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Dyes and Pigments 74 (2007) 622–629

DYES and PIGMENTS

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Degradation of *Reactive Black* 5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes

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Received 17 February 2006; accepted 19 April 2006
Available online 13 June 2006

Abstract

The feasibility of employing different photoxidation systems, like Fenton/UV-C and ferrioxalate/H_2O_2/solar light in the decolorization and mineralization of an azo dye, has been investigated. Batch experiments were carried out to evaluate, on the first stage, the influence of different processes on *Reactive Black* 5 (RB5) decolorization. During the second stage were investigated the optimal operational conditions of Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes, like pH, H_2O_2 dosage, iron dosage, RB5 concentration and source of light. The experiments indicate that RB5 can be effectively decolorized using Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes with a small difference between the two processes, 98.1% and 93.2%, respectively, after 30 min. Although there is lesser difference in dye decolorization, significant increment in TOC removal was found with Fenton/UV-C process (46.4% TOC removal) relative to ferrioxalate/H_2O_2/solar light process (29.6% TOC removal). This fact reveals that UV-C low-pressure mercury lamp although with its small effect on dye decolorization is particularly important in dye mineralization, when compared to solar light. However, ferrioxalate/H_2O_2/solar light system shows large potential on photochemical treatment of textile wastewater with particular interest from the economical point of view.

Keywords: Textile wastewater; *Reactive Black* 5; Advanced Oxidation Processes; Fenton's reagent; Ferrioxalate; UV-C radiation; Solar light

1. Introduction

Textile industry is one of the highest water consuming sectors, between 25 and 250 m^3 per ton of product depending on the processes – and the largest consumer of colorants for various dyeing, printing and finishing processes [1,2]. This water consumption, allied to high dosages of dyes, originates effluents that are extremely colorized. The release of these wastewaters to natural environments is described as very problematic to aquatic life [3] and mutagenic to human [4].

The conventional treatment techniques applied in textile wastewaters, such as chemical coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) or elimination by activated carbon adsorption, are not only costly, but also result in phase transfer of pollutants. Biological treatment is not an efficient solution to these effluents due to the complex structure of some dyes that provokes resistances to biodegradation. Hence, the resource to Advanced Oxidation Processes (AOPs) could be a good alternative to treat and remove textile dyes from the wastewaters.

The azo dyes, characterized by an azo group (–N=N–), are the largest class of dyes used in textile industry for dyeing several natural and synthetic materials [1,5]. Between the several azo dyes (acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur) the most used are the 'reactive' type. These dyes are the most problematic pollutants of textile wastewaters. This fact occurs because, after the dyeing process, more than 15% of the textile dyes are lost in wastewater stream [6]. Therefore, in this study was selected the azo dye *Reactive Black* 5 (RB5) as a representative dye pollutant of textile wastewaters.

Advanced Oxidation Processes offer a highly reactive, nonspecific oxidant, namely hydroxyl radicals ($HO^\bullet$), capable of

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doi:10.1016/j.dyepig.2006.04.005

destroying a wide range of organic pollutants in water and wastewater [7,8]. Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. In an acid environment if hydrogen peroxide is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction will occur [9–11]. The overall reaction is

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

The ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $HO^\bullet$ [12,13]. Hydroxyl radicals are capable of rapidly attacking organic substrates and causing chemical decomposition of these compounds by H-abstraction and addition to C=C unsatured bonds [14].

The addition of UV radiation to Fenton's reagent process could be an interesting allied in dye decolorization due to its capacity in influencing direct formation of $HO^\bullet$ radicals [15,16]. This AOP combination has gained progressive attention in recent years due to its higher efficiency when compared to the dark process. In Fenton/UV-C process, in addition to Eq. (1), the formation of hydroxyl radical also occurs by the following reactions (Eqs. (2) and (3)):

$$H_2O_2 + UV \rightarrow HO^\bullet + HO^\bullet \qquad (2)$$

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

Recently, other processes have been studied trying to use solar light instead of artificial UV radiation. Ferrioxalate, used for decades as a chemical actinometer, has been applied in the Fenton's reagent process as iron source thus allowing further benefit from solar radiation [17]. The use of ferrioxalate in the degradation of organic pollutants was reported to be very effective, and using solar light was found to be an economic alternative when compared to artificial UV radiation [18–20]. The photolysis of ferrioxalate generates Fe(II) in acid solutions reported as follows [18,21]:

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \qquad (4)$$

$$C_2O_4^{-\bullet} + [Fe(C_2O_4)_3]^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \qquad (5)$$

$$C_2O_4^{-\bullet} + O_2 \rightarrow O_2^{-\bullet} + 2CO_2 \qquad (6)$$

The main objective of this study is to analyse the feasibility of decolorization and mineralization of RB5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. The influence of different operational parameters (source and intensity of light, pH and H_2O_2, iron and RB5 concentration) that affect the efficiency of Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes during the oxidation of *Reactive Black* 5 are studied.

