

# Photocatalytic Degradation of Dyes by TiO<sub>2</sub> Process in Batch Photoreactor

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**Abstract:** Chemical contamination in water caused by pollutants is becoming a severe environmental problem. The combination of photocatalysis and solar technologies are a valuable method for water pollution reduction caused by dyeing composites. Therefore, this study aims to determine the effects of operating parameters on the dyes photocatalytic degradation using titanium dioxide (TiO<sub>2</sub>)-based photocatalyst. Different types of dyes were used in this study, such as methylene blue, congo red, and methyl orange. The different weights of TiO<sub>2</sub> were mixed respectively in 500 ml of 10 mg/L dye solutions, which was set up in the photoreactor priorly. Later, the sample extractions were carried and analyzed using a UV-Vis spectrophotometer. The dye removal efficiency was investigated by changing conditions (catalyst dosage, light sources, and aeration). The results showed methylene blue photocatalytic degradation was best with 0.0547 min<sup>-1</sup> degradation rate at conditions of 3.0 g/L of TiO<sub>2</sub>, presence of UVC lamp, and aeration. Congo red photocatalytic degradation was best with 0.0254 min<sup>-1</sup> degradation rate at conditions of 1.0 g/L of TiO<sub>2</sub>, presence of sunlight, and aeration. Methyl orange photocatalytic degradation was best with 0.0094 min<sup>-1</sup> degradation rate using 1g/L of TiO<sub>2</sub>, presence of UVC lamp, and aeration. These findings can be used as an effective option in industrial wastewater treatment.

**Keywords:** methylene blue; congo red; methyl orange; titanium dioxide; photocatalytic degradation.

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## 1. Introduction

Human civilization development has grown rapidly due to the industrial revolution in the late 19<sup>th</sup> century. However, the increase in the human population and industry sectors over the years has degraded the quality of surroundings [1, 2]. Chemical contamination of water is a wide range of pollutants that has become a serious environmental problem due to its potential toxicity towards organisms and humans. Industrial wastewater contained either organic or inorganic pollutants. For instance, a textile processing industry uses a massive amount of water and generates large volumes of effluent from different steps in wet processing operations. Starting in 2016, a load of pollution and wastewater increase by dye-based textile industries [3]. The effluent colors discharged into the ecosystem affects the surrounding environment and cause severe environmental diseases. Some of these dyes are toxic or carcinogenic. Moreover, dyes can accumulate in soils, especially at the point where wastewater discharges and alters the ecological balance in the environment. Some more, it may also increase the level of toxicity in

the aquatic ecosystem once discharge excess dyestuffs into the water stream. This is lead by the presence of toxic by-products produced from an incomplete azo dyes synthesis such as aromatic amines [4].

Non-biodegradable or toxic substances cannot be treated by biological treatment methods [5]. This wastewater treatment works (i.e., aerobic systems such as activated sludge and trickling filters) do not achieve satisfactory color removal. As a result, colored effluent enters the water bodies. This issue leads to an increase in the number of complaints due to aesthetic reasons. Dyes removal from wastewater using economical methods is a significant problem faced by textile industries and dye-based industries. The selection of treatment technologies depends on the wastewater type and economic aspect requirements [6]. Highly polluted water containing color materials have to be treated with tertiary water treatment technologies. The tertiary treatment, such as micro and ultrafiltration and reverse osmosis, produce high pollutant concentration. They transfer the contamination between different phases generating a different pollution type; hence, further treatment is necessary [7]. Membrane life has been considered two to five years, which are dependent on wastewater nature. The flux and permeate quality may decrease over a long time period due to membrane fouling. However, porous membranes not efficient in eliminating organic compounds [8]. Membrane clogging occurs by foreign substances in wastewater considers as a problem while the treatment process is expensive [9].

Other than that, a single oxidation system is not sufficient for organic pollutants to be decomposed completely. Advanced Oxidation Processes (AOPs), which involve more than one oxidation process, are needed. AOPs design produces and uses hydroxyl free radicals as a strong oxidant to destroy organic pollutants [10]. Boczkaj & Fernandes [11], stated that the photocatalytic processes are described as an effective AOP type in order to degrade organic compounds.  $\text{TiO}_2$  is said to be the most studied semiconductor photocatalyst [12]. Photocatalytic surface excites the electrons in the valence band to the conduction band, resulting in a positive hole ( $p^+$ ) formation in the valence band and an electron ( $e^-$ ) in the conduction band once illuminated by light with sufficient energy [13, 14].

