

## Photodegradation study of TiO<sub>2</sub> and ZnO in suspension using miniaturized tests

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### ABSTRACT

Miniaturization has been a trend in the instrumentation of chemical analyzes. The interest in miniaturization stems from the perceived benefits of faster, easier, less expensive and less wasteful analyzes than the tradition analyses. Thus, this work proposes a miniaturization of photocatalytic tests using a microplate reader for the analysis of several results, using only microliters of solution. The present work investigates the heterogeneous photocatalysis of the eosin yellow, acid yellow 73 and basic yellow 2 dyes, in the presence of zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>) catalysts, under irradiation in the visible light and ultraviolet light. Dye degradation was evaluated using a microplate reader (Elisa Polaris®), a photometric device that performs colorimetric readings in the 0-3 absorbance (ABS) range at wavelengths of 405, 450, 492 and 630 nm. The kinetic study was performed using the Langmuir-Hinshelwood law. It was verified that the degradation rates were higher than 90% over a period of 120 minutes for all the studied systems, especially the system composed of acid yellow dye 73 and the ZnO catalyst, which reached a degradation of 96.23% in 120 minutes.

**Keywords:** heterogeneous photocatalysis, kinetic study, miniaturized assays.

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### 1. INTRODUÇÃO

Dye are usually categorized according to their chemical structures or according to their applications, they can also be classified in relation to their solubility in water [1, 2]. Anionic dyes, for example, are pigments widely used in the detergent, soap, textile, printing and cosmetic industries, being commercially known as acid dyes [3]. Acid yellow 73 (AY73) and eosin yellow (EY) dyes are examples of this class, also marketed as fluorescent dyes.

On the other hand, cationic dyes are synthetic pigments, commercially known as basic dyes, widely used in the textile industry in various processes such as acrylic, nylon, silk and wool dyeing [1,4,5]. An example of this class of dyes is the 4,4-dimethylaminobenzophenoneimide dye, known in the market as basic yellow 2 (BY2), used in the textile industry and the leather industry [6].

The effluents, industrial and laboratory-based dyes, are considered significant environmental pollutants, mainly due to the low biodegradability [7,8]. Each year, tons of dyestuffs are discharged as wastewater through textile effluents [9]. Such residues are rich in organic matter and are discarded in water resources, causing pollution and seriously affecting the aquatic ecosystem by preventing the penetration of light into water, making it impossible to carry out photosynthesis [10,11].

To solve the issues related to water pollution, studies were conducted to optimize methods for the removal of dye residues, which include treatments such as precipitation followed by filtration [3], coagulation [12], the adsorption of activated carbon [13], ionic exchange [12], ozonization [14], and aerobic and anaerobic microbial degradation [10]. The most of these methods involve the transfer of pollutants from one stage to another, requiring a secondary treatment of wastewater, rendering it ineffective in the decontamina-

tion of effluents [8,12,15].

Therefore, a sustainable and environmentally correct method has been used to treat water pollution, which consists on the usage of Advanced Oxidative Processes (AOPs) [7,12,15]. The AOPs are based on the in-situ production of hydroxyl radicals ( $\text{HO}\cdot$ ), reactive species of high potential standard of reduction (2.72 V) generated from visible or ultraviolet radiation [16], which are capable of causing the mineralization of several organic molecules [17,18], due to their high oxidative capacity. These reactive species react quickly and without specificity with most of the organic compounds leading to the mineralization process with formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [8].

These oxidative processes are divided into two major groups, according to the number of phases present in the system: homogeneous processes and heterogeneous processes [19]. In homogeneous systems, the catalyst is dissolved in the solution forming a single phase. Ozone, transition metal oxide and photo-Fenton systems are examples of catalysts of homogeneous systems [20]. In heterogeneous systems, the catalyst is in the solid state; usually inorganic semiconductors, for example metal oxides, like titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) [21]. These oxides are the most widely used, due mainly to their non-toxicity, high photochemical activity, low cost, stability in aqueous systems and chemical stability over a wide pH range [15,22,23,24]. Lv et al. [29], studied the photocatalytic activity of  $\text{ZnO}$  in the degradation of the rhodamine B dye under UV-Vis (sunlight) and under UV radiation. The degradation rate of rhodamine B was approximately 100%, in 40 minutes of reaction, under UV-Vis radiation. Under UV radiation (36 W), the  $\text{ZnO}$  also showed efficient photocatalytic activity, with values close to 90% degradation of the rhodamine B dye.

