

# A study of the photocatalytic degradation of the textile dye Reactive Yellow 17 in aqueous solution by TiO<sub>2</sub>-coated non-woven fibres in a batch photoreactor

S. Alahiane\*, A. Sennaoui, F. Sakr, S. Qourzal, M. Dinne, A. Assabbane

*Laboratory of Electrochemistry, Catalysis and Environment, Catalysis and Environment Team, Department of Chemistry, Faculty of Science, IbnZohr University, PO Box 8106 City Dakhla, Agadir, Morocco.*

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[alahiansaid@gmail.com](mailto:alahiansaid@gmail.com)

(+212) 5 28 22 09 54

## Abstract

In this work we are interested in the degradation of an azo dye RY17 by heterogeneous photocatalysis. We have studied in the first place, the adsorption of this dye on TiO<sub>2</sub>-coated non-woven fibres, in order to determine the optimal conditions for the degradation of the dye, the results show that the adsorption equilibrium is reached after 30 min of adsorption and that the Langmuir describes better the adsorption by report to the Freundlich isotherm. Then, we have discussed the influence of some experimental parameters such as the initial dye concentrations, the initial pH of aqueous solution and the addition of H<sub>2</sub>O<sub>2</sub> on the degradation of the solution studied.

## 1. Introduction

The azo dyes represent approximately 50-70% of the dyes available in the market. They can be divided into monoazo, diazo, triazo classes according to the presence of one or more azo bonds (–N=N–) and are found in various categories, i.e. acid, basic, direct, disperse, azoic and pigments [1, 2].

Several studies [3, 4] have shown the effects toxic and/or carcinogenic azo dyes. Furthermore, their non biodegradability is due to their high molecular weight and to their complex structure, thus, the azo dyes are reluctant to oxidative catabolism under aerobic environmental conditions, because of their electronic impairments, that is generated by the electro-attraction of azo groups. The presence of these dyes in drinking water with concentrations greater than 3.1 µg.L<sup>-1</sup>, generates health problems for the human being [5].

The various conventional processes, used for decontamination of these wastewater that is either of the processes physical, chemical and/or biological, present a major disadvantage in transforming the pollution of an aqueous phase toward a new phase, by the formation of concentrated sludge, thus creating a problem of secondary waste, or leading to a regeneration of materials, often very expensive.

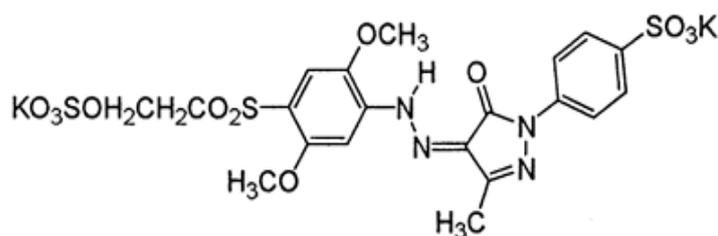
The most recent advances in the field of water treatment have been made in the oxidation of organic compounds "biologically recalcitrant" strongly present in the effluents of releases textiles. These methods rely on the formation of chemical entities very reactive which will decompose the more recalcitrant molecules into biologically degradable molecules or in mineral compounds such as CO<sub>2</sub> and H<sub>2</sub>O, these are the Advanced Oxidation Processes (AOPs). The heterogeneous photocatalysis is part of these processes, and offers the possibility of clean up but also to disinfect the waters and effluents closing this type of organic pollutants.

The objective of this study is to show the interest of heterogeneous photocatalysis on the degradation of textile dye. In this context, the study is focused on the oxidation of azo dye RY17 solution in view of the application to the cleanup of a real effluent from the textile industry. This dye has been chosen because of its high use in the industry of Moroccan textile. The effect of some experimental parameters (initial concentration of RY17, initial pH of the medium and addition of H<sub>2</sub>O<sub>2</sub>) on the kinetics of photodegradation was also studied.