The main objectives of this study are to investigate the degradation rates of different dyes by  $\text{TiO}_2$  photocatalysis and to determine the effect of critical parameters, which are catalyst dosage, aeration, and type of UV sources on photocatalysis performance.

## 2. Materials and Methods

### 2.1. Material selection.

Chemicals and equipment used for conducting the study were titanium dioxide ( $\text{TiO}_2$ ), methylene blue (Bendosen), Congo red (Bendosen), methyl orange (R & M), UVC lamp (7 W), magnetic stirrer, aerator (speed: 3.5 L/min), UV-Vis spectrophotometry (UV-1800; Shimadzu) and Centrifuge (Eppendorf 5702 R).

### 2.2. Photoreactor set up.

A simple custom-made photoreactor was designed and fabricated to comprise a UVC lamp, magnetic stirrer, aerator, and opaque box. The function of the box was to prevent any penetration of other light sources. The dimension and space of the box should fit a 500 ml beaker.

### 2.3. Reaction experiments.

The TiO<sub>2</sub> weighed 1.0 g and 3.0 g, respectively, were mixed into 10 mg/L of every dye (methylene blue, Congo red, and methyl orange) in a 500 ml beaker, which was set up in the photoreactor. The mixture was set for 30 min of stirring using a magnetic stirrer without the presence of light to maintain mixing uniformity. After that, on the presence of light, the sample extraction is carried out with a time interval of 15 min in the first hour, 30 min time interval in the second hour, and 60 min time interval in the last hour.

The duration of each experiment is 3 hrs. The samples were centrifuged using Centrifuge (Eppendorf 5702 R) to separate the components in the samples according to their densities before taken for further analysis. Overall, there were 12 sets of experiments for every dye in various conditions, as shown in Table 1, with every set had the average reading as experimental data.

**Table 1.** Set of experiments conducted for methylene blue, Congo red, and methyl orange with conditions 1, 2, and 3.

Catalyst load (g/L)	Light sources	Aeration
1.0	UVC lamp	With aeration
1.0	UVC lamp	Without aeration
1.0	Sunlight	With aeration
1.0	Sunlight	Without aeration
3.0	UVC lamp	With aeration
3.0	UVC lamp	Without aeration
3.0	Sunlight	With aeration
3.0	Sunlight	Without aeration

The total experiments conducted were 36 experiments, which were conducted at the Fluid Mechanics Laboratory, Universiti Malaysia Terengganu. The details of the conditions are listed as follows:

- Condition 1: Catalyst load (1.0 g/L and 3.0 g/L)
- Condition 2: Light sources (UVC lamp and sunlight)
- Condition 3: Aeration (with aeration and without aeration)

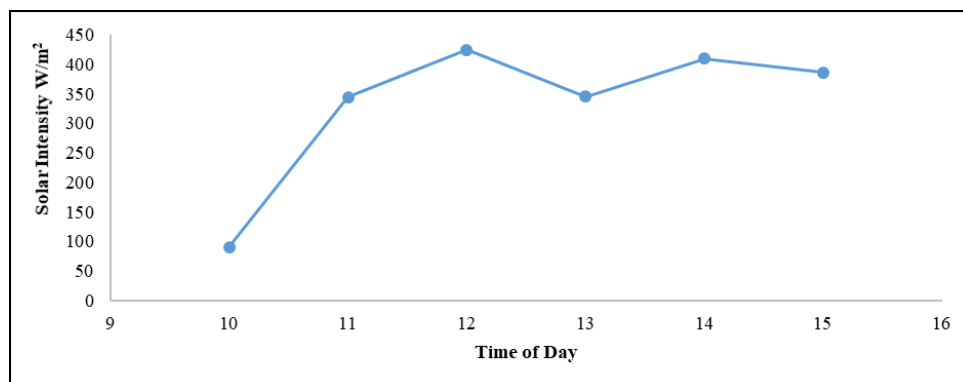
### 2.4. Analytical technique.

The analytical technique used for this study extracted scientific data from the carried experiment and analyzed the data for results and discussion. The wastewater degradation was analyzed using a UV-Vis spectrophotometry (UV-1800; Shimadzu) to detect the adsorption of dyes throughout the experiment. This step helped to study the kinetics mechanism of photocatalytic degradation of the dyes.

