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Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation

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Abstract

The oxidative decolorization of Reactive Black 5 (RB5) in aqueous solution has been studied using Fenton (H_2O_2/Fe^{2+}) and photo-Fenton ($H_2O_2/Fe^{2+}/UV$) processes. This investigation reveals that both methods can remove the color of RB5. Batch experiments were carried out to investigate the process's optimal operational conditions: pH, H_2O_2 dosage, Fe^{2+} dosage, RB5 concentration and optimal $[Fe^{2+}]_0/[H_2O_2]_0/[RB5]_0$ ratio, to obtain the bests results at low cost, render AOP competitive with other processes. The optimal conditions found were a ratio $[H_2O_2]_0/[RB5]_0$ of 4.9:1, a ratio $[H_2O_2]_0/[Fe^{2+}]_0$ of 9.6:1 and pH = 3.0. The decolorization experiments indicate that RB5 can be effectively decolorized using Fenton and photo-Fenton processes with a little difference between the two processes, 97.5% and 98.1%, respectively, for optimal conditions. This small difference in dye decolorization is not similar to TOC removal: with photo-Fenton process there is a significant increment (46.4% TOC removal) relatively to Fenton process (only 21.6% TOC removal). This fact indicates that although UV low-pressure mercury lamp has little effect on dye decolorization it is particularly important in dye mineralization.

Keywords: Textile wastewater; Azo dye; Reactive Black 5; Advanced Oxidation Processes (AOP's); Fenton process; Photo-Fenton process

1. Introduction

Textile wastewaters are a large problem for conventional treatment plants in the entire world. The release of these wastewaters in natural environments is very problematic to aquatic life [1] and mutagenic to human [2]. The traditional treatment techniques applied in textile wastewaters, such as coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or elimination by activated carbon adsorption, only do a phase transfer of the pollutant, and biological treatment is not a complete solution to the problem due to biological resistance of some dyes. Hence, the resource to Advanced Oxidation Processes (AOP's), like Fenton and photo-Fenton processes, could be a good option to treat and eliminate textile dyes. These processes appear to have the capacity to completely decolorize and partially mineralize the textile industry dyes in short reaction time, as it was related by some studies [3–7].

There are many kinds of dyes available in the market. Based on the chemical structure or chromophore, 20–30 different groups of dyes can be discerned. Anthraquinone, phthalocyanine, triarylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms (—N═N—), are the largest class of dyes used in textile industry [8]. Inside the azo dyes we have a wide types of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes. Between these, the most used are the reactive azo dyes. Additionally, these dyes are the most problematic pollutants of textile wastewaters.

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This fact occurs because after the reactive dyeing process is finished, more than 15% of the textile dyes is lost in wastewater stream during dyeing operation [9]. So, in this work, we have selected the dye Reactive Black 5 (RB5), one of the most used reactive dyes for textile finishing, as a representative dye pollutant of these industrial wastewaters.

Advanced Oxidation Processes are oxidation processes that offer a highly reactive, non-specific oxidant namely hydroxyl radicals ($HO^{\bullet}$), capable of destroying wide range of organic pollutants in water and wastewater [10]. Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment [11]. In an acidic environment if hydrogen peroxide is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction will occur [12–14]. The overall reaction is:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (1)$$

The ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $HO^{\bullet}$ [15,16]. Hydroxyl radicals are powerful oxidation agents that have an oxidation potential only lower than fluorine and higher than ozone and H_2O_2: 3.0 V for fluorine, 2.8 V for $HO^{\bullet}$, 2.07 V for ozone and 1.78 V for H_2O_2. Then, hydroxyl radicals are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of these compounds by H-abstraction and addition to C–C unsaturated bonds [17]:

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (3)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \quad (4)$$

Numerous competing reactions which involve Fe^{2+}, Fe^{3+}, H_2O_2, hydroxyl radicals, hydroperoxyl radicals and radicals derived from the substrate, may also be involved. Hydroxyl radicals may be scavenged by reacting with Fe^{2+} or hydrogen peroxide:

$$HO^{\bullet} + Fe^{2+} \rightarrow HO^- + Fe^{3+} \quad (5)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (6)$$

Fe^{3+} formed through reactions (1) and (5) can react with H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, with regeneration of Fe^{2+} [16,18]:

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe{-}OOH^{2+} + H^+ \quad (7)$$

$$Fe{-}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (8)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^- \quad (9)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (10)$$

In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reactions (Eqs. (11) and (12)):

$$H_2O_2 + UV \rightarrow HO^{\bullet} + HO^{\bullet} \quad (11)$$

$$Fe^{3+} + H_2O + UV \rightarrow HO^{\bullet} + Fe^{2+} + H^+ \quad (12)$$

The addition of UV to Fenton's process could be an interesting allied in dye decolorization due to its capacity to influence the direct formation of $^{\bullet}OH$ radicals [6,19]. The main objective of this study is to analyse the feasibility of decolorization and mineralization of RB5 by Fenton and photo-Fenton processes. The influence of different operational parameters (pH, H_2O_2 dosage, Fe^{2+} dosage, RB5 concentration and optimal $[Fe^{2+}]_0/[H_2O_2]_0/[RB5]_0$ ratio) which affect the efficiency of Fenton and photo-Fenton reactions, in Reactive Black 5 (RB5) oxidation was also investigated.

