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Kinetic Study of Fenton-Like Degradation of Methylene Blue in Aqueous Solution Using Calcium Peroxide

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ABSTRACT

The textile industry is one of the fastest-growing industries that significantly contribute to the economic growth in Malaysia. Dyeing wastewater is one of the more difficult to control in industrial wastewater. Methylene blue is a widely used dye in the textile industry, which cannot be discharged directly into the natural environment without treatment. The present study involves the degradation of methylene blue by a Fenton-like system using calcium peroxide (CaO_2, CP). The process of degradation was recorded spectrophotometrically. The field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) were measured for testing the purchased commercial calcium peroxide. The effect of pH, the initial dosage of CaO_2, and temperatures were studied with kinetics modeling, respectively. The results indicated that 97.07% removal of methylene blue took place at the optimum condition (pH=3.0, initial CaO_2 dosage=3.0 g, 65°C, 150 rpm, contact time=60 minutes). Over four models (zero-order, first-order, second-order, Behnajady, Modirshahla, and Ghanbary (BMG) model) applied in this study, the BMG model with the R^2=0.9935 was in accordance with the experimental data.

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INTRODUCTION

The textile industry has always been the fastest growing and most widely used industry in Malaysia; what follows is that this industry also has high water consumption and subsequently produces a

high discharge rate of wastewater with a high load of contaminants (Pang & Abdullah, 2013). Dyeing wastewater is present in a large amount of effluent. Each ton of textile processing consumes 100 to 200 tons of water, of which 80 to 90% becomes wastewater. The release of dyes into the environment during textile fiber dyeing and finishing processes is the main source of water pollution. The problems with dyeing wastewater are the content of organic matter that is non-biodegradable, toxic, and high chroma. Therefore many difficulties are added to the design of wastewater treatment process and operation management, which is a type of industrial wastewater with great environmental hazards (Yaseen & Scholz, 2019). Individual wastewater treatment through physical, biological, or chemical methods is often very costly and results in large sludge. Therefore, finding an effective method to complete fast and high rate decolorization for dye wastewater has been focused on in recent years.

Dye effluents released from numerous dye-utilizing industries are harmful to the environment and living things. Dyeing wastewater should be treated first before release to minimize its negative impacts on the environment and living things (Katheresan et al., 2018a). Dyes are colorful substances designed to give fabrics, papers, or any colorable materials a hue. It is possible as dyes can attach themselves to any amenable materials (Yagub et al., 2014). It has been reported that the main methods for dye removal can be separated into three categories: biological, chemical, and physical treatments. Among these, chemical oxidation is the main method for decolorization of dye wastewater, with the commonly used oxidants being ozone or chlorine and its oxygen-containing compounds (Ameta et al., 2014). In contrast, ozone is expensive and inconvenient to put into practice. Additionally, chlorine and its oxygen-containing compounds as oxidants can eventually generate chlorine-containing organic compounds resulting in secondary pollution (Cuerda-Correa et al., 2020). Also, the use of one individual process may often not be sufficient to achieve complete decolorization (Sun et al., 2019). It leads to the study of other more effective methods, such as the Fenton-like system employed in this work, one of the advanced oxidation processes applied for dye removal (Girard, 2013).

Methylene blue is 3,7-bis(dimethylamino)-phenothiazine-5-ium chloride with the molecular formula $C_{16}H_{18}N_3SCl$ (molecular structure as shown in Figure 1, molecular weight = 371.91). This dye belongs to the class of thiazine dye at room temperature, which appears as a solid, odorless, dark green powder. The color of the dye solution in water is blue. It absorbs at 663-667 nm. Moreover, methylene blue is widely used in chemical indicators, dyes, biological stains, and pharmaceuticals, especially in the dyeing industry for the manufacture of

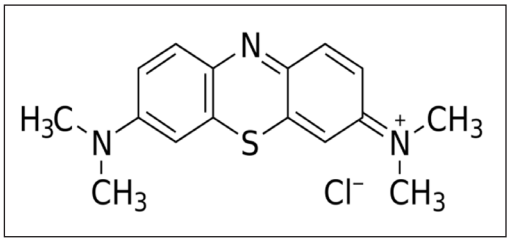


Figure 1. Structure of methylene blue

inks. However, due to its toxicity and removal difficulty, methylene blue has caused serious harm to the ecological environment and also caused irreversible damage to the human body.

