

Photocatalytic oxidation of Cibacron Yellow LS-R

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Abstract

The photocatalytic degradation of Cibacron Yellow LS-R (CIY), an azo dye, has been investigated in aqueous heterogeneous solutions containing semiconductor oxides as photocatalysts. The disappearance of the organic molecule follows approximately a pseudo-first kinetic order according to the Langmuir–Hinshelwood model. Various commercial photocatalysts are compared with respect to their decolorization efficiency, the COD, as well as the toxicity reduction. The effect of the temperature on the reaction rate is ascertained.
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1. Introduction

The textile industry is one of those producing large amounts of wastewater. In a typical dyeing and finishing mill, about 1000 L of water are consumed on the average for every ton of cloth processed [1]. There is a great variation in the characteristics of these wastewater, since the chemicals used change daily or even more times every day, depending on the quality and the colour of the fabric being dyed. Most of these dyes are not readily degraded under the aerobic conditions prevailing in biological treatment plants [2]. The studies related to the treatment of this kind of wastewater, deal with the removal of the colour and the organic matter as well as the salt additives, in order to reach the suitable conditions for recirculating and reusing these. In this context, proper treatment methods is highly requested. Destructive oxidation methods, such as heterogeneous photocatalysis (TiO₂/UV-A), ozonation, H₂O₂/UV-B, Photo-Fenton, etc., could result in a substantial solution of the detoxification of different kind of wastewater, exactly at the sight where they are released.

Heterogeneous and homogeneous solar photocatalytic oxidation (TiO₂/H₂O₂, Fe³⁺/H₂O₂) have shown to be effective with a variety of different kind of chemicals (pesticides, organics, etc.) and different kinds of wastewater (industrial and municipal, groundwater, contaminated air and water, etc.) [3–5]. Recently,

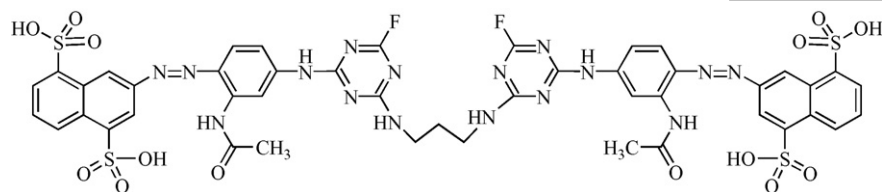
a number of research groups have dealt with the heterogeneous photocatalytic decomposition of various types of dyes in the presence of near UV (UV-A) or visible light [6–11] with very encouraging results.

General description of heterogeneous photocatalysis under artificial or solar irradiation is presented in several excellent review articles [4,12,13]. A brief summary is presented here only for the sake of completeness.

It is well established, that by the irradiation of an aqueous TiO₂ suspension with light energy greater than the band gap energy of the semiconductor ($E_g > 3.2$ eV), conduction band electrons (e^-) and valence band holes (h^+) are generated. Part of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons, act as powerful oxidants and reductants, respectively. The photogenerated electrons react with the adsorbed molecular O₂ on the Ti(III)-sites, reducing it to superoxide radical anion O₂⁻, while the photogenerated holes can oxidize either the organic molecules directly, or the OH⁻ ions and the H₂O molecules adsorbed at the TiO₂ surface to OH• radicals. These radicals together with other highly oxidant species (e.g. peroxide radicals) are reported to be responsible for the primary oxidizing step in photocatalysis. The OH• radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with a standard reduction potential of 2.8 V. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading finally to their complete mineralisation.

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Our present study provides results describing the heterogeneous photocatalytic decolourisation and oxidation of Cibacron Yellow LS (CIY), an azo dye, used in the dyeing of cellulose, over semiconducting powders such as TiO_2 and ZnO under various experimental conditions. Its structure is presented below.



