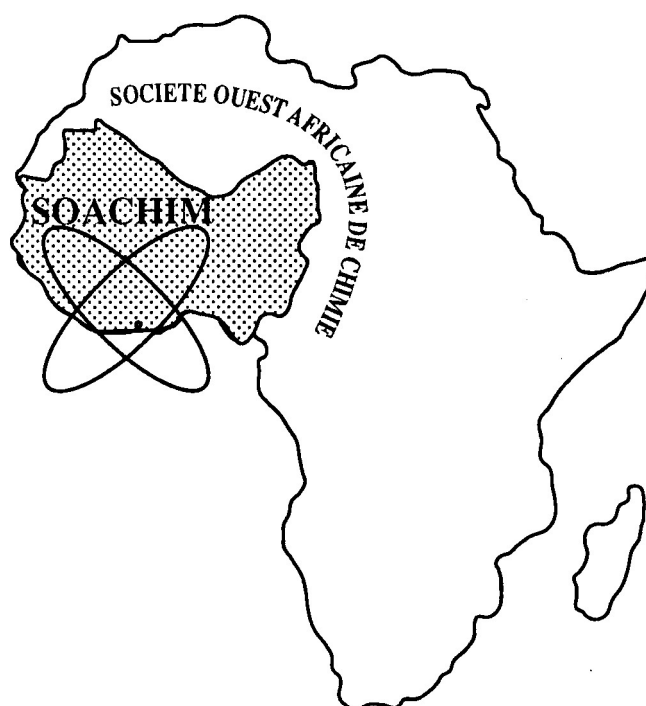


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Oxidation of rhodamine B using the Fenton process: optimization, kinetics and inorganic ions studies

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Abstract: In this work, the oxidation of rhodamine B (RhB) was performed by Fenton process in the presence of inorganic ions (NO_3^- ; Cl^- ; SO_4^{2-} ; PO_4^{3-}). The concentration of RhB was monitored using a UV-visible spectrophotometer. RhB oxidation by Fenton process was a simple and rapid method because the reaction occurred within the first 20 minutes. Fenton process produced hydroxide radicals responsible for the oxidation of RhB. For optimal oxidation of RhB, the pH must be less than or equal to 2. For $\text{pH} > 2$, the oxidation rate decreases due to parasitic reactions. Parasitic reactions also occur if the ratio $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}]$ is higher than 35.7. The oxidation of RhB was faster for low concentrations than for high concentrations of RhB. According to this work for maximum oxidation (99.42%) of 5 mg/L RhB, $8.4 \cdot 10^{-4}$ mg/L Fe^{2+} , $3 \cdot 10^{-3}$ M H_2O_2 and $\text{pH} = 2$ are required. The rate of discoloration decreases with the concentration of inorganic ions. Inorganic ions strongly decrease the rate of RhB degradation in the following order: $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$.

Keys words: Optimisation, Oxydation, Rhodamine B, Fenton Process

Oxydation de la rhodamine B par le procédé de Fenton : optimisation, études cinétiques et des ions inorganiques

Résumé : Dans ce travail, l'oxydation de la rhodamine B (RhB) a été réalisée par le procédé Fenton en présence d'ions inorganiques (NO_3^- ; Cl^- ; SO_4^{2-} ; PO_4^{3-}). La concentration de RhB a été suivie à l'aide d'un spectrophotomètre UV-visible. L'oxydation de RhB par le procédé Fenton a été une méthode simple et rapide car la réaction s'est déroulée dans les 20 premières minutes. Le procédé Fenton a permis de produire des radicaux hydroxydes responsables de l'oxydation de RhB. Pour une oxydation optimale de RhB, le pH doit être inférieur ou égale à 2. Pour $\text{pH} > 2$, le taux d'oxydation diminue à cause des réactions parasites. Des réactions parasites se produisent également si le ratio $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}]$ est supérieur à 35.7. L'oxydation de RhB a été plus rapide pour les faibles concentrations que pour les concentrations fortes en RhB. Selon ces travaux pour une oxydation maximale (99,42 %) de 5 mg/L de RhB, il faut $8,4 \cdot 10^{-4}$ mg/L de Fe^{2+} , $3 \cdot 10^{-3}$ M de H_2O_2 et $\text{pH} = 2$. Le taux de décoloration diminue avec la concentration en ions inorganiques. Les ions inorganiques diminuent fortement le taux de dégradation de RhB dans l'ordre suivant : $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$.

Mots Clés : Optimisation, Oxydation, Rhodamine B, Procédé fenton

1. Introduction

Water is the central element of all economic and social processes, and its human need grows in line with the increase in agro-industrial activities and the degree of development ^[1]. Water used in the various industrial sectors contains more and more pollutants ^[2, 3]. Dyes are among the most dangerous pollutants. They are used in many industrial sectors such as food, cosmetic and clinical products, in particular in the textile industries ^[4, 5]. According to literature, the molecules of these dyes are hardly biodegradable and difficult to degrade by conventional methods ^[6-8].

