International Journal of PharmTech Research
CODEN (USA): IJPRIF, ISSN: 0974-4304
Vol.8, No.2, pp 289-297, 2015

# Photocatalytic Decolorization of Brilliant Cresyl Blue using Zinc Oxide

**Hazim Y. Al-Gubury[1]*, and Ghadeer S Al – Murshidy[2]**

**[1,2] Babylon University, College of Science for Women, Chemistry Department-Iraq.**

**Abstract:** This research include, photocatalytic decolorization of an aqueous solution of 3 ppm of brilliant cresyl blue in a suspension of 0.11gm/100 ml of ZnO metal oxide semiconductor as a catalyst, was carried out by using 125Watts mercury lamp from external source inside a Pyrex photoreaction cell of 100 ml at room temperature 298 K. The effect of various parameters, such as mass of catalyst, initial dye concentration, and light intensity was studied. The disappearance of original colored dye concentration with irradiation time was monitored by using UV-VIS spectrophotometer. The results indicate that this photoreaction is a pseudo first order reaction according to the Langmuir -Hinshelwood relationship. It has been observed that the increase of light intensity leads to the increase of decolorization rate of brilliant cresyl blue.

**Keywords:** Photcatalytic process, Decolorization, Brilliant **c**resyl blue .Zinc oxide, and Irradiation.

## Introduction

In few years ago, environmental contaminations has been major problem because excess use of various dyes in the textile industry, this led to polluted the surface water and groundwater by releasing the toxic and colored effluents[1,2].

Different ways used to wastewater treatment, the most important one of them advanced oxide processes (AOP) method .It has attracted public concern for its ability to convert the pollutants into the harmless substances directly in the waste water.

In these manner, hydroxyl radicals (˙OH) was generated as strong oxidizing agents $E$ = 2.8 V, this reactive radical capable of mineralizing organic pollutants[3,4].

Advanced Oxidation Processes, used to treat the organic pollutants to $CO_2$ and inorganic acids[5] by using heterogeneous photo-catalytic oxidation process, Zinc oxide metal oxide semiconductor used in this method as a catalyst and has the ability to de-toxificate water from a number of organic and complete destruction of dyes pollutants such as pesticides[6]. Zinc oxide is n-type metal oxide semiconductor with band gap (3.37 eV) .Zinc oxide used extensively in rubber, paint, cosmetics and textile industry[7].

When zinc oxide semiconductor irradiated using UV light with energy equal to or greater than the band gap[8], electrons are promoted from the valence band to the conduction band of the zinc oxide semiconducting oxide to give electron–hole pairs. The valence band hole($h^+$) potential is positive enough to generate hydroxyl radicals at the surface. Also, the conduction band electron ($e^-$) is negative enough to reduce the oxygen molecules, present in the solution, which in turn leads to the generation of another series of hydroxyl radicals[9,10].

As shown in figure (1) :

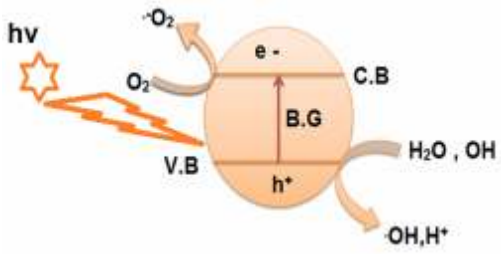



**Figure1: mechanism of UV / ZnO photocatalysis**

## Materials and Methods

### Chemicals:

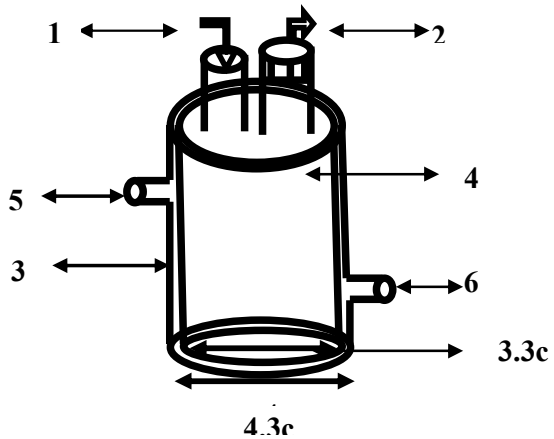
1-Zinc oxide ( ZnO ) : purity ( 98%) , supplied by Fluka AG.

2 – brilliant cresyl blue supplied by sigma – Aldrich .

