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# Photocatalytic degradation of methylene blue in aqueous suspensions using $TiO_2$ and ZnO

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## ABSTRACT

The non-biodegradability of textile wastewater is mainly due to the presence of synthetic dyes. Resistance to bacterial degradation led to the development of new techniques where solar photocatalysis appears to be the best method for this type of application. methylene blue (MB) degradation was studied in $TiO_2$ and ZnO aqueous suspension using solar energy in a tubular reactor. This study was conducted to evaluate the performance of the prototype and explore the feasibility of this concept for solar photocatalytic oxidation. The main objective of this work was to compare the efficiency of two types of catalysts, which are titanium dioxide ($TiO_2$) and zinc oxide (ZnO). The use of $TiO_2$ as a catalyst enables a good degradation of MB which can achieve a disposal rate of 98% after 270 min with a $TiO_2$ concentration of 0.75 g/L. The same removal rate can be achieved by ZnO but for a much smaller concentration which was 0.025 g/L after 140 min.

*Keywords:* Photocatalysis; Methylene blue (MB); Solar energy; Titanium dioxide ($TiO_2$); Zinc oxide (ZnO)

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## 1. Introduction

The presence of dyes and pigments in water causes considerable damage in the aquatic environment [1–3]. Even with very low concentrations, the color of this kind of contaminants can be noticed, as the presence of dyes in water is highly visible. This effect is undesirable because it prevents sunlight access to the aquatic flora and fauna and reduces the photosynthetic action within the ecosystem [4–6]. The most used dye is methylene blue (MB) which is also applied to manufactured products. In addition, this type of dye has been used in textile, plastics, paper mill industry, and in toxicology. It is also used in clinical medicine as an indicator dye and in the

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treatment of symptomatic methemoglobinemia as an antidote [7].

The effluents resulting from the dyeing process of textile fibers and fabric have a significant impact on the ecosystem, which reduce the transparency of water and the sunlight penetration, and thereby, alter the photosynthetic activity and the solubility of gases. Up to 40% of the loads of these effluents may consist of dyes used in dyeing processes [8,9].

Many processes have been extensively applied to the treatment of wastewater containing dye such as: incineration, biological treatment, ozonation, and adsorption on solid phases [10–13].

However, these procedures have some drawbacks, For example:

(1) the incineration can produce toxic volatiles;
(2) biological treatment demands long periods of treatment and emit bad smell; and
(3) ozonation presents a short half-life and ozone stability is affected by the presence of salts, pH, and temperature.

In this way, the heterogeneous photocatalysis becomes a suitable alternative for dye degradation. This technique presents many advantages over conventional technologies such as the dye degradation into innocuous final products [14,15]. However, most of the azo dyes are generally resistant to biological decolorization. Recently, heterogeneous photocatalysis using semiconductors such as titanium dioxide has attracted much attention because of its ability to decolorize dye-containing wastewater [16,17]. This process can mineralize organic dyes completely into $H_2O$, $CO_2$, and other nontoxic inorganic compounds without bringing secondary pollution [18].

If the used energy comes from the sun, the process is called solar photocatalysis. Solar photocatalysis for wastewater treatment has proven to be a highly effective technology which most researchers have employed [19]. The efficiency of solar photocatalysis would be directly controlled by the production of free radicals, which significantly depends on the activation of photocatalysts and oxidants upon light irradiation.

Photocatalytic degradation of organic pollutants in water using semiconductive particles, such as $TiO_2$ and ZnO, has attracted extensive attention in the past two decades [20–24].

Titanium dioxide is widely used as a photocatalyst because it is photochemically stable, non toxic, and low cost [25–28]. ZnO also has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity, stability, and wide band gap.

Even $TiO_2$ is widely employed as a photocatalyst, ZnO is a suitable alternative as it has a similar band-gap energy (3.2 eV), larger quantum efficiency than $TiO_2$, and higher photocatalytic efficiencies as reported by Height et al. [24].