Thus, for the industrial world, the treatment of dyes has become a priority. The development of effective methods to treat these dyes is the subject of much research. Currently, the most recent advances in wastewater treatment have been made in advanced oxidation processes (AOPs), which appear to be more effective techniques for the destruction of organic pollutants ^[9-13]. AOPs are treatment techniques using highly reactive radical intermediates, particularly hydroxyl radicals (HO[•]) at room temperature. The development of AOPs for the treatment of organically contaminated waters is an attempt to take advantage of the non-selectivity and rapid reaction time of HO[•] ^[14, 15].

Fenton process is one of the advanced oxidation techniques, based on the formation of hydroxyl radicals (HO[•]) possessing an oxidizing power superior to that of traditional oxidants such as Cl₂, ClO₂ or O₃. These radicals are able to partially or totally mineralizing most organic compounds [16-18]. In the literature, the process has been used to degrade rhodamine B (RhB) ^[19, 20]. However, this work did not completely degrade RhB ^[19, 20]. Moreover, in the literature very few authors have studied the influence of inorganic ions on organic compounds oxidation ^[21, 22]. Thus our objective is to optimize the RhB oxidation by Fenton process and to study the influence inorganic ions on RhB oxidation.

2. Materials and methods

2.1. Determination of Rhodamine B concentration

The spectrophotometric method of RhB quantification is a method which makes it possible to follow only the RhB concentration and all the compounds absorbing at the same frequency as RhB. In this study, absorbance was measured using a Ultraviolet-visible spectrophotometer (HACH DR-6000).

Characteristics of RhB are listed in **Table I** and **Figure 1**.

Table I. Rhodamine B characteristics

Parameters	Values
Suggested name	Rhodamine B
Aspect	Solid green
Color	Red
Odeur	Odorless
C.I. number	45170
C.I. name	Basic violet 10
Class	Rhodamine
λ_{max}	554 nm
Molecular formula	C ₂₈ H ₃₁ N ₂ O ₃ Cl
Formula weight	479.02

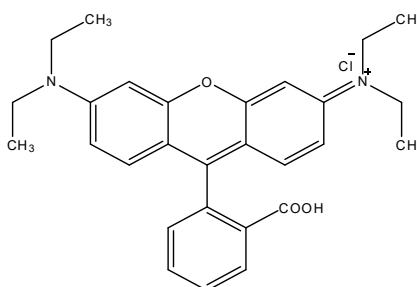


Figure 1: Molecular structure of rhodamine B

2.2. Reagents

Hydrogen peroxide (H_2O_2) were manufactured SCHARLAU. Ferrous sulfate (FeSO_4), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3) and sodium phosphates (Na_3PO_4 , 12 H_2O) have been manufactured by the company Merck. Sulfuric acid (H_2SO_4) was supplied by the company Fluka.

2.3. Experiments

A stock solution of RhB (100 mg / L) was prepared in distilled water. Several sets of 500 mL reaction mixture are prepared with the RhB solutions, hydrogen peroxide and ferrous ions. The pH of the reaction mixture was adjusted with sodium hydroxide solution and sulfuric acid solution. One of the following parameters is varied: RhB concentration, Fe^{2+} concentration, H_2O_2 concentration, pH and inorganic ions concentration setting the other parameters. Regarding the influence of inorganic ions, a given concentration is added to the reaction mixture. Then 2 mL of the reaction media is taken every 5 minutes and the absorbance is measured using a HACH DR-6000 UV-visible spectrophotometer. Before each spectrophotometer reading, the collected solution is filtered through filter paper. The exact concentration of RhB remaining in the reaction mixture is determined using a calibration curve. The absorbances of several RhB solutions of known concentration were measured. For a given concentration, the measurements were performed 3 times and an average of the values was calculated. The values obtained were used to plot the absorbance curve as a function of the RhB concentration. The calibration curve obtained is an equation line:

$$\text{Absorbance} = 0.2765 C \quad (1)$$

All the experiments were made at ambient temperature of 25 °C.

3. Results and discussion

3.1. Influence of H_2O_2 concentration

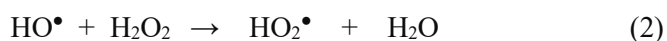
Figure 2 shows the spectra measured at regular time intervals (5 min) during the RhB oxidation (5 mg / L) in the presence of Fe^{2+} (10^{-3} M), H_2O_2 (10^{-2} M) at pH = 3. This figure shows that the maximum absorbance is obtained at the wavelength of 554 nm. We also note the

absorbance decreases during the reaction indicating the degradation of rhodamine B.

Figure 3 shows the influence of H_2O_2 concentration on RhB discoloration. The concentrations of RhB and Fe^{2+} were respectively set at 5 mg / L and 10^{-3} mol / L. The pH was fixed to 3 and the concentration of hydrogen peroxide was varied from 0.01 M To 0.05 M. In this figure 3, we noticed a rapid change in the degradation rate from 0 to 10 min using all the H_2O_2 concentrations. In addition, a slow increase in the degradation rate was observed from 10 to 30 min. Beyond 30 min, the degradation rate remained constant. Consequently, 30 min was fixed for RhB degradation in following experiments.