### Photo reactor and Procedure:

Experiments were carried out in glass photochemical reactor. The cylindrical annular – type reactor consisted of two parts. The first part was an outside thimble, Running water was passed through the thimble to cool the reaction solution. Owing to the continuous cooling, the temperature of the reaction solution was maintained of room temperature. The second part was an inside thimble and the reaction solution (volume 100 ml) was put in the reaction chamber.

Schematic diagram of photochemical reaction as shown in figure (2) :




**1- Air inlet**
**2- Air outlet and sampling**
**3- Cooling Chamber**
**4- Reaction Chamber**
**5- Water inlet**
**6- Water outlet**

**Figure 2 : Main parts of the photocatalytic cell used in Photcatalytic degradation of brilliant cresyl blue**

### Irradiation System :

A block diagram of photolysis apparatus is shown in figure ( 3 ) a 125Watts mercury lamp source is a focusing fitted with a focusing lens to ensure parallel beam of light .

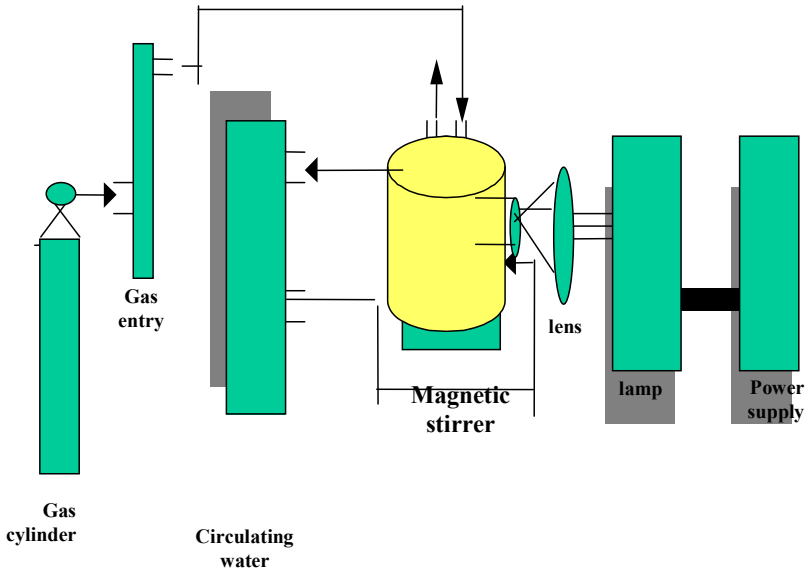



**Figure 3 : Schematic diagram of the experimental apparatus.**

## Results and Discussion

### Effect of Different Parameters on Photocatalyst Decolorization of brilliant cresyl blue :

### 1 - Effect of mass catalyst of zinc oxide on photo catalytic degradation of brilliant cresyl blue :

The effect of photocatalyst mass of zinc oxide on the photocatalytic decolorization of brilliant cresyl blue was investigated under experimental condition with initial brilliant cresyl blue concentration of 3ppm, light intensity equal to 8.22 $mW.cm^{-2}$, temperature equal to 298K and flow rate of air 10 ml/min. This behavior can be explained on the basis that on increasing catalyst concentration the active site on the catalyst surface increases.

Table (1) and Figure (4) represent photo catalytic degradation processes of brilliant cresyl blue at different loaded mass of zinc oxide. Photocatalytic decolorization of brilliant cresyl blue, gradually increases as the masses of zinc oxide increases due to increasing the active site on the catalyst surface until reach to the optimum photocatalytic activity 0.11 gm/100ml , then gradually decreases. When the mass of zinc oxide equal 0.11 gm /100ml the semiconductor zinc oxide can provide the highest absorption of light. The decrease in the efficiency of phtocatalytic degradation process at the masses of zinc oxide higher than 0.11 gm /100 ml due to the light absorption will be limited only to the first layers of brilliant cresyl blue and the other layers of solution do not receive light photons. Moreover light scattering at high zinc oxide loading , this lead to decrease the photon intensity, so the strong absorption of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel .Many workers studied this effect[11,12]. At the loading mass of zinc oxide below the optimum value 0.11 gm /100 ml the rate of photodegradation of brilliant cresyl blue also decrease due to the quantity of mass of zinc oxide decrease that mean the surface area decrease which lead to decrease of light absorption of light by zinc oxide which cause lower photodegradation rate of brilliant cresyl blue.