2. Experimental

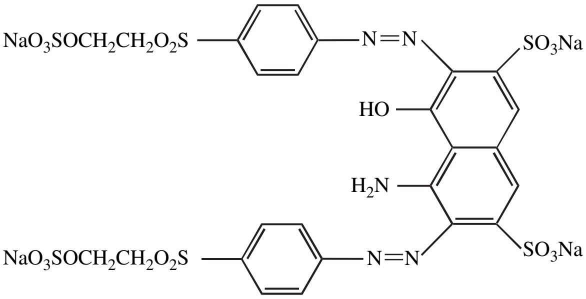
2.1. Material

The azo dye, Reactive Black 5 (Color Index 20505), was kindly provided by DyStar (Portugal) and used as received without further purification. Molecular structure of RB5 in non-hydrolyzed form is illustrated in Table 1. $FeSO_4 \cdot 7H_2O$ (Panreac), H_2O_2 (Merck, Perhydrol, 30% w/w) and Na_2SO_3 (M&B) were used as reagent grade. Solutions were prepared by dissolving requisite quantity of dye in deionised water from a Millipore purification system. pH of the reaction solutions was adjusted using H_2SO_4 and NaOH solutions. Initial pH of the solution was monitored using a Basic pH Meter from Denver Instrument Company.

2.2. Photoreactor

Batch experiments, for Fenton and photo-Fenton oxidation, were performed in a *Heraeus* photoreactor. The cylindrical reactor of 800 mL capacity was made of

Table 1
Chemical structure, absorption maxima and molecular weight of RB5

Name	Chemical structure	λ_{max} (nm)	Molecular weight (g/mol)
Reactive black 5 (diazo dye)		310 and 595	991.8

borosilicate glass and with lateral-top ports for sampling. For photo-Fenton oxidation was used a low-pressure mercury vapor lamp *Heraeus* TNN 15/32 placed in axial position inside the reactor. The spectral output of the low-pressure mercury vapor lamp emits mainly (85–90%) at 253.7 nm and about 7–10% at 184.9 nm. The reaction temperature was kept at the desired value within ±0.5 °C by using a thermostatically controlled outer water jacket. For every experiment performed, the reactor was initially loaded with 500 mL of RB5 aqueous solution and continuous mixing was maintained by means of a magnetic stirrer.

2.3. Analysis

A desired quantity of dye/Fe^{2+}/H_2O_2 solution was freshly prepared from $FeSO_4\cdot 7H_2O$, H_2O_2 and the dye stock solution. Most experiments were carried out at pH = 5 of the solution. The required amounts of Fe^{2+} and H_2O_2 were added simultaneously into the dye solution. In Fenton process the reaction time was recorded when the H_2O_2 solution was added, for photo-Fenton process it is recorded when the UV lamp is turned on. Samples of the dye solution were withdrawn during the course of the reaction, at periodic intervals, and analysed in a UV–visible scanning spectrum 200–800 nm, using a Jasco V-530 UV/VIS (Tokyo, Japan) double-beam spectrophotometer. Na_2SO_3 solution was used to quench the oxidation before the spectrophotometer analyses. The color of the dye solution in the reaction mixture at different times, was obtained by the measure of the absorbance at maximum wavelength ($\lambda_{max} = 595$ nm) and by computing the concentration from calibration curve. Total Organic Carbon (TOC) measurements were carried out with a SKALAR SK12 analyser.

3. Results and discussion

Absorption spectra of the dye solutions were recorded. From the observation it is visible that no new absorption peaks occurred near the original maximum wavelength. From this, it is possible to conclude that intermediate oxidation products do not disturb the absorption bands. The concentration of the residual dye in solution was calculated by Beer–Lambert's law using the optical density and molar extinction observed at the characteristic wavelength ($\lambda_{max} = 595$ nm):

$$A = l\varepsilon C$$

where A is the absorbency, l the path length (cm), ε the molar extinction coefficient (L/mol/cm), and C the dye concentration at time t (mol/L). Dye decolorization was analysed as follows:

$$\text{Dye decolorization} = \left(\frac{1 - C_{\text{dye},t}}{C_{\text{dye},0}}\right) \times 100\%$$

where $C_{\text{dye},t}$ and $C_{\text{dye},0}$ are the concentrations of dye at reaction time t and 0, respectively.

3.1. Chemical degradability of Reactive Black 5

To evaluate the efficiency and the benefit of each condition on the dye degradation experiments were carried out under the following conditions: (1) dye + H_2O_2, (2) dye + UV, (3) dye + UV + H_2O_2, (4) dye + UV + Fe^{2+}, (5) dye + Fe^{2+} + H_2O_2 (Fenton process), (6) dye + UV + Fe^{2+} + H_2O_2 (photo-Fenton process). In Fig. 1 are represented the results of decolorization. From the results it is possible to observe that dye is resistant to the oxidation from H_2O_2 alone. For UV alone it was observed that the dye decolorized about 79.7% in 240 min. The combined action of UV and H_2O_2 caused 99.3% decolorization in 180 min. For UV and Fe^{2+} color removal observed was 92.6% in 240 min. In Fenton process color removal was 72.6%, 90.9%, 95.0% and 97.5% at 1, 7.5, 15, 30 min, respectively. For photo-Fenton process 71.8%, 93.6%, 97.7% and 98.1% of decolorization was obtained at 1, 7.5, 15 and 30 min,