Calcium peroxide (CaO_2, CP) is an odorless, tasteless, safe, and non-toxic oxygen release agent regarded as the solid form of H_2O_2. The dried product is quite stable at room temperature and easy to store and transfer compared with liquid H_2O_2. It is used for water-soluble dye wastewater treatment due to its significantly effective decolorization rate (Olyaie et al., 2012). Calcium peroxide in the presence of Fe^{2+} in an acidic medium can release highly active, strong oxidizing hydroxyl free radicals (·OH), resulting in a higher decolorization rate. The reaction mechanism is as follows:

$$CaO_2 + 2H^+ \rightarrow Ca^{2+} + H_2O_2$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \cdot OH,$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-,$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\cdot,$$

$$HO_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + \cdot OH$$

$$\cdot OH + \text{organics(MB)} \rightarrow \text{products(3, 7 bis-dimethylaminophenothiazine ion)} + CO_2 + H_2O$$

Under the acid condition, CaO_2 is converted to H_2O_2. Then, H_2O_2 reacts rapidly with Fe^{2+} to generate OH radicals and Fe^{3+} with strong oxidizing ability. Moreover, Fe^{3+} reacts with H_2O_2 to slowly form Fe^{2+}, OH radicals attack organic molecules, oxidizes, and destroy the chromophoric groups to achieve the purpose of degradation (Liu, 2018). That is to say, as mentioned previously, the methylene blue solution is blue naturally. When encountering strong oxidants, it will lose electrons to form colorless 3, 7 bis-dimethylaminophenothiazine ions. In addition, the degradation process of MB triggers the decrease of toxicity due to the destruction of chemical structure. Based on the reactions above, it can be concluded that the oxidized by-products are CO_2 and H_2O, which are nontoxic.

In recent years, ample evidence exists to support the view that the Fenton system, as a typical advanced oxidation process (AOPs), is extremely efficient in treating wastewater containing MB and any other dye molecules, such as chromotrope 2R, methyl orange, phenol red (Katheresan et al., 2018b). Therefore, according to several kinetic models, it is vital to assess the rate of dye decolorization. More importantly, kinetic models developed on a laboratory scale are essential for reactor design, scale-up, and performance prediction. Only a first-order linear model has been employed in a few recent kinetics investigations of wastewater via Fenton processes. However, certain correlation coefficients defining reaction kinetics (R^2) were lower than 0.9 (Hou et al., 2016), indicating that the first-order model is not always the most appropriate. To summarize, the current work aims to conduct

the investigations on different models (zero-, first-, second-order, and BMG—Behnajady, Modirshahla, and Ghanbary). Here, it is worth mentioning that the BMG model is a kinetic model established to predict the decolorization by the Fenton process under various operating circumstances. This model can be applied to study a system that includes the effects of hydrogen peroxide, Fe(II), and dye concentrations or temperatures (Behnajady et al., 2007).

Previous researchers have reported on the removal of methylene blue from wastewater, but the cost of those methods is still quite high; meanwhile, the process will also generate other by-products or by-waste. In this work, commercial calcium peroxide, as a solid form of hydrogen peroxide under the catalysis of Ferrous ion ($FeSO_4$), was used for methylene blue removal from wastewater. Furthermore, the effect of pH, the effect of initial calcium peroxide dosage, and temperature were also reported with four kinetics models applied.

MATERIALS AND METHODOLOGY

Chemical Reagents and Instruments

Methylene blue, calcium peroxide (65%, commercial), ferrous sulfate ($FeSO_4$), sodium sulfite (Na_2SO_3, 2.0 M), sodium hydroxide, hydrochloric acid, hydrogen peroxide (H_2O_2, 30%, 9.8 M), and other chemicals employed in the present study were of analytical grade chemicals. The pH of the solution was measured by the digital pH meter (Model: Sartorius PB-10). The desired pH of the solution was adjusted by the addition of previously standardized 0.1 N hydrochloric acid and 0.1 N sodium hydroxide solutions. UV spectrophotometer (Model: HALO DB-20) was used to monitor the degradation process.

Methodology

Calcium peroxide (65%, commercial) was purchased, with field emission scanning electron microscope (FESEM) and energy dispersive X-ray analysis (EDX) applied to identify the particle appearance, size range together with the elemental composition of materials. 10 ppm solution of methylene blue was prepared in a volumetric flask with distilled water and stored as a stock solution. This solution was further used as a standard dye solution in the desired wastewater environment. Ferrous sulfate ($FeSO_4$), as the source of Fe^{2+}, was prepared at the concentration of 0.5 mmol L^{-1}. The pH value was adjusted at pH=3.0 as the optimal reaction pH for the Fenton-like system using standardized 0.1 N hydrochloric acid and 0.1 N sodium hydroxide solutions. The analysis of the concentration of the MB was carried out by using UV-Vis spectroscopy, in which the MB molecule exhibits an absorbance spectrum at 665 nm. In order to quench the Fenton-like reaction, 0.5 mL sodium sulfite (Na_2SO_3) was added into each sample before absorbance determination to consume residual

H_2O_2 instantaneously. The calibration curve of methylene blue (R^2=0.9958) was prepared, as well. Ultimately, dye removal percentage was calculated by the following Equation 1:

$$\text{Total Dye Removal Percentage} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \qquad [1]$$

where C_0 and C_t are the concentration of dye (methylene blue) at initial and a given contact time t, respectively.
The following parameters were studied in the present study:

Effect of pH

The effect of pH on methylene blue removal was evaluated at the pH value of 3, 7, and 11. In this set, experiments were conducted with other parameters retained (3.0 g CaO_2, 100 mL 10 ppm MB solution, 150 rpm, RT=25 ± 2°C, contact time= 60 minutes) while the absorbance values were acquired for every 10 minutes.

