



## Photocatalytic Decomposition of Dye polluted Wastewater Using Titanium Dioxide and Graphitic Carbon Nitride.



Abdelaziz A. Noaman \*

Minia University, Faculty of Engineering, Chemical Eng. Dept., Minia, P.O. Box 61519, Egypt.

### Abstract

Advanced oxidation process (AOPs) is an alternative to the classical wastewater treatment methods which are environmentally friendly, producing harmless end-products such as CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. APOs are in-situ treatment processes characterized by the generation of highly reactive intermediates (OH radicals) which can oxidize the target organic pollutants.

This paper studied the operational parameters influencing the photocatalytic degradation rate of methylene blue in dye polluted wastewater treatment. These parameters are initial dye concentration, catalyst concentration, H<sub>2</sub>O<sub>2</sub> volume. The catalysts used were titanium dioxide (TiO<sub>2</sub>) and supported Graphene (g-C<sub>3</sub>N<sub>4</sub>). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used in all experimental work to increase the efficiency of the UV / TiO<sub>2</sub> process and supported Graphene (g-C<sub>3</sub>N<sub>4</sub>).

The experiments of UV lamp revealed that the best degradation is at 5 ppm initial dye concentration, 0.5 g from g-C<sub>3</sub>N<sub>4</sub> and 5 ml/dm<sup>3</sup> H<sub>2</sub>O<sub>2</sub> with efficiency 54.8 % at 180 minutes by using solar UV. The experiments of solar UV illustrated that the best degradation is at 15 ppm initial dye concentration, 0.5 g from g-C<sub>3</sub>N<sub>4</sub> and 5 ml H<sub>2</sub>O<sub>2</sub> with efficiency 80.64 % at 120 minutes. It's confirmed that using the solar unit is the best choice for the photocatalytic oxidation process

**Keywords:** TiO<sub>2</sub>, UV, AOPs, H<sub>2</sub>O<sub>2</sub>, photocatalytic, Graphene

### Introduction

The textile industry produces large quantities of highly colored effluents which are generally toxic and resistant to destruction by biological treatment methods [1]. Due to the large degree of organics present in these molecules and stability of modern textile dyes, conventional biological treatment methods are ineffective for their decolorization and degradation. In the recent years advanced oxidation processes have been developed to meet the increasing need of an effective wastewater treatment [2].

AOP generates powerful oxidizing agent hydroxyl radicals which completely destroy the pollutants in wastewater [3]. Heterogeneous photocatalysis through illumination of UV or solar light on a semiconductor surface is an attractive advanced oxidation process. AOPs include photo-catalysis systems such as a combination of a semiconductor and UV light [4].

Photocatalytic oxidation of pollutants with solar light can make it an economically viable process since solar energy is an abundant natural energy source. This solar energy can be used instead of artificial light sources. The artificial light sources need high electrical power

which is costly and hazardous. Solar energy has been successfully used for photo-catalytic degradation of pollutants [5]. It is demonstrated how the photo decolorization of some dyes could be achieved by solar light irradiation. In photocatalysis, UV irradiation source stands up among other sources to avoid this problem [6].

A way to increase TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> photocatalytic activity is the preparation of a nanostructure to get a high surface area that is directly related with catalytic activity. The design of titanium oxide photocatalyst and (g-C<sub>3</sub>N<sub>4</sub>), anchored or embedded onto support materials with large surface areas, which could condense diluted polluted substances would be of great significance, not only to avoid the filtration of small photocatalyst particles, but also to obtain higher efficiency [7,8].

The efficiency of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> is influenced by its crystal structure, particle size, specific surface area and porosity. Ultrafine powders of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> show a good catalytic activity. However, agglomeration can take place and engendering the production of larger particles and resulting in the

\*Corresponding author e-mail: [zizomoo@yahoo.com](mailto:zizomoo@yahoo.com); (Abdelaziz A. Noaman).

Receive Date: 09 March 2021, Revise Date: 04 April 2021, Accept Date: 17 April 2021

DOI: 10.21608/EJCHEM.2021.67049.3444

©2021 National Information and Documentation Center (NIDOC)

reduction or even complete loss of catalytic efficiency [9,10].

Enrico Mendes Saggiaro et al., showed that the photocatalytic degradation of two commercial azo dyes mediated by  $\text{TiO}_2$ . It has been observed that the increase in the initial dye concentration led to a decrease in the photodegradation. [11].

