

# Kinetics of photocatalytic degradation of reactive dyes in a TiO<sub>2</sub> slurry reactor

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## Abstract

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Dyes are extensively used and hence wastewaters discharged in rivers or public sewage treatment plants are highly contaminated. In this work, a detailed investigation of the adsorption and photocatalytic degradation of the safira HEXL dye, an anionic azo dye of reactive class, is presented. H<sub>2</sub>O<sub>2</sub> and UV light have a negligible effect when they are used on their own. The adsorption of dye on the semiconductor shows a strong dependence on the pH and follows a Langmuir adsorption model. The photodegradation kinetics is discussed in terms of the Langmuir–Hinshelwood model.

The effect of pH, amount of photocatalyst, UV light intensity and hydrogen peroxide concentration is discussed. The relative photonic efficiency of the system is reported using phenol as a standard organic compound. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Photocatalysis; Decolourization; Semiconductor; Dye

## 1. Introduction

Dye pollutants from the textile industry are an important source of environmental contamination. It is estimated that from 1 to 15% of the dye is lost during dyeing processes and is released in wastewaters [1]. The release of these coloured wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life [2].

A variety of physical, chemical and biological methods are presently available for treatment of textile wastewater. Biological treatment is a proven technology and is cost-effective. However, it has been reported that the majority of dyes are only adsorbed on the sludge and are not degraded [3]. Physical methods such as ion-exchange, adsorption, air stripping, etc., are also ineffective on pollutants which are not readily adsorbable or volatile, and have the further disadvantage that they simply transfer the pollutants to another phase rather than destroying them.

The efficiency of advanced oxidation processes for the degradation of recalcitrant compounds has been extensively studied. Photocatalytic reactions take place when the semiconductor particle absorbs a photon of light which is more energetic than its bandgap. Thus, the electron is excited from the valence bond to the conduction band, forming a

hole–electron pair, able to initiate the oxidation and reduction processes of adsorbed substrates [4]. In aqueous solutions the holes are scavenged by surface hydroxyl groups to generate the strong oxidizing hydroxyl radical (OH<sup>•</sup>), which can promote the oxidation of organic compounds.

Several studies of photocatalytic degradation of dyes have been reported [4–11]. Factors influencing the photodegradation rate of aqueous systems have been studied in the subjects such as the effect of pH values, dissolved oxygen contents and amounts of photocatalyst added to the aqueous solution [12–14]. There are very few studies related to the use of semiconductors in the photodegradation of photostable dyes [15–17].

In this work, we studied the photocatalytic degradation of an azo dye of reactive class that is extensively used by the textile industry. The effect of pH of the dispersion on the adsorption of the reactive dye on the TiO<sub>2</sub> surface and consequently on the degradation rate was examined to determine whether the degradation occurs on the TiO<sub>2</sub> surface or in bulk solution.

## 2. Experimental details

### 2.1. Materials

The anatase form of titanium dioxide (Degussa P25), with a particle size of 30 nm and a surface area of 50 m<sup>2</sup> g<sup>-1</sup>,

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according to the manufacturer's specifications, without further treatment in all experiments. Safira dye HEXL, an anionic azo dye from reactive class, was obtained from Dystar and used as such without further purification. Hydrogen peroxide (30%, w/w) was obtained from Nuclear. All reagents were of analytical purity.

## 2.2. Device

Irradiations were carried out using an 80, 125 or 150 W medium pressure mercury lamp without the glass cover, in an immersion well photochemical reactor. The pH of the solution was adjusted using dilute hydrochloric acid and sodium hydroxide solutions. Hydrochloric acid was chosen because its effect on the adsorption surface properties of the  $\text{TiO}_2$  is negligible [18].

The solution inside the photoreactor was continuously agitated by a mechanical stirrer. A constant-temperature water bath was connected to the reactor and the thermostat was set to 25 °C. The experimental apparatus is shown in Fig. 1.