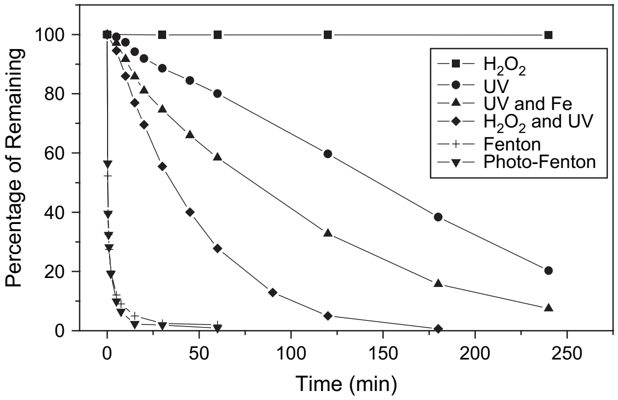


Fig. 1. Chemical degradability of RB5 under different conditions. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [Fe^{2+}] = 1.5×10^{-4} mol/L; [H_2O_2] = 7.3×10^{-4} mol/L; temperature = 20 °C; pH = 4.9; UV lamp = TNN 15/32 *Heraeus*.

respectively. Therefore, photo-Fenton process alone is more efficient than other experimental conditions.

The relative efficiencies of the above processes are in the following order: $Fe^{2+} + H_2O_2$ + UV (photo-Fenton) > $Fe^{2+} + H_2O_2$ (Fenton) > H_2O_2 + UV > UV + Fe^{2+} > UV > H_2O_2. The high efficiency of photo-Fenton process is due to the formation of more hydroxyl radical than the other processes. This signifies that UV lamp has a sensible increase on dye decolorization comparatively to the Fenton process. It is also possible to say that the iron catalysed decomposition of H_2O_2 is more efficient than the UV catalysed decomposition of H_2O_2. With the combination of UV and H_2O_2, the chemical bonds of azo compounds can be directly photolyzed by UV irradiation, but this is a slow process that can be substantially improved in the presence of H_2O_2 [20]. Adding Fe^{2+} to UV radiation improves the action of the UV wavelength on the dye decolorization. UV alone can remove dye color but at a lower percentage. At last, the H_2O_2 alone does not have any influence on dye decolorization. It is possible to conclude that the oxidizing power of H_2O_2 it is not enough to bring about RB5 decomposition.

3.2. Kinetic analysis

In all the experiments the disappearance of dye during the first 2 min of oxidation could be described as a first order reaction kinetics with regard to dye concentration as it may be seen from the data in Table 2. Initial decolorization rate constants were determined from the slope of $-\ln(C/C_0)$ vs t (min) plots, where C_0 and C are dye concentration at zero and t time, respectively. Also, to have a better knowledge on the decolorization process is presented the time necessary to reduce to 50% the initial concentration of RB5 – the half-life time ($t_{1/2}$).

Table 2
First order rate kinetics (K) and half-life ($t_{1/2}$) of dye decolorization

Oxidation processes	K (min^{-1})	$t_{1/2}$ (min)
H_2O_2	–	–
UV	0.0038	147.0
UV + Fe^{2+}	0.0109	77.8
UV + H_2O_2	0.0186	35.2
Fenton	1.225	0.568
Photo-Fenton	1.234	0.556

As it can be seen in Fig. 1 and comparing K values and $t_{1/2}$ in Table 2, photo-Fenton process, when compared to Fenton process, is better but the results are very similar. This fact is due to the little effect of UV radiation on initial minutes of the reaction. Low-pressure mercury vapor lamp TNN 15/32 has little power, only 15 W. However the use of a simple UV lamp in Fenton reaction may be very important to increase the degradation capacity of Reactive Black 5 after few minutes. This is because UV light wavelength can significantly influence direct formation of $^{\bullet}OH$ radicals as well as the photo-reduction rate of Fe^{3+} to Fe^{2+} (Eq. (12)). So, to have a complete knowledge of optimal conditions for each process, the next steps of this work are to assess the capacity of each process (Fenton and photo-Fenton), to oxidize Reactive Black 5, evaluating the effect of each parameter fixing the values of the others.

3.3. Effect of pH

The effect of pH on the decolorization of RB5 by Fenton and photo-Fenton processes is shown in Fig. 2. This figure shows that pH significantly influences the conversion of RB5. The experiments were carried out at pH between 1 and 8. At low pH (1 and 2) we have a very low decolorization both in Fenton and photo-Fenton processes. In the Fenton process the decolorization percentage, obtained at 30 min, is 8% and 51.6% for pH 1 and 2,

