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#, ΔH# and ΔS#) 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 electrodeggradation [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 and OH-) generated in the persulfate system [30, 31]. It offers some advantages over other oxidants: Ease of storage and transport, high stability, high aqueous solubility
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]:

\[ \text{SO}_4^{2-} + \text{heat/UV} \rightarrow 2\text{SO}_4^{2-} \]

The present work is focused on the kinetic study of the discoloration of Rhodamine 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 Rhodamine B, transition metals concentration, and salts concentration was studied. A comparison between the degradation of Rhodamine 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 (C_{28}H_{31}N_{2}O_{3}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 \times 10^{-5} M) of Rhodamine 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 Rhodamine 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 (Co(NO_3)_2, Ni(NO_3)_2, and CuSO_4), were also prepared to study the matrix effect on the discoloration rate. 5 \times 10^{-2} M of AgNO_3, Fe^{2+}(NH_4)_2(SO_4)_2, 6 H_2O, 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 Rhodamine B with KSP.

**Kinetic Study**

The order with respect to Rhodamine 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} (4.18 \times 10^{-5} M) of Rhodamine B, (7-x) mL of H_2O and 2 mL of 5 \times 10^{-2} M KSP ([KSP]: 0.11 M). Quickly after the addition of the dye, the absorbance of the solution was recorded every 1 min. during 60 minutes at 560 nm (\lambda_{max} of Rhodamine B). The rate expression for the discoloration reaction is:

\[ \text{Rate} = k[S_2O_8^{2-}][\text{Rhod B}]^m = k_{app}[\text{Rhod B}]^n \]

where \( k \) is the rate constant of the reaction, m and n are the pseudo order of the reaction with respect to Rhodamine B and K_{2}S_{2}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} Rhodamine B ([RhodB]: 0.93 \times 10^{-5} M), 2 mL of 5 \times 10^{-2} M of KSP (KSP): 0.11 M, 5 mL of the acid...
or the base (5x10^{-3} M – 5x10^{-3} M).

**Metal activation**

Concerning the effect of metal salts, several experiments were done at fixed concentration of KSP and Rhod B in the mixture as follow: 3 mL of 20 mg L^{-1} Rhod B ([Rhd B]: 1.25x10^{-5} M), 2 mL of a predetermined concentration of KSP ranging from 5x10^{-2} M to 10^{-3} M, x mL of Fe(II) (Fe^{II}(NH_{4})_{2}(SO_{4})_{2} \cdot 6 H_{2}O, 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_{2}SO_{4}, and Na_{2}CO_{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 Rhod B decreases slowly with time especially the absorbance at 560 nm (\(\lambda_{\text{max}}\) of Rhod B). The general shape of Rhod B spectrum does not vary during its reaction with KSP. The reaction between Rhod B and KSP leads to total discoloration of Rhod 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 Rhod 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 Rhod 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 Rhod 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 Rhod B/ KSP mixture become colorless. The discoloration of low concentration of Rhod 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 Rhod B. No blue shift (progressive decrease from 560 to 498 nm) is observed during the discoloration as observed during the degradation of Rhod B under visible light ir-

![Fig. 2a, 2b: Evolution of the Rhod B spectra in presence of an excess of KSP as a function of time at 290 K. (a):10 mg L^{-1} Rhod B (2.1x10^{-3} M), 2.5x10^{-2} M KSP, spectrum taken every 1min during 1h). (b): 100 mg L^{-1} Rhod B (21x10^{-5} M), 2.5x10^{-2} M KSP.](image)

![Fig. 3. TLC of the mixture (Rhd B + KSP) done at various moments during one day (from left to right) (21x10^{-5} M Rhod B, 2.5x10^{-2} M KSP, 290 K). The spot to the left corresponds to Rhod B.](image)
radiation by Zn\textsubscript{1-x}Cd\textsubscript{x}S/TiO\textsubscript{2} \[47\], and ZnCd/TiO\textsubscript{2} \[48\]. The degradation products of Rhd B are function of the oxidant used \[49, 50\]. There are several pathways for the Rhd B degradation:

- N-deethylating (formation of Rhd B110), followed by deamination \[49, 52\].
- Break in the chemical bond of xanthone molecule between the C\textsubscript{1} and C\textsubscript{15} atoms (elimination of the phe-
- nyl 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\textsubscript{630}).
- Further degradation of these intermediate is possible \[27, 51, 52\].

**Order with respect to Rhd B**

Rhodamine B shows a strong absorption band at 560 nm and follows Beer’s law for low concentrations (2–8 mg L\textsuperscript{-1}). The relation found between the absorbance A\textsubscript{560} and Rhd B concentration in mg L\textsuperscript{-1} is \( A = 0.196 \times [\text{Rhd B}] \) (mg L\textsuperscript{-1}) \( R^2: 0.993 \). The order with respect to Rhd B is not zero according to the plot of A\textsubscript{560} vs. time (Fig.4a).