The results illustrated in figure 5 which shows the pseudo first order reaction curve for various catalyst concentration according to Langmuir Hinshelwood relationship. The kinetic results are plotted in figure 6 which shows that the rate constant of reaction generally increases with increase of photocatalyst concentration.

**Table 1 The change of $A_t/A_0$ with irradiation time using different masses of zinc oxide.**

| Catalyst mass g /100 ml | 0.02 | 0.04 | 0.11 | 0.30 | 0.50 |
|---|---|---|---|---|---|
| Irradiation Time/min | $A_t/A_0$ | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 10 | 0.78 | 0.66 | 0.50 | 0.84 | 0.92 |
| 20 | 0.55 | 0.42 | 0.23 | 0.64 | 0.77 |
| 30 | 0.30 | 0.22 | 0.10 | 0.45 | 0.64 |
| 40 | 0.23 | 0.15 | 0.06 | 0.37 | 0.53 |
| 50 | 0.21 | 0.12 | 0.04 | 0.30 | 0.45 |
| 60 | 0.18 | 0.11 | 0.02 | 0.28 | 0.44 |

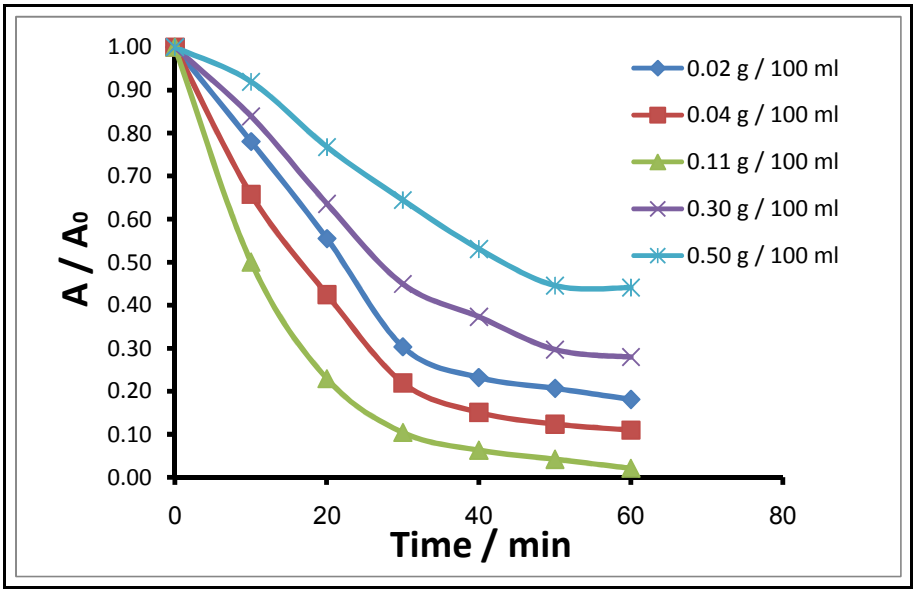



**Figure 4 The effect masses of zinc oxide on Photcatalytic degradation of brilliant cresyl blue .**

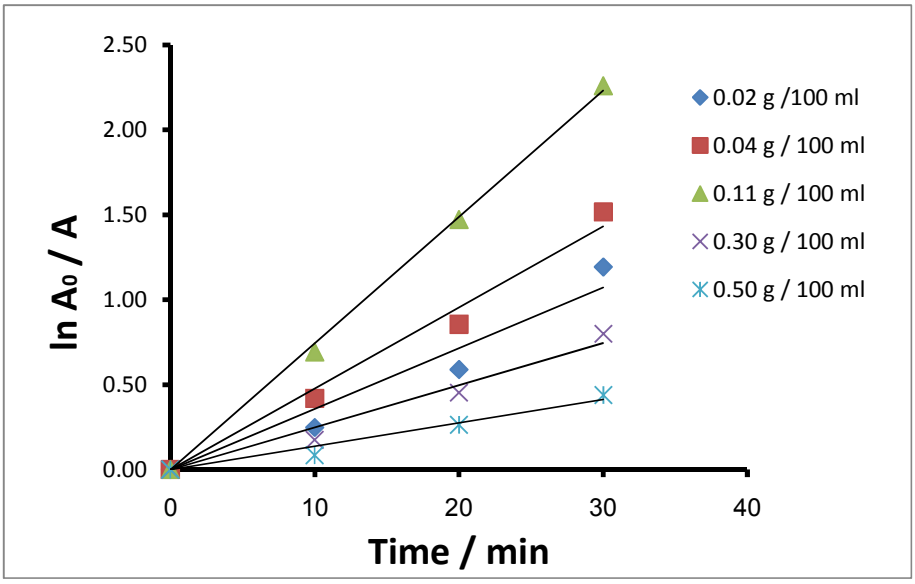



**Figure 5 : The change of $lnC/C_0$ with irradiation time at different masses of ZnO.**

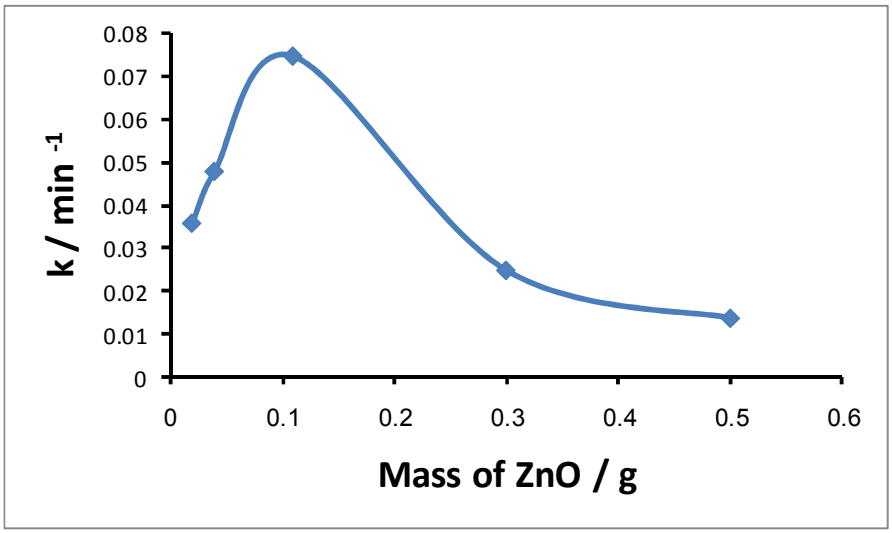



**Figure 6 : Effect of masses of ZnO on rate constant.**

**2- The Effect of initial brilliant cresyl blue concentration on photo catalytic degradation processes:**

A different experiments have been done, the effect of change initial rang (3–30 ppm) on photocatalytic degradation process of brilliant cresyl blue was studied using the optimum mass of zinc oxide 0.11gm / 100 ml, the light intensity equal to 8.22 mW/cm$^2$, and temperature equal to 298 K. The results are listed in Table 2 and plotted in figure 7. It has been