Effect of Initial Dosage of CaO_2

The effect of CaO_2 dosage on the rate of degradation was investigated by varying the initial dosage of CaO_2 from 0.5, 1.5, and 3.0 g. Next, 100 mL 10 ppm of methylene blue solution was added into a conical flask. The initial pH of MB solution was tested at pH=5.65 naturally and adjusted to pH=3.0. Then, the solution was placed into a water bath shaker and agitated at 150 rpm. The experiment was conducted at room temperature, around 25°C. The sample was withdrawn from the flask every 10 minutes in duration of 1 h and was filtered through 0.25 μm filter paper. Then, 2 mL of the filtered sample was filled into a cuvette to determine the absorbance and concentration by using a UV-Vis spectrophotometer.

Effect of Temperature

The effect of temperature on methylene blue removal was evaluated at 25 ± 2°C (room temperature), 45, 65°C. In this set, experiments were conducted with retaining other parameters (3.0 g CaO_2, 100 mL 10 ppm MB solution, pH=3.0, 150 rpm, contact time= 60 minutes) while the absorbance values were acquired every 10 minutes.

Kinetics Study

Four kinetic models (zero-order, first-order, second-order models, and BMG models) were applied in this work for kinetics studies (Santana et al., 2019). The modeling equations are listed in Table 1, respectively:

Table 1
Kinetic modelling equations

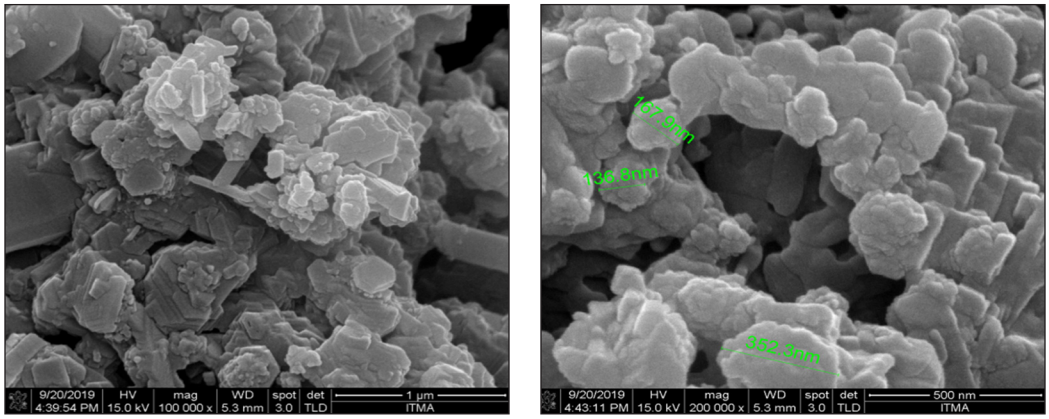
Order	Equation Applied	Linear Form by Intergration
Zero-order	$\frac{dC_t}{dt} = -k_0$	$C_t = C_0 - k_0 \cdot t$
First-order	$\frac{dC_t}{dt} = -k_1 \cdot C_t$	$ln\, C_t = lnC_0 - k_1 \cdot t$
Second-order	$\frac{dC_t}{dt} = -k_2 \cdot (C_t)^2$	$\frac{1}{C_t} = \frac{1}{C_0} + k_2 \cdot t$
BMG model	$\frac{C_1}{C_0} = 1 - \left[\frac{t}{(m + b \cdot t)}\right]$	$\frac{t}{\left[1 - \left(\frac{C_t}{C_0}\right)\right]} = m + bt$

Note. k_0, k_1, and k_2 are apparent kinetic rate constants of zero-, first-, and second-order models, respectively, *t* is reaction time, and C_t is dye concentration at a given time t; where m and b are two constants concerning initial reaction rate and maximum oxidation capacity, respectively)

RESULTS AND DISCUSSION

Field Emission Scanning Electron Microscope (FESEM)

The morphology of samples was evaluated by FESEM images (Rashid et al., 2018). Figures 2 (a) and (b) indicate that commercial calcium peroxide [a): 100,000x, b): 200,000x] appears irregular flake shapes of particles, along with excessive aggregation, which lowers surface area and reaction efficiency. The particle size ranges from 130 nm to 355 nm, which is greatly larger than nanoparticles measured in typical research conducted (Madan et al., 2016).



(a) (b)

Figure 2. FESEM images of commercial calcium peroxide (130 nm - 355 nm): (a) 100,000×; (b) 200,000 ×

Energy Dispersive X-ray (EDX) Result

The chemical purity and stoichiometry of the samples were studied by EDX (Soltani et al., 2021). Figure 3 presents the main peaks of calcium and oxygen in a commercial CaO_2 sample. The atomic % of Ca and O are 23.12% and 58.43%, respectively. Peaks assigned to the Pt are presented as well because Pt properly coated the sample. The overall weight% and atomic% are also reported in Table 2. Furthermore, the EDX result confirmed the presence of C elements in the nanoparticles due to the impurities during the synthesis process.