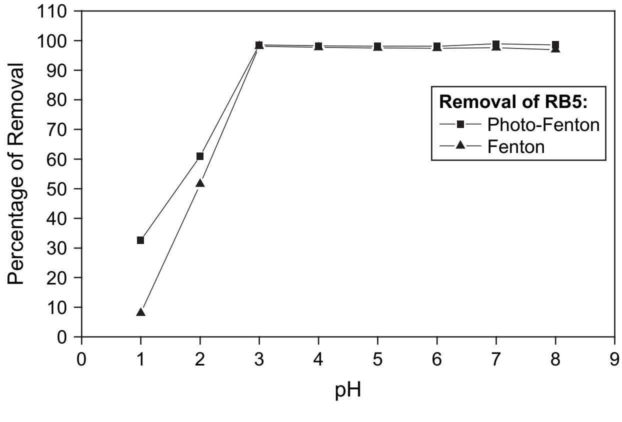


Fig. 2. Effect of pH on the decolorization of RB5 by Fenton and photo-Fenton processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [Fe^{2+}] = 1.5×10^{-4} mol/L; [H_2O_2] = 7.3×10^{-4} mol/L; temperature = 20 °C; UV lamp = TNN 15/32 *Heraeus*; reaction time = 30 min.

respectively. For photo-Fenton the decolorization is higher than Fenton process at this pH. At pH 1 the decolorization percentage is 32.6% and for pH 2 is 61% at 30 min. By increasing the pH to 3 we can obtain the highest decolorization, 98.1% and 98.6% for Fenton and photo-Fenton, respectively. For pH above 3 the decolorization is similar for Fenton and photo-Fenton processes having a color removal of about 98% for all pH. For pH values below 3, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing the reduction in hydroxyl radical production. Inhibition of radical $HO^{\bullet}$ formation at pH below 3 seems also to be due to the small amount of soluble iron (Fe^{3+}), responsible for the continuity of the oxidation process, occurring in the formation of $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ [21]. The low decolorization at pH 1 and 2 is also due to the hydroxyl radical scavenging of H^+ ions (Eq. (13)) [22].

$$HO^{\bullet} + H^+ + e^- \rightarrow H_2O \tag{13}$$

3.4. Effect of H_2O_2 dosage

Figs. 3 and 4 show the relationship between the degradation of dye and the initial concentration of H_2O_2 in the Fenton and photo-Fenton processes. To render the Fenton and photo-Fenton processes competitive with other processes, it is essential that their applications represent a low cost operation, which basically implies a better control of H_2O_2 dosage. The objective of this evaluation is to select the best operational dosage of H_2O_2 in Fenton and photo-Fenton processes. For the Fenton process, the addition of H_2O_2 from 2.4×10^{-4} to 9.8×10^{-4} mol/L increases the decolorization from 79% to 94% at 7.5 min. In the photo-Fenton process, the addition of H_2O_2 between 2.4×10^{-4} and 9.8×10^{-4} mol/L increases decolorization from 84% to 98%, respectively. Further increase from 7.3×10^{-4} to 9.8×10^{-4} mol/L causes no significant change in decolorization even for Fenton and photo-Fenton processes. This little increase is due to the fact that at a higher H_2O_2 concentration scavenging of OH radicals will occur, which can be expressed by the Eqs. (6) and (14) [23,24]:

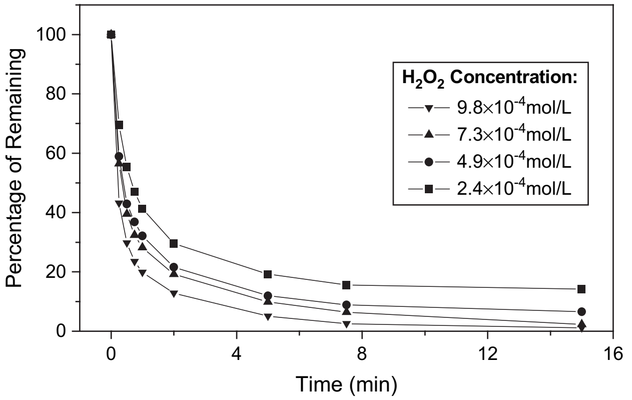


Fig. 4. Effect of the addition of H_2O_2 on the decolorization of RB5 by photo-Fenton process. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [Fe^{2+}] = 1.5×10^{-4} mol/L; temperature = 20 °C; pH = 5; UV lamp = TNN 15/32 *Heraeus*.

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{14}$$

The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H_2O_2. In Fenton and photo-Fenton processes the decolorization efficiency is not significantly different at the end. Hence, 7.3×10^{-4} mol/L of H_2O_2 appears as an optimal dosage for Fenton and photo-Fenton processes.

3.5. Effect of ferrous dosage

The effect of the addition of Fe^{2+} ion on the decolorization of RB5 has been studied. The results are shown in Figs. 5 and 6. The amount of ferrous ion is one of the main parameters influencing the Fenton and

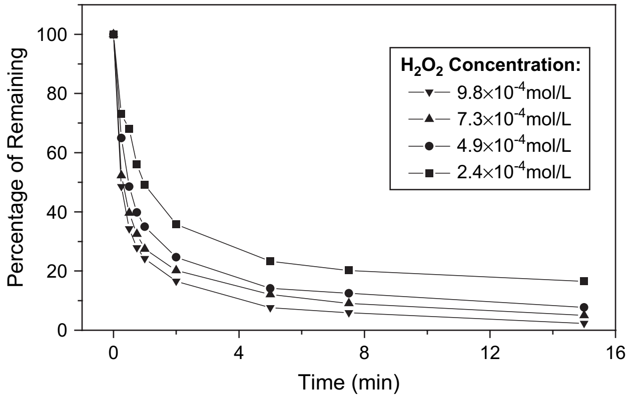


Fig. 3. Effect of the addition of H_2O_2 on the decolorization of RB5 by Fenton process. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [Fe^{2+}] = 1.5×10^{-4} mol/L; temperature = 20 °C; pH = 5.

