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Discoloration of red 5B and reactive blue 5G dyes in synthetic textile dye effluent by photo-Fenton process

Leandro Finger[1+]; Ismael Laurindo Costa Junior[1]; Poliana Paula Quitaiski[1]; Juliana Bortoli Rodrigues Mees[1]

[1] Universidade Tecnológica Federal do Paraná (UTFPR) Campus Medianeira, Paraná, Brazil

[+]Corresponding author: Leandro Finger, e-mail address: fingerleandro@hotmail.com

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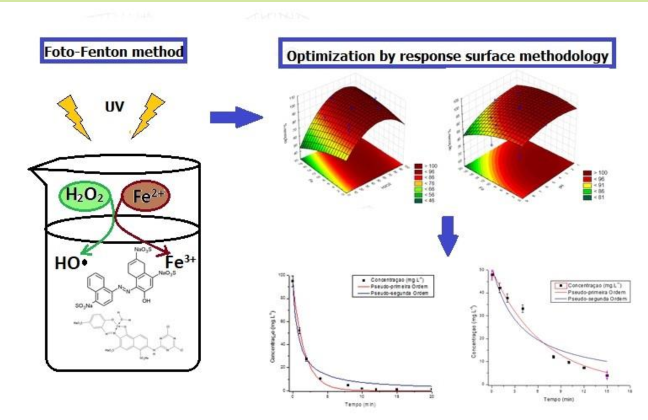
ABSTRACT: Effluents from textile industries are difficult to treat because they are loaded with non-biodegradable dyes. In this context, the Advanced Oxidation Processes (AOPs) are presented as alternatives to be studied for the treatment of these effluents. The objective of this work was to evaluate the efficiency of the discoloration of red 4B and 5G blue dyes in synthetic solution by means of the advanced oxidation Photo-Fenton. The best pH for discoloration of Red 4B was pH 3 and for Blue 5G dye was pH 1.6. The obtained results report a good discoloration when using H_2O_2 and Fe^{2+} ions. With a H_2O_2 concentration of 66.80 mg L^{-1}, Fe^{2+} of 9.66 mg L^{-1} and pH 5.81 with a predicted percentage discoloration of 100.01 % for Red 4B dye. And for Blue Reactive 5G dye a concentration of H_2O_2 of 55.04 mg L^{-1}, Fe^{2+} ions of 10.34 mg L^{-1} and pH 2.59 with an expected percentage discoloration of 100.56 %. The kinetics was that pseudo-first order with k_1 of 0.597 min^{-1} and $t_{1/2}$ of 1.16 min for red 4B and k_1 of 0.150 min^{-1} and $t_{1/2}$ of 4.60 for blue 5G. The results indicate the application of photo-Fenton as promising for the dyes discoloration in aqueous solutions.



1. Introduction

The environmental contamination has global proportions due, especially the continuous emission of large volume of domestic and industrial wastewater, with high polluting potential when not treated in a proper way. Regarding industrial activities, textile fiber dyeing operations deserve attention due to the high volumes of liquid waste, with high organic load and intense coloration[1].

The interest of environmental research related to the treatment of effluents from the textile industry is increasing, since these are highly complex, because they have different physical and chemical compositions, great diversity of synthetic dyes and different toxicity potentialities, thus making them difficult treatment and high pollution capacity[2].

In this sense, the advanced oxidation processes (AOPs) have been gaining visibility as a consequence of the great contribution potential with the conventional processes of effluent treatment, since the hydroxyl radicals generated have high reactivity and low selectivity, being able to act in the chemical oxidation of a large number of substances[3]. The photo-Fenton process ($UV/H_2O_2/Fe^{+2}$) has been prominent among AOPs, since it provides oxidations in shorter times when compared to others, besides being simple, since it is based on the reaction between ferrous salts (Fe^{2+}) and hydrogen peroxide (H_2O_2), associated with UV irradiation[4].