Table 2
The overall percentage of calcium peroxide based on EDX

Element	Weight%	Atomic%
C	4.92	12.78
O	29.95	58.43
Ca	29.69	23.12
Pt	35.44	5.67
Total	100.00	100.00

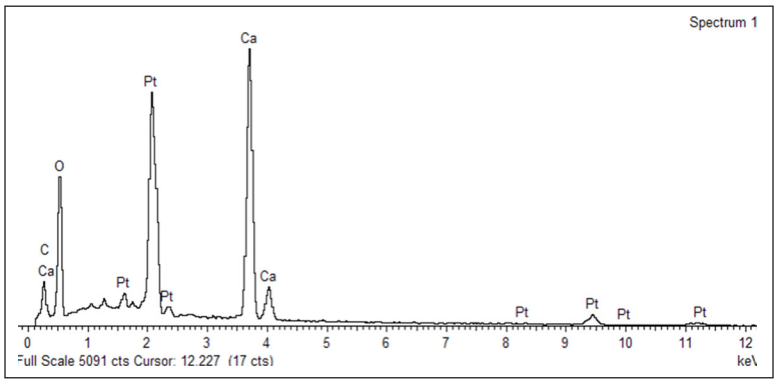


Figure 3. EDX spectrum of commercial calcium peroxide

Effect of pH

As is mentioned earlier, pH is another essential parameter for the Fenton system. In the Fenton process, the H^+ concentration greatly affects the formation of H_2O_2, which in turn controls the generation of the hydroxyl radical. Therefore, pH is one of the most important factors to study. Since the form of iron in the solution is restricted by the pH, the Fenton reagent only works under acidic conditions. In neutral and alkaline environments, Fe cannot catalyze the production of H_2O_2 completely, resulting in lower removal. In this study, as shown in Figure 4, the optimal pH was obtained at pH=3.0, with a total removal percentage of 87.57%. Beside that, removal percentage achieved 67.70% and 43.90% over pH=7.0 and pH=11.0, respectively. Prior researchers have reported that when pH value is in the range of 2 to 4, the removal effect is higher, and the optimal occurs at pH=2.5 - 3.5. A representative work conducted previously suggested that the optimum pH for dyeing wastewater treatment was 3, with over 20 dyes studied (Xu et al., 2004). Tran and coworkers reported that at pH=3.0 using the Fenton process, the maximal removal percentage (91.91%)

was obtained for glyphosate removal (Tran et al., 2021). It is also reported that among solid peroxides, such as CaO_2, Na_2O_2, and liquid H_2O_2, the optimal pH is 2.5 (Trovó et al., 2016). To conclude, pH=3.0 is regarded as the optimum pH for the removal of methylene blue using a Fenton-like reagent. When it comes to the kinetics modeling shown in Figure 5 and Table 3, it can be concluded that the second-order fit the reaction the most with R^2 value= 0.9498 compared to the other models. Aiming at the BMG model, pH=3.0 showed the best suitability with R^2 value= 0.9925. Setup (pH= 11.0) could not fit the BMG model due to low decay based on the experimental data.

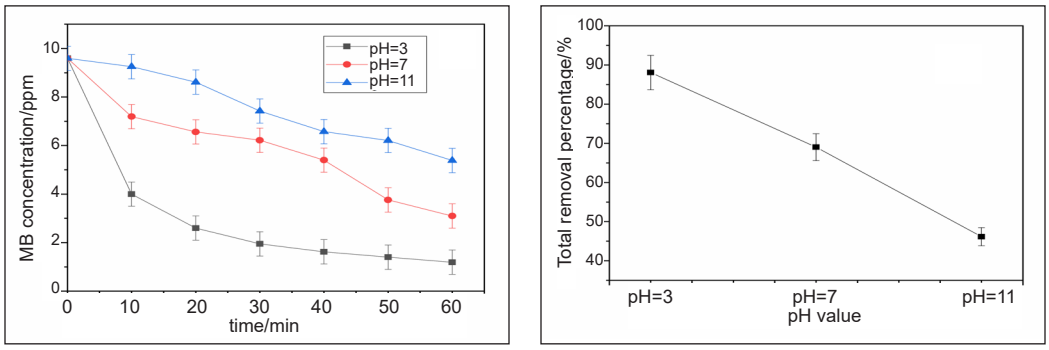


Figure 4. (a) Degradation of the MB concentration over time on different pH at 3,7,11. (b) Effect of different pH on removal percentage of MB (initial MB concentration = 10 ppm, RT, 150 rpm, Time = 60 min)