The constant k\textsubscript{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 Rhd B by UV/KSP \[29\], by photo- Fenton reagent \[22\], and by photo-degradation in presence of TiO\textsubscript{2} \[9\].

**Order with respect to KSP**

The increase in KSP concentration increases the discoloration rate of Rhd B. For 10\textsuperscript{-3} M of KSP (in the mixture), the absorbance of Rhd B remained the same during 1 h, but with 10\textsuperscript{-2} M of KSP, the absorb-
- ance decreases significantly. The rate constant (k\textsubscript{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 Rhd B degradation rate during UV/S\textsubscript{2}O\textsubscript{8}\textsuperscript{-} system. Rhd B is stable in acidic and in basic medium, it does not lose its color with time in these mediums. Its maximum
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 $\cdot \text{SO}_4^-$ is rather stable and more numerous at low pH, while increasing system pH results in the transformation of $\cdot \text{SO}_4^-$ to hydroxyl radical OH$^*$ ($\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \cdot \text{OH}^+ + \text{SO}_4^2^- + \text{H}^+$) [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 5x$10^{-2}$ M (or 5x$10^{-3}$ 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 5x$10^{-2}$ 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 5x$10^{-3}$ M of KSP and 10$^{-3}$ M of Fe(II) (instead of 5x$10^{-3}$ 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 3x$10^{-3}$ M – 4x$10^{-3}$ M) (Fig.5a). Linear relation is observed between $k_\text{obs}$ and Fe(II) ($R^2$: 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$^{-4}$ 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].**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>BrO$_3$ / Br$_2$</th>
<th>ClO$_3$ / Br$_2$</th>
<th>H$_2$O$_2$ / H$_2$O</th>
<th>O$_3$/O$_2$</th>
<th>OH$^*$</th>
<th>S$_2$O$_8^{2-}$/SO$_4^{2-}$</th>
</tr>
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<tbody>
<tr>
<td>$E^0$ (V)</td>
<td>1.51</td>
<td>1.46</td>
<td>1.76</td>
<td>2.07</td>
<td>2.38</td>
<td>2.01</td>
</tr>
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</table>

Fig. 5a. Effect of Fe(II) on the discoloration rate of Rhd B with KSP (6 mg L$^{-1}$ Rhd B (1.25x$10^{-5}$ M), 1x$10^{-3}$ 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 (1.25x$10^{-5}$ M), [KSP]$_0$ = [Fe(II)]$_0$ = 10$^{-3}$ M, 290 K).
The optimum ratio of Fe(II)/[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 (5x10^{-2} M), the addition of x ml of 5x10^{-2} M Ag(I) (0 ≤ x ≤ 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 ($k_{obs} = 0.226×[Ag^+] + 2×10^{-5}$, 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) (2.5x10^{-3} 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]:

\[
\begin{align*}
SO_4^{2-} + Cl^- & \leftrightarrow SO_4^{2+} + Cl^- \\
Cl^- + Cl^- & \leftrightarrow Cl_2^- \\
Cl_2^- + Cl_2^- & \leftrightarrow Cl^- + Cl_2^{-}
\end{align*}
\]

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. 6. Effect of Ag(I) concentration on the discoloration rate constant of Rhd B with KSP. (6 mg L^{-1} Rhd B (1.25x10^{-5} M), 0.01 M KSP, 290 K).

Fig. 7a. Effect of salts concentration on the degradation of Rhd B by KSP (6 mg L^{-1} Rhd B (2.5x10^{-5} M), 0.01 M KSP, 290 K)

Fig. 7b. Arrhenius plot of ln$k_{obs}$ vs. 1/T. (12 mg L^{-1} Rhd B (2.5x10^{-5} M) + 0.01 M K_2S_2O_8).

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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 Rhd 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 $(1 \times 10^{-4} - 4 \times 10^{-4} \text{M})$ did not affect the discoloration rate of Rhd 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 $(15^\circ \text{C} – 33^\circ \text{C})$ increases the discoloration rate of Rhd 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 Rhd B is pseudo first order with respect to Rhd 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 Rhd B with KSP leads probably to total mineralization of the dye.

**REFERENCES**


<table>
<thead>
<tr>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^\circ_{298}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.5 (27.3)</td>
<td>34 (24.8)</td>
<td>- 0.198 (-0.201)</td>
<td>93.0 (86.8)</td>
</tr>
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</table>

Table 2. Activation thermodynamic parameters of the degradation of Rhd B by persulfate. (12 mg L$^{-1}$ Rhd B (2.5x10$^{-5}$ M) + 0.01 M K$_2$S$_2$O$_8$) The values between () correspond to those in presence of 5x10$^{-3}$ M Fe(II).


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