Siew Teng Ong et al., showed that the immobilized  $\text{TiO}_2$  is able to remove MB under the illumination of either UV or sunlight. The results revealed that the  $\text{TiO}_2$  loading plays an important role in determining the photocatalytic decoloring efficiency of MB. [12].

Meeti Mehra et al., showed that the photocatalytic activity of  $\text{TiO}_2$  is greater in the presence of solar light compared to the UV light. It has been found that the initial rate of photo decolorization increased with increase in the catalyst dose up to an optimum loading after that it did not show any effect [13].

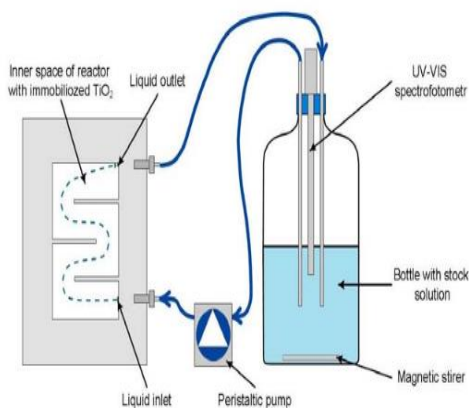
Salmin, S. Al-Shamali showed that the photocatalytic degradation of MB was examined using  $\text{TiO}_2$  catalyst under direct solar light. Some parameters such as pH of solution, loading of catalyst and concentration were studied for influencing on the efficiency of photocatalysis process [14].

The purpose of this work is to study the effect of solar photocatalytic oxidation of an azo dye (methylene blue) which are extensively used in the textile industry by using the solar parabolic collector under the effect of the catalysts ( $\text{g-C}_3\text{N}_4$  and  $\text{TiO}_2$ ). The effect of solar UV light irradiation and the amount of photocatalyst were examined as well.

## Experimental Work

### 2.1. UV lamp Setup:

The experimental setup used is a closed cycle as shown in figure 1.

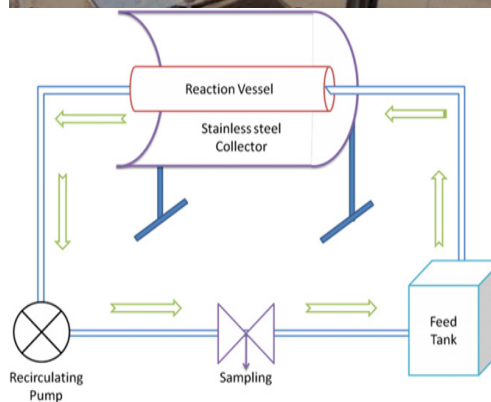


**Figure. 1: UV Lamp Setup and Schematic Diagram.**

It includes the feed tank which is a plastic beaker and its volume is 5 liters, this tank contains polluted feed water which will be subjected to treatment, the tank is connected with the inlet and outlet of a tubular reactor of UV lamp, the tubular reactor is 45 cm long and 10 cm diameter.

### 2.2 Solar UV Setup:

The experimental setup used is a closed cycle as illustrated in figure 2.

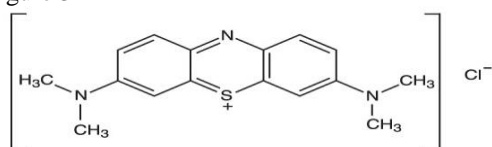


**Figure 2: Solar UV Setup and Schematic Diagram**

It consists of feed tank which is a plastic beaker, its volume is 5 liters, this tank contains polluted feed water which will be subjected to treatment, the tank is connected with the inlet and outlet of a glass tube. The glass tube is the reactor which the treatment is happened, it consists of input and output stream of water. Curved plate of stainless steel, it assembles the sunlight and focuses it on the glass tube.

