

KINETIC STUDY OF THE DISCOLORATION OF RHODAMINE B WITH PERSULFATE, IRON ACTIVATION

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ABSTRACT

The discoloration of the fluorescent dye, Rhodamine B (Rhd B) by persulphate (KSP), was investigated by spectrophotometric methods. The discoloration reaction of Rhd B by KSP is slow. It's first order with respect to Rhd B and KSP. It's effective at any pH and was found to increase linearly for $pH < 4$, temperature, and after addition of Fe(II) and Ag(I). The rate of discoloration remained the same after addition of Co(II), Ni(II), Cu(II) and carbonate salts, but decreased after addition of ethanol and chloride salts. The TLC experiment showed the formation of colored intermediates. The activation parameters (E_a , ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger) of the discoloration reaction of Rhd B by KSP in absence and in presence of Fe(II) were calculated.

Keywords: Rhodamine B, persulfate, metal activation, matrix effect, kinetic.

INTRODUCTION

Textile industry produces a large amount of dyed wastewater. The non-biodegradable nature of the spent dye baths constitutes serious environmental problems [1]. Rhodamine B (Rhd B), is one of the important xanthene cationic dyes, is largely applied in industry as a dye for paper, silk, wool, jute leather, cotton (Fig. 1). The xanthene dyes (Rose Bengal, Eosin Y and Rhodamine 6G,...) are used also as fluorescent markers in structural microscopic studies, photosensitizers, and laser dyes. They have long been known to be toxic to insects (insecticide). They are harmful if swallowed by human and animals, and cause irritation to the skin, eyes and lung [2-3].

The main technologies available for the treatment of dyes involve the transfer of the pollutant from a liquid phase to another phase, concentrating the dye on an adsorbent (for example) so that it can later be discarded in a landfill or incinerated [4-5]. This phase exchange is

not an ideal remedy. Destructive oxidation treatments provide more permanent solutions such as electrodegradation [6, 7], photodegradation using TiO_2 [8-13] are applied for removal of dyes (especially cationic dyes) from textile effluents.

Chemical oxidation of contaminants by oxidants has been studied to develop novel remediation technologies: $KBrO_3$ [14, 15], $KClO_3$ [16], O_3 [17], UV/O_3 [18], activated O_2 [19], Fenton's reagent [20 -21], photo Fenton [22], H_2O_2 [23] have been widely tested in laboratory for the degradation of basic dyes.

The use of persulfate (KSP) has recently been the focus of attention for an alternative oxidant in the chemical oxidation of contaminants [24-37]. It's one of the strongest oxidants known in aqueous solution (Table 1) [27, 38]. It has great capability for degrading numerous organic contaminants through free radicals ($SO_4^{\cdot-}$ and OH^{\cdot}) generated in the persulfate system [30, 31]. It offers some advantages over other oxidants: Ease of storage and transport, high stability, high aqueous solubility

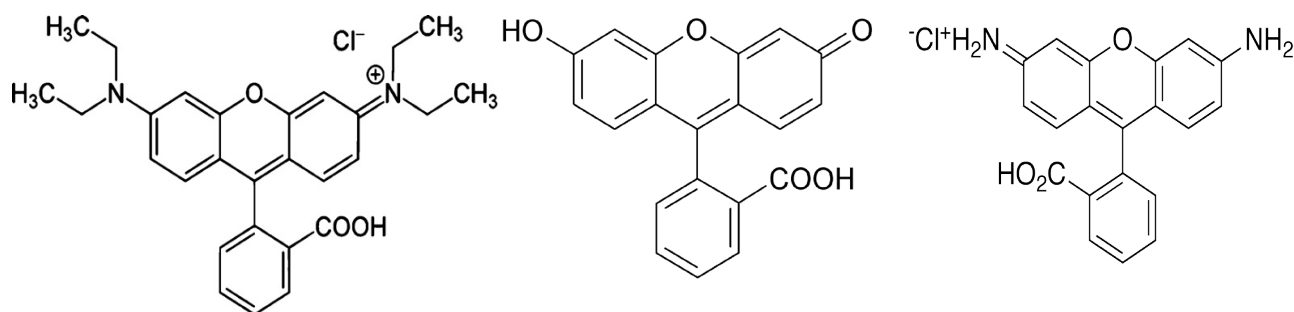
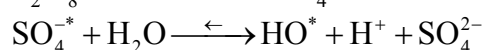
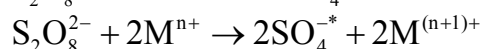
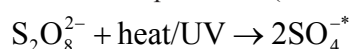


