Fine Chemical Engineering
http://ojs.wiserpub.com/index.php/FCE/

UNIVERSAL WISER
PUBLISHER

Research Article

Photo-Degradation of Orange G as an Environmental Pollutant with TiO_2-ZnO Composite Material

Md Abdullah Bin Samad[1*], **Md. Amjad Hossain**[2], **Tajmeri S. A. Islam**[2], **Waziha Farha**[1]

[1]Department of Textile Engineering, Bangladesh University of Business and Technology, BUBT, Dhaka, Bangladesh
[2]University of Dhaka, Dhaka-1000, Bangladesh
Email: samad@bubt.edu.bd

Received: 24 September 2021; **Revised:** 01 December 2021; **Accepted:** 14 December 2021

Abstract: The increasing water pollution is a great concern as millions of people don't have access to pure water in Bangladesh. A considerable number of people are dying of contaminated water each year not only in Bangladesh but all over the world. Many industries, tanneries, companies, etc. are emitting lots of environmentally hazardous materials into the surrounding water. Many of these pollutants are industrial dyes. The dyes loss from the industrial water during dyeing operation damage the esthetic merit of surface water. They minimize light penetration, hamper aquatic lives and hinder photosynthesis. Some dyes may also have toxic, mutagenic, and carcinogenic characteristics. The purpose of this research is to get rid of the pollutant dye Orange G before the water is contaminated. A method named photo-degradation using different light sources is used to mineralize Orange G dye with composite materials including TiO_2-ZnO. This composite was prepared by the hydrothermal method. The photocatalytic behavior of the prepared composite TiO_2-ZnO helps in minimizing the effect of this dye to save the water from contamination. The composite compound was studied by experimenting on photo-degradation with Orange G under different light sources such as visible light, UV light, and sunlight. The photo-degradation percentage was found to maximum of 79.60 in the presence of sunlight. The percentages of photo-degradation under UV light and visible light were 48.0 and 18.40 respectively.

***Keywords*:** photo-degradation, pollutant, Orange G, composite, TiO_2-ZnO, light sources

1. Introduction

Environmental pollution is one of the great concerns the modern world is facing recently because a large number of people are dying each year and many people are carrying chronic diseases. So, the shortage of potable water is becoming very severe due to the pollution of source water. The widespread presence of organic pollutants, especially dyes in industrial wastewater from textile, apparel, leather, leather products, footwear and paper industries, plays a vital role in water contamination. In addition, artificial dyes are also used in almost all branches of consumer goods industries. Furthermore, the industrial effluents collected after different operations are usually highly colored, non-biodegradable, toxic, carcinogenic, and colored pigments causing damage to humans. The artificial and organic dyes are resistant to sunlight as well as other degradative environmental conditions. That is why it is necessary to remediate these industrial effluents before they get released into the aquatic environment. Regretfully, the traditional methods for remedying contaminated water with dyes are not so effective for the total mineralization of these organic dyes.