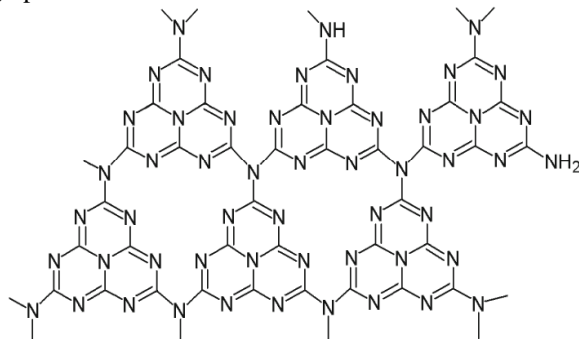
### 2.3 Materials:

The materials used in the experiments include distilled water which is prepared in chemical engineering department laboratories. Methylene blue dyestuff ( $\lambda_{\max}$  664 nm), a heterocyclic basic dye having a molecular weight of 373.9 g/mol. Its scientific name is basic blue (9) with the molecular Formula  $C_{16}H_{18}N_3S$ . The structural formula is illustrated in figure 3



**Figure 3. Structural Formula of Pollutants**

Catalysts which include  $TiO_2$  (anatase type), the specifications of this type used as a photocatalyst in the experimental work are particle size of 0.05  $\mu m$ , density of 3.78  $g/cm^3$  and purity of 98.5 % graphitic carbon nitride ( $g-C_3N_4$ ), the first type which is melamine type should be used in the experimental work. Figure 4 displays the structural formula of graphitic carbon nitride.



**Figure 4 Structural Formula of Graphitic Carbon Nitride**

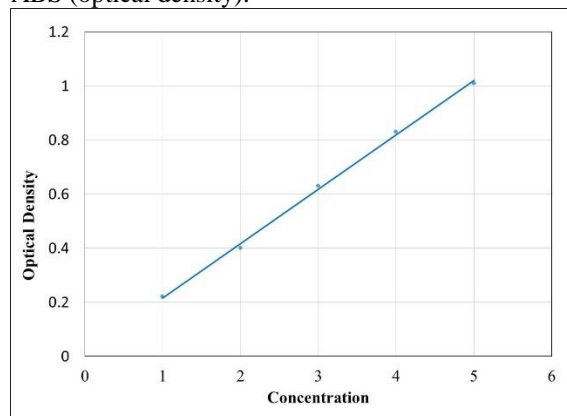
The parameters used include the initial dye concentration (methylene blue), the mass of catalyst ( $TiO_2$ ) & ( $g-C_3N_4$ ) and the volume of  $H_2O_2$ . Dilutions of concentrated samples were undertaken in order that the reduced optical density as found from the Spectrophotometer was in the range from 0.2 to 1, it has been observed that more accurate results were obtained in this range. Then by multiplying these reduced optical densities by their dilution factor, the optical density of the original stock solution was obtained. All tests were carried out at room temperature ( $\pm 25^\circ C$ ) to eliminate any temperature effects, unless otherwise stated. The calibration curve

for dye (methylene blue) was prepared by recording the absorbance (optical density) values for a range of known concentrations of methylene blue solution at the wavelength for maximum optical density. This value,  $\lambda_{\max}$ , was found from a full scan of the methylene blue spectrum. The value of  $\lambda_{\max}$  was determined using a Spectrophotometer and this value which is (664) nm was used in all subsequent investigations using Spectrophotometer (type). Optical density readings for various samples as shown in table 1 were compared with the calibration curve in figure 5 and transformed into concentration (ppm) terms.

**Table 1. Optical Density Readings for Various Concentrations**

Concentration (ppm)	Optical Density
0	0
1	0.23
2	0.384
3	0.646
4	0.841
5	1.025

In accordance with the beer lambert's law and using least-squares method applied to the straight line shown in figure 5, the optical density follows a linear relationship to concentration, optical density = 0.02077 X concentration, concentration = 4.815 X ABS (optical density).