2. Experimental

2.1. Material

The azo dye, *Reactive Black* 5 (Color Index 20505), was kindly provided by *DyStar Anilinas Têxteis Lda.* (Portugal) and used as received without further purification. UV–vis absorption spectra and molecular structure of RB5 in non-hydrolyzed form are illustrated in Fig. 1. The chemicals used in the experiments, $FeCl_3$ (*Riedel-de-Haën*), $C_2H_2O_4$ (*Fluka*), $FeSO_4 \cdot 7H_2O$ (*Panreac*), H_2O_2 (*Merck*, Perhydrol, 30% w/w) and Na_2SO_3 (*M&B*) were of reagent grade. All the solutions were prepared by dissolving requisite quantity of dye in deionised water from a *Millipore* purification system. When appropriate, the pH of the solution was adjusted using H_2SO_4 and NaOH solutions. Initial pH of solution was monitored using a Basic pH Meter from *Denver Instrument Company*.

2.2. Photoreactor

Batch experiments for Fenton/UV-C oxidation, were performed in a *Heraeus* photoreactor. The cylindrical reactor of 800 mL capacity was made of borosilicate glass with ports, at the top, for sampling. For Fenton/UV-C oxidation was used a low-pressure mercury vapor lamp, *Heraeus TNN 15/32*, placed in an axial position inside the reactor. 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. Ferrioxalate/H_2O_2/solar light experiments were carried out, in open air, at the University of Trás-os-Montes and Alto Douro campus, Portugal (41°18′N; 7°45′W) under clear sky conditions. All photocatalytic experiments were carried out under similar conditions on sunny days of May–August, between 11 AM and 3 PM. Solar reactions were conducted in a glass reactor wrapped externally with aluminium foil to avoid lateral penetration of irradiation through the sidewalls. During the experiments solar light intensity was measured at 5-min intervals using a *Macam Q102 PAR* Radiometer (400–1000 nm). The measurements were standardized in the way such that the sensor was always set in the horizontal position. The average light intensity over the duration of each experiment was calculated.

2.3. Analysis

For Fenton/UV-C process 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 of the experiments were carried out at pH = 5 of the solution. The required amount of Fe^{2+} was added into the dye solution. In ferrioxalate/H_2O_2/solar light process the required amounts of Fe^{3+} and oxalic acid were added simultaneously into the dye solution and mixed by means of a magnetic stirrer. Finally, in both processes, the desired volume of H_2O_2 was injected into the

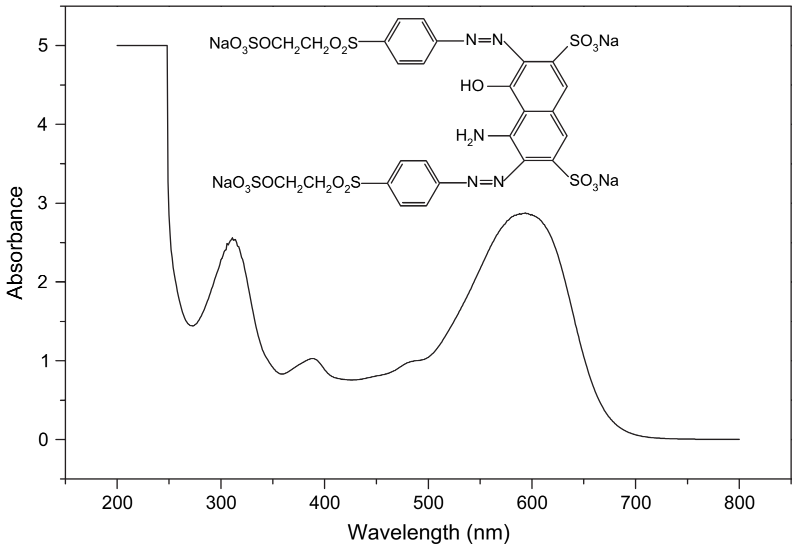

Fig. 1. UV–vis absorption spectra and chemical structure of *Reactive Black* 5.

solution. In Fenton/UV-C process the reaction time was recorded when the UV lamp was turned on, and in ferrioxalate/H_2O_2/solar light process when the solution was exposed to solar irradiation. Samples of dye solution were withdrawn during the course of the reaction, at periodic intervals, and analysed in a UV–vis 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 oxidation in the samples before spectrophotometric analysis. The color of dye solution in the reaction mixture was obtained by the measure of the absorbance at maximum wavelength ($\lambda_{max} = 595$ nm) and computing the concentration from calibration curve. Total Organic Carbon (TOC) measurements were carried out with a *Skalar Formacs* TOC/TN analyser.