Cibacron Yellow LS-R (CI: Reactive Yellow 208)

2. Experimental

2.1. Reagents

Cibacron Yellow LS-R ($\text{C}_{42}\text{H}_{38}\text{O}_{14}\text{N}_{16}\text{S}_4\text{F}_2$) (CI: Reactive Yellow 208), was a product of Ciba GmbH and was used as received. TiO_2 P-25 Degussa (75% anatase and 25% rutile with a specific BET surface area of $56\text{ m}^2\text{ g}^{-1}$ and a primary particle size of 25 nm nonporous) [14], TiO_2 Tronox (Mc Gee) (pure anatase, $10\text{ m}^2\text{ g}^{-1}$), TiO_2 UV-100 Hombikat (100% pure anatase with a specific BET surface area $>250\text{ m}^2\text{ g}^{-1}$) and ZnO (Merck, with a specific BET surface area $9.2\text{ m}^2\text{ g}^{-1}$) were used for all photocatalytic experiments.

2.2. Procedures and analysis

Experiments were performed in a closed Pyrex cell of 300 mL capacity. The reaction mixture in the cell was maintained as a suspension by magnetic stirring. The suspension was left for 30 min in the dark in order to achieve the maximum adsorption of the dye onto the semiconductor surface. The reaction vessel was fitted with a central lamp and had inlet and outlet ports for bubbling the desired gas under which the reaction was taking place. The spectral response of the irradiation source (Osram Dulux S 9W/78, UVA) according to the producer, ranged between 350 and 400 nm with maximum at 366 nm. The photon flow per unit volume of the incident light was determined by chemical actinometry using potassium ferrioxalate [15,16]. The initial light intensity, under exact the same conditions as in the photocatalytic experiments, was evaluated to be $1.83 \times 10^{-4}\text{ Einstein min}^{-1}$. In all cases during the experiments 250 mL of the CIY solution containing the appropriate quantity of the semiconductor powder was magnetically stirred, before and during the illumination, while the solution was purged with CO_2 free air. At specific time intervals samples of 6 mL were withdrawn. To remove the TiO_2 particles, the solution was filtered through a $0.45\text{ }\mu\text{m}$ filter (Schleicher and Schuell). All photocatalytic experiments, except where otherwise mentioned in the text, were carried out at an initial pH value of 6.

Changes in the concentration of CIY were observed from its characteristic absorption band at 400 nm using an UV–vis spectrophotometer (Shimadzu UV-160 A). In order to determine

the extent of mineralisation, samples were taken out at regular time intervals and the Chemical Oxygen Demand (COD) were measured according to [17].

Some photocatalytic experiments were repeated three times in order to check the reproducibility of the experimental results.

The accuracy of the optical density values was within $\pm 5\%$, while the respective values of the dilute organic carbon (DOC) reduction during the mineralization experiments was $\pm 10\%$.

Toxicity measurements were done using bioluminescent bacteria with LUMISTox 300 (Dr Lange). To all the samples, 2 vol.% NaCl was added and the pH was adjusted to a value between 6.8 and 7.2 by addition of HCl or NaOH, respectively. After reactivation of the bacteria for 15 min at $15\text{ }^\circ\text{C}$, 0.5 mL of the sample and 0.5 mL of the bacteria suspension, was added in the measuring cell and incubated for 30 min at $15\text{ }^\circ\text{C}$. The inhibition of the luminescence was measured in comparison to a blank sample of 0.5 mL of 2% NaCl solution and 0.5 mL of the bacteria suspension using a LUMISTox-multiplier unit (Dr. Lange).

3. Results and discussion

3.1. Photocatalytic oxidation

Fig. 1 shows the changes in the optical absorption spectrum of a 25 mg L^{-1} CIY solution containing 0.5 g L^{-1} TiO_2 P-25 as a function of irradiation time. The absorption spectrum is seen to decrease in intensity with increasing irradiation time, vanishing almost completely within 30 min. The rapid disappearance of the 400 nm absorption band in Fig. 1 suggests that the chromophore