**Figure 5. Calibration Curve of Methylene Blue ( $\lambda_{\max}$  =664 nm)**

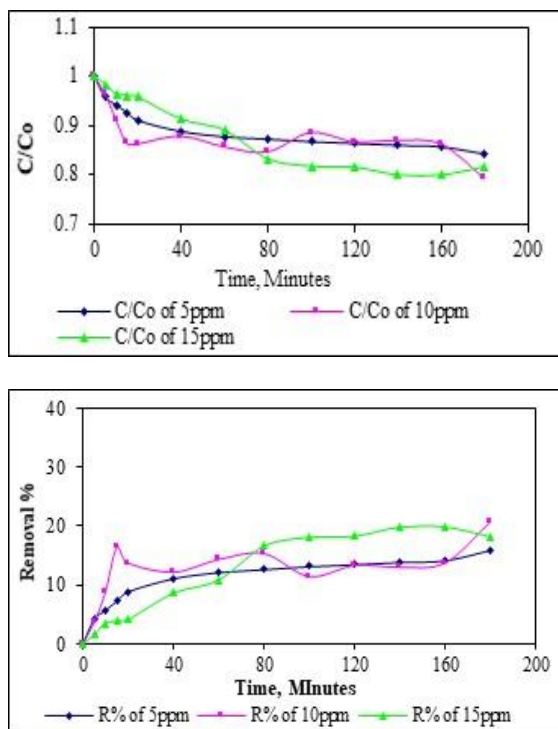
The experimental procedures include the methylene blue was made in stock solution of concentration 1000 ppm and was diluted to the required concentrations by using distilled water. Standard solutions of methylene blue strengths ranging from 5 to 15 ppm were prepared by using the distilled water as a solvent., pollutant solution was prepared according to the required concentration by dissolving the predetermined amount of the dye (methylene blue) in distilled water. The prepared volume was 5 liters.  $TiO_2$  or  $g-C_3N_4$  was added to the solution as a catalyst. To eliminate the

effect of adsorption, the suspension was subjected to mixing for 3-5 minutes in the absence of UV light. In the UV lamp test, the pump was connected to the tank and operated at specific discharge rate so the pollutant solution was circulated from the tank to the tubular reactor and again to the tank, this cycle was repeated. In the solar UV test, the pump was connected to the tank and was operated at specific discharge rate so the pollutant solution was circulated from the tank to the glass tube and again to the tank, this cycle was repeated. The mass of  $\text{TiO}_2$  or  $\text{g-C}_3\text{N}_4$  was changed every time to study the effect of increasing mass of photo-catalyst on the reaction rate. Samples were taken periodically for the analysis. Samples were centrifuged for separation of  $\text{TiO}_2$  powder or  $\text{g-C}_3\text{N}_4$ . Samples were diluted to the concentration range of calibration curve. Analysis was performed on spectrophotometer to determine pollutant concentration in samples taken at the beginning, end and intermediate time intervals throughout the experiment.

## Results & Discussions

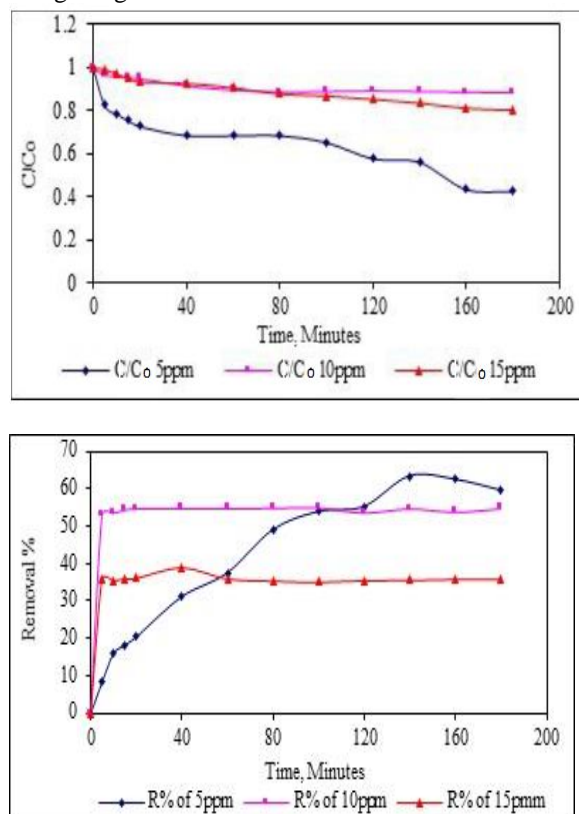
### 3.1. Effect of Different Dye Concentrations at UV Lamp

Figure 6 Illustrates the relationship between the percent removal and  $C/C_0$  with time at different dye concentrations at room temperature.