In this sense, the objective of this work was to evaluate the efficiency of the discoloration of red 4B and blue 5G in synthetic solution by means of the photo-Fenton reaction ($UV/H_2O_2/Fe^{+2}$), by optimizing a discoloration condition for the variables pH, Fe^{2+} ions concentration and H_2O_2 concentration and kinetic study of the process.

2. Experimental

2.1 Solutions and Analytical Determinations

Stock standard solutions of red 4B and blue 5G dyes were prepared using ultrapure water at 1000 mg L^{-1} concentration. The pH adjustments by 0.1 mol L^{-1} HCl (Biotec) and 0.01 mol L^{-1} NaOH solutions (Vtec) were also prepared. For the photo-Fenton process, H_2O_2 1000 mg L^{-1} (Alphatec) and $FeSO_4\ 7H_2O$ 100 mg L^{-1} (Merck) were used.

For the quantification, initially scans of the solution of each dye were performed to determine the absorption maximum. The calibration curve was constructed by absorbance readings in the maximum length of solutions with known dye concentrations (0.5 to 50 mg L^{-1}) using the dual beam scanning UV/VIS molecular absorption spectrophotometer, Perkin Elmer brand, model Lambda 45, in the range of 400 to 800 nm with resolution of 2 nm and quartz cuvettes with optical path of 1 cm.

2.2 Optimization of Discoloration Conditions

The experiments with the synthetic effluent were carried out in a laboratory-scale reactor, operating in a batch system, consisting of a beaker with 250 mL of capacity and a magnetic stirrer to homogenize the solution, positioned inside a wooden box (80 cm x 40 cm x 60 cm) coated with aluminum foil to increase the radiation incidence in the solution and equipped with a UV source (high pressure Mercury vapor lamp without the bulb – 250W) fixed at the top about 20 cm from the solution. The inner temperature, after 20 min, was maintained at about 45 °C (Figure 1).

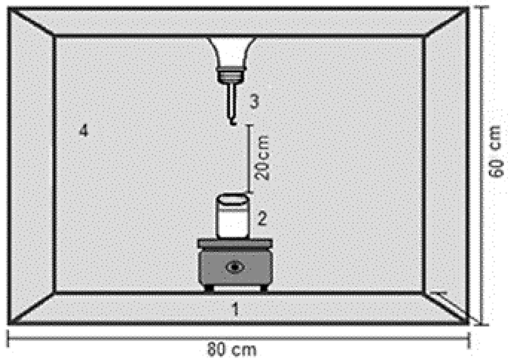


Figure 1. Photo-Fenton process reactor.
Caption:
1 – Magnetic stirrer.
2 – Reactor.
3 – UV source.
4 – Wooden box coated with aluminum foil.

Samples were withdrawn at pre-established intervals, 0-20 min for red 4B dye, and 0-15 min for blue 5G dye, and immediately the remaining concentration in the solution was determined using the dual beam scanning UV/VIS molecular absorption spectrophotometer by the calibration curve.

In order to verify the influence of the H_2O_2 concentration, Fe^{2+} ions concentration and pH and to obtain an optimum discoloration condition, a central composite rotational design (CCRD) 2^3 was elaborated with 2 replicates at the central point, using Statistica 8.0 software and the desirability function as tool. As the response variable in the statistical analysis the percentage of discoloration of the analytes (Red 4B and Blue 5G dyes) was used. The experimental data were adjusted to the linear and quadratic models it was evaluated using the Analysis of Variance (ANOVA) at the 95 % confidence level.

2.3 Discoloration Kinetic Study of Dyes in Water

In the study of kinetics of dye discoloration, solutions were used with concentration of 100 mg L^{-1} for red 4B and 50 mg L^{-1} for blue 5G in 250 mL beakers. Aliquots were taken in the time intervals of 0; 1; 2; 4; 8; 10; 12; 15 and 20 min to the red 4B dye, and 0; 1; 2; 4; 8; 10; 12 and 15 min to the blue 5G dye, with determination based on the previously determined maximum wavelength.

