

# Photocatalytic and Kinetics Study of Copper Oxide on the Degradation of Methylene Blue Dye

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## ABSTRACT

Methylene blue dyes in is widely used various industries in Indonesia, especially in the textile industry. Methylene blue in waters is toxic and difficult to degrade. One of the methods used is to overcome this problem is photocatalysis under visible light. CuO photocatalyst was prepared using an easy hydrothermal preparation using common autoclave at low temperature. The photocatalytic activity on methylene blue showed degradation up to 63.44%, with optimum pH 9 and the optimum irradiation time of 120 minutes. The photocatalytic activity is influenced by the formation of hydroxyl radicals in CuO, which can degrade dyestuffs. The reaction rate follows second order kinetics.

**Keywords:** methylene blue, photocatalyst, CuO

## 1. INTRODUCTION

Methylene blue (MB) is a dye used in various areas, especially in the industrial sector. It is used as dyes for silk, wool, textiles, office supplies, and cosmetics. The presence of MB in water affects water quality, endanger health, and cause toxic effects. MB degradation has been widely carried out, such as using adsorption and photocatalytic degradation with the help of UV radiation. Dwijayanti et. al, carried out the adsorption of MB with fly ash coal and obtained an adsorption capacity of 500mg/g [1]. The photocatalytic degradation of MB using Zeolite-WO<sub>3</sub> weight variation obtained degradation of 99.66% [2]. The use of nanoparticles or nanocomposite catalysts is used in various recent studies, especially on the degradation of dye waste. Such that conducted using ZnO-CuO nanocomposite, on the application of Methyl Orange photocatalyst degradation [3].

Various methods have been carried out of the synthesis of nanoparticles, nanostructures, and nanocomposites. The method used produces nanomaterials with different optical, structural, and magnetic properties. Some commonly used methods are the sol-gel method, hydrothermal/solvothermal, sonochemical, polyol, and co-precipitation. Application of nanomaterials itself is broad including photocatalytic degradation of metal oxides in various dyestuffs, nanomaterials as gas sensors, and much more. CuO

nanomaterials have been developed and widely used synthesis using various methods. CuO is a p-type semiconductor with a narrow bandgap ( $E_g = 1,2$  eV) that has been investigated in solar energy conversion, lithium-ion batteries, gas sensors, electrochemistry, and catalysis. CuO nanoparticles and MXene hybrid composite has been utilized to detect toluene gas [4]. Jana et al, made a comparison on CuO produced from hydrothermal and reflux processes to know the ability of the device to improve the electrical parameters based on the Schottky diode barrier [5].

The results show that CuO by reflux has a better ability than CuO (Reflux) to flow current in Schottky's barrier diode system. CuO (Hydrothermal) showed 93% response to light while CuO (Reflux) was 62%. Zhang et al., carried out the hydrothermal synthesis of three-dimensional CuO with a butterfly-like structure. The precursors used were CuCl<sub>2</sub>·2H<sub>2</sub>O and NaOH with surfactant sodium dodecyl benzenesulfonate (SDBS) heated for 15 hours at 100° C [6]. The crystals obtained are 6 nm long, 2-4 nm wide, with a sheet thickness of 60 nm. Salehi researched CuO-ZnO composites to grade direct blue dye 71 [7].

The effectiveness of the degradation obtained is 89.58% at optimal pH 3.9. The catalyst concentration used was 1.85 g/L, and the dye concentration was 20.34. mg/L at the optimum time of 177 minutes. Nogueira et al. increased photocatalytic activity CuBi<sub>2</sub>O<sub>4</sub>/CuO

heterojunction to degrade MB and metronidazole [8]. The precursors used were  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  with solvent ratio water: ethanol (1:1 v/v) applying the hydrothermal method. On the photodegradation of methylene blue with visible light,  $\text{CuBi}_2\text{O}_4/\text{CuO}$  showed good photocatalytic to degrade more than 80% MB in just 10 minutes. The optimum time is 60 minutes to degrade up to 98%. Some of the descriptions above are related to the synthesis of CuO and nanomaterials. For its application, CuO synthesis will be carried out using the hydrothermal method utilising a common autoclave with low temperature with photocatalyst application on the degradation of MB.

