OPTIMIZATION AND EFFECTS OF SOME ELECTRON ACCEPTORS ON THE PHOTOCATALYTIC DEGRADATION OF DIRECT RED 23 AZO DYE

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ABSTRACT

The photocatalytic degradation of aqueous solution of commercial azo textile dye, direct red 23 (DR23), was carried out in TiO₂ suspension at 30°C with the use of artificial and solar light sources. The photoreaction followed the first-order behavior with respect to the azo dye as a function of irradiation time. A 2³ factorial design was carried out, in order to obtain the best experimental conditions, using the rate constant of DR23 degradation as the analytical response. Seven chemical species were determined from the normalized UV-Vis spectra during the DR23 degradation through Imbrie Q mode factor analysis followed by varimax and Imbrie oblique rotations. The addition of electron acceptors, such as H₂O₂, S₂O₈²⁻, and ClO₃⁻ on the optimized conditions, was carried out to increase the DR23 degradation rate. Comparison of degradation efficiencies under artificial and solar radiation was examined in the presence of oxidants.

Keywords: degradation; direct red 23; inorganic oxidant; photocatalysis; factorial design.

INTRODUCTION

Dyes have been widely used in many industries such as textile, paint, ink, and cosmetics. There are many different classes of dyes, such as azo, anthraquinone, metal complex, azo metal complex and phthalocyanine, reflecting the chromophoric structure of their constituent molecules. Of these dyestuffs, the azo dyes are the most frequently used due to the synthesis facility and good fixation capacity. These compounds belong to a class of synthetic dyes characterized by the presence of one or more azo groups (-N=N-) bonded to aromatic rings. According to the number of such groups the dyes are described as mono-, di-, tri-, tetra- azo dyes. Among these, the direct red 23 (DR23) is a direct dye mainly used for dyeing of cotton, viscose, silk and cellulose fabrics. The release of large amounts of this and other highly colored dyes into the ecosystem creates environmental problems like aesthetic pollution and perturbation of aquatic life ¹⁻³. Their toxicities, stabilities to natural decomposition, and persistence in the environment have been the cause of much concern to regulatory societies and regulation authorities around the world ⁴. Various chemical and physical decolorization processes have been utilized, including neutralization, flocculation, coagulation, settling, carbon adsorption, detoxification, and biological treatment. However, these treatment methods only provide separation of the dyes without any degradation, creating a waste disposal problem with large quantities of sludge produced. Thus, the decolorization and degradation of dye effluents has received increasing attention ⁵⁻⁷. During the past two decades, photocatalytic processes involving TiO₂ particles under UV light illumination has been shown to be potentially advantageous and useful in the treatment of wastewater pollutants. Earlier studies have shown that a wide range of organic substrates can be completely photomineralized in the presence of TiO₂ and oxygen and this process can be used for removing coloring material from the dye effluent ³.

There are no examples in the literature where statistical design and Q mode factor analyses are used simultaneously in studies involving dyes. The aim of this work was to use statistical experimental design for the establishment of optimal experimental conditions for degradation and decolorization of direct red 23 azo dye (DR23) (Fig. 1) by titanium dioxide. The effects of the azo dye and the semiconductor concentrations, pH, and temperature were investigated simultaneously by a 2³ factorial design. In this work, we extend these studies to the kinetics of simultaneous structural transformations of the azo dye during the irradiation ⁸. Imbrie Q mode factor analysis followed by varimax and Imbrie oblique rotations were applied to the UV-Vis spectral data in order to investigate the formation of the DR23 intermediates and products obtained in degradation and decolorization of direct red 23 azo dye. The chemometric methods used here permit one to deduce the relative concentrations from observed spectral changes and resolve the absorption spectra of the species without any experimental separation procedures. Furthermore, electron acceptors such as persulfate ion, chlorate ion, and hydrogen peroxide were added to the suspension at the optimized conditions to make the degradation easier and faster, as well as to compare the degradation rate efficiencies, under artificial and solar irradiations.

Figure 1.- Chemical structure of direct red 23.

