



## Solar photocatalytic degradation of methylene blue in a fixed bed reactor

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### ABSTRACT

In sustainable development context, solar energy may be adapted to improve the development of green technologies in wastewater treatment. In this paper, the photocatalytic elimination of Methylene Blue (MB) as a reference dye is performed in a fixed bed photoreactor. A commercial  $\text{TiO}_2$  catalyst is immobilized on a cement support irradiated by solar light. The effects of some parameters such as the light source, pH of the solution as well as the pollutant initial concentration were investigated. The results show that the quantity of catalyst affects positively the MB degradation rate unlike the pollutant initial concentration which decreases the degradation efficiency. The degradation efficiency was found higher at around basic pH values (93%–97%). In addition, the degradation rate of pollutant was higher with solar light irradiation (97%) rather than with artificial irradiation (16%). This solar photocatalytic device is a potential application for organic dyes elimination.

*Keywords:* Solar energy; Wastewater treatment; Organic pollutant; Solar photocatalysis; Immobilized catalyst; Cement

### 1. Introduction

The integration of renewable resources in wastewater treatment is becoming increasingly attractive. Given Algerian's abundant solar, wind resources, biomass, geothermal, etc. represent a potential market for renewable energy technologies.

Water pollution due to toxic organic compounds remains a serious problem for human life. Wastewater released from several industrial companies needs to be treated before discharge to the environment by cost-effective technologies. Among these technologies, Advanced Oxidation Processes (AOP's) for purification of wastewater are promising methods [1–4]. One of these (AOP's) is the solar photocatalysis, which is considered as green technology by excellence for the treatment of organics pollutant. Efficient photocatalyst that can be used in solar light conversion technologies is Titanium dioxide. Photocatalysis reactors can be designed in two configurations: reactors in which the catalyst is suspended in the

reaction mixture and reactors that utilize the photocatalyst immobilized/deposited on different surfaces (glass, metals, membranes, etc).

$\text{TiO}_2$  photocatalyst is used in different applications such as self-cleaning surfaces, water purification, air purification, anticorrosion applications and photocatalytic lithography. This study will focus on the application of immobilized  $\text{TiO}_2$  for photodegradation of organic compounds.

Several research works have reported the  $\text{TiO}_2$  mixing procedure with water and cement. Cement is one of the most used man-made substances, applied on a large scale in the production of spectra of cement-based construction materials (mortars, concrete, and renders).

Extremely large surfaces of cement-based materials in build environment and infrastructural objects (buildings, industrial plants, tunnels, pavements, roads, tunnels, bridges, etc.) are exposed to changes and increasingly polluted environment, causing gradual deterioration of both surface properties and structural characteristics of different construction materials. Prolonged durability and lower costs

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of the maintenance of build environment surfaces is one of the main challenges in developing new construction materials of improved properties [5].

The increasing interest in combining photocatalytic active material with cementitious material has been recognized in a number of publications [6–10] as well as in the development of some commercial products [11]. Most of the published research refers to the application of nano-sized  $\text{TiO}_2$  semiconductor as photocatalytic active material [6,10,12–14]. Also some of serious challenges which need to be approached in developing new functionality: achieving sufficient and stable photocatalytic activity in changing conditions of real environment. Maintaining or even improving the key building material properties in the modified structure, especially physical and mechanical; developing of photocatalytic active material having adequate compatibility with the substrate and therefore durability in aggressive outdoor environment [6,7,15]. Different techniques for  $\text{TiO}_2$  application in the cement-based matrix have been used, such as: mixing with the cementitious materials, sputtering, spray coating and sol-gel dip coating [16].

Turchi and Ollis [17] made a detailed investigation on the reaction mechanism of  $\text{TiO}_2$ -photocatalysis. It has been reported in the literature that initial rates of photodegradation of different compounds are pretty close under identical conditions.