Figures 3a and **3b** show that the degradation rate increases when the initial H_2O_2 concentration increases from 0.01 M to 0.03 M. Using 0.03 M H_2O_2 , the degradation rate of 95.94 % was reached. Beyond 0.03 M, the degradation rate of RhB decreases such as 94.74 % for 0.04 M and 90.60 % for 0.05 M. This result indicated that 0.03 M was the optimal concentration of H_2O_2 necessary for the RhB degradation under the study conditions.

The results obtained can be explained by the fact that increasing the H_2O_2 concentration causes an increase in the amount of OH^\bullet and therefore increases the RhB degradation efficiency. However, too high a concentration of H_2O_2 causes trapping of hydroxyl radicals (equation 2) due to excess H_2O_2 forming hydroperoxyl radicals (HO_2^\bullet) and slows down the degradation of the dye [23, 24].



3.2. Kinetic model of the RhB oxidation

The study of the kinetic model applicable to RhB oxidation by Fenton process was investigated. Experimental data were applied to 0, 1 and 2 pseudo-order models which are shown in Figures 4a, 4b and 4b. Consider the constant production kinetic of hydroxyl radicals and their stable concentration during the process, we have:

For the equation:



The kinetic equation is given by;

$$\frac{-d[RhB]}{dt} = k[OH^\bullet]^\alpha [RhB]^\beta \quad (4)$$

α : partial order with respect to OH^\bullet

β : partial order with respect to RhB

Since the concentration of hydroxyl radicals is constant, the oxidation kinetic of the organic compound can be described by an apparent kinetic law of order 1 with respect to the concentration of organic compound (equation 5):

Which gives:

Order 1 reaction

$$\frac{-d[RhB]}{dt} = k_{app}[RhB] \quad (5)$$

$$\ln\left(\frac{RhB}{RhB_0}\right) = -k_{app}t \quad (6)$$

Where k_{app} is the pseudo-constant of apparent kinetic of order 1, which is in agreement with recent work concerning the reaction of the hydroxyl radical with organic compounds [25].

Order 2 reaction

$$\frac{-d[RhB]}{dt} = k_{app}[RhB]^2 \quad (7)$$

$$\frac{1}{[RhB]} = \frac{1}{[RhB]_0} + k_{app}t \quad (8)$$

Order 0 reaction

$$\frac{-d[RhB]}{dt} = k_{app}[RhB]^0 \quad (9)$$

$$[RhB]_t = [RhB]_0 - k_{app}t \quad (10)$$

The curves in Figure 4 were used to determine the parameters of the 0, 1 and 2 order kinetics models. The values of constants for both kinetic models are given in Table II. This table shows that the values of the correlation coefficients obtained from the order 2 kinetic model are higher than those obtained with the kinetic model of order 0 and 1 regardless of H_2O_2 concentration. This indicates that the kinetic model suitable for our study is the second order kinetic model. Besides, Table II shows that the maximum value of the apparent velocity pseudo-constant is maximum when the H_2O_2 concentration is equal to 0.03 M. This confirms that the reaction kinetics are maximum when the H_2O_2 concentration is equal to 0.03 M.

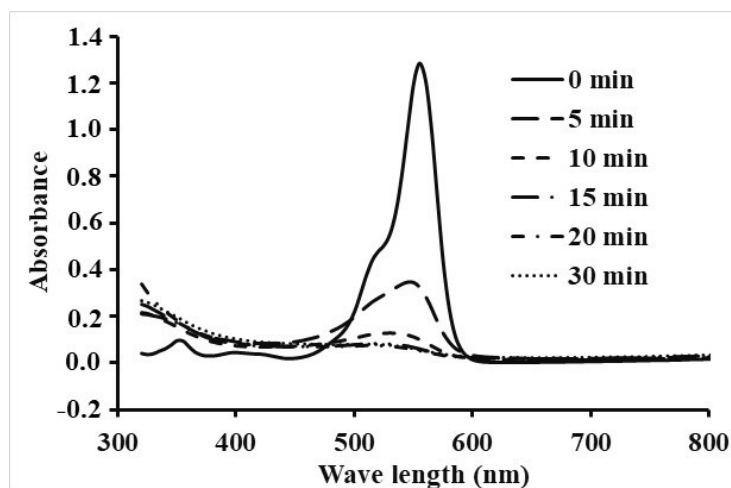


Figure 2: Rhodamine B spectrum (5 mg / L) in the presence of Fe^{2+} (10^{-3} M), H_2O_2 (10^{-2} M), pH = 3