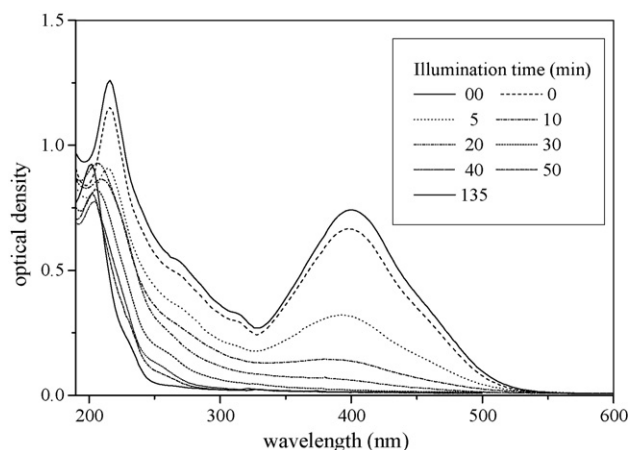


Fig. 1. Spectral response of 25 mg L^{-1} CIY during the photocatalytic degradation in the presence of 0.5 g L^{-1} TiO_2 P-25 at $\text{pH}_{\text{eq}} 6$ (00: a 25 mg L^{-1} CIY solution without catalyst; 0: a 25 mg L^{-1} CIY solution in the presence of 0.5 g L^{-1} TiO_2 in the dark).

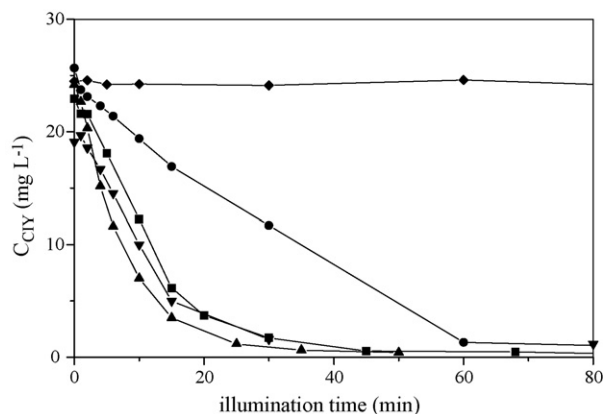


Fig. 2. Photodegradation of 25 mg L⁻¹ CIY as a function of the irradiation time in the presence of (■) 1 g L⁻¹ TiO₂ P-25, (▼) 1 g L⁻¹ TiO₂ UV-100, (●) 1 g L⁻¹ TiO₂ Tronox and (▲) 1 g L⁻¹ ZnO, (◆) without catalyst, at pH_{eq} 6.

responsible for the characteristic colour of the azo dye is breaking down. Apart from the degradation of the coloured group, as one can see in the same figure, there is a drastic decrease of the absorbance values at wavelengths below 300 nm, due to the OH[•] radical attack and breaking of the aromatic rings in the dye molecule.

Results of the photolysis of a 25 mg L⁻¹ CIY solution in the presence of various semiconducting oxides as photocatalysts are shown in Fig. 2. Three different TiO₂ commercial products (P-25, Tronox and UV-100) and ZnO were tested, in suspensions of 1 g L⁻¹ of the photocatalyst and 25 mg L⁻¹ of CIY. The amount of the dye present in the supernatant is plotted as a function of irradiation time. Under these experimental conditions and after 30 min of light exposure in the presence of 1 g L⁻¹ TiO₂ P-25 and TiO₂ UV-100 the decolorisation of the solution was almost complete (94% of the colour of CIY disappeared), while in the presence of ZnO the decolorization of the solution by the end of the 30 min was complete. On the contrary the decolorization in the presence of TiO₂-Tronox, as can be seen in Fig. 2, is a slower process and after 30 min of illumination 45% of the initial concentration of CIY remains in the solution.

The blank experiments for either illuminated CIY solution or the suspension containing TiO₂ and CIY in the dark showed that both, illumination and catalyst were necessary for the destruction of the dye.

The influence of the initial concentration of the solute on the photocatalytic degradation rate of most organic compounds is described by a pseudo-first kinetic order, which is rationalised in terms of the Langmuir–Hinshelwood model, modified to accommodate reactions occurring at a solid–liquid interface [18–20]. The rate dependence on reagent concentration can be approximated by the equation:

$$r_0 = -\frac{dC}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \quad (1)$$

where r_0 is the initial rate of disappearance of the organic substrate, k_r and K the apparent rate constants and adsorption coefficients respectively and C_{eq} is the equilibrium reactant concentration. This equation can be used when data demonstrate