## 2. Materials and methods

### 2.1. Reagents

The various reagents used in this study were used without prior purification. The Reactive Yellow 17 is an azo dye synthetic organic used in the textile industry, which is provided by the firm Sigma-Aldrich. Its chemical structure is represented in figure 1. The table 1 summarizes the main physico-chemical characteristics of the dye used in this work.



**Figure 1:** Chemical structure of RY17.

**Table 1:** Physico-chemical properties of the RY17 dye.

Dye	RY17
Family	reactivedye
Brute formula	$C_{20}H_{20}N_4O_{12}S_3 \cdot 2K$
Molecularweight (g/mol)	682.77
$\lambda_{max}$ (nm)	408
Origin	Sigma-Aldrich
Purity (%)	99.9

The immobilized photocatalyst used in this study is the Titanium dioxide PC500 of a brand Millennium inorganic chemicals S.A (anatase: >99%, specific surface area  $350 - 400 \text{ m}^2 \cdot \text{g}^{-1}$ , crystallites mean size = 5 - 10 nm). Titania PC500 was coated on non-woven fibers (natural and synthetic fibers  $254 \mu\text{m}$  of thickness) using an inorganic binder. The binder was an aqueous dispersion of colloidal  $\text{SiO}_2$ . A specific surface area extender (zeolite,  $2000 \text{ m}^2 \cdot \text{g}^{-1}$ ) was used to increase adsorption properties of the photocatalyst.

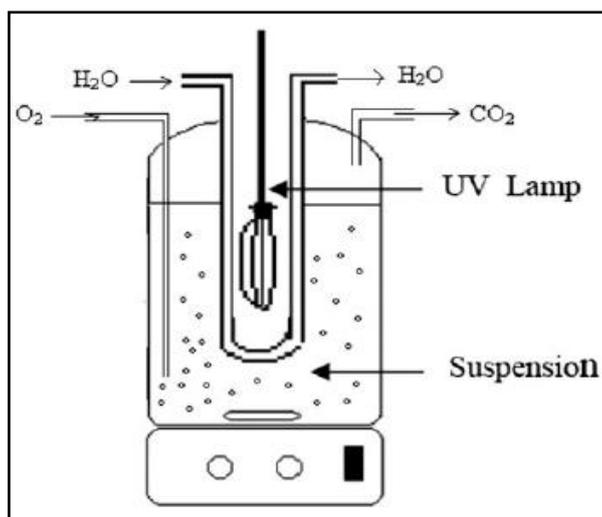
### 2.2. Instruments and experimental procedures

The adsorption experiments of RY17 on  $\text{TiO}_2$  surface were performed at different initial concentrations between  $5 \text{ mg} \cdot \text{L}^{-1}$  and  $40 \text{ mg} \cdot \text{L}^{-1}$ . The adsorbed quantity is calculated by measuring the concentration of the solution before and after adsorption using the following equation:

$$Q_e = \Delta C \cdot V / m$$

Where,  $Q_e$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the adsorbed quantity of RY17 per unit weight of the photocatalyst at adsorption equilibrium,  $\Delta C$  ( $\text{mg} \cdot \text{L}^{-1}$ ) is the difference between the initial concentration ( $C_0$ ) and the equilibrium concentration ( $C_e$ ),  $V$  (L) is the volume of solution and  $m$  (g) is the mass of the photocatalyst.

The photodegradation experiments were carried out by loading 500 ml of the dye solutions RY17 of known titre in the photoreactor (Figure 2) recovered inside by the photocatalytic  $\text{TiO}_2$ -coated non-woven fibres ( $11 \text{ cm} \times 25 \text{ cm}$ ) (equivalent to 1g of  $\text{TiO}_2$ ). The pH was adjusted to a given value in the range 3 – 11.5 by addition of  $\text{HNO}_3$  (1N) or  $\text{NaOH}$  (1N), which were obtained from Merck. The mixture is kept under constant magnetic stirring in the dark during an hour and a half, so that the RY17 adsorption equilibrium on the catalyst surface is established. Then, we expose the reaction mixture to UV radiation. Experiments were performed in room temperature.