## 3. Results and Discussion

### 3.1. Solar intensity.

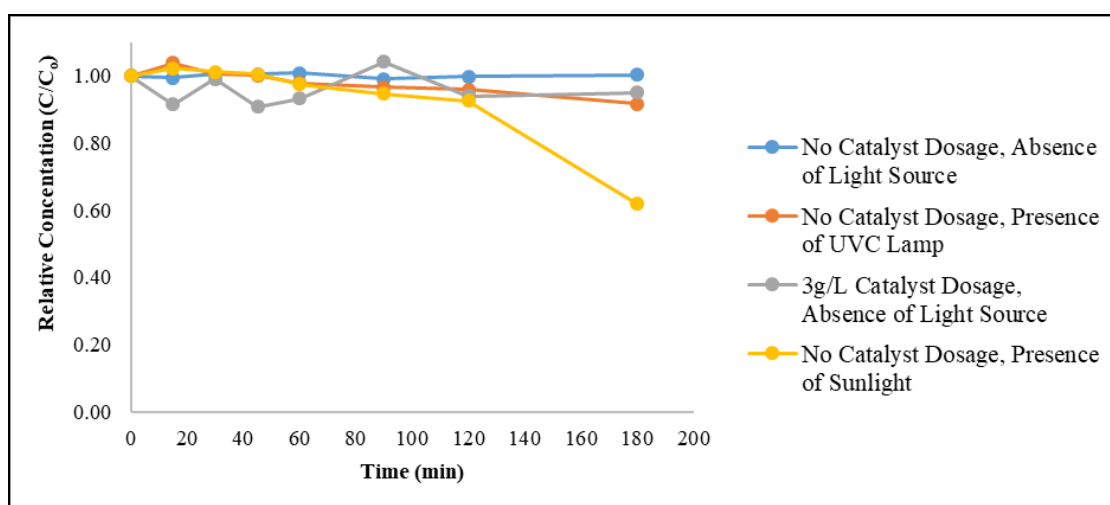
The average solar irradiation over daytime is shown in Figure 1. The sunlight is an accessible natural energy source where it can be utilized for the semiconductors in the pollutant photodegradation. It also recognized as a vital source of renewable energy for water treatment technologies [15, 16]. The solar light application is a cheap and environmentally friendly method and also gain an efficient photocatalytic system [17]. The experiments were conducted from 11 a.m. to 1 p.m. due to its high solar irradiation intensity.



**Figure 1.** Average solar intensity vs. time of the experiment.

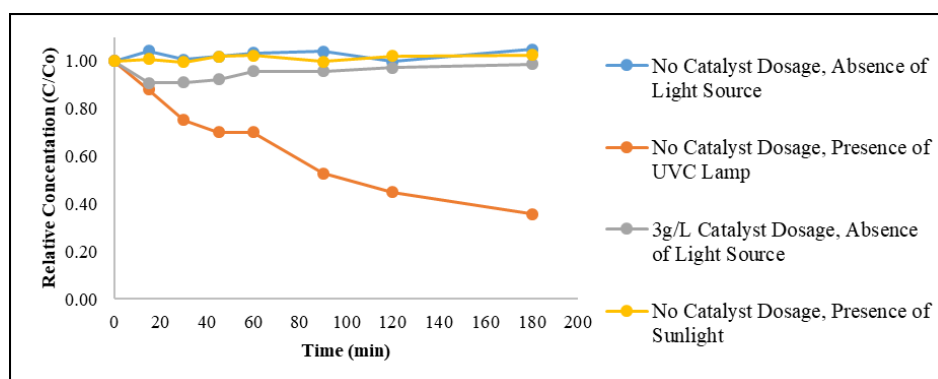
### 3.2. Control experiments.

Figure 2 shows the methylene blue degradation profile under several conditions. The addition of TiO<sub>2</sub> to the methylene blue aqueous solution in the absence of light sources for 180 min showed no measurable of decrement in the concentration of the dye. This result specifies that no dye adsorption on the catalyst occurred. Thus, there was no degradation occurred with TiO<sub>2</sub> alone. The effect of light on the photolysis degradation of methylene blue was studied by changing the light sources, which were the UVC lamp and sunlight. The methylene blue dye did not decompose at all under the UVC lamp. The methylene blue dye concentration in the presence of sunlight decreased steadily after 120 min. This result indicates that there was photolysis degradation by sunlight without TiO<sub>2</sub> after a specific period.