3. Results and discussion

Absorption spectra of the dye solutions were recorded. The concentration of residual dye in solution was calculated by Beer–Lambert law using the optical density and the molar extinction observed at the characteristic wavelength ($\lambda_{max} = 595$ nm):

$$A = l\varepsilon C \tag{7}$$

where A is the absorbance, l, the path length (cm), ε, the molar extinction coefficient (L mol^{-1} cm^{-1}), and C, the dye concentration at time t (mol/L). Dye decolorization was calculated as follows:

$$\text{Dye decolorization} = \left(1 - C_{\text{dye},t}/C_{\text{dye},0}\right) \times 100\% \tag{8}$$

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

3.1. Photochemical decolorization of Reactive Black 5

Initially, the photochemical degradability of dye RB5 was carried out with Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes to compare the decolorization capacity of each one. From Fig. 2 it is possible to verify that the decolorization of RB5 solutions was efficiently induced by both processes. However, Fenton/UV-C process has a better decolorization capacity than ferrioxalate/H_2O_2/solar light process. Although from the results it is not possible to evaluate, for example, whether the higher decolorization of Fenton/UV-C process is due to the source of iron or from the source of light.

Therefore, to analyse the influence of each parameter on dye decolorization several experiments were carried out that permits to evaluate the employment of UV-C radiation, solar light and different sources of iron (ferrous and ferrioxalate).

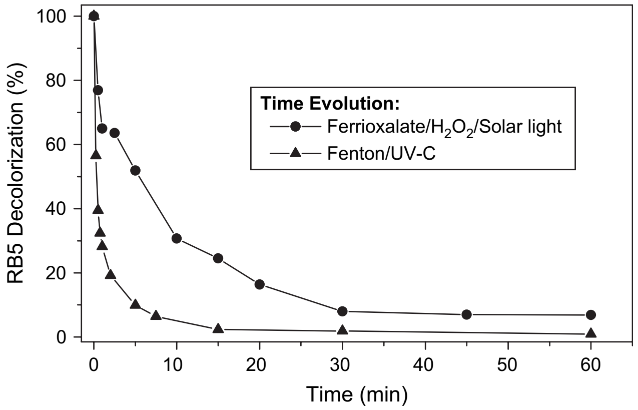

Fig. 2. *Reactive Black* 5 decolorization evolution during Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; iron concentration = 1.5×10^{-4} mol/L; oxalic acid = 9.0×10^{-3} mol/L; [H_2O_2] = 1.5×10^{-3} mol/L; pH = 5; solar light intensity average = 530 W m^{-2}; UV lamp = TNN 15/32 *Heraeus*; and reaction time = 60 min.

Table 1
Reactive Black 5 decolorization efficiencies with different processes

Process	Conditions	Reaction time (min)	RB5 decolorization (%)
(1) RB5 + solar light	Sunny day	60	0
(2) RB5 + UV-C	UV lamp	30	11.4
(3) RB5 + Fe^{2+} + solar light	$Fe^{2+} = 1.5 \times 10^{-4}$ mol/L; sunny day	60	0
(4) RB5 + Fe^{2+} + UV-C	$Fe^{2+} = 1.5 \times 10^{-4}$ mol/L; UV lamp	30	25.4
(5) RB5 + ferrioxalate + solar light	$Fe^{3+} = 1.5 \times 10^{-4}$ mol/L; sunny day	30	16.4
(6) RB5 + ferrioxalate + UV-C	$Fe^{3+} = 1.5 \times 10^{-4}$ mol/L; UV lamp	30	53.5
(7) RB5 + H_2O_2 + solar light	$H_2O_2 = 1.5 \times 10^{-3}$ mol/L; sunny day	60	0
(8) RB5 + Fe^{2+} + H_2O_2 + dark	$Fe^{2+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L	30	97.4
(9) RB5 + Fe^{2+} + H_2O_2 + solar light	$Fe^{2+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L; sunny day	30	97.5
(10) RB5 + Fe^{2+} + H_2O_2 + UV-C	$Fe^{2+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L; UV lamp	30	98.1
(11) RB5 + ferrioxalate + H_2O_2 + dark	$Fe^{3+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L	60	0
(12) RB5 + ferrioxalate + H_2O_2 + solar light	$Fe^{3+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L; sunny day	30	93.2
(13) RB5 + ferrioxalate + H_2O_2 + UV-C	$Fe^{3+} = 1.5 \times 10^{-4}$ mol/L; $H_2O_2 = 1.5 \times 10^{-3}$ mol/L; UV lamp	30	98.7

$[RB5]_0 = 1.0 \times 10^{-4}$ mol/L; oxalic acid $= 9.0 \times 10^{-3}$ mol/L; pH = 5; solar light intensity average (sunny day) = 530 W m^{-2}; and UV lamp = TNN 15/32 *Heraeus*.