Fig.1. Chemical structures of Rhodamine B, Fluorescein, and Rhodamine 110.

and relatively low cost.

Base activation [36, 37], UV-irradiation [25, 26, 35], thermal activation [34, 39-41], metal activation [42-46], and soil mineral activation [30] have been used to generate a sulfate radical (E° : 2.5- 3.1V), a stronger oxidant than persulfate (2.01 V) [41, 45]:



The present work is focused on the kinetic study of the discoloration of Rhd B (model molecule of xanthenes dye) with persulfate by UV- Visible spectrophotometry. The effect of various parameters such as initial pH, initial concentration of persulfate and Rhd B, transition metals concentration, and salts concentration was studied. A comparison between the degradation of Rhd B and Fluorescein (which has similar structure (Fig.1) with persulfate is undertaken to interpret better the results.

EXPERIMENTAL

Rhodamine B is used as purchased from Sigma ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$, CAS: 81-88-9, MW: 479.02 g). The other chemical reagents used are from BDH (Analar or GPR). 20 mg L^{-1} (4.18×10^{-5} M) of Rhd B solution is prepared in distilled water in order to study its discoloration by KSP. The concentration of the dye in the reactional mixture is selected in such a way the absorbance of the dye at 560 nm followed Beer's law. The concentration of KSP in the reactional mixture (0.01 M) is selected in such a way the rate of the reaction is not very slow. The kinetic study of the discoloration of Rhd B by persulfate was carried on a double beam spectrophotometer, Specord 200 (Analytical Jena). 1 M of salt solutions (carbonate, chloride, and sulfate), and 0.1 M of transition

metal solutions ($\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and CuSO_4), were also prepared to study the matrix effect on the discoloration rate. 5×10^{-2} M of AgNO_3 , $\text{Fe}^{\text{II}}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$, and 10^{-2} M of the surfactant (SDS) were also prepared for the same reason. H_2SO_4 and NaOH solutions were used to study the effect of pH on the discoloration rate of Rhd B with KSP.

Kinetic Study

The order with respect to Rhd B was carried out in the presence of a large excess of persulfate. The reactional mixture was prepared as follows: x ml ($2 < x < 4$) of 20 mg L^{-1} (0.93×10^{-5} M $< [\text{RhdB}]_f < 1.85 \times 10^{-5}$ M) of Rhd B, (7- x) mL of H_2O and 2 mL of 5×10^{-2} M KSP ($[\text{KSP}]_f$: 0.11 M).

The order with respect to persulfate was determined in the presence of different excess amounts of it, while the other parameters were kept constant: x mL of 5×10^{-2} M KSP ($2 < x < 4$) (7-x) mL of H_2O and 2 mL of 20 mg L^{-1} Rhd B ($[\text{RhdB}]_f$: 0.93×10^{-5} M). Quickly after the addition of the dye, the absorbance of the solution was recorded every 1 min. during 60 minutes at 560 nm (λ_{max} of Rhd B). The rate expression for the discoloration reaction is:

$$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^n[\text{Rhd B}]^m = k_{\text{app}}[\text{Rhd B}]^m$$

$$\text{with } k_{\text{app}} = k[\text{S}_2\text{O}_8^{2-}]^n$$

where k is the rate constant of the reaction, m and n are the pseudo order of the reaction with respect to Rhd B and $\text{K}_2\text{S}_2\text{O}_8$ respectively.