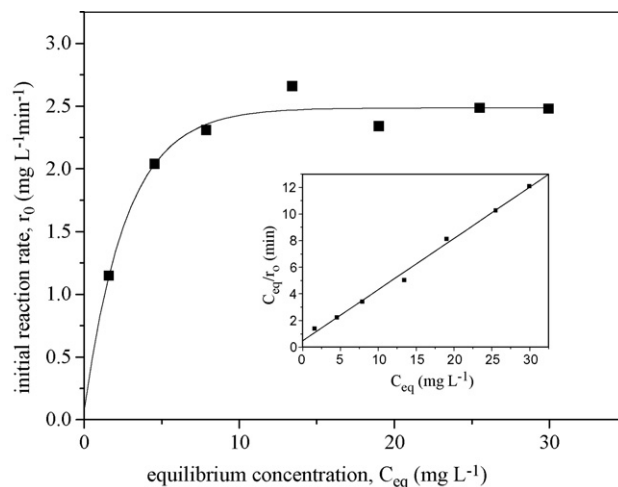


Fig. 3. Plot of r_0 vs. C_{eq} at different initial concentrations of Cibacron Yellow LS in the presence of 1 g L⁻¹ TiO₂ P-25. Inset: linear transform of C_{eq}/r_0 vs. C_{eq} according to Eq. (2).

linearity when plotted as follows:

$$\frac{C_{eq}}{r_0} = \frac{1}{k_r K} + \frac{C_{eq}}{k_r} \quad (2)$$

Such a linearisation is commonly taken to indicate that the rate-determining process involves reaction events between reactant species adsorbed onto the surface of the catalyst, which is the case in our study.

The effect of altering the equilibrium concentration of CIY on the initial reaction rate (r_0) of photodegradation is shown in Fig. 3. The curve is reminiscent of a Langmuir type isotherm, for which the rate value of decomposition first increases sharply and then reaches a saturation value at high concentrations of CIY. The r_0 values were independently obtained by a linear fit of the $C_{eq} - t$ data in the range of 1.5–30 mg L⁻¹ initial CIY concentration. Only the experimental data obtained during the first 5 min illumination were used in calculating the initial reaction rates, in order to minimise variations as a result of the competitive effects of the intermediates, pH changes, etc. The dependence of C_{eq}/r_0 values on the respective equilibrium concentrations of CIY for constant concentration of TiO₂ P-25 at 1 g L⁻¹ is shown in inset of Fig. 3. The k_r and K values calculated according to Eq. (2) from the slope of the straight line ($R^2 = 0.999$) and from the intercept with the C_{eq}/r_0 axis were 2.6 ± 0.13 mg L⁻¹ min⁻¹ and 1.24 ± 0.04 mg L⁻¹, respectively. As already mentioned, K represents the equilibrium constant for the adsorption of CIY onto TiO₂ P-25 and k_r reflects the limiting rate of reaction at maximum coverage for the given experimental conditions and therefore has no absolute meaning.

The effect of varying the quantity of TiO₂ P-25 on the observed photodegradation of CIY is presented in Fig. 4. As the TiO₂ concentration increases from 0.1 to 4 g L⁻¹ the rate of photodecomposition of the CIY increases by a factor of 3.3. The curve is reminiscent of a Langmuir type isotherm suggesting that r_0 may reach a saturation value at higher TiO₂ concentrations, as has been reported in similar cases [6,21,22]. Increasing further the amount of TiO₂ leads to enhancement of the light

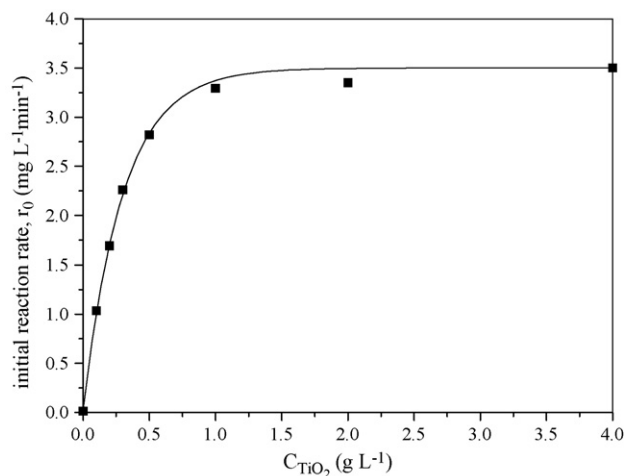


Fig. 4. Plot of r_0 vs. C_{TiO_2} for 25 mg L^{-1} of CIY at different concentrations of TiO_2 P-25.

reflectance and consequently to a decrease in the efficiency of the photodegradation of CIY [23].