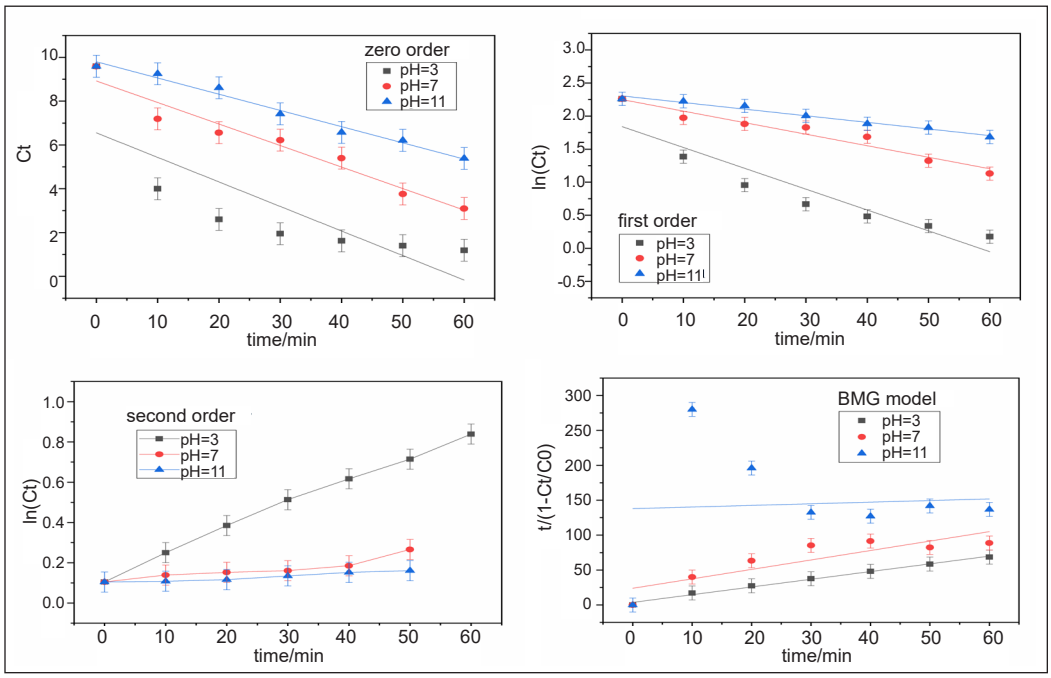


Figure 5. Degradation data of methylene blue using different kinetic models under different pH

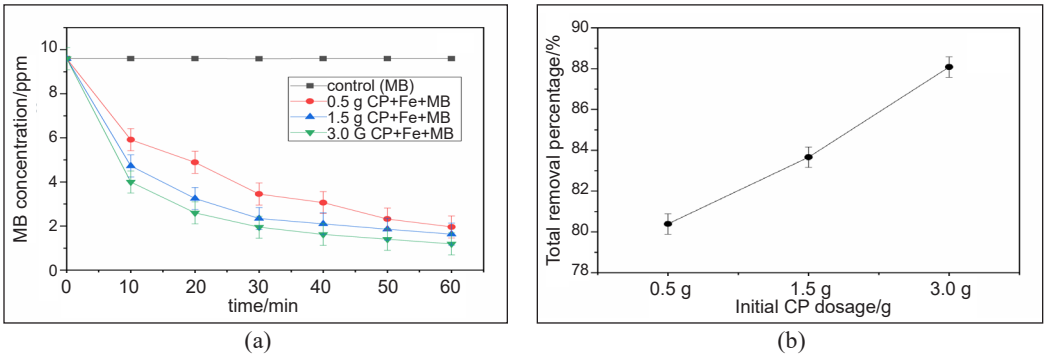
Table 3
MB degradation percentages after 60 min through Fenton-like processes at different pH, apparent kinetic rate constants of the zero- (k_0), first- (k_1), and second-order(k_2), parameters obtained from the BMG model (1/m and 1/b) and correlation coefficients (R^2) obtained after data fits

		Zero-order		First-order		Second-order		BMG Model		
pH	**Removal (%)**	**K_0**	**R^2**	**K_1**	**R^2**	**K_2**	**R^2**	**1/m**	**1/b**	**R^2**
3	87.57	0.1120	0.6616	0.0315	0.8818	0.0120	0.9959	0.2716	0.9060	0.9925
7	67.70	0.0982	0.9488	0.0174	0.9473	0.0037	0.8896	0.3224	0.7396	0.7502
11	43.90	0.0741	0.9824	0.0100	0.9789	0.0014	0.9638	-	-	-
Average R^2			**0.8641**		**0.9360**		**0.9498**			**0.8713**

Effect of Initial Dosage of Calcium Peroxide

To the main point, the kinetic study on different initial dosages in the range of 0.5 to 3.0 g was shown in Figure 6 (a), and on the right side, the overall removal percentages with different initial CaO_2 dosages were also presented in Figure 6 (b). It can be seen that with the increase of initial dosage (0.5 g-3.0 g), a higher removal percentage was obtained (80.39%, 83.66%, 88.08%). As observed from the plot, there is a sharp plunge of concentration in the first hour of contacting time, which reveals the Fenton-like system is a rapid and effective reaction at the initial stage.