This can only be explained by a rate limiting step consisting of hydroxyl radical formation or attack. Since, adsorption is considered critical in the heterogeneous photocatalytic process, the Langmuir-Hinshelwood model was used to describe the photo-oxidation kinetics of dyes by a few previous researchers [18]. Langmuir-Hinshelwood pseudo first order kinetic model, modified to accommodate reactions occurring at a solid-liquid interface is as follows [19]:

$$(r) = -\frac{dC}{dt} = \frac{kKC}{1+KC} = \frac{k_{app}C}{1+kC+K_sC_s} \quad (1)$$

where  $r$ , is the rate of degradation of the pollutant (mg/L min),  $k$ , the rate constant reaction in mg/L.min,  $K$ , adsorption equilibrium constant of the reactant in L/mg;  $C$ , the pollutant concentration of solution at any time  $t$  in mg/L,  $k_{app}$ , apparent rate constant of degradation in min<sup>-1</sup>,  $K_sC_s$ , contribution of solvent.

Two cases are possible:

- For a dilute solutions  $KC \ll 1$

$$(r) = -\frac{dC}{dt} = kKC = k_{app}C \quad (2)$$

where  $k_{app}$  of pseudo first order differential Eq. (2) can be integrated according to:

$$\ln(C_0/C) = k_{app} \cdot t \quad (3)$$

The apparent rate constant  $k_{app}$  is determined by the slope of the curve obtained by representing  $\ln(C_0/C)$  as a function of time  $t$ .

- At high concentrations, Eq. (1) can be simplified and reduced to a zero-order kinetics, its integral form is given by Eq. (4):

$$(C_0/C) = k_{app} \cdot t \quad (4)$$

The aim of this work is to study the efficiency of the catalyst fixed bed on the cement surface for the degradation of some recalcitrant pollutants under solar irradiation. The photocatalytic cementitious system was used to degrade Methylene Blue (MB) in aqueous solution. The photocatalytic study was targeting the evaluation of kinetic and the effect of some parameters affecting MB degradation such as the effects of light source, amount of catalyst, pH and the pollutant initial concentration.

## 2. Materials and methods

### 2.1. Chemicals and reagents

The photoreactor is made of an Algerian cement “Sarie brand,” composed of 6%–9% tricalcium aluminate  $\text{C}_3\text{A}$  and has a finess following the Blaine method (NA231) (3,500–4,500).

The pollutant Methylene Blue (Fig. 1)  $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ , azoic dye used as model to prove photocatalytic activity by ISO 10678:2010, with the max absorption wavelength of 664 nm, provided by Biochem Chemopharma (Montreal, Quebec).

The photocatalyst used in our experiments is commercial  $\text{TiO}_2$  produced by the Chemical Factory “BIOCHEM Chemo Pharma” (Quebec, Canada). The surface area, particle size, morphology, and other characteristics of  $\text{TiO}_2$  catalyst were determined.

### 2.2. Composite $\text{TiO}_2$ -cement preparation

The commercial titanium dioxide was supported on the cement surface by wet impregnation method. An amount of  $\text{TiO}_2$  is mixed with the minimal amount of water that is necessary to wet the solid catalyst to be easily dispersed on the cement surface. Following slow evaporation of water, the cement surface is dried in the oven.

### 2.3. Solar photoreactor

The photocatalytic degradation of pollutant was carried out in a photoreactor developed at the Unit of Solar Equipment Development (UDES) on the north of Algeria (latitude  $36^\circ.39'$ ; longitude  $2^\circ.42'$  at sea level), during the period from July to August 2013, using solar light irradiation.

The photoreactor is a Pyrex glass tank with effective volume of 5 L (32 cm Length  $\times$  24 cm Wide  $\times$  6.5 cm Height) as shown in Fig. 2.

The tank is filled with cement having a thickness of 2 cm and 1 g of  $\text{TiO}_2$  powder which was impregnated in the last step of the mixture cement preparation.



Fig. 1. Chemical structure of Methylene Blue.