Experimental methods

Reagents and solutions

The diazo dye direct red 23 (CI 29610) was kindly supplied by Chimical, Brazil and used as such without any further purification. The water used in all experiments was purified with a USF Elga Maxima system. The photocatalyst, TiO₂ P25, consisting of 80 % anatase and 20 % rutile was a gift from Degussa/Brazil. With a specific surface area (BET) of 50 m² g⁻¹ and a particle size of 30 nm, the semiconductor was used as the photocatalyst without further treatment. Hydrogen peroxide (60 %, P.A.) and potassium persulfate (98 %, P.A.) were purchased from Nuclear/Brazil. Sodium chlorate (99%, P.A.) was obtained from Vetec/Brazil. The other chemicals used in this study were analytical grade and used without previous purification. Solutions of the azo dye were prepared in purified water. The pH value of about 6.9, hereafter referred to as the natural pH, was measured before and after the irradiation.

Methods

An immersion well reactor, made of borosilicate glass equipped with a magnetic stirring bar and a water-circulating jacket, was used ^{9,10}. For the irradiation experiments, 150 mL of the azo dye solution was placed in the photoreactor and the required amount of photocatalyst was added in large excess with respect to the azo dye in order to maintain the pseudo first order conditions. The TiO₂ suspension containing the azo dye was stirred (600 rpm) for 45 min in the dark at 30.0±0.1 °C to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solutions kept in the dark and then submitted to irradiation. Irradiations were performed using a 125 W mercury lamp without a bulb. The radiation intensity was measured through a radiometer (Topcon UVR-2) at 365 nm [227.00±9.50 μW cm⁻²]. The distance between the lamp and the reactor was 13 cm. Samples of 1.5 mL were withdrawn before and at regular intervals during the irradiation and filtrated before analysis. Solar irradiations were carried out placing the whole set-up at ambient temperature from 10 am to 2 pm on March 28 and 31, and April 1, 2006 and the average intensity during this period was 3613±248 μW cm⁻². The temperature varied from 28 to 42 °C during the 4 h irradiation period in the reactor.

The decolorization and the degradation of the DR23 was monitored by using a UV-Vis spectrophotometer (Hitachi U-3000) recording the spectra between 200 and 900 nm. The concentration of DR23 was calculated from a calibration curve of the azo dye absorbance at 505 nm. A first-order decolorization rate constant, *k*_{obs}, was evaluated from the slope of the linear plot of the natural logarithm of the DR23 concentration against irradiation time.

Experimental design

The degradation and decolorization were studied under different conditions for temperature, substrate, pH, and semiconductor concentrations. First, a 2³

full factorial design ¹¹, was used to evaluate the effects of three variables pH, substrate and semiconductor concentrations on degradation and decolorization of the DR23. The decolorization rate constant was used as analytical response. The low and high levels of the DR23 concentrations were 0.5×10^{-4} and 1.5×10^{-4} mol L⁻¹; those for TiO₂ were 0.75 and 1.75 g L⁻¹ while the pH was set at 4.0 and 6.9. All the experiments were carried out at 30°C and the rate constants are presented in Table 1. Since the temperature was maintained constant in the first design, a second one was carried out to determine also the temperature effect on of the decolorization rate of DR23 in presence of UV light. In this design the temperature, the azo dye, and semiconductor concentrations were varied. A center point, with experimental conditions at the averages of the three low and high factor levels was added to the design in order to check the response surface for curvature. Low (1.5×10^{-4} mol L⁻¹), intermediate (2.25×10^{-4} mol L⁻¹), and high (3.0×10^{-4} mol L⁻¹) levels for the DR23 and TiO₂ concentrations (1.75; 2.50; and 3.25 g L⁻¹) were used. Temperature levels of 20.0, 30.0, and 40.0 °C were studied. The rate constants are given in Table 2.

RESULTS AND DISCUSSION

Decolorization and degradation of irradiated sample

From Table 1 it can be inferred that the concentrations of the semiconductor, substrate, and pH influence the decolorization rate constant of the DR23 azo dye. The highest response of the rate constant (5.59×10^{-3} min⁻¹) was obtained by irradiating 1.50×10^{-4} mol L⁻¹ DR23 in a suspension containing 1.75 g L⁻¹ TiO₂ at the natural pH (6.9) and at 30.0°C. The decrease of the natural pH from 6.9 to 4.4 for the fastest decolorization (run 8, Table 1) after 6 h irradiation was attributed to the proton transfer and hydroxyl radical production in the valence band by the water molecule. The highest rate constants for the 1st and 5th runs shown in Table 2 correspond to exactly the same experimental conditions of the Table 1.