In Table 1 are represented the results of that experiments. Through this it is possible to observe that for an RB5 concentration of 1.0×10^{-4} mol/L, at pH 5, and with a solar light intensity average of 530 W m^{-2}, the dye decolorization is null after 60 min for the following processes: (1) RB5 + solar light; (3) RB5 + Fe^{2+} + solar light; (7) RB5 + H_2O_2 + solar light and (11) RB5 + ferrioxalate + H_2O_2 + dark. In process (2) RB5 + UV-C was observed a small dye decolorization of about 11.4% in 30 min. In process (7), where could be expected a significant decolorization due to the use of a powerful oxidant − hydrogen peroxide ($H_2O_2 = 1.78$ V), the RB5 decolorization does not happen. This result reveals that RB5 azo dye has a complex and resistant molecular structure (Fig. 1). Therefore, decolorization of *Reactive Black* 5 could be primarily attributed to the hydroxyl radicals, with a higher redox potential ($HO^\bullet = 2.80$ V), generated from Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes.

Comparing processes (1) and (2) results reveal a better RB5 decolorization capacity of the UV-C radiation than solar light. The addition of Fe^{2+} to the UV-C radiation (process (4)) promotes an increase in dye decolorization, compared to process (2), achieving the value of 25.4%. However, the addition of Fe^{2+} to process (3) RB5 + solar light does not effect positively to the dye decolorization.

By adding H_2O_2 to processes (3) and (4) (processes (9) RB5 + Fe^{2+} + H_2O_2 + solar light and (10) RB5 + Fe^{2+} + H_2O_2 + UV-C) it is visible that decolorization capacity increases significantly for both processes, achieving a very similar decolorization percentage of 97.5% and 98.1%, respectively. Process (8) RB5 + Fe^{2+} + H_2O_2 + dark shows a decolorization of 97.4%. With a ferrioxalate iron source (processes (5) and (6)) the UV-C radiation for a time reaction of 30 min, have a higher decolorization capacity than solar light (53.5% and 16.4%, respectively). By comparing processes (11) (dark, 0%) and (12) (solar light, 93.2%), it is patent that light is absolutely necessary for processes involving ferrioxalate. Processes (12) and (13) present a decolorization capacity of 93.2% and 98.7%, respectively, evidencing that artificial UV-C light leads to a better performance than solar light.

The higher efficiency of processes (10) RB5 + Fe^{2+} + H_2O_2 + UV-C and (13) RB5 + ferrioxalate + H_2O_2 + UV-C, achieving a decolorization of 98.1% and 98.7%, signifies that the combination between UV-C lamp, ferrous ions and ferrioxalate has a sensible increase on dye decolorization when compared to the experiments with solar light.

3.2. Kinetic analysis of ferrioxalate processes

For a better knowledge of decolorization processes with ferrioxalate were also evaluated the reaction kinetics and the half-life time ($t_{1/2}$). As shown in Table 2 the disappearance of dye during the first 30 min of oxidation could be described as a first-order reaction kinetics with regard to dye concentration. 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 concentrations at time zero and t, respectively.

As it can be seen in Table 1 and comparing K values and $t_{1/2}$ in Table 2 it follows that process (13) RB5 + ferrioxalate + H_2O_2 + UV-C, when compared to process (12) RB5 + ferrioxalate + H_2O_2 + solar light, presents an improved decolorization capacity. This fact is due to the little effect of solar light radiation as can be seen for the small K value process (5) RB5 + ferrioxalate + solar light. In process (6) RB5 + ferrioxalate + UV-C, although there is little power of the low-pressure mercury vapor lamp TNN 15/32, the K value is six times higher than that obtained in process (5). This result

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)
(5) RB5 + ferrioxalate + solar light	0.0044	–
(6) RB5 + ferrioxalate + UV-C	0.0264	27.2
(11) RB5 + ferrioxalate + H_2O_2 + dark	–	–
(12) RB5 + ferrioxalate + H_2O_2 + solar light	0.0772	5.4
(13) RB5 + ferrioxalate + H_2O_2 + UV-C	0.0922	3.7

permits defined as more efficient, with these experimental conditions, the (13) RB5 + ferrioxalate + H_2O_2 + UV-C process. However, to have a complete knowledge of optimal conditions the next steps of this work are to assess the capacity of each principal process (Fenton/UV-C and ferrioxalate/H_2O_2/solar light) that oxidizes the *Reactive Black* 5 azo dye.

3.3. Effect of pH

The effect of pH on RB5 decolorization by processes (10) RB5 + Fe^{2+} + H_2O_2 + UV-C and (12) RB5 + ferrioxalate + H_2O_2 + solar light ferrioxalate/H_2O_2/solar light is shown in Fig. 3. This figure shows that pH significantly influences the conversion of RB5 in both processes. The experiments were carried out at pH between 1 and 8. At low pH (1 and 2) was obtained a very low decolorization in both processes. In the Fenton/UV-C process the decolorization percentage, for a reaction time of 30 min, was 32% and 46% for pH 1 and 2, respectively. For ferrioxalate/H_2O_2/solar light process the decolorization was minor than Fenton/UV-C process at this pH, achieving a decolorization of 2% for pH 1 and 39% for pH 2. The low decolorization at pH 1 and 2 is probably due to the hydroxyl radical scavenging by the H^+ ions (Eq. (13)) [16].