Linear regression analyses based on zero-, first-, and second-order reaction kinetics for the removal of methylene blue (MB) through Fenton-like processes were conducted to obtain the values of k_0, k_1, and k_2, as well as the BMG model, for which the results are shown in Table 4 and Figure 7. According to the correlation coefficient values(R^2), the second-order reaction kinetics was the most fitted to present degradation process for the reason that the highest R^2=0.9871 was obtained, followed by the BMG model (R^2=0.9761), subsequently first-order reaction model (R^2=0.9115) and zero-order model (R^2=0.7407) as the lowest correlation coefficient values (R^2). Considering parameter 1/b obtained by the



(a) (b)

Figure 6. (a) Degradation of the MB concentration over time on different initial dosages in the range of 0.5 g to 3.0 g. (b) Effect of CaO_2 dosage on the removal of MB (initial MB concentration = 10 ppm, Temperature = 25 ± 2°C, 150 rpm, Time = 60 min)

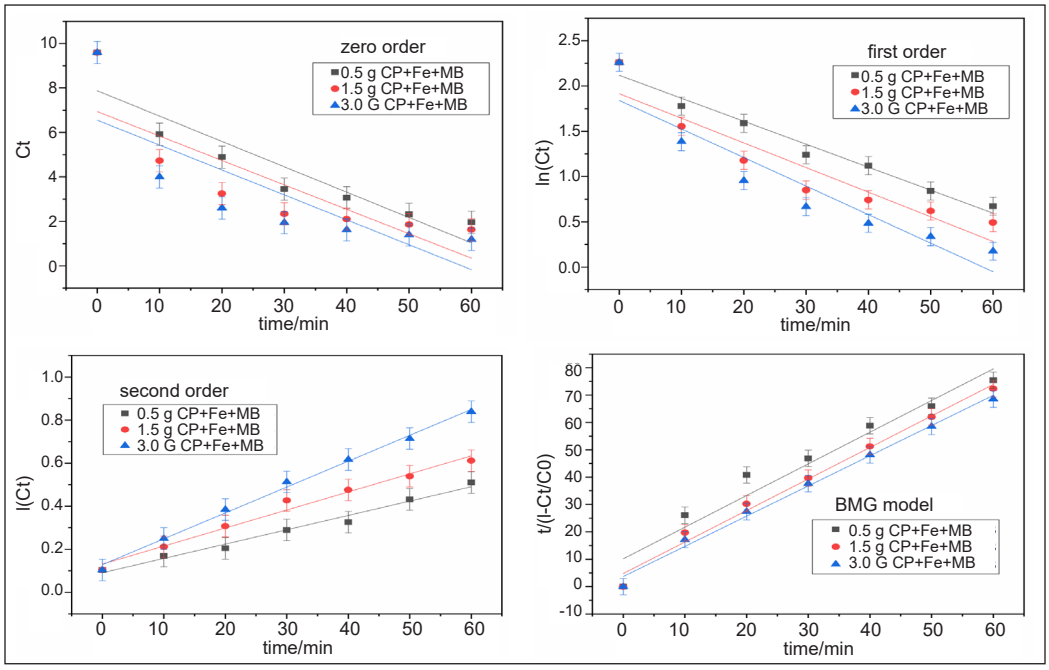


Figure 7. Degradation data of methylene blue using different kinetic models under different initial calcium peroxide dosage

Table 4
MB degradation percentages after 60 min through Fenton-like processes at different initial CP dosages, apparent kinetic rate constants of the zero- (k_0), first- (k_1), and second-order(k_2), parameters obtained from the BMG model (1/m and 1/b) and correlation coefficients (R^2) obtained after data fits

CP Initial dosage(g)	Removal (%)	Zero-order		First-order		Second-order		BMG Model		
		K_0	R^2	K_1	R^2	K_2	R^2	1/m	1/b	R^2
0.5	79.56	0.1121	0.8572	0.0254	0.9737	0.0067	0.9834	0.0986	0.8645	0.9470
1.5	82.69	0.1099	0.7039	0.0272	0.8805	0.0084	0.9824	0.2236	0.8683	0.9885
3.0	87.57	0.1121	0.6610	0.0315	0.8802	0.0120	0.9955	0.2729	0.9060	0.9927
Average R^2			**0.7407**		**0.9115**		**0.9871**			**0.9761**

BMG model, it is possible to observe that the maximum oxidation capacity (Defined as 1/b) is quite close at each dosage. In terms of parameter 1/m (Initial Degradation Rate), which keeps an upward tendency, it indicates that with 3.0 g calcium peroxide dosage holds the most initial degradation rate. In addition, a sharp surge of initial degradation rate happened from the dosage of 0.5 to 3.0 g initial calcium peroxide dosage. It can be estimated that initial CP dosage impacts both initial degradation rate and total removal percentage. Besides, the oxidation of organic compounds by Fenton processes using Fe^{2+} as a catalyst generally proceeds via two stages: a fast one and a much slower one. The last stage is attributed to a reaction between Fe^{2+} and H_2O_2, while the slower one is due to the

accumulation of Fe^{3+} and low recovery of Fe^{2+} by H_2O_2 (León et al., 2021). Since R^2 >0.9 was inferred from the first order, second order, and BMG model, it is also can be found that the suitability of more than one kinetic model is also common for modeling study.

