Ashdin Publishing
Journal of Advanced Chemical Engineering
Vol. 1 (2011), Article ID A110301, 8 pages
doi:10.4303/jace/A110301

*Research Article*

# Photocatalytic Degradation of Solophenyl Red 3 BL in an Aqueous Suspension of Titanium Dioxide

**A. Boukhennoufa,[1] M. Bouhelassa,[1] and A. Zoulalian[2]**

*[1] LIPE Laboratory, Department of Industrial Chemistry, Faculty of Engineering Sciences, University Mentouri Constantine, 25000 Constantine, Algeria*

*[2] Wood-Material Study and Research Laboratory (LERMAB), Faculty of Science, Henri Poincaré University, Nancy I, BP 70239, 54506 Vandoeuvre lès Nancy Cédex, France*

*Address correspondence to A. Zoulalian, andre.zoulalian@lermab.uhp-nancy.fr*

Received 8 March 2011; Revised 26 August 2011; Accepted 29 August 2011

**Abstract** The wastewater from the textile industry generates a serious problem for environment by the presence of compounds such as dyes, resistant to the natural and conventional treatment. In this work, the photocatalytic degradation of aqueous solution of an azo-dye as Solophenyl red 3 BL was investigated, using a semiconductor ($TiO_2$) and a UV lamp. The decolorization of dye aqueous solution was controlled by spectrophotometry. Photolysis is enhanced by the addition of $TiO_2$ particles. The degradation rate depends on the initial pH of the suspension and it goes through a minimum at neutral pH. For a fixed concentration of dye, degradation rate increases with the oxygen concentration and temperature. The influence of temperature on the rate constant corresponds to activation energy of $31.9$ kJ/mol. Intensity and geometry of UV radiation and the addition of hydrogen peroxide, are significant parameters whose influence is directly related to changes in the concentrations of $OH^\bullet$ and $O_2^{-\bullet}$ radicals.

**Keywords** azo-dye; solophenyl red 3 BL; photocatalytic degradation; titanium dioxide

## 1 Introduction

Dyes are usually resistant compounds that can be found in industrial wastewater, producing important environmental problems [4]. Different biological treatments [3] and traditional methods like ultrafiltration, extraction and carbon adsorption [19] have been applied to remove such compounds. A disadvantage of most of these processes is that they are non-destructive; they simply transfer the pollutant from one phase to another [24]. Over the past few years, several advanced oxidation processes (AOPs) have been proposed as alternative routes for water purification. Among them, oxidation via ozonation or hydrogen peroxide was one method [6, 14]. Nevertheless, the photocatalytic process seems to be the most successful one for water decontamination, since it involves very oxidizing species such as hydroxyl radicals [15, 16, 21, 26]. The photocatalytic degradation rate of different compounds depends on various parameters (concentration of semiconductor, initial concentration of the pollutant, initial pH, temperature, light intensity, addition of salts and oxidants, partial pressure of oxygen, etc.) [5, 13]. Since the azo-dyes are considered the most common dyes present in textile industry wastewater [20], we are interested, in this work, in the decolorization of an aqueous solution containing this type of dyes such as Solophenyl red 3 BL which was previously investigated [8, 9]. Effects of some parameters such as initial pH, temperature, light intensity and addition of $H_2O_2$ on the photodegradation of this direct dye were investigated.

A photocatalytic process is based on the action of light on the surface of a semiconductor, which causes a jump of electrons from the valence band to the conduction band (electronically) within the superficial atoms of semi driver. This process can be summarized, in brief, in three steps:

(1) the production of pairs of electron-positive holes: under the effect of UV irradiation, provided that the photon energy is greater than or equal to the difference in energy between the valence band and conduction band (band gap) [10], an electron can move from the valence band to a vacant orbital of the conduction band as follows:

$$TiO_2 + h\nu \longrightarrow e_{CB}^- + h_{VB}^+; \tag{1}$$

(2) the separation of electrons and holes: the lifetime of the pairs $(e_{CB}^-/h_{VB}^+)$ is a few nanoseconds and recombination is accompanied by heat:

$$e_{CB}^- + h_{VB}^+ \longrightarrow \text{heat}. \tag{2}$$

Recombination of electrons and holes is the main factor limiting the rate of oxidation of organic substrates [11]. The recombination should be avoided, for an efficient

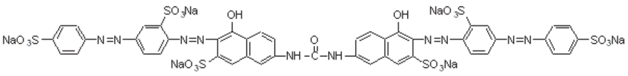


Figure 1: Chemical structure of Solophenyl red 3 BL.

photocatalyst. This is made possible by the transfer and trapping of free charges to intermediate energy levels (irregularities of structure or adsorbed molecules). For example, the electron trapping occurs at sites of defective $Ti^{3+}$ (instead of $Ti^{4+}$) or molecular oxygen adsorbed, forming superoxide radicals:

$$e_{CB}^{-} + O_2 \text{ (adsorbed)} \longrightarrow O_2^{-\bullet}, \quad (3)$$

(3) the oxidation and reduction: the charges created migrate to the surface of the catalyst and react with adsorbed substances likely to accept electrons (i.e. oxidizing) or give electrons (i.e. reducing). These are oxidation or reduction substances which are interesting for remediation.

Thus, in an aqueous medium, the hydroxyl groups OH, adsorbed on the surface of titanium, react and produce free radicals $OH^{\bullet}$. In fact, the main reactions are [27] as follows:

$$h_{VB}^{+} + H_2O \text{ (adsorbed)} \longrightarrow OH^{\bullet} + H^{+}, \quad (4)$$

$$h_{VB}^{+} + OH^{-} \text{ (surface)} \longrightarrow OH^{\bullet}. \quad (5)$$

In addition, hydrogen peroxide can be formed in the solution or at the solid-liquid interface [12, 18].