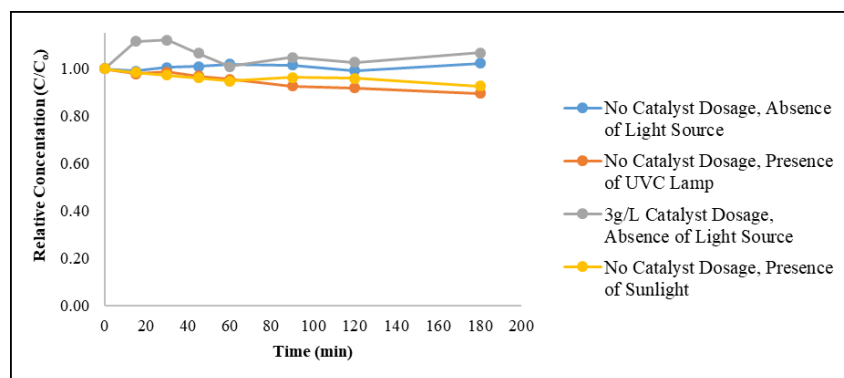
**Figure 2.** Relative concentration vs. time for methylene blue control experiments.

Figure 3 shows, the Congo red degradation profile under several conditions. The addition of TiO<sub>2</sub> to Congo red dye solution in the absence of light sources for 180 min showed no changes in the dye concentration. This result indicates that no dye adsorption on the catalyst happened. Hence, there is no degradation with TiO<sub>2</sub> alone. The light effect on the photolysis degradation of Congo red was studied using various light sources, which were UVC lamps and sunlight. The presence of the UVC lamp on the aqueous solution of Congo red showed a gradual decrease in the concentration of the dye. This result indicates that there was photolysis degradation with UVC lamp without the presence of TiO<sub>2</sub>.



**Figure 3.** Relative concentration vs. time for congo red control experiments.

Figure 4 shows the methyl orange degradation outlined under several conditions. The addition of TiO<sub>2</sub> to methyl orange solution in the absence of light sources for 180 min showed no changes in the dye concentration. This result specifies that no dye adsorption on the catalyst happened. So, there is no degradation with TiO<sub>2</sub> alone. There is no methyl orange degradation in the presence of a catalyst without light irradiation, which demonstrating the importance of light illumination [18]. The light effect on the photolysis degradation of methyl orange was studied by changing the light sources, which were the UVC lamp and sunlight. The presence of the UVC lamp and sunlight to the aqueous solution of methyl orange showed a slight reduction in the dye concentration after 20 min. This result indicates that there was photolysis degradation with light irradiation alone without TiO<sub>2</sub> after such a long time.



**Figure 4.** Relative concentration vs. time for methyl orange control experiments.

### 3.3. Methylene blue experiments.

#### 3.3.1. Catalyst dosage dependence of the photocatalytic activity.

The effects of the amount of the catalysts were studied by varying the amounts of the TiO<sub>2</sub>, which were 1.0 g/L and 3.0 g/L. The methylene blue dye concentration was 10 mg/L in all experiments. The experimental data of photocatalytic degradation of methylene blue with catalyst dosage 1.0 g/L after 180 min with the presence of UVC lamp, sunlight, with and without aeration are shown in Table 2. The results demonstrate that the photocatalytic activity of methylene blue dye was the lowest in the case of 1.0 g/L catalyst by a degradation rate of 0.0276 min<sup>-1</sup>.

The experimental data of photocatalytic degradation of methylene blue with catalyst dosage 3.0 g/L after 180 min presence of UVC lamp, sunlight, with and without aeration are shown in Table 3. The maximum degradation of methylene blue occurred at 3.0 g/L catalyst by a degradation rate of 0.0547 min<sup>-1</sup>. The efficiency of degradation increases when increasing

the dosage of catalyst. This is due to the availability of higher active site numbers, which increasing hydroxyl radical production [19]. An optimal catalyst dosage is required for improving the rate of degradation and decreasing unnecessary waste, and in this experiment, the ideal quantity was 3.0 g/L.

