Kinetic evaluation of methylene blue decolorization by CuO as a Fenton-like catalyst

Y Tiandho\textsuperscript{1,\,*}, F Afriani\textsuperscript{1}, Evi.J\textsuperscript{1}, R Lingga\textsuperscript{2} and Handoyo\textsuperscript{3,4}

\textsuperscript{1}Department of Physics, Universitas Bangka Belitung, Indonesia
\textsuperscript{2}Department of Biology, Universitas Bangka Belitung, Indonesia
\textsuperscript{3}Geophysical Engineering, Institut Teknologi Sumatera, Indonesia
\textsuperscript{4}Facultat de Ciencies de La Terra, Universitat de Barcelona, Spain

\*E-mail: yuant@ubb.ac.id

Abstract. The presence of dyes in wastewater is one of the main problems in wastewater treatment. Wastewater containing dyes can damage the ecosystem because it can block sunlight into the water and is often accompanied by toxic materials. This paper proposes an alternative method to decolorize dyes in water using CuO as a Fenton-like catalyst, especially for wastewater contaminated by methylene blue dye. The Fenton method is an advanced oxidation process method with a radical group of \( \text{H}_2\text{O}_2 \) acting as the primary decolorizing agent. By measuring the concentration using a UV-Vis spectrophotometer, we found that the proposed decolorization method effectively degraded the color of methylene blue. To understand the decolorization mechanism, we investigated the reaction kinetics of the decolorization process. We found that compared to the pseudo-first-order and second-order reaction kinetics models, the BMG model had higher accuracy and conformed to the color concentration degradation curve.

1. Introduction

One of the main problems in water pollution is caused by the presence of dyes in wastewater. These dyes can come from various sources such as the textile industry, printing industry, and various other industries. The presence of dyes in aquatic systems can threaten aquatic ecosystems. In addition to being often toxic, the presence of dyes in aquatic systems will block sunlight from entering the water. It will disrupt various organisms that need sunlight for metabolism and photosynthesis [1, 2].

There are various kinds of dye treatment in wastewater, such as adsorption [3], electrocoagulation [4, 5], ultrasonic decomposition [6], nanofiltration [7], and various advanced oxidation processes (AOPs) methods [8]. Among these methods, AOPs is a hot method that is studied now. There have been several developments in AOPs methods, such as the most popular being Fenton-based oxidation [9], sonophotocatalysis [10], and electrochemical AOPs [11]. AOPs are treatment technologies to degrade and mineralize pollutants from wastewater through reactions with hydroxyl radicals [12].

The Fenton-based oxidation method utilizes hydroxyl radicals for wastewater treatment purposes using Fe\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2} catalysts as a source of hydroxyl radicals [9]. This method has high effectiveness for the wastewater decolorization process. Various development efforts were also carried out, such as integrating with various other systems such as sonication [10], UV and looking for other alternative catalysts [9]. One alternative catalyst that has the potential to be used as Fenton-like oxidation is CuO. Cu is an element with an oxidation number of +1 and +2 to break down H\textsubscript{2}O\textsubscript{2} into HO\textsubscript{2}\textsuperscript{-} and HO\textsuperscript{+} radicals [13].
In this study, we utilized CuO as a catalyst in the Fenton reaction to decolorize methylene blue (MB). MB is a dye model that is often used in the textile industry. The presence of these dyes in wastewater can pose a risk of causing eye irritation and indigestion. We conducted a kinetic study of the decolorization process that occurred. It is because the kinetic model of AOPs is complex and has not been well explained.

2. Method
We used commercial CuO (>99%) from Xilong Chemical Co. Ltd. as a Fenton-like catalyst. As a source of oxidant radicals, technical grade H$_2$O$_2$ (35%) is used. The decolorization process was carried out in a 2.5 ppm methylene blue (MB) solution. For further analysis and simplifying calculations, we refer to this solution as the initial MB solution with a concentration of 100% MB (C$_0$ = 100%). The decolorization mechanism was carried out by mixing 0.5 grams of CuO and 1 ml of H$_2$O$_2$ into the initial 100 ml MB solution. The kinetics evaluation of the decolorization process was carried out by measuring the concentration of MB using a UV-Vis spectrophotometer.

3. Result and Discussion
In Figure 1, the absorbance curve of MB at different concentrations is presented. It appears that the peak of the highest absorbance curve for all concentrations occurs at 664 nm. It is consistent with various other studies which state that the absorbance peak using a UV-Vis spectrophotometer for MB occurs in the range of 663 – 665 nm [14]. Through Figure 1, it can be seen that there is a decrease in the peak value of MB absorbance along with the concentration of MB. Therefore, through the Lambert-Beer law, which relates the relationship between concentration and absorbance, namely [15]:

$$A = \varepsilon C l$$

where $A$ is absorbance, $\varepsilon$ is absorption coefficient, $C$ is concentration, and $l$ is optical path length, then the absorbance peak pattern of MB solution can be used to determine MB concentration.