Analytical control samples were taken at convenient times and filtered by a 0.22  $\mu\text{m}$  membrane filter. The filtered liquid was then analysed by a UV–Vis spectrophotometer (Hach) to measure the concentration of dye in the suspension.

Total UV incident radiation flux was determined by potassium ferrioxalate actinometry [19]. The actinometer was irradiated under conditions similar to those of the photoreaction used.

## 2.3. Adsorption tests

The adsorption tests were performed using aqueous solutions of dye at different pH values. The 200 ml aqueous solutions at different dye concentrations were put in contact with 1.0 g of  $\text{TiO}_2$  for 4 h, at 25 °C.

After, the solutions were centrifugated and filtered through a 0.22  $\mu\text{m}$  membrane filter and the remnant dye concentration was measured by a UV–Vis spectrophotome-

ter. The amount of dye adsorbed was determined by mass balance.

## 3. Results and discussion

### 3.1. Equilibrium of adsorption in dark conditions

Previous tests showed that there was no observable loss of dye when the irradiation was carried out in the absence of  $\text{TiO}_2$ . It is likely that sorption of the dye is an important parameter in determining photocatalytic degradation rates. The adsorbed dye on the surface of the semiconductor particles acts as an electron donor, injecting electrons from its excited state to the conduction band of the semiconductor under UV irradiation.

Adsorption tests in dark conditions were carried out in order to evaluate the equilibrium constants of the adsorption of dye on the  $\text{TiO}_2$  surface at different pH (Fig. 2). All isotherms showed a type of L-shape according to the classification of Giles et al. [20]. The L-shape of the isotherms means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites.

The experimental data was fitted to the Langmuir equation (Eq. (1)) to describe the adsorption of dye on the homogeneous surface of  $\text{TiO}_2$ :

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where  $q_m$  is the maximum amount of dye adsorbed forming a complete monolayer,  $b$  the equilibrium parameter,  $C_e$  the concentration of dye in aqueous solution, and  $q_e$  the concentration of dye in the solid. The Langmuir equilibrium constants ( $K_a = q_m b$ ) are shown in Table 1 and are discussed in Section 3.5.

The point of zero charge (pzc) of the  $\text{TiO}_2$  is at pH 6.8 [6]. The  $\text{TiO}_2$  surface is positively charged in acid media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8).

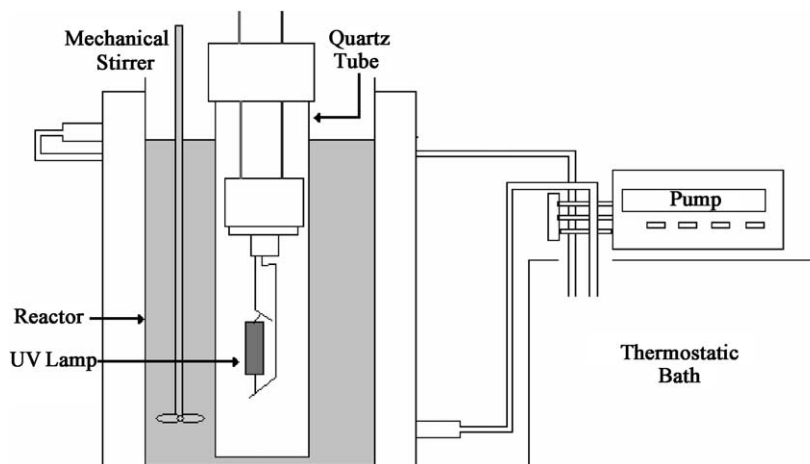


Fig. 1. Photocatalytic reactor scheme.