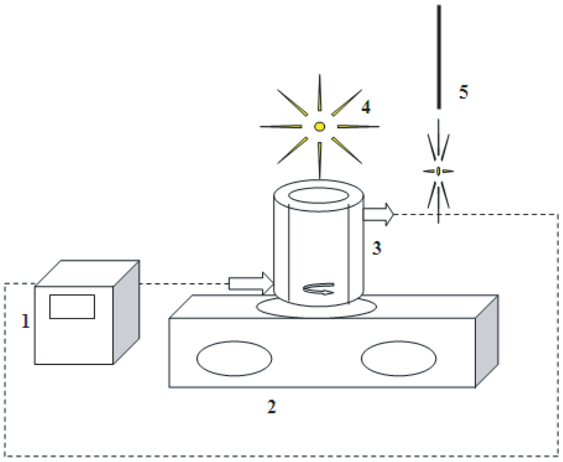
## 2 Materials and methods

### 2.1 Chemicals

The dye chosen as a model molecule in this work is a water soluble azo-dye: Solophenyl red 3 BL which is used without further purification (manufactured by COLOREY). Its chemical structure is presented in Figure 1. $TiO_2$ powder was supplied by Sigma and the manufacturer's values are minimum 99.0%, mainly the anatase form, and the density of the titania is $d = 3.9\ \text{g/cm}^3$.

### 2.2 Experimental device

All the experiments were performed in a batch photoreactor represented by a cylindrical Pyrex vessel with a double envelope and with respective values of diameter and height ($di = 5.4$ cm, $L = 12.8$ cm); see Figure 2. To maintain the temperature constant, water was flowing through the double envelope from a Lauda RC6 thermostatic bath. Bi-distilled water was used throughout the experiments. To verify the adsorption capacity of the azo dye on $TiO_2$ particles, samples were collected on an aqueous dispersion of particles of $TiO_2$ and dye, at regular time intervals.



1. Thermostatic bath. 2. Magnetic agitator. 3. Pyrex vessel.
4. Lamp wood (not immersed projection lamp). 5. Lamp HPK 125 (immersed lamp).

Figure 2: Experimental setup for photocatalytic process in the presence of two different lamps (used separately).

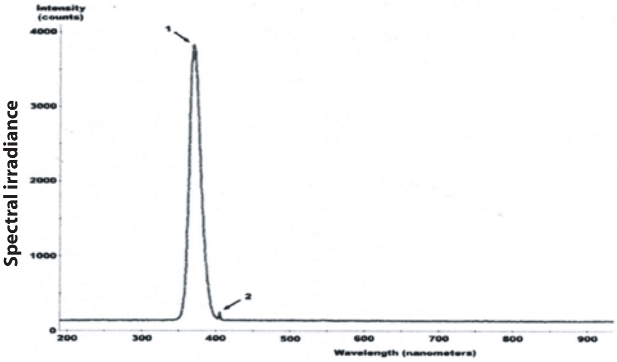


Figure 3: Relative spectral distribution, characteristic of light to lamp 1 (lamp wood).

In case of photolysis and photocatalysis processes, the aqueous dye solution (in the presence of $TiO_2$ in case of photocatalysis) was contained in the Pyrex vessel (200 mL) and was subjected to a magnetic stirring. Irradiation of this solution is made (separately) from two different monochromatic UV lamps: Lamp Wood (lamp 1: B-100AP, 100 W, type Spot, not immersed projection lamp, $\lambda_{\max} = 366$ nm) and Lamp HPK 125 (lamp 2: immersed lamp, $\lambda_{\max} = 366$ nm). Light spectra of the two lamps are shown in Figures 3 and 4, respectively. The distance between the free area of azo dye aqueous solution and the lamp 1 is 10 cm.

The data of luminous intensity of two lamps were obtained experimentally using the actinometry method. The principle of the actinometry is based on irradiation of a reference substance called chemical actinometer whose quantum yield is known and is constant in wavelength emitted by the lamp.

In this work, we used a complex mixture of a solution of oxalic acid ($5 \cdot 10^{-2}$ M) and a solution of uranyl sulfate

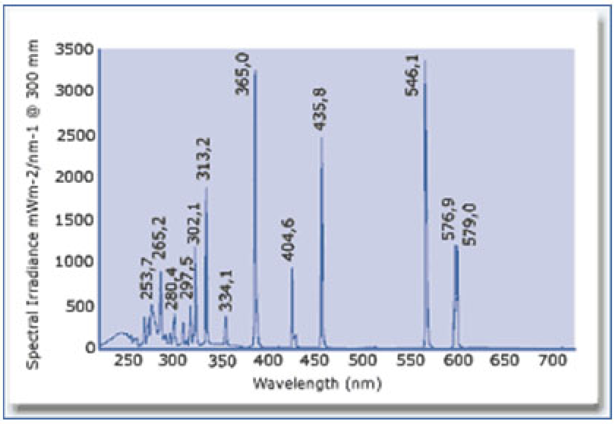


**Figure 4:** Relative spectral distribution, characteristic of light to lamp 2 (lamp HPK 125 Philips).

($10^{-2}$ M). This mixing leads to the formation of complexes of uranyl oxalate: $UO_2(C_2O_4)_2^{-2}$ and $UO_2C_2O_4$. The luminous intensity values found, respectively, for lamps 1 and 2 are $4.42 \cdot 10^{-9}$ and $7.30 \cdot 10^{-9}$ Einstein/s.