Macha et al. [30], investigated the heterogeneous photocatalysis of organic pollutants in municipal wastewater using photocatalysts of the type  $\text{TiO}_2$  and  $\text{TiO}_2$  with metals (Ag, Cu and Fe), under ultraviolet radiation and solar radiation. The results demonstrate that the photocatalysts were effective under both UV and UV-Vis irradiation, presenting degradation levels higher than 95%, thus overcoming the limitation that the  $\text{TiO}_2$  catalyst was only effective under ultraviolet radiation.

The principle of heterogeneous photocatalysis involves the activation of a semiconductor by natural or artificial light. A semiconductor is characterized by valence bands and conduction bands, the region between the valence band and the conduction band is called band gap [25]. When a semiconductor is irradiated with energy greater than the energy of band gap, electrons are generated ( $e_{CB}^-$ ) in the conduction band, and holes ( $h_{VB}^+$ ) in the valence band [20]. The photogenerated electrons can react with both the dye and acceptor electrons, as oxygen molecules adsorbed on the surface of the semiconductor or dissolved in the water, generating superoxide anions ( $\text{O}_2^{\cdot-}$ ) [26]. The photogenerated holes can oxidize the organic molecule to form radicals  $\text{R}^+$ , or react with  $\text{OH}^-$  or  $\text{H}_2\text{O}$ , oxidizing these species to  $\text{HO}\cdot$  [14,23]. Other highly oxidizing species, such as hydrogen peroxide, are responsible for heterogeneous photodecomposition with semiconductors on organic substrates, such as dyes.

The relevant reactions that occur on the surface of the semiconductor that form the reactive species are [12,20,26,27,28]:



Many studies show that  $\text{ZnO}$  can be as efficient as  $\text{TiO}_2$  in the photocatalytic degradation of some organic substances and even in some cases,  $\text{ZnO}$  has higher photocatalytic activity than  $\text{TiO}_2$  [31]. Poullos et al. [32] investigated the photocatalytic degradation of basic yellow 2 dye. Under the experimental conditions applied in the study, a degradation of 95% was achieved after 60 min exposure to UV light, using the  $\text{TiO}_2$  P-25 catalyst, while in the presence of  $\text{ZnO}$  the solution degraded approximately 100% at the end of 60 min. The superior efficiency of  $\text{ZnO}$  over  $\text{TiO}_2$  has also been demonstrated in the study of Muruganandham et al. [33], which studied the photocatalytic degradation of the reactive yellow 14 dye in aqueous solution. The study revealed the following order of reactivity:  $\text{ZnO} > \text{TiO}_2\text{-P25} > \text{TiO}_2$  (anatase). Tian et al. [34], studied the efficiency of  $\text{ZnO}$  semiconductors prepared using calcination of zinc acetate dihydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ) and  $\text{TiO}_2\text{-P25}$  (Degussa) in the photodegradation of the orange methyl dye, concluding that the rate of degra-

dation using the ZnO catalyst was four times higher when compared to the use of the catalyst TiO<sub>2</sub>-P25 (Degussa).

Kansal et al. [35] studied the degradation of the orange of methyl and rhodamine 6G dyes, using the heterogeneous photocatalytic process. The experimental results indicated that the maximum degradation (above 90%) of the dyes occurred with the use of the ZnO catalyst and basic pH, besides that, the performance of the photocatalytic system using ZnO/sunlight was observed to be more efficient than the ZnO/UV system.

Concern about the residual water treatment is not restricted to the industrial field, a new concept of sustainable chemistry has recently emerged that advocates the minimization of waste whether in industrial or laboratory effluents. The concept of sustainable chemistry is the creation, development and application of chemical products and processes to reduce or eliminate the use and generation of toxic substances. This requires a new chemical behavior for the improvement of processes, with the fundamental objective of decreasing generation of toxic wastes and effluents [38].