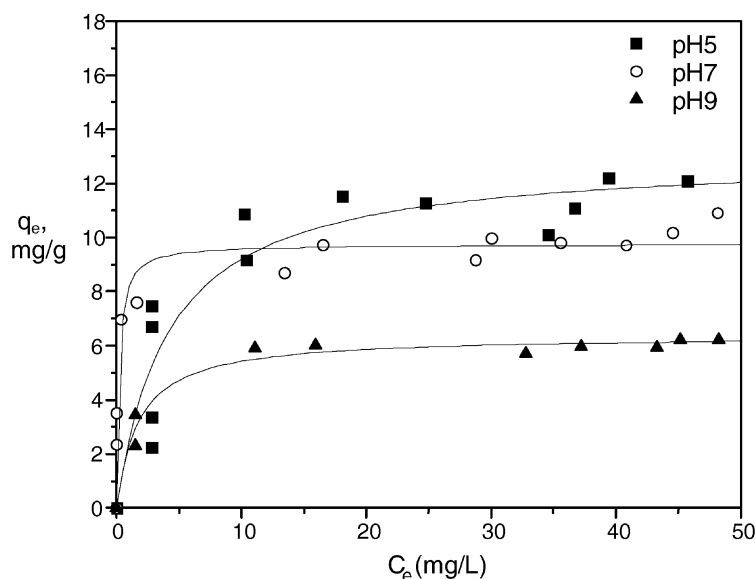


Fig. 2. Adsorption isotherms of dye on  $\text{TiO}_2$  surface at different pH: points, experimental data; line, Langmuir isotherm model.

It may be observed (Table 1) that the adsorption of safira dye is favoured at pH near the pzc of  $\text{TiO}_2$ . The suitable charge distribution on  $\text{TiO}_2$  could explain the effect of pH on the adsorption. At  $\text{pH} > 6.8$ , as the solid surface is negatively charged, the anionic safira dye is repulsed and so it is scarcely adsorbed.

### 3.2. Decolourization analysis

Fig. 3 shows a typical time-dependent UV–Vis spectrum of safira dye solution during photoirradiation. The absorption peaks corresponding to the dye diminished and finally disappear under reaction, indicating the degradation of the dye. No new absorption bands appear in either the visible or ultraviolet regions, especially absorption bands of aromatic moieties and other similar intermediates.

### 3.3. Effect of catalyst concentration

Experiments performed with different concentrations of catalyst (Table 2) showed that the rate increased with an increase in the amount of catalyst and that it remained almost constant above a certain level.

As the concentration of catalyst is increased, the number of photons absorbed and the number of dye molecules

adsorbed are increased owing to an increase in the number of  $\text{TiO}_2$  particles. The density of particles in the area of illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of  $\text{TiO}_2$  particles. Hence the additional catalyst powder is not involved in the catalyst's activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit. The aggregation of  $\text{TiO}_2$  particles at high concentrations must also be considered, which causes a decrease in the number of surface active sites.

Galindo et al. [1] reported an empirical relationship between the initial decolourization rate and  $\text{TiO}_2$  concentration,  $r_0 \propto [\text{TiO}_2]^n [\text{dye}]$ , where  $n$  is an exponent less than 1 for all the dyes studied, in relation to low concentration of  $\text{TiO}_2$ . In this work, the dependence of the  $\text{TiO}_2$  concentration on the initial decolourization rate follows a similar relationship ( $r_0 \propto [\text{TiO}_2]^{0.93}$ ), when the  $\text{TiO}_2$  concentration is less than 1 g/l (Fig. 4).

### 3.4. Effect of initial dye concentration

The kinetics of disappearance of Safira dye is represented in Fig. 5. It is evident that the photodegradation rate depends on the initial concentration of the dye. Since the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. High dye concentrations logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolourization rate.