Effect of initial pH

The effect of pH on the degradation rate was studied in presence of several concentrations of NaOH or H_2SO_4 . The following mixtures were prepared for this purpose: 2 mL of 20 mg L^{-1} Rhd B ($[\text{RhdB}]_f$: 0.93×10^{-5} M), 2 mL of 5×10^{-2} M of KSP ($[\text{KSP}]_f$: 0.11 M), 5 mL of the acid

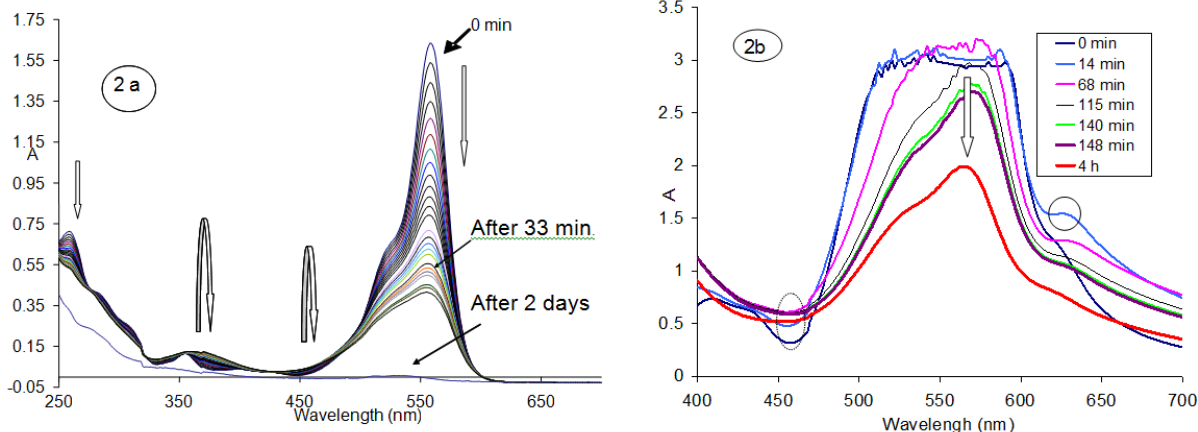


Fig. 2a, 2b: Evolution of the Rhd B spectra in presence of an excess of KSP as a function of time at 290 K. (a): 10 mg L⁻¹ Rhd B (2.1×10^{-5} M), 2.5×10^{-2} M KSP, spectrum taken every 1 min during 1h. (b): 100 mg L⁻¹ Rhd B (21×10^{-5} M), 2.5×10^{-2} M KSP.

or the base (5×10^{-1} M – 5×10^{-3} M).

Metal activation

Concerning the effect of metal salts, several experiments were done at fixed concentration of KSP and Rhd B in the mixture as follow: 3 mL of 20 mg L⁻¹ Rhd B ($[Rhd\ B]_f: 1.25 \times 10^{-5}$ M), 2 mL of a predetermined concentration of KSP ranging from 5×10^{-2} M to 10^{-3} M, x mL of Fe(II) ($Fe^{II}(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$), or Ag(I) solution of the same initial concentration of KSP and (5-x) mL of water.

Matrix effect

The effect of salt such as KCl, Na_2SO_4 , and Na_2CO_3 (1 M), on the rate constant was carried out at several concentrations of the mentioned salts by replacing some volume of water by the salt solution (x mL, with $0 \leq x \leq 5$), while keeping the concentration of the others reactants constant. The effect of the surfactant (SDS) and ethanol, on the discoloration rate were also studied in the same manner.

RESULTS AND DISCUSSION

UV-Visible spectroscopy and TLC Analysis

The visible spectrum of Rhd B decreases slowly with time especially the absorbance at 560 nm (λ_{max} of Rhd B). The general shape of Rhd B spectrum does not vary during its reaction with KSP. The reaction between Rhd B and KSP leads to total discoloration of Rhd B (Fig. 2a). The discoloration is very slow compared to that with crystal violet and malachite green [27]. The

slow decrease in the intense peaks of Rhd B at 560 and 260 nm is accompanied for the first time by an increase in the absorbance at 630, 470 and 370 nm (Fig. 2a, 2b). Then the decrease continues in the whole spectrum.