Table 1.- Rate constants obtained from the 2³ factorial design by varying the TiO₂ and DR23 concentrations and the pH at 30.0°C.

run	[TiO ₂]/g L ⁻¹	[DR23]/mol L ⁻¹	pH	$k_{obs} / 10^{-3} \text{ min}^{-1}$
1	0.75	0.5×10^{-4}	4.0	0.05
2	1.75	0.5×10^{-4}	4.0	0.27
3	0.75	1.5×10^{-4}	4.0	1.49
4	1.75	1.5×10^{-4}	4.0	0.35
5	0.75	0.5×10^{-4}	6.9	0.30
6	1.75	0.5×10^{-4}	6.9	0.65
7	0.75	1.5×10^{-4}	6.9	2.90
8	1.75	1.5×10^{-4}	6.9	5.59

The most important parameters, Table 2, which affect the decolorization rate constant, were the substrate (DR23) and semiconductor concentrations (TiO₂). TiO₂ concentration has an insignificant main effect (-0.32 ± 0.123 g L⁻¹) on the decolorization rate constant, while substrate concentration (DR23) has a significant main effect ($-2.45 \pm 0.123 \times 10^{-4}$ mol L⁻¹). On the other hand, semiconductor and substrate concentrations showed a significant synergic effect on of the decolorization rate constant ($1.72 \pm 0.123 \times 10^{-3}$ min⁻¹). The statistical significance of the ratio of mean square variation due regression and mean square residual error was tested using analysis of variance (ANOVA). The results show that the model does not present lack of fit at the 95 % confidence level. Fig. 2 shows the response surface obtained for model; $\hat{y} = b_0 - b_1x_1 - b_2x_2 + b_{12}x_1x_2$, fit to the results in Table 2.

Table 2. Rate constants obtained by varying the DR23 and TiO₂ concentrations and the temperature for the 2³ factorial design with a center point.

run	[TiO ₂]/g L ⁻¹	[DR23]/mol L ⁻¹	t/°C	$k_{obs} / 10^{-3} \text{ min}^{-1}$
1	1.75	1.5×10^{-4}	20.0	5.32
2	3.25	1.5×10^{-4}	20.0	3.33
3	1.75	3.0×10^{-4}	20.0	1.37
4	3.25	3.0×10^{-4}	20.0	2.98
5	1.75	1.5×10^{-4}	40.0	5.40
6	3.25	1.5×10^{-4}	40.0	3.31
7	1.75	3.0×10^{-4}	40.0	1.01
8	3.25	3.0×10^{-4}	40.0	2.20
9	2.50	2.25×10^{-4}	30.0	2.71
10	2.50	2.25×10^{-4}	30.0	2.35
11	2.50	2.25×10^{-4}	30.0	2.58

The contour plots given in Fig. 2 show the relative effects with pH and temperature kept constant. The results demonstrate that the surface has a maximum when the semiconductor and substrate concentrations are lower. Under these conditions, the experimental values agreed with the values predicted by the model.

Figure 2.- Contour of the response surface of the decolorization rate constant of direct red 23 showing the interactive effect of semiconductor and substrate concentrations.

As there was not any significant difference between these results when the temperature was enhanced from 20 to 40.0 °C, the temperature of 30°C was chosen, since it is close to the local room temperature.

The changes in the absorption spectra of DR23 solution with a maximum at 505 nm, during the photocatalytic process at different irradiation time, are shown in Fig. 3.

Figure 3.- Spectral changes of DR23 (1.50×10^{-4} mol L $^{-1}$) decolorization and degradation in TiO $_2$ (1.75 g L $^{-1}$) suspension at natural pH at 30.0°C during 6 h irradiation.

The color remove is attributed to the rupture of the double bond between the two nitrogen atoms ($-N=N-$) and related as the most active site for oxidative attack⁵. The decrease of the bands with maximum absorptions at 240 and 310 nm indicates the disappearance of the aromatic groups. Taking into account that the decolorization is related to the nitrogen double bond rupture, the elemental analysis for carbon was performed after sample irradiation for 6 h. As the initial concentration of total carbon for azo dye was 21.5% and 0.45% after 6h, this means that 97.9% of DR23 were degraded during the photocatalytic process, as it was reported in previous work⁸.