Therefore, this study proposes the miniaturization of photocatalytic tests to evaluate and compare the efficiency of photodegradation using minimized amounts of dyes (basic yellow 2, acid yellow 73 and eosin yellow), with the catalysts ZnO and TiO<sub>2</sub>, both in suspension and irradiated with visible and ultraviolet lights.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The catalysts used in the photodegradation tests were titanium dioxide (TiO<sub>2</sub> - 99.99% purity) and zinc oxide (ZnO - 99.99% purity). The dyes used were basic yellow 2 (BY2), acid yellow 73 (AY73) and eosin yellow (EY). All dyes were used without prior purification.

Solution concentrations  $5.25 \times 10^{-5}$  mol.L<sup>-1</sup>,  $1.23 \times 10^{-5}$  mol.L<sup>-1</sup> and  $5.25 \times 10^{-5}$  mol.L<sup>-1</sup> of basic yellow 2, acid yellow 73 and eosin yellow green were used respectively. A calibration curve was performed for each dye evaluated, from the calibration curves were chosen as the initial concentration for the each dye so that were not demonstrated absorbance greater than 1, according to Lambert-Beer law for the basic yellow dye 2, acid yellow 73 and eosin yellow dyes at wavelengths 450 nm, 492 nm and 530 nm respectively [34].

### 2.2 Preparation of Solutions

In conical tubes (1.50 mL), 0.50 mL of aqueous solution of dye was added to the concentrations  $1.05 \times 10^{-4}$  mol.L<sup>-1</sup>,  $2.46 \times 10^{-5}$  mol.L<sup>-1</sup> and  $1.05 \times 10^{-4}$  mol.L<sup>-1</sup> for BY2, AA73 and EY respectively. Thereafter 0.5 mL of distilled water were added, thereby obtaining the desired concentrations of  $5 \times 10^{-5}$  mol.L<sup>-1</sup>,  $1 \times 10^{-5}$  mol.L<sup>-1</sup> and  $5 \times 10^{-5}$  mol.L<sup>-1</sup> for BY2, AA73 and EY, respectively. To this solution was added 0.001 g.mL<sup>-1</sup> of TiO<sub>2</sub> or ZnO.

### 2.3 Calibration curves

The great majority of the photodegradation studies uses a cuvette spectrophotometer to analyze the absorbance of the solutions generated by the catalytic process. However, this study proposes the use of miniaturized assays to analyze such solutions, that is, it is suggested to carry out the photocatalytic study of the dyes through the use of a microplate reader to read the absorbances, in this way it is possible to carry out up to 96 readings simultaneously, with minimal usage of reagents.

The need to realize the calibration curve is due to the conversion of the result obtained by the spectrophotometer into a physical value. Thus, by means of the Lambert-Beer law, for diluted solutions, there is a linear dependence between the absorbance and the concentration of the substances present in the sample, according to equation 7 [34]:

