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Homogeneous photodegradation of C.I. Reactive Blue 4 using a photo-Fenton process under artificial and solar irradiation

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Abstract

The oxidation of C.I. Reactive Blue 4 (RB4) by photo-Fenton process mediated by ferrioxalate was investigated under artificial and solar irradiation. The RB4 degradation in acidic medium (pH 2.5) was evaluated by the decrease in Total Organic Carbon (TOC) content and color, measured by the decrease in chromophore absorption band (600 nm). The influence of ferrioxalate and H_2O_2 concentrations on the dye degradation was studied and best results were obtained using 1.0 mM ferrioxalate and 10 mM of hydrogen peroxide. Under these experimental conditions, 80% of TOC and 100% of color removal were obtained for a 0.1 mM RB4 dye in 35 min of solar irradiation.

Keywords: Anthraquinone dye; Photo-Fenton; Decolorization; Degradation; Reactive Blue 4

1. Introduction

Dyes are substances that possess high coloration degree and are, in general, employed in the textile, pharmaceutical, cosmetics, plastics, photographic, paper and food industry [1]. The diversity of dyes available is justified if we consider that the dyeing process is one of the fundamental factors in the commercial success of the textile products.

Many dyes are difficult to fade due to their complex structure and synthetic origin. There are many structural varieties, such as direct, reactive, acidic, basic, disperse, azo, diazo, anthraquinone-based and metal complex dyes [1–3]. Over 700,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide. From this amount, about 20% are discharged as industrial effluents during the textile dyeing and finishing processes without previous treatment [4]. The color and toxicity of dyes influence the quality of life by causing health problems besides influencing the efficiency of some water treatment techniques [1,5–7].

Considering the volume and chemical composition of the effluent discharge, the textile dyeing and finishing industry is one of the major polluters among industrial sectors. Therefore, establishing removal technologies for dyes is an urgent problem. The most commonly used method for the treatment of textile wastewater is the combination of biological oxidation and physical–chemical treatment [8]. However, these processes are quite ineffective in color removal of wastewater since dyestuff, such as anthraquinone-based dye, are biorecalcitrant due to their aromatic structure, while physical–chemical treatments provide only a phase transfer of dyes and produce large quantities of sludge.

Chemical oxidation aims at the mineralization of contaminants to carbon dioxide, water and inorganics or, at least, their transformation into biodegradable or harmless products. During the last two decades, advanced oxidation process (AOPs) has been applied for the removal of refractory organic pollutants and xenobiotics [9]. Destructive oxidation of dyes and textile effluents has recently received considerable attention since colored aromatic compounds have proven to be degraded effectively by a variety of homogeneous and heterogeneous AOPs. Recently, the system Fe^{3+} (or Fe^{2+})/H_2O_2/hν (photo-Fenton) has attracted much attention due to its high efficiency in the oxidation of a variety of organic compounds, including dyes [4,10–13].

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The success of photo-Fenton process for the oxidation of a variety of organic contaminants is attributed to the generation of hydroxyl radicals formed during the catalytic decomposition of hydrogen peroxide in acidic media [14] as represented by $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet}$. Besides the high efficiency of the reaction, iron is a non-toxic element and can be separated from treated wastewater by coagulation, while H_2O_2 is easy to handle, environmentally safe and is consumed during usual degradation process.

In addition, the rate of degradation of organic compounds via Fenton process is strongly accelerated by irradiation with UV–vis light called photo-Fenton process, which is also improved by the use of ferrioxalate as mediator reaction [15,16]. Ferrioxalate is the oldest and best-known photoactive example of Fe^{3+}–polycarboxylate complexes. It is well known that irradiation of ferrioxalate in acidic solution generates carbon dioxide and ferrous ions free or complexed with oxalate [17], which in combination with H_2O_2 provides a continuous source of Fenton's reagent as demonstrated by equations below:

$$[Fe^{III}(C_2O_4)_3]^{-3} + h\nu \rightarrow [Fe^{II}(C_2O_4)_2]^{-2} + C_2O_4^{\bullet-} \quad (1)$$

$$C_2O_4^{\bullet-} + [Fe^{III}(C_2O_4)_3]^{-3} \rightarrow [Fe^{II}(C_2O_4)_2]^{-2} + C_2O_4^{-2} + 2CO_2 \quad (2)$$

$$C_2O_4^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + 2CO_2 \quad (3)$$

The high efficiency of this process is attributed mainly to the broad absorption range of ferrioxalate (up to 450 nm) thus utilizing more efficiently the UV–vis radiation and to the high quantum yield of Fe^{2+} (1.0–1.2) over the range of irradiation [17].