DOI: https://doi.org/10.37256/fce.3120221170

The most recent works were devoted to investigating the removal of organic pollutants from the environment, especially from the water body. In this regard, titanium dioxide (TiO_2) with zinc oxide (ZnO) was evaluated to degrade the various kinds of organic dyes under light sources, including visible light and ultra-violet light.[1] The kinetic study of Orange G on the surface of ZnO and ZnO/Ag photocatalyst was investigated to get an accurate model.[2] The composite materials (composites of two different or more oxides) were applied as a photocatalyst for the removal of organic pollutants.[3,4] Photo-degradation reaction with ZnO/biomass activated carbon was studied under visible and UV light sources to get rid of environmentally hazardous material Orange G.[5] The material, ZnO, was also studied to minimize the effect of azo-dyes.[6] Titanium oxide, ZnO, and Graphene oxide were applied to study the removal of the dye methyl orange under visible light.[7] The compounds TiO_2 and ZnO with different ratios were used to degrade an organic dye, methylene blue.[8] The compounds, TiO_2/ZnO[9], ZnO/CdS[10,16], and ZnO/TiO_2/CdS[11] etc. were commonly used as the photocatalysts in photo-degradation process. Methylene blue and Brilliant golden yellow were mineralized by TiO_2 and TiO_2-ZnO respectively under UV light source.[12-14,22] The azo-reactive dyes and Brilliant Orange dye were reported to be removed by the photo-degradation.[15] As ZnO was reported to have higher photocatalytic efficiency than TiO_2, the prepared TiO_2-ZnO[13,17] was used as a photocatalyst to decolorize organic pollutants/dyes. TiO_2 and ZnO, etc. were studied to minimize the effect of dyes including Methyl Orange (MO) and Rhodamine 6G (R6G).[18] The photocatalytic reaction of titanium oxide was investigated to decolorize yellow 14 and azo dyes under UV light.[19,20] The widespread use of aromatic compounds was curbed by the photochemical degradation of Remazol Brilliant blue and Uniblue A dyes.[21,23-25] Recently, as a photocatalyst, semiconductor helps to investigate the various kinds of organic and inorganic pollutants for photo-degradation. TiO_2, a semiconductor, is one of widely used photocatalysts for its high photocatalytic activity, non-toxicity, and cost-effectiveness. It was thus of interest to obtain double systems consisting of semiconductors differing in the width of the forbidden bands such as TiO_2-CdS, TiO_2-WO_3, TiO_2-SnO_2, TiO_2-MoO_3, and TiO_2-Fe_2O_3.[3,13] Therefore, it is clear that the photo-degradation of organic pollutants/dyes under sunlight was not well reported in previous researches.

The purpose of the current research work is to investigate the prepared composite TiO_2-ZnO at two distinctly temperatures 450 °C and 750 °C denoted as A and B to degrade Orange G dye (Figure 1) under three light sources like visible light, UV light and sunlight. This dye, Orange G, is extensively used in textile and dyeing industries. The percentages of photo-degradation of Orange G under these light sources will be compared. Finally, the activities of the composite A and B will also be compared. Furthermore, this research will predict that the percentage of Orange G's photo-degradation will be maximum under sunlight than under the visible and UV light sources.

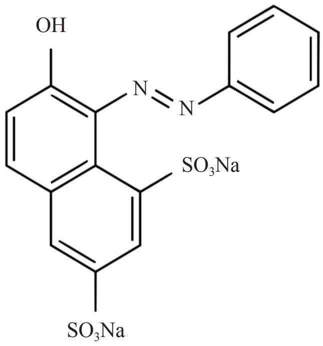

Figure 1. Structure of Orang G dye

2. Materials and methods

2.1 *Chemicals, apparatus, and instrument*

TiO_2 (Merck KG Germany), Orange G dye (reagent grade), and Prepared TiO_2-ZnO were used in research work. Analytical instrument namely Electric balance (FR-200, NDO-450ND, Japan), UV-visible spectrophotometer (UV-160A, Shimadzu, Japan), Magnetic stirrer and pH meter, Laboratory centrifuge machine (3000 cps, Heka, BHG), and UV light source wavelength 254 nm (Applied photolysis, England) were used in different steps of research work. The particle sizes of the composite were characterized by SEM (JSM-6490LA, JEOL, Tokyo, Japan). Different glass apparatuses including a graduated pipette, volumetric flask, and beaker were used during the photo-degradation experiment. All the chemicals are analytical grade.

2.2 *Photo-irradiation experiments*

10 mL de-ionized water and 0.2 g of TiO_2-ZnO composite were taken in a 100 mL beaker and kept in it overnight. Then, 0.6 mL 0.01 M Orange G solution and 89.40 mL de-ionized water were added into it to prepare 6×10^{-5} M. The pH of the suspension recorded was 6.67. The prepared solution then faced 40 minutes' adsorption, and also the suspension was magnetically stirred while irradiated for two hours (Figure 2). The pH of the suspension was recorded again. Afterward, the suspension was centrifuged and ready for taking absorbance using a UV spectrophotometer. The photo-degradation percentage was calculated as a % photo-degradation = $(a_0 - a_t)/a_t \times 100$ (assuming photo-degradation following the same trend as that of de-colorization), where a_0 was the absorbance at time 0 minute and a_t was the absorbance at time t minute. The irradiation experiments were studied under visible light, UV light and sunlight at the same concentration of Orange G dye and the same amount (0.2 g) of prepared composite TiO_2-ZnO.