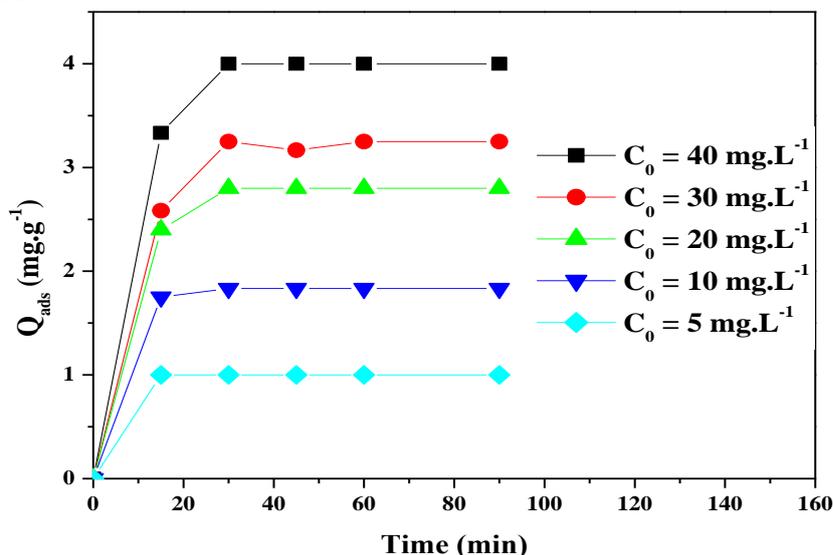
**Figure 2:** Schematic diagram of photoreactor.

The samples taken were filtered with cellulose filters having pore sizes equal to  $0.45\mu\text{m}$ . The remaining concentration of RY17 in the solution was measured using UV-Vis Spectrophotometer (Jasco V-630). The wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) is  $408\text{nm}$ . The calibration curve of the dye was carried out, with concentrations of RY17 varying from  $5$  to  $40\text{mg.L}^{-1}$ .

### 3. Results and discussion

#### 3.1. adsorption Study

The adsorption of the pollutant to the surface of the photocatalytic media is an important step in the process of photocatalytic degradation. In order to highlight the optimal conditions for the degradation of our dye, we first started by the study of its adsorption on the titanium dioxide coated media. The adsorption kinetics are shown in figure 3. The results show that the adsorbed quantity on the photocatalyst increases with increasing initial dye concentration (Table 2). This is due to the presence of a high number of molecules that will diffuse towards the sites of the  $\text{TiO}_2$  surface.



**Figure 3:** Adsorption kinetics of RY17.

The figure also shows that for the first 10 minutes, a rapid increase in the quantity of RY17 adsorbed in mg per g of  $\text{TiO}_2$ , up to reach a constant value after 30 minutes whatsoever the initial concentration. This contact time of 30 min is therefore the time of adsorption equilibrium. This can be explained by the formation of repulsive forces between the dye molecules on the catalyst surface in solution, which prevents the vacant surface sites on the surface from being occupied. On the other hand, the average size of