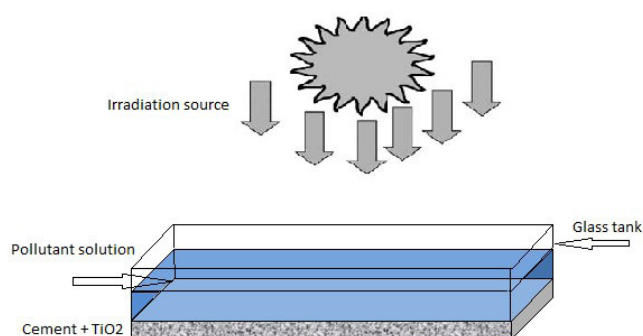


Fig. 2. The solar photoreactor.

#### 2.4. Procedure and analysis

The photoreactor was irradiated by both artificial and solar light. 2 Phillips PL-L 24 W/10/4 P lamps ( $\lambda_{\max} = 365$  nm) were used as artificial irradiation. Solar light was used as natural irradiation source, the solar light intensity was measured by Pyranometer KIPP & Zonen, CMP 11 (285 to 2,800 nm).

One liter of the dye solution with different initial concentrations (5–30 mg/L) in the presence of 1 g of  $\text{TiO}_2$ . The pH of the solution was not adjusted (natural solution pH) except in the section 3.4 (effect of pH) and the temperature was not controlled, it was varying from 25°C to 35°C.

A series of reactors with immobilized  $\text{TiO}_2$  on cement fixed bed with several amount of titanium dioxide (0.65, 1.3 and 2.6 mg/cm<sup>2</sup>) was prepared to study the effect of catalyst amount on dye photodegradation. A sample of 2 mL was pipetted out at 10 min interval. A change in transparency of the dye solution was observed. The dye concentration was recorded by UV Visible spectrophotometer (Shimadzu-1800).

### 3. Results and discussion

#### 3.1. Catalyst characterization

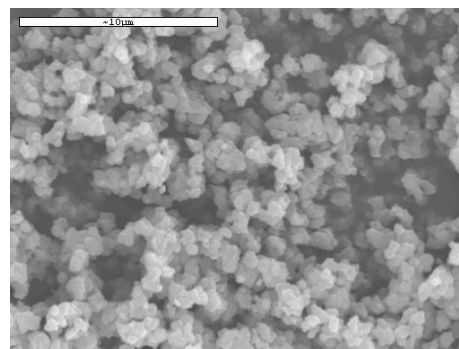
The surface area, particle size, morphology, and other characteristics of  $\text{TiO}_2$  catalyst were determined. The transmission electron microscope (TEM, JEOL JEM-2000EXII) was used to determine the morphology and pore structure of the mesoporous  $\text{TiO}_2$  particle. Scanning electron microscopy (SEM) images given in Fig. 3 are done by microscope PHILIPS XL 30 with a probe microanalysis and imaging X (EDS analysis) type -Princeton, Gamma-Tech.

Measurements of X-ray diffraction were performed on a PW 1729X-RAY GENERATOR brand PHILIPS device. The analysis shows that  $\text{TiO}_2$  has a structure of 90% Anatase and 10% Rutile (Fig. 4).

The Brunauer, Emmett and Teller (BET) surface area was obtained from nitrogen adsorption–desorption data (Micromeritics, ASAP-2010 Surface Area analyzer and reach 4.61 m<sup>2</sup>.g<sup>-1</sup>, mean particle diameter of  $\text{TiO}_2$  is 48 nm.

#### 3.2. Effect of catalyst amount

The quantity of the photocatalyst is most essential parameter that affects the rate of photocatalytic degradation. Experiments were carried with 1 L solution volume, 10 mg/L



Elmt	Spect. Type	Element	Atomic %	Atomic %
C	K	ED	40.42	53.18
O	K	ED	41.30	40.79
Ti	K	ED	18.28	6.03