The TLC study (Silica gel – pure ethanol) shows the appearance of two spots other than that of Rhd B: the lower one, orange less intense than the upper one (violet) (Fig. 3). The two color intermediate products disappear with time, in favors of two others intermediates with higher R_f . The Rhd B spot persists even after long time (one day) but its color faded, and then it disappears completely. The same behavior is observed with the other spots. Finally the Rhd B/ KSP mixture become colorless. The discoloration of low concentration of Rhd B by KSP leads to the formation of colored intermediates undetectable clearly by UV-visible spectroscopy. The decrease in the whole UV - visible spectrum is probably a consequence of total mineralization of Rhd B. No blue shift (progressive decrease from 560 to 498 nm) is observed during the discoloration as observed during the degradation of Rhd B under visible light ir-

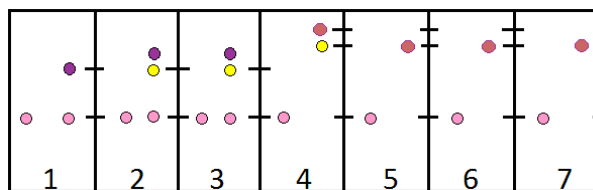


Fig. 3. TLC of the mixture (Rhd B + KSP) done at various moments during one day (from left to right) (21×10^{-5} M Rhd B, 2.5×10^{-2} M KSP, 290 K). The spot to the left corresponds to Rhd B.

radiation by $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{TiO}_2$ [47], and ZnCd/TiO_2 [48]. The degradation products of Rhod B are function of the oxidant used [49, 50]. There are several pathways for the Rhod B degradation:

N-deethylation (formation of Rhod B110), followed by deamination [49, 52].

Break in the chemical bond of xanthone molecule between the C_1 and C_{15} atoms (elimination of the phenyl ring containing COOH) leading to the formation of Pyronin G [50].

A break in the -O- bridge giving an intermediate having a similar structure to malachite green (increase in A_{630}).

Further degradation of these intermediate is possible [27, 51, 52].

Order with respect to Rhod B

Rhodamine B shows a strong absorption band at 560 nm and follows Beer's law for low concentrations ($2-8 \text{ mg L}^{-1}$). The relation found between the absorbance A_{560} and Rhod B concentration in mg L^{-1} is $A = 0.196 \times [\text{Rhod B}]$ (mg L^{-1}) $R^2: 0.993$). The order with respect to Rhod B is not zero according to the plot of A_{560} vs. time (Fig.4a). The functions $\ln A$ and $1/A$ vary linearly with time. The constant k_{obs} is the slope of the plot

$$\ln A_{560} \text{ or } \frac{1}{A_{560}} \text{ vs time } (k_{\text{obs}} \propto k_{\text{app}}).$$

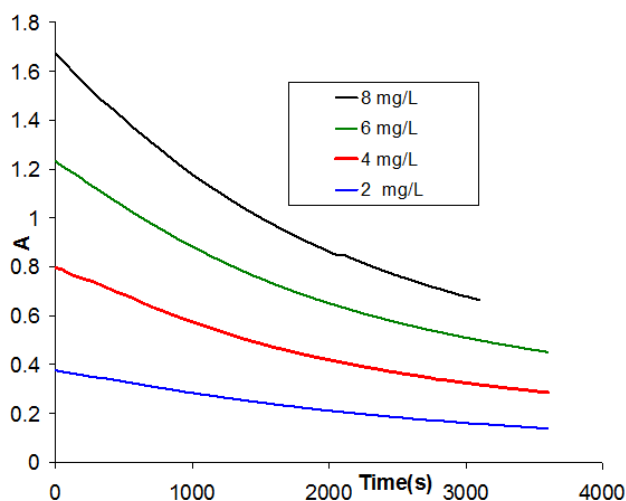


Fig. 4a: Variation of the absorbance of Rhod B (A_{560}) as a function of time for several concentrations of Rhod B in presence of 0.01 M of KSP at 290 K.