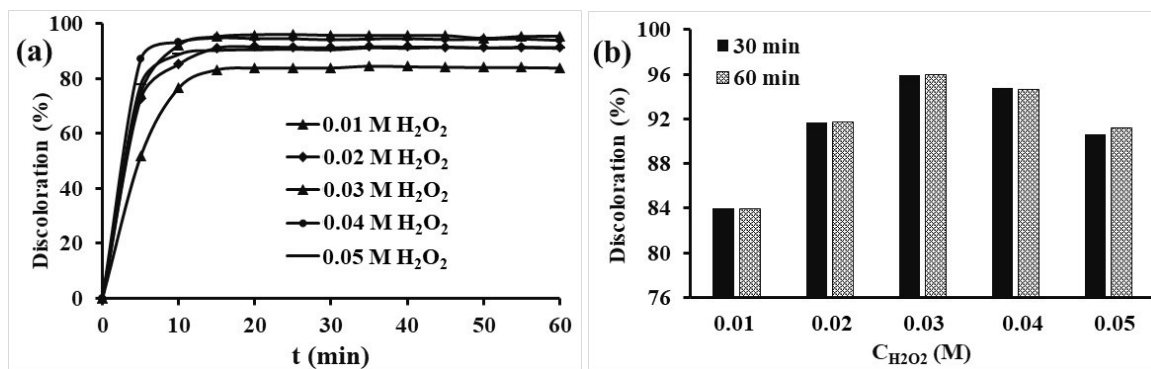


Figure 3: (a) Effect of H_2O_2 concentration on RhB degradation as a function of time; (b) RhB discoloration rate after 30 and 60 minutes; pH = 3; [RhB] = 5 mg / L; $[Fe^{2+}] = 10^{-3}$ M.

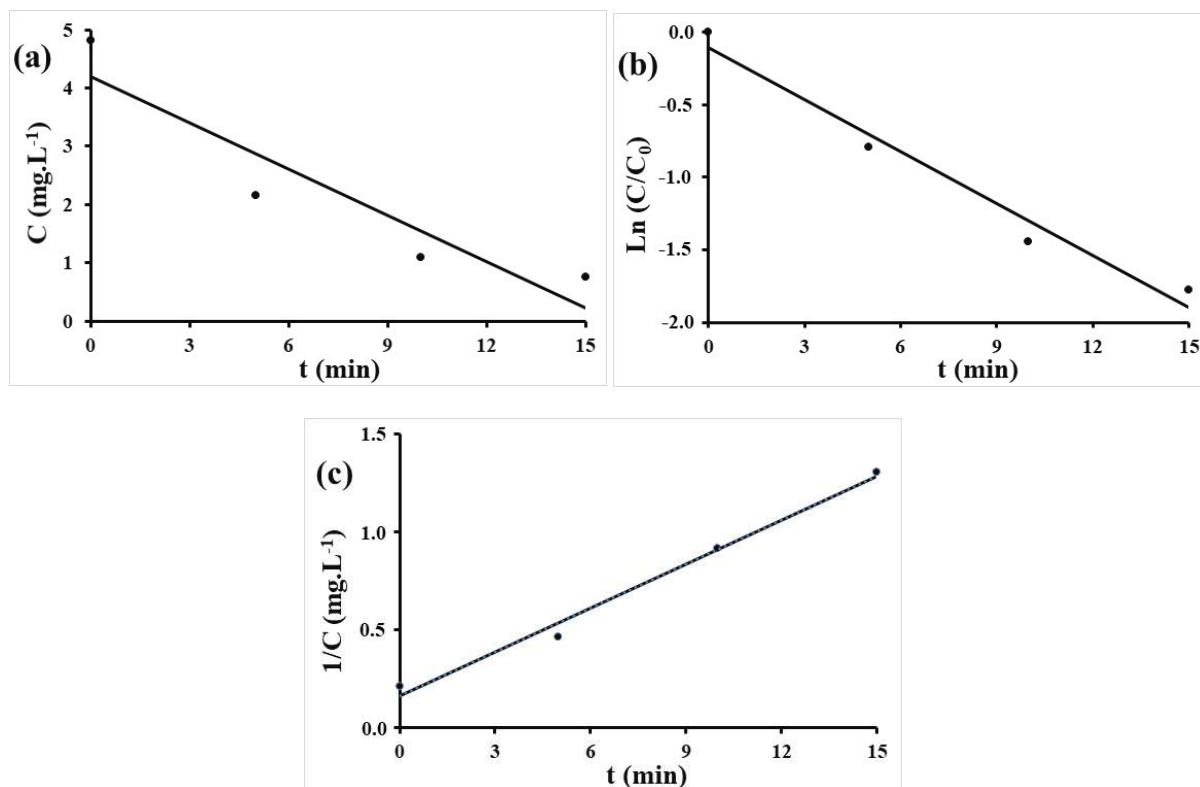


Figure 4: Application of the pseudo-order 0 (a), pseudo-order 1 (b) and pseudo-order 2 (c) models to RhB adsorption; pH = 3; [RhB] = 5 mg / L; $[Fe^{2+}] = 10^{-3}$ M; $[H_2O_2] = 0.1$ M.

Table II: Constants of the kinetics models

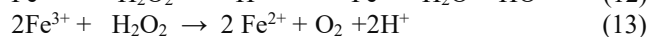
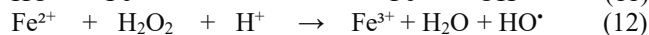
H_2O_2 Concentration	Pseudo-order 0 kinetic model		Pseudo-order 1 kinetic model		Pseudo-order 2 kinetic model	
	R^2	k_{app} (min ⁻¹)	R^2	k_{app} (min ⁻¹)	R^2	k_{app} (mol ⁻¹ .L.min ⁻¹)
0.1 M	0.862	-0.264	0.959	0.120	0.989	0.075
0.2 M	0.766	-0.277	0.941	0.158	0.972	0.167
0.3 M	0.771	-0.292	0.933	0.206	0.940	0.384
0.4 M	0.668	-0.282	0.857	0.193	0.996	0.354
0.5 M	0.711	-0.268	0.864	0.154	0.970	0.160

3.3. Influence of Fe^{2+} concentration

The influence of Fe^{2+} concentration on RhB oxidation has been studied and **Figures 5a** and **5b** drawn to indicate the obtained results.

