experimentally proven [8, 9].

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Several physicochemical processes such as adsorption, filtration, coagulation/flocculation, and electrocoagulation have been used to remove dyes from water. However, these physical processes are separatives but not degradatives.

Furthermore, the biological treatments of wastewater are often not recommended due to the toxicity of the dyes to micro-organisms.

The degradation of basic dyes by chemical oxidation has been widely tested in several laboratories. Examples of oxidants are: persulfate [10 - 13], O₃ [14], UV/O₃ [15], activated O₂ [16], Fenton's reagent [17, 18], photo Fenton [19], H₂O₂ [20], and photodegradation using TiO₂ [21- 26].

In recent years, the use of electrochemical technologies has shown a great interest because they offer effective means to solve environmental problems related to industrial processes, and are adaptable to a wide range of dyes [27-31]. Electrochemical methods for wastewater treatment mainly involve the direct and indirect electrochemical oxidation [32-34]. In indirect oxidation, the main oxidizing agents are Cl₂ and HOCl [33, 35]. Chlorine molecules have the ability to mineralize organic molecules quickly, but they can interact easily with organic molecules to form carcinogenic halogenated compounds [36-38].

The efficiency of the electrochemical oxidation of dyes is a function of the electrode and the supporting electrolyte [38-46]. At Pt electrode, the supporting electrolyte is divided into two types: inactive such as sulfate and nitrate, and active such as chloride (production of Cl₂, and HClO). The discoloration rate of rhodamine B (Rhd B) observed at the RuO₂-PdO-TiO₂/Ti electrode was faster than those with one component electrodes [43]. The total mineralization of Rhd B was observed with OH^{*}, which was electrogenerated by the electro-Fenton process, with Pt and BDD electrodes [44]. Therefore, it is of interest to study the effect of some experimental parameters such as pH, temperature, current intensity, and others, on the discoloration rate of rhodamine B with Pt and BDD anodes in the presence of KCl, nitrate, and sulfate.

Experimental

Rhodamine B (Fig. 1) was purchased from Sigma (C₂₈H₃₁N₂O₃Cl, CAS: 81-88-9, MW: 479.02 g), while the other chemical reagents were purchased from BDH (Analar or GPR). In order to study the discoloration by indirect oxidation with Pt and BDD electrodes, 100 mgL⁻¹ of Rhd B solution were prepared in distilled water. The concentration of the dye in the reaction mixture was selected in such a way that the absorbance of the dye at 550 nm followed Beer's law ($A_{550}:0.194x$ [Rhd B] in mg L⁻¹, R²: 0.998). The majority of the experiments were done at room temperature (293 K), in the presence of 8 mgL⁻¹ Rhd B, 0.1M KX (X = Cl⁻, Br⁻) or 0.1 M sulfate, at pH 2, with a current of 5 mA. Experiments were carried out in a single combined electrolytic cell. The electrolyzed solution was prepared by mixing 8 mL of 100 mgL⁻¹ of Rhd B, 10 mL of 0.1 M H₂SO₄, 10 mL of 1 M supporting electrolyte and 72 mL H₂O.

The Pt wire electrodes (d: 1.5 mm, l: 15 mm) were purchased from Taccusel (France), and the bipolar BDD electrodes (plate: 50x25x3 mm) from NeoCoaT

(Switzerland). The distance between the two electrodes is 5 cm. The electrolysis was done in Chrono-Amperostat, type CEAMD-6, from Taccusel.

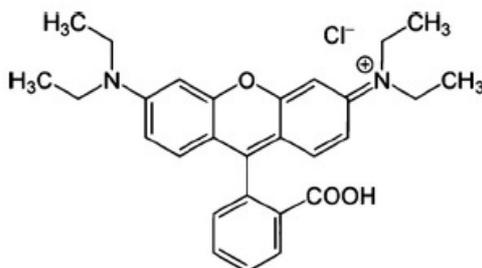


Figure 1: Structure of rhodamine B.