For all the experiments concerning the determination with respect to Rhod B, the correlation coefficient (R^2) for order one is closer to one than that for 2nd order. Order one is confirmed by applying the differential method ($\ln V_o = 1.27 \times \ln[\text{Rhod B}]_o - 10.27$, $R^2: 1$). The constant k_{obs} remains the same with the increase in the dye concentration ($k_{\text{obs}} = 2.9 \times 10^{-4}$). Order one is also observed by discoloration of Rhod B by UV/KSP [29], by photo-Fenton reagent [22], and by photo-degradation in presence of TiO_2 [9].

Order with respect to KSP

The increase in KSP concentration increases the discoloration rate of Rhod B. For 10^{-3} M of KSP (in the mixture), the absorbance of Rhod B remained the same during 1 h, but with 10^{-2} M of KSP, the absorbance decreases significantly. The rate constant (k_{obs}) increases linearly with the increase in KSP concentration ($k_{\text{obs}} \times 10^4 = 200 \times [\text{KSP}]$, $R^2: 0.983$). So the order with respect to KSP is one. Order one is also observed for the degradation of crystal violet by KSP [27].

Effect of initial pH

Initial pH of solution had great effect on Rhod B degradation rate during $\text{UV}/\text{S}_2\text{O}_8^{2-}$ system. Rhod B is stable in acidic and in basic medium, it does not loose its color with time in these mediums. Its maximum

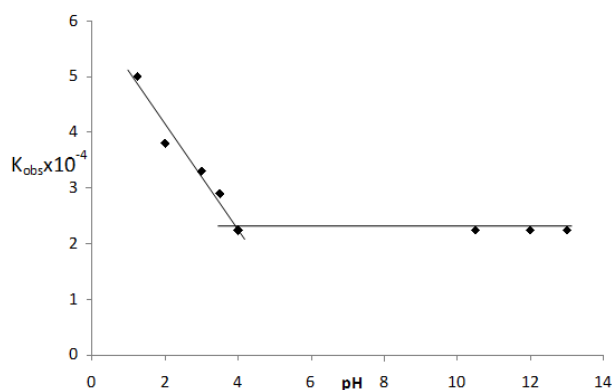


Fig. 4b: Effect of initial pH on the discoloration rate constant (k_{obs}). (6 mg L^{-1} Rhod B ($1.25 \times 10^{-5} \text{ M}$), 0.01M KSP, 290 K).