From **figure 5**, it was observed a variation of RhB degradation rate with the Fe^{2+} concentration. Indeed, when going from 5.10^{-4} M to $8.4.10^{-4}$ M the degradation rate increases from 94.43% to 96.02%. These results are in agreement with literature indicating that the addition of Fe^{2+} improves the RhB destruction rate [26-28]. Then, it is observed that beyond $8.4.10^{-4}$ M, it decreases to reach 85.42% at $1.25.10^{-3}$ M. That showed that the optimum degradation rate of RhB is reached for a Fe^{2+} concentration equal $8.4.10^{-4}$ M. Thus, for optimum degradation of RhB, the $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}]$ ratio equal to 35.7.

Above $8.4.10^{-4}$ M, Fe^{2+} is engaged in a secondary reaction by consuming hydroxyl radicals, hence the decrease in the RhB degradation. According to Panizza and Cerisola [29], when the Fe^{2+} concentration is very high, side reactions occur (equation 11 to 13). These reactions compete with the degradation reaction of organic compounds. This reduces the organic compounds oxidation.



According to Equation 12, Fe^{2+} react with H_2O_2 to form Fe^{3+} . So if the Fe^{2+} concentration is high, the amount of Fe^{3+} produced will be high. Fe^{3+} reacts with H_2O_2 according to equation 13. The sharp decrease in degradation with an excess of Fe^{2+} would also be linked to the decomposition of H_2O_2 by the Fe^{2+} produced.

3.4. Influence of RhB concentration

The amount of material to be degraded is one of the factors that determines the efficiency of the treatment process. Thus, various initial RhB concentrations were studied by fixing the concentration values $[\text{H}_2\text{O}_2] = 0.03$ M and $[\text{Fe}^{2+}] = 8.4.10^{-4}$ M. The obtained results are presented in FIGS. 6a and 6b.

From **Figures 6a** and **6b**, the degradation efficiency decreases as the initial RhB concentration increases. This is in agreement with literature data [30, 31]. In addition, an almost total degradation (98.52%) is

observed after 5 min for the low concentrations of RhB (1.5 mg / L). At high concentrations (10 mg / L), degradation is relatively slow with a rate of 94.27% after 30 min.

The gradual decrease in degradation rates with initial concentration could be explained by competition reactions between the dye molecules and those of the intermediates formed during the Fenton oxidation process [32]. The dye molecules as well as the intermediate products formed will compete to react with the HO^\bullet radicals. The amount of degradation intermediates formed is proportional to the initial concentration of the dye, so the decrease in the RhB degradation efficiency is a direct consequence of the increase in this competitive effect with the initial concentration of RhB [32].

3.5. Influence of pH

The media pH is one of the most important parameters influencing the degradation of organic pollutants by advanced oxidation processes. In this work, the RhB degradation was carried out at different pH values (1.5; 2; 3; 4). **Figures 7a** and **7b** show the obtained results.

From these figures, it was observed that the degradation rates are higher in a very acidic media (pH between 1.5 and 2) than for pH between 3 and 4. RhB degradation rate is constant at equal pH 1.5 and 2. A degradation rate of 99.42% was obtained for a pH equal to 1.5 or 2. These latter values therefore constitute the optimum conditions for RhB degradation. Several studies reported that pH dramatically influences the transformation of synthetic dyes in aqueous solutions, and generally the optimum value is ranged between 1 and 3 [23, 33].

In the area of water treatment, the pH brings about a modification in the ionization degree of the organic molecule which appears in different forms depending on its ionizable functions. RhB carries a carboxylic acid function having a $\text{pK}_a = 3$. If the media is characterized by a pH below this value, the cationic form of RhB (RhB^+) is predominant. Its cationic form is predominant for pH greater than 3.7 [34].

The acceleration of degradation kinetics in an acidic media (pH between 1 and 3) is therefore probably due to the protonation of the functional site $-\text{COOH}$, which improves the hydrophobicity of the RhB molecules. Results showed that the efficiency of the capture of HO^\bullet radicals by RhB molecules is greater in acidic conditions, due to the strong regeneration of H_2O_2 molecules [23].