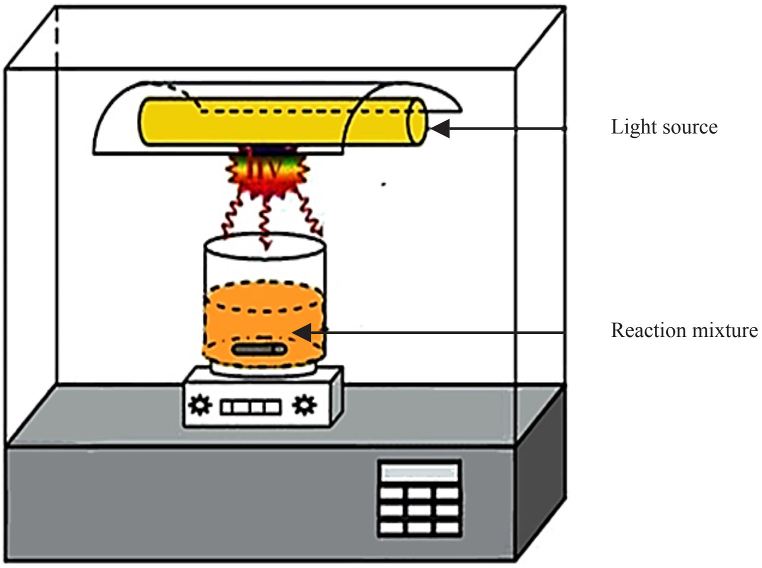

Figure 2. Schematic diagram for the reactor where irradiation was carried out

2.3 *Synthesis of TiO_2-ZnO composite*

To synthesize TiO_2-ZnO composite, initially, $ZnCO_3$ was prepared by the reaction of $ZnSO_4 \cdot 7H_2O$ and $(NH_4)_2CO_3$. After the formation of $ZnCO_3$, commercial TiO_2 was added to it slowly with continuous stirring until a solid layer formed at the bottom of the beaker. During the addition of TiO_2, the heat was applied moderately to speed up the reaction. In the final stage, the suspended liquid was transferred, and solid TiO_2-ZnO portion was taken into crucible and heated in a muffle furnace at two different temperatures for 3 hours.

In the photo-degradation reaction of Orange G dye with composite, A/B was converted to mineralized products as presented in Figure 3.

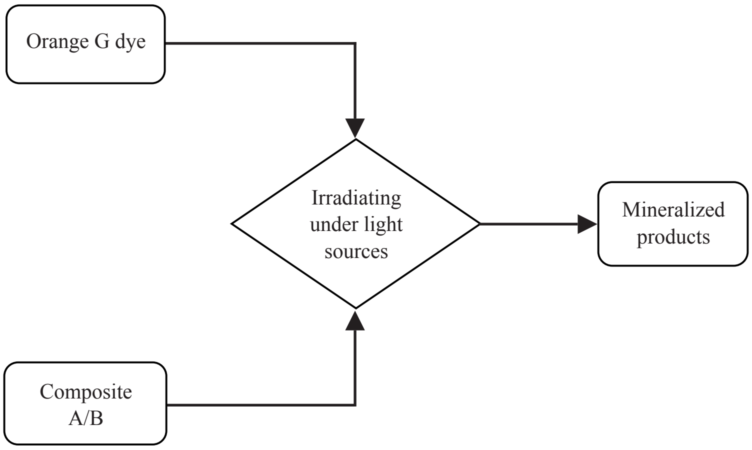

Figure 3. Flow chart of the reaction pathway of Orange G with composite A/B

3. Results and discussions

3.1 *Characterization of TiO_2-ZnO composite by SEM*

In Figure 4, the prepared TiO_2-ZnO composites A and B were analyzed with the help of the images of the SEM (Scanning Electron Microscope) to understand surface topography. The particle sizes of composite A were found to be in the range from 85 nm to 95 nm dimension. On other hand, particle sizes of composite B were found to be in the range from 150 nm to 200 nm dimension.[3,23] The larger particle sizes of B might be accounted for the accumulation of particles at higher temperatures and vice-versa for A.