Fig. 5 shows the COD reduction versus illumination time of a solution containing 25 mg L^{-1} CIY in the presence of 1 g L^{-1} TiO_2 P-25, ZnO and TiO_2 Tronox. ZnO seems to be a better catalyst under the given experimental conditions and after 90 min of illumination a 80% COD reduction can be achieved, while in the same time the presence of TiO_2 P-25 leads only to a COD reduction of 67%.

3.2. Influence of the temperature

Although the temperature in a chemical reaction play an important role, very little information concerning the temperature effect on the heterogeneous photocatalytic degradation of pollutants in aqueous solutions is available. This is due to the fact that the heterogeneous photocatalytic reactions are usually not very temperature-sensitive because the band-gap energy of TiO_2 is too high ($\sim 3.2 \text{ eV}$) to be overcome by the thermal activa-

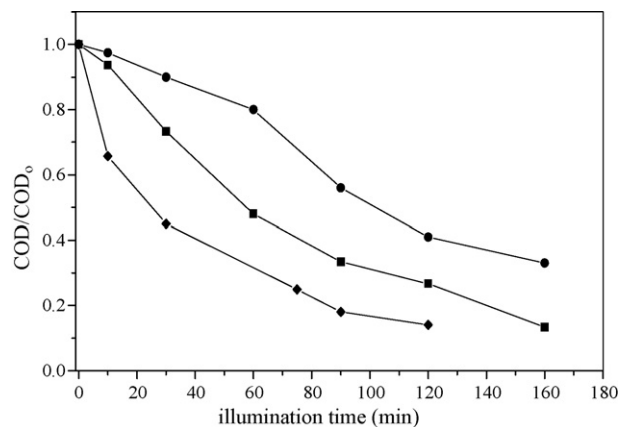


Fig. 5. COD/COD_0 plotted vs. the irradiation time for 25 mg L^{-1} of Cibacron Yellow LS, for $(\blacksquare) 1 \text{ g L}^{-1}$ TiO_2 P-25 at $\text{pH}_{\text{eq}} 6$, $(\bullet) 1 \text{ g L}^{-1}$ TiO_2 Tronox at $\text{pH}_{\text{eq}} 6$, $(\blacklozenge) 1 \text{ g L}^{-1}$ ZnO, at $\text{pH}_{\text{eq}} 7.5$.

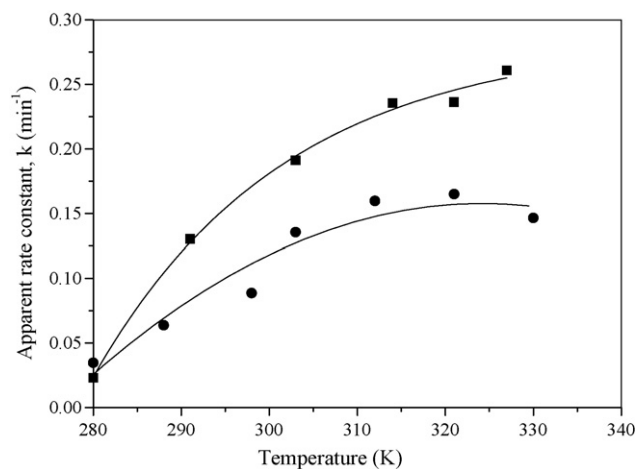


Fig. 6. The dependence of the apparent rate constant, k of the photocatalytic degradation of 15 mg L^{-1} CIY vs. the reaction temperature for $(\bullet) 0.5 \text{ g L}^{-1}$ TiO_2 P-25 at $\text{pH}_{\text{eq}} 6$ and $(\blacktriangle) 0.5 \text{ g L}^{-1}$ ZnO, at $\text{pH}_{\text{eq}} 7.5$.

tion energy ($kT = 0.026 \text{ eV}$ at room temperature). Increasing the reaction temperature may increase the oxidation rate of organic compounds at the interface, but it also reduces the adsorptive capacities associated with the organics and dissolved oxygen [12,24].