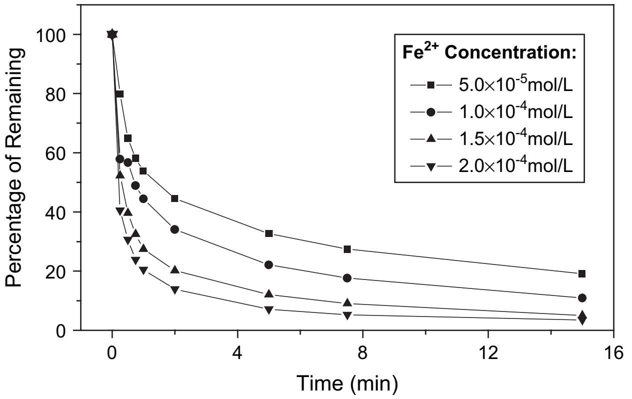


Fig. 5. Effect of the addition of Fe^{2+} on the decolorization of RB5 by Fenton process. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [H_2O_2] = 7.3×10^{-4} mol/L; temperature = 20 °C; pH = 5.

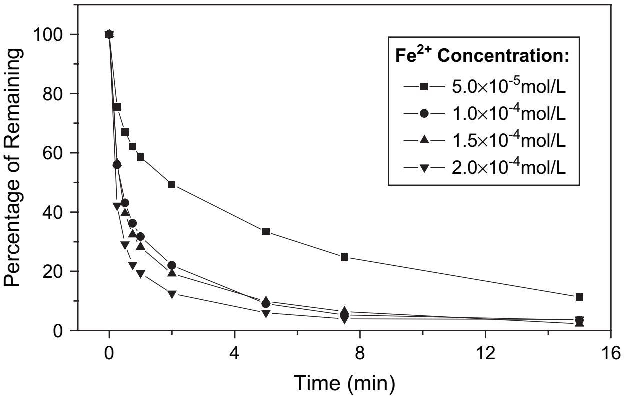


Fig. 6. Effect of the addition of Fe^{2+} on the decolorization of RB5 by photo-Fenton process. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; temperature = 20 °C; pH = 5; UV lamp = TNN 15/32 *Heraeus*.

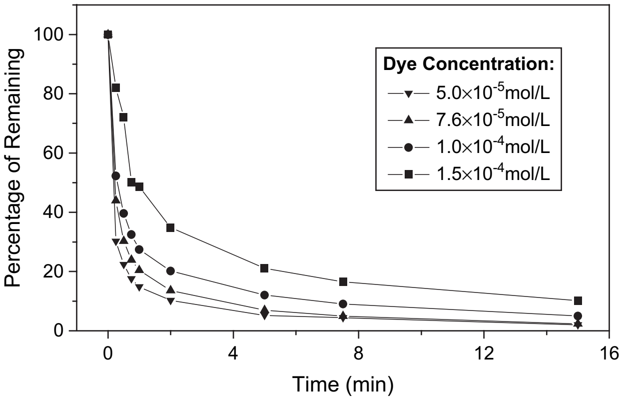


Fig. 7. Effect of dye concentration on the decolorization of RB5 by Fenton process. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; temperature = 20 °C; pH = 5.

photo-Fenton processes. The results indicate that the extent of degradation increases with the increase in initial Fe^{2+} concentration. Fenton process addition of Fe^{2+} from 5.0×10^{-5} to 2.0×10^{-4} mol/L increases color removal from 72% to 95% at 7.5 min and in photo-Fenton process the increase is from 75% to 96% for the same time. From the results it is possible to say that the efficiency of the RB5 destruction increases with increasing initial Fe^{2+} concentration. Although, the increase is from 1.5×10^{-4} to 2.0×10^{-4} it is very soft. It may be explained by the redox reactions since $HO^{\bullet}$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule as below. The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest $HO^{\bullet}$ radicals production available for oxidation. Fe^{2+} of 1.5×10^{-4} mol/L can be used as an optimum dosage for both the processes.

3.6. Effect of dye concentration

The effect of initial dye concentration of aqueous solution of RB5 on the Fenton and photo-Fenton processes was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of the concentration is shown in Figs. 7 and 8. From these figures it is possible to see that the extent of degradation decreases with the increase in the initial dye concentration. Increase of dye from 5.0×10^{-5} mol/L to 1.5×10^{-4} mol/L decreases the decolorization from 96% to 83% for Fenton and from 98% to 88% for photo-Fenton process in 7.5 min. The increase in dye concentration increases the number of dye molecules and not the HO radical concentration and so the removal rate decreases. In photo-Fenton process at high dye concentration the penetration of photons entering into solution decreases thereby lowering the hydroxyl radical concentration.