$$HO^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \tag{9}$$

By increasing the pH for 3 was obtained the highest decolorization for Fenton/UV-C, 98.6%. For pH above 3 the Fenton/UV-C process decolorization capacity is very similar to that for pH 3, achieving a color removal of about 98% for all pH. In the ferrioxalate/H_2O_2/solar light process for pH 3 a color removal of 69% was achieved, with increasing decolorization capacity until pH 5, the highest value for this process being 90%. For pH above 5 the color removal capacity decreases until the value of 72% for pH 8. This behavior could be explained by the formation of ferric hydroxo complexes during the reaction, which blocks the decomposition of hydrogen peroxide catalyzed by the ferrous iron [22].

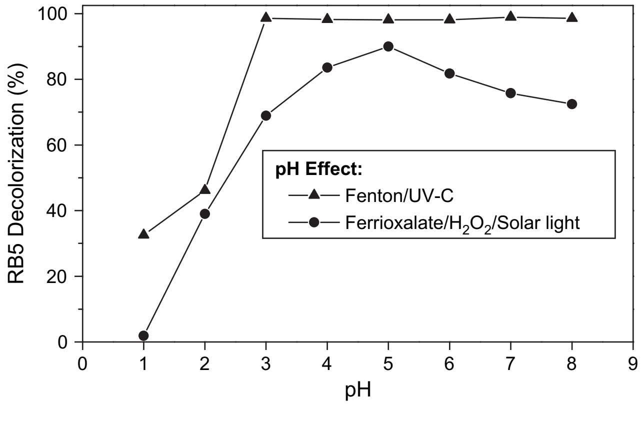

Fig. 3. Effect of pH on the decolorization of RB5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; Iron concentration = 1.5×10^{-4} mol/L; Oxalic acid = 9.0×10^{-3} mol/L; [H_2O_2] = 1.5×10^{-3} mol/L; UV lamp = TNN 15/32 *Heraeus*; Reaction time = 30 min; solar light intensity average = 530 W m^{-2}.

3.4. Effect of H_2O_2 dosage

Fig. 4a and b shows the relationship between degradation of dye and initial dosage of H_2O_2 in the Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. The objective of this evaluation is to select the best operational dosage of H_2O_2 in both processes. In Fenton/UV-C process, the addition of H_2O_2 between 0.5×10^{-3} and 2.0×10^{-3} mol/L increases the decolorization from 86% to 99%, respectively, at 20 min. For ferrioxalate/H_2O_2/solar light process is achieved an RB5 decolorization of 78% to a H_2O_2 dosage of 1.5×10^{-3} mol/L. However, increasing the peroxide dosage to 2.0×10^{-3} mol/L, dye decolorization decreases to 73%, also for a reaction time of 20 min. This decrease is probably due to the scavenging of $HO^{\bullet}$ radicals by H_2O_2, which can be expressed by Eqs. (10) and (11) [23,24]:

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{10}$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \tag{11}$$

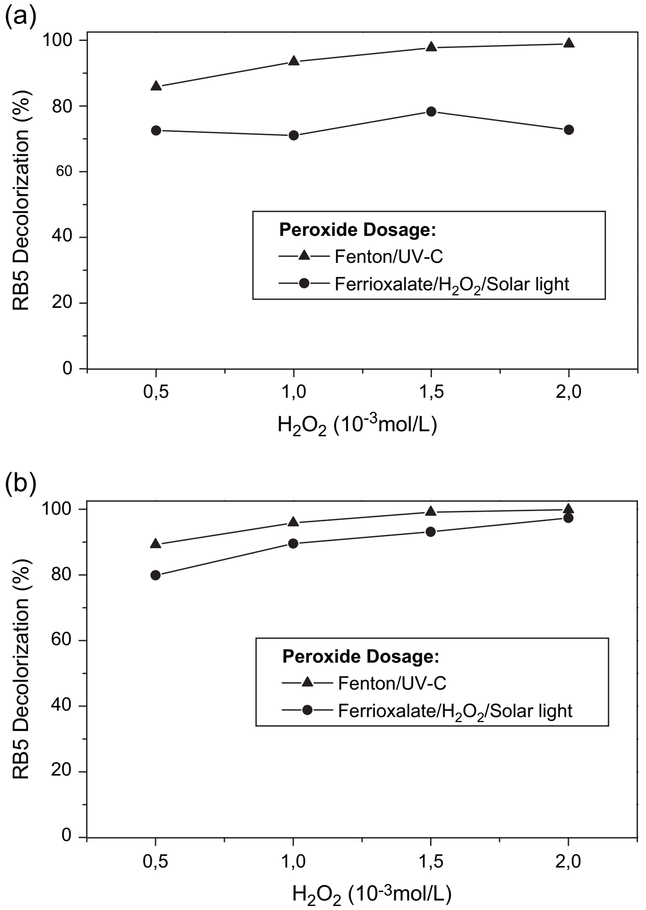

Fig. 4. Effect of peroxide dosage on the decolorization of RB5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; iron concentration = 1.5×10^{-4} mol/L; oxalic acid = 9.0×10^{-3} mol/L; pH = 5; UV lamp = TNN 15/32 *Heraeus*; solar light intensity average = 530 W m^{-2}. (a) reaction time = 20 min; (b) reaction time = 60 min.