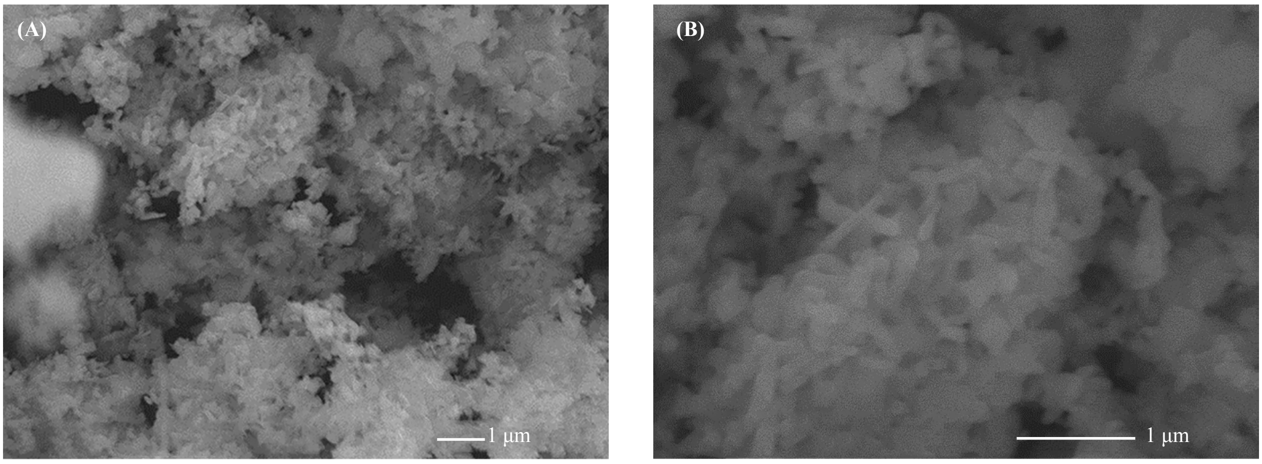

Figure 4. SEM images of prepared composites A and B

3.2 *Construction of calibration curve of Orange G*

Beer-Lambert law describes the absorption of a monochromatic beam of light by an absorbing system.

One form of the law is expressed by $A = \log\frac{I_0}{I_t} = \varepsilon cl$, where,

I_0 = Intensity of the light incident upon the sample in a cell of path length l cm,

I_t = Intensity of the light leaving the sample cell,

A = Absorbance,

c = Molar concentration of absorbing species,

ε = Molar absorption coefficient or molar extinction coefficient or molar absorptivity.

From Figure 5 based on Table 1, the molar extinction co-efficient of Orange G in aqueous solution at room temperature (30 °C) and at λ_{max} = 478 nm is 13567 L $mol^{-1}cm^{-1}$.

Table 1. Absorbance of different concentrations of Orange G solution at λ_{max}

Concentrations of Orange G × 10^5 (M)	Absorbance at λ_{max}
0.0	0.00
1.0	0.152
2.0	0.268
4.0	0.542
6.0	0.813
8.0	1.091
10.0	1.359
12.0	1.639
15.0	2.022