$$A = \epsilon bc \quad (7)$$

**A** is absorbance,  $\epsilon$  is the molar absorptivity, **b** is the optical path, and **c** is the concentration.

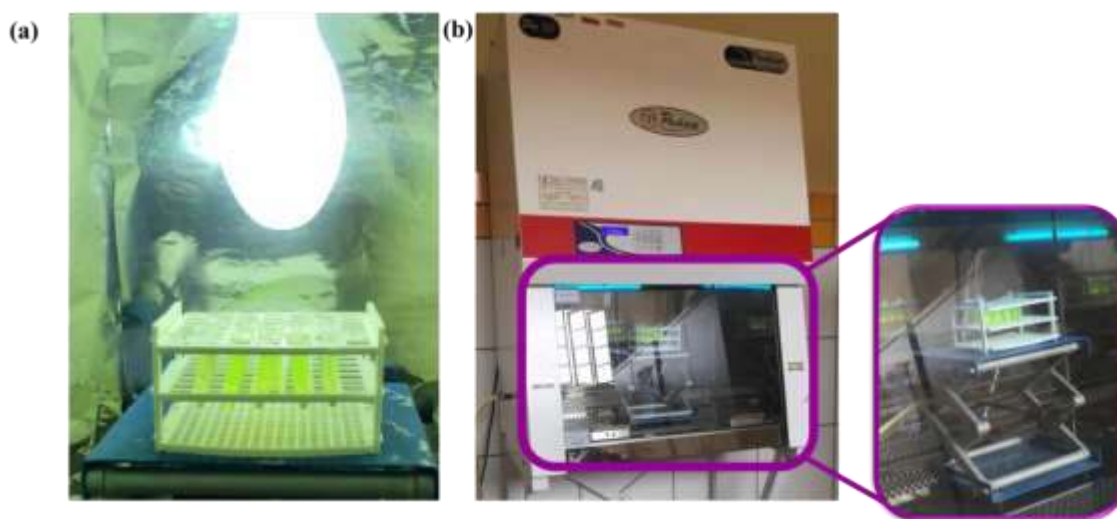
A solution of the BY2, AY73 and EY dyes having a concentration  $5.25 \times 10^{-5}$  mol.L<sup>-1</sup>,  $1.23 \times 10^{-5}$  mol.L<sup>-1</sup> and  $5.25 \times 10^{-5}$  mol.L<sup>-1</sup> respectively was prepared; this solutions were considered the standard solutions. Thus, all the solutions analyzed by the Polaris spectrophotometer, equivalent to the points in the calibration curve, were originated from this initial solutions. The calibration curve was obtained through a series of

dilutions,  $1.44 \times 10^{-1} \text{ g.L}^{-1}$  to  $3.2 \times 10^{-3} \text{ g.L}^{-1}$ , for BY2,  $8 \times 10^{-3} \text{ g.L}^{-1}$  to  $8 \times 10^{-5} \text{ g.L}^{-1}$ , for AY73 and  $1.73 \times 10^{-2} \text{ g.L}^{-1}$  to  $2.31 \times 10^{-3} \text{ g.L}^{-1}$ , for EY.

The absorbances of the dye BY2, dye AY73 and dye EY were measured at a wavelength of 405 nm [6], 490 nm [36] and 492 nm [37], which are the absorption wavelength of each dye, respectively .

## 2.4 Photocatalytic degradation experiments

The photocatalytic experiments were performed on conical tubess (1.5 mL) containing  $1.00 \times 10^{-3} \text{ g.mL}^{-1}$  of catalyst and 1 mL of aqueous solutions of the dyes. The mixture was illuminated in a hood when irradiated with a 160 W lamp emitting radiation in the region of the UV-Vis (365-1000 nm) and in a Pachane Pa50 laminar flow bench when irradiated by the UV lamp 15W ( $\lambda_{\text{max}} = 365 \text{ nm}$ ). The system temperature was maintained at approximately 30 °C by the use of a  $0.45 \text{ m.s}^{-1}$  air recirculation flow, Figure 1.



**Figure 1:** (a) System irradiated by a UV-Vis light (b) system irradiated by UV light.

Aliquots of the aqueous suspension were withdrawn at 0, 10, 20, 40, 60, 80 and 120 minutes from the conical tubess and then centrifuged in an conical tubes centrifuge to remove the suspended catalyst. The absorbances of the solutions were measured using an microplate reader (Elisa Polaris®) at wavelengths of 405 nm for BY2, 492 nm for AA73 and EY for calculation of the concentration of dyes as a function of the irradiation time.

The efficiency of the degradation reaction was determined using equation 8 [26,29,31]:

$$D(\%) = \left( \frac{A_0 - A_t}{A_0} \right) \cdot 100 \quad (8)$$

$A_0$  is the initial absorbance of the dye solution and  $A_t$  the absorbance in time  $t$ , which relate respectively to the initial concentrations ( $C_0$ ) in time  $t$  ( $C_t$ ) according to the Lambert-Beer law.

Systems composed of three dyes were studied: BY2, AY73 and EY; two catalysts: zinc oxide and titanium oxide; and 2 types of irradiation: UV light and UV-Vis light. Table 1 summarizes the systems studied in this work.

**Table 1:** Dye photodegradation systems (basic yellow 2, acid yellow 73 and eosin yellow) by catalysts ( $\text{TiO}_2$  and  $\text{ZnO}$ ).