Effect of Temperature

Among the parameters relating to the Fenton process, temperature and initial reaction pH affect removal reaction in significant measure (Sun et al., 2019). Generally, temperature plays an important part in many chemical reactions, which means the reaction rate will increase with temperature (Soltani et al., 2017; Rashid et al., 2018). Some studies demonstrated that as the reaction temperature increases, the degradation rate of contaminant also increases steadily in the Fenton system (Emami et al., 2010). Nevertheless, in some research, it has been reported that for the Fenton system, once the temperature reaches a certain degree, the reaction will slow down or stop, in turn declining the total removal percentage of contaminants. Most probably, the generation rate of •OH is enhanced at a high temperature, but when the temperature approaches a certain point, hydrogen peroxide undergoes self-accelerating decomposition, thus reducing the concentration of •OH (Soltani et al., 2020). Likewise, it was reported that while reaching more than 30°C, the removal rate down slowly. At low temperature, activation energy is insufficient, inhibiting the synthesis of HO•, while at high temperature, the decomposition of H_2O_2 into HO• becomes faster, the concentration of HO• increases (Zhou et al., 2012). Both sides claimed that temperature increment had a positive and promoting impact on the degradation process. In this work, seen from Figure 8, as the temperature goes up, the degradation is greater and faster as revealed at 65°C with the highest total removal percentage= 97.07% within 60 minutes. While 92.76% removal of MB at T=45°C and 87.57% removal of MB at RT were achieved. It is also worth noting that the decolorization reaction takes less time at

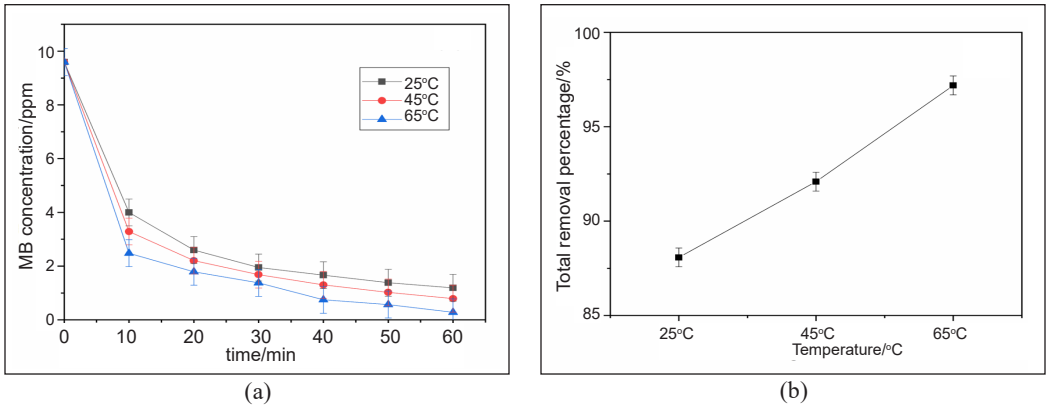


Figure 8. (a) Degradation of the MB concentration over time on the different temperatures at 25°C, 45°C, 65°C. (b) Effect of different temperatures on removal of MB (Initial MB concentration = 10 ppm, pH=3.0, 150 rpm, Time = 60 min)

higher temperatures, as shown in Figure 8(a). The process at 65°C has already reached the practically total removal % value of the process at RT (25°C) in roughly 30 minutes.

Four kinetic models were applied to test the reaction at different temperatures. The kinetic parameter plots and data are shown in Figure 9 and Table 5. Regarding the three classical kinetic models, the increase in the apparent rate constant as a function of temperature can be verified. As for the BMG model, due to the increase in temperature, an increase in oxidation capacity (1/b) and a faster initial reaction rate (1/m) can be observed. In this set of experiments, the BMG model fits the experimental data well, and R^2=0.9935

