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EVALUATION OF MINERAL-BASED HYDROXYAPATITE/ZnO NANOCOMPOSITE AS PHOTOCATALYST FOR METHYLENE BLUE DEGRADATION

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Abstract

The use of dyes in the textile industry has increased significantly, raising concerns about their potential to pollute the environment and harm human health. Methylene blue is a widely used synthetic dye, necessitating effective methods for its degradation. Photodegradation is a promising approach to decompose dyes into simpler, less harmful compounds. In this study, hydroxyapatite combined with ZnO was employed as a photocatalyst material to enhance photocatalytic performance. The research aims to degrade methylene blue using a Hydroxyapatite/ZnO (HAp/ZnO) nanocomposite through photodegradation. The optimization of the photodegradation process was investigated by varying irradiation time, methylene blue concentration, and pH. The optimum degradation of methylene blue was achieved using 20 mg of HAp/ZnO nanocomposite at an irradiation time of 120 minutes, an initial methylene blue concentration of 5 ppm, and pH 7. Adsorption isotherm modeling revealed that the process followed the Langmuir isotherm model, with a maximum adsorption capacity (q_{max}) of 0.3353 mg/g. The degradation followed pseudo-second-order kinetics with a reaction rate constant of 4.0026×10^5 L/mol·s.

INTRODUCTION

The rapid development of the textile industry has contributed to environmental pollution due to the increased use of dyes [1]. In this industry, large quantities of dyes are used to color products, making it a major source of dye waste, particularly synthetic dyes [2]. The presence of dyes and other pollutants in water sources not only threatens aquatic ecosystems but also poses significant risks to human health if these contaminated sources are used for daily activities [3-4]. One of the most commonly used dyes in the textile industry is methylene blue [5]. Prolonged accumulation of methylene blue in the human body can lead to severe health issues, including hypersensitive dermatitis, mental disorders, nausea, abdominal pain, cancer, and genetic mutations [5].

Additionally, a high concentration of dye molecules in water can disrupt the photosynthesis process, further impacting aquatic life [6]. A significant portion of these dye wastes is discharged into the environment without proper treatment, leading to severe ecological damage and pollution of water bodies [7-8].

Photodegradation is an effective method for decomposing dyes into harmless compounds in a simple and efficient manner [9]. This approach offers several advantages, including environmental friendliness, low operational costs, high efficiency, and minimal production of secondary pollutants [10]. The effectiveness of the method largely depends on the choice of semiconductor photocatalyst material [11]. The photocatalysis mechanism begins when electrons (e^-) in the valence band are excited to the conduction band, creating holes (h^+) in the valence band. These holes interact with water (H_2O) or hydroxide ions (OH^-) to generate hydroxyl radicals (OH•), which can degrade harmful organic compounds into simpler or fully mineralized forms. Simultaneously, the excited electrons react with oxygen molecules to form superoxide radicals, further enhancing the degradation process [12].

Extensive research has been conducted on the use of hydroxyapatite as a support material to enhance the photocatalytic performance of catalysts [13–16]. However, combining hydroxyapatite with semiconductor catalysts such as ZnO can further improve photocatalytic activity [12,17]. ZnO exhibits strong oxidizing ability, excellent photocatalytic properties, high photosensitivity, chemical stability, biocompatibility, non-toxicity, as well as electronic and piezoelectric characteristics. Due to its similarities with TiO_2, ZnO is considered a suitable alternative to TiO_2-based semiconductors [18–19].

In photocatalysis, modified hydroxyapatite is increasingly recognized as a promising class of photocatalysts for pollution remediation [20–23]. Hybrid metal oxide semiconductors serve as effective photocatalysts due to their environmental safety and ability to degrade organic pollutants under UV or visible light exposure, making them valuable for water purification [7,24]. To mitigate environmental damage, wastewater discharged into aquatic ecosystems must first undergo proper treatment to prevent ecological harm [25]. The photocatalyst material used in this study was synthesized in previous research [26] and has been employed as a mineral-based photocatalyst for the UV-assisted degradation of methylene blue (MB).

EXPERIMENT

Material

The materials used in this study include a hydroxyapatite/ZnO nanocomposite photocatalyst derived from the limestone of PT. Kurnia Artha Pratiwi Padalarang, 96% ethanol, methylene blue (MB), and distilled water.

Instrumentation

This study utilizes a centrifuge (PLC-05), a magnetic stirrer, and a UV-Vis spectrophotometer (Shimadzu UV-1800).

Procedure

Preparation of the MB Calibration Curve

A total of 0.01 g of methylene blue (MB) dye was weighed and dissolved in a 100-mL volumetric flask, then ethanol was added up to the calibration mark. This process resulted in a 100 ppm methylene blue stock solution, which was subsequently diluted to obtain standard solutions with concentrations of 1, 3, 5, 7, 10, and 12 ppm. The maximum absorption wavelength was then determined (**Figure 1**). The absorbance of each standard solution was measured using a UV-Vis spectrophotometer at the identified maximum wavelength (**Figure 2**).