observed that the rate of photocatalytic degradation gradually decreases with the increasing of initial brilliant cresyl blue concentration when the brilliant cresyl blue concentration decreases, the decolorization of dye increases, this behavior is due to the decrease of the concentration $OH^-$ adsorbed on catalyst surface with the increase of dye concentration. The concentration 3ppm was the optimum concentration to cover the largest area of the zinc oxide particles, therefore absorbed maximum exciting photons to generate higher concentration of the activated zinc oxide semiconductor. Another reason for this behavior is the strong absorption of light by the brilliant cresyl blue in the sample which contain high concentration that 3 ppm, brilliant cresyl blue on 0.11 gm /100ml of titanium dioxide . The excess of brilliant cresyl blue prevent the penetration of light through the successive layers of brilliant cresyl blue on the zinc oxide surface is weak to generate the required excited state of the brilliant cresyl blue adsorbed on zinc oxide[13,14]. The results illustrated in figure 8 which shows the pseudo first order reaction curve for various catalyst concentration according to Langmuir Hinshelwood relationship. Figures 9 show that the inverse proportionality of rate constant of decolorization reaction with dye concentration is due to decreases of light intensity which reaches to the catalyst surface and consequently photon absorption on surface of catalyst is reduced with the increasing the dye concentration. When the dye concentration increases, the path length of photon entering the solution is decrease and as a result, the rate of decolorization of dye decreases.