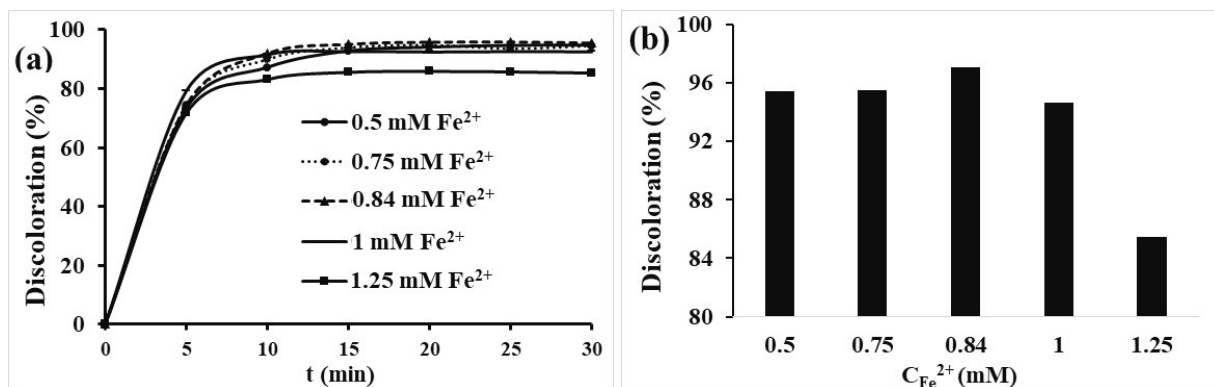


Figure 5: (a) Effect of Fe^{2+} concentration on the RhB degradation versus time; (b) RhB concentration reduction rate for different Fe^{2+} concentrations; pH = 3; $[\text{RB}] = 5 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 3.10^{-2} \text{ M}$.

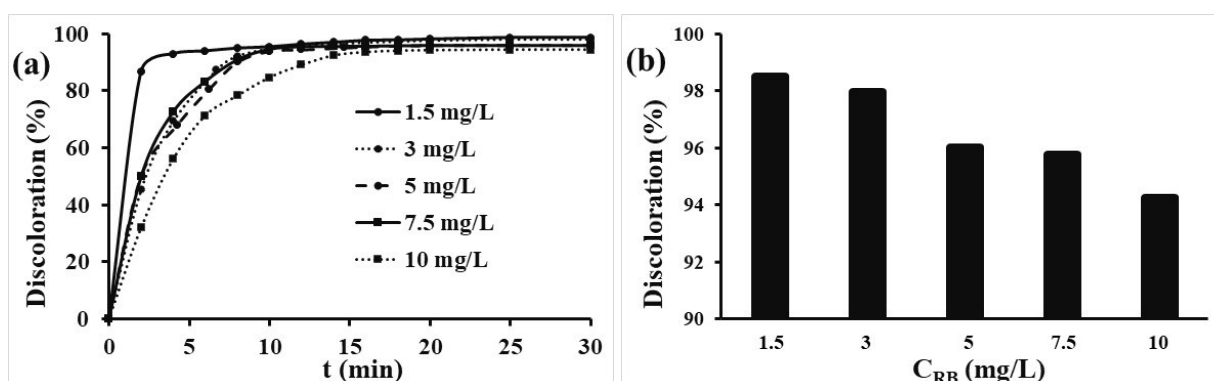


Figure 6: (a) Effect of RhB concentration on degradation versus time; (b) RhB concentration reduction rate for different initial RhB concentration over a period of 20 min; pH = 3; $[\text{H}_2\text{O}_2] = 3.10^{-2} \text{ M}$; $[\text{Fe}^{2+}] = 8.4.10^{-4} \text{ M}$

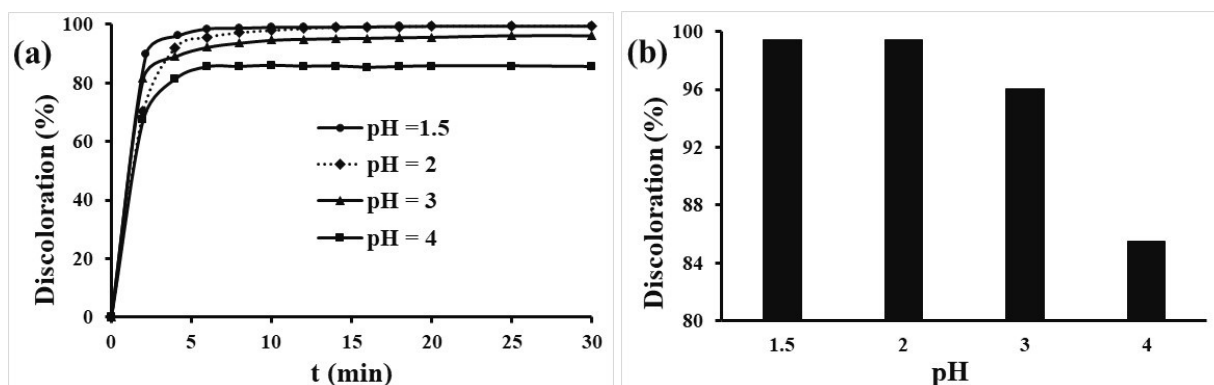


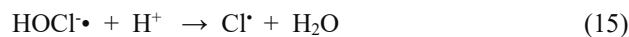
Figure 7: (a) Effect of pH on RhB degradation versus time; (b) RhB concentration reduction rate for different pHs over a period of 30 minutes; $[\text{RhB}] = 5 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 3.10^{-2} \text{ M}$; $[\text{Fe}^{2+}] = 8.4.10^{-4} \text{ M}$.