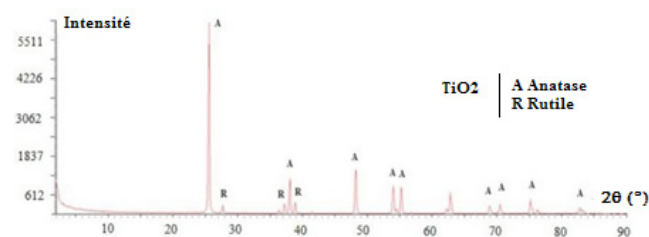
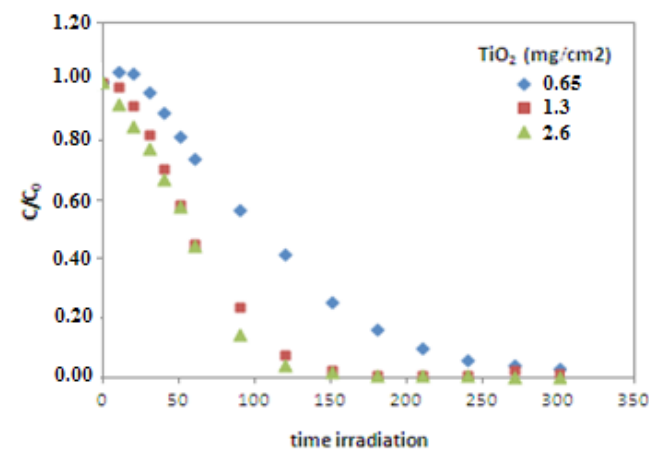
Fig. 3. SEM image of  $\text{TiO}_2$  catalyst using 5,000 Magnification and EDS results.

Fig. 4. X-ray diffraction spectrum.

Fig. 5. Effect of catalyst amount on MB photocatalytic degradation. (MB = 10 mg/L, pH: natural, solar intensity  $Q = 815$  W/m<sup>2</sup>,  $V = 1$  L).

dye concentration, at natural pH in different photoreactors with different catalyst amount 0.65, 1.3 and 2.6 mg/cm<sup>2</sup>. Fig. 5 Shows the MB reduced concentration evolution for different  $\text{TiO}_2$  quantity during 300 min sunshine.

The shapes of the curves are decayed exponentially and predict that the kinetic of Methylene Blue degradation is pseudo-first order. This is confirmed by the trace of  $\ln(C/C_0)$

Table 1

Values of kinetic constants, initial velocities, degradation rate and reaction half-time after 300 min of solar irradiation for different amount of  $\text{TiO}_2$ .  $C_0 = 10 \text{ mg/L}$ , pH: natural,  $V = 1 \text{ L}$

$\text{TiO}_2$ ( $\text{mg}/\text{cm}^2$ )	$K_{\text{app}}$ ( $\text{min}^{-1}$ )	$r_0$ ( $\text{mg}/\text{L}\cdot\text{min}$ )	$t_{1/2}$ (min)	X (%)	$R^2$
0.65	0.010	0.10	6.93	97	0.983
1.30	0.019	0.19	3.65	98	0.992
2.60	0.021	0.21	3.30	99	0.978

vs. time, which is a line through the origin where the apparent rate constant  $k_{\text{app}}$  represents the slope of the line. Table 1 summarizes values of kinetic constants, initial rates, degradation rate and reaction half-time after 300 min of solar irradiation for different amount of  $\text{TiO}_2$ .

In order to define the optimal catalyst quantity, we compared the degradation performance and the reaction half-time. As included in Table 1. We notice that using 0.65, 1.30 and 2.60  $\text{mg}/\text{cm}^2$  as catalyst amount the obtained results are 97, 98 and 99% of MB elimination, respectively. Unlike the half-life, it was doubled for 2.6  $\text{mg}/\text{cm}^2$  of catalyst compared with 0.65  $\text{mg}/\text{cm}^2$ . We concluded that for this mass range the quantity of the catalyst does not affect the rate of degradation. So that, for the rest of the study we used 1.3  $\text{mg}/\text{cm}^2$  to minimize the cost of the product.