Although for a reaction time of 60 min the decolorization percentage achieved for Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes are similar to all peroxide dosages. The difference between the two processes, for the same peroxide dosage, is minor for a reaction time of 60 min than for 20 min. Ferrioxalate/H_2O_2/solar light process increases its decolorization capacity with time, revealing that reaction time is very important in RB5 decolorization. For an RB5 concentration of 1.0×10^{-4} mol/L, 1.5×10^{-3} mol/L of H_2O_2 could be defined as the optimum dosage.

3.5. Effect of iron dosage

The effect of adding iron on RB5 decolorization has been studied. The results are shown in Fig. 5a and b. The amount of iron is one of the main parameters that influence the Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. The results indicate that the extent of decolorization increases with a higher initial iron concentration.

In Fenton/UV-C process addition of Fe^{2+} from 0.5×10^{-4} to 2.0×10^{-4} mol/L increases color removal from 89% to 96% for a reaction time of 20 min. From the results it is possible to say that efficiency of RB5 destruction increases with a higher initial Fe^{2+} concentration. Although, by increasing the iron dosage from 1.5×10^{-4} to 2.0×10^{-4} mol/L only a small decrease in decolorization is verified. It may be explained by redox reactions that $HO^{\bullet}$ radicals may be scavenged either by the reaction with hydrogen peroxide present or with another Fe^{2+} molecule as mentioned below (Eqs. (12) and (13)) [25].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \tag{12}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow HO^{-} + Fe^{3+} \tag{13}$$

In ferrioxalate/H_2O_2/solar light process, to the same reaction time, addition of Fe^{3+} from 0.5×10^{-4} to 2.0×10^{-4} mol/L increases color removal from 48% to 79%. The lower decolorization capacity at small concentration of iron is probably due to the lowest $HO^{\bullet}$ radicals production available for oxidation. But for a reaction time of 60 min it a significant increase in RB5 decolorization is observed in both processes. However, in the ferrioxalate/H_2O_2/solar light process the enhancement in the decolorization is higher. The decolorization increases, for the same iron dosage, from 79% to 93% for the ferrioxalate/H_2O_2/solar light process and from 96% to 99% for Fenton/UV-C process. This reveals an important dependence of the ferrioxalate/H_2O_2/solar light process on the reaction time. For both processes 1.5×10^{-4} mol/L of iron can be used as the optimum dosage.

3.6. Effect of dye concentration

The effect of initial dye concentration on the Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of the concentration is shown in Fig. 6a and b. From the figures it is possible to observe that the extent of degradation decreases with the increase in the initial dye concentration. The increase of RB5 concentration from 0.5×10^{-4} mol/L to 1.5×10^{-4} mol/L decreases the decolorization from 99% to 93% for Fenton/UV-C and from 98% to 22% for ferrioxalate/H_2O_2/solar light process in 20 min. A higher concentration increases the number of dye molecules, but not the $HO^{\bullet}$ radical concentration, and so the removal rate diminishes. In both processes the high color of dye concentration makes the penetration of photons difficult, even from UV-C and from solar light into the dye solution, thereby decreasing the hydroxyl radical concentration [15]. After 60 min of reaction time the ferrioxalate/H_2O_2/solar light process reveals a better performance achieved, even for the highest RB5 concentration studied – an 83% color removal.