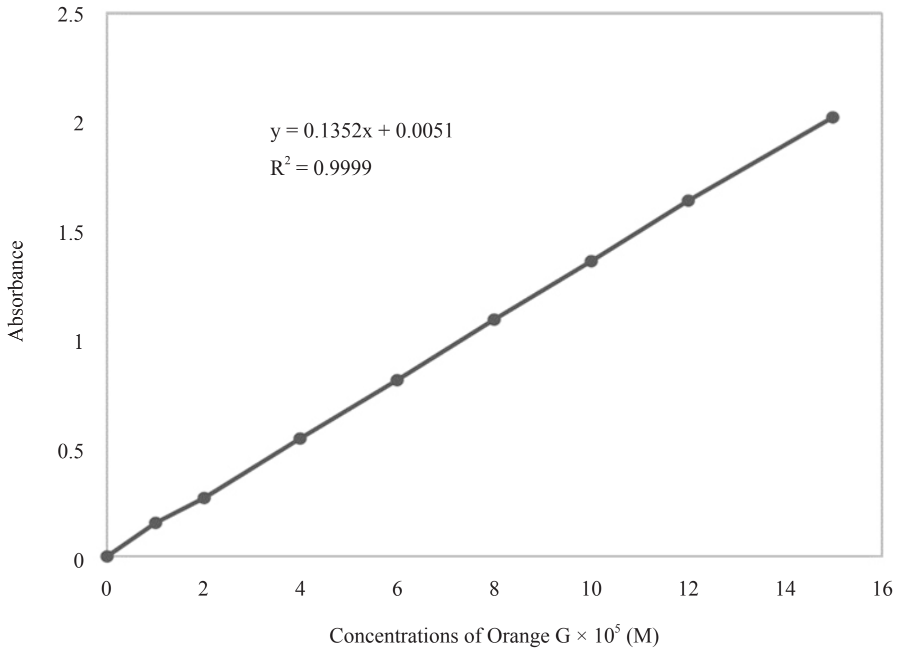

Figure 5. Calibration curve of Orange G at λ_{max}

3.3 *Comparison of photo-degradation results between sunlight, UV-light, and visible light sources for sample A*

Photo-degradation experiments of Orange G dye using A under the same conditions were carried out (Figure 6 and Table 2). From Figure 6 and Table 2, it was clear that the percentage of photo-degradation by using sunlight was maximum because of a higher intensity of sunlight. As a result, maximum photo-degradation of Orange G was observed and a higher percentage of photo-degradation was obtained. This result was similar to the photo-degradation.[3] The minimum percentage of photo-degradation was recorded under visible light due to the lower intensity of visible light compared with sunlight. The photo-degradation of Orange G under UV light was in between sunlight and visible light because the intensity of UV light is greater than that of visible light but lower than that of sunlight.

Table 2. Data of % photo-degradation of Orange G in the suspension of 0.20 g composite A under different light sources

Sources	Irradiation time (Min)	% Photo-degradation of Orange G
Visible light	120	18.40
UV light	120	48.00
Sunlight	120	79.60

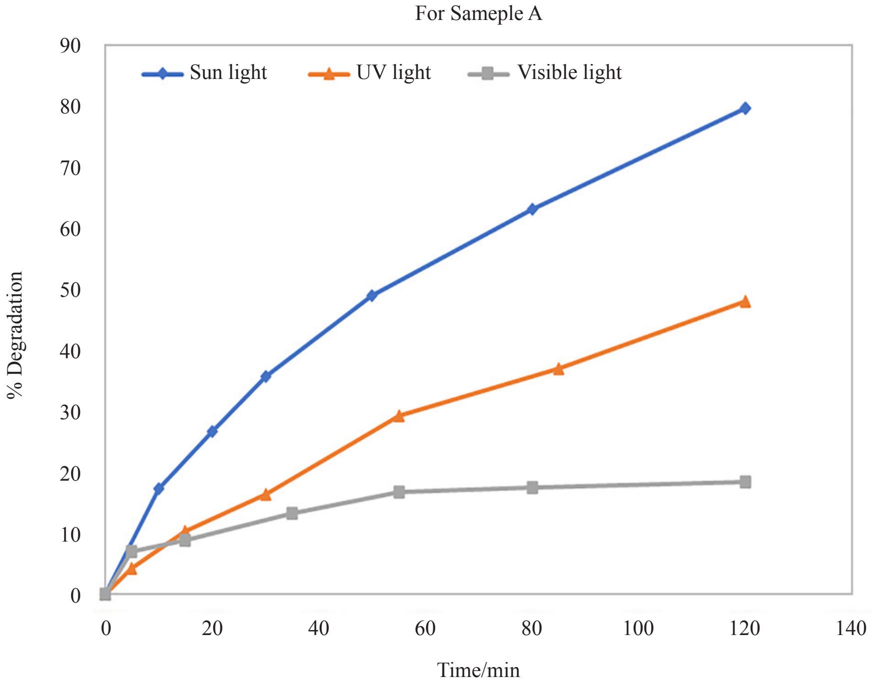

Figure 6. Photo-degradation percentage versus time under three different sources

3.4 *Comparison of photo-degradation results between sunlight, UV-light, and visible light sources for sample B*