The application of photo-Fenton process for the treatment of wastewater containing reactive dyes has long been pointed out as very promising [18]. Recently, the possibility of combining the solar photo-Fenton and biological process has also been proposed considering the increase in biodegradability after photo-Fenton process [19].

The purpose of the present study is to evaluate the efficiency of the photo-Fenton process for the decolorization and photodegradation of the C.I. Reactive Blue 4 (C.I. 61205). The efficiency of degradation was compared using solar and artificial irradiation. The photo-Fenton reaction under solar irradiation was studied with the aim to propose a lower cost alternative for the treatment of wastewaters dye contamination, becoming more attractive for industrial applications. C.I. Reactive Blue 4 (Fig. 1), a commercial reactive dye based on anthraquinone group as chromophore and dichlorotriazine group as reactive site is very much used for dyeing cotton fibers. The influence of initial potassium ferrioxalate (FeOx) as source of iron, H_2O_2 and dye concentration as well as light source was investigated following the Total Organic Carbon (TOC) concentrations and color removal by the measurement of absorbance decrease of chromophore band (600 nm).

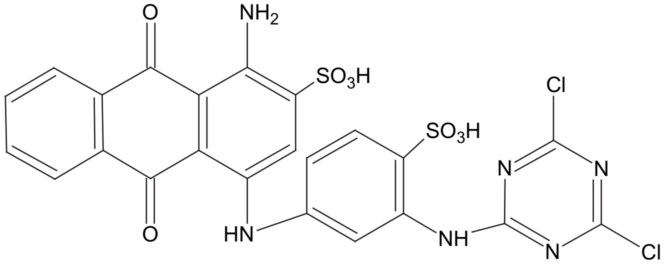

Fig. 1. Molecular structure of the C.I. Reactive Blue 4 dye.

2. Experimental

2.1. Chemicals

Solutions of C.I. Reactive Blue 4 (RB4, $C_{23}H_{13}O_8N_6S_2Cl_2$, 636.43 g mol^{-1}) were prepared with deionized water (Millipore Milli-Q system) without further purification (Aldrich 35% purity). The potassium ferrioxalate [$K_3Fe(C_2O_4)_3 \cdot 3H_2O$] was synthesized by the reaction of potassium oxalate with iron chloride (III) ($FeCl_3$), as described previously [17]. Aqueous 0.25 M ferrioxalate (FeOx) stock solution was prepared and stored in the dark at room temperature for a maximum of one week. For the experiments with artificial and solar irradiation the pH of the RB4 dye solution was adjusted to pH 2.5 with H_2SO_4 and appropriate volumes of FeOx and H_2O_2 30% were added in this order.

2.2. Photoreactor and photodegradation procedure

For evaluation of the influence of different parameters on the photodegradation of model RB4 dye, experiments were performed with artificial irradiation to assure stable conditions of light intensity in the reactor using a 15 W blacklight lamp and an upflow photoreactor similar to that of previously described [20], characteristics are shown in Table 1. The photoreactor was operated in a recirculation mode using a peristaltic pump (Ismatec IPC). The light intensity of the blacklight lamp used was measured at 365 nm using a radiometer (Cole Parmer 9811-50), which was 26.2 W m^{-2}. Dye solution was pumped into the reactor immediately after the addition of FeOx and H_2O_2 in the reservoir solution under magnetic stirring. The lamp was switched on when the reactor was completely filled and the time start to be monitored. Aliquots of 5 mL were taken at 5 or 10 min intervals for immediate analysis. It is important to note that the irradiation time differs from the total experimental time, since only a portion of the total volume is exposed to the light at any time and is corrected by the following equation:

$$t_{irradiation} = t_{total} \times V_{reactor}/V_{total} \quad (4)$$

where, t is the time in minutes and V is the volume in mL. The initial total volume of dye solution was 1000 mL. The solution was recirculated continuously for 1 h through the reactor.