The discoloration was evaluated using the photo-Fenton process ($UV/H_2O_2/Fe^{+2}$) by kinetic models. The order of the reaction is the dependence of the speed of the reaction with the concentration. With C_0 being the initial

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concentration of the reagent, and C the concentration of the reagent elapsed at time t of reaction and n the order of the reaction. When n = 1 the reaction is of pseudo-first order (Equation 1) and n = 2 of pseudo-second order (Equation 2).

$$\ln C = \ln C_0 - k_1.t \;\therefore\; C = C_0.e^{-k_1 t} \quad (1)$$

$$\frac{1}{C} = \frac{1}{C_o} + k.t \;\therefore\; C = \frac{C_o}{1+C_o.k.t} \quad (2)$$

The experimental data obtained in the discoloration assays were fitted to these models in order to evaluate their decay during the experiment time, as well as to determine the half-life of each analyte according to the equation of pseudo-first order (Equation 3) and of pseudo-second order (Equation 4).

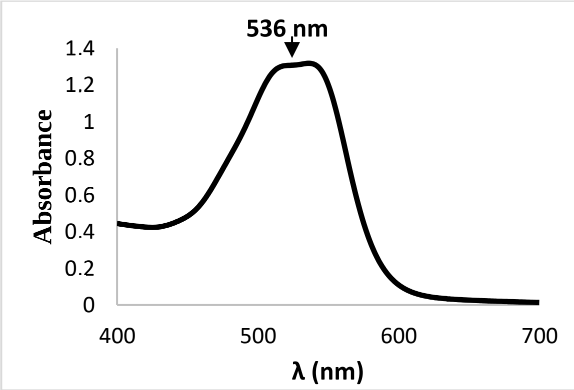
$$t_{\frac{1}{2}} = \frac{ln2}{K_1} \quad (3)$$

$$t_{\frac{1}{2}} = \frac{1}{K.C_o} \quad (4)$$

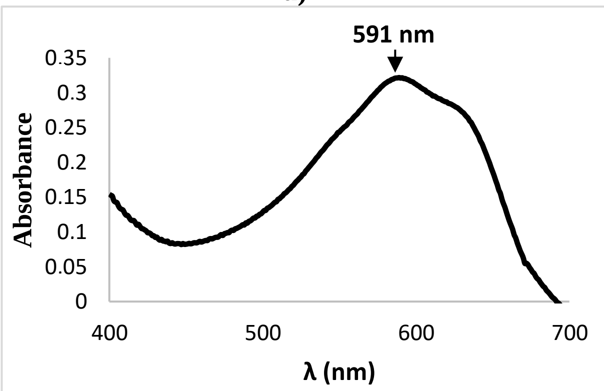
3. Results and Discussions

3.1 Spectrophotometric Evaluation

In order to determine the amount of dye removed, the optimum wavelength definition for the red 4B and blue 5G dyes reagent was first determined. This definition was obtained by double beam spectrophotometer scanning, where the molecular absorption spectrum was obtained, indicating the maximum absorbance band at 536 nm for red 4B dye and at 591 nm for blue 5G dye (Figure 2).



a)



b)

Figura 2. a) UV absorption spectrum in aqueous solution at 50 mg L^{-1} concentration for red 4B dye and b) blue 5G dye.

3.2 Optimization of Discoloration Conditions Employing Photo-Fenton Process

The experimental matrix for the 2^3 central composite rotational design (CCRD) delineation is presented in Table 1, with the levels of each factor, the actual values and the response variable obtained for the discoloration of red 4B and blue 5G dye in the photo-Fenton process ($UV/H_2O_2/Fe^{+2}$) in the course of 16 runs performed randomly.

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Table 1. CCDR 2^3 planning matrix with the factors coded (and real) and responses regarding the discoloration efficiency of 4B red and 5G blue dyes.