Photo-degradation experiments of Orange G dye using B followed the same pattern as A under the same experimental conditions (Figure 7 and Table 3). From Figure 7 and Table 3, the percentage of photo-degradation by using sunlight was higher because of a higher intensity of sunlight. This result was similar to photo-degradation.[3] The lower percentage of photo-degradation (Figure 7 and Table 3) was recorded under visible light indicating minimum de-colorization of Orange G for the lower intensity of visible light compared to sunlight. The photo-degradation of Orange G under UV light (from Figure 7 and Table 3) was in between sunlight and visible light because the intensity of UV light is greater than that of visible light but lower than that of sunlight. So, the photo-degradation of Orange G by the composite catalysts A and B followed the same patterns under the same experimental conditions.

Comparing the results of both Figure 6 & 7 and Table 2 & 3, it was found that composite A was the better photocatalyst than B. The higher calcined temperature of composite B was responsible for the lower efficiency of Orange G photo-degradation. At higher temperatures, the agglomeration of the particle's size became larger and surface area decreased, which leads to lower adsorption of Orange G. Conversely, at lower calcined temperature, photocatalysts possessed larger surface area and a large number of active sites for adsorption of Orange G dye. Thus, prepared composite A at lower calcined temperature was more efficient than prepared composite B at higher calcined temperature.[3]

Table 3. Data of % photo-degradation of Orange G in the suspension of 0.20 g composite B under different light sources

Sources	Irradiation time (Min)	% Photo-degradation of Orange G
Visible light	120	15.98
UV light	120	37.16
sunlight	120	66.99

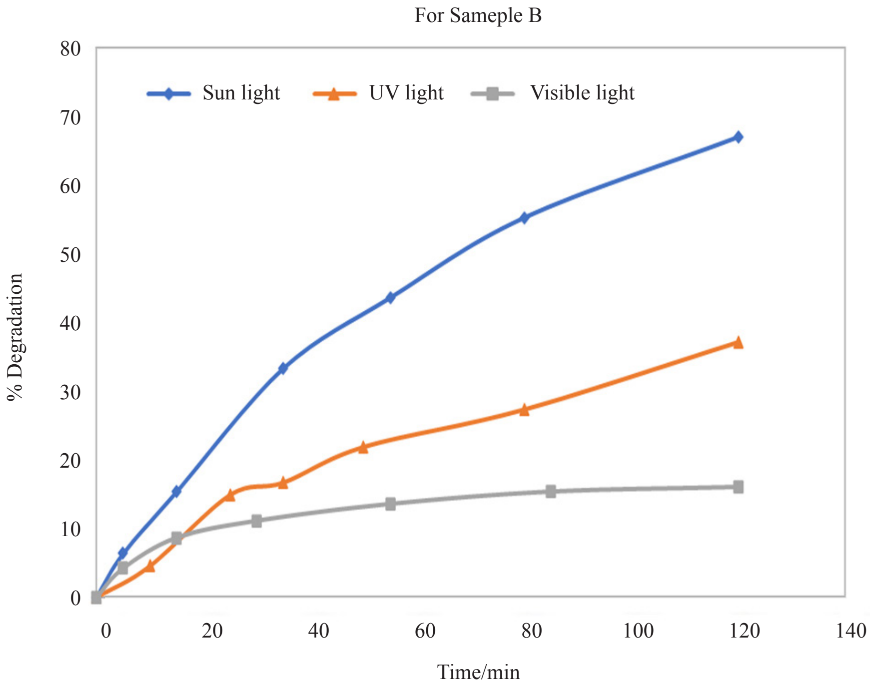

Figure 7. Photo-degradation percentage versus time under three different sources

3.5 *Kinetics study of photo-degradation of Orange G*

Table 4. Data for the extracted slopes from the graph

Composites	Light sources	Pseudo-first order rate constants, k (min^{-1})
	Visible light	1.91×10^{-3}
A	UV light	5.62×10^{-3}
	Sunlight	13.21×10^{-3}
	Visible light	1.82×10^{-3}
B	UV light	4.18×10^{-3}
	Sunlight	9.72×10^{-3}