**Figure 6** Effect of Different Dye Concentrations at UV Lamp

Tests are run on figure 6 showed the effect of different dye concentrations on the process of photocatalytic degradation. In this case the dye concentration of 5 ppm showed the best results of photocatalytic degradation UV lamp process. Figure 6 showed the limits of dye concentrations which we can remove it easily, (5 ppm) gave the best results of pollutant degradation. 3.1.1. Effect of different dye concentrations at 0.5 g of  $\text{TiO}_2$  and 5 ml of  $\text{H}_2\text{O}_2$  Figure 7 reveals the relationship between the removal and  $C/C_0$  with time at different concentrations at by using 0.5 g of  $\text{TiO}_2$  and 5 ml of  $\text{H}_2\text{O}_2$



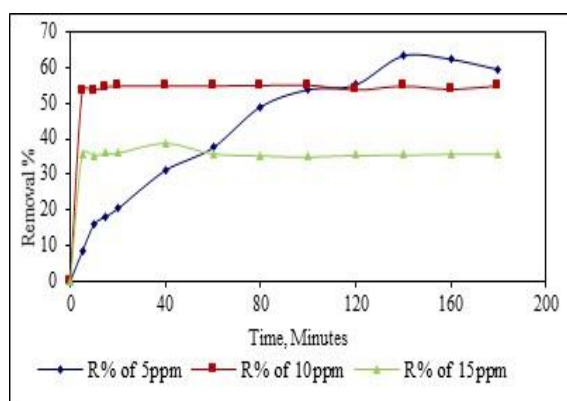
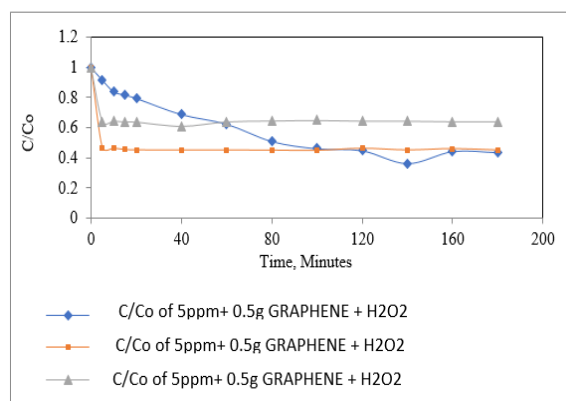
**Figure 7.** Effect of Different Dye Concentrations at 0.5 g of  $\text{TiO}_2$  and 5 ml of  $\text{H}_2\text{O}_2$

Test run of figure 7 reveals the effect of dye concentrations on the process of photocatalytic degradation. In this case the concentration of 5 ppm showed the best results of photocatalytic degradation at 0.5 g of  $\text{TiO}_2$  and 5 ml of  $\text{H}_2\text{O}_2$ . The presence of  $\text{TiO}_2$  has a pronounced positive effect on the rate of pollutant degradation. Besides, increasing the concentration of catalyst (up to optimum limit) increases the degree of pollutant degradation.

### 3.1.2. Effect of Different Concentrations of Dye Solution at 0.5 g of $\text{g-C}_3\text{N}_4$ and 5 ml of $\text{H}_2\text{O}_2$

Figure 8 illustrates the relationship between the removal and  $C/C_0$  with time at different concentrations at by using 0.5 g of  $\text{g-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$



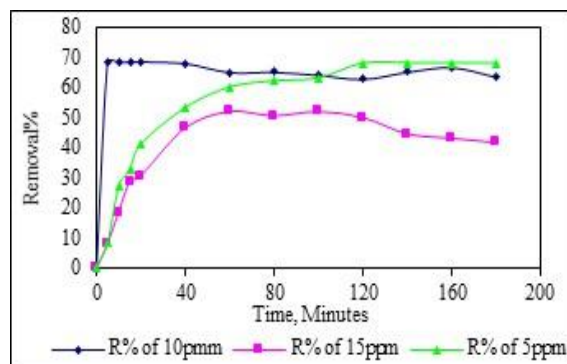
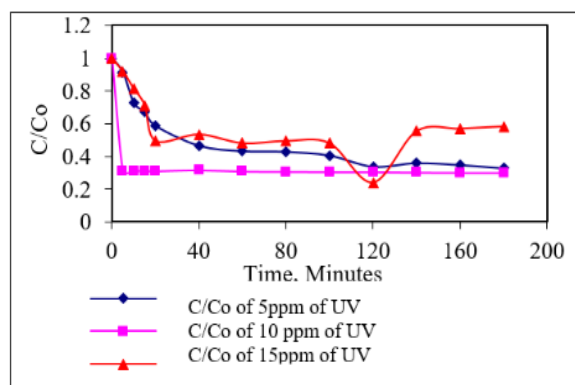


**Figure 8. Effect of Different Concentrations of Dye Solution at 0.5 g of  $g\text{-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$**

Tests are run on figure 8 reveals the effect of dye concentrations on the process of photocatalytic degradation. It has been noticed that the concentration of 5 ppm shows the best results of photocatalytic degradation at 0.5 g of  $g\text{-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$ . The presence of  $g\text{-C}_3\text{N}_4$  has a pronounced positive effect on the rate of pollutant degradation. Besides, increasing the concentration of catalyst (up to optimum limit) increases the degree of pollutant degradation.