According to a great number of researchers [1,14,21,22], the influence of the initial concentration of the solute on the photocatalytic degradation rate of most organic compounds

Table 1  
Langmuir equilibrium constants for the adsorption of safira dye on  $\text{TiO}_2$

pH	$K_a$ (g/l)
5.0	2.94
7.0	38.51
9.0	2.33
11.0	None

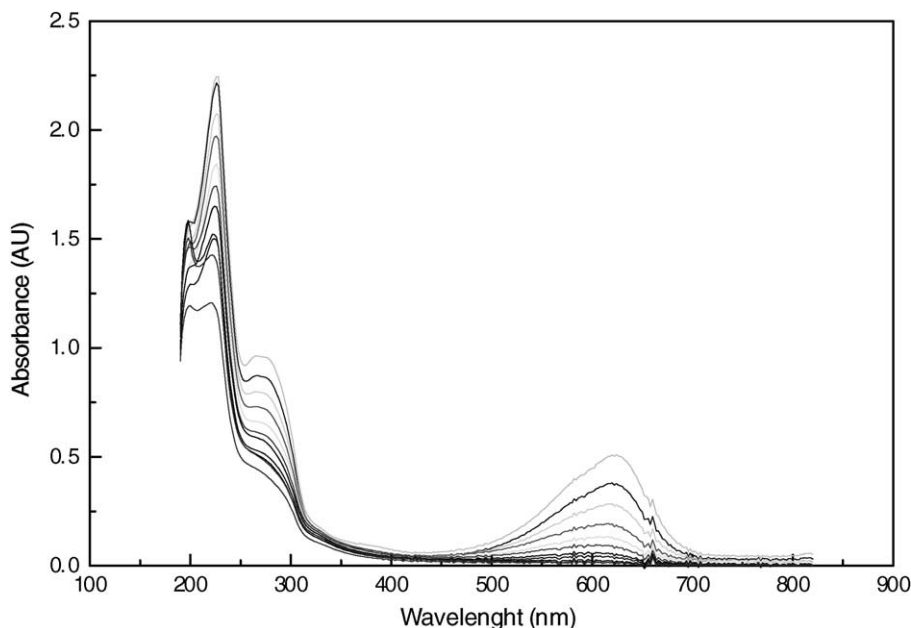


Fig. 3. Spectral changes that occur during photocatalytic degradation of aqueous solution of safira dye after time interval of 10 min; pH = 5.8; [TiO<sub>2</sub>] = 1.0 g/l; C<sub>0</sub> = 50 ppm.

Table 2

Effect of TiO<sub>2</sub> load on the decolourization rate during the photocatalytic oxidation (C<sub>0</sub> = 50 ppm; pH = 7.0)

[TiO <sub>2</sub> ] (g/l)	r <sub>0</sub> (mg/lmin)
0.1	0.99
0.3	1.92
0.5	2.96
1.0	9.33
1.5	8.05
2.0	8.00

is described by a pseudo-first-order kinetics, which is rationalized in terms of the Langmuir–Hinshelwood model (Eq. (2)), modified to accommodate reactions occurring at a

solid–liquid interface [6]. A linear expression can be conveniently obtained by plotting the reciprocal initial rate against the reciprocal initial concentration (Fig. 6):

$$r_0 = -\frac{dC}{dt} = \frac{k_v K_e C_0}{1 + K_e C_0} \quad (2)$$

where  $k_v$  reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions.  $K_e$  represents the equilibrium constant for adsorption of dye on to illuminated TiO<sub>2</sub>, and according to Cassano et al. [23], can incorporate other kinetic constants. In Eq. (2),  $k_v$  represents the apparent rate constant because it is also dependent on the source UV light and the radiation field inside a photocatalytic reactor [24].