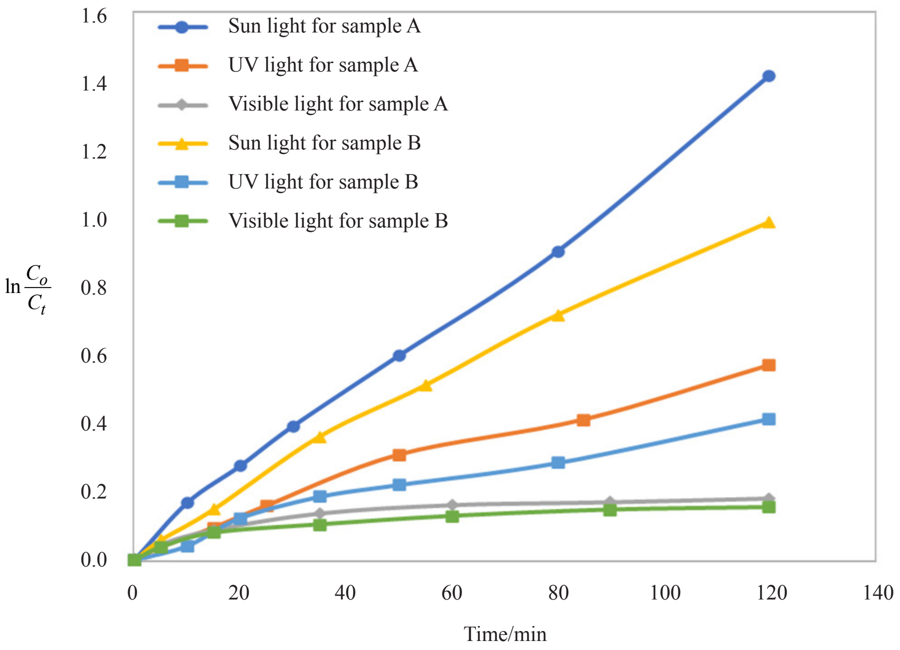

Figure 8. $\ln \frac{C_o}{C_t}$ versus time plot to determine pseudo-first-order rate constant

The kinetics study of photo-degradation of Orange G was conducted. The first-order rate equation is commonly expressed by

$$\ln \frac{C_o}{C_t} = \text{kt}.$$

The concentration of dye at zero minute is C_o, the concentration at any time (t minute) is C_t and k (Table 4) is the pseudo-first-order rate constant. From Figure 8, the plot of $\ln \frac{C_o}{C_t}$ versus time t for A and B under sunlight and UV light followed the first-order integrated rate equation. This result was similar to kinetics study.[6,9,13] But in the case of visible light, the plot became curvature initially, which might be due to very rapid photo-degradation initially compared with a later time. Thus, the photo-degradation of Orange G using A and B under sunlight and UV light followed pseudo-first-order kinetics but under visible light did not.

4. Conclusion

The TiO_2-ZnO composite exhibited a varying photocatalytic activity towards degradation of Orange G dye under different light sources including sunlight, UV light, and visible light, with the same experimental conditions. The photo-degradations under visible light, UV light and sunlight were 18.40%, 48.0% and 79.60% respectively by irradiating Orange G dye for 2 hours in the suspension of A. But the photo-degradations of Orange G on the surface of B under visible light, UV light and sunlight were 15.98%, 37.16% and 66.99% respectively with the same experimental conditions as A. Henceforth, A was a better photocatalyst to decolorize organic pollutant Orange G under sunlight compared to visible light and UV light. It was also established that A acted as a better composite photocatalyst than B. In a future study, the characterizations like XRD, EDX, and FTIR of the prepared composite A will be studied. Moreover, it will be studied how the percentage photo-degradation of dye will change with parameters including catalyst loading, solution pH, the concentration of dye, calcined temperature, etc.

Declaration of interests

The authors announce that they are not aware of competing for financial issues or personal contacts that could have seemed to sway the work published in this paper.

Acknowledgment

The authors of this paper were indebted to the Department of Chemistry, the University of Dhaka for providing its lab facilities, instruments, and machinery.