The number of intermediates and products as a consequence of the DR23 degradation was obtained through the normalized UV-Vis spectra using the Imbrie Q mode factor analysis followed by varimax and Imbrie oblique rotations¹²⁻¹⁴. Normalization to unit length was accomplished by dividing each absorbance in the spectrum (vector) by the square root of the sum of all the square values of the vector. When factor analysis is performed on the normalized data, it decomposes the data matrix into a score or concentration matrix and a spectral or loading matrix. The rows of the spectral matrix are the estimated spectral signatures of each constituent comprising the sample. If there is no noise in the data, the number of factors necessary to describe the data is equal to the number of chemical constituents comprising the sample. The score and loading matrices obtained from factor analysis are mathematical solutions devoid of chemical meaning. For this reason, varimax and oblique rotations are used to rotate the score and loading matrices from an abstract coordinate system to one that is based on the spectral profiles of the constituents comprising the sample. After the score and loading matrices are rotated, they must be transformed back to the original measurement space, i.e. the effects of normalization to unit length and range scaling must be removed to make these matrices interpretable. Details of this procedure are given in reference 15. The factor analysis showed that six factors explained around 99% of the total variance of the spectral data. This result indicates the existence of seven chemical species for the DR23 degradation because the factors are linearly independent. Therefore, seven factors were subjected to varimax rotation and oblique rotation. The relative concentrations for the seven species calculated by Imbrie's oblique rotation, and their profiles are shown in Fig. 4¹⁵. The spectral profiles (loadings) before oblique rotations are shown in Fig. 5.

Figure 4.- Normalized relative concentrations of seven chemical species obtained by analysis of Q mode factors by deconvolution of UV-Vis spectra vs irradiation time. A represents the azo dye; C, D, E, F, and G, the intermediates and B, the product.

Figure 5.- Factor loadings obtained by Q mode factor analysis. A represents the azo dye; C, D, E, F, and G, the intermediates and B, the product.

From Fig. 5, one can observe that really there is information on the seven loading factors, that is, A represents the spectral information of the azo dye and C, D, E, F, and G the intermediates that appear and disappear as a function of time with B being the product in Fig. 4. The eighth factor is only noise. Song et al¹⁶ degraded DR23 in aqueous solutions under UV irradiation using SrTiO $_3$ /CeO $_2$ composite surface as the photocatalyst, and showed that the increase of UV power enhances the decolorization rate and detected nine intermediates. The smaller degradation time and larger number of intermediates during the irradiation with respect to our results are attributed mainly to the large photocatalytic activity of SrTiO $_3$ /CeO $_2$ in comparison to TiO $_2$ and the fact of, in our case, the determination has been carried out without any experimental separation procedure.

Effect of electron acceptors

In order to enhance the formation of hydroxyl radicals and also inhibit undesired electron/hole pair recombination, and hence permit the degradation of highly toxic wastewater to become faster and easier^{4, 17, 18}, some electron acceptors were added to the TiO $_2$ suspension containing direct red 23. Hydrogen peroxide, persulfate ion, and chlorate ion oxidants were added at the optimized conditions, obtained from the experimental design for azo dye degradation. The addition of each oxidant was carried out into suspensions containing 1.75

g L⁻¹ TiO₂ and 1.5x10⁻⁴ mol L⁻¹ DR23 at natural pH and 30.0 °C for all the irradiations. Blank experiments were carried out by irradiating the aqueous solutions of the dye containing the oxidant in the absence of the photocatalyst. There is no observable loss of dye, since the rate constants remained practically constant during the irradiation, as shown in Fig. 6 – 8.

Hydrogen peroxide

The effect of the hydrogen peroxide addition ($E^\circ = 1.78$ V)¹⁹ was investigated from 5.0x10⁻⁵ to 5.0x10⁻² mol L⁻¹ in the TiO₂ suspension containing the DR23 azo dye at pH 6.9 and 30 °C. The initial pH decreased respectively to 6.8 and 6.5 with the addition of H₂O₂ in this concentration range. This small pH dependence with respect to H₂O₂ may be due to the simultaneous H⁺ consumption in the valence band and production in the conduction band²⁰. The variation of the decolorization rate constants is shown in Fig. 6.