### 3.3. Effect of initial pollutant concentration

The kinetics of MB degradation under sunlight irradiation performed in the reactor for different initial concentrations is represented in Fig. 6. The diffusion of reactive species from  $\text{TiO}_2$  surface to the solution is quite low. The adsorption of organic compounds on the surface of semiconductor particles is a parameter that will strongly impact the efficiency of photocatalysis. The relationship between the degradation rates and the initial concentrations of the organic compounds is often modeled by the model of Langmuir–Hinshelwood [20].

The shape of the curves is decayed exponentially and predicts that the kinetics of MB degradation is pseudo-first order. This is confirmed by the trace of  $\ln(C/C_0)$  vs. time as shown in Fig. 7, which is a line through the origin where the apparent rate constant  $k_{\text{app}}$  represents the slope of the line.

The results show that the degradation rate decreases with increasing MB initial concentration; it is 100% and 60% for 5 and 30  $\text{mg}/\text{L}$  of MB initial concentration, respectively. Kinetic constants for each concentration were determined by linear regression from the plot of the evolution of  $\ln(C/C_0)$  vs. time (Fig. 7). The values of kinetic constants, initial rates, degradation rate and reaction half-time after 300 min of solar irradiation for different MB initial concentrations are summarized in Table 2.

Table 2 shows that the photocatalytic degradation of MB is faster at low concentrations, which is confirmed by the values of the initial rate  $r_0$  (0.24  $\text{mg}/\text{L}\cdot\text{min}$  for 5  $\text{mg}/\text{L}$ ) against 0.03  $\text{mg}/\text{L}\cdot\text{min}$  for 30  $\text{mg}/\text{L}$ . The results predict us to increase the amount of catalyst for the high MB concentrations in the future studies.

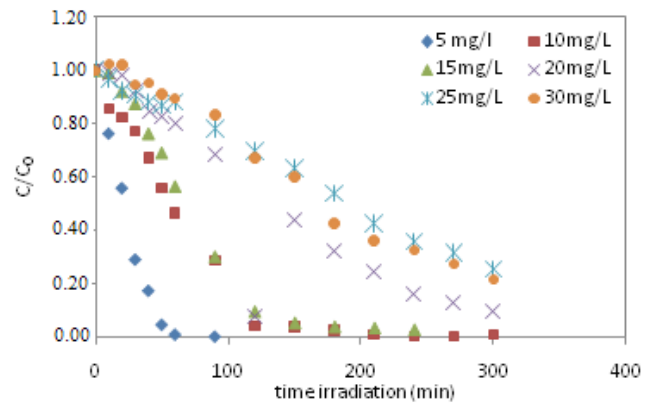


Fig. 6. Effect of the initial concentration of MB. ( $\text{TiO}_2$ : 1.3  $\text{mg}/\text{cm}^2$ , pH: natural, solar intensity  $Q = 815 \text{ W}/\text{m}^2$ ,  $V = 1 \text{ L}$ ).

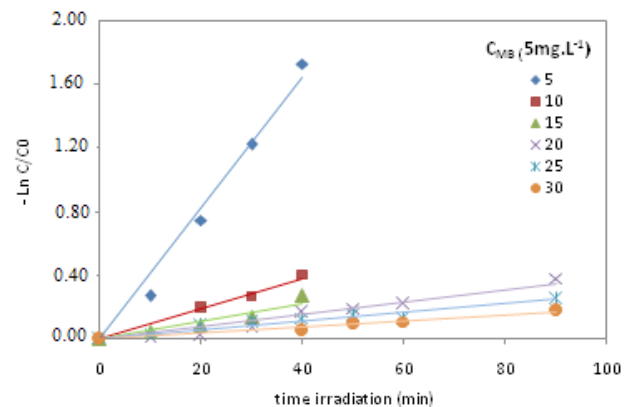


Fig. 7. Kinetics of MB degradation for different initial concentrations. ( $\text{TiO}_2$ : 1.3  $\text{mg}/\text{cm}^2$ , pH: natural, solar intensity  $Q = 815 \text{ W}/\text{m}^2$ ,  $V = 1 \text{ L}$ ).