### 2.3 Experimental procedure

After 30 min of agitation (average speed) and adsorption of dye on $TiO_2$ particles, the suspension was sampled (3 mL) at regular intervals irradiation time and then filtered through a millipore membrane filter (pore size, 0.20 $\mu$m) to remove the residual powder of $TiO_2$. In different cases, the decolorization of solution was monitored by absorbance measurements at the wavelength of 531 nm by using a spectrophotometer (Shimadzu 160 A). All reagents were analytical grade. The pH has been changed by adding to the solution different amounts of $H_2SO_4$ or NaOH. The oxygen needed for the photoreaction is derived from the direct contact of the suspension with atmospheric air or by introducing the air or the oxygen through a tube in the Pyrex vessel.

## 3 Results and discussion

### 3.1 UV-visible spectra of solopheny red 3 BL solution

Figure 5 shows the electronic absorption spectra of Solophenyl red 3 BL in water (pH = 6.82). The UV-visible spectrum of Solophenyl red 3 BL dye ($C_0$ = 30 mg/L) consists of many absorption bands. It has been noticed that the absorption spectrum of Solophenyl red 3 BL is characterized by two bands in the visible region, with their maxima located at 531 nm and 380 nm, and by two bands in the ultraviolet region located at 220 nm and 280 nm. The absorbance bands in the visible region are due to the chromophore containing azo linkage. It seems that the less intense band centered around 380 nm is due to the partly forbidden $n \rightarrow \pi^*$ transition. The absorbance bands at 220 nm and 280 nm are due to the benzene and naphthalene rings of 3 BL, respectively, and are assigned to a $\pi \rightarrow \pi^*$ transition.

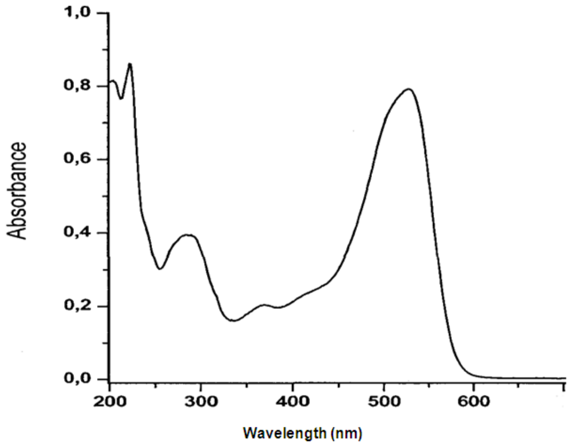


**Figure 5:** UV-visible absorption spectrum of Solophenyl red 3 BL in water ($C_0$ = 30 mg/L, optical path of cell ($l$ = 1 cm)).

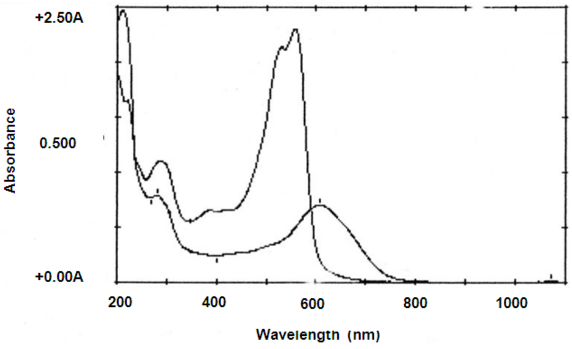


**Figure 6:** UV-visible absorption spectrum of both highly acidic solution (pH = 1) and strongly basic solution (pH = 14) of Solophenyl red 3 BL, in water ($C_0$ = 100 mg/L, optical path of cell ($l$ = 1 cm)).

The absorption spectra of Solophenyl red 3 BL were determined about highly acidic (pH = 1) and highly basic solutions (pH = 14); see Figure 6. At pH = 1, the solution changes color and takes on a dark blue one. However, the strongly basic solution takes on a dark purple color and shows a larger effect bathochrome and a very remarkable disappearance of the dye molecules. In the range of initial pH between 2 and 12, the appearance of absorption spectra remains similar to that obtained for the water solution (pH = 6.82).

### 3.2 Photocatalytic degradation

To examine the photodegradation feasibility of dye solution, experiments are carried out in the presence of UV lamp wood (lamp 1). Figure 7 displays the illumination of dye in three cases: adsorption, photolysis and photocatalysis. In

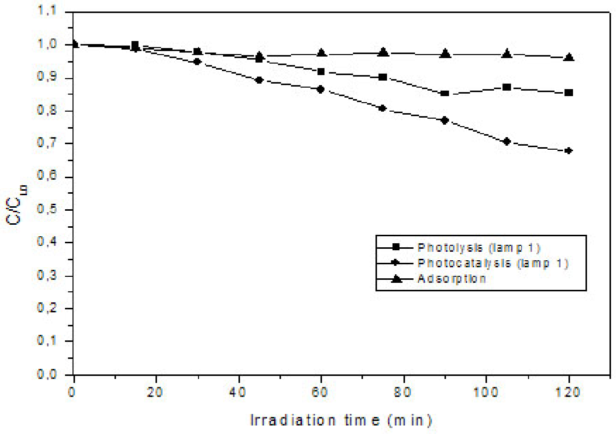


**Figure 7:** Temporal evolution of normalized residual concentration of Solophenyl red 3 BL, in the presence of lamp 1 ($C_0 = 100$ mg/L, $C_{TiO_2} = 1$ g/L, $T = 25$ °C, pH $= 6.82$, in the presence of atmospheric air with direct contact of the liquid surface).

case of the direct photolysis (in absence of semiconductor particles), a certain decolorization of the solution of the red solophenyl 3 BL was noted. The addition of a certain quantity of $TiO_2$ (1 g/L) in the irradiated medium clearly improved the rate of decolorization of the solution colored by the red Solophenyl 3 BL. The rate of decolorization increased from 14.7% to 32.2% at the end of 2 h.