![Figure 1. UV-Vis spectrophotometer absorbance curve of methylene blue solution](image)

Figure 2 shows a calibration curve of the relationship between MB concentration and the absorbance curve at 664 nm. It appears that the two parameters have an excellent linearity relationship. It is indicated by the value of the coefficient of determination $R^2 = 0.99$. Explicitly, the mathematical relationship between concentration and absorption of the MB solution satisfies:

$$A = 0.0057C_{MB} + 0.0089$$

(2)
where $A$ is the absorbance value at a wavelength of 664 nm, and $C_{MB}$ is the concentration of MB. Next, we use equation (2) to determine the concentration present in the MB solution in the decolorization process.

\[
C_{MB} = \frac{C_{0MB} - A}{0.76 - A} \times 100%
\]  

(3)

Figure 2. Calibration curve of the relationship between MB concentration and absorbance at a wavelength of 664 nm

In Figure 3, the changes in the absorbance curve of MB around the wavelength of 664 nm when decolorized with different reaction times: 20 minutes, 60 minutes, and 120 minutes are presented. It appears that the more prolonged reaction, the absorbance peak decreases. According to the Lambert-Beer law in equation (1), this indicates that the longer the decolorization reaction through a Fenton-like mechanism occurs, the concentration of MB in solution will decrease.

Figure 3. Absorbance curve of MB solution when decolorized at different reaction times

Through the relationship between the absorbance value at a wavelength of 664 nm and the MB concentration as in equation (2), it can be determined the MB concentration value after the decolorization process with different reaction times, as shown in Figure 4(a). In addition, the degree of decolorization ($\%$Decolorization) can be calculated as:

\[
\%\text{Decolorization} = \frac{C_{0MB} - C_{MB}}{C_{0MB}} \times 100%
\]  

(3)
The percent value of MB decolorization in this study is shown in Figure 4(b). It appears that the decolorization process at the beginning of time occurs very quickly. However, the longer the decolorization process becomes, the slower. It is due to the decreasing concentration of MB or the concentration of reactive H_2O_2 and CuO.

![Figure 4. The percent value of: (a) MB concentration after decolorization process and (b) decolorization of MB](image)

Like in the Fenton reaction, CuO as a catalyst in Fenton-like reactions plays a role in accelerating the breakdown of H_2O_2 into hydroxyl radical groups such as HO^- and HO_2^•. However, the reaction kinetics of the decolorization process using hydroxyl radicals tends to be complicated. Therefore, we tried to analyze several models of the reaction kinetics following the experimental results. Several kinetic models analyzed are kinetic models: pseudo-first-order, second-order, and BMG models. The general rate (R) law of the decolorization in Fenton or Fenton-like reaction is:

\[ R = -\frac{dC_{MB}}{dt} = k_{OH}\cdot C_{OH}\cdot C_{MB} + \sum_{i} k_{Ox_i}\cdot C_{Ox_i}\cdot C_{MB} \]  

(4)

the \(O_{ox}\) term represents other oxidants besides HO^- as an active oxidant. The problem is, the concentration of HO^- can not be directly measured. Several models that may accommodate the reaction kinetics of Fenton or Fenton-like reactions are pseudo-first-order, second-order, and BMG models.

The pseudo-first-order reaction equation is derived from the second-order reaction with the provision that in the initial conditions, the concentration of one reactant has a much greater value than the other reactants. In this case, the initial CMB concentration is much greater than the HO• radical concentration. Thus, the mathematical expression is:

\[ C_{MB} = C_{0MB}e^{-k_1t} \]  

(5)

where \(k_1\) is a constant related to the rate of pseudo-first-order reaction kinetics. The second-order kinetics are derived from the rate relationship:

\[ \frac{dC_{MB}}{dt} = -k_2\left(C_{MB}\right)^2 \]  

(6)

Through integration, the solution for the second-order reaction can be obtained:

\[ \frac{1}{C_{MB}} = \frac{1}{C_{0MB}} + k_2t \]  

(7)

where \(k_2\) is a constant related to the rate of second-order reaction kinetics, the BMG kinetic model is a model proposed by Behnajady et al. (2007) to answer the complex problem of the Fenton reaction. In the model, it is proposed that the rate of reaction kinetics satisfies [16]:

\[ \frac{dC_{MB}}{dt} = C_{0MB}\left(\frac{-m}{m + bt^s}\right) \]  