Figure 6.- Rate constants for decolorization of DR23 (1.5x10⁻⁴ mol L⁻¹) in the presence of H₂O₂ (●) and TiO₂/H₂O₂ (■) at natural pH under UV irradiation as a function of hydrogen peroxide concentration at 30°C.

From this figure it is observed that the rate constant enhanced from 12.23x10⁻³ min⁻¹ at 5.0x10⁻⁵ mol L⁻¹ H₂O₂ to 20.90x10⁻³ min⁻¹ at 5.0x10⁻³ mol L⁻¹. In this concentration DR23 was degraded about 97.8% in 2 h irradiation. The rate constant enhancement is due to the reaction of the photogenerated electrons with hydrogen peroxide, producing hydroxyl radical and inhibiting the electron-hole combination according to (1)^{19, 21-24}.

The slight decrease in the rate constant from 20.90x10⁻³ to 20.26x10⁻³ min⁻¹ respectively at 5.0x10⁻³ and 2.0x10⁻² mol L⁻¹ range is attributed to the hole (2) and hydroxyl radical (3) scavenging by hydrogen peroxide as well as the reaction of hydroxyl radical with hydroperoxyl radical (4)^{17, 19}.

Besides this, hydrogen peroxide can compete with azo dye by the adsorption sites as well as modify the photocatalyst surface and decrease its catalytic activity^{17, 25}.

Persulfate ion

The influence of the persulfate ion addition, a strong oxidant ($E^\circ = 2.01$ V)²⁶, on the decolorization rate constant was studied in the range between 0.1x10⁻⁴ and 2.0x10⁻⁴ mol L⁻¹ at 30° C at natural pH of 6.9 as shown in the Fig. 7. The initial pH lowered respectively to 6.7 and 5.7 with the persulfate addition.

Figure 7.- Rate constants for decolorization of DR23 (1.5x10⁻⁴ mol L⁻¹) in the presence of S₂O₈²⁻ (●) and TiO₂/S₂O₈²⁻ (■) at natural pH under UV irradiation as a function of persulfate ion concentration at 30°C.

From this figure the rate constant increased from 11.91x10⁻³ min⁻¹ at 1.0x10⁻⁵ mol L⁻¹ S₂O₈²⁻ to 32.92x10⁻³ min⁻¹ at 2.0x10⁻⁴ mol L⁻¹. The gradual and continuous increase of the rate constant is attributed to the reaction of this oxidant with a photogenerated electron, producing a strong oxidant, such as sulfate anion radical, SO₄•⁻ ($E = 1.10$ V)²⁷, according to the following equation (5):

This anion radical produces hydroxyl radical (6) when it reacts with H₂O and in subsequent step the molecular oxygen (7)^{17, 18}, decreasing the medium pH.

Because the rate constant did not attain the maximum value in this concentration range, it was added 2.5x10⁻⁴ mol L⁻¹ S₂O₈²⁻ and then, 97.6% of DR23 was decolorized in 1 min irradiation. This unexpected result suggest that after the consumption of photogenerated electrons by persulfate, avoiding the recombination of electron-hole pair, more sulfate anion radical would be produced by photolysis (8) and reduction (5), enhancing the decolorization rate. This means that the more S₂O₈²⁻ concentration is added the more decolorization is.

Chlorate ion

The influence of the chlorate ion on DR23 decolorization was investigated by varying the concentration from 1.0x10⁻⁴ to 4.0x10⁻³ mol L⁻¹ at 6.9 and 30° C as shown the Fig. 8. The addition of this oxidant enhanced the initial pH respectively to 7.4 and 6.0.

Figure 8.– Rate constants for decolorization of DR23 (1.5×10^{-4} mol L⁻¹) in the presence of ClO_3^- (●) and $\text{TiO}_2/\text{ClO}_3^-$ (■) at natural pH under UV irradiation as a function of chlorate ion concentration at 30°C.