Table 1
Characteristics of the lamp reactor

$D_{\text{int.}}$ cylinder (mm)	D_{lamp} (mm)	Path length (mm)	V_{reactor} (mL)	V_{total} (mL)	Q (mL min^{-1})	θ (min)	$\bar{I}_{365}$ (W m^{-2})
52.9	37.1	15.4	400	1000	36	11	26.2

$D_{\text{int.}}$ = internal diameter; V_{reactor} = volume of the photoreactor; V_{total} = total volume for photodegradation; Q = flow rate; θ = residence time; $\bar{I}_{365}$ = average light intensity of the lamp at 365 nm and D_{lamp} = diameter of the lamp.

2.3. Solar light experiments and light intensity measurements

Solar experiments were conduced by exposing directly to sunlight 250 mL dye solutions using dark glass vessels, 7.2 cm depth and 8.5 cm in diameter with an exposition area of 57 cm^2 with no stirring. This procedure was adopted to simulate a shallow pound type reactor where the solar irradiation would penetrate only through the upper open surface, as dicussed previously [21]. The experiments were performed at the Chemistry Institute of the University, at the city of Araraquara, Brazil (21°47′ S; 48°10′ W), during the summer (December and January), between 11:00 am and 2:00 pm. The average solar light intensity calculated for each experiment was 29.3 W m^{-2} in clear sky, while under cloudy days it decreased to 11.3 W m^{-2}.

2.4. Chemical analysis

The mineralization of organic matter in the solution during photodegradation was monitored by determinations of Total Organic Carbon (TOC) using a Total Organic Carbon Analyzer (TOC 5000A Shimadzu). TOC concentration includes the carbon content of the dye, oxalate and intermediates generated during photodegradation. The contribution of oxalate in the initial total content of carbon varied from 51 to 78% on the different experiments depending on the initial ferrioxalate and dye concentrations. For instance, a 0.1 mM RB4 solution contains 28 mg L^{-1} TOC, which in the presence of 1 mM ferrioxalate, increases to 99.6 mg L^{-1}.

The RB4 dye photodegradation was also monitored by spectrophotometry in the UV–vis region using a diode array HP 8453 spectrophotometer. Qualitative information was obtained from absorbance spectrum in the region between 200 and 800 nm that can be related mainly to iron complex and intermediates formed during the photodegradation. Quantitative information was obtained by monitoring the absorption band of chromophore (600 nm). The color removal during the degradation process is expressed as relative absorption (A/A_0).

The samples were analyzed immediately after the retreat of aliquots (4.0–5.0 mL) during the photodegradation.

3. Results and discussion

3.1. Artificial photodegradation of RB4 dye

3.1.1. Effect of initial FeOx concentrations

The initial concentrations of ferrioxalate (FeOx) and hydrogen peroxide play a very important role in the oxidation of organic compounds. The Fe (II) produced during the photolysis of ferrioxalate catalyzes the decomposition of hydrogen peroxide to generate the highly reactive hydroxyl radicals.

The effect of the initial FeOx concentration on dye photodegradation was investigated from 0.5 to 1.0 mM by color removal (Fig. 2A) and Total Organic Carbon (TOC) measurements (Fig. 2B). The concentrations of hydrogen peroxide and dye were fixed as 10 and 0.1 mM, respectively.

When comparing the removal of TOC from dye solution (Fig. 2B) in the presence of three different FeOx concentrations as 0.5, 0.7 and 1.0 mM, it is observed that dye photodegradation reaction is limited at 0.5 mM, due probably to low iron concentration in solution. In the presence of 0.7 or 1.0 mM, a slight improvement is obtained in relation to 0.5 mM. However, the TOC removal is very similar showing that no improvement of dye photodegradation is achieved when increasing the FeOx concentration from 0.7 to 1.0 mM.