Absorption spectra were recorded on a double beam UV- Visible Specord 200 spectro-meter (Analytic Jena, AG Germany) and the fluorescence spectra were recorded on LS-50B (PerkinElmer) spectrofluorimeter equipped with a Xenon discharge lamp, 1 cm quartz cell (λ_{ex} : 550 nm, λ_{em} : 578 nm). Schott Gerate CG 819 pH-meter Schott Gerate CG 819 pH-meter was used to measure pH.

In order to determine the discoloration rate of the dye and the effect of the experimental parameters, the visible spectra of the solution were recorded at various times of the electrolysis. The slope of the line A_{550} vs. time (k_{obs}) yielded an explanation about the discoloration rate value. The discoloration was studied as a function of several parameters such as the concentration of dye, the initial pH, the nature and the concentration of the electrolyte, the intensity of the current, and ionic strength.

Results and discussions

Electrolysis with Pt/Pt electrodes

Visible spectroscopy analysis

The discoloration of Rhd B was not observed in the presence of sulfate or nitrate at any pH (no direct reaction with Pt electrode). However, in the presence of 0.1 M KCl short time (8 min., pH: 2) was sufficient for total discoloration (Fig. 2). The time required for total discoloration was a function of the operational parameters which will be discussed later. No wavelength shift was observed during the discoloration of Rhd B as was the case with fluorescein (red shift) [37]. The absorbance (or the fluorescence) in the whole spectrum decreases during the electrolysis, which means that there are no fixation of chlorine on the aromatic rings of Rhd B and no N- deethylation, in contrast to the results reported by Watanabe et al. and by Zhao et al. (Fig. 2) [47, 48]. The evolutions of the visible spectra during electrolysis are similar to those obtained with Wenqi et al. and Ben Salah et al. [15, 46]. No colored intermediates were detected during the oxidation of Rhd B since the TLC test at different electrolysis times showed only one colored spot, corresponding to Rhd B. The oxidation mechanism of Rhd B with chlorine is different from that with persulfate because several colored spots were observed on TLC with persulfate [49]. The absorbance A_{550} (inset of Fig. 2) or the fluorescence signal (S_{578}) decreases linearly with time. The addition

of Rhod B solution to a freshly saturated solution with electro-generated chlorine species leads to a sudden discoloration of Rhod B. This means that the reaction between chlorine species and Rhod B is very fast. Therefore, the procedure used to measure the absorbance is not suitable for the determination of the order of the reaction. However the slope of the line A_{550} vs. time is useful to study the effect of the operational parameters on the discoloration rate.

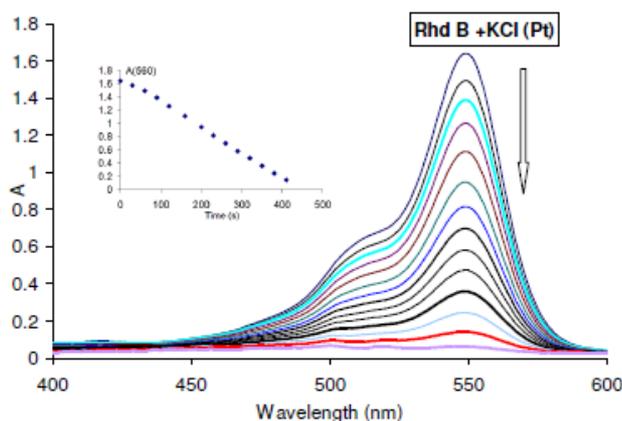


Figure 2. Variation of the visible spectrum of Rhod B as a function of electrolysis time at Pt electrode (0 s - 400 s) (10 mgL^{-1} Rhod B, 0.1 M KCl, 5 mA, pH_0 : 2, 293 K).