The influence of adsorption of Solophenyl red 3 BL on $TiO_2$ particles is also examined in this study; an experiment was carried out in the same Pyrex vessel, under the same operating conditions, with absence of light. Figure 7 shows a negligible decrease of the residual dye concentration. The photocatalytic process improves the rate of decolorization of the azo-dye. This result is due to the increase of $OH^{\bullet}$ and $O_2^{-\bullet}$ radicals in the solution. Subsequently, we will examine various operating parameters for changing the concentrations of oxidizing free radicals.

### 3.3 Effect of pH

The photocatalytic degradation of the dye (100 mg/L) has been studied in the pH of 2–14 under UV irradiation (Lamp Wood) for 60 min with particles of $TiO_2$ (1 g/L). The result is depicted in Figure 8 and the observation indicates that there is a strong dependence between the pH of the solution and the heterogenous photon process. The pH of the solution is an important parameter in the photocatalytic reactions taking place on the surface of the $TiO_2$ particles as it revealed by the charge on the particles surface and the size of the aggregate it forms. In case of $TiO_2$, the zero point charge pH ($pH_{zpc}$) is at pH 6. Hence, at acidic pH values the particle surface is positively charged and at basic pH values it is negatively charged, as shown in Figure 9 [23].

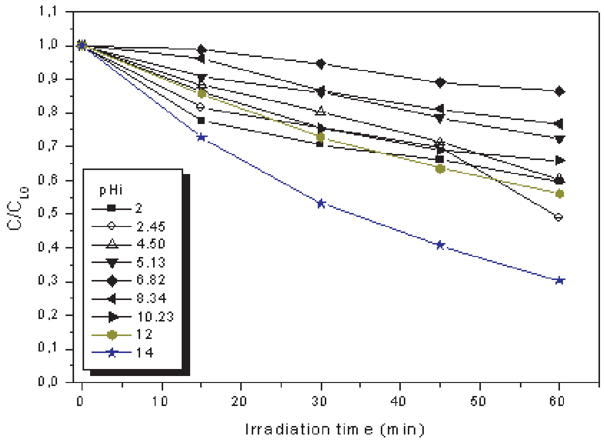


**Figure 8:** Temporal evolution of normalized residual concentration of dye for various initial pH (lamp 1, $C_0 = 100$ mg/L, $C_{TiO_2} = 1$ g/L, $T = 25$ °C, in the presence of atmospheric air with direct contact of the liquid surface).

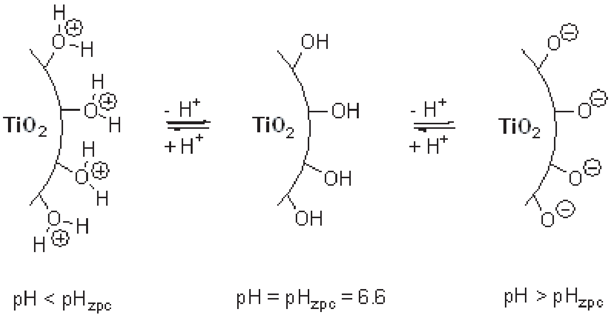


**Figure 9:** Changing the surface charge of $TiO_2$ as a function of pH.

The initial kinetic rate values of dye degradation obtained by performing photodegradation reactions under different initial pH are reported in Figure 10. These rate values indicate that the reaction rate is high at strong acidic pH for Solophenyl red (pH $=$ 2). The photoreactivity decreases with the increase of initial pH until pH $=$ 6.82 (natural pH). However, the kinetic rate values at pH $<$ 6.82 are lower for those corresponding to the runs carried out at the initial pH $>$ 6.82. A similar behavior was obtained in the study carried out by Augulgliaro et al. [1] on the degradation of a common azo-dye (orange II), in the presence of polycrystalline $TiO_2$ irradiated by sunlight. In the same way, Gouvêa et al. [7] noted the same effect of the pH on the degradation of a reactive dye (Remazol Brillant Blue R), in the presence of ZnO as a photocatalyst.

Although it is not easy to fully explain the behavior of the dye at various initial pH. Tang et al. [25] have noticed that the interpretation of pH effects on the efficiency of the photochemical process is a very difficult task, because three

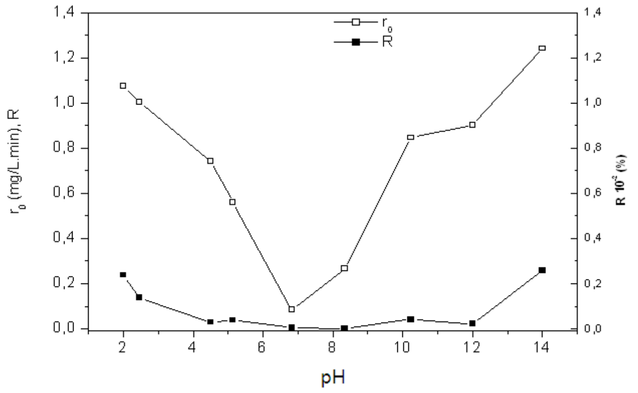


**Figure 10:** Effect of initial pH on the initial rate of decolorization of Solophenyl red 3 BL (lamp 1, $C_0 = 100$ mg/L, $C_{\text{TiO}_2} = 1$ g/L, $T = 25$ °C, in the presence of atmospheric air with direct contact of the liquid surface).