In the present paper the CIY decolorization was also studied as a function of temperature under the same operating conditions for both illuminated TiO_2 P-25 and ZnO systems.

The results concerning the dependence of the rate constant k of the photocatalytic degradation of CIY from the reaction temperature, from 5 to 57°C , are shown in Fig. 6. It is clear that by increasing the reaction temperature an increase of the apparent reaction rate constant k is achieved for both photocatalytic systems. By plotting the natural logarithm of k as a function of the reciprocal absolute temperature (T), a linear behaviour was obtained for both TiO_2 P-25 and ZnO catalysts as shown in Fig. 7. The activation energy (E_a) was determined according to

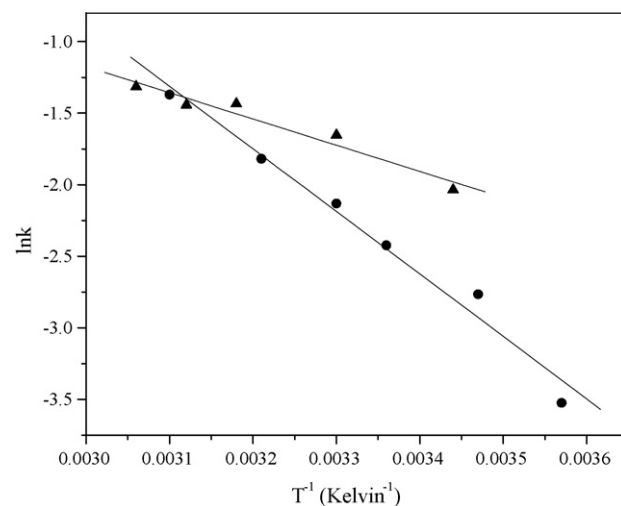


Fig. 7. Plot of $\ln k$ vs. T^{-1} for 15 mg L^{-1} of Cibacron Yellow LS, for $(\bullet) 0.5 \text{ g L}^{-1}$ TiO_2 P-25 at $\text{pH}_{\text{eq}} 6$, $(\blacktriangle) 0.5 \text{ g L}^{-1}$ ZnO, at $\text{pH}_{\text{eq}} 7.5$.

Table 1
Activation energy for the photocatalytic decolourisation of Cibacron Yellow LS (CIY)

Photocatalytic system	Activation energy, E_a (kJ mol ⁻¹)
0.5 g L ⁻¹ TiO ₂ P-25 at pH _{eq} 6	36.316 ± 2.644
0.5 g L ⁻¹ ZnO, at pH _{eq} 7.5	15.232 ± 2.020

Arrhenius equation (Eq. (3)) and the results are given in Table 1:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

3.3. Toxicity measurements

The photocatalytic degradation of the organic compounds is a promising method for eliminating these from water. However, the question of partial versus total oxidation is quite important since some incompletely oxidized compounds can be more toxic than the parent contaminants. In our study, toxicity measurements of the treated solutions were carried out in order to give a more complete evaluation of the efficiency of the methodology that have been used. The toxicity of unirradiated stock solution and of several samples (collected after different times of irradiation of solutions of CIY in the presence of different catalysts) were examined by means of a LUMIStox-Test (LCK484 of Dr. Lange GmbH) determining the inhibition of luminescence of bacteria *Vibrio fischeri* after 30 min of incubation. The bioluminescence test, in this series of experiments, was chosen as a reproducible and sensitive screening method to determine the overall toxicity during the treatment. In order to be able to indicate the changes in the toxicity, instead of presenting the percentage inhibition, the results are being converted to the *relative toxicity index* (RTI), according to the following equation [25,26]:

$$\text{RTI} = \frac{\% \text{ inhibition at } t}{\% \text{ inhibition at } t_0} \quad (4)$$

The results obtained after 30 min exposure of the bacteria to the samples are presented to Fig. 8. The increase of the toxicity after 25 min of treatment when using TiO₂ P-25, is probably due to the release of toxic intermediates. After 60 min of irradiation, there is almost a 97% decrease of the inhibition provoked during the irradiation and 87% of the initial inhibition. When using TiO₂ Tronox, although not so toxic intermediates seem to appear, finally there is a 70% decrease of the initial inhibition, after almost 160 min of irradiation.