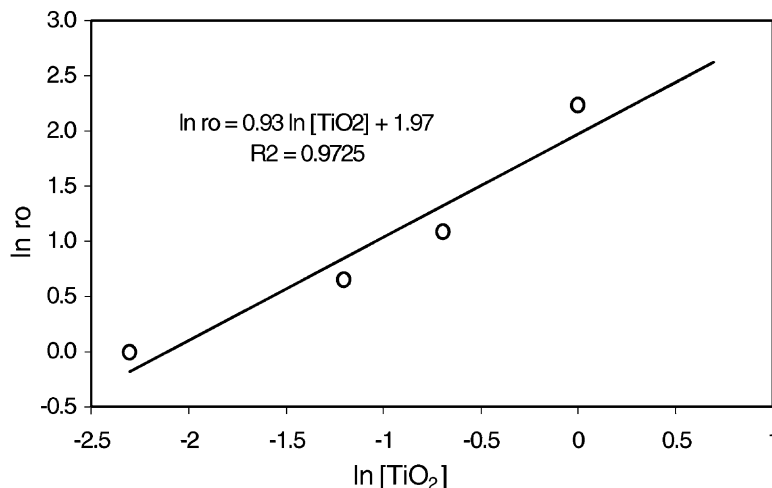


Fig. 4. Relationship between  $\ln r_0$  and the amount of TiO<sub>2</sub>; pH = 7.0; C<sub>0</sub> = 50 ppm.

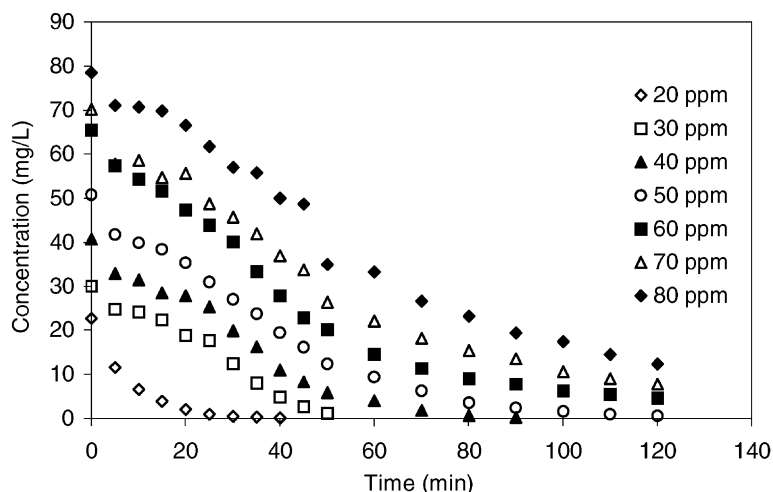


Fig. 5. Kinetics of decolourization at different initial concentrations:  $[\text{TiO}_2] = 1 \text{ g/l}$ ;  $\text{pH} = 7.0$ .

### 3.5. Effect of pH

The pH is a complex parameter since it is related to the ionization state of the surface (Eqs. (3) and (4)) as well as to that of reactants and products such as acids and amines:



Three possible reaction mechanisms can contribute to dye degradation: hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band, depending on the nature of the substrate and pH [25].

The safira dye is an anionic dye in aqueous solution whose optical spectrum remains invariant in the pH range 5–11. In our experiments, any changes in the initial degradation rate with varying pH values must be ascribed to variations of the acid/base properties of the  $\text{TiO}_2$  particle surface.

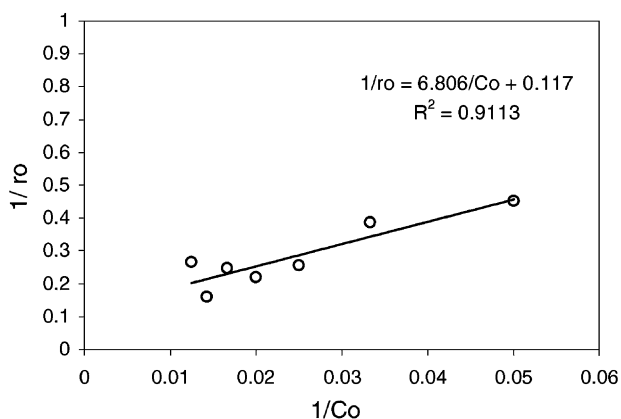


Fig. 6. Representation of Langmuir-Hinshelwood equation:  $\text{pH} = 7.0$ ;  $[\text{TiO}_2] = 1.0 \text{ g/l}$ .