Similar effect is observed when considering the absorbance of the solution at 600 nm (Fig. 2A), which decreases during irradiation independently of the initial concentration of FeOx up to 25 min. After this time, the absorbance starts to increase at higher concentrations of FeOx above 0.7 mM. This increase in absorbance is not related to the chromophore band of the dye but to iron hydroxide absorption, generated during photodegradation reaction. This is better explained in Fig. 3 where the changes in RB4 dye UV–vis spectra during the photodegradation are shown. Typical UV–vis spectrum of RB4 dye presents absorption bands at 595 nm attributed to the transition

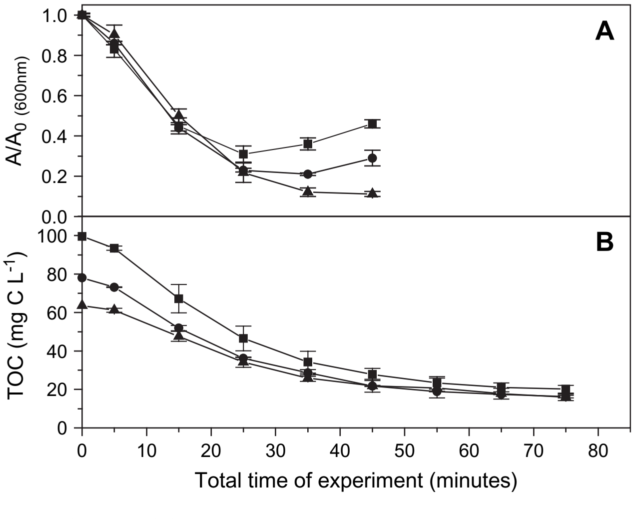

Fig. 2. Influence of ferrioxalate concentration on the photodegradation of RB4 dye under artificial light. [H_2O_2] = 10 × 10^{-3} mol L^{-1}, [dye] = 0.1 × 10^{-3} mol L^{-1} and [FeOx] = (▲) 0.5 × 10^{-3} mol L^{-1}, (●) 0.7 × 10^{-3} mol L^{-1} and (■) 1.0 × 10^{-3} mol L^{-1}. A – Color removal and B – TOC removal.

$n \rightarrow \pi^*$ (chromophore group), two other bands at 296 nm (transitions $\pi \rightarrow \pi^*$ of the anthraquinone function) and 256 nm attributed to the dichlorotriazine group or the other transitions of the chromophore [1]. The results indicated that TOC removal reaches 76% and color abatement is 80% after 25 min of irradiation, suggesting that active oxidant species formed in the photolysis of FeOx complexes in the aqueous solutions promote expressive photodegradation of RB4 dye. Nevertheless, during the process the occurrence of hydroxyl-compounds of iron decreases the transparence of the final solution, but visible fading of the solution is observed when iron species deposits on the bottom of the reservatory leading to 100% of color removal, as shown in the Fig. 3.

3.1.2. *Effect of initial H_2O_2 concentrations*

The effect of the initial concentration of H_2O_2 (7.0, 10 and 20 mM) on the photochemical efficiency of the system was investigated using fixed concentrations of FeOx and dye at 1.0 and 0.1 mM, respectively. The results show that for all H_2O_2 concentrations tested, no significant difference in TOC removal was observed, achieving 80% mineralization after 75 min (Fig. 4). This indicates that the excess of H_2O_2 is decomposed without promoting further degradation or hindering the reaction. This decomposition may be attributed to the generation of water and oxygen ($2H_2O_2 \rightarrow O_2 + H_2O$) since no detrimental effect is observed in the mineralization process that could indicate hydroxyl radical scavenging ($H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$), as already observed in other cases [22]. Further experiments were carried out using 10 mM H_2O_2.