Effect of Rhod B concentration

At Pt electrode, the degradation rate (slope of the line A_{550} vs. time) is approximately the same when the concentration varies in the range $4 \text{ mgL}^{-1} - 10 \text{ mgL}^{-1}$, but the time needed to have total discoloration is proportional to the concentration of Rhod B. The result is in accordance with the linear variation of A (550 nm) as a function of electrolysis time (inset in Fig. 2).

Effect of the nature of the supporting electrolyte

It is interesting to investigate the effect of the nature of the strong electrolyte added on the discoloration rate (with Pt electrode). The electrolysis is done in presence of 0.1 M of the following supporting electrolytes: Na_2SO_4 , NaNO_3 , KCl, KBr and KI (each added separately). The results show that discoloration in presence of sulfate or nitrate did not occur. The addition of KI to Rhod B solution provoked the precipitation of Rhod B. The rate of precipitation is proportional to iodide concentration. Therefore, it is possible to eliminate Rhod B from aqueous solution by precipitation. The discoloration of Rhod B in the presence of KCl and KBr is efficient and fast. However, for the same concentration of electrolyte, it is ~ 10 times faster with KBr than with KCl.

Effect of pH

It is well understood that pH is one of the important factors that affect the performance of the electrochemical process. Rhod B has no acid-base property, so the general shape and the absorbance of the dye is independent of the pH of the solution ($2 < \text{pH} < 11$). However, the oxidant strength of chlorine is a function of pH. Electrolysis at different initial pH (pH_0) shows that the discoloration rate of

Rhd B increases linearly with the decrease in pH_0 (Table 1). This is due to the increase in HClO/Cl_2 amount in acidic medium, which has higher standard potential than that of $(\text{ClO}^-/\text{Cl}^-)$. Similar results were reported for the degradation of azo dyes [34] and methylene blue [38]. No effect of pH is observed in the presence of KBr.

Table 1. Effect of the operational parameters on the discoloration rate of Rhd B at Pt electrode.

Parameter	$k_{\text{obs}} \times 10^3$
Rhd B concentration*	No effect
Initial pH (KCl)* Initial pH (KBr)*	$-0.447 \times [\text{pH}] + 5.34$, $R^2: 0.997$ No effect
[Strong electrolyte]*	$43.2 \times [\text{KCl}]$, $R^2: 0.98$ $744 \times [\text{KBr}]^2 + 631 \times [\text{Br}]$, $R^2: 0.99$ No discoloration (with Na_2SO_4)
Current intensity (KCl)*	$0.965 \times I(\text{mA})$, $R^2: 0.993$
Ionic force*	No effect
Effect of temperature	$-0.188 \times T(\text{K}) + 61.2$, $R^2: 0.993$

(* the study has been done at 293 K)

Effect of halide salt concentration

To study the effect of KCl concentration on the discoloration rate, the electrolysis is done with 8 mgL^{-1} of Rhd B solution at $\text{pH}_0: 2$, with 5 mA. Linear relation is observed between KCl concentration and the discoloration rate, but it is polynomial (equation of 2nd degree) with KBr (Table 1). This result confirms the discoloration of the organic compounds via the electro-generated halide species [29, 30].

Effect of ionic strength

The effect of the ionic strength on the discoloration rate of Rhd B was investigated with 8 mgL^{-1} of Rhd B solution, at $\text{pH}_0: 2$, with 2.5 mA, and in the presence of 0.1 M KCl by varying the concentration of Na_2SO_4 or NaNO_3 in the medium (0.03 M- 0.2 M). The results obtained showed no effect of the ionic strength on the discoloration rate ($k_{\text{obs}} \sim \text{constant}$).

Effect of current intensity

Current intensity is an important variable in electrolysis. The generation of chlorine species by electrolysis was done in acidic medium ($\text{pH}_0: 2$) in presence of 8 mgL^{-1} Rhd B and 0.1 M KCl, at several constant currents ranging from 1 mA to 20 mA. The results depict that the discoloration rate increases linearly with the increase of the current intensity (Table 1).

Linear relation was also observed with other organic compounds [37, 38]. The increase in discoloration rate with the applied current is due to the increase in the production of active chlorine products.