## 2. METHOD

The instruments used include glassware, magnetic stirrer, autoclave, calcination furnace, Shimadzu 1800 UV-visible spectrophotometer Shimadzu-1700 UV-vis, reactor photocatalytic, oven, centrifuge, and digital balance. Chemicals used in the manufacture is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , distilled water, aqua demineralization, NaOH,  $\text{H}_2\text{SO}_4$ , MB and ethanol (95%); All ingredients' Chemicals were used as received without prior purification.

### 2.1 CuO synthesis

Adapting from ref [9], the synthesis of CuO is using the hydrothermal method. copper oxide solution precursor was prepared by dissolving 6.25 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 mL aqua demineralization. The precursor solution was made alkali by adding a solution of 0.1 M NaOH while stirring continuously until a black coloured precipitate was formed. The resulting solution is put into an autoclave, then heated in an oven at 120 °C for 5 hours. The resulting solid was separated from the solution phase by centrifugation. The solids are washed and dried in the oven overnight at 200 °C.

### 2.2 Preparation of MB standard solution

Preparation of a standard solution of MB with a concentration of 100 ppm was carried out by Weighing 0.1 grams of MB crystals, then dissolve them with distilled water and dilute them to 1000 ml using a 1000 ml volumetric flask. as much as 100 ml of 100 ppm MB mother liquor was dissolved with distilled water and diluted with a 1000 ml volumetric flask to the mark (10 ppm). The absorbance in standard solutions in the wavelength range of 650-700 nm was analysed using a UV-Vis spectrophotometer. After that, a standard curve was created that relates the concentration of each standard solution with absorbance obtained.

### 2.3 Determination of the optimum pH

The adsorption process was carried out using the batch method. As much as 0.5 grams, CuO was reacted with 50 mL of 10 ppm MB solution with a pH variation of 3, 5, 7, 9, 11, and 13 accompanied by 60 minutes of stirring and irradiating with tungsten lights. The concentration of MB is determined by measuring its absorbance at the maximum wavelength.

### 2.4 Effect of irradiation time

The adsorption process was carried out by mixing 0.05 g of CuO with 50 mL of 10 ppm MB at the optimum pH and stirred with a stirring variation of 15, 30, 45, 60, 90, 120, 180, 240, and 360 minutes. Further, centrifugation was carried out for 15 minutes, and the filtrate was measured at determined maximum wavelength

### 2.5 Photocatalytic degradation of MB

The degradation of MB was carried out photocatalytically under lamp tungsten irradiation at room temperature. The experiments were carried out in the reactor batch utilizing 100 mL MB at an initial concentration of 10 mg L<sup>-1</sup> and catalyst loading of 0.05 g. The irradiation source is a tungsten lamp with maximum emission at 665 nm. Before irradiation, the suspension was stirred in the dark for 10 minutes to ensure the balance adsorption and desorption. The suspension sample was collected and filtered to separate solid particles at regular time intervals. The filtrate was analysed on the maximum wavelength at 665 nm in the UV-vis spectrum MB using a Shimadzu-1700 UV-vis Spectrophotometer. MB concentration calculated using the Beer-Lambert equation

## 3. RESULTS AND DISCUSSION

### 3.1 CuO synthesis

The development of synthesis methods has been carried out extensively and includes fundamental interests to know, understand, and apply to materials nano. nanomaterials synthesis depends on various parameters such as morphology, particle size, size distribution [10]. The hydrothermal reaction synthesis method involves water which is pressurized in a closed container, and the reaction temperature exceeds the critical point of a solution, has been used widely because of the simple reaction system, toxic, low cost, and environmentally friendly [11].