The combination of TiO₂ P-25 and H₂O₂ decreases after only 20 min of irradiation the initial inhibition to 98%. On the other hand the use of ZnO leads to a very toxic solution for the bacteria *Vibrio fischeri*, as a result of dissolution and photodissolution of ZnO [27]. This is confirmed by measurements of Zn²⁺ presented in Fig. 9 (EC₅₀ of zinc is 1.62 mg L⁻¹ [28]) and by the difference in the toxic response between the 5 and 15 min exposure, which is characteristic of the metal ions [29]. This makes, in the case of ZnO impossible any conclusion concerning the toxicity of the photoproducts.

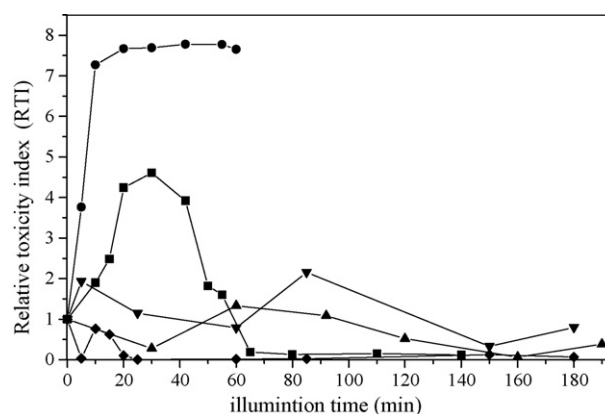


Fig. 8. Relative toxicity index plotted vs. the irradiation time for 25 mg L⁻¹ of Cibacron Yellow LS, for (■) 1 g L⁻¹ TiO₂ P-25 at pH_{eq} 6 (●) 1 g L⁻¹ ZnO, at pH_{eq} 7.5 (▼) 1 g L⁻¹ TiO₂ Tronox at pH_{eq} 6, and (◆) 1 g L⁻¹ TiO₂ P-25 and 85 mg L⁻¹ H₂O₂ at pH_{eq} 6.

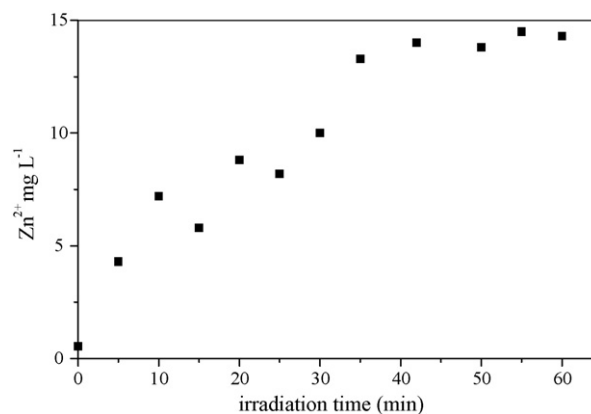


Fig. 9. Zn²⁺ concentration vs. irradiation time in a 25 mg L⁻¹ CIY solution and 1 g L⁻¹ ZnO.

4. Conclusions

In this work the photocatalytic oxidative degradation of the azo dye Cibacron Yellow LS-R, has been studied under artificial illumination. It is observed that TiO₂ P-25 as well as ZnO are efficient photocatalysts, both in respect of decolorization as well as mineralization. Additionally, a drastic decrease in the parent compound toxicity has been observed after treatment in the presence of TiO₂ P-25.

From the results of the present work and the respective literature one could claim that the photocatalytic treatment of the waste water of the textile industry, one of the most polluting industrial sectors, could be employed as a powerful tool for the decolorization and the reduction of the organic content of this liquid waste. The use of a low cost and biologically inactive catalyst and the possibility of activating it with solar light, combined with the simple technology required for this method, can offer economically reasonable and practical solutions to the processing of this liquid waste, especially in regions of abundant sunlight.

An integrated photocatalytic-nanofiltration system, under solar exposure, for the decolorization, COD reduction and inor-

ganic salts removal, seems a logical choice for the treatment and reuse of waste waters such as those coming from the textile processing industry.

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