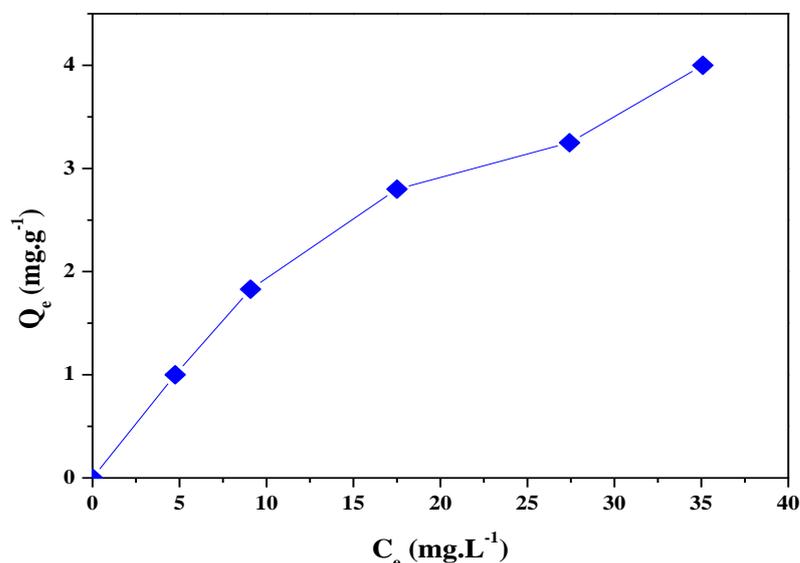
molecules of RY17 promotes a rapid and easy diffusion in the internal pores up to saturation, which leads to a reduction of the mass transfer between the liquid and solid phase with time and by the Following decrease in the adsorption rate. It's therefore necessary to leave the agitation of the mixture at least during this time before proceeding to the photodegradation.

**Table2:** Adsorbed quantity of RY17 on the TiO<sub>2</sub> at different initial dye concentration.

Initial concentration of RY17	5	10	20	30	40
Q <sub>max</sub> (mg <sub>RY17</sub> /g <sub>TiO2</sub> )	1	1.83	2.8	3.25	4

### 3.1.1. Adsorption Isotherms

The adsorption isotherm expresses the existing relationship at the adsorption equilibrium between the adsorbed quantity and the concentration of RY17 in a given solvent at a constant temperature. The adsorption experiments of RY17 on the TiO<sub>2</sub> surface were carried out at various initial concentrations (5, 10, 20, 30 and 40 mg.L<sup>-1</sup>) (Figure 4). The type of adsorption isotherm model is very important to understand the adsorption behavior of solid-liquid system [6]. In this study, the Langmuir and Freundlich models were tested to study the adsorption behavior of RY17.



**Figure 4:** Adsorption isotherm of RY17.

Several works [7, 8] have shown that the adsorption of many organic compound on TiO<sub>2</sub> is described by the Langmuir model whose expression is given below:

$$Q_e = Q_{\max} (K_{\text{ads}} C_e / (1 + K_{\text{ads}} C_e))$$

Where, Q<sub>max</sub>(mg.g<sup>-1</sup>) is the maximum adsorbed quantity and K<sub>ads</sub> is the equilibrium constant for adsorption.

The linear form of the Langmuir isotherm is given as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_{\max}} + \frac{1}{Q_{\max} K_L C_e}$$

The values of K<sub>L</sub>, Q<sub>max</sub> are calculated from the plot of figure 5, these kinetic constants of equilibrium adsorption are shown in table 3.

The adsorption isotherm of Freundlich is based on the following empirical equation:

$$Q = K_f C_e^{1/n_f}$$

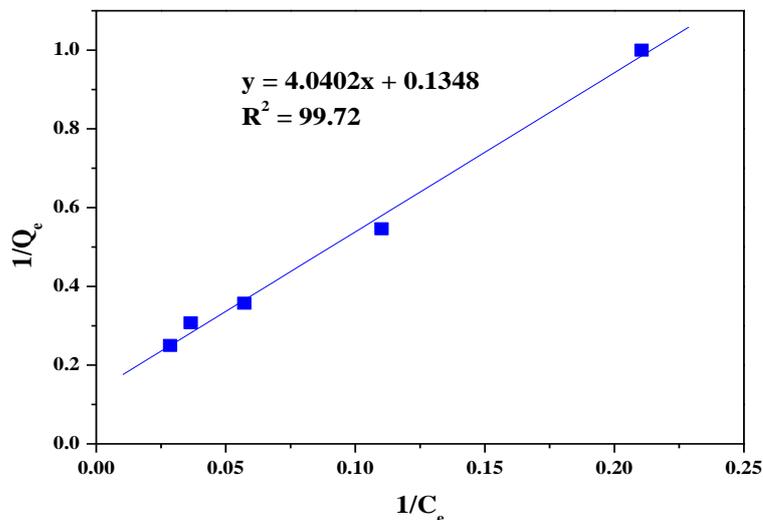
Where, K<sub>f</sub> and n are Freundlich constants