Effect of temperature

In general, any increase in temperature decreases the solubility of $\text{Cl}_2(\text{g})$ in aqueous solution and therefore decreases the discoloration rate of the dyes (Table 1). The discoloration rate decreases from 6.36×10^{-3} a.u. to 3.93×10^{-3} a.u. when the temperature increases from 293 to 306 K. This behavior was also observed with another xanthene dye [37].

Effect of electrolysis time

It was observed that when the electrolysis was stopped just after discoloration (8 min) or after longer time (30 min), the transparent solution re-gained its color slowly. The reappearance of the color is function of light and temperature. At room temperature, and under indoor light, it takes one week for the development of the color (with successive blue shift of λ_{max} from 540 to 510 nm) (Fig. 3a), but in sunlight it takes one day only. The final product (compound X) is fluorescent and the color of its aqueous solution (red- orange, $\lambda_{\text{max}} \sim 510$ nm, λ_{em} : 530 nm) is different from that of Rhd B (red, λ_{max} : 550 nm). The UV spectrum of Rhd B is approximately similar to that of the final product (bands at: 250, 290 and 340 nm). Apparently the electro-generated chlorine species did not breakdown Rhd B totally, but leads to a product with minor change in the functional group attached to the aromatic rings. In order to prevent the formation of the fluorescent colored compound and have total mineralization, the electrolysis was allowed to continue for a longer time (3h, 8 h, and 16 h) (Fig. 3b), but this tentative has failed, since a precipitate with light pink color is obtained after putting the solution at rest overnight. After 3-4 h of electrolysis, the Rhd B solution became transparent in UV zone, because the slightly pink water insoluble product floats on the surface of the solution or precipitates on the immersed part of the electrode. This result is well in line with that obtained with Chen et al. [45]. The precipitate is insoluble in DMSO and acetone, but soluble in ethanol (λ_{max} : 510nm), and its NMR and FTIR spectra showed the presence of aromatic H and aromatic C=C respectively. Therefore, based on the λ_{em} (530 nm) of the slightly pink precipitate and the FTIR and NMR data obtained we can deduce that the slightly pink precipitate is not a simple aromatic molecule.

Electrolysis with BDD/BDD electrodes

In the presence of KCl, the replacement of the Pt electrode by BDD electrode gave approximately the same colored compound and the same precipitate, since in both cases Cl_2 is generated at the anode. For the same KCl concentration, the discoloration rate is as fast as with Pt electrode (Fig. 4a). In the presence of sulfate, the discoloration occurred with BDD electrode slowly (~ 8 times slower than in the presence of KCl (Fig. 4b). No recoloration and no formation of the slightly pink precipitate after setting the electrolysis at rest. This might imply total mineralization. Therefore, the discoloration of Rhd B with sulfate at BDD

electrode is convenient for wastewater treatment. The results obtained with BDD electrode in the presence of sulfate are in accordance with those of Ben Salah et al. [46] and with Oturan et al. in the presence of ($O_2 + Fe(II)$), since in both cases OH radical is reacted with Rhd B [44]. The disagreement of our results in using Pt and BDD electrodes in the presence of KCl, with those of Oturan et al. is attributed to the nature of the electro-generated species. In the presence of sulfate, the discoloration rate increases with the increase in current intensity (k_{obs} : $0.3 \times 10^{-4} \times I(\text{mA})$, $R^2:0.92$), with the decrease in pH (k_{obs} : $2 \times 10^{-4} \times \text{pH}^{-0.58}$, $R^2:0.92$), but it is independent of the Rhd B concentration. The discoloration rate in the presence of nitrate is higher than that with sulfate at pH: 2, but at neutral pH, it is much slower.