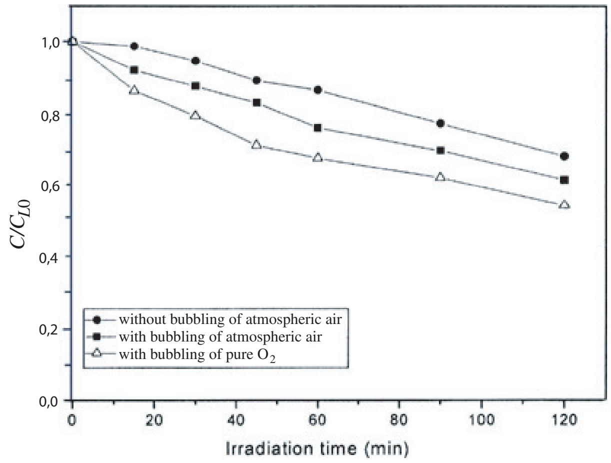


**Figure 11:** Temporal evolution of normalized residual concentration of dye for various dissolved concentrations of oxygen (lamp 1, $C_0 = 100$ mg/L, $C_{\text{TiO}_2} = 1$ g/L, $T = 25$ °C, pH = 6.82).

possible reaction mechanisms can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band. The importance of each one depends on the substrate nature and on the pH.

The significantly higher reaction rate found at pH = 2 corresponding to the substrates disappearance can suggest the occurrence of fast primary attacks by oxidant species to the dyes strongly, interacting with the positively charged catalyst surface. This is confirmed by a better dye adsorption onto the catalyst surface observed at pH = 2 (see Figure 10).

The adsorption ratio R is determined by expression (6):

$$\text{R}(\%) = \left(\frac{C_{L0} - C_{30}}{C_{L0}}\right) * 100, \tag{6}$$

where $C_{L0}$ and $C_{30}$ are the initial dye concentration and the dye concentration after 30 min of adsorption process (without irradiation).

Also, a significant enhancement on the decolorization process of Solophenyl red at pH between 6.82 and 14 has been observed. This behavior was probably due to the fact that the main reaction is represented by the hydroxyl radical attack, which can be highly fostered by the high concentration of adsorbed hydroxyl groups at high pH values. Consequently, the yield of photocatalytic degradation is mostly affected by the pH value.

### 3.4 Effect of oxygen

Experiments were carried out to determining the effect of the oxygen concentration in the liquid phase on the photodegradation process.

The decolorization was studied in three cases: the first case was performed in the presence of atmospheric air by direct contact of the liquid surface with the atmosphere; the second case by bubbling the atmospheric air through a tube that is introduced in the dye solution. The third case consists of bubbling the pure $O_2$. Figure 11 shows that the bubbling of dye solution by pure $O_2$ gives the best results and indicates that the oxygen concentration in the liquid phase is very important in the photodegradation process. In fact, the rate of production of $O_2^{-\bullet}$ radicals is favored.

### 3.5 Effect of temperature

Generally, the rates of photocatalytic reactions increase with increasing temperature [2]. In this work, we examine five values of temperature (15, 25, 35, 45 and 55 °C) under the same other operating conditions. The results of the reduced pollutant concentration versus irradiation time are shown in Figure 12. The results of the initial rate versus temperature are shown in Figure 13. These figures show that an increase of the temperature leads to an increase in the rate of photocatalytic degradation of Solophenyl red 3 BL, over the range 15 °C to 55 °C. Same, if the increase of temperature increases the desorption of physical and chemical adsorbates, the reactional steps are favored.

With the chosen operating conditions, the experimental values of the degradation of the dye show that there is a linear relationship between the natural logarithm of the $C_t/C_{L0}$ ratio and time (see Figure 14):

$$-\text{Ln}\,\frac{C_t}{C_{L0}} = kt, \tag{7}$$

where $C_t$ represents the concentration of the substrate in solution at time $t$ of illumination, $C_{L0}$ is the initial residual concentration (after adsorption) and $k$ represents the apparent rate constant ($\text{min}^{-1}$). The relationship (7) shows that the kinetic law of degradation of the dye is of first-order kinetics with respect to the concentration of the dye.

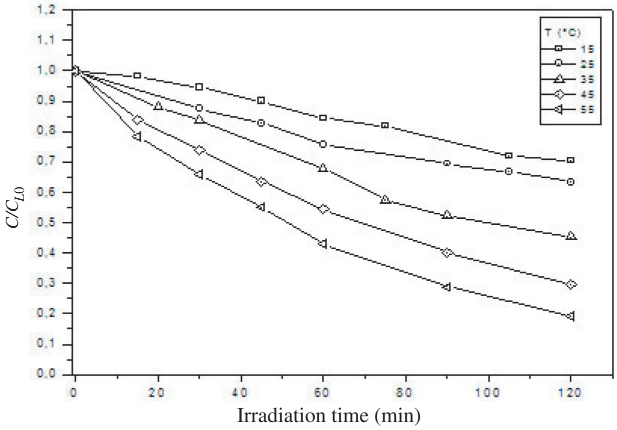


**Figure 12:** Temporal variation of normalized residual concentration of dye for various temperatures (lamp 1, $C_0 = 100\,\mathrm{mg/L}$, $C_{\mathrm{TiO_2}} = 1\,\mathrm{g/L}$, pH $= 6.82$, with continuous bubbling of atmospheric air).