The transformed linear allow to verify the validity of this equation, obtained by passing in the logarithmic scale [9] :

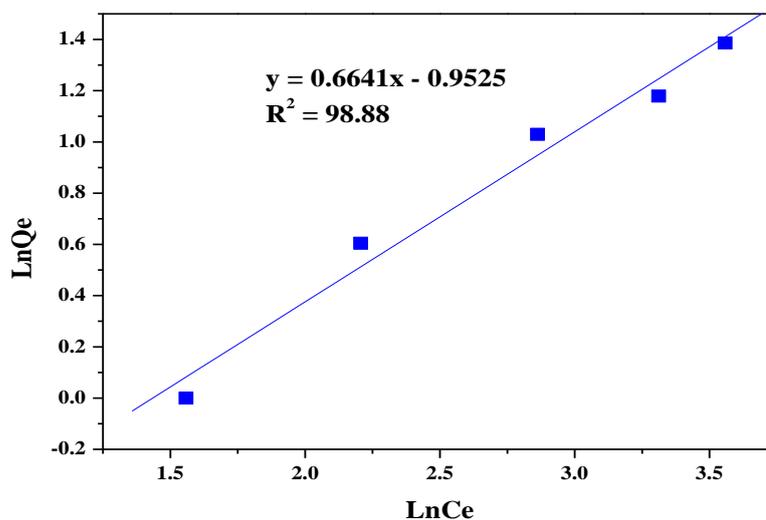
$$\ln Q_e = \ln K_f + 1/n_f \ln C_e$$

By plotting ln Q<sub>e</sub> versus ln C<sub>e</sub>, we obtain a straight line of slope 1/n<sub>f</sub> and the intercept ln K<sub>f</sub> (Figure 6).

According to the two straight lines obtained, the adsorption of RY17 on the TiO<sub>2</sub> in the absence of UV light obeys the Langmuir model under its linear form because it presents a correlation coefficient greater than the one obtained in the Freundlich model, which implies A monolayer adsorption model.



**Figure 5:** Linear transformation of the Langmuir isotherm.



**Figure 6:** Linear transformation of the Freundlich isotherm.

**Table 3:** Kinetic constants of Langmuir and Freundlich.

Isotherme	Langmuir Isotherm			Freundlich Isotherm		
Parameters	$Q_{\max}$ (mg.g <sup>-1</sup> )	$K_L$ (L.mg <sup>-1</sup> )	$R_L^2$	$K_f$ (mg.g <sup>-1</sup> )	$n_f$	$R_f^2$
	7.418	0.033	99.72	0.386	1.506	98.88

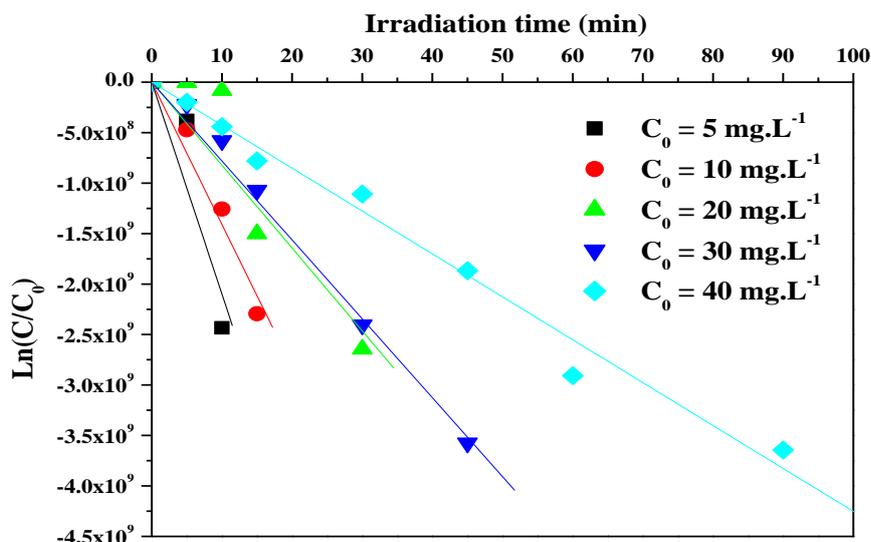
### 3.2. Degradation of RY17 by heterogeneous photocatalysis