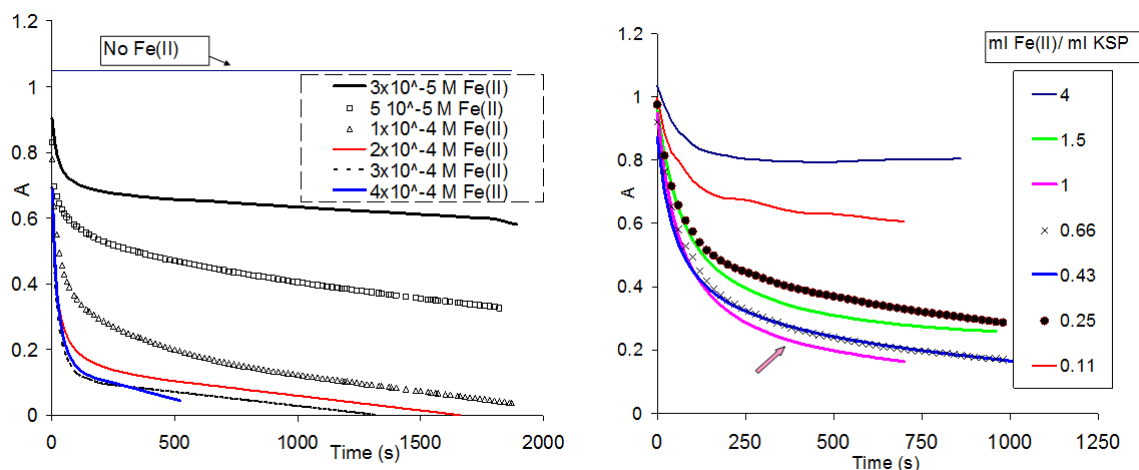


Fig. 5a. Effect of Fe(II) on the discoloration rate of Rhd B with KSP (6 mg L⁻¹ Rhd B (1.25x10⁻⁵ M), 1x10⁻³ M KSP, 290 K).
 Fig. 5b. Effect of the ratio [Fe(II)]/[KSP] on the discoloration rate of Rhd B with KSP (6 mg L⁻¹ Rhd B (1.25x10⁻⁵ M), [KSP]₀ = [Fe(II)]₀ = 10⁻³ M, 290 K).

wavelength remained the same whatever the pH. The results showed that, the discoloration rate constant does not vary in neutral and in basic medium, but increases linearly with the decrease in pH for pH ≤ 4 (Fig. 4b). The radical SO₄^{•-} is rather stable and more numerous at low pH, while increasing system pH results in the transformation of SO₄^{•-} to hydroxyl radical OH[•] (SO₄^{•-} + H₂O → OH[•] + SO₄⁻ + H⁺) [29]. The acidic medium has positive effect on the Rhd B discoloration due to shift to right in the equilibrium of the reaction mentioned. The obtained result is in accordance with that obtained by action of UV/ KSP on Rhd B [29] and by action of KSP on Orange G [45].

Matrix effect

Metal Activation

The chemical oxidation of organic pollutants by persulfate can be accelerated by metal ion activation, through enhancing sulfate radical generation. In the present case Ni(II), Co(II) and Cu(II) did not increase the discoloration rate constant, whereas the ions Ag(I) and Fe(II) accelerate it considerably (Fig. 5 and 6). For the same concentration of metal ion, Fe(II) decolorizes the mixture (Rhd B + KSP) faster than Ag(I). The discoloration behavior of Rhd B in presence of Fe(II)

is somehow special:

The control mixture (presence of Fe(II) without KSP) shows no discoloration of Rhd B. For 5x10⁻² M (or 5x10⁻³ M) as initial concentration of KSP and Fe(II): The decrease in Fe(II) concentration in the medium increases the discoloration rate (result not shown). For the experiment done with 5x10⁻² M of KSP and Fe(II), the mixtures with Fe(II)/[KSP] ≥ 2, the discoloration is completely stopped, but for other mixtures with low ratio (≤ 0.5), the color disappears completely in less than 1 minute.

The repetition of the experiment mentioned above with 5x10⁻³ M of KSP and 10⁻³ M of Fe(II) (instead of 5x10⁻³ M) as initial concentration showed different attitude: the discoloration rate increases with the increase in Fe(II) volume (0.3 ml < x < 4 ml or 3x10⁻⁵ M – 4x10⁻⁵ M) (Fig.5a). Linear relation is observed between k_{obs} and Fe(II) (R²: 0.97). This behavior is the opposite of that observed with higher concentrations of KSP and Fe(II).

Basing on this, we think about the existence of an optimum ratio of Fe(II)/[KSP]. This ratio corresponds to 1 when using 10⁻³ M as initial concentration of KSP and Fe(II) (2 ml of 10⁻³ M KSP + x ml of 10⁻³ M Fe(II)).

Table 1. The standards potentials of some oxidants used in advanced chemical oxidation [27, 38].