Table 2

Values of kinetic constants, initial rates, degradation rate and the reaction half-time after 300 min of solar irradiation for different initial MB concentrations. ( $\text{TiO}_2$  1.3  $\text{mg}/\text{cm}^2$ , pH: Natural, Solar UV,  $V = 1 \text{ L}$ )

$C_{\text{MB}}$ ( $\text{mg}\cdot\text{L}^{-1}$ )	$k_{\text{app}}$ ( $\text{min}^{-1}$ )	$r_0$ ( $\text{mg}/\text{L}\cdot\text{min}$ )	$t_{1/2}$ (min)	X (%)	$R^2$
5	0.041	0.205	17	100	0.983
10	0.009	0.090	77	99	0.989
15	0.005	0.075	139	99	0.895
20	0.003	0.060	231	90	0.941
25	0.003	0.090	231	74	0.921
30	0.002	0.050	346	60	0.952

### 3.4. Effect of irradiation source

The objective of this experiment is the comparison of two light sources, one artificial light (UV lamp) and the other natural (Solar UV). The photoreactor was irradiated by a 2 Phillips PL-L 24 W/10/4 P lamps ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) and a solar light, for the different radiation sources tested, solar and



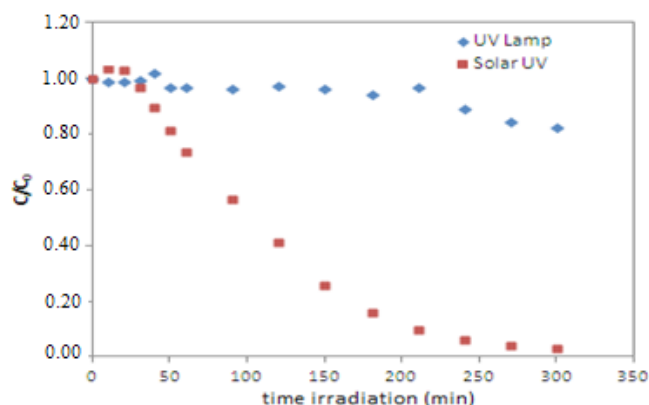


Fig. 8. The temporal variation of the performance degradation of MB for solar and lamp irradiation.

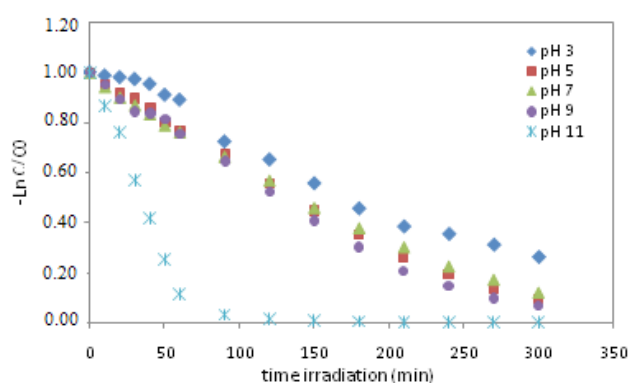


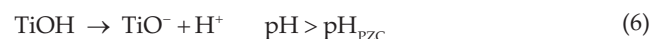
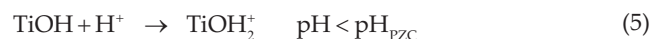
Fig. 9. Solar degradation of MB at different pH values. ( $\text{TiO}_2$  1.3 mg/cm<sup>2</sup>,  $\text{MB}_0 = 10 \text{ mg.L}^{-1}$ , solar intensity  $Q = 815 \text{ W/m}^2$ ,  $V = 1 \text{ L}$ ).

lamp same experiments was carried. Fig. 8 shows the temporal variation of the performance degradation of MB for solar and lamp radiation.

The obtained results show that the degradation rate of methylene blue using sunlight was higher, it attained 97% against the UV lamp and it was only 16%. This can be due to the absorbance of MB in visible light at 664 nm.

### 3.5. Effect of pH

The pH is a complex parameter since it is related to the ionization state of the surface and the pH Zéro Charge ( $\text{pH}_{\text{PZC}}$ ). For  $\text{TiO}_2$ , the  $\text{pH}_{\text{PZC}}$  is between 6 and 6.5 [21].