3.7. Effect of the relation $[H_2O_2]_0/[RB5]_0$ and $[H_2O_2]_0/[Fe^{2+}]_0$

To observe the optimal initial concentration ratio $[Fe^{2+}]_0/[H_2O_2]_0/[RB5]$ on the degradation of dye, different initial concentrations of Fe^{2+} at fixed $[H_2O_2]_0 = 7.3 \times 10^{-4}$ mol/L and $[RB5]_0 = 1.0 \times 10^{-4}$ mol/L to evaluate the optimal rate Fe^{2+}/H_2O_2 were experimented. We also experimented the relation H_2O_2/dye at different initial concentration of RB5 and fixed $[H_2O_2]_0 = 7.3 \times 10^{-4}$ mol/L. Fig. 9 shows the degradation of dye with the variation of $[H_2O_2]_0/[RB5]_0$ for a reaction time of 30 min. The results indicate that the extent of degradation increases until the optimum value of 9.6 for $[H_2O_2]_0/[RB5]_0$ ratio, either for Fenton or for photo-Fenton processes. For a bigger value of $[H_2O_2]_0/[RB5]_0$ it is visible from Fig. 9 that the RB5 degradation decreases. This is due to the fact that at higher H_2O_2 concentration,

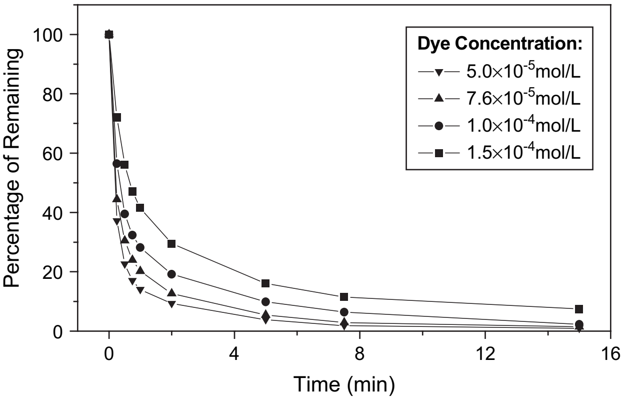


Fig. 8. Effect of dye concentration on the decolorization of RB5 by photo-Fenton process. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; temperature = 20 °C; pH = 5; UV lamp = TNN 15/32 *Heraeus*.

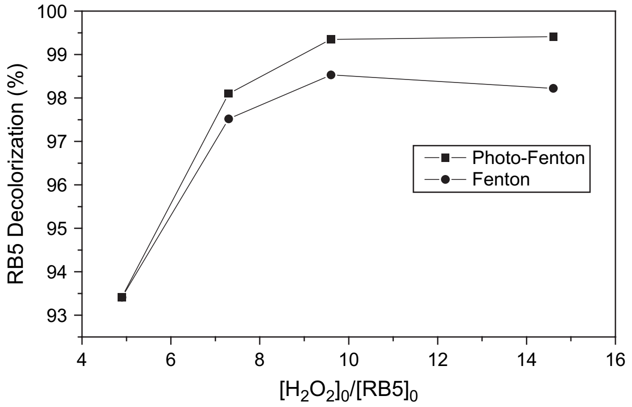


Fig. 9. Effect of initial $[H_2O_2]_0/[RB5]_0$ ratio on dye decolorization by Fenton and photo-Fenton processes. Experimental conditions: $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; temperature = 20 °C; UV lamp = TNN 15/32 *Heraeus*; reaction time = 30 min.

scavenging of OH radicals will occur (Eq. (6)) decreasing the RB5 decolorization (Fig. 9).

From Fig. 10 it is clear that the best $[H_2O_2]_0/[Fe^{2+}]_0$ ratio is at the value of 4.9. The increase on the H_2O_2 dosage induces the $HO^{\bullet}$ scavenge, decreasing the oxidation effect. In the photo-Fenton process this does not happen probably due to the UV lamp employment that maintains the oxidation capacity.

3.8. UV–visible spectra of the RB5 oxidized by photo-Fenton process

To study the decolorization of RB5, UV–visible absorption spectra of 1.0×10^{-4} mol/L RB5 solution were considered before and after the treatment with photo-Fenton process ($[H_2O_2] = 7.3 \times 10^{-4}$ mol/L, $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol/L and the UV lamp TNN 15/32), as it can be observed in Fig. 11. Before treatment, UV–visible spectra of RB5 consist of two main characteristic absorption bands. One is in UV region (310 nm) and another is in visible region (595 nm). UV band is characteristic of two adjacent rings, whereas visible band ows to long conjugated π system linked by two azo groups [25]. When 1.0×10^{-4} mol/L of RB5 solution was degraded by the photo-Fenton process it was clearly observed that the intensity of absorption peak in visible region (595 nm) disappears very fast after a few seconds. The UV band at 310 nm was also observed to vanish but at a lower rate than that of visible band. During photo-Fenton degradation, the absorbance values diminish all over the spectral window and no more specific peak remains after 5 min of reaction (Fig. 11).