Assays	Factors			Variable Response	
	$[H_2O_2]$* (mg L^{-1})	[Fe]* (mg L^{-1})	pH*	Red 4B discoloration (%)	Blue 5G discoloration (%)
1	-1 (25.0)	-1 (5.0)	-1 (3.0)	95.31	86.35
2	-1 (25.0)	-1 (5.0)	+1 (7.0)	87.41	18.34
3	-1 (25.0)	+1 (15.0)	-1 (3.0)	85.76	81.16
4	-1 (25.0)	+1 (15.0)	+1 (7.0)	74.18	55.67
5	+1 (75.0)	-1 (5.0)	-1 (3.0)	100.00	100.00
6	+1 (75.0)	-1 (5.0)	+1 (7.0)	95.61	39.84
7	+1 (75.0)	+1 (15.0)	-1 (3.0)	98.75	73.75
8	+1 (75.0)	+1 (15.0)	+1 (7.0)	92.61	78.82
9	-1.68 (8.0)	0 (10.0)	0 (5.0)	65.04	72.64
10	+1.68 (92.0)	0 (10.0)	0 (5.0)	98.20	86.79
11	0 (50.0)	-1.68 (1.6)	0 (5.0)	95.06	16.24
12	0 (50.0)	+1.68 (18.4)	0 (5.0)	96.22	77.60
13	0 (50.0)	0 (10.0)	-1.68 (1.6)	95.12	100.56
14	0 (50.0)	0 (10.0)	+1.68 (8.4)	95.68	80.62
15	0 (50.0)	0 (10.0)	0 (5.0)	98.60	80.57
16	0 (50.0)	0 (10.0)	0 (5.0)	98.31	82.67

More effective discolorations were observed in assays 5, 7, 10, 14, 15 and 16 for both dyes, where H_2O_2 concentrations were applied at higher levels and pH was more acidic.

With the experimental results obtained in the discoloration of the dyes by photo-Fenton from CCDR 2^3, the values of the estimated effects of each parameter (concentration of H_2O_2 and Fe^{2+} ions, and pH) on the response variables presented in Table 1 were obtained, values that presented p-value less than 0.05 were considered significant for the 95 % confidence interval. From the significant values, the mathematical equation of the quadratic regression model and its respective determination coefficients (R^2) were obtained (Table 2).

Table 2. Mathematical models and determination coefficients (R^2) of the models adjusted for discoloration of the red 4B and blue 5G dyes.

Response	Model	R^2 (%)
Red 4B discoloration (%)	$98.37 + 7.33H_2O_2 – 5.78(H_2O_2)^2 - 1.84Fe^{2+} – 2.13pH – 0.89(pH)^2 + 2.31H_2O_2.Fe^{2+} + 1.12\ H_2O_2.pH$	88.56
Blue 5G discoloration (%)	$82.13 + 5.47H_2O_2 + 10.84Fe^{2+} – 13.49(Fe)^2 - 13.34pH + 13.47Fe.pH$	87.42

For the discoloration of the red 4B and blue 5G dyes respectively the R^2 values show that 88.56 % and 87.42 % of the responses were explained by the models, and the linear effects of pH and concentrations of $[H_2O_2]$ (mg L^{-1}) and $[Fe^{2+}]$ (mg L^{-1}) were the most important to describe the behavior of discoloration of the analytes by the photo-Fenton process.

To verify the fit quality of the model, the analysis of variance (ANOVA) was used, evaluating the determination coefficients (R^2) and the F test for both discolorations (Table 3).

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Table 3. ANOVA of the quadratic model to remove red 4B and blue 5G dyes.