**Table 2.** Rate reaction vs. time interval for methylene blue with catalyst dosage of 1.0 g/L.

Experiments	Degradation rate (min <sup>-1</sup> )
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0276
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0304
1.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0504
1.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0424

**Table 3.** Rate reaction vs. time interval for methylene blue with catalyst dosage of 3.0 g/L

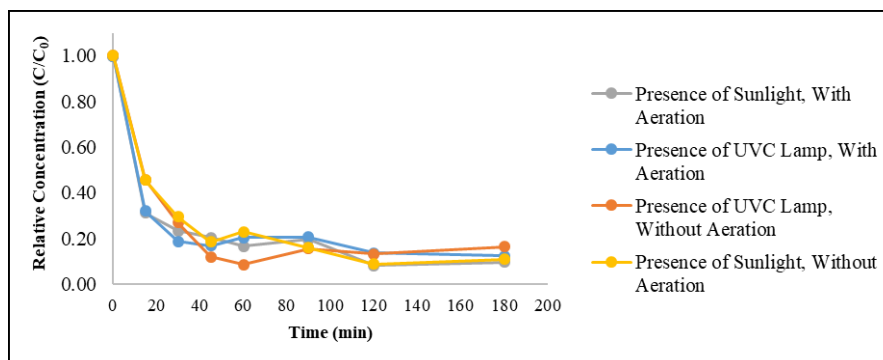
Experiments	Degradation rate (min <sup>-1</sup> )
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0547
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0406
3.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0532
3.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0420

### 3.3.2. Light source dependence of the photocatalytic activity.

The experiments were conducted by varying light sources, which were the UVC lamp and sunlight. In these experiments, the UVC lamp intensity was set at 7W. As presented in Figure 5, the relative concentration of methylene blue dye decreases sharply in the presence of UVC lamp, which is 0.19 after 30 min. This result is due to the UVC lamp light irradiation on the TiO<sub>2</sub> surface, which gave impact to the generation of hydroxyl free radicals. The relative concentration of methylene blue dye was slightly decreased in the presence of sunlight, which is 0.23 after 30 min. This is due to the low solar intensity transmitted through the suspension. UVC lamp has a smaller wavelength that can provide greater efficiency of degradation [19].

### 3.3.3. Aeration dependence of the photocatalytic activity.

The experiments were conducted by varying the presence of aeration. As shown in Figure 5, in 30 min with 3.5 L/min aeration, the relative concentration of the dye in the presence of 3.0 g/L of catalyst and UVC lamp was 0.19. In 30 min without aeration, the relative concentration of the dye was 0.27. Aeration created continuous shaking in the suspension were produced a homogenous suspension. The flow of suspension increase along the surface of photocatalysts. Aeration enhances the photocatalysts and dye mixtures in the wastewater and increases dye photodegradation efficiency [20].



**Figure 5.** Relative concentration vs. time for methylene blue with catalyst dosage of 3.0 g/L.



### 3.4. Congo red experiments.

#### 3.4.1. Catalyst dosage dependence of the photocatalytic activity.

The effects of the amount of catalysts were investigated by varying the amounts, which were 1.0 g/L and 3.0 g/L of TiO<sub>2</sub>. The Congo red dye concentration was 10 mg/L in all experiments. The experimental data of the photocatalytic degradation of Congo red with a catalyst dosage of 1.0 g/L after 180 min presence of UVC lamp, sunlight, with and without aeration are shown in Table 4. The maximum degradation of Congo red occurred at 1.0 g/L catalyst by degradation rate of 0.0254 min<sup>-1</sup>.

**Table 4.** Rate reaction vs. time interval for Congo red with catalyst dosage of 1.0 g/L.

Experiments	Degradation rate (min <sup>-1</sup> )
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0221
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0095
1.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0254
1.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0118

The experimental information about the photocatalytic degradation of Congo red dye with a catalyst dosage of 3.0 g/L after 180 min presence of UVC lamp, sunlight, with and without aeration are displayed in Table 5. The outcome reveals that the photocatalytic activity of the Congo red dye was the lowest in the case of 3.0 g/L of the catalyst, with its degradation rate of 0.0087 min<sup>-1</sup>. The high quantity of catalyst had decreased the rate of Congo red degradation. This is caused by increased turbidity or cloudiness and reduces light penetration through the solution [21]. Furthermore, the low degradation at a higher catalyst dosage could be due to the sedimentation of the TiO<sub>2</sub> particles.