DYE	UV light	UV-Vis light	$\text{TiO}_2$	$\text{ZnO}$
Basic Yellow 2 (BY2)	X	X	X	X
Acid Yellow 73 (AY73)	X	X	X	X

Eosin Yellow (EY)	X		X	
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### 3. RESULTS AND DISCUSSION

#### 3.1 Calibration Curves

The calibration curves, shown in Figure 2, demonstrate that the acid yellow dye presented lower dispersion, followed by basic yellow 2 and eosin yellow. It was obtained  $R^2$  over 0.98 for all the calibration curves, confirming that the system developed for the absorbance analysis of the solutions generated by the photocatalytic reaction is validated.

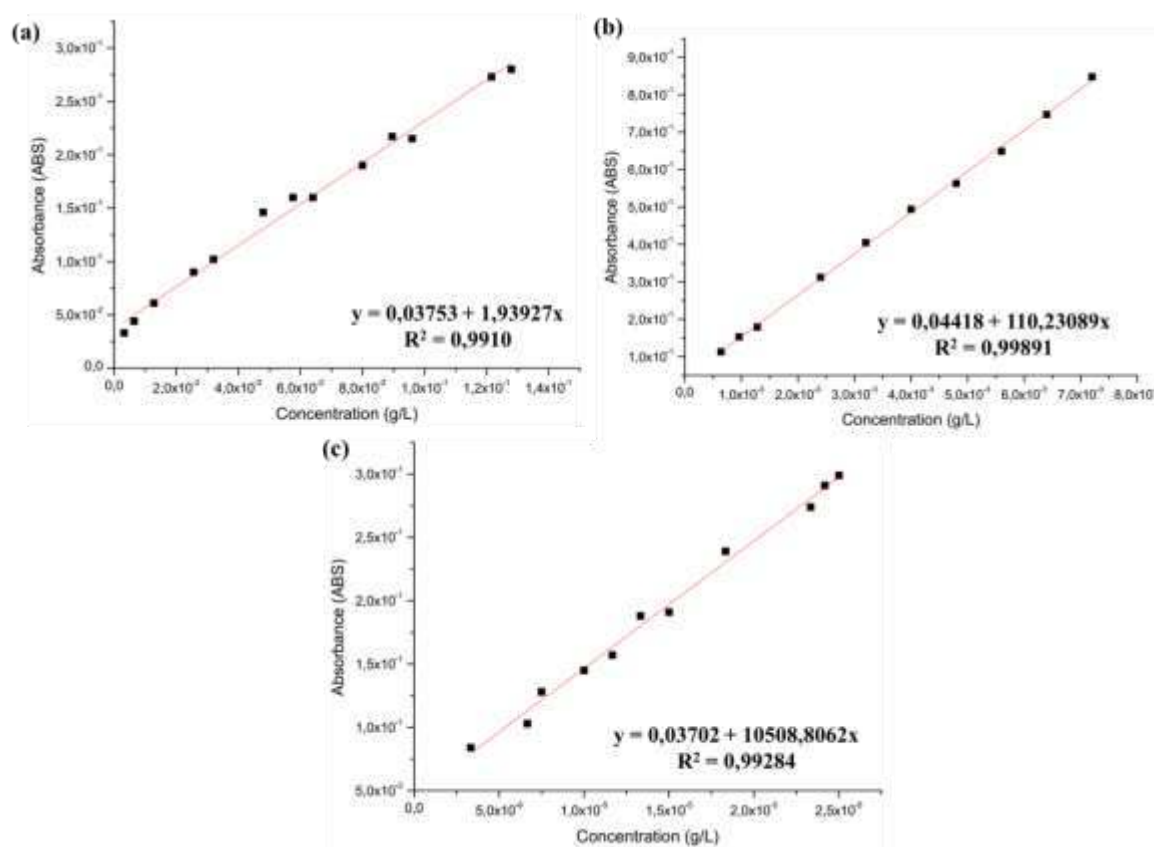


Figure 2: Calibration curves (a) basic yellow 2 (b) yellow acid 73 (c) yellow eosin.