	Sources of Variation	SQ	GL	MQ	F_{cal} (95%)	F_{tab} (95%)	F_{cal}/F_{tab}
Red 4B	Regression (model)	1249.64	9	138.85	5.16	4.10	1.26
	Residuals	161.34	6	26.89	-	-	-
	Lack of Adjusted	161.30	5	32.26	786.83	230.00	3.42
	Error	0.041	1	0.041	-	-	-
	Total	1410.98	15				
Blue 5G	Regression (model)	8591.58	9	954.62	5.10	4.10	1.24
	Residuals	1122.36	6	187.06	-	-	-
	Lack of Adjusted	1120.14	5	224.03	101.23	230.00	0.44
	Error	2.21	1	2.21	-	-	-
	Total	9713.93	15				

It is observed in Table 3 that the ratio of F_{cal} to F_{tab} for the regression presented a statistically significant value for the equation of discoloration of both dyes, a fact evidenced by a value higher than 1. Moreover, for the blue 5G dye, it was not observed (Figure 2). In this study, the F_{cal}/F_{tab} ratio for the lack of fit was lower than 1[5].

On the other hand, for the discoloration of red 4B dye the regression model generated was significant ($p \leq 0.05$) because $F_{cal} = 5.10$ was higher than the $F_{tab} = 4.10$. However, the lack of fit was also significant ($F_{cal} = 786.83 > F_{tab} = 230$), although the ideal was a value of $F_{cal} < F_{tab}$, and therefore not significant. However, since the means at the central points were very close and the pure error very low (reasons for the F of the lack of high fit), the model was considered valid for predictive purposes[5].

The Figure 3 shows the behavior of the process regarding the discoloration efficiency of red 4B according to the relation of the dependent variables by the surface response graph.

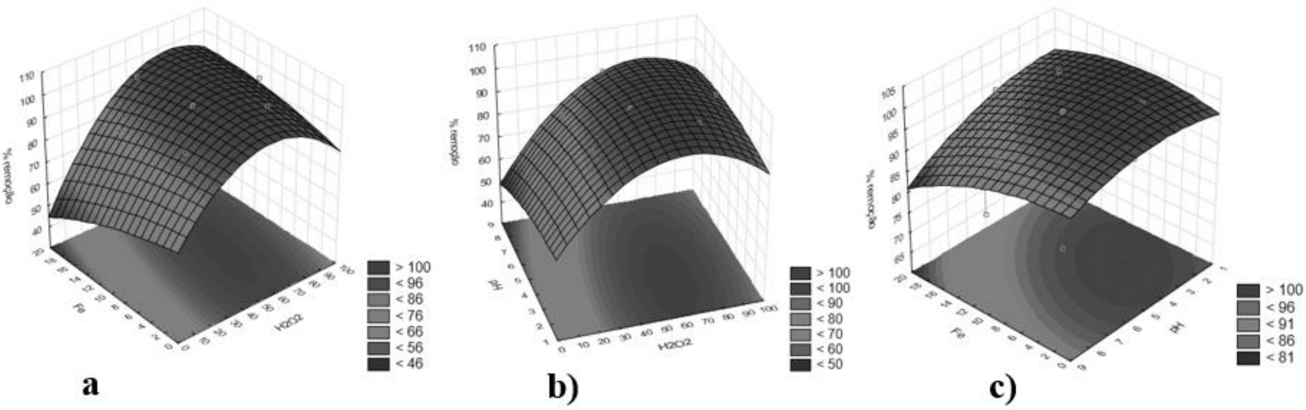

Figure 3. Response surface for discoloration efficiency red 4B dye by a) Fe^{2+} (mg L^{-1}) and H_2O_2 (mg L^{-1}); b) pH and H_2O_2 (mg L^{-1}); c) Fe^{2+} (mg L^{-1}) and pH.

In Figure 3, it can be observed that the discoloration efficiency of red 4B dye presented mean values between 65.04 % and 100.00 %. The best discoloration efficiency values, 98.75 % and 100.00 %, were obtained with pH 3, H_2O_2 concentration of 75 mg L^{-1}, Fe^{+2} concentration of 5 and 15 mg L^{-1}, respectively.