### 3.1.3. Effect of catalyst on dye degradation at Different Concentrations of Dye Solution at 0.5 g of $g\text{-C}_3\text{N}_4$ and 5 ml of $\text{H}_2\text{O}_2$

Figure 9 displays the effect of catalyst on dye degradation at different concentrations of dye Solution at 0.5 g of  $g\text{-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$

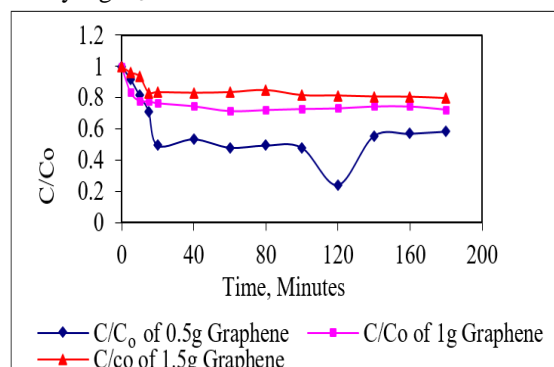


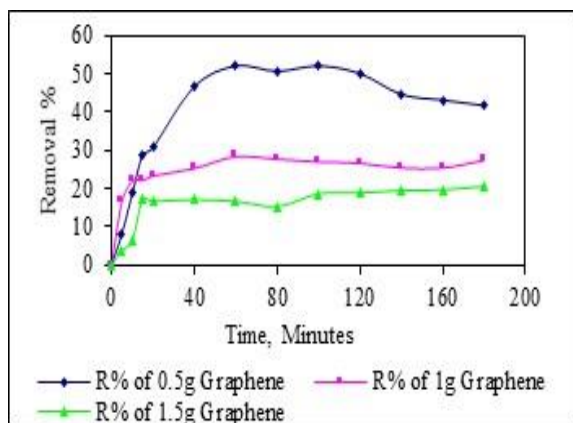
**Figure 9. Effect of catalyst on dye degradation at Different Concentrations of Dye Solution at 0.5 g of  $g\text{-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$**

Tests are run on figure 9 illustrates the effect of dye concentrations on the process of photocatalytic degradation. It has been noticed that the concentration of 5 ppm shows the best results of photo-catalytic degradation at 0.5 g of  $g\text{-C}_3\text{N}_4$  and 5 ml of  $\text{H}_2\text{O}_2$ . The graphitic carbon nitride  $g\text{-C}_3\text{N}_4$  has better effect than  $\text{TiO}_2$  pollutant degradation.

### 3.1.4. Effect of 15 ppm concentrations of dye solution at different weights of $g\text{-C}_3\text{N}_4$

Figure 10 illustrates the effect of 15 ppm concentrations of dye solution at different weights of catalyst  $g\text{-C}_3\text{N}_4$





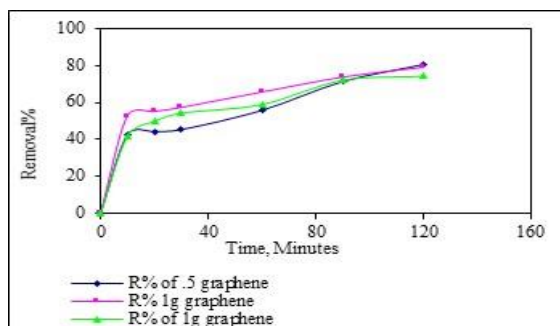
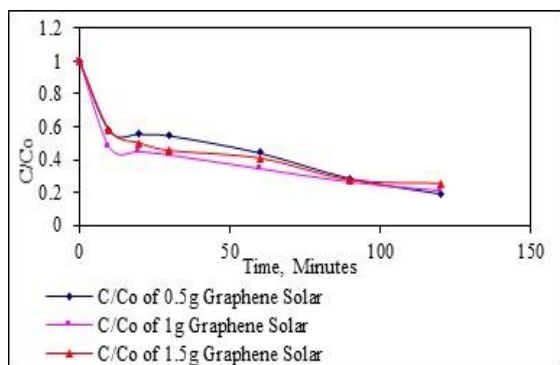
**Figure 10.** Effect of 15 ppm concentrations of dye solution at different weights of catalyst  $g-C_3N_4$