#### 3.2 Kinetics of Photodegradation

Initially, the study of photolysis was carried out. This study consisted of analyzing the effect of UV radiation on the dye solution without the presence of the photocatalysts for 120 minutes. According to the data obtained, negligible degradation efficiency was found to be below 10% for basic yellow 2, eosin yellow and a degradation efficiency of 19% for acid yellow 73 dye, indicating that only ultraviolet or visible radiation is insufficient for the degradation of the dyes.

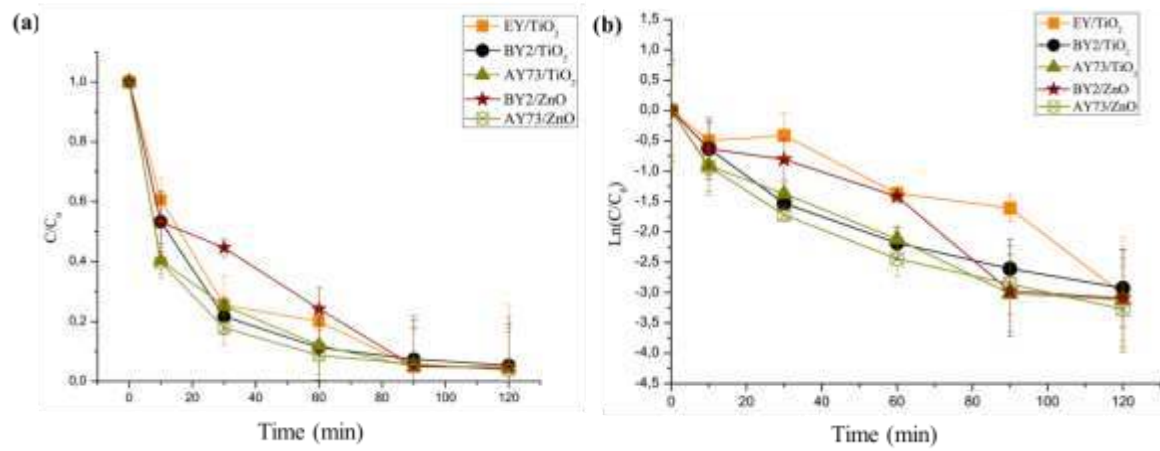
Then, the photocatalysis study was carried out using  $TiO_2$  or  $ZnO$  as catalysts. The kinetic study shows systems irradiated by light in the UV-Vis region reached degradation efficiency above 90% with both catalysts in 90 minutes.

However, for systems irradiated by UV light the degradation efficiency above 90% with both catalysts was achieved in up to 60 minutes for all dyes, Figure 3.

The results from the degradation of dyes eosin yellow, acid yellow 73 and basic yellow 2, as a func-

tion of the time of exposure to UV light in the presence of the catalysts ZnO and TiO<sub>2</sub> are shown in Figure 3 (a). During the experiments, the concentration of the catalysts, pH and temperature of the solutions were kept constant.

The linearity obtained in the graph Ln (C<sub>0</sub>/C<sub>t</sub>) versus t, observed in Figure 3 (b), confirms the applicability of the Langmuir-Hinshelwood equation for photocatalytic degradation of dyes under UV radiation.



**Figure 3:** (a) Process for the degradation of dyes with radiation in the UV region. (b) kinetics of degradation of dyes.

All systems showed degradation higher than 90% with 120 minutes of reaction, and the rate of degradation of the dyes in the aqueous solution described by Langmuir-Hinshelwood kinetic model of pseudo-first order [7,21]:

$$r = -\frac{dC}{dt} = \frac{CKk_r}{1+KC} \quad (9)$$

"r" represents the rate of degradation, "K" represents the equilibrium constant for the adsorption of the dye on the surface of the catalyst and "k<sub>r</sub>" is the kinetic constant for the degradation reaction.