In the present study, we have investigated the photocatalytic degradation of MB dye solution synthetically polluted. The photocatalytic reaction is based on the adsorption of light radiation by the catalyst, usually a semiconductor, which is titanium dioxide ($TiO_2$). The advantage of this method is that no chemical compounds other than $TiO_2$ were introduced in the solution to be treated and this after the treatment of the target pollutant. In a region with high sunshine rate, such as Algeria, the use of solar radiation for the treatment of chemical pollution in water is an asset. Photocatalysis is gradually becoming an alternative technology for water pollution control as it is part of a sustainable development perspective when using the sun as a renewable energy source.

The aim of the present work is to study the photocatalytic decomposition of MB using $TiO_2$ and ZnO with the objective of comparing their performance.

## 2. Experimental

### 2.1. Chemicals and reagents

#### 2.1.1. Pollutant

MB ($C_{16}H_{18}ClN_3S$) was provided by “BIOCHEM ChemoPharma” (Quebec, Canada). It is a greenish powder with a molecular weight of 319.8 (g/mol).

MB degradation was evaluated by measuring the absorbance using a spectrophotometer UV–visible, of Shimatzu UV 1800 type. The maximum absorption band was located at 664 nm. A correlation curve between MB (Fig. 1) concentration and the absorption was pre-established.

#### 2.1.2. Photocatalysts

A commercially available titanium dioxide ($TiO_2$), used as a photocatalyst, was produced by the Chemical Factory “BIOCHEM ChemoPharma”

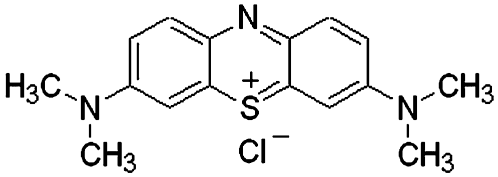

Fig. 1. Chemical structure of methylene blue (MB).

(Quebec, Canada). This photocatalyst is in anatase (90% anatase) form with BET specific surface area of 4.61 ($m^2 g^{-1}$) and a particle diameter of 48 nm.

A second type of catalyst ZnO is used for comparison, it is produced by Aldrich Chemical Company. This photocatalyst has a structure of 100% Zincite form with BET specific surface area of 9 $m^2 g^{-1}$ and an average size of 1.5 μm.

X-ray diffraction (XRD) patterns of ZnO and $TiO_2$ catalysts were obtained using a Philips diffractometer PW 1729X-RAY GENERATOR with monochromated high intensity CuKα1 ($\lambda$ = 15,406 Å). CuKa in the scan range 2$y$ between 101 and 701 (Fig. 2).

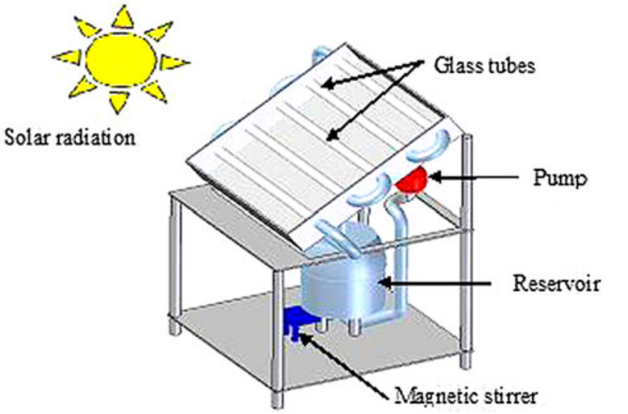

Fig. 3. Experimental set-up.

## 2.2. Photoreactor

Photocatalytic experiments were carried out in a pilot plan developed specially for photocatalytic application installed at the Solar Equipment Development Unit (UDES) located in the north of Algeria (latitude 36˚.39´; longitude 2˚.42´) using natural sunlight irradiation. Solar ultraviolet radiation (UV) was measured by global UV radiometer (KIPP and ZONZN, CMP11) mounted on a platform tilted 36˚ as the reactor.

The solar photocatalytic reactor (Fig. 3) used in this experiment is based on compound collector technology [29]. This small prototype consists of one photoreactor module with 05 tubes out of glass assembled in series (1 m length × 65 mm interne diameter × 2 mm thickness) and mounted on an aluminum reflector. A volume of 10 L is placed in the supply reservoir and mixed with photocatalyst powder. The temperature was not controlled and it could vary from 20 to 30˚C.