Oxidant	BrO ₃ ⁻ / Br ₂	ClO ₃ ⁻ / Br ₂	H ₂ O ₂ / H ₂ O	O ₃ /O ₂	OH [•]	S ₂ O ₈ ²⁻ /SO ₄ ²⁻
E ⁰ (V)	1.51	1.46	1.76	2.07	2.38	2.01

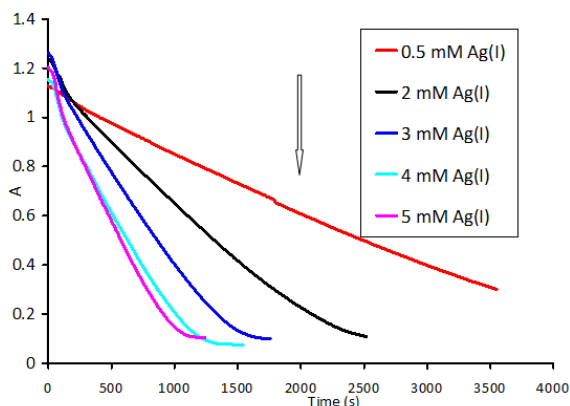


Fig. 6. Effect of Ag(I) concentration on the discoloration rate constant of Rhd B with KSP. (6 mg L^{-1} Rhd B ($1.25 \times 10^{-5} \text{ M}$), 0.01 M KSP, 290 K).

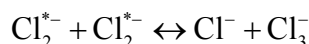
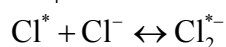
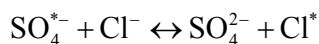
The optimum ratio of $\text{Fe(II)}/[\text{KSP}]$ is also confirmed by varying the volume of 10^{-3} M KSP with respect to that of 10^{-3} M Fe(II) (Fig. 5b). There is scavenger effect [27, 45].

Concerning the effect of Ag(I), the control mixture (presence of Ag(I) without KSP) shows no discoloration of Rhd B. For an initial concentration of KSP ($5 \times 10^{-2} \text{ M}$), the addition of $x \text{ ml}$ of $5 \times 10^{-2} \text{ M}$ Ag(I) ($0 \leq x \leq 5$), the discoloration of Rhd B became very fast, and increased linearly with the increase of Ag(I) concentration. The repetition of the experiment with an initial concentration of KSP and Ag(I) equal to 0.01 M gave the same results but the discoloration is slower ($k_{\text{obs}} = 0.226 \times [\text{Ag}^+] + 2 \times 10^{-5}$, with $R^2: 0.982$) (Fig. 6). No Scavenger effect is observed with Ag(I) as was the case with Fe(II) . Similar result is observed during the

discoloration of crystal violet by KSP [27]. For another initial concentration of KSP and Ag(I) ($2.5 \times 10^{-3} \text{ M}$), the increase in Ag(I) concentration in the reactional mixture increases slightly the rate constant, whereas in the same conditions, the rate constant is higher with Fe(II) . The order with respect to Rhd B in presence of Ag(I) becomes zero order, whereas it is rather 2 in presence of Fe(II) , so the action of Ag(I) on the discoloration of Rhd B by KSP is different from that of Fe(II) .

Effect of wastewater constituents

The high redox potential of sulfate free radical makes it very reactive in destroying organic contaminants. However, parallel reactions with other species, could result in scavenging of sulfate radical and could possibly limit its oxidation efficiency. Competition for sulfate radical could be from wastewater constituents such as chloride ions, carbonate and phosphate [45]. The equations below show the chemical reaction mechanism of persulfate with chlorides in aqueous solutions [31]:



When chloride concentrations were less than 0.05 M , presence of chloride ions had insignificant impacts on Rhd B degradation. However, beyond these concentration levels, Rhd B degradation rates reduced significantly with an increase in chloride concentrations (Fig. 7a) The presence of sulfate or carbonate even in high concentration (0.5 M) did not reduce the discoloration

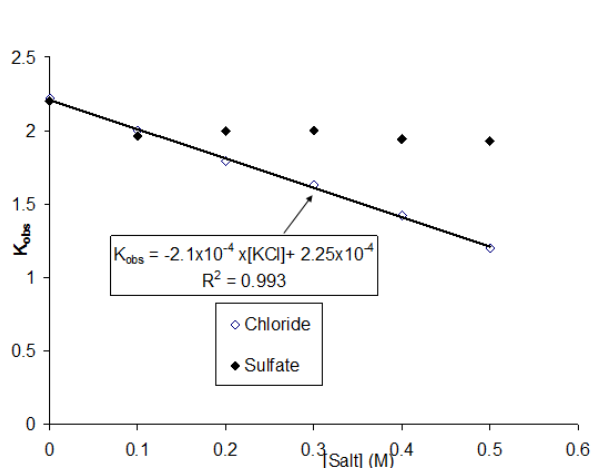


Fig. 7a. Effect of salts concentration on the degradation of Rhd B by KSP (6 mg L^{-1} Rhd B ($2.5 \times 10^{-5} \text{ M}$), 0.01 M KSP, 290 K)