References

[1] Cambrussi, A. N. C. O.; Morais, A. Í. S.; Neris, A. D. M.; Osajima, J. A.; Silva, E. C. D.; Ribeiro, A. B. *Material (Rio J).* **2019,** *4*, 24.

[2] Tekin, D.; Tekin, T.; Kiziltas, H. *Sci. Rep.* **2019,** *9*, 1-7.

[3] Hossain, M. A., Samad, M. A. B., Khan, M. D., Ara, N. J., Islam, T. S. A. *IOSR-JESTFT.* **2018,** *12*, 58-67.

[4] Mendoza-Mendoza, E.; Nuñez-Briones, A. G.; García-Cerda, L. A.; Peralta-Rodríguez, R. D.; Montes-Luna, A. J. *Ceram.* **2018,** *44*, 6176-6180.

[5] Vinayagam, M.; Ramachandran, S.; Ramya, V.; Sivasamy, A. *J. Environ. Chem. Eng.* **2018,** *6*, 3726-3734.

[6] Chen, X.; Wu, Z.; Liu, D.; Gao, Z. *Nanoscale Res. Lett.* **2017,** *12*, 1-10.

[7] Raliya, R.; Avery, C.; Chakrabarti, S.; Biswas, P. *Appl. Nanosci.* **2017,** *7*, 253-259.

[8] Teixeira, S.; Martins, P. M.; Lanceros-Méndez, S.; Kühn, K.; Cuniberti, G. *Appl. Surf. Sci.* **2016,** *384*, 497-504.

[9] Zaharieva, K.; Milenova, K.; Cherkezova-Zheleva, Z.; Kunev, B.; Dimova, S.; Mitov, I. *J. Int. Sci. Publ.* **2014,** *8*, 250-258.

[10] Dinesh, S.; Duchaniya, R. K. *J. Nano-Electron. Phys.* **2013,** *5*, 03015.

[11] Lin, C.; Song, Y.; Cao, L.; Chen, S. *J. Chinese Adv. Mater. Soc.* **2013,** *1*, 188-199.

[12] Sima, J.; Hasal, P. *Chem. Eng. Trans.* **2013,** *32*, 79-84.

[13] Habib, M. A., Shahadat, M. T., Bahadur, N. M., Ismail, I. M., Mahmood, A. *J. Int. Nano Lett.* **2013,** *3*, 1-8.

[14] Dotto, G. L.; Vieira, M. L. G.; Goncalves, J. O.; Pinto, L. D. A. *Química. Nova.* **2011,** *34*, 1193-1199.

[15] Islam, M. S., Islam, T. S. *Dhaka Univ. J. Sci.* **2011,** *59*, 241-244.

[16] Luo, Y. *J. Colloid Sci.* **2009,** *71*, 370-374.
[17] Thamaphat, K.; Limsuwan, P.; Ngotawornchai, B. *Agric. Nat.* **2008,** *42*, 357-361.
[18] Kansal, S. K.; Singh, M.; Sud, D. *J. Hazard. Mater.* **2007,** *141*, 581-590.
[19] Muruganandham, M.; Swaminathan, M. *J. Hazard. Mater.* **2006,** *135*, 78-86.
[20] Konstantinou, I. K.; Albanis, T. A. *Appl. Catal. B.* **2004,** *49*, 1-14.
[21] Viswanathan, R.; Lilly, G. D.; Gale, W. F.; Gupta, R. B. *Ind. Eng. Chem. Res.* **2003,** *42*, 5535-5540.
[22] Georgiou, D.; Melidis, P.; Aivasidis, A.; Gimouhopoulos, K. *Dyes. Pigm.* **2002,** *52*, 69-78.
[23] Marci, G., Augugliaro, V., López-Muñoz, M. J., Martin, C., Palmisano, L., Rives, V., Schiavello, M., Tilley, R. J.; Venezia, A. M. *J. Phys. Chem.* **2001,** *105*, 1026-1032.
[24] Herrera, F.; Kiwi, J.; Lopez, A.; Nadtochenko, V. *Environ. Sci. Technol.* **1999,** *33*, 3145-3151.
[25] Oussi D.; Mokrini A.; Esplugas S. *Trends Photochem Photobiol.* **1997,** *1*, 77-83.