**Table 2 The change of $A_t$ /$A_0$ with irradiation time using different concentration of brilliant cresyl blue**

| Concentration of brilliant cresyl blue / ppm | 3 | 5 | 10 | 15 | 30 |
|---|---|---|---|---|---|
| Irradiation Time/min | $A_t$ /$A_0$ | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 10 | 0.69 | 0.77 | 0.85 | 0.88 | 0.93 |
| 20 | 0.53 | 0.65 | 0.70 | 0.76 | 0.87 |
| 30 | 0.40 | 0.54 | 0.65 | 0.71 | 0.80 |
| 40 | 0.27 | 0.47 | 0.56 | 0.65 | 0.73 |
| 50 | 0.13 | 0.38 | 0.49 | 0.59 | 0.67 |
| 60 | 0.11 | 0.32 | 0.49 | 0.59 | 0.67 |

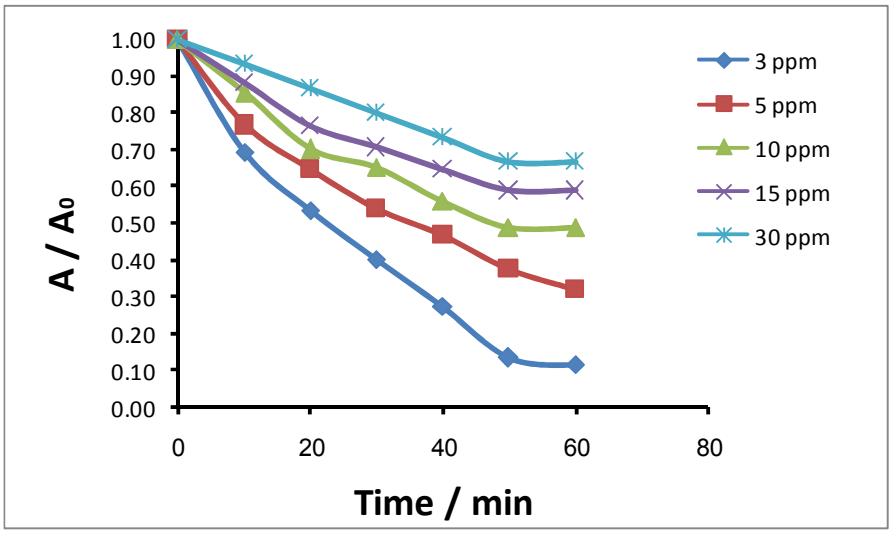



**Figure 7 : The change of ( A / $A_0$ )with irradiation time at concentration of brilliant cresyl blue .**

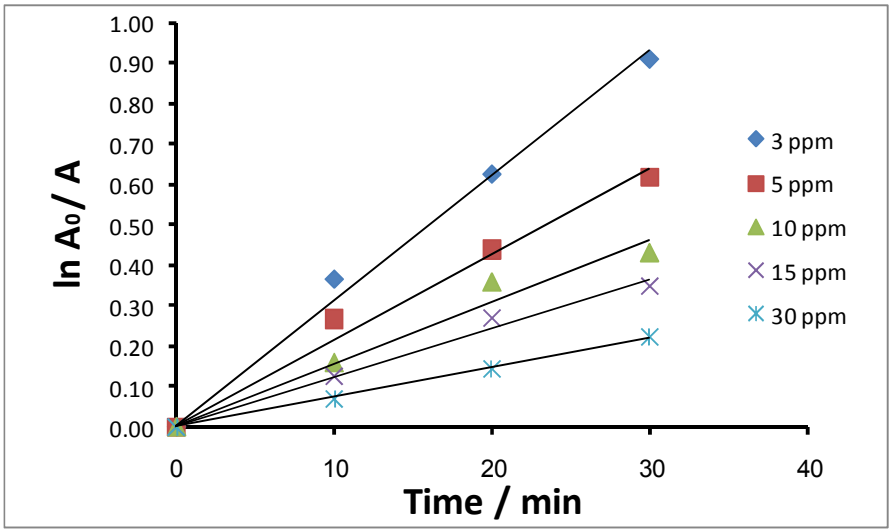



**Figure 8 : The change of ln$C/C_0$ with irradiation time at different concentration of brilliant cresyl blue .**

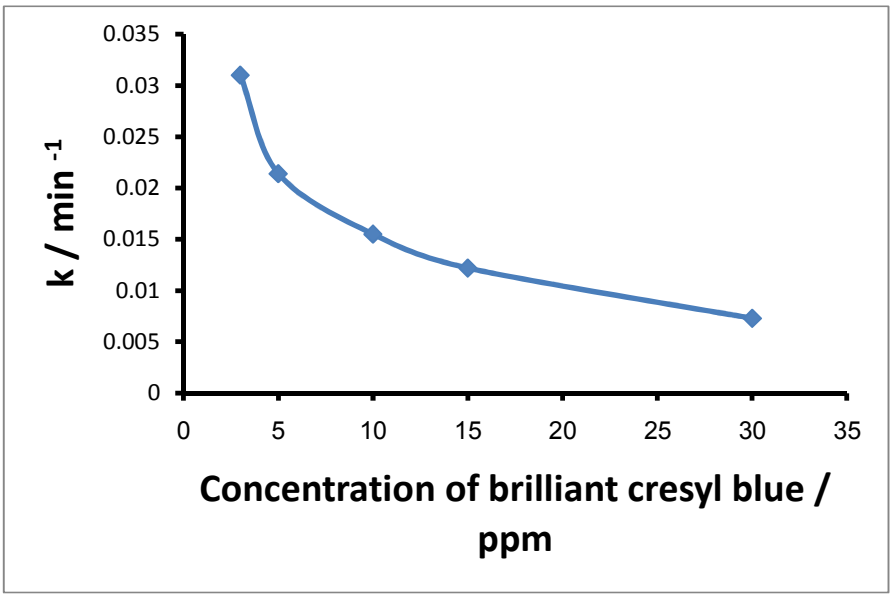



**Figure 9 : Effect of concentration of brilliant cresyl blue on rate constant.**

**3 – Effect of light intensity on photocatalytic degradation process of brilliant cresyl blue.**

A serious of experiment were carry out to study the effect of light intensity range (2.15 – 8.22) mW/cm$^2$ from high mercury lamp 125 watts, all experiments was studied using optimum condition, the weight of loaded of zinc oxide 0.11gm/ 100 ml and the initial concentration of brilliant cresyl blue 3 ppm, with flow rate of air bubbling is kept constant at 10 ml/min, at room temperature 298K.