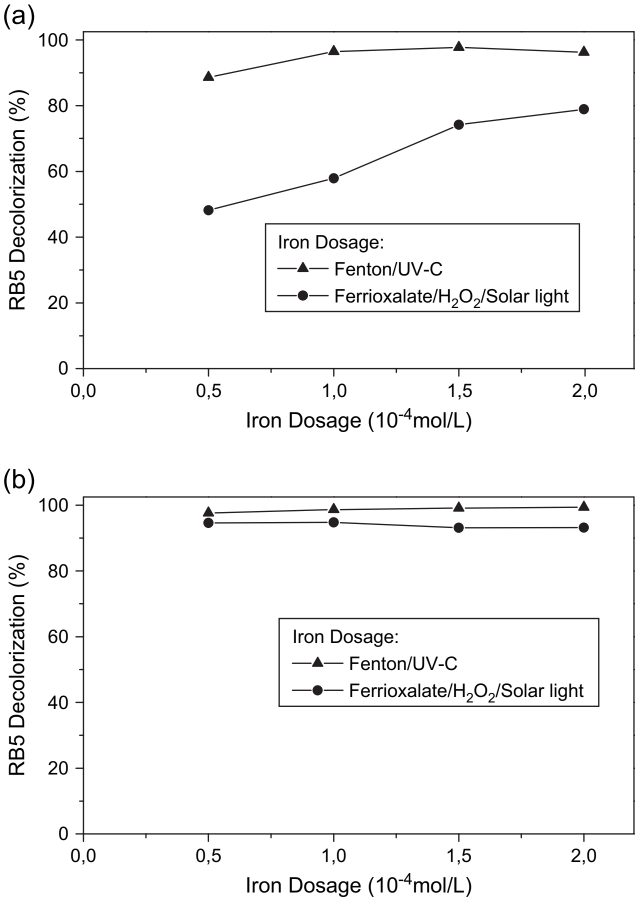

Fig. 5. Effect of the iron dosage on the decolorization of RB5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: [RB5] = 1.0×10^{-4} mol/L; [H_2O_2] = 1.5×10^{-3} mol/L; oxalic acid = 9.0×10^{-3} mol/L; pH = 5; UV lamp = TNN 15/32 *Heraeus*; solar light intensity average = 530 W m^{-2}. (a) reaction time = 20 min; (b) reaction time = 60 min.

3.7. Effect of solar light intensity

The solar light intensity changes during the day and with the climatic conditions. Therefore, to evaluate the effect of solar light intensity in the ferrioxalate/H_2O_2/solar light process were performed several experiments at different weather

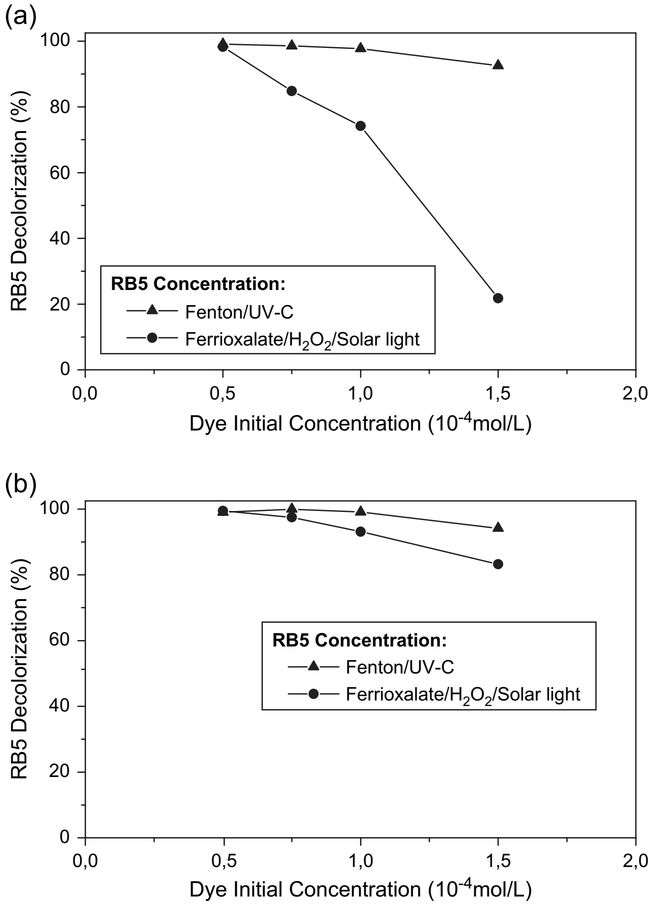

Fig. 6. Effect of dye initial concentration on the decolorization of RB5 by Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: iron concentration = 1.5×10^{-4} mol/L; $[H_2O_2] = 1.5 \times 10^{-3}$ mol/L; oxalic acid = 9.0×10^{-3} mol/L; pH = 5; UV lamp = TNN 15/32 *Heraeus*; solar light intensity average = 530 W m^{-2}. (a) reaction time = 20 min; (b) reaction time = 60 min.

conditions — sunny day and cloudy day — at the same hour of the day. From Fig. 7 it is visible that RB5 decolorization is significantly different during the first minutes — half an hour — to experiments with sunny or cloudy day. In the cloudy day the decolorization achieved at 30 min is 75% and in the sunny day for the same reaction time it is 92%. However, for a reaction time of 60 min the decolorization capacity of both experiments is the same — 93%. From these results it is possible to conclude that if the solar light intensity was minor a higher retention time in the reactor could be sufficient to find the same color removal.