3.6. Influence of inorganic ions

The influence of the chloride (Cl^-) concentration on RhB oxidation was studied at pH 2 in the presence of 5 mg/L RhB, 3.10^{-2} M H_2O_2 and $8.4.10^{-4} \text{ M}$ Fe^{2+} . The results obtained (Figure 8a) show that the addition of chloride reduces the RhB discoloration rate. The reduction in the rate of discoloration increases as the chloride concentration increases.

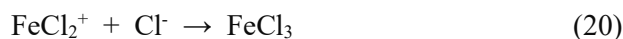
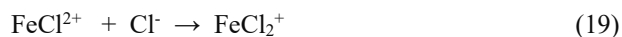
The Figure 8b shows that the RhB discoloration rates are respectively 99.42%, 97.72%, 96.96%, 92.42%, 81.53% and 76.54% for a chloride concentration of 0.65 mM, 1.19 mM, 2.91 mM, 7.03 mM and 10 mM. This shows that the chloride inhibits the degradation reaction of RhB and this inhibition may be due to complexation and radical scavenging [35]. As shown in equations (14) and (15), chloride react with hydroxyl radicals competing with the RhB oxidation

reaction, leading to inhibition of oxidation, and therefore slowing down the oxidation rate [36].



Cl^- can undergo complexing reactions with ferrous and ferric ions, which prevents the reaction causing the formation of hydroxyl radicals product.

Equations (16) - (20) describe the Complexation reactions [37].



Based on the above reactions, the Fenton reaction was inhibited because ferrous and ferric complexes cannot catalyze hydrogen peroxide to produce hydroxyl radicals as efficiently as when they are free. At the initial stage of the Fenton reaction, the species of iron is the ferrous ion Fe^{2+} . The reactivity of ferrous ion complexed with chloride is much lower than the one of Fe^{2+} only [35]. This causes a decrease in the RhB discoloration rate. The values in Table 1 show that the chloride inhibit the RhB discoloration. The RhB discoloration rate decreases with increasing chloride concentration. This table confirmed that the oxidation of RhB is described by the pseudo-order 2 kinetic model.

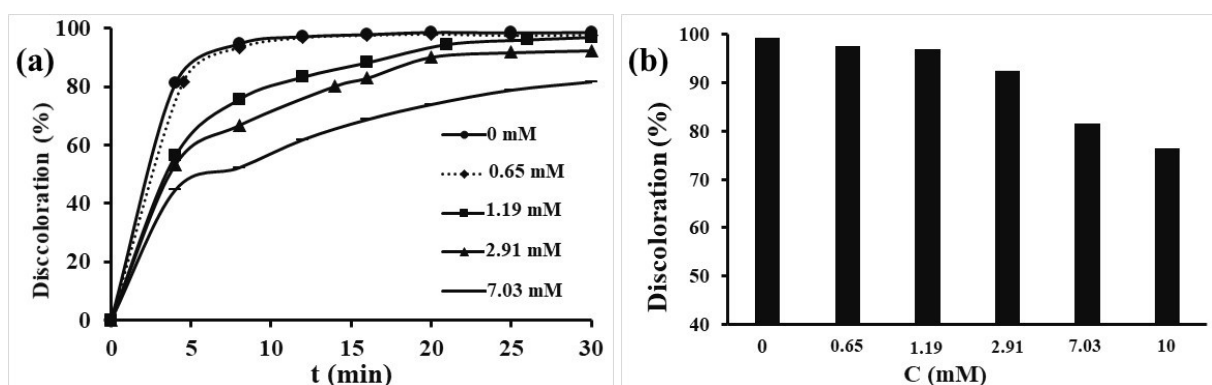


Figure 8: Effect of chloride on RhB discoloration; pH = 2; [RhB] = 5 mg / L; $[\text{H}_2\text{O}_2] = 3.10^{-2}$ M; $[\text{Fe}^{2+}] = 8.4.10^{-4}$ M

Table III: Parameters of the kinetics models

Cl ⁻ Concentration	Pseudo-order 1 kinetic model		Pseudo-order 1 kinetic model		Pseudo-order 2 kinetic model	
	R ²	k _{app} (min ⁻¹)	R ²	k _{app} (min ⁻¹)	R ²	k _{app} (mol ⁻¹ . L. min ⁻¹)
0 M	0.636	- 0.290	0.922	0.206	0.981	1.345
6.49.10 ⁻⁴ M	0.623	- 0.287	0.862	0.184	0.944	0.967
1.19.10 ⁻³ M	0.881	- 0.272	0.945	0.135	0.993	0.343
2.91.10 ⁻³ M	0.818	- 0.233	0.964	0.105	0.990	0.064
7.03.10 ⁻³ M	0.819	- 0.197	0.926	0.067	0.984	0.027