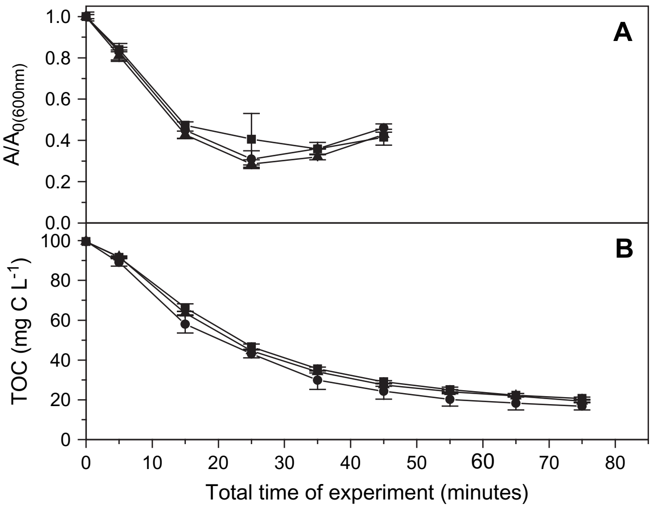

Fig. 4. Influence of H_2O_2initial concentration on the degradation of RB4 dye under artificial light. $[FeOx] = 1.0 \times 10^{-3}$ mol L^{-1}, $[dye] = 0.1 \times 10^{-3}$ mol L^{-1} and $[H_2O_2] =$ (▲) 7.0×10^{-3} mol L^{-1}, (●) 10×10^{-3} mol L^{-1} and (■) 20×10^{-3} mol L^{-1}. A – Color removal and B – TOC removal.

3.1.3. *Effect of initial RB4 dye concentration*

Photochemical processes are strongly dependent on solution absorption once penetration of light can be strongly limited in high absorption solutions such as dyes. Therefore, influence of the RB4 dye on its photodegradation was examined in this study, varying dye concentration from 0.075 to 0.25 mM. The concentrations of FeOx and H_2O_2 were maintained as 1.0 and 7.0 mM and the solution was irradiated with blacklight. The strong light absorption of the dye solution at a concentration of 0.25 mM has limited the application. Therefore, the photodegradation process is hindered as denoted by the small TOC and color removal values obtained (Fig. 5). This occurs because iron is in the complexed form in the investigated system and it is not available to react with H_2O_2, making the reaction strongly dependent on irradiation. At low concentration (0.075 and 0.1 mM) the photodegradation rate increases with the decrease in the dye concentration.

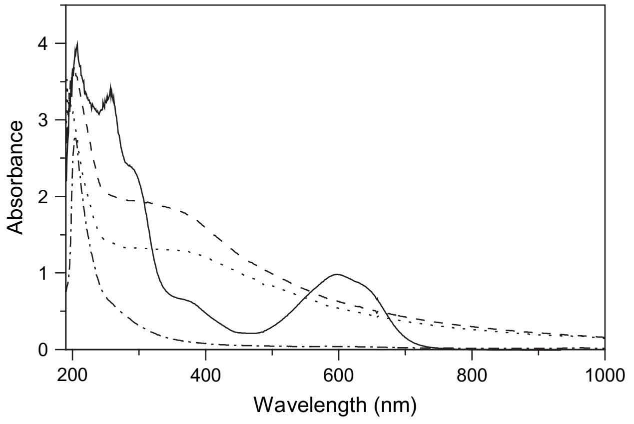

Fig. 3. UV-Vis spectra during photodecolorization of RB4 dye by photo-Fenton process under: (- - -) artificial light after 60 min, (···) solar light after 60 min, (—·—·) after 3 h in rest, (—) Original dye (not irradiated); $[FeOx] = 1.0 \times 10^{-3}$ mol L^{-1}; $[H_2O_2] = 10 \times 10^{-3}$ mol L^{-1}, $[dye] = 0.1 \times 10^{-3}$ mol L^{-1}.