The mixture was stirred for 10 min in the dark before starting the circulation from $t = 0$ mn (origin time). The reaction system was continuously stirred to achieve a homogenous suspension. At certain reaction

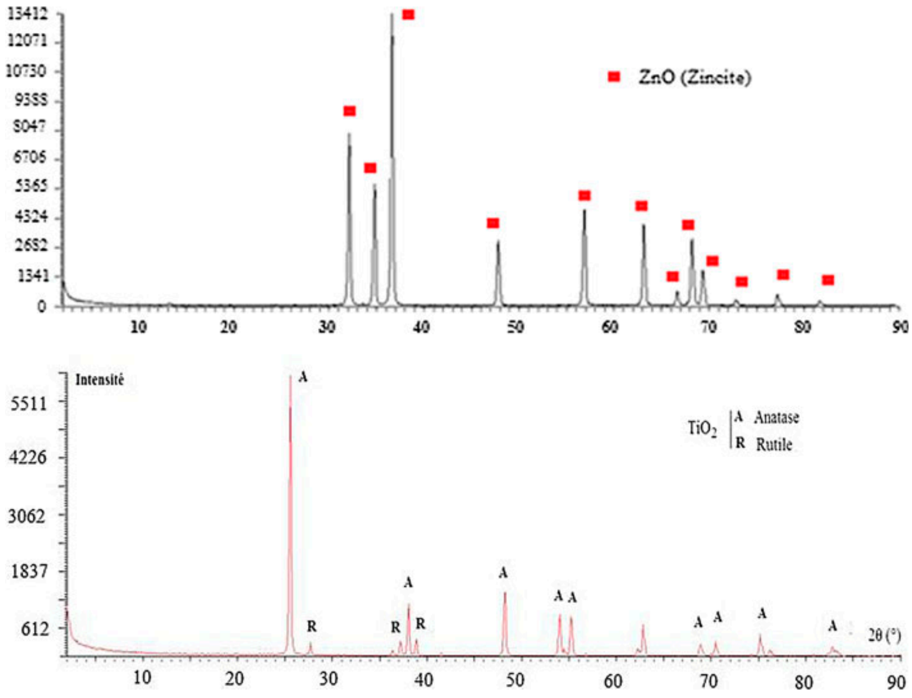

Fig. 2. XRD patterns of ZnO and $TiO_2$ photocatalysts.

intervals, 5 mL of sample was withdrawn, filtered on a Millipore filter of 0.45 µm. The dye concentration was analyzed with a UV–visible spectrophotometer SHIMADZU kind 1800.

## 3. Results and discussion

### 3.1. Effect of photocatalyst loading

It is important to study the dependence of the photocatalytic reaction rate on the concentration of photocatalyst. Hence, the effect of photocatalyst dosage on the degradation of MB was investigated using $TiO_2$ and ZnO at different concentration, keeping all other parameters stable. As shown in Fig. 4, the photocatalytic degradation rate was found to increase as the photocatalyst dosage increases.

Both catalysts were used under the same experimental conditions. MB concentration = 10 mg/L in 10 L solution, under sun light radiation, flow rate = 25.8 L/min.

For both photocatalysts ($TiO_2$ and ZnO), the MB degradation is almost complete. With an increased $TiO_2$ catalyst loading from 0.25 to 1.25 g/L, the rate of dye which is degraded after 270 min increased from 85 to 98%. In the case of ZnO, the increase in catalyst loading from 0.025 to 0.3 g did not have an impact on the rate of MB degradation. In this concentration interval, the elimination rate is around 97% after 140 min of irradiation time.

According to Table 1, MB degradation follows the pseudo-first order kinetic model. The apparent rate constants for each photocatalyst concentration were determined by linear regression form (ln $(C/C_0)$ vs. time). The slope of the straight lines corresponding to the kinetic rate constants of degradation increases with the amount of photocatalyst, until it reaches an optimum value under sunlight. We can see that the constant rate $k_{app}$ is more important in the case of ZnO. The quantum efficiency of ZnO powder is significantly larger than the $TiO_2$ powder, and higher catalytic efficiencies have been reported for ZnO [30]. The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than $TiO_2$. For this reasons, ZnO photocatalyst is the most suitable for organic dye in presence on sunlight [23].