Since the photooxidation of dyes is accompanied by the release of protons [6], its efficiency may then change because of the reversible protonation of the  $\text{TiO}_2$  surface. In Fig. 7, the initial reaction rate values of the photodegradation of S-dye are given in the pH range 5–11, at different initial concentrations.

Photocatalytic activity reached a maximum in acidic conditions, followed by a decrease of  $r_0$  in the pH range 7–11. This behaviour is characteristic for many photocatalytic systems and similar results have been obtained by the photodegradation of other dyes [6].

The effect of pH on the photocatalytic reaction can be largely explained by the surface charge of  $\text{TiO}_2$  ( $\text{pzc}$  of  $\text{TiO}_2 \approx 6.8$ ) and its relation to the acid dissociation

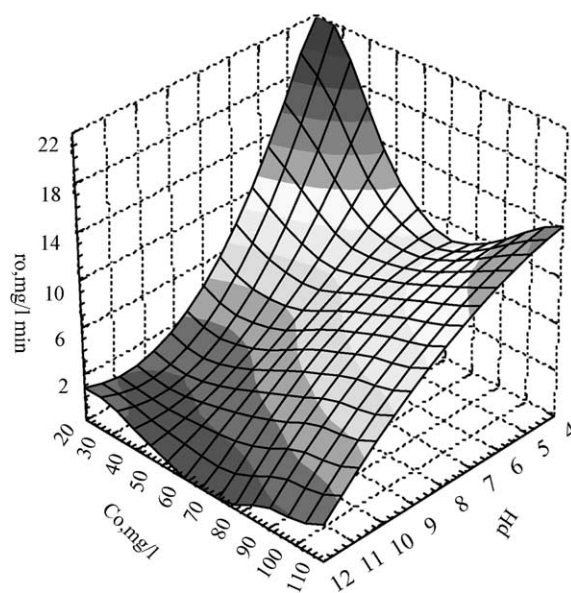


Fig. 7. Effect of pH on the initial rate of photocatalytic degradation of safira dye:  $[\text{TiO}_2] = 1.0 \text{ g/l}$ ;  $C_0$ , ppm and  $r_0$ ,  $\text{mg/l min}$ .

Table 3  
Langmuir–Hinshelwood constants for the photodegradation of S-dye at different pH values

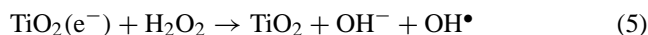
pH	$K_e$ (l/mg)	$k_v$ (min <sup>-1</sup> )
5.0	0.0158	14.36
7.0	0.0035	38.31
9.0	~0	27.23
11.0	0.0020	9.27

constants of S-dye. Below pH 6, while pH decreases, a strong adsorption of the dye on to the TiO<sub>2</sub> particles as a result of the electrostatic attraction of the positively charged TiO<sub>2</sub> with the ionized S-dye is observed. This can also be seen with the naked eye, while the catalyst turns blue. On the other hand, above pH 6 a decrease in the reaction rate has been observed, with a minimum at pH 11, reflecting the difficulty of anionic dye in approaching the negatively charged TiO<sub>2</sub> surface when increasing the solution pH. These results are reflected by the  $k_v$  and  $K_e$  values of the Langmuir–Hinshelwood equation (Eq. (1)) shown in Table 3.

It is worth noting that the adsorption constant  $K_a$  (Table 1) obtained from the dark adsorption isotherm is significantly different to the  $K_e$  determined from the L–H equation (Table 3) in the photocatalytic process. Similar results have been reported by other researchers [7,26,27]. Zhang et al. [7] showed that the adsorption constant for eosin in the dark is about 14 times less than that in TiO<sub>2</sub>-assisted photodegradation under UV irradiation. The photoadsorption and the fast photoreaction of substrate on the TiO<sub>2</sub> surface make the observed  $K_e$  under irradiation conditions different from that ( $K_a$ ) in the dark. Chen et al. [12] has demonstrated that the  $K_e$  from Eq. (1) is an apparent constant that also incorporates other kinetic constants.