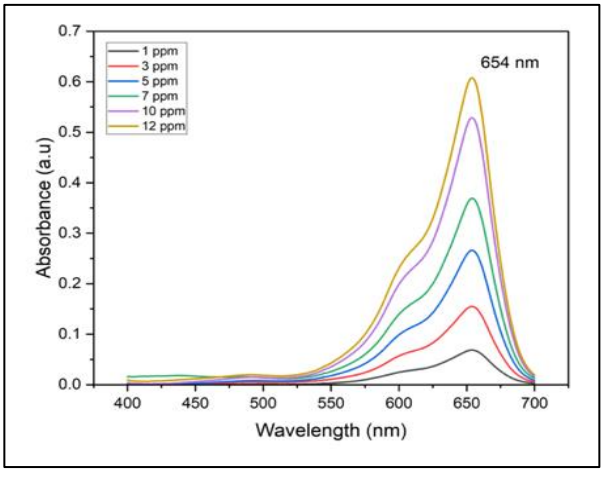


Figure 1. Visible spectrum of MB standard solution series.

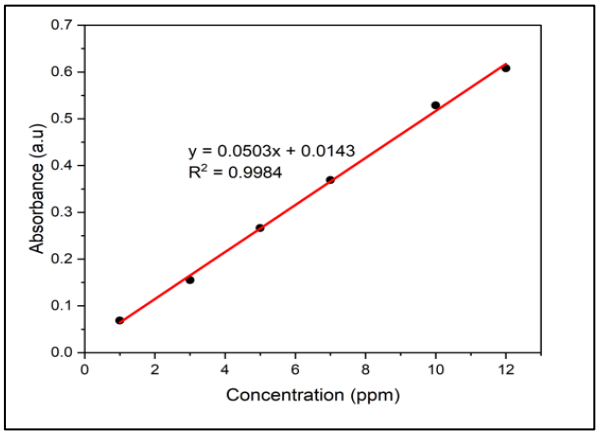


Figure 2. Linear regression of absorbance as a function of MB concentration.

Optimization of Photodegradation Parameters

Variation on MB initial concentration

A total of 0.02 grams of the HAp/ZnO nanocomposite was weighed and placed into a 150-mL beaker. Then, 10 mL of methylene blue (MB) solution was added, with concentrations varied to 5, 6, 7, 8, 9, and 10 ppm. The mixture was then exposed to UV light for 120 minutes while being stirred with a magnetic stirrer. Afterward, the filtrate was separated from the composite residue using a centrifuge. The absorbance of the obtained filtrate was measured using a UV-Vis spectrophotometer [27].

Variation on irradiation time

A total of 0.02 grams of the HAp/ZnO nanocomposite was weighed and placed into a 150-mL beaker. Then, 10 mL of methylene blue (MB) solution with a concentration of 8 ppm was added. Irradiation under UV light was carried out with eight time variations: -30, -20, -10, (without irradiation) 30, 60, 90, and 120 minutes (with irradiation), while stirring with a magnetic stirrer. The filtrate was then separated from the composite residue using a centrifuge. The absorbance of the obtained filtrate was measured using a UV-Vis spectrophotometer [27].

Variation on pH solution

A total of 0.02 grams of the HAp/ZnO nanocomposite was weighed and placed into a 150-mL beaker. It was then mixed with 10 mL of methylene blue (MB) solution with a concentration of 7 ppm. The pH of the solution was adjusted to 3, 7, and 11 by adding HCl and NaOH. Next, the solution was exposed to UV light for 120 minutes while being stirred with a magnetic stirrer. Following this, the filtrate was separated from the composite residue using a centrifuge. The absorbance of the obtained filtrate was then measured using a UV-Vis spectrophotometer.

Adsorption Isotherm Study

The adsorption isotherm [28] was then analyzed to determine the adsorption capacity and the interaction between the adsorbent and adsorbate. To model the adsorption isotherm, the concentration of methylene blue was monitored during the 120-minute photocatalytic process while maintaining a constant pH level. The adsorption isotherm was modeled using the Langmuir, Freundlich, and Temkin (**equation 1-3**) [29].

$$\frac{c_e}{q_e} = \frac{1}{K_l \times q_0} + \frac{c_e}{q_e} \qquad (1)$$

The variable q_o represents the maximum amount of adsorbent (mg/g), while K_L represents the Langmuir constant (L/mg).

$$Log\ q_e = Log\ K_f + \frac{1}{n}\ Log\ C_e \qquad (2)$$

In this equation, K_F represents the adsorption capacity (L/mg), while 1/n represents the adsorption intensity or surface heterogeneity.

$$q_e = \frac{RT}{b}\ ln\ C_e + \frac{RT}{b}\ ln\ K_m \qquad (3)$$

Where R is the universal gas constant (J/mol.K), T is the temperature (K), b is the Temkin constant related to sorption heat (J/mol), and K_m is the Temkin isotherm constant (L/mg).