The rate constant increased from 8.65×10^{-3} to 24.50×10^{-3} min⁻¹ following a similar trend with smaller values in relation to those obtained from persulfate addition. In contrast to the persulfate case, the rate constant enhancement through the chlorate addition ($E^\circ = 1.15$ V)²⁸ can be attributed to the formation of oxidizing species such as $\text{ClO}_2^\bullet$ radical (9), that reacts with the azo dye, RH, to produce a radical, $\text{R}^\bullet$ (10).

When it was added 5.0×10^{-3} mol L⁻¹ ClO_3^- , a similar behavior to that discussed for $\text{S}_2\text{O}_8^{2-}$ was observed, that is, the azo dye was decolorized about 95.9% in 1 min, attributed to the scavenging of the photogenerated electron by the reduction agent (9). In this case the rate constant was lower, due to the larger bonding energy between chlorine and oxygen atoms (269.1 kJ mol⁻¹)²⁹ in chlorate anion in comparison to the O-O bonding energy (146 kJ mol⁻¹)³⁰ in $\text{S}_2\text{O}_8^{2-}$.

Comparison of the irradiation times of the DR23 decolorization in the presence of oxidants

Comparable decolorization percentages were obtained for DR23 in the presence of three oxidants. Among these, the persulfate ion showed the highest efficiency, because 2.5×10^{-4} mol L⁻¹ decolorized 97.3 % azo dye in 1 min, followed by chlorate ion using 5.0×10^{-3} mol L⁻¹ and 95.7 % also in 1 min and, 97.8 % in 4 h through the addition of 5.0×10^{-3} mol L⁻¹ hydrogen peroxide. In the absence of any oxidant 98.6% was decolorized after 6 h irradiation and resulting in a rate constant of 5.59×10^{-3} min⁻¹ as presented in Table 3.

Table 3. Decolorization percentages and irradiation times of DR23 in the presence of catalyst and oxidant at natural pH at 30.0°C. [DR23] = 1.5×10^{-4} mol L⁻¹; $[\text{TiO}_2] = 1.75$ g L⁻¹.

oxidant	[oxidant]/10 ⁻⁴ mol L ⁻¹	decolorization/%	irradiation time/min
$\text{S}_2\text{O}_8^{2-}$	2.5	97.3	1.0
ClO_3^-	50.0	95.7	1.0
H_2O_2	50.0	97.8	120.0
--	--	98.6	360.0

This means that through the addition of persulfate and chlorate ions, DR23 was degraded decreasing the irradiation time by a factor of, at least, 360 relative to the irradiation time in their absence. This ratio dropped to 3 when the hydrogen peroxide was used. This behavior may be justified in terms of the pH variation during 3 h irradiation as well as the hydroxyl radical production, as it was the case of the hydrogen peroxide and persulfate ion, or of the reduction

potential of several oxidant species, as it occurred with the chlorate ion.

The formation of sulfate anion radical (5) and the subsequent hydroxyl radical production (6) from the reaction between persulfate and photogenerated electron let more acidic the medium and cause the rate constant enhancement. This acidity may be observed, when 1.0×10^{-3} and 2.50×10^{-4} mol L⁻¹ persulfate were added to the TiO_2 suspension, the initial pH (6.9) decreased to 6.7 and 5.5 respectively. Conversely, the pH decrease through the hydrogen peroxide addition was smaller, that is, 6.8 when it was used 5.0×10^{-4} mol L⁻¹ and 6.5 for 5.0×10^{-2} mol L⁻¹. This smaller difference in the pH values for hydrogen peroxide may be attributed to the formation of hydroxide ion when this oxidant reacts with photogenerated electron, the medium becomes alkaline rather than acid as it occurs with the sulfate anion radical (6 – 7). It may be attributed that the reaction takes place more rapidly due to the hydroxyl radical (6) and molecular oxygen (7).

On the other hand, the initial pH increased for 7.4 when 1.0×10^{-4} mol L⁻¹ chlorate was added and a decrease to 6.0 for 4.0×10^{-3} mol L⁻¹. These results suggest that the rate constant enhancement is due to the reactions (8 – 11) in which each oxidant species captures a photogenerated electron preventing the electron-hole pair recombination.

From these results, the persulfate and chlorate ions in the presence of TiO_2 and UV radiation represent a promising alternative for the treatment and purification of aquatic environment contaminated by azo dye.