The Figure 4 shows the behavior of the process regarding the discoloration efficiency of the blue 5G dye according to the relation of the dependent variables by the surface response graph.

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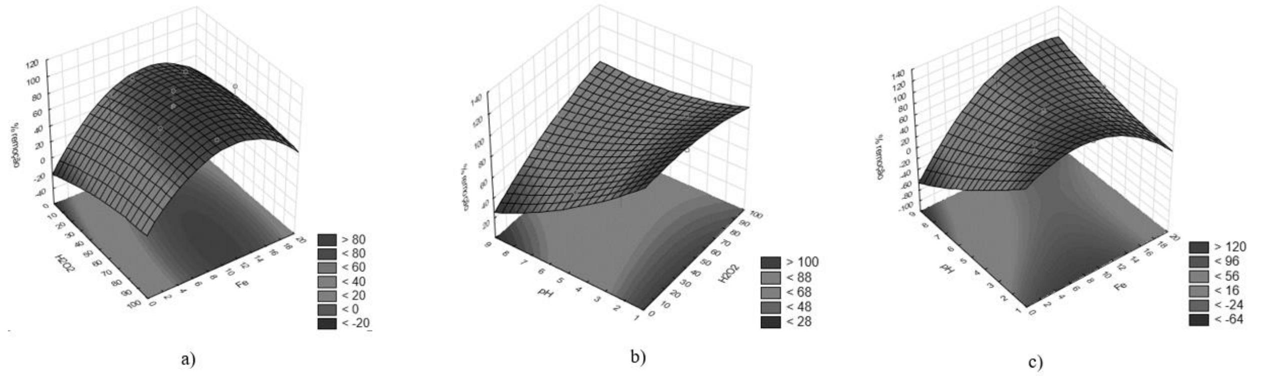

Figure 4. Response surface for blue 5G dye discoloration efficiency by a) Fe^{2+} ions (mg L^{-1}) and H_2O_2 (mg L^{-1}); b) pH and H_2O_2 (mg L^{-1}); c) Fe^{2+} ions (mg L^{-1}) and pH.

In Figure 4 it is observed that the discoloration efficiency of the blue 5G dye presented average values between 16.24 % and 100.00 %. The best discoloration efficiency values, both at 100.00 %, were obtained with pH 3 and 1.6, H_2O_2 concentration of 75 mg L^{-1} and 50 mg L^{-1}, and Fe^{+2} concentration of 5 and 10 mg L^{-1}.

Analyzing Figures 3 and 4 it is possible to verify that the concentration of H_2O_2 and Fe^{2+} ions showed a positive effect on the discoloration efficiency of red 4B and blue 5G dyes and that the pH variable had a negative effect on the discoloration efficiency, indicating that the highest discolorations were achieved with the decrease of this variable.

Škodič *et al.* demonstrated that the additions of moderate concentrations of H_2O_2 and Fe^{+2} ions catalyst during the AOPs obviously increased the decolorization efficiencies within the first few minutes of the processing time (5–10 min) for Reactive Blue 4 and Reactive Blue 268 dyes[4].

As a more favorable response to the discoloration of dyes in aqueous solution, the optimization tool employing the desirability function indicated a H_2O_2 concentration of 66.80 mg L^{-1}, Fe^{2+} ions of 9.66 mg L^{-1} and pH 5.81 with a percentage of 100.01 % discoloration to red 4B dye. For the blue 5G dye, a H_2O_2 concentration of 55.04 mg L^{-1}, Fe^{2+} ions of 10.34 mg L^{-1} and pH 2.59 with a predicted percent discoloration of 100.56 %.

3.3 Discoloration Kinetics Employing the Photo-Fenton Process (Uv / H_2O_2 / Fe^{+2} ions)

The optimum conditions were used in the kinetic study for both dyes. The pseudo-first order and pseudo-second order models fitted to the experimental data are shown in Figure 5.