#### 3.2.1. Effect of initial dye concentration

The concentration of pollutants is a very important parameter in the treatment, the effect of the initial concentration of RY17 on the photocatalytic degradation rate has been investigated at different initial concentrations of the dye ranging from 5 to 40 mg.L<sup>-1</sup>, and the experimental results are presented in figure 7. All the concentration profiles could be correlated by the following exponential function with good agreement:

$$C = C_0 \exp(-k_{app}.t)$$

With,  $C$  and  $C_0$  ( $\text{mg.L}^{-1}$ ) are the concentration at time  $t$  and initial time,  $K_{\text{app}}$  ( $\text{min}^{-1}$ ) is the apparent rate constant and  $t$  (min) is the illumination time.

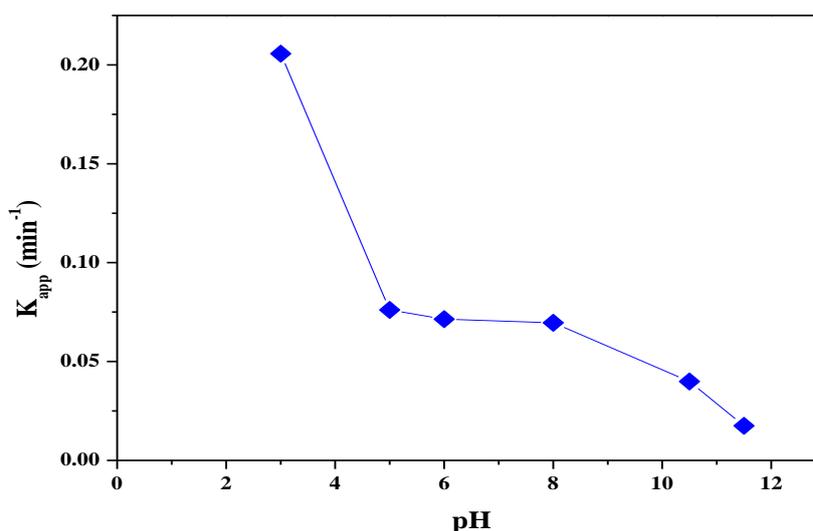


**Figure7:** Effect of initial RY17 concentration on the removal efficiency.  $[\text{TiO}_2] = 1\text{g.L}^{-1}$ ;  $\text{pH}_i = 5$  ;  $T = 22 \text{ }^\circ\text{C}$ .

The apparent rate constant  $k_{\text{app}}$  in above equation decreased with the increasing in the initial concentration of RY17 when other parameters are maintained unchanged. Therefore, the degradation rate was Pseudo-first-order by report to the concentration within the experimental range.

### 3.2.2. Effect of pH

All experiments were carried out in the natural pH of the solution of the dye RY17 which is 5. However, the effluents industrial real can cover a wide range of pH. To evaluate the degradation efficiency by  $\text{TiO}_2$  supported, solutions of several values of pH (3, 5, 6, 8, 10.5 and 11.5) have been studied. The relationship between the apparent rate constant and pH is shown in figure 8.



**Figure 8:** Effect of pH on the photodegradation of RY17.  $[\text{RY17}]_0 = 30 \text{ mg.L}^{-1}$ ;  $[\text{TiO}_2] = 1\text{g.L}^{-1}$ ;  $T = 22^\circ\text{C}$ .