Hydrothermal synthesis of CuO has been carried out using precursor  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as much as 24.95 g in the form of light blue fine powder dissolved with 1000 mL of water. The solution was made alkaline to pH 12 by adding 0.1 M. NaOH drops with continuous stirring

until a black precipitate formed. The solution is then put into an autoclave and heated at a temperature of 120°C for 5 hours, and a black powder is formed, which is still present. The water content was then washed with H<sub>2</sub>O and ethanol. Next in dry at 200°C for 12 hours. CuO has a hydrothermally synthesized size of 300-800 nm. The addition of NaOH serves to form Cu (OH)<sub>2</sub>, which is the core of CuO crystals. CuO crystal growth occurs with a heating aid which will remove the moisture content [9].

### 3.2. Determination of Maximum Wavelength

The wavelength in the spectroscopic analysis is used to determine the absorption intensity in a solution. Each solution has a length of different waves depending on the maximum absorption of the solution. The maximum wavelength is used in a quantitative analysis, where the maximum wavelength occurs at the time of maximum absorption. Determination of the maximum wavelength of the MB solution measured the absorption with the highest value of the measured solution in the range wavelength of 600-700 nm using a UV-Vis spectrophotometer. The results obtained are in the form of the relationship between the absorbance value and the wavelength so that if it is described, it will form a long absorbance absorption peak maximum wave.

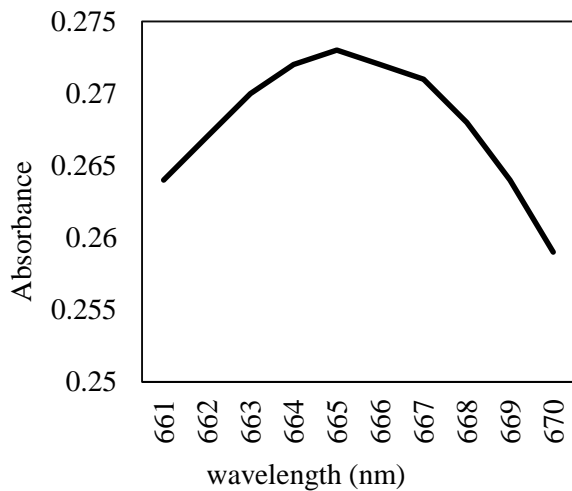


Figure 1. maximum wavelength of MB

Based on Figure 1. the maximum wavelength MB is 665 nm, similar to some references. This wavelength is used as a reference for making calibration curves.

### 3.3. Calibration curve of MB concentration

A calibration curve in the analysis was used to compare the effect of analyte levels with the tool's response (instrument). Curve calibration shows the relationship between concentration and absorbance in a straight line where the x-axis is the concentration of the standard solution of MB and the y-axis is the absorbance at the maximum wavelength. According to

Lambert's law- Beer, absorption is directly proportional to concentration, so it gets more considerable concentration, the greater the absorbance value.

The calibration curve for the standard solution of MB was made using standard solution of MB with concentrations of 1, 2, 3, 4, and 5 ppm analysed by a UV-Vis spectrophotometer at a maximum wavelength of 665 nm. Measurement results in a standard solution of MB are as follows.

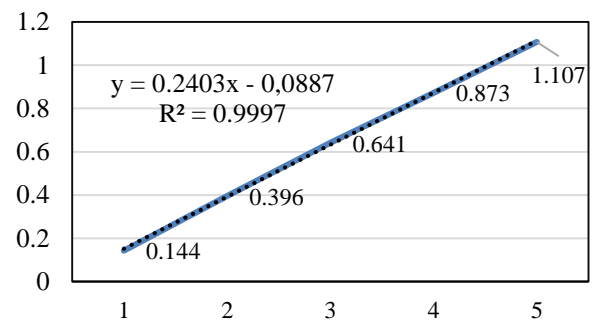


Figure 2. Calibration curve of MB standard solution

The MB calibration curve obtained in Figure 2 shows the linear relationship between concentration and absorbance. It can be seen from the linear regression equation obtained,  $y = 0.2403x - 0.0887$  with the value of  $R^2 = 0.9997$ . This result follows the Law Lambert-Beer. R-value<sup>2</sup> close to 1 indicates the feasibility of the graph in testing.