Five pH values have been selected: two acidic (3 and 5), two basic (9 and 11) and neutral pH (7). The pH values were adjusted by adding a basic (NaOH: 1 M.) or acidic (HCl: 1 M.) solution to the feed. The solar degradation of MB for the five pH values was given in Fig. 9.

It can be seen that the solar degradation of MB was favored at basic and neutral pH. The MB degradation

Table 3

Values of kinetic constants, initial rates, degradation rate and the reaction half-time after 300 min of solar irradiation for different initial pH of solution. ( $\text{TiO}_2$  1.3 mg/cm<sup>2</sup>,  $C_{\text{MB}} = 10 \text{ mg.L}^{-1}$ , Solar UV,  $V = 1 \text{ L}$ )

pH	$k_{\text{app}}$ (min <sup>-1</sup> )	$r_0$ (mg/L.min)	$t_{1/2}$ (min)	X (%)	$R^2$
3	0.001	0.01	693	74	0.959
5	0.004	0.04	173	88	0.983
7	0.004	0.04	173	90	0.991
9	0.004	0.04	173	93	0.966
11	0.019	0.19	36	99	0.976

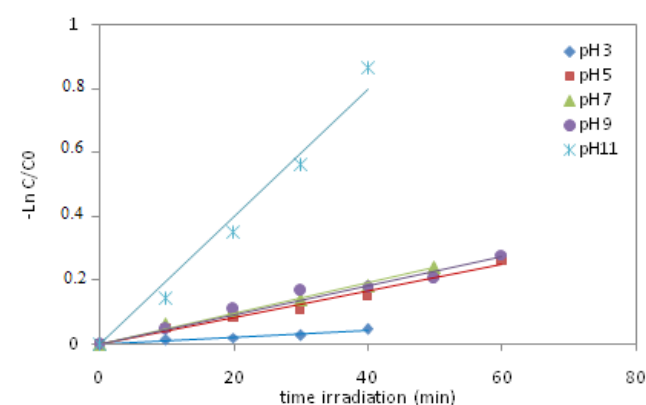


Fig. 10. Rate of the photocatalytic degradation of MB at different pH values. ( $\text{TiO}_2$  1.3 mg/cm<sup>2</sup>,  $\text{MB}_0 = 10 \text{ mg.L}^{-1}$ , solar UV,  $V = 1 \text{ L}$ ).

increases with increasing pH of the solution (Fig. 9). Increases in rate of MB photocatalytic degradation may be due to more availability to  $\text{OH}^-$  ions by combining with holes, which are performed due to electronic excitation in catalyst in pH range 11. Formation of hydroxyl radicals are responsible more for photocatalytic degradation than supra oxide ( $\text{O}_2^-$ ) [22].

As shown in the Table 3 and Fig. 10, the photodegradation rate of MB is important for neutral to basic pH values, where the degradation percentage reach 99% in the case of pH 11. The lowest reaction half-time is noted for the same pH.

## 4. Conclusion

The present study consists on the use of cement catalyst system for wastewater treatment under solar irradiation. The efficiency of this process has been proven by experiments using  $\text{TiO}_2$  as catalyst fixed on the cement support by impregnation method.

The photocatalytic degradation of MB was effective and reaches more than 90% after 300 min of solar irradiation. A total discoloration of the solution was observed for 5 mg/L of MB initial concentration using 1.6 mg/cm<sup>2</sup> of catalyst after few minutes of the reaction.

For the range of 0.65–2.6 mg/cm<sup>2</sup> of catalyst the obtained results show that the same rate of degradation is achieved. The degradation of Methylene Blue has been investigated in various experimental conditions. The results suggested that

the Kinetic of MB photocatalytic degradation is first order. Basic and neutral pH promotes the photocatalytic degradation of MB.

The photocatalytic degradation of the colored effluents using TiO<sub>2</sub>-cement system has the potential to improve the quality of the wastewater from textile and other industries.

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