### 3.2. Effect of initial dye concentration

The effect of the initial dye concentration on the rate of dye degradation was studied by varying the initial dye concentration from 5 to 30 mg/L with constant optimum catalyst loading (0.75 g/L $TiO_2$ and 0.025 g/L ZnO), the results are reported in Table 2.

Figs. 5(a) and 4(b) reveal that the initial dye concentration influences the rate of degradation of the dye. It is obvious that the rate increases with decreasing dye concentration.

The degradation rate relates to the formation of $^{\cdot}OH$ radical which is the critical species in the degradation process. The equilibrium adsorption of reactants on the catalyst surface and the rate of reaction of $^{\cdot}OH$ radicals with other chemicals are also significant in the rate of degradation.

Furthermore, as the initial dye concentration increases, the path length of photons entering to the solution decreases, and in low concentration the reverse effect is observed [31].

Hence, it can be concluded that as the initial concentration of dye increases, the catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the $OH^{\cdot}$ and $O_2^{2-}$ species attacking the dye molecules decrease in dye concentration [23]. This proves that the rate of decolorization and degradation decrease considerably

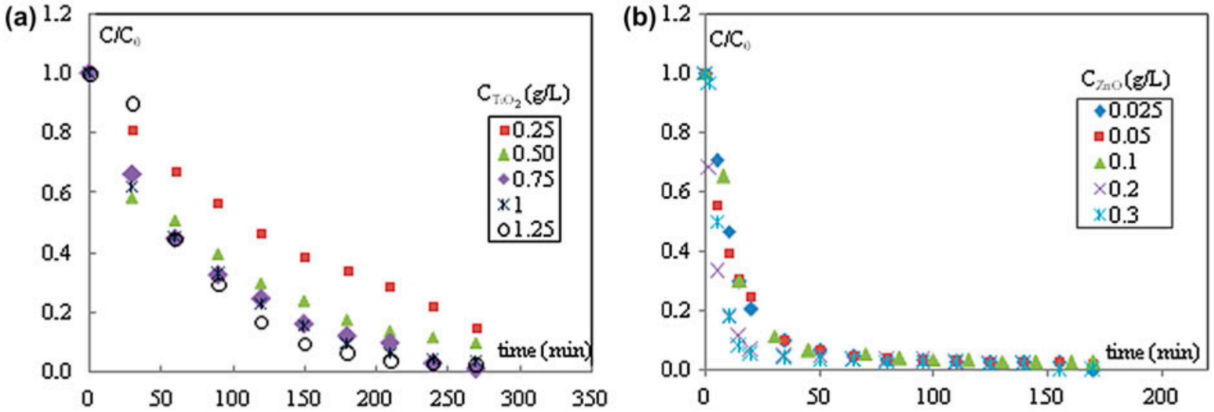

Fig. 4. Effect of catalyst loading ($C_{MB}$ = 10 mg $L^{-1}$; $Q$ = 25.8 L $min^{-1}$) (a) using $TiO_2$ and (b) using ZnO.

Table 1
Value of kinetic constants, times of half reaction for different photocatalyst concentration under solar radiation

| $TiO_2$ catalyst | | | | | ZnO catalyst | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$ (g $L^{-1}$) | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) | ZnO (g $L^{-1}$) | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) |
| 0.25 | 85 | 0.006 | 0.06 | 115 | 0.025 | 97 | 0.078 | 0.69 | 9 |
| 0.50 | 90 | 0.009 | 0.09 | 77 | 0.05 | 97 | 0.070 | 0.60 | 10 |
| 0.75 | 99 | 0.011 | 0.11 | 63 | 0.10 | 97 | 0.072 | 0.64 | 10 |
| 1.00 | 96 | 0.012 | 0.12 | 58 | 0.20 | 98 | 0.144 | 1.25 | 5 |
| 1.25 | 98 | 0.015 | 0.15 | 46 | 0.30 | 98 | 0.154 | 1.39 | 4 |