### 3.4. Effect of pH in the photocatalysis

The pH parameter is one of the parameters used in the photocatalytic process. pH affects the surface charge of the catalyst, and the degree of ionization. variations of pH are known to affect the rate of degradation at some point. The pH variation in the MB solution used is pH 3, 5, 7, 9, 11, and 13 by adding HCl and NaOH, then Stirring was carried out for 60 minutes under visible irradiation.

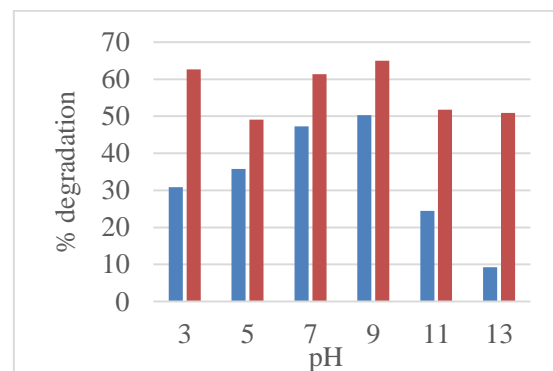


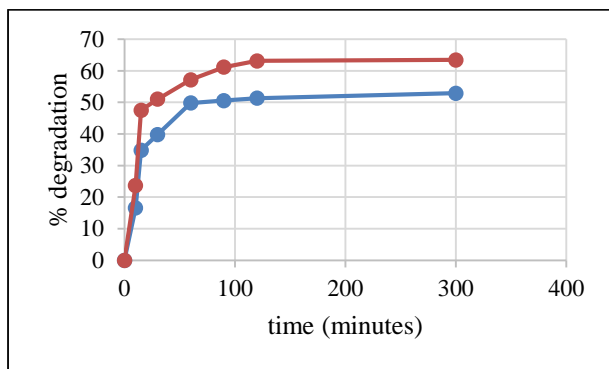
Figure 3. Decrease in MB at variations in pH (Red = under visible light irradiation, blue under dark condition)

The maximum decrease in the concentration of MB is at pH 9, equal to 64.97% as presented in Figure 3. Closed catalyst surface at acidic pH by dye molecules cause absorption of light radiation on the catalyst surface decreases [12]. In a low pH environment, the high concentration of H<sup>+</sup> ions inhibits MB's degradation rate, thereby reducing the positive charge on the catalyst as a radical forming agent hydroxyl on the catalyst [13]. Meanwhile, there is an excess of OH anions at a higher pH, which facilitates the photodegradation of OH radicals. Changes in pH shift the redox potential of the valence and conduction bands that can affect the charge transfer interface. Li et al., [14] modified CeO/CuO in degradation of MB on CuO optimal at pH nine, whereas for CeO/CuO composite was optimal at pH 4.

This result is because when exposed to light, Cu ions will react under alkaline conditions, producing HO<sub>2</sub>• species formed in the medium alkaline and reacts with OH• and H<sub>2</sub>O<sub>2</sub>. Another interpretation of the effect of pH is the acid-base nature of the surface. Metal oxides can be described as a zero-point charge (ZPC) basis. Adsorption of water molecules at the metal surface site is followed by the OH- group charge dissociation, which leads to the chemical equilibrium of the metal hydroxyl groups (M-OH). The surface of CuO is positively charged below pH 9 and negatively charged above this pH.

### 3.5. Effect of Variation of Exposure Time

The measurement of irradiation time is used to determine the optimum time catalyst required in degrading the dye solution. This process was performed by adding 0.1 grams of CuO to 100 mL of 10 ppm MB accompanied by stirring and irradiation with visible light.