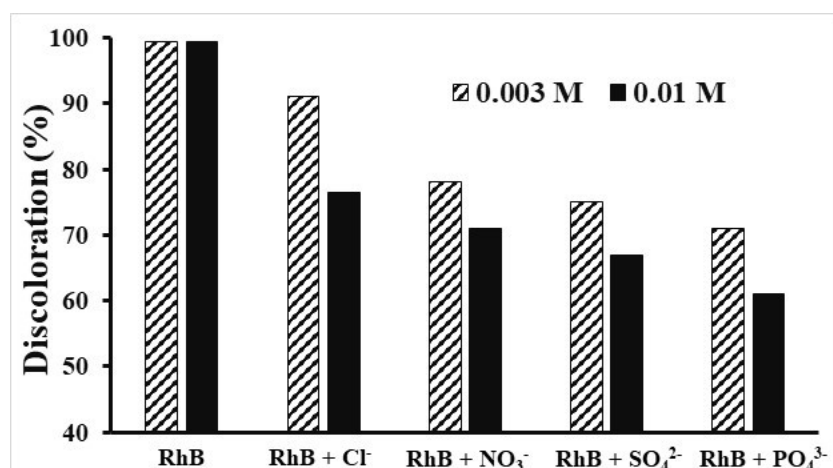


Figure 9: Effect of inorganic ions on RhB degradation; pH = 3, [RhB] = 5 mg / L; [H₂O₂] = 3.10⁻² M; [Fe²⁺] = 8.4.10⁻⁴ M.

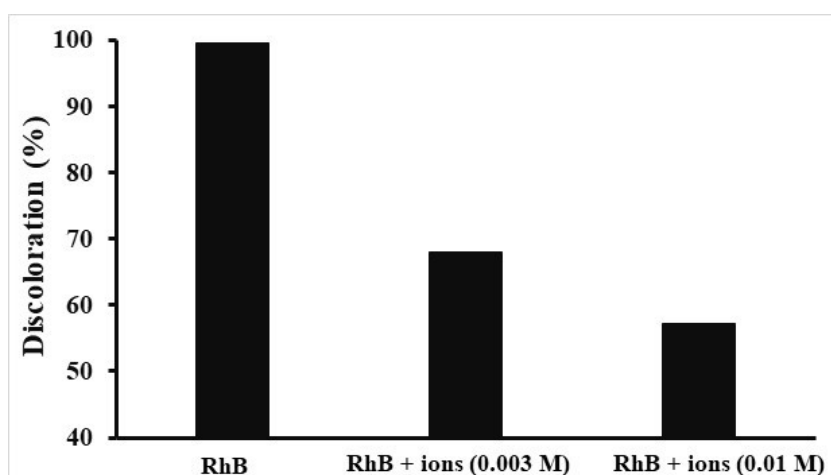
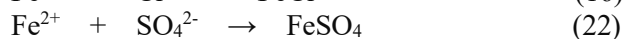


Figure 10: RhB concentration reduction rate in the presence of different inorganic ions (NO₃⁻ + Cl⁻ + SO₄²⁻ + PO₄³⁻) with a concentration of 0.003 M and 0.01 M each; Δt = 30 min, pH = 3; [RhB] = 5 mg / L; [H₂O₂] = 3.10⁻² M; [Fe²⁺] = 8.4.10⁻⁴ M.

The influence of inorganic ions on RhB degradation rate has been investigated and obtained results are shown in **Figure 9**. This figure shows a decrease in the RhB degradation rate in the presence of inorganic ions. In addition, it is noted that for a given ion, the higher its concentration, the more the RhB degradation rate decreases. This figure indicated that the presence of Cl⁻ has a less negative influence on RhB degradation, compared to nitrate, sulphate and phosphate ions. From results, inorganic ions strongly slow down the RhB degradation rate in the following order: Cl⁻ < NO₃⁻ < SO₄²⁻ < PO₄³⁻. Thaís D. de Oliveira et al [38] showed that sulfate ions inhibited the oxidation reaction of caffeine by Fenton process more than chloride. In fact, the Fenton process is very sensitive to inorganic ions present in solution

[39]. These ions can form complexes with Fe (II) (equation 16 and 22 to 24) thus affecting the distribution and reactivity of free Fe²⁺.



The presence of Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ leads to competition between organic matter and hydroxyl radicals, which delays the RhB oxidation. Inorganic ions react with hydroxyl radicals to produce inorganic radicals with less powerful oxidizing powers compared to hydroxyl radicals.

The influence of the synergistic effect of the above anions has been examined. Results (Figure 10) shows that the presence of several ions (NO_3^- ; Cl^- ; SO_4^{2-} ; PO_4^{3-}) in the reaction media greatly reduces the RhB degradation rate. This reduction in the abatement rate is more accentuated as the ion concentration increases.

4. Conclusion

This study showed that the mixture of H_2O_2 and Fe^{2+} significantly degrades RhB. This mixture produces hydroxide radicals responsible for the RhB degradation. The study of pH influence on RhB oxidation revealed that for a maximal oxidation of RhB, the pH must be less than or equal to 2. Parasitic reactions also occur if the ratio $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}]$ is higher than 35.7. RhB oxidation was faster for low concentrations than for high concentrations of RhB. According to this work for maximum oxidation (99.42%) of 5 mg/L RhB, $8.4 \cdot 10^{-4}$ mg/L Fe^{2+} , $3 \cdot 10^{-3}$ M H_2O_2 and pH = 2 are required. The rate of discoloration decreases with the concentration of inorganic ions. Inorganic ions strongly decrease the rate of RhB degradation in the following order: $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. RhB oxidation by Fenton process was a simple and rapid method because the reaction occurred within the first 20 minutes.

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