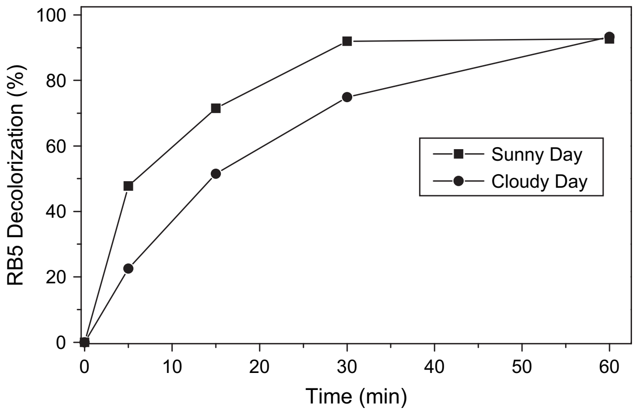

Fig. 7. Effect of solar light intensity on the decolorization of RB5 by ferrioxalate/H_2O_2/solar light processes. Experimental conditions: iron concentration = 1.5×10^{-4} mol/L; $[H_2O_2] = 1.5 \times 10^{-3}$ mol/L; oxalic acid = 9.0×10^{-3} mol/L; pH = 5; and solar light intensity average: sunny day = 530 W m^{-2}; cloudy day = 230 W m^{-2}.

3.8. Mineralization study

It is known that reaction intermediates can be formed during the oxidation of azo dyes and some of them could be long-lived and even more toxic than the parent compounds. Therefore, it is necessary understand the mineralization degree of the azo dye RB5 to evaluate the degradation level applied by Fenton/UV-C and ferrioxalate/H_2O_2/solar light 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:

$$\text{TOC removal ratio} = (1 - \text{TOC}_t/\text{TOC}_0) \times 100\% \qquad (14)$$

where TOC_t and TOC_0 are the TOC values at reaction time t and 0, respectively.

Fig. 8 presents the color degradation and TOC removal ratio of the azo dye RB5 with Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. As could be seen, dye decolorization is much higher than TOC removal even in Fenton/UV-C and also in ferrioxalate/H_2O_2/solar light processes. Although, it is visible from the figure that Fenton/UV-C process presents a TOC removal higher than ferrioxalate/H_2O_2/solar light process, 46.4% and 29.6%, respectively. So, from this analysis it is evident that neither Fenton/UV-C nor ferrioxalate/H_2O_2/solar light has the capacity of eliminate the RB5 dye. However, the employment of UV lamp benefits the azo dye mineralization when compared to the solar light. Although from the economical point of view, the use of solar light could be a good alternative in dye decolorization.

4. Conclusions

In this work was evaluated the decolorization and mineralization capacity of two advanced photochemical processes: Fenton/UV-C and ferrioxalate/H_2O_2/solar light on *Reactive Black* 5. From the results the following conclusions can be drawn:

- Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes, within the used experimental conditions, lead to more than 90% of *Reactive Black* 5 decolorization in half an hour.
- The experiments with RB5 + ferrioxalate follow a first-order kinetic law even with UV-C or solar light alone and with hydrogen peroxide addition. However, when UV-C lamp + H_2O_2 was employed the kinetic rate (K) was higher compared to the solar light + H_2O_2 combination, achieving, consequently, a minor half-life time ($t_{1/2}$).

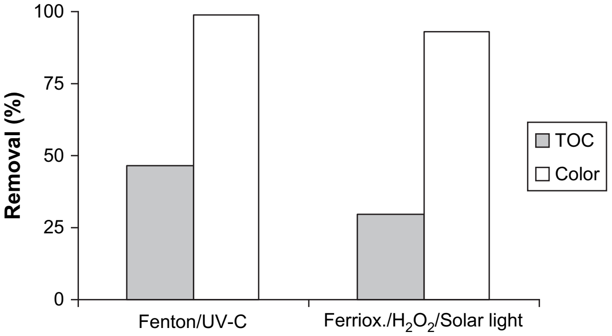

Fig. 8. Comparison between decolorization and TOC removal of RB5 after Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes. Experimental conditions: $[RB5] = 1.0 \times 10^{-4}$ mol/L; $[H_2O_2] = 1.5 \times 10^{-3}$ mol/L; oxalic acid $= 9.0 \times 10^{-3}$ mol/L; iron concentration $= 1.5 \times 10^{-4}$ mol/L; UV lamp = TNN 15/32 *Heraeus*; solar light intensity average $= 530\ \mathrm{W\,m^{-2}}$; and reaction time = 1 h; pH = 5.

- Optimal experimental conditions for both processes, with an RB5 concentration of 1.0×10^{-4} mol/L, can be summarized as: pH = 5, hydrogen peroxide dosage $= 1.5 \times 10^{-3}$ mol/L and iron dosage $= 1.5 \times 10^{-4}$ mol/L.
- The Fenton/UV-C and ferrioxalate/H_2O_2/solar light processes do not only decolorize the dye solutions but also partially mineralize the azo dye RB5.
- Although the very similar decolorization is noted in both processes, the employment of the UV lamp benefits the azo dye degradation. However, from the economical point of view the employment of the natural resource – solar light – could be an interesting option due to its low cost and the fact of being environmentally harmless.

Acknowledgement

Marco S. Lucas thank FCT (Fundação para a Ciência e Tecnologia – Portugal) for the PhD grant (BDE/15576/2005) and for the financial support that made this study possible.

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