(8)
where \( m \) and \( b \) are the two characteristic constants in the Fenton reaction. Physically, \( 1/m \) corresponds to the methylene blue removal rate, while \( 1/b \) corresponds to the theoretical maximum methylene blue removal fraction. Therefore, the rate on the BMG model meets:

\[
C_{MB} = C_{0,MB} \left( 1 - \frac{t}{m + bt} \right)
\]

To validate the three models according to the experimental results of MB decolorization using CuO as a Fenton-like catalyst, we performed a regression analysis of the three models, and the results are shown in Figure 5 and Table 1. It can be seen that in the pseudo-first-order, the value of \( k_1 = 0.0792 \) is obtained, in the second-order \( k_2 = 0.0012 \), and the BMG model obtained characteristic constants \( m = 1.8548 \) and \( b = 1.0775 \). Based on the comparison of the coefficient of determination adjusted \( R^2 \), the BMG model is the most suitable compared to the others.

Table 1. The parameters of kinetic models and correlation coefficients for the decolorization of MB

| Condition                  | Pseudo-first-order | Second-order | BMG model |
|----------------------------|--------------------|--------------|------------|
|                            | \( k_1 \) (min\(^{-1}\)) | \( k_2 \) (%\(^{-1}\) min\(^{-1}\)) | \( m \) | \( b \) | adj.\( R^2 \) |
| Methylene Blue (\( C_0 = 100\% \)) | 0.0792 | 0.0012 | 1.8548 | 1.0775 | 0.999 |

Figure 5. Kinetics of methylene blue decolorization reaction using CuO as a Fenton-like catalyst: (a) Pseudo-first-order, (b) Second-order, and (c) BMG model

4. Conclusion

The use of CuO as a catalyst in Fenton-like reactions for decolorizing methylene blue has been studied. The experimental results show that the longer the decolorization process using CuO and \( \text{H}_2\text{O}_2 \), the greater the percentage of decolorization that occurs in methylene blue. Based on the comparison of the three reaction kinetics models, namely: pseudo-first-order reaction kinetics model, second-order reaction kinetics model, and BMG model, it is known that the BMG model has a degree of suitability.
compared to others. This decolorization process can be an alternative method for treating wastewater containing dyes such as methylene blue.

References
[1] Al-Tohamy R, Sun J, Fareed M F, Kenawy E R and Ali S S 2020 Scientific Reports 10 1
[2] De-Luca P, Chiodo A, Macario A, Siciliano C, Nagy J B and Van der Bruggen B 2021 Applied Sciences 11 1687
[3] Hamad M T and Saied M S 2021 Applied Water Science 11 1
[4] Sandi, Afriani F and Tiandho Y 2020 IOP Conf. Series: Earth and Environmental Sciences 599 012069
[5] Gusa R F, Sari D N, Afriani F, Sunanda W and Tiandho Y 2020 IOP Conf. Series: Earth and Environmental Science 599 012061
[6] Maheshwari K, Solanki Y S, Ridoy M S H, Agarwal M, Dohare R and Gupta R 2020 Environmental Progress & Sustainable Energy 39 e13410
[7] Donkadokula N Y, Kola A K and Saroj D 2020 Sustainable Environment Research 30 1
[8] Thanavel M, Bankole P O, Selvam R, Govindwar S P and Sadasivam S K 2020 Scientific reports 10 1
[9] Farinelli G, Minella M, Pazzi M, Giannakis S, Pulgarin C, Vione D and Tiraferri A 2020 Journal of Hazardous Materials 393 122413
[10] Sun M, Yao Y, Ding W and Anandan S 2020 Journal of Alloys and Compounds 820 153172
[11] Samarghandi M R, Dargahi A, Shabanloo A, Nasab H Z, Vaziri Y and Ansari A 2020 Arabian Journal of Chemistry 13 6847
[12] Garrido-Cardenas J A, Esteban-García B, Agüera A, Sánchez-Pérez J A and Manzano-Agugliaro F 2020 International Journal of Environmental Research and Public Health 17 170
[13] Zhang T, Dong L, Du J, Qian C and Wang Y 2020 RSC Advances 10 23431
[14] Hadisantoso E P, Ayu Z D, Listiani P and Setiadji S 2021 IOP Conf. Series: Materials Science and Engineering 1098 062066
[15] Gusa R F, Sari D N, Afriani F, Sunanda W and Tiandho Y 2021 Jurnal Ilmiah Pendidikan Fisika Al-Biruni 10 139
[16] Behnajady M A, Modirshahla N and Ghanbary F 2007 Journal of Hazardous Materials 148 98

Acknowledgments
This research was funded by the LPPM-Universitas Bangka Belitung through the PU scheme in 2021 and for publication was funded by the RKAKL of Faculty of Engineering, Universitas Bangka Belitung.