3.9. Color and aromatic fragment degradation

To make a clear comparison of color rates (595 nm) and aromatic fragment (310 nm) degradation, the absorbance of 1.0×10^{-4} mol/L RB5 solution at 595 and 310 nm, as a function of time, was measured, for photo-Fenton process, and is presented in Fig. 12. This figure suggests that the action of the $HO^{\bullet}$ radicals first attack azo groups and open the N=N bonds, destructing the long conjugated π systems, and consequently causing decolorization. Second, owing to the fact that N=N bonds are easier to be destructed than aromatic ring structures, the elimination of adjacent ring structure needs a longer time.

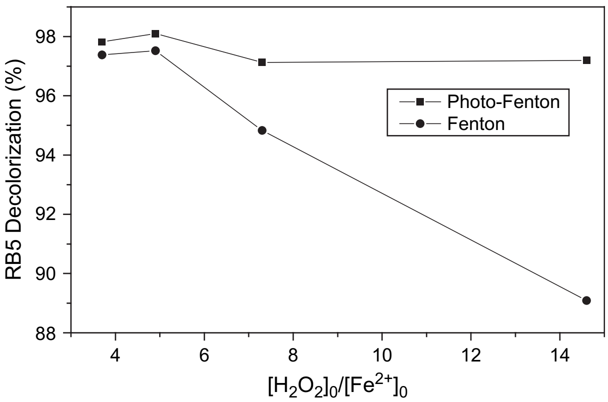


Fig. 10. Effect of initial $[H_2O_2]_0/[Fe^{2+}]_0$ ratio on dye decolorization by Fenton and photo-Fenton processes. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; temperature = 20 °C; UV lamp = TNN 15/32 *Heraeus*; reaction time = 30 min.

The plot (Fig. 12) indicates a high decolorization rate in the first 2–5 min, followed by a slower variation. The point of inflexion might indicate the separation between two different steps. These observations support the hypothesis that Fenton process could be theoretically divided into two-stages [26]. The first one is named as the Fe^{2+}/H_2O_2 stage. In this first step the hydroxyl radicals,

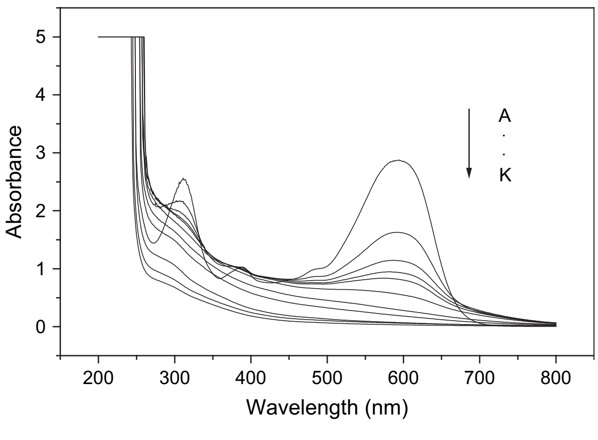


Fig. 11. UV–visible absorption spectra of RB5 solution during degradation with photo-Fenton process. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[H_2O_2] = 7.3 \times 10^{-4}$ mol/L; $[Fe^{2+}] = 1.5 \times 10^{-4}$ mol/L; UV lamp = TNN 15/32 *Heraeus*; reaction time = 1 h; pH = 5. A = 0 s, B = 15 s, C = 30 s, D = 45 s, E = 1 min, F = 2 min, G = 5 min, H = 7.5 min, I = 15 min, J = 30 min, K = 1 h.

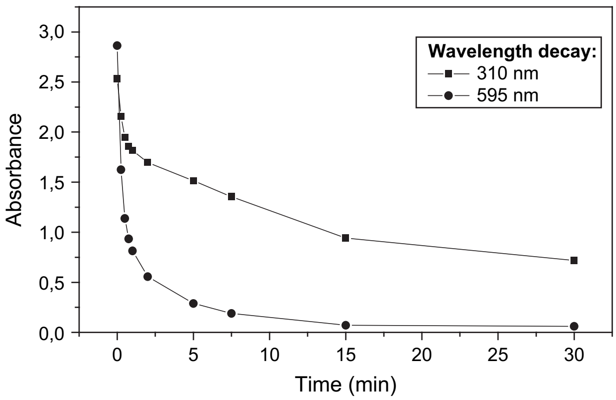


Fig. 12. Comparison between the color removal (595 nm) and aromatic fragment degradation (310 nm) from the [RB5] = 1.0×10^{-4} mol/L solution after oxidation with the photo-Fenton process.