Table 3 and figure 10 , illustrate the effect of light intensity on the photocatalytic degradation of brilliant cresyl blue. The results indicate that the photocatalytic degradation of brilliant cresyl blue increases with the increase of light intensity, the maximum value of light intensity 8.22 mW/cm$^2$. In general the used lamp production photons, this photons increase electrons transfer from valance band to conduction band in the zinc oxide lead to the increase of the number of electron–hole pairs and increases the decolorization efficiency of brilliant cresyl blue[15,16].

The results illustrated in figure 11 which shows the pseudo first order reaction curve for various catalyst concentration according to Langmuir Hinshelwood relationship. The results also show that the effect of light intensity on rate constant of photocatalyst decolorization of brilliant cresyl blue increase of the light intensity leading to the increase of rate constant. These results which are plotted in figures 12. the recombination rate of photogeneration electron-hole pairs increase, preventing the generation rate of $OH^{\bullet}$ radical. The rate constant is proportional to the generation of $OH^{\bullet}$ radicals on catalyst surface.

**Table 3 The change of $A_t/A_0$ with irradiation time using different light intensity.**

| light intensity/ mW/cm$^2$ | 8.22 | 4.00 | 2.80 | 2.15 |
|---|---|---|---|---|
| Irradiation Time/min | $A_t/A_0$ | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 |
| 10 | 0.62 | 0.71 | 0.89 | 0.93 |
| 20 | 0.39 | 0.57 | 0.82 | 0.91 |
| 30 | 0.21 | 0.48 | 0.77 | 0.88 |
| 40 | 0.15 | 0.43 | 0.72 | 0.86 |
| 50 | 0.13 | 0.35 | 0.68 | 0.82 |
| 60 | 0.11 | 0.33 | 0.66 | 0.80 |