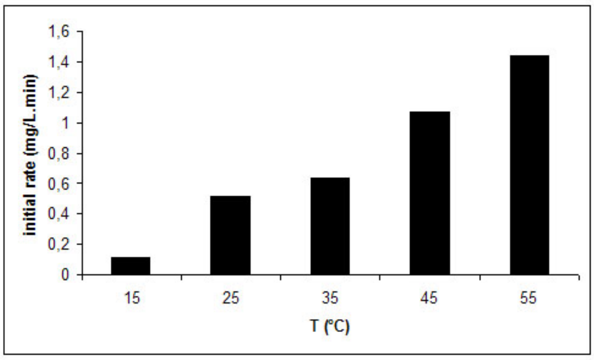


**Figure 13:** Variation of initial rate versus different temperatures (lamp 1, $C_0 = 100\,\mathrm{mg/L}$, $C_{\mathrm{TiO_2}} = 1\,\mathrm{g/L}$, pH $= 6.82$, with continuous bubbling of atmospheric air).

The rate constant $k$ increases with temperature. Let us assumes that this variation obeys the Arrhenius relationship:

$$k = k_0 \exp(-Ea/R\mathrm{T}), \tag{8}$$

where $k_0$ represents the pre-exponential factor, $Ea$ is the activation energy [J/mol], $R$ is the gas constant [J/mol.K], T is the temperature [K] and $k$ is the rate constant [M/s].

The value of the activation energy deduced from the curve $\ln(k)$ versus $1/\mathrm{T}$ (Figure 15) is estimated to $Ea = 31,90\,\mathrm{kJ/mol}$.

This value of the activation energy is higher than activation energies obtained under different illumination intensities; 13.6 kJ/mol was obtained by Bahnemann et al. [2] when illumination was carried out with $4.5\,\mu$E/s, and 18.8 kJ/mol for $1.5\,\mu$E/s.

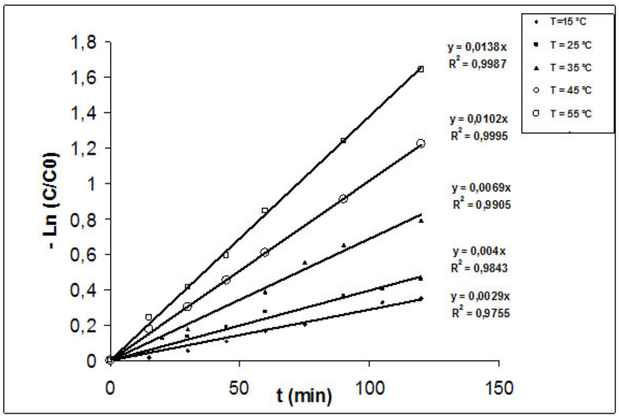


**Figure 14:** Variation of $-\,\mathrm{Ln}(C/C_0)$ versus irradiation time for different temperatures (lamp 1, $C_0 = 100\,\mathrm{mg/L}$, $C_{\mathrm{TiO_2}} = 1\,\mathrm{g/L}$, pH $= 6.82$, with continuous bubbling of atmospheric air).

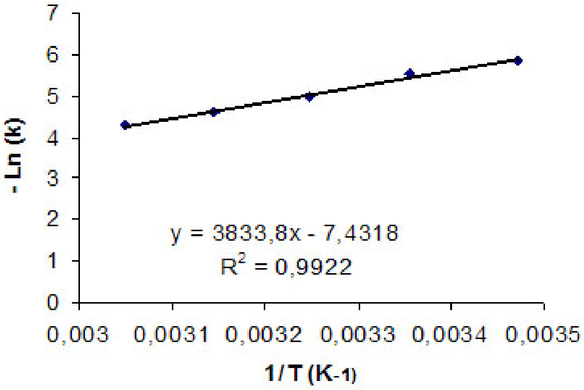


**Figure 15:** Variation of $-\,\mathrm{Ln}(k)$ versus inverse of temperature (lamp 1, $C_0 = 100\,\mathrm{mg/L}$, $C_{\mathrm{TiO_2}} = 1\,\mathrm{g/L}$, pH $= 6.82$).

### 3.6 Sensitive parameters for the growth of the degradation rate of the dye

#### *3.6.1 Effect of light intensity*

The influence of light intensity is determined by using two different lamps: the lamp 1 (Lamp Wood, B-100AP, 100 W, type Spot, projection lamp) set at the outside of the reactor and the lamp 2 (type HPK 125, 125 W) directly immerged in the liquid in the vessel with, respectively, the luminous intensity values of $4.42 \cdot 10^{-9}$ and $7.30 \cdot 10^{-9}$ Einstein/s.

Figure 16 shows that the efficiency of photocatalysis reaction increases with increasing the incident light intensity. The initial rate of photodegradation of Solophenyl red 3 BL goes from $0.521\,\mathrm{mg/L{\cdot}min}$ in case of the first lamp (lamp 1) to $2.566\,\mathrm{mg/L{\cdot}min}$ in case of the second lamp (lamp 2), while the rate of decolorization passes from 24% (lamp 1) to 83% (lamp 2), at the end of

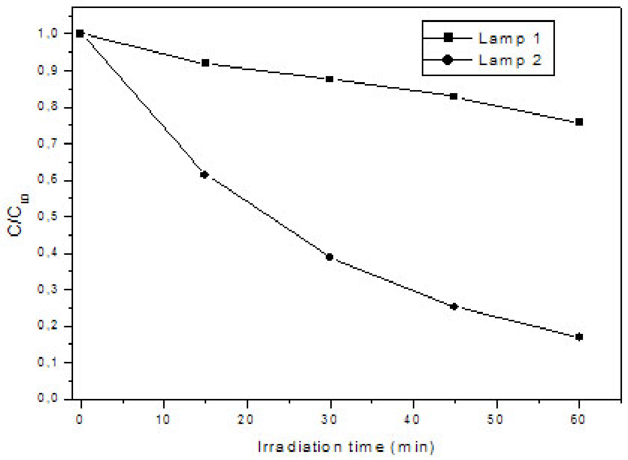


**Figure 16:** Temporal variation of normalized residual concentration for two different photoreactor systems, ($C_0 = 100\,\text{mg/L}$, $C_{\text{TiO}_2} = 1\,\text{g/L}$, $T = 25\,°\text{C}$, pH $= 6.83$, with continuous bubbling of atmospheric air).