**Table 5.** Rate reaction vs. time interval for Congo red with catalyst dosage of 3.0 g/L.

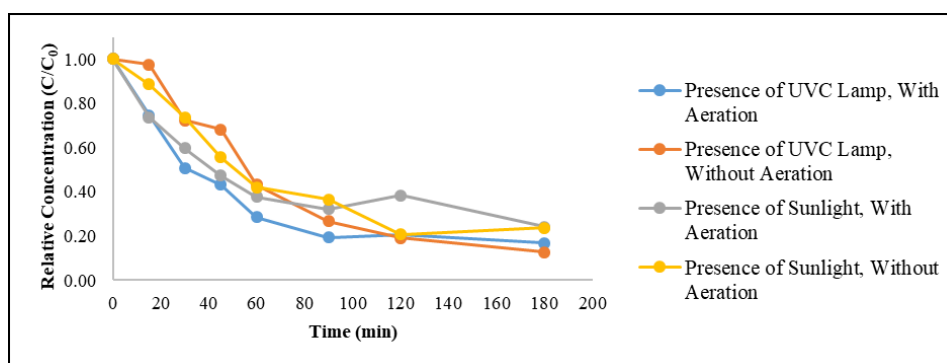
Experiments	Degradation rate (min <sup>-1</sup> )
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0147
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0087
3.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0135
3.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0097

#### 3.4.2. Light source dependence of the photocatalytic activity.

The experiments were conducted by varying light sources, which were UVC lamps and sunlight. In these experiments, the UVC lamp intensity was 7W. As demonstrated in Figure 6, the relative concentration of Congo red dye decreased in the presence of UVC lamp, which was 0.75, whereas, in the presence of sunlight was 0.74 within 15 min. In the present work, the Congo red has excellent photocatalytic degradation under the sunlight compared to the UVC lamp. The photocatalyst is able to degrade dyes by the mechanism of photocatalytic oxidation when used sunlight as a radiation source [22].

#### 3.4.3. Aeration dependence of the photocatalytic activity.

The experiments were conducted by varying the presence of aeration. As shown in Figure 6, in 30 min with 3.5 L/min aeration, the relative concentration of dye in the presence of 1.0 g/L of the catalyst under sunlight irradiation was 0.60. In 30 min without aeration, the relative concentration of dye was 0.74. The aeration rates helped in increasing the degradation rate of Congo red dye. The aeration source is not only sustained satisfactory suspension and mixed well the solution but offers an adequate quantity of oxygen [23].



**Figure 6.** Relative concentration vs. time for Congo red with catalyst dosage of 1.0 g/L.

### 3.5. Methyl orange experiments.

#### 3.5.1. Catalyst dosage dependence of the photocatalytic activity.

The effects of the number of catalysts were investigated by varying the amounts, which were 1.0 g/L and 3.0 g/L TiO<sub>2</sub>. The concentration of the methyl orange dye was 10 mg/L in all experiments. The experimental data of the photocatalytic degradation of methyl orange with a catalyst dosage of 1.0 g/L after 180 min presence of UVC lamp or sunlight, with and without aeration, are shown in Table 6. The maximum degradation of methyl orange dye occurred at 1.0 g/L catalyst by a degradation rate of 0.0094 min<sup>-1</sup> due to the rise of active sites with the catalyst dosage suspension.

**Table 6.** Rate reaction vs. time interval for methyl orange dye with catalyst dosage of 1.0 g/L.

Experiments	Degradation rate (min <sup>-1</sup> )
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0094
1.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0054
1.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0051
1.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0086

The experimental data of the photocatalytic degradation of methyl orange with a catalyst dosage of 3.0 g/L after 180 min presence of UVC lamp or sunlight, with and without aeration, are presented in Table 7. The outcomes reveal that the photocatalytic activity of methyl orange dye was the lowest in the case of the 3.0 g/L catalyst by a degradation rate of 0.0011 min<sup>-1</sup>. The degradation rate decreased due to the rise of the catalyst concentration. This result caused by the light scattering of suspended catalyst. The penetration of light through the dye solution with the increasing dosage of the catalyst made the photo-activated suspension volume reduced [24]. In this state, some parts of the catalyst surface turned out to be inaccessible for the absorption of photon and dye [25].