Tests are run on figure 10 shows the effect of dye concentrations on the process of photocatalytic degradation. It has been noticed that the concentration of 5 ppm shows the best results of photocatalytic degradation at 0.5 g of  $g-C_3N_4$

### 3.2. Effect of Different Dye Concentrations at Solar UV

#### 3.2.1. Results of 15 ppm Concentrations of Dye Solution at Different weights of $g-C_3N_4$

Figure 11 indicates the results of 15 ppm concentrations of dye solution at different weights of  $g-C_3N_4$



**Figure 11.** Results of 15 ppm Concentrations of Dye Solution at Different weights of  $g-C_3N_4$

Tests are run on figure 11 illustrate the effect of 15 ppm dye concentrations on the process of photocatalytic degradation. It can be noticed that the 1g from  $g-C_3N_4$  shows the best results of photocatalytic degradation.

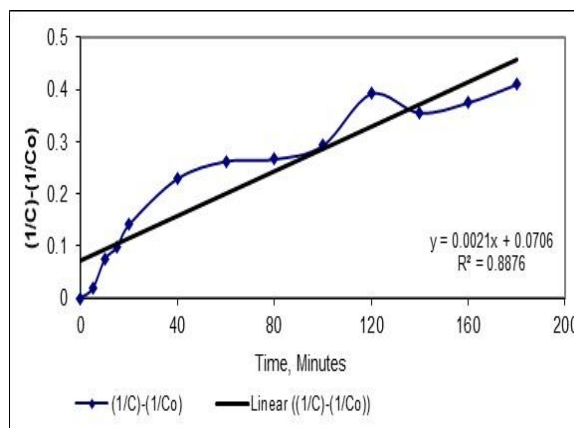
### 3.3 Kinetic studies

Table 2 reveals the reaction rate of 5 ppm concentration of dye and 0.5 g of  $g-C_3N_4$

**Table 2.** Reaction Rate of 5 ppm concentration of dye, 0.5 g of  $g-C_3N_4$

Reaction rate equation	Kinetic equation	Rate of reaction (K)	R <sup>2</sup>
Zero order equation	$C-C_0=0.0149t$	$0.0149 S^{-1}$	0.6978
First order equation	$\ln (C_0/C) =0.0054t$	$0.0054 S^{-1}$	0.8051
Second order equation	$(1/C) -(1/C_0) =0.0021t$	$0.0021 S^{-1}$	0.8876

Figure 12 shows the reaction rate of 5 ppm concentration of dye and 0.5 g of  $g-C_3N_4$



**Figure 12** Reaction Rate of 5 ppm concentration of dye, 0.5 g of  $g-C_3N_4$ , Second order

### 4. Conclusions

The presence of  $TiO_2$  has a pronounced positive effect on the rate of pollutant degradation. Besides, increasing the concentration of catalyst (up to optimum limit) increases the degree of pollutant degradation (in the UV-lamp Experiment the best removal is 69.81 % when using 0.5 gram  $TiO_2$  / L of pollutant solution). The effect of initial dye concentrations on the photocatalytic degradation shows the limits of concentrations which can be removed easily, it has been noticed that 5 ppm at the

both experiments give the best results of pollutant degradation. The graphitic carbon nitride  $g\text{-C}_3\text{N}_4$  has better effect than  $\text{TiO}_2$  pollutant degradation. Using  $g\text{-C}_3\text{N}_4$  can reach up to 50 % removal in UV lamp and up to 80.6% removal in solar UV. Adding 5ml from  $\text{H}_2\text{O}_2$  to the pollutant stream enhances the photocatalytic degradation of pollutant. Adding  $\text{H}_2\text{O}_2$  increase the generation of highly reactive intermediates (OH radicals) which can oxidize the target organic pollutants.