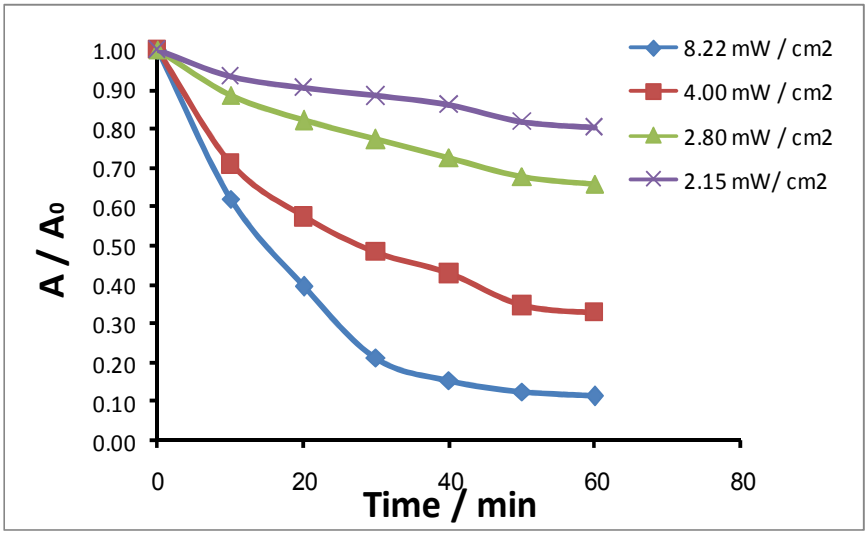



**Figure 10 : The change of ( A / $A_0$ )with irradiation time at different light intensity with 0.11 gm/100ml zinc oxide on photocatalytic decolorization of brilliant cresyl blue .**

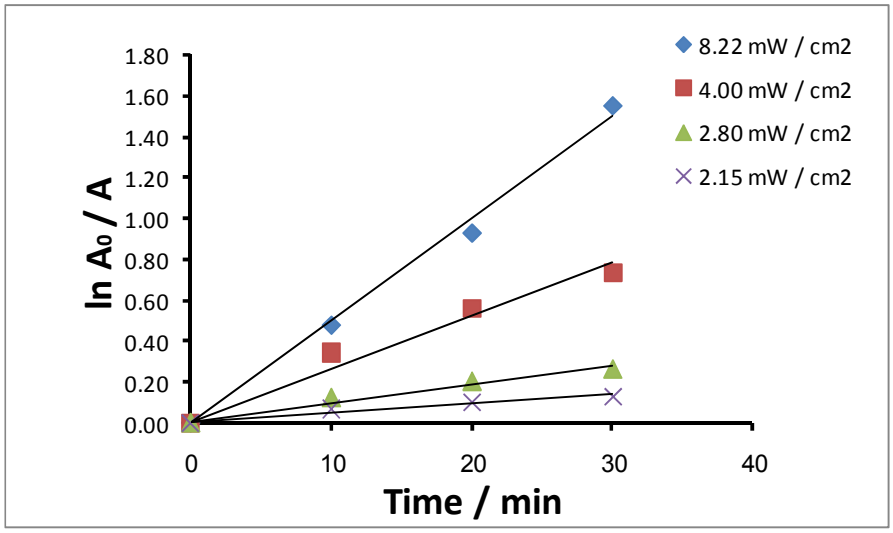



**Figure 11 : The change of ln$C/C_0$ with irradiation time at different light intensity.**

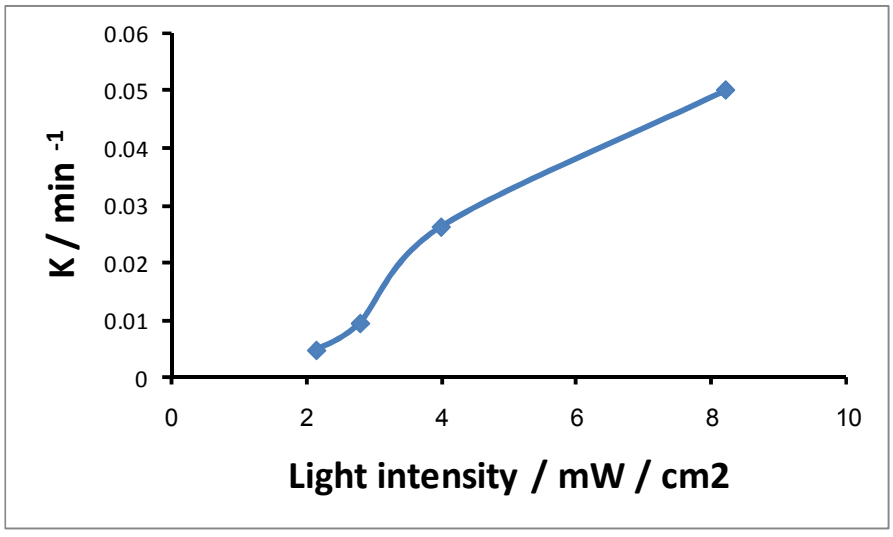



**Figure 12 : Effect of light intensity on rate constant.**

## Conclusion

1 – The compound has been not degraded in case of absent of catalyst.

2 – The compound has been successfully degraded when used the catalyst with the light.