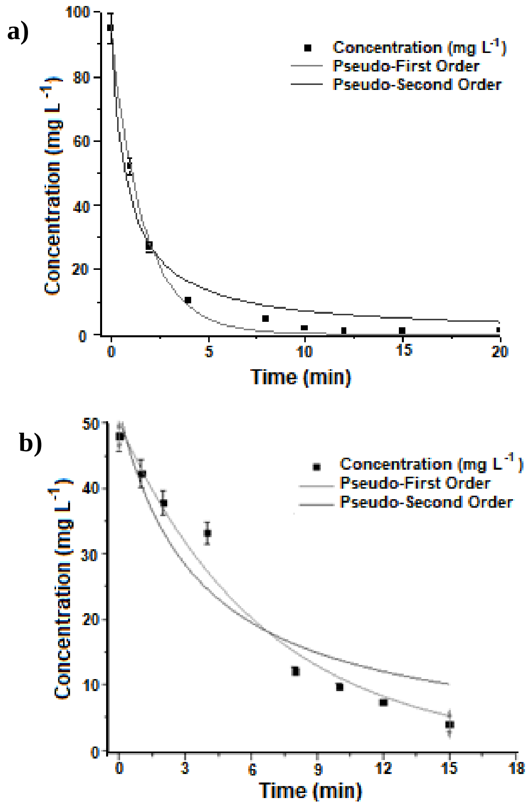

Figure 5. Adjustment of the experimental data of dye discoloration to the kinetic models of Pseudo-first order and Pseudo-second order. a) Red 4B; b) Blue 5G.

By means of this adjustment, it was possible to obtain the kinetic constant of pseudo-first order (k_1) and pseudo-second order (k_2), correlation coefficient (R^2) and half-life time ($t_{1/2}$), indicated in Table 4, for the discoloration of the red 4B and blue 5G dyes.

Santana *et al.* also obtained a good kinetic adjustment for the pseudo-first order for the removal of reactive blue dyes 5G and remazol red RB 133 % by photo-Fenton process[6].

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Table 4. Kinetic data for the photo-Fenton process ($UV/H_2O_2/Fe^{+2}$) of the red 4B and blue 5G dyes.

Dye	pH	Model Pseudo-First Order K_1 (min^{-1})	$t_{1/2}$ (min)	R^2
Red 4B	5.8	0.597	1.16	0.99
Blue 5G	2.6	0.150	4.60	0.97

Half-life times of 1.16 min for red 4B and 4.60 min for blue 5G dyes were observed. It was also verified that there was a greater speed of dye discoloration in the pseudo-first order model, besides a better adjustment in both treatments.

According to Núñes *et al.*, taking into account that the concentration of the reactive species needs to reach a steady state during the process, and once the oxidant concentration can be considered constant, the kinetics of the discoloration process can be treated as pseudo-first order, in terms of the consumption of the organic compound, in this case, the dye[7]. Generally, advanced discoloration processes obey the pseudo-first order kinetics[8].

4. Conclusions

The advanced photo-Fenton oxidative process ($UV/H_2O_2/Fe^{+2}$) proved to be very efficient in the discoloration of the synthetic solutions of red 4B and blue 5G dyes, allowing to eliminate the color of the aqueous media in times less than 20 min.

By means of the kinetic models evaluated, it was verified that the mathematical model of pseudo-first order was the one that best represented the experimental data of discoloration. However, it was observed that for red dye 4B the discoloration was faster, as indicated by the kinetic constant, that is, the half-life time was lower for the red4B compared to the blue 5G dye. It was also found that the concentrations of H_2O_2 and Fe^{2+} ions exhibited a positive effect on the discoloration for the studied dyes, increasing efficiency.

Further studies on the application of this process in real textile effluent are required, as well as in larger effluent volumes to compare the results with those obtained in this study. Studies using advanced chromatography techniques or total organic carbon are also necessary to verify possible degradation of the dyes in these effluents.

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