The obtained results demonstrate that photodegradation and photodecolorization are faster for diluted solution of RB4 dye. Nevertheless, the results are also satisfactory for dye concentrations up to 0.1 mM, which demonstrate that the method is

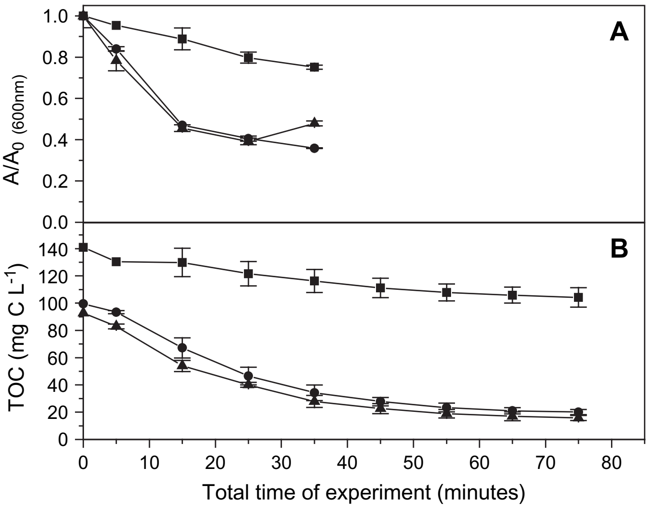

Fig. 5. Influence of RB4 dye initial concentration on its photodegradation under artificial light. $[FeOx] = 1.0 \times 10^{-3}$ mol L^{-1}, $[H_2O_2] = 10 \times 10^{-3}$ mol L^{-1}and $[dye] =$ (▲) 0.075×10^{-3} mol L^{-1}, (●) 0.1×10^{-3} mol L^{-1}and (■) 0.25×10^{-3} mol L^{-1}. A – Color removal and B – TOC removal.

relevant, once high mineralization efficiencies are obtained. A previous work showed about 60% degradation of the initial 25 mg L^{-1} (0.04 mM) of Reactive Blue 4 under UV irradiation in the presence of $FeCl_3$, in 60 min of irradiation [18]. Comparing these results with the one obtained in the present work, it can be stated that the use of ferrioxalate has improved the efficiency of the process, once higher degradation was achieved in shorter time.

In summary, a satisfactory color removal of the RB4 solutions can be obtained by the photo-Fenton method with artificial irradiation. The best results were obtained for diluted dye solutions up to concentration ≤ 0.1 mM. The best concentrations of hydrogen peroxide and ferrioxalate were 7.0 and 0.7 mM, respectively. However, even the best results lead to a maximum of 80% mineralization. The limitation of mineralization reaction at longer times indicates the formation of recalcitrant compounds resistant to the photodegradation under these conditions, the identification of which is not within the scope of this work. Although the increase in hydrogen peroxide's initial concentration from 7 to 20 mM did not improve the dye mineralization, the total consumption of peroxide could be responsible for the limited degradation as has been observed previously [20]. In such cases, further additions of peroxide during irradiation would improve the mineralization.

3.2. Solar photodegradation of RB4 dye

3.2.1. Effect of solar light intensity

Considering the abundance of solar irradiation in tropical countries like Brazil, the use of the photo-Fenton process with solar irradiation would be an advantage when compared to artificial light. The sunlight intensity is highly variable during the day or the year, and therefore this was considered during evaluation of solar-driven processes. The effect of solar light intensity on dye degradation was investigated using the concentrations 0.1 mM of the dye, 10 mM of H_2O_2 and 1.0 mM of the FeOx. The efficiency of dye degradation was compared between clear sky days ($I = 29.3$ W m^{-2}) and cloudy sky days ($I = 11.3$ W m^{-2}) during the summer by comparing the performance of color removal (Fig. 6A) and TOC reduction (Fig. 6B). The data were also compared to those obtained under artificial irradiation ($I = 26.2$ W m^{-2}). As expected, the removal of TOC under clear sky days is faster than in cloudy days or with artificial irradiation reaching 70% TOC removal in only 15 min of exposition, while only 15 and 25% were obtained under cloudy days and artificial irradiation in the same time, respectively (Fig. 6B). However, after 75 min exposition similar TOC removal percentages were obtained in all the three cases, for which reductions are 81, 77 and 74% under clear sky days, cloudy and artificial irradiation, respectively.

In the same way, an accentuated decrease in absorbance at 600 nm is observed in clear sky days. Eighty-six percentage of its initial absorbance is diminished in 5 min of exposition reaching 100% in 15 min. At cloudy days, the required time to reach 100% decrease in absorbance is 35 min, showing that this difference happens only due to the variation of light intensity.