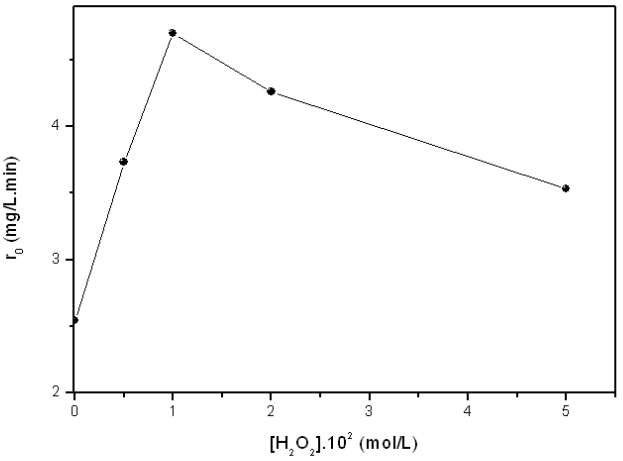


**Figure 17:** Effect of addition of $H_2O_2$ on the initial rate of decolorization of Solophenyl red 3 BL (lamp 2, $C_0 = 100\,\text{mg/L}$, $C_{\text{TiO}_2} = 1\,\text{g/L}$, $T = 25\,°\text{C}$, with continuous bubbling of atmospheric air).

60 min of photocatalytic process. The light intensity on the semiconductor is favorable for creating positive hole and electron (relation (1)).

Moreover, the great difference obtained between the two lamps shows that the photocatalytic process of Solophenyl red 3 BL is dependent not only by the luminous intensity but also by the geometry of optical field received by the dye solution.

### *3.6.2 Effect of the addition of $H_2O_2$*

Experiments were conducted to evaluate the effect of addition of $H_2O_2$ ($0.5 \cdot 10^{-2}$–$5 \cdot 10^{-2}$ mol/L) on the Solophenyl red photodegradation, in the presence of the HPK 125 lamp. The results are shown in Figure 17 and indicate that decolorization efficiency increases notably as the concentration of $H_2O_2$ increases and reaches an optimum at $10^{-2}$ mol/L. Several researchers have obtained the same results and have reported the beneficial effect of $H_2O_2$ on the photocatalytic degradation [17, 22]. The enhancement of decolorization by the addition of $H_2O_2$ is due to an increase in the hydroxyl radical concentration since it inhibits the $e^-_{\text{CB}}$, $h^+_{\text{BV}}$ recombination (relation (2)).

$H_2O_2$ is considered as having two functions in the photocatalytic degradation: it accepts a photogenerated conduction band electron that promotes the charge separation and it also forms $OH^\bullet$:

$$\text{TiO}_{2(e-)} + H_2O_2 \longrightarrow \text{TiO}_2 + OH^- + OH^\bullet. \tag{9}$$

$H_2O_2$ also reacts with superoxide anion to form OH radical:

$$H_2O_2 + O_2^{-\bullet} \longrightarrow OH^- + OH^\bullet + O_2. \tag{10}$$

At high concentration ($2.10^{-2}$ mol/L) of $H_2O_2$, the rate of decolorization decreases due to its hydroxyl radical scavenging effect. When the $H_2O_2$ concentration is higher, the formed $HO_2^\bullet$ is significantly less reactive than the formed $OH^\bullet$:

$$H_2O_2 + OH^\bullet \longrightarrow H_2O + HO_2^\bullet, \tag{11}$$

$$HO_2^\bullet + OH^\bullet \longrightarrow H_2O + O_2. \tag{12}$$

Ultimately, the addition of the hydrogen peroxide can be very favorable provided to adjust its concentration in the production of hydroxyl radicals relatively to $HO_2^\bullet$ radicals.

## 4 Conclusions

The study confirms that the degradation of Solophenyl red 3 BL dye can be achieved by photocatalysis in the presence of an aqueous suspension of anatase $\text{TiO}_2$. The degradation rate depends on the intensity of UV radiation; however, the influence of radiation is not limited to the intensity but also to the arrangement and geometry of the radiation to respect to the irradiated solution. The degradation rate increases with oxygen concentration (for $O_2^{-\bullet}$ radicals formation) and with temperature. The influence of temperature is noticeable between 15 °C and 55 °C. The rate of degradation can be significantly increased by adding in the middle of the hydrogen peroxide. However, the concentration of hydrogen peroxide should be optimized so as not to favoring the production of $HO_2^{-\bullet}$ radicals at the expense of $OH^\bullet$ radicals whose oxidative activity is higher than the previous. Finally, the degradation rate is favored in acidic medium, but in the case of industrial discharges, on the environmental plan, consideration should be given to the deterioration in the natural state, by varying the temperature level and addition of hydrogen peroxide to increase the kinetics of degradation of the dye.

## References

[1] V. Augugliaro, C. Baiocchi, A. B. Prevot, E. Garcia-Lopez, V. Loddo, S. Malato, et al., *Azo-dyes photocatalytic degradation in aqueous suspension of* $TiO_2$ *under solar irradiation*, Chemosphere, 49 (2002), 1223–1230.