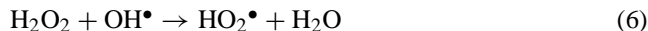
### 3.6. Effect of H<sub>2</sub>O<sub>2</sub>

The addition of hydrogen peroxide to the heterogeneous system increases the concentration of OH•, since it inhibits the electron–hole recombination, according to the following equation:



Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation [6]. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation, and it also forms OH•, according to Eq. (5).

The addition of H<sub>2</sub>O<sub>2</sub> is known to increase the rate of photocatalytic degradation by allowing an enhancement in the quantum yield of formation of hydroxyl radical [11,28]. Consequently, the degradation rate is expected to be enhanced. But at high dosage, H<sub>2</sub>O<sub>2</sub> is a powerful OH• scavenger [1,6] (Eqs. (6) and (7)):



However, we can observe in Fig. 8 that at pH 5.0 and 7.0 the rate goes through a maximum when increasing the concentration of the hydrogen peroxide. This effect has been reported due to the competition for adsorption between the dye and the hydrogen peroxide [11]. The increase in the concentration of H<sub>2</sub>O<sub>2</sub> above 0.2 g/l at pH 5 and 0.1 g/l at pH 7 could cause Eqs. (6) and (7) to become predominant.

### 3.7. Effect of light intensity

Three different lamps were used in this work: 80, 125 and 250 W. The total UV incident radiation flux was  $1.6 \times 10^{-4}$ ,  $1.6 \times 10^{-4}$  and  $2.3 \times 10^{-4}$ , respectively.

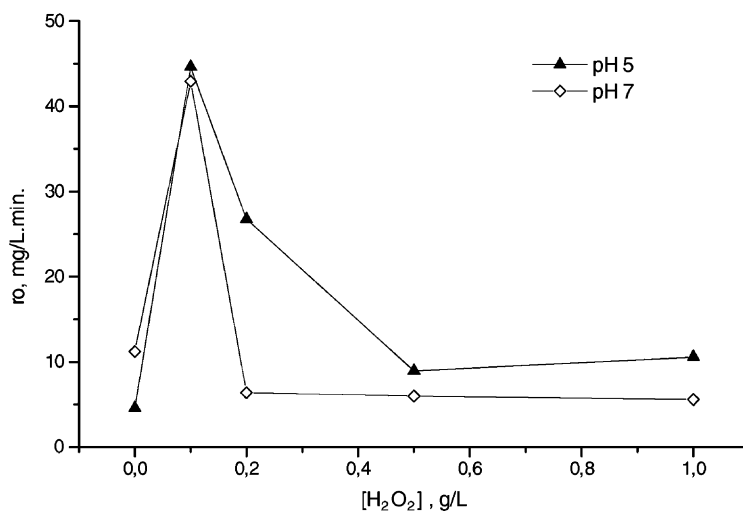


Fig. 8. Effect of H<sub>2</sub>O<sub>2</sub> concentration on the initial rate at pH 5 and 7: C<sub>0</sub> = 70 ppm; [TiO<sub>2</sub>] = 1.0 g/l.

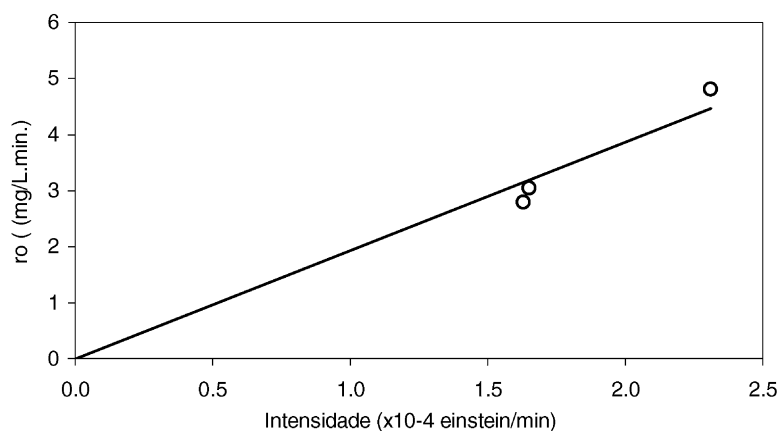


Fig. 9. Effect of light intensity on the rate of dye decolourization:  $C_0 = 70$  ppm; pH = 7.0;  $[\text{TiO}_2] = 1.0$  g/l.