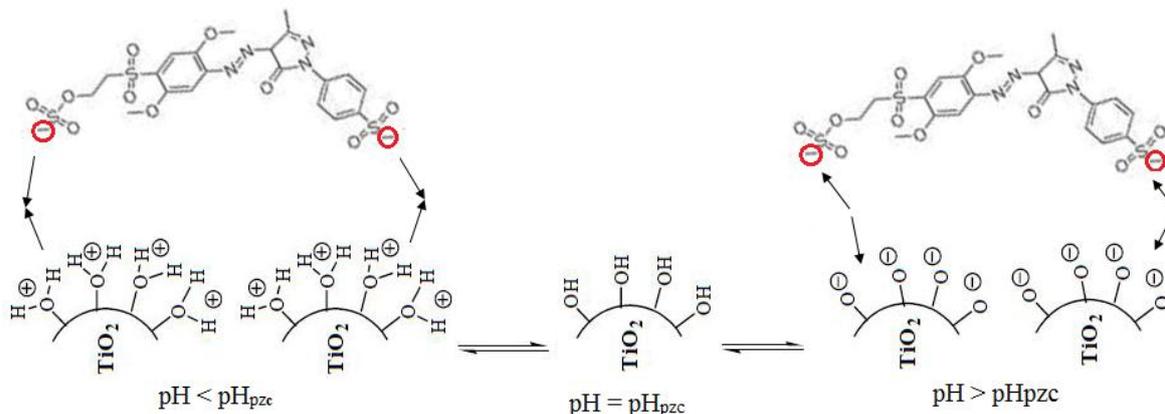
It is clearly seen that the apparent rate constants decreases when pH values increase in order: (pH)  $3 > 5 > 6 > 8 > 10 > 11$ .

It is known that the metal oxide particles in water present an amphoteric behavior and react readily with the dye by a mechanism which can be described by the following chemical equilibria [10-12]:



The  $\text{TiO}_2$  charge depends on the pH of the solution. The pH of zero point of charge ( $\text{pH}_{\text{PZC}}$ ) for  $\text{TiO}_2$  is about 6.3 [13]. Thus, the  $\text{TiO}_2$  surface is positively charged in an acid medium ( $\text{pH} < \text{pH}_{\text{PZC}}$ ) and negatively charged under alkaline conditions ( $\text{pH} > \text{pH}_{\text{PZC}}$ ) (Figure 9).

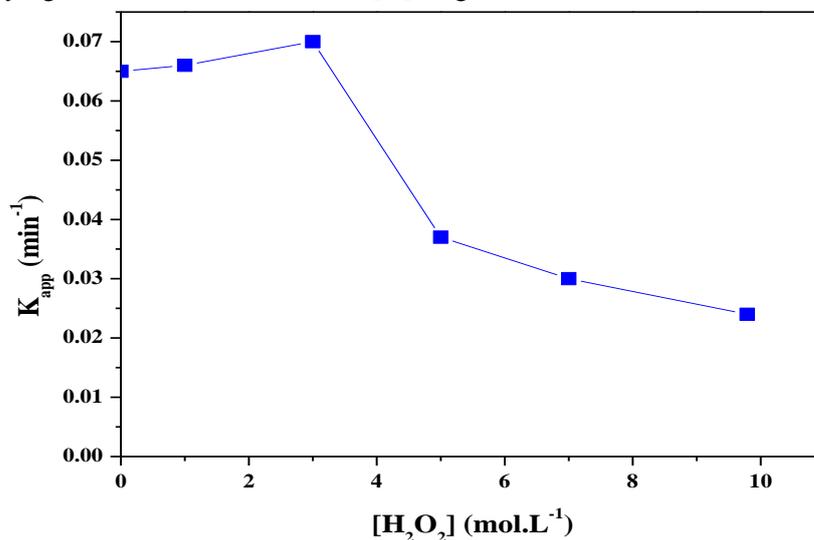
At a pH below  $\text{pH}_{\text{PZC}}$ , the  $\text{TiO}_2$  surface acquires a positive charge, indicated by (1), and therefore attracts the skeleton of RY17 dye negatively charged, which leads to a large number of dye molecules being attracted (or adsorbed) On the paper surface. As the concentration of the dye on the surface increases, the photodegradation activity also increases, as observed at pH 3. At a pH above  $\text{pH}_{\text{PZC}}$ , the electrostatic repulsion between the negative charge on the paper surface as shown in (2) and the skeleton of anionic dye delays the accumulation of the dye molecules on the surface leading to a decrease in the Photodegradation activity [14].