Fig. 7b. Arrhenius plot of $\ln k_{\text{obs}}$ vs. $1/T$. (12 mg L^{-1} Rhd B ($2.5 \times 10^{-5} \text{ M}$) + 0.01 M $\text{K}_2\text{S}_2\text{O}_8$).

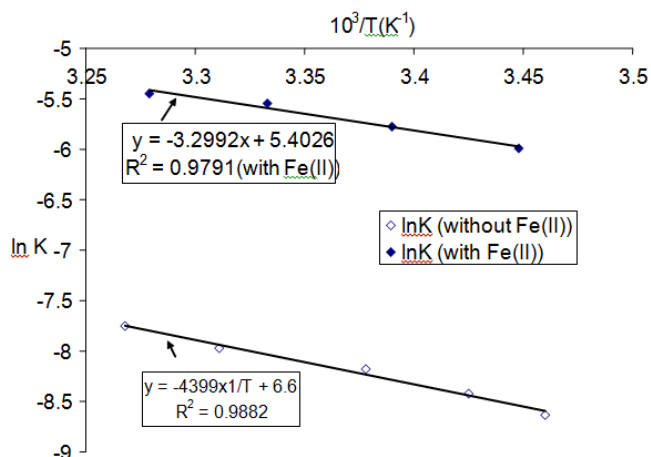


Table 2. Activation thermodynamic parameters of the degradation of Rhod B by persulfate. (12 mg L⁻¹ Rhod B (2.5x10⁻⁵ M) + 0.01 M K₂S₂O₈) The values between () correspond to those in presence of 5x10⁻³ M Fe(II).

E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (kJ.mol ⁻¹ K ⁻¹)	ΔG^\ddagger_{298} (kJ mol ⁻¹)
36.5 (27.3)	34 (24.8)	- 0.198 (-0.201)	93.0 (86.8)

rate significantly. Chloride was the ion that had the most negative effect. The reaction between sulfate and sulfate radical will generates sulfate radical. Similar results are observed with Lee et al. [31] and Soares et al. [12].

Effect ethanol and surfactant

Ethanol decreases the discoloration rate of Rhod B. Linear relation is observed between k_{obs} and the volume of pure ethanol added ($k_{obs} = -0.373 \times V(\text{ethanol}) + 1.87$ with $R^2:0.985$). The presence of SDS in low concentration (1x10⁻⁴ M - 4x10⁻⁴ M) did not affect the discoloration rate of Rhod B by KSP. The increase in SDS concentration did not allow the measurement of the absorbance accurately due to the micelle formation.

Effect of Temperature

The increase in temperature (15°C – 33°C) increases the discoloration rate of Rhod B (Fig. 7b). The activation parameters associated with the discoloration are calculated according to Arrhenius and Eyring equations [27] (Table 2). The activation energy in presence of Fe(II) is lower than in its absence. The decrease in the activation energy in presence of Fe(II) confirms the catalyst effect of Fe(II) (metal activation).

CONCLUSIONS

The discoloration of Rhod B is pseudo first order with respect to Rhod B and to persulfate. The discoloration increases with temperature, in acidic medium, after addition of Fe(II) and Ag(I), but decreases with the addition of NaCl and ethanol. There was no effect on the rate constant upon addition of Cu (II), Ni(II), or Co(II) and carbonate. Colored intermediate products are observed by TLC during the discoloration. The reaction of Rhod B with KSP leads probably to total mineralization of the dye.

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