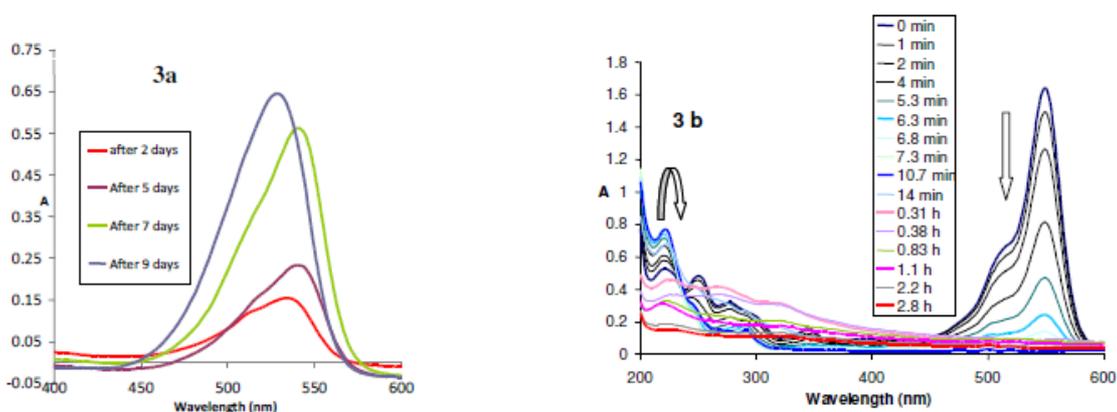


Figure 3. **a:** Reappearance of color with time after stopping electrolysis; **b:** evolution of the UV-Visible spectrum of Rhd B during long time of electrolysis at Pt electrode in presence of KCl (10 mg L^{-1} Rhd B, 0.1 M KCl , $\text{pH}_0: 2$, 5 mA , 293 K).

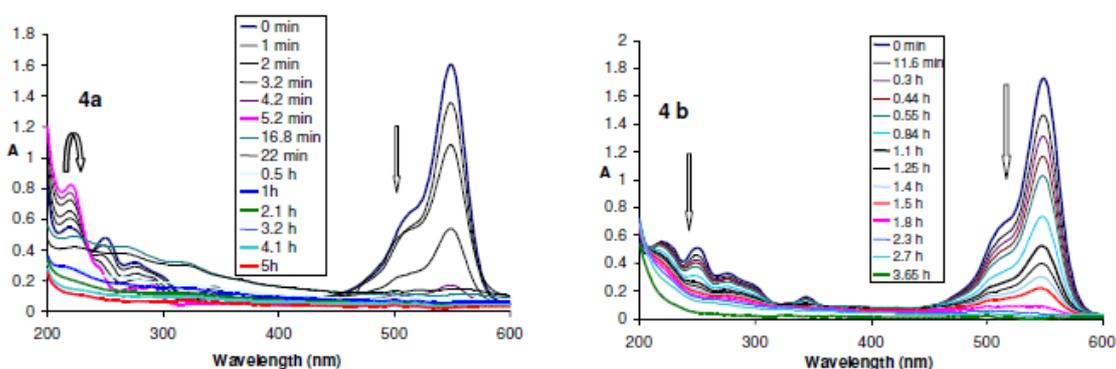


Figure 4. Evolution of the UV-Visible spectrum during long time of electrolysis at BDD electrode in presence of 0.1 M KCl (**a**) and in presence of $0.1 \text{ Na}_2\text{SO}_4$ (**b**) (10 mg L^{-1} Rhd B, $\text{pH}_0: 2$, 5 mA , 293 K).

Conclusion

The discoloration of Rhd B using Pt and BDD electrodes in the presence of KCl and KBr is fast, but no mineralization occurred under these conditions even for an extended electrolysis time. The discoloration and the mineralization of Rhd B using BDD electrode are slow in the presence of sulfate and nitrate. The

discoloration using Pt electrode increases with the increase in the current intensity and KCl concentration, but decreases with the increase in pH and temperature. The discoloration rate is independent of the Rhd B concentration and the ionic strength. The effects of the operating parameters on the discoloration rate using BDD and Pt electrodes are similar.

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