Ollis et al. [29] reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalysis process and stated that at low light intensities, the rate would increase linearly with increasing light intensity, at intermediate light intensities the rate would depend on the square root of the light intensity, and at high light intensities the rate is independent of light intensity. Several studies [29–31] have attributed this variation to the recombination of photo-generated electron–hole pairs at high light intensity. This is detrimental to the photocatalytic process as the quantum efficiency decreases. In this work, the enhancement of the rate of decolourization as the light intensity increased (Fig. 9) was also observed.

To compare process and efficiencies in heterogeneous photocatalysis, the relative photonic efficiency ( $\zeta_r$ ) can be used (Eq. (8)) [32]:

$$\zeta_r = \frac{\text{rate of disappearance of dye}}{\text{rate of disappearance of phenol}} \quad (8)$$

where both (initial) rates are obtained under exactly the same conditions.

Ideally,  $\zeta_r$  values should not depend on light intensity or reactor geometry, or on other parameters such as pH, photocatalyst concentration, substrate concentration or temperature [32]. The parameters that can influence  $\zeta_r$  are those that may have an effect on the adsorption–desorption properties of the substrate on  $\text{TiO}_2$  (such as concentration of the organic substrate, pH and temperature). Also, since the kinetics ( $r = f(C)$ ) of dye photodegradation follows a Langmuir–Hinshelwood mechanism, with a linear increase of  $r$  at low concentrations, this catalytic quantum yield could be consequently higher for higher concentrations [33].

The photodegradation of phenol using an identical reactor was studied by Cesconeto [34], using identical experimental conditions to those used in this work. The relative photonic efficiency of the dye degradation is reported in Table 4. All the efficiencies are greater than unity, indicating that the initial photocatalysed oxidative degradation of the dye is more efficient than for phenol. As expected, the  $\zeta_r$  data

Table 4  
Relative photonic efficiencies for the dye photodegradation under various conditions (relative to phenol)

pH	Light intensity (einstein/min)	$[\text{TiO}_2]$ (g/l)	$C_0$ (ppm)	Relative photonic efficiency
5	$1.6 \times 10^{-4}$	1.0	30	41.88
			50	20.05
			70	8.52
7	$1.6 \times 10^{-4}$	1.0	50	5.40
			0.1	8.12
			0.3	13.37
			0.5	9.38
			1.0	13.49
			20	6.98
			30	8.26
9	$2.31 \times 10^{-4}$	1.0	40	7.41
			50	16.41
			60	33.04
			70	31.90
			50	7.83
			70	5.15
			70	1.96
11	$1.6 \times 10^{-4}$	1.0	30	12.29
			50	4.63
			70	7.97

shows a strong dependence on the pH and the light intensity and varies in the range 2–42.

#### 4. Conclusions

Safira dye, an anionic azo dye of reactive class, is easily degraded by a  $\text{TiO}_2$ -assisted method in aqueous dispersions under irradiation by UV light. The adsorption of dye is a prerequisite for the degradation. Both adsorption and photodegradation occur more extensively when the pH is near the pzc. The photodegradation kinetics follows a Langmuir–Hinshelwood model and depends on the  $\text{TiO}_2$  concentration, pH, UV light intensity and hydrogen peroxide concentration. The decolourization rate goes through

a maximum when increasing the concentration of the hydrogen peroxide. This effect could be ascribed to the competition for adsorption between the dye and the hydrogen peroxide.

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