[2] D. W. Bahnemann, D. Bockelmann, R. Goslich, M. Hilgendorff, and D. Weichgrebe, *Photocatalytic detoxification: Novel catalysts, mechanisms and solar applications*, in Photocatalytic Purification and Treatment of Water and Air, D. F. Ollis and H. Al-Ekabi, eds., vol. 3, Elsevier Science Publishers B.V., Amsterdam, 1993.

[3] I. M. Banat, P. Nigam, D. Singh, and R. Marchant, *Microbial decolorization of textile-dye-containing effluents: A review*, Biores Technol, 58 (1996), 217–227.

[4] A. Bianco Prevot, C. Baiocchi, M. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, et al., *Photocatalytic degradation of acid blue* 80 *in aqueous solutions containing* $TiO_2$ *suspensions*, Environ Sci Technol, 35 (2001), 971–976.

[5] L. Chen, *Effects of factors and interacted factors on the optimal decolorization process of methyl orange by ozone*, Water Res, 34 (2000), 974–982.

[6] P. Cooper, ed., *Color in Dyehouse Effluent*, Society of Dyers and Colourists, England, 1995.

[7] C. A. K. Gouvêa, F. Wypych, S. G. Moraes, N. Duran, N. Nagata, and P. Peralta-Zamora, *Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution*, Chemosphere, 40 (2000), 433–440.

[8] M. H. Habibi, A. Hassanzadeh, and S. Mahdavi, *The effect of operational parameters on the photocatalytic degradation of three textile azo dyes in aqueous* $TiO_2$ *suspensions*, J Photochem Photobiol A Chem, 172 (2005), 89–96.

[9] M. H. Habibi, A. Hassanzadeh, and A. Zeini-Isfahani, *Spectroscopic studies of solophenyl red 3BL polyazo dye tautomerism in different solvents using UV-visible,* $^1H$ *NMR and steady-state fluorescence techniques*, Dyes and Pigments, 69 (2006), 93–101.

[10] J.-M. Herrmann, *Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants*, Catal Today, 53 (1999), 115–129.

[11] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Environmental applications of semiconductor photocatalysis*, Chem Rev, 95 (1995), 69–96.

[12] Z. Hua, Z. Manping, X. Zongfeng, and G. K.-C. Low, *Titanium dioxide mediated photocatalytic degradation of monocrotophos*, Wat Res, 29 (1995), 2681–2688.

[13] F. Kiriakidou, D. I. Kondarides, and X. E. Verykios, *The effect of operational parameters and* $TiO_2$*-doping on the photocatalytic degradation of azo-dyes*, Catal Today, 54 (1999), 119–130.

[14] W. G. Kuo, *Decolorizing dye wastewater with Fenton's reagent*, Water Res, 26 (1992), 881–886.

[15] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, et al., *Photocatalytic degradation of various types of dyes (Alzarin S., Crocein Orange G., Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania*, Appl Catal B, 39 (2002), 75–90.

[16] R. W. Matthews, *Photocatalysis in water purification: Possibilities, problems and prospects*, in Photocatalysis Purification and Treatment of Water and Air, D. F. Ollis and H. Al-Ekabi, eds., Elsevier Science Publishers B.V., Amsterdam, 1993, 121–137.

[17] M. Muruganandham and M. Swaminathan, $TiO_2$*-UV photocatalytic oxidation of reactive yellow 14: Effect of orerational parameters*, J Hazardous Materials, 135 (2006), 78–86.

[18] D. F. Ollis, E. Pelizetti, and N. Serpone, *Photocatalyzed destruction of water contaminants*, Envir Sci Technol, 25 (1991), 1522–1529.

[19] A. S. Özcan, B. Erdem, and A. Özcan, *Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite*, J Colloid Interface Sci, 280 (2004), 44–54.

[20] C. Sahoo, A. K. Gupta, and A. Pal, *Photocatalytic degradation of Methyl Red in aqueous solutions under UV irradiation using* $Ag^+$ *doped* $TiO_2$, Desalination, 181 (2005), 91–100.

[21] M. Schiavello, *Heterogeneous photocatalysis*, in Photoscience and Photoengineering, vol. 3 of Wiley Series, John Wiley & Sons, Chichester, 1997.

[22] S. Senthilkumaar, K. Porkodi, and R. Vidyalakshmi, *Photodegradation of a textile dye catalysed by sol-gel derived nanocrystalline* $TiO_2$ *via ultrasonic irradiation*, J Photochem Photobiol A Chem, 170 (2005), 225–232.

[23] C. G. Silva, W. Wang, and J. L. Faria, *Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation*, J Photochem Photobiol A Chem, 181 (2006), 314–324.

[24] S. S. Tahir and N. Rauf, *Removal of a cationic dye from aqueous solutions by adsorption onto bentonic clay*, Chemosphere, 63 (2006), 1842–1848.

[25] W. Z. Tang, Z. Zhang, H. An, M. O. Quintama, and D. F. Torres, $TiO_2$*/UV photodegradation of azo dyes in aqueous solutions*, Environ Technol, 18 (1997), 1–12.

[26] P. C. Vandevivere, R. Bianchi, and W. Verstraete, *Review: Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies*, J Chem Technol Biotechnol, 72 (1998), 289–302.

[27] S. Wen, J. Zhao, G. Sheng, J. Fu, and P. Peng, *Photocatalytic reactions of phenanthrene at* $TiO_2$*/water interfaces*, Chemosphere, 46 (2002), 871–877.