**Figure 4.** The optimum time of degradation of MB with CuO (Red = under visible light irradiation, blue under dark condition)

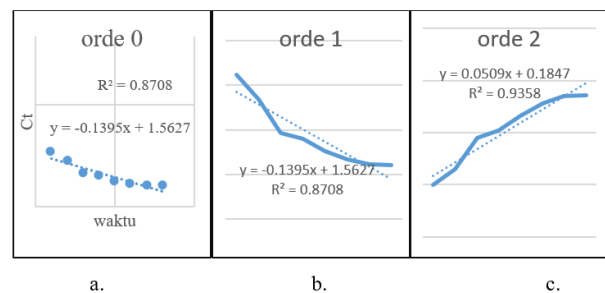
Figure 4. shows a rapid decrease in the concentration of MB at under 50 minutes. Furthermore, the optimum degradation time is at 120 minutes with a degradation ability of 63.44%. The treatment without irradiation was

carried out as a comparison. Without irradiation, the degradation of MB is lower at 52.8%. The activity of the catalyst is influenced by physical parameters related to the catalyst surface, such as particle size, shape, and structure. The smaller the particle size, the bigger the MB degradation. The larger the surface area, the more catalyst sites adsorb organic compounds. The results of the degradation of MB using CuO in Figure 4 shows that the longer the irradiation time, the more MB was degraded. This result is due to the presence of electrons in the valence band of CuO that are excited to the conduction band, causing a hole or positive hole (h<sup>+</sup>). Positive holes will react with H<sub>2</sub>O or hydroxyl to form a hydroxyl radical (OH•), decomposing MB organic compound [10].

### 3.6. Evaluation of kinetics

In the photocatalysis, there is a photooxidation reaction and photoreduction. Photooxidation occurs in the valence band where holes (h<sup>+</sup>) react with H<sub>2</sub>O/OH<sup>-</sup> will form hydroxyl radicals OH• with the help of photon energy from light. Meanwhile, the conduction band will be going on to reduce O<sub>2</sub> into radical's superoxide (O<sub>2</sub>•-) and hydroxyl radicals (OH•). Degradation of organic MB dye is carried out by the hydroxyl radicals formed on the CuO produces intermediate organic compounds before being completely degraded into CO<sub>2</sub> and H<sub>2</sub>O.

The rate of decrease in the concentration of MB by CuO The rate of decrease in concentration or reaction kinetics is used to determine the adsorption speed of CuO to MB and its effect on time. The rate test is used to estimate the order of the reaction. Reaction order of a chemical reaction can be defined as the rate of a chemical reaction. A first-order reaction is a reaction whose rate is directly proportional to the reactants. Meanwhile, A second-order reaction is when a reaction rate is proportional to the square of the reactant concentration.



**Figure 5.** Reaction rate of CuO against MB (a) zero order, (b) 1<sup>st</sup> order (c) 2<sup>nd</sup> order

The linear curve ln Ct concerning time is used for the kinetic model of order reaction one and a linear 1/Ct curve for order two. Linear regression equation is obtained from the second order, the value of the reaction As presented in Figure 5, the photocatalytic reaction showed to follow second order reaction kinetics.

#### 4. CONCLUSION

CuO photocatalytic activity on MB showed degradation of 63.44%, at the optimum pH 9 with the optimum irradiation time of 120 minutes. Photocatalytic activity is influenced by the formation of hydroxyl radicals which can degrade dyestuffs. The photodegradation mechanism occurs due to the presence of hydroxyl radicals and holes. The reaction rate follows second order kinetics.

#### AUTHORS' CONTRIBUTIONS

All authors have contributions about CONCEPT, METHOD, and ANALYSIS. The contribution in EDITING is A.R. All authors provided feedback, discussed result and contributed to the final manuscript.

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