Integrating equation (9), obtain the irradiation time t, for concentration C<sub>t</sub> of the dye:

$$t = \left(\frac{1}{Kk_r}\right) \ln\left(\frac{C_0}{C_t}\right) + \frac{C_0 - C_t}{k_r} \quad (10)$$

C<sub>0</sub> represents the initial concentration of the dye. Therefore at low C<sub>0</sub>, the second term in equation 10 becomes insignificant and hence can be neglected:

$$\ln\left(\frac{C_0}{C_t}\right) = k_r K t = k_{app} t \quad (11)$$

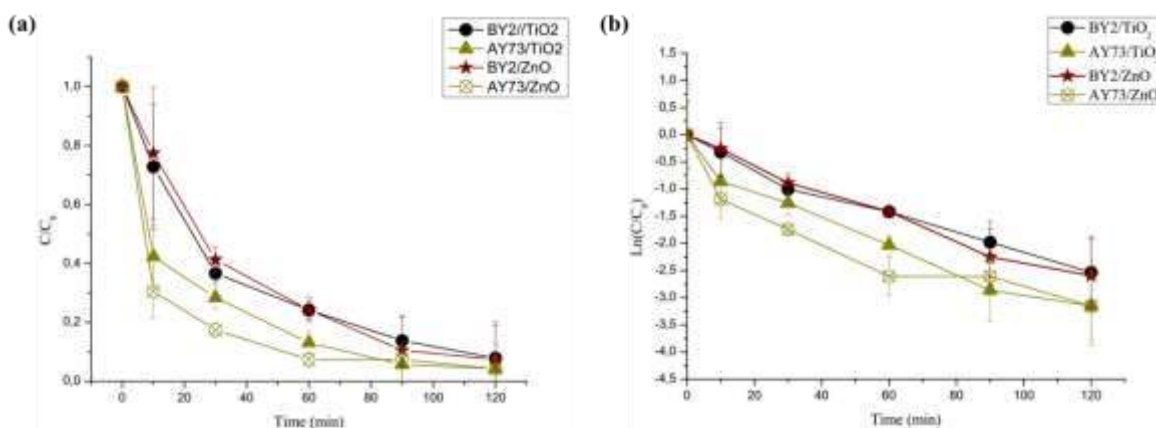
k<sub>app</sub> is the apparent degradation rate constant of the photocatalytic reaction. The results of the rate constants are described in Table 2.

**Table 2:** Constants obtained in the process of degradation of the dyes under UV light irradiation.

Dye	Catalyst	%Degradation	k <sub>app</sub> , 10 <sup>-2</sup> (min <sup>-1</sup> )
EY	TiO <sub>2</sub>	95.17%	2.52 ± 0.009
BY2	TiO <sub>2</sub>	94.65%	2.44 ± 0.004
AY73	TiO <sub>2</sub>	95.57%	2.60 ± 0.013
BY2	ZnO	95.48%	2.58 ± 0.005

AY73	ZnO	96.22%	$2.73 \pm 0.017$
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The Figure 4 (a) shows the results obtained from the degradation of the dyes acid yellow 73 and basic yellow 2, in the concentrations  $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$  mol. L<sup>-1</sup>, respectively, as a function of the time of exposure to visible light in the presence of the catalysts ZnO and TiO<sub>2</sub>. During the experiments, the concentration of the catalysts, pH and temperature of the solutions were kept constant.



**Figure 4:** (a) Process of degradation of dyes with UV-Vis light; (b) Kinetics of dye degradation.

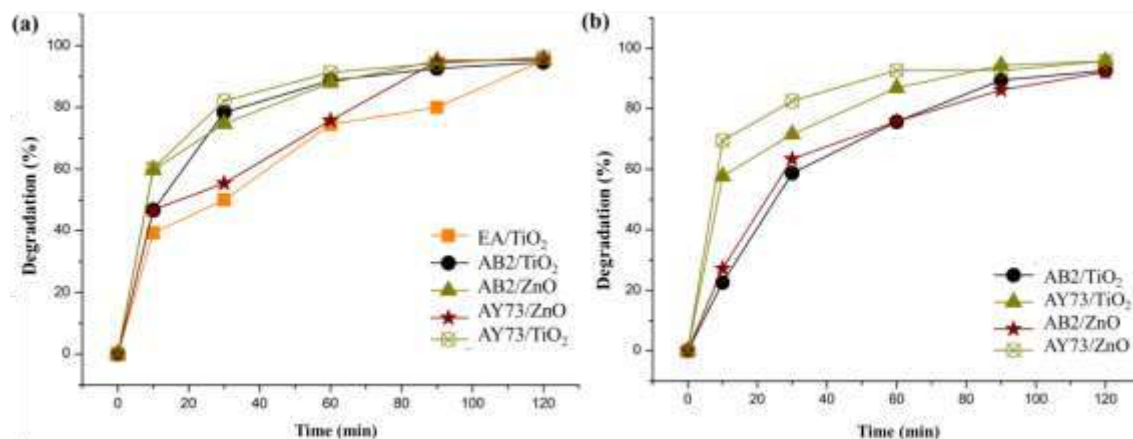
The linearity obtained through the graph  $\ln(C_0/C_t)$  versus  $t$ , observed in Figure 4 (b), confirms the applicability of the Langmuir-Hinshelwood equation for photocatalytic degradation of dyes under UV-Vis radiation. The rate constants are shown in Table 3.