## References

- [1] F. H. Hussein and T. A. Abass, " Photocatalytic Treatment of Textile Industrial Wastewater", *Int. J. Chem. Sci.*, 8(3), 1353-1364, (2010).
- [2] Y. V. E. S. Parent, D. Blake, K. M. Bair, C. Lyons, C. Turchi, A. Watt, E. Wolfrum, M. Pairie, "Solar Photocatalytic Processes for the Purification of Water: State of Development and Barriers to Commercialization", *J. F. Solar Energy Vol. 56 (5)*, pp. 429-437, (1996).
- [3] J. Antonio Rivera Márquez, Consuelo Mendoza Herrera, Mirna López Fuentes, Leydi Medel Rosas, "Effect of Three Operating Variables on Degradation of Methylene Blue by Zn Electrodeposited: Response Surface Methodology", *International Journal of Electrochemical Science*, 7, p 11043 - 11051, (2012).
- [4] N.P. Mohabansi, V. B. Patil, N. Yenkie, "A Comparative Study on Photodegradation of Methylene Blue Dye Effluent by Advanced Oxidation Process by Using  $\text{TiO}_2/\text{ZnO}$  Photocatalyst", *Rasayan, J. Chem.*, Vol.4, No.4, (2011).
- [5] G.M. Madhu, M.A. Lourdu Antony Raj, K. Vasantha Kumar Pai, "Titanium dioxide ( $\text{TiO}_2$ ) assisted photocatalytic degradation of methylene blue", *Journal of Environmental Biology*, (2009).
- [6] Rahmatollah Rahimi, Mahboube Rabbani, Samaneh Safalou Moghaddam, "Application of N, S-codoped  $\text{TiO}_2$  photocatalyst for degradation of methylene blue", 16th International Electronic Conference on Synthetic Organic Chemistry, (2012).
- [7] V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann, S.C. Pillai, " Visible Light Activation of  $\text{TiO}_2$  Photocatalysts: Advances in Theory and Experiments", *J. Photochem. Photobiol. C Photochem. Rev.* 25, 1-29, (2015).
- [8] Cátia Gil Maia, Anabela Sousa, Oliveira, Enrico Mendes Saggioro, Josino Costa Moreira, "Optimization of the photocatalytic degradation of commercial azo dyes in aqueous  $\text{TiO}_2$  suspensions", *Reaction Kinetics, Mechanisms and Catalysis*, (2014).
- [9] Seo, D.C.; Lee, H.J.; Hwang, H.N.; Park, M.R.; Kwak, N.W.; Cho, I.J.; Cho, J.S.; Seo, J.Y.; Joo, W.H. Heo, J.S., "Treatment of non-biodegradable cutting oil wastewater by Ultrasonification-Fenton oxidation process. *Water Sc. Technol*", 55 (1-2), p 251-259, (2007).
- [10] Kwon, S.; Fan, M.; Cooper, A.T.; Yang, H., "Photocatalytic applications of micro- and nano- $\text{TiO}_2$  in environmental engineering", *Environ. Sci. Technol.*, p. 38, 197-226, (2008).
- [11] Enrico Mendes Saggioro, Anabela Sousa Oliveira, Thelma Pavesi, Cátia Gil Maia, Luis Filipe Vieira Ferreira, Josino Costa Moreira, "Use of Titanium Dioxide Photocatalysis on the Remediation of Model Textile Wastewaters Containing Azo Dyes", *Molecules*, (2011).
- [12] Siew-Teng Ong, Wai-Sim Cheong, Yung-Tse Hung, "Photodegradation of Commercial Dye, Methylene Blue Using Immobilized  $\text{TiO}_2$ ", 4<sup>th</sup> International Conference on Chemical, Biological and Environmental Engineering IPCBEE Vol.43, (2012).
- [13] Meeti Mehra, T. R. Sharma, "Photocatalytic degradation of two commercial dyes in aqueous phase using photo catalyst  $\text{TiO}_2$  ", *Pelagia Research Library*, (2013).
- [14] Dr. Salmin S. Al-Shamali, "Photocatalytic Degradation of Methylene Blue in the Presence of  $\text{TiO}_2$  Catalyst Assisted Solar Radiation", *Australian Journal of Basic and Applied Sciences*, 7(4): 172, 176, ISSN 1991-8178, (2013).