formed by the reaction between ferrous ions and hydrogen peroxide (Eq. (1), $K = 76\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$), decomposes azo bonds very quickly, due to high reactivity of the hydroxyl radicals [27], resulting in a fast decrease of wavelength color (595 nm), as it could be seen in Fig. 12. The ferric ions, produced in the first stage (Eq. (1)), can react with hydrogen peroxide to produce hydroperoxyl radicals ($HO_2^{\bullet}$) and ferrous ions (Eqs. (7) and (8), $K = 0.01$–$0.02\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$). Here begins the second stage, known as Fe^{3+}/H_2O_2 stage. In this step, reproduced ferrous ions (Eq. (8)) react with hydrogen peroxide (Eq. (1)) to produce hydroxyl radicals. Hydroxyl radicals and hydroperoxyl radicals thus formed are able to continue dye degradation. But the oxidation rate of this second stage was slower than the first stage due to slow production of Fe^{2+} from Fe^{3+} (Eqs. (7) and (8), $K = 0.01$–$0.02\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) comparatively to radical reaction constant between the hydroxyl radical and RB5 (Eq. (2), $K = 10^8$–$10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$). These kinetic considerations are evident, in practice, in a slower dye decolorization. However in this second stage, with the formation of $HO^{\bullet}$ radicals and hydroperoxyl radicals, the aromatic fragment has a higher removal. As suggested by some authors [26,28], the first stage have the duration of few minutes, between 1 and 5 min. In this case after 1 min of degradation, the peak at 595 nm has a decrease of 72% and the peak at 310 nm only have a decrease of 28%. So, it is possible to deduce that the highest decolorization occurs in first minute during the first stage of Fenton reaction (Fe^{2+}/H_2O_2). Degradation of aromatic fragment occurs in both stages of Fenton process but at high percentage during the second stage (stage Fe^{3+}/H_2O_2). From the results it is visible that between 1 and 30 min occurs a degradation of 44% of the aromatic peak, in opposite to the first minute where we have only a peak reduction of 28%. This result is also justified by the use of UV lamp. The action of UV lamp in the first stage is negligible due to duration of first stage being only a few minutes. But in second stage UV lamp have an important role due to increment of $HO^{\bullet}$ radicals production during the period of time of this phase (~25 min) (Eqs. (11) and (12)). Although after 30 min of photo-Fenton degradation, it is observable from Fig. 12 that the 310 nm peak has not yet completely degraded. The wavelength of the color was decolorized 98% but the wavelength related to the aromatic fragment was reduced by only 72%, suggesting that the original chemical structure of RB5 namely the aromatic fraction was not completely degraded.

3.10. Mineralization study

It is known that reaction intermediates can form during the oxidation of azo dyes and some of them could be long-lived and even more toxic than their parent compounds. Therefore, it is necessary to understand the mineralization degree of the azo dye RB5 to evaluate the degradation level applied by Fenton and photo-Fenton processes. To quantitatively characterize the mineralization of azo dyes in the solution, the TOC removal ratio is used in the study, which is defined as follows:

$$\text{TOC removal ratio} = \left(\frac{1 - \text{TOC}_t}{\text{TOC}_0}\right) \times 100\%$$

where TOC_t and TOC_0 are the TOC values at reaction time *t* and 0, respectively. Fig. 13 presents the color degradation and TOC removal ratio of the azo dye RB5 with Fenton and photo-Fenton processes. As could be seen, dye decolorization is much higher than TOC removal even in Fenton and photo-Fenton. Although, it is visible from this figure that photo-Fenton process presents a TOC removal higher than Fenton process, 46.4% and 21.6%, respectively. So, from this analysis it is evident that, even though the same decolorization occurs in both processes, the employment of the UV lamp benefits the azo dye degradation. It is possible to conclude that the UV lamp, though has little power, is very useful in Fenton process to aid the dye degradation.

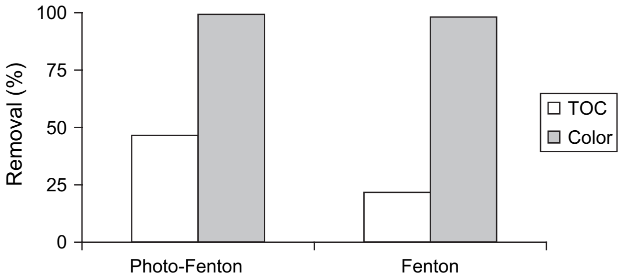


Fig. 13. Comparison between the decolorization and TOC removal of dye RB5 after Fenton and photo-Fenton processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [H_2O_2] = 7.3×10^{-4} mol/L; [Fe^{2+}] = 1.5×10^{-4} mol/L; UV lamp = TNN 15/32 *Heraeus*; reaction time = 1 h; pH = 5.

With this result it is verified that the RB5 did not totally degrade with photo-Fenton, like was suggested from the analyses of the peak at 310 nm.

4. Conclusions

From the Fenton and photo-Fenton oxidation studies of Reactive Black 5 (RB5), a model compound of textile wastewaters, the following conclusions can be drawn:

- Fenton and photo-Fenton processes lead to complete decolorization of Reactive Black 5 dye in relatively short time (~15 min).
- RB5 degradation follows, even for Fenton and photo-Fenton, a first order kinetic law in the first 2 min. This decolorization could be separated into two phases, the Fe^{2+}/H_2O_2 and the Fe^{3+}/H_2O_2 phases. The first one is much faster and with a high decolorization power and the second lowest but with a highest degradation capacity of the aromatic fragment.
- The optimal parameters, for both processes, under the same operational conditions are: ratio $[H_2O_2]_0/[RB5]_0 = 9.6:1$, ratio $[H_2O_2]_0/[Fe^{2+}]_0 = 4.9:1$ and $pH = 3.0$.
- The Fenton and photo-Fenton processes only decolorize the dye solutions but also partially mineralize the azo dye RB5.
- Although the decolorization is very similar in both processes, the employment of the UV lamp benefits the azo dye degradation. So, it is possible conclude that the UV lamp, though has little power (15 W), is very useful in Fenton process to increase the dye degradation.

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