**Table 3:** Constants obtained in the process of degradation of the dyes under irradiation UV-Vis light.

Dye	Catalyst	%Degradation	$k_{app}, 10^{-2} (\text{min}^{-1})$
BY2	TiO <sub>2</sub>	92.53%	$2.16 \pm 0.001$
AY73	TiO <sub>2</sub>	95.73%	$2.62 \pm 0.002$
BY2	ZnO	92.08%	$2.11 \pm 0.001$
AY73	ZnO	95.71%	$2.63 \pm 0.004$

### 3.3 Effect of radiation source and photocatalyst

Figure 5 illustrates the effect of the radiation source on degradation of the dye solutions for each photocatalysts. It is observed that degradation achieved about 95% degradation with both lights for all evaluated dyes.



**Figura 5:** (a) Process of degradation of dyes under UV-Vis light; (b) Process of degradation of dyes under UV light.

Therefore, the present study corroborates with the literature about the efficiency of UV radiation and UV-Vis radiation in the heterogeneous photocatalysis of organic molecules using ZnO or TiO<sub>2</sub>.

Comparing the rate constants of Tables 1 and 2, all of them are in the same order of magnitude, confirming the efficiency of both semiconductors in the heterogeneous photocatalysis of the dyes treated in this study. However, it is possible to note a greater efficiency with the use of the ZnO catalyst in the degradation of the acid yellow dye 73.

Thus, by presenting values of 92 to 97% degradation of basic yellow dyes 2, acid yellow 73 and eosin yellow using TiO<sub>2</sub> and ZnO in suspension as catalysts in the heterogeneous photocatalysis of dyes, this study is in agreement with the results presented in the literature, which discuss the best efficiency of ZnO when compared to TiO<sub>2</sub> [26]. A hypothesis that may explain the higher efficiency of ZnO is related to its ability to absorb a wide range of solar spectrum [25].

#### 4. CONCLUSIONS

In order to develop a miniaturized method of photocatalytic tests, aiming at the lower use of reagents and rate in reading the results, in this paper we propose for the first time the use of small reactors to perform the photocatalytic reactions and a microplate reader that allows up to 96 solutions at the same wavelength.

The results obtained in this study allow us to conclude that the heterogeneous photocatalysis of the basic yellow 2, yellow acid 73 and eosin yellow dyes using UV and UV-Vis radiation sources is satisfactory in all analyzed systems. The highest color degradation occurred in the system composed of acid yellow dye 73, using the ZnO semiconductor under UV radiation.

It is observed that both semiconductors, TiO<sub>2</sub> and ZnO, were efficient as photocatalysts, in the heterogeneous photocatalytic process, to reduce the color of the basic yellow dyes 2, yellow acid 73 and yellow eosin, showing that ZnO is the best catalyst for the systems studied.

Finally, it was concluded that the use of miniaturized assays to study heterogeneous photocatalysis is adequate, minimizing waste in the laboratory effluent, in addition to allowing rapid results due to the possibility of carrying out multiple tests simultaneously.

#### 5. ACKNOWLEDGMENTS

The authors thank to Danny Color Dyes for providing the basic yellow dyes 2 and yellow sour 73, the Federal University of Paraíba for supplying TiO<sub>2</sub> and the Federal University of Piauí (UFPI) to provide the others work research conditions.

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