Table 2
Value of kinetic constants, times of half reaction for different initial MB concentration under solar radiation

| [$TiO_2$] = 0.75 g/L | | | | | [ZnO] = 0.025 g/L | | | | |
|---|---|---|---|---|---|---|---|---|---|
| [BM] (mg $L^{-1}$) | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) | [BM] (mg $L^{-1}$) | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) |
| 5 | 99 | 0.009 | 0.03 | 77 | 5 | 95.6 | 0.067 | 0.335 | 10 |
| 10 | 99 | 0.012 | 0.09 | 58 | 10 | 97.3 | 0.078 | 0.780 | 09 |
| 20 | 95 | 0.009 | 0.17 | 77 | 20 | 95.4 | 0.027 | 0.540 | 26 |
| 30 | 74 | 0.004 | 0.10 | 173 | 30 | 43.9 | 0.009 | 0.270 | 77 |

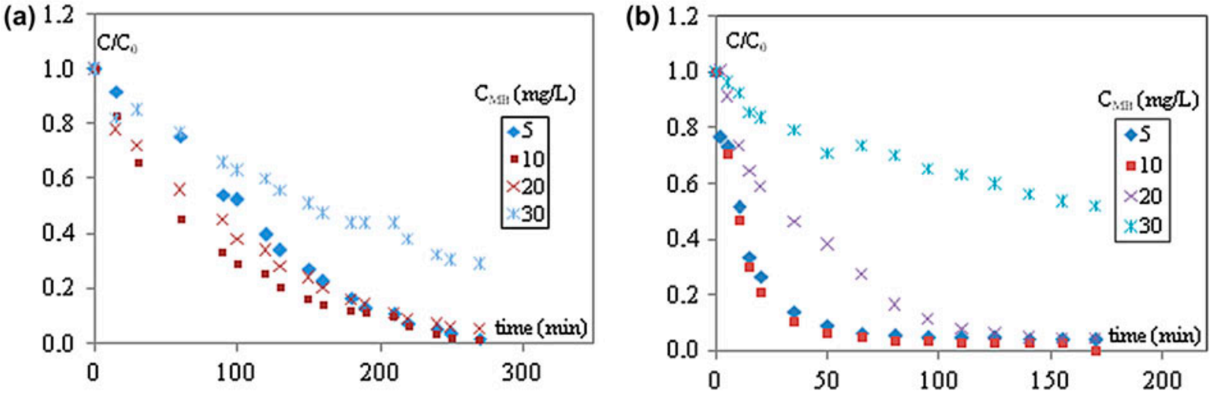

Fig. 5. Effect of initial Methylene Blue concentration (a) using 0.75 g/L $TiO_2$ and (b) using 0.025 g/L ZnO.

with dye concentration increase. Additionally, in terms of process costs, the commercial ZnO achieved greater MB degradation than the commercial $TiO_2$ with a lower catalyst concentration [32].

### 3.3. Influence of pH

Another important parameter in the heterogeneous photocatalysis process is the pH reaction. It influences the surface charge properties of the photocatalyst and therefore, the adsorption behavior of the pH pollutant of the dye solution was adjusted by adding NaOH or HCl.

The role of pH on the rate of photocatalytic degradation was studied in the pH range 3–12 at constant dye concentration (10 mg $L^{-1}$) and catalyst amount 0.75 g/L $TiO_2$ and 0.025 g/L ZnO.

The obtained Results, with varying pH from 3 to 12, were illustrated in Fig. 6. Table 3 summarizes the calculated $k_{app}$ and $t_{1/2}$. The complete degradation (100%) of MB was obtained at pH value of 6.3 (natural solution) after an irradiation time of 270 min