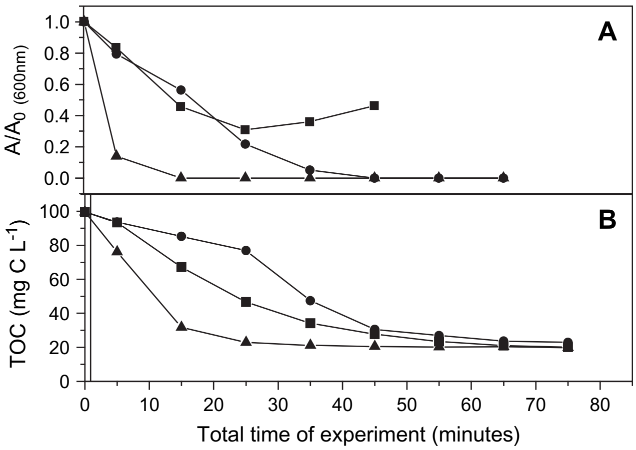

Fig. 6. Solar degradation of RB4 dye under (▲) clear days I = 29.3 W $m^{-2}$and (●) cloudy days I = 11.3 W $m^{-2}$and (■) under artificial light I = 26.2 W m^{-2}. [FeOx] = 1.0×10^{-3} mol L^{-1}, [H_2O_2] = 10×10^{-3} mol $L^{-1}$and [dye] = 0.1×10^{-3} mol L^{-1}. A – Color removal and B – TOC removal.

From the results demonstrated in Fig. 6 it is clear that the efficiency of the photo-Fenton process using solar irradiation for degradation of the RB4 dye is higher than when blacklight irradiation is used, for both TOC and color removal. Nevertheless, it is necessary to consider three points in this comparison: light intensity, reactor geometry and ferrioxalate absorption. The light intensity of the blacklight lamp used is about 10% smaller than the solar irradiation at 365 nm, what implies in lower efficiency since less photons reach the solution. The geometry of the solar and lamp reactors is very different. In the reactor based on UV lamp, only part of the total volume is effectively irradiated during the experiments, yielding a time of irradiation smaller than total experimental time. At the solar reactor, the experimental time is equal to irradiation time. Considering that some dark reaction could also occur in the reservoir, the total experimental time was used in the comparison of the processes under different irradiation sources. In addition, potassium ferrioxalate absorbs up to wavelength close to 500 nm, using more efficiently the visible solar energy than the blacklight irradiation [16].

Although the experimental conditions are not the same, the results suggest that photo-Fenton process coupled to solar light irradiation is a feasible technique for RB4 dye degradation and for wastewater treatment containing anthraquinone dyes. The use of solar light could be an excellent alternative since this natural source of energy could reduce the costs for the treatment of textile wastewater.

4. Conclusions

The feasibility of photo-Fenton process mediated by ferrioxalate complex for the degradation of dyes based on anthraquinone group was demonstrated in this work. Concentrations of RB4 up to 0.1 mM can be photodegraded resulting in 80% mineralization and 100% color removal under solar irradiation at summer clear sky days in 35 min exposition in the presence of 1.0 mM ferrioxalate and 10 mM H_2O_2. However, when studying the influence of initial FeOx and H_2O_2 concentrations, it was observed that 0.7 mM of FeOx and 7.0 mM H_2O_2 were sufficient to obtain similar photodegradation.

It is possible to conclude that the photodegradation of the RB4 dye under solar irradiation is highly dependent on the irradiation intensity. The yellow coloration characteristic of Fe (III) species was observed for both solar and artificial irradiation conditions, but the residue generated is easily removed after rest for 4 h, when 100% decolorization is obtained. These results indicate that visible irradiation can effectively accelerate the generation of hydroxyl radicals, due to the regeneration of Fe^{2+}.

The rate of the reaction is diminished on cloudy days. However, the lower cost intrinsic to solar energy utilization can compensate for small differences in photodegradation rates, especially in tropical regions where solar energy is abundant. The homogeneous photo-Fenton system presents the advantage that larger reactors are not necessary since the results presented here were obtained with small exposition areas of about 57 cm^2.

Acknowledgements

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