Effect of radiation source

The influence of the radiation source on the rate of azo dye decolorization has been examined at constant dye concentration (1.50×10^{-4} mol L⁻¹, natural pH) in the absence and presence of catalyst loading (1.75 g L⁻¹). The irradiation was carried out at the smallest concentration of the three oxidants with the aim of knowing the influence of the light intensity (irradiance) using solar radiation and artificial illumination at 30°C on the DR23 decolorization. The decolorization rate constants are displayed in Table 4. The experiments using solar radiation were carried out at the State University of Londrina, Exact Sciences Center, Department of Chemistry (latitude 23°19'39" S, longitude 51°11'59" W) from 10 am to 2 pm, taking into account that the solar radiation presents a larger angle of incidence on the Earth's surface in the Southern Hemisphere. The temperature inside of the reactor increased from 26.0 to 34.0°C in this period.

When the reaction was performed in the presence of TiO_2 , the decolorization rate constant increased more than double under solar radiation (15.65×10^{-3} min⁻¹) relative to the value under artificial conditions (5.59×10^{-3} min⁻¹). On the other hand, the rate constant was enhanced by about 30% under solar radiation (0.54×10^{-3} min⁻¹) relative to artificial light (0.41×10^{-3} min⁻¹) in the absence of TiO_2 . The addition of an oxidant as persulfate increased the rate constant to 33.40×10^{-3} min⁻¹ under solar radiation, and to 11.93×10^{-3} min⁻¹ under artificial radiation at 30°C, while the rate constants were 0.99×10^{-3} and 1.33×10^{-3} min⁻¹ on photolysis in the presence of persulfate using artificial and solar radiation respectively. In the presence of 0.50×10^{-4} mol L⁻¹ hydrogen peroxide the rate constants attained respectively 12.23×10^{-3} and 40.36×10^{-3} min⁻¹ for artificial and solar illuminations. This behavior was attributed to the higher oxidation potential of the hydroxyl radical (2.8 V) in comparison to sulfate anion radical (1.10 V)²⁷ or $\text{ClO}_2^\bullet$ (1.15 V), produced by the respective oxidants.

Table 4. Rate constants of DR23 decolorization obtained from artificial and solar illumination. [DR23] = 1.50×10^{-4} mol L⁻¹.

$[\text{TiO}_2]$ / g L ⁻¹	oxidant	[oxidant]/10 ⁻⁴ mol L ⁻¹	k _{obs} / 10 ⁻³ min ⁻¹ (artificial light)	k _{obs} / 10 ⁻³ min ⁻¹ (solar radiation)
1.75	-	-	5.59	15.65
1.75	H_2O_2	0.50	12.23	40.36
1.75	$\text{S}_2\text{O}_8^{2-}$	0.50	11.91	33.40
1.75	ClO_3^-	1.00	8.65	32.20
-	-	-	0.41	0.54
-	H_2O_2	0.50	0.91	1.42
-	$\text{S}_2\text{O}_8^{2-}$	0.50	0.99	1.33
-	ClO_3^-	1.00	0.88	1.26

Taking into account that the average intensity of solar radiation during the solar illumination was 3613 ± 248 $\mu\text{W cm}^{-2}$ and from the 125 W Hg vapor lamp it was 227.0 ± 9.5 $\mu\text{W cm}^{-2}$, the rate constants were ca. three fold larger

in the presence of TiO_2 and ca. 30% more upon photolysis by means solar illumination. This confirms that a higher light intensity increases the amount of h_{ν}^+ , OH radicals and other highly oxidative radicals generated at the TiO_2 surface.

CONCLUSION

Direct red 23 azo dye was simultaneously decolorized and degraded in 6 h of artificial irradiation in the presence of titanium dioxide following the 1st order kinetic behavior. The most favorable experimental conditions were determined using a 2³ factorial design by varying the substrate and the catalyst concentrations, and the pH. Seven chemical species were determined from the UV-Vis normalized spectra during the DR23 degradation. The addition of oxidants such as persulfate ion, chlorate ion, and hydrogen peroxide enhanced the rate constants. Concentrations equivalent to 2.5×10^{-4} mol L⁻¹ persulfate ion and 5.0×10^{-3} mol L⁻¹ chlorate showed that the persulfate ion decolorized the dye more rapidly than the others. In addition, the degradation was faster under solar illumination when compared to the artificial one.

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