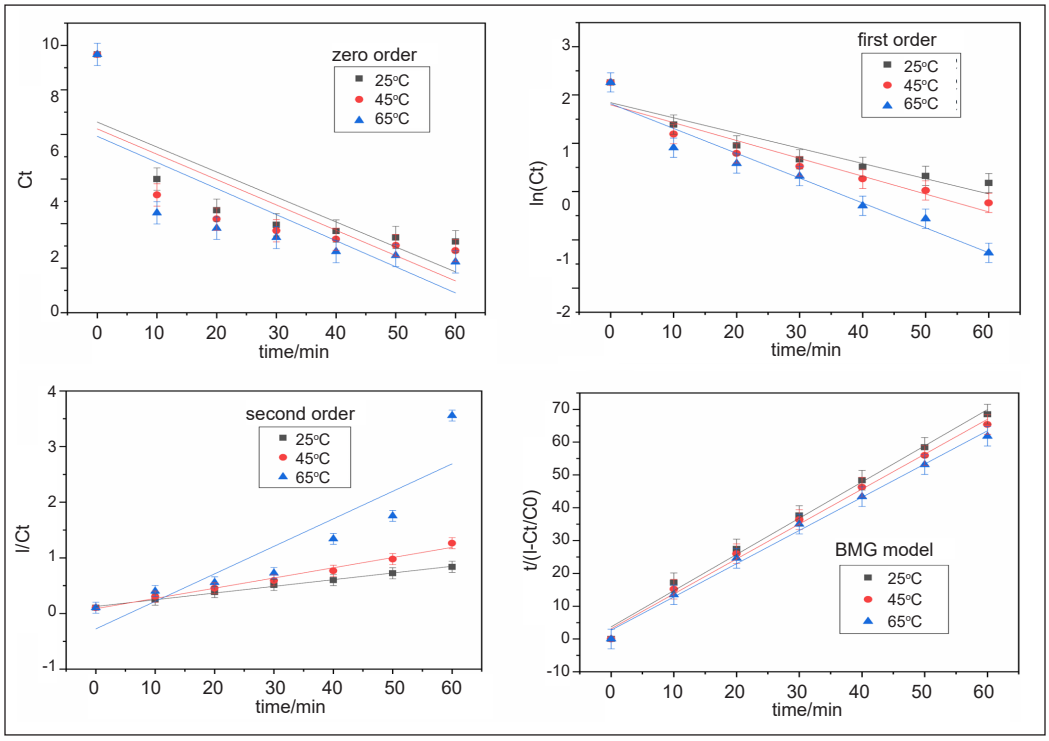


Figure 9. Degradation data of methylene blue using different kinetic models under different temperatures

Table 5
MB degradation percentages after 60 min through Fenton-like processes at different temperatures, apparent kinetic rate constants of the zero- (k_0), first- (k_1), and second-order(k_2), parameters obtained from the BMG model (1/m and 1/b) and correlation coefficients (R^2) obtained after data fits

		Zero-order		First-order		Second-order		BMG Model		
Temperature (°C)	**Removal (%)**	**K_0**	**R^2**	**K_1**	**R^2**	**K_2**	**R^2**	**1/m**	**1/b**	**R^2**
25	87.57	0.1120	0.6616	0.0315	0.8818	0.0120	0.9959	0.2716	0.9060	0.9925
45	91.76	0.1137	0.6307	0.0370	0.9020	0.0184	0.9868	0.3224	0.9397	0.9940
65	97.07	0.1171	0.6030	0.0514	0.9444	0.0495	0.8192	0.3727	0.9875	0.9941
Average R^2			**0.6318**		**0.9094**		**0.9339**			**0.9935**

is obtained. This increment is due to a higher temperature, which increases the reaction rate between hydrogen peroxide and iron, thereby increasing the production of reactive oxygen species, such as HO• radicals.

Comparison of Dye Removal in Wastewater by Fenton (Fenton-like) Processes

Table 6 summarizes the previous works in terms of dyeing wastewater treatment through Fenton and Fenton-like processes. It demonstrated that Fenton and Fenton-like processes perform outstandingly for soluble and insoluble dyes suggesting its superior cost-effectiveness in removing various dyes. The present work provides a new approach for Fenton processes in wastewater treatment, which can be employed further in the industrial field considering the cost and efficiency.

Table 6
Comparison of dye removal in wastewater by Fenton (Fenton-like) processes

Dye	Condition	Result	Maximum removal/%	Reference
Direct Blue 71	Batch reactor; iron^{2+}=3 mg/L , 100 mg/L(dye concentration), 3 (initial pH), 132 mg/L (hydrogen peroxide concentration), 20–60°C; 20 min	50.7% COD removal	94%	Ertugay & Acar, 2017
Methylene Blue	Optimum: pH = 4, 10 mg/L MB, [H_2O_2] = 23.58 mmol/L, 0.372 g/L Fc(catalyst), 60°C	Novelty: Ferrocene is catalyst; following the the pseudo- first-order kinetic model	99.50%	Wang et al., 2013
Acid Orange 24	Optimal condition: Fe^{2+}=0.75 g/L, [hydrogen peroxide]= 0.75 g/L, [dye]=3 ml/L, pH=3 , reaction time= 40 min.	95.5% COD removal	95%	Ebrahiem et al., 2017
Disperse Red 343	pH=3.82, [Fe]= 0.33 mmol L^{-1}, [H_2O_2]= 0.54 mmol L^{-}, time= 1 hr, RT	No residual H_2O_2	100%	Fernandes et al., 2018
Methylene Blue	Optimal condition: pH=3, [initial dye]= 10 ppm, [Fe]= 0.5 mmol L^{-1}, CaO_2 dosage= 3.0 g, 65°C, 60 minutes	Significant performance; All effects gave a strong correlation toward the degradation of methylene blue	97.07%	Present study

CONCLUSION

In the present work, the degradation of methylene blue in a Fenton-like system was investigated using commercial calcium peroxide as an oxidant. Various parameters such as the effect of pH, initial calcium peroxide dosage, and temperature were studied with kinetic models applied, respectively. Based on the results, under conditions (pH=3.0, initial CP dosage= 3.0 g, Fe^{2+} as a catalyst, contact time= 60 minutes, 65°C), 97.07% degradation was

achieved, which demonstrated that calcium peroxide is a significantly effective oxidant for degradation of methylene blue dye wastewater. Additionally, among the four kinetic models studied, the second-order kinetic model fitted the reactions well, and the BMG model was the most appropriate with the initial dosage and temperature study. To sum up, all effects gave a strong correlation toward the degradation of methylene blue. The Fenton-like process can be widely used to treat water discharge containing dyes such as methylene blue in an effective and less expensive approach compared to conventional processes.

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