3 – The optimum condition for the Photcatalytic decolorization of brilliant cresyl blue equal 0.11 gm / 100 ml mass of zinc oxide and 3 ppm concentration of brilliant cresyl blue and 8.22 $mW/cm^2$.

4 – The hydrogen peroxide increases photocatalytic degradation of brilliant cresyl blue.

**Acknowledgements**

Insincerely thank for the University of Babylon, College of Science for Women-Iraq, for providing the necessary infrastructural facilities during my research.

## References

1. Yuanjie S., Ya Y.,Hulin Z., Yannan X., Zhiming W.,Yadong J., Naoki F., Yoshio B. and Zhong L.W., Enhanced photodegradation of methyl orange with $TiO_2$ nanoparticles using a triboelectric nanogenerator, Nanotechnology, 2013, 24, 6, 2013.
2. Lis S., and Nor H., Parveen J., Immobilization of $TiO_2$ with cement: Photocatalytic degradation of phenol and its kinetic studies, Indian Journal of chemical Technology,2011,18,263-270.
3. Pankaj N., Sayli D.,and Parag R., Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation, Ultrasonics Sonochemistry,2014, 21 , 1770–1777.
4. Alok D., and Wonyong C., Review of iron-free Fenton-like systems for activating $H_2O_2$ in advanced oxidation processes, Journal of Hazardous Materials,2014, 275 ,121–135.
5. Meeti M, and Sharma T. , Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst $TiO_2$ , Advances in Applied Science Research,2012, 3( 2), 849-853.
6. El Yadini A., Marouane B., Ahmido A., Dunlop P., Anthony Byrne J. , EL Azzouzi1 M., and EL Hajjaji S., Photolysis and photodegradation of Fenamiphos insecticide by using slurry and supported $TiO_2$, J. Mater. Environ. Sci. 2013,4 (6), 973-980.
7. Surabhi S., Putcha V., Vanka R. and Gollapalli N., Synthesis, characterization and optical properties of zinc oxide nanoparticles, International Nano Letters 2013, 1- 6.
8. Patrick W., and Dietmar S., Photodegradation of rhodamine B in aqueous solution via $SiO_2/TiO_2$ nano-spheres, Journal of Photochemistry and Photobiology A: Chemistry,2007, 185, 19–25.
9. Hadj B ., Messaoud C., Thierry S. , Jérémy G., Angélique L., Stéphanie D. , Michel C., and Benoît H. , Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol–gel process, Alexandria Engineering Journal,2013,52(3),517 – 523 .
10. Zulkarnain Z., Lee K., Mohd Z., Abdul Halim, A., and Imad R., Characterization of TiO2–Chitosan/Glass photocatalyst for the removal of a monoazo dye via photodegradation–adsorption process, Journal of Hazardous Materials, 2009,164,138 – 145 .
11. Kai W., Juan X., Xia H., Na L., Mindong Ch., Fei T., Yongfa Z., and WenqingY., Highly efficient photodegradation of RhB–MO mixture dye wastewater by$Ag_3PO_4$ dodecahedrons under acidic condition, Journal of Molecular Catalysis A: Chemical,2014,393,302 – 308 .
12. Hazim Y. Al-gubury and Hedear H. Alsaady, Photcatalytic Degradation of Rhodamine b using Titanium Dioxide, International Journal of Multidisciplinary and Current Research, 2015,3 .
13. Charanpahari A., Umare S., and Sasikala R., Enhanced photodegradation of dyes on Bi2O3 microflakes: Effect of $GeO_2$ addition on photocatalytic activity, Separation and Purification Technology,2014,133, 438– 442.
14. Junfeng N., Lilan Z., Yang L., Jinbo Z., Sidan L., and Keqing X., Effects of environmental factors on sulfamethoxazole photodegradation undersimulated sunlight irradiation: Kinetics and mechanism, Journal of Environmental Sciences, 2013, 25(6) 1098–1106.
15. Meena R.,and Ram P. ,Photocatalytic degradation of model textile azo dyes in textile wastewater using methylene blue immobilized resin dowex-11,Journal of Scientific Industrial Research ,2009,68,730–734.
16. Modh S.,Anil K.,Mukesh P.,Rameshwar A., and Khandelwal R.,Degradation of organic effluents containing wastewater by photo-Fenton oxidation process, Indian Journal of Chemistry,2008,47A,1681 – 1684.

*****