**Table 7.** Rate reaction vs. time interval for methyl orange with catalyst dosage of 3.0 g/L.

Experiments	Degradation rate (min <sup>-1</sup> )
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, With Aeration	0.0043
3.0 g/L Catalyst Dosage, Presence of UVC Lamp, Without Aeration	0.0011
3.0 g/L Catalyst Dosage, Presence of Sunlight, With Aeration	0.0014
3.0 g/L Catalyst Dosage, Presence of Sunlight, Without Aeration	0.0016

#### 3.5.2. Light source dependence of the photocatalytic activity.

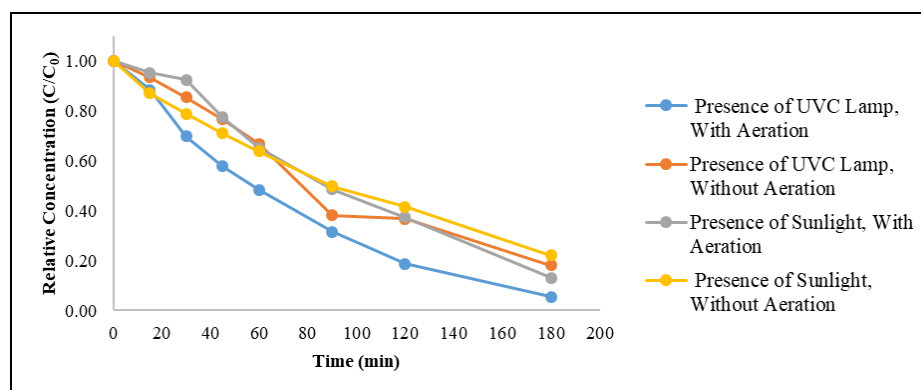
The experiments were conducted by varying the light sources that were the UVC lamp and sunlight. In these experiments, the UVC lamp intensity was 7 W. As demonstrated in Figure 7, the relative concentration of methyl orange dye sharply decreased in the presence of



UVC lamp, which was 0.58 and slightly decreased in the presence of sunlight, which was 0.77 within 45 min. Undoped TiO<sub>2</sub> is the best and effective photocatalyst for methyl orange degradation in water under UV irradiation. The doped TiO<sub>2</sub> mostly might be a photocatalytically reactive under solar light irradiation [26]. Based on Nasirian & Mehrvar [27] research, they stated that UVC light has a lower wavelength and greater energy. Methyl orange degradation was higher and quicker due to more electron/hole pair production since TiO<sub>2</sub> activated under UV light, which has a lesser wavelength (<389nm).

### 3.5.3. Aeration dependence of the photocatalytic activity.

The experiments were conducted by varying the presence of aeration. As shown in Figure 7, in 30 min with 3.5 L/min aeration, the relative concentration of dye in the presence of 1.0 g/L catalyst and UVC lamp was 0.70. In 30 min without aeration, the relative concentration of dye was 0.85. The aeration rates helped in increasing the degradation rate of the methyl orange dye. It provides well mixing in the suspension and enables the catalyst surface to contact with dye surface. Moga *et al.* [28] indicated that the performance of the oxygenation process improved by aeration systems.



**Figure 7.** Relative concentration vs. time for methyl orange dye with catalyst dosage of 1.0 g/L.

## 4. Conclusions

TiO<sub>2</sub> is widely utilized in environmental-based applications because of its physical and chemical stabilities, low cost, non-poisonous, and resistant to corrosion. The rates of degradation of methylene blue, Congo red, and methyl orange dyes by TiO<sub>2</sub> photocatalysis investigated. The effects of catalyst dosage, aeration, and type of UV source on photocatalysis performance examined. The results obtained from the conducted study showed that the methylene blue photocatalytic degradation was the best with a catalyst dosage of 3.0 g/L of TiO<sub>2</sub> under the UVC lamp and presence of aeration with a degradation rate of 0.0547. The Congo red photocatalytic degradation was the best with a catalyst dosage of 1.0 g/L of TiO<sub>2</sub> under sunlight and aeration with the degradation rate of 0.0254. The methyl orange photocatalytic degradation was the best with a catalyst dosage of 1.0 g/L of TiO<sub>2</sub> under the UVC lamp and aeration with the degradation rate of 0.0094. Overall, this research encourages the industries to be drawn to this method of dye treatment and adapt it as a practical approach that will benefit the industries, humans, and ecosystems.

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## Conflicts of Interest

We have no conflicts of interest.

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