**Figure 9:** Scheme of interaction between RY17 and  $\text{TiO}_2$  as a function of pH.

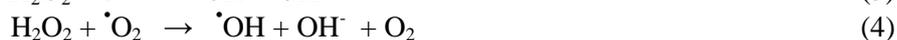
### 3.2.3. Effect of Addition of $\text{H}_2\text{O}_2$

To highlight the role of the hydroxyl radicals ( $\cdot\text{OH}$ ) in the degradation of the dye, we realized the photocatalytic tests in the presence of the hydrogen peroxide, considered an important generation source of these radicals [15]. The influence of the concentration of  $\text{H}_2\text{O}_2$  on the photocatalytic activity of  $\text{TiO}_2$  for the photodegradation of RY17 was studied by varying the concentration of the  $\text{H}_2\text{O}_2$  (Figure 10).



**Figure 10:** Effect of addition of  $\text{H}_2\text{O}_2$  on the apparent rate constant of photodegradation of RY17  
 $[\text{RY17}]_0 = 30 \text{ mg.L}^{-1}$ ;  $[\text{TiO}_2] = 1 \text{ g.L}^{-1}$ ;  $\text{pH}_i = 5$ ;  $T = 22^\circ\text{C}$ .

The results show that the apparent rate constant increased with increasing the concentration of  $\text{H}_2\text{O}_2$  from 0 to 3 mol.L<sup>-1</sup>, then  $\cdot\text{OH}$  decreased from 3 to 10 mol.L<sup>-1</sup> (Figure 10), that refer to the increase in the formation of  $\cdot\text{OH}$  radicals and besides inhibiting the recombination of hole-electron by following equation [16, 17]:



While, at high concentrations of H<sub>2</sub>O<sub>2</sub>, the photocatalytic processes decrease because H<sub>2</sub>O<sub>2</sub> is a scavenger for  $\cdot\text{OH}$  radicals, according to the following equations [18]:



The rate of photocatalytic degradation was decreased at higher concentration of H<sub>2</sub>O<sub>2</sub>, this negative effect of H<sub>2</sub>O<sub>2</sub> at higher concentration may occur due to inhibition of  $\cdot\text{OH}$ , because at high concentration of H<sub>2</sub>O<sub>2</sub>, the amount of  $\cdot\text{OH}$  formed on the surface was increased quickly and hence the annihilation  $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$  rate which consider faster than the degradation rate of RY17 [19].

## Conclusion

The results obtained in this study show that :

- The adsorption equilibrium is described better by the Langmuir isotherm.
- The photocatalytic degradation of RY17 in aqueous solution by TiO<sub>2</sub>-coated non-woven fibres follows a pseudo-first-order kinetics.
- The photodegradation rate decreases with increase in pH, the efficiency is very high at pH values strongly acid. Because, an adsorption OH on TiO<sub>2</sub> surface liberate  $\cdot\text{OH}$ , which is essential for photocatalysis process.
- The addition of electron acceptor (H<sub>2</sub>O<sub>2</sub>) enhances the degradation rate of the dye until a maximum concentration value equal 3 whereas for concentrations more than 3 the addition of H<sub>2</sub>O<sub>2</sub> led to decrease photocatalytic degradation rate.

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