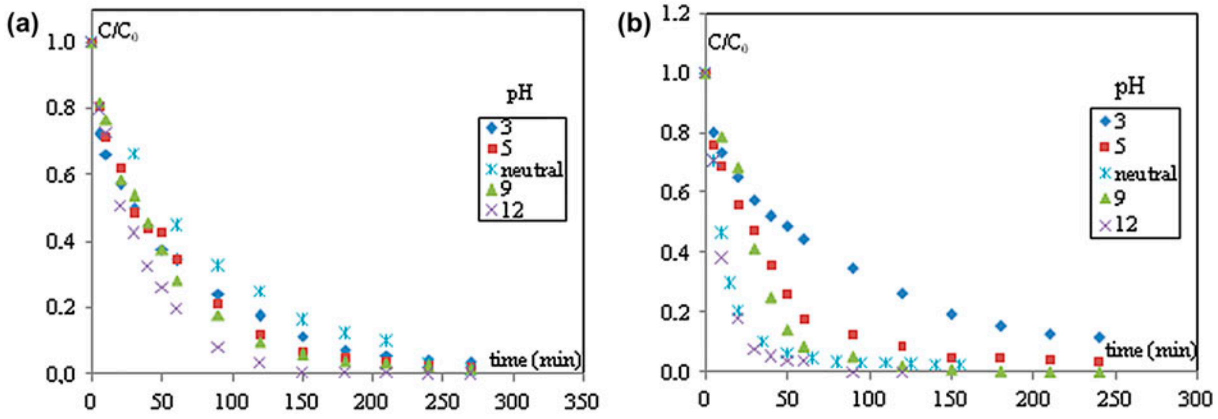

Fig. 6. Effect of initial solution pH on Methylene Blue photodegradation (a) using 0.75 g/L $TiO_2$ and (b) using 0.025 g/L ZnO.

Table 3
Value of kinetic constants, times of half reaction for different pH under solar radiation

| $TiO_2$ catalyst | | | | | ZnO catalyst | | | | |
|---|---|---|---|---|---|---|---|---|---|
| pH | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) | pH | $X$ (%) | $k_{app}$ ($min^{-1}$) | $r_0$ (mg $L^{-1}$ $min^{-1}$) | $t_{1/2}$ (min) |
| 3 | 96 | 0.014 | 0.14154 | 49 | 3 | 88 | 0.016 | 0.1512 | 43 |
| 5 | 98 | 0.017 | 0.14416 | 41 | 5 | 96 | 0.027 | 0.26244 | 26 |
| Free | 99 | 0.011 | 0.08063 | 63 | Free | 100 | 0.07 | 0.6237 | 10 |
| 9 | 99 | 0.019 | 0.1615 | 37 | 9 | 100 | 0.036 | 0.31356 | 19 |
| 12 | 100 | 0.028 | 0.21924 | 25 | 12 | 100 | 0.078 | 0.31356 | 9 |

for $TiO_2$ and 90 min for ZnO. As the pH increased from 6 to 12, the degradation time also increased from 270 to 200 min for $TiO_2$ and from 90 to 60 min for ZnO.

Kinetics were fitted as a function of time ($C = f(t)$) for the two catalysts ($TiO_2$/ZnO). $k_{app}$ values could be respectively obtained from the slopes of the regression curves representing by $\ln(C/C_0)$ vs. time. The obtained results are summarized in Table 3. As pH increased, high kinetic constant were obtained in both cases.

## 4. Conclusion

Solar light induced degradation of a dye as an organic pollutant and MB has been completely degraded by both ZnO and $TiO_2$ catalysts. MB solution was completely decolorized. However, complete degradation was observed within 140 and 270 min by ZnO and $TiO_2$, respectively. Therefore, it may be concluded that in solar applications, ZnO will be the best catalyst for the pollutants degradation for less catalyst loading and less time of treatment, best degradation rate was observed.

## Acknowledgments

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## List of symbols

$C_0$ — initial dye concentration, mg $L^{-1}$
$C$ — dye concentration at rime $t$, mg $L^{-1}$
$k_{app}$ — apparent constant kinetic, $min^{-1}$
MB — methylene blue
$r_0$ — initial rate of dye degradation, mg $min^{-1}$
$r$ — reaction rate, mg $min^{-1}$
$R^2$ — linear regression coefficient
$t$ — duration of irradiation, s
$t_{1/2}$ — half-time reaction, min
$TiO_2$ — titanium dioxide
UV — ultraviolet
$X$ % — MB reduced percentage, %
ZnO zinc oxide

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