Reaction Kinetics Study

Changes in the chemical reaction during the photodegradation process were observed by monitoring the breakdown of methylene blue over 120 minutes at a concentration of 8 ppm with pH control. The reaction kinetics were analyzed using pseudo-zero-order, pseudo-first-order, and pseudo-second-order models, represented by (**equation 4-6**) [30].

$$C_o - C_t = -k_0 t \qquad (4)$$

$$lnC_t = lnC_o - k_1 t \quad (5)$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \quad (6)$$

Where C_0 is the initial concentration of methylene blue (ppm), C_t is the concentration of methylene blue at a certain time (ppm), and t is the photocatalyst reaction time (min). The value of k_0 is the pseudo-zeroth order reaction rate constant ($mgL^{-1}min^{-1}$), k_1 is the pseudo-first-order reaction rate constant (min^{-1}) and k_2 is the pseudo-second-order reaction rate constant ($L\ mg^{-1}s^{-1}$).

RESULT AND DISCUSSION

Photocatalyst Performance Test

The Effect of MB Initial Concentration

As the concentration of the dye solution increased, the percentage of dye degradation decreased. The optimum degradation occurred at a concentration of 5 ppm, achieving 44.8% degradation (**Figure 3**). This decline in degradation efficiency may be attributed to the accumulation of dye molecules on the surface of the photocatalyst as the solution concentration increases. This accumulation forms a layer that covers the photocatalyst's active sites, reducing their availability for interaction with methylene blue. As a result, fewer hydroxyl radicals are generated to break down the pollutants, and the catalytic efficiency decreases. Additionally, the presence of a higher concentration of dye molecules reduces light penetration, as the dye itself absorbs most of the photons. This limits the number of photons reaching the photocatalyst surface, thereby decreasing the excitation of electrons and holes required for the photocatalytic reaction [27,31-34].

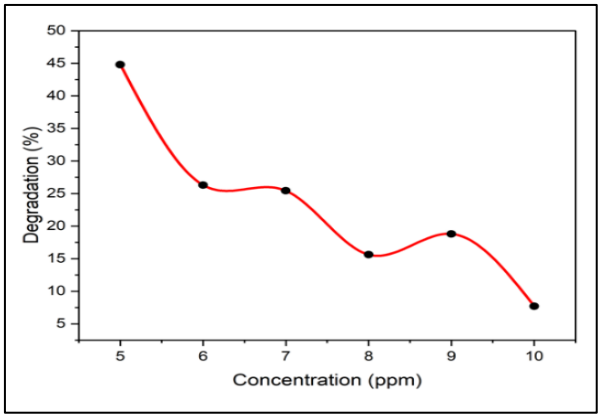


Figure 3. The effect of MB concentration on the MB degradation percentage.

Effect of Irradiation Time

The percentage of methylene blue (MB) degradation increased with contact time. At an MB concentration of 8 ppm, the optimum irradiation time was 120 minutes, achieving a degradation percentage of 15.75% (**Figure 4**). This increase in degradation efficiency can be attributed to the prolonged interaction between the photocatalyst and UV light, which enhances energy generation within the photocatalyst. As a result, more reactive species are produced, leading to a higher degradation rate.

The energy generated during the process is used to produce hydroxyl radicals. As the photodegradation progresses, the OH^- radicals become increasingly active in breaking down dye molecules [31,35]. However, over time, the availability of active sites on the catalyst surface decreases due to the repulsive forces between adsorbed molecules, making it more difficult for additional dye molecules to interact with the catalyst [36]. Consequently, the degradation percentage tends to plateau after a certain period, typically around 60 minutes [37].

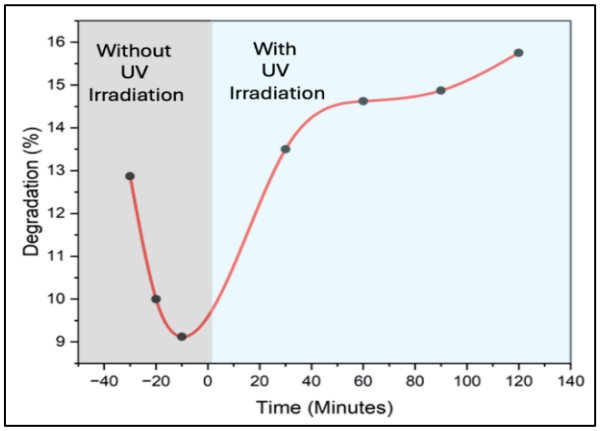


Figure 4. The effect of irradiation time on MB degradation percentage.

Effect of pH Solution

In this study, the pH of the methylene blue solution was varied at 3, 7, and 11. As shown in **Figure 5**, the optimum condition for methylene blue degradation occurred at pH 7, achieving a degradation percentage of 59.71%. According to previous research [38], pH 7 has been identified as the most effective condition for breaking down mercaptobenzoxazole using an HAp/ZnO nanocomposite. At this pH, the positively charged catalyst surface interacts favorably with the positively charged dye molecules due to

electrostatic attraction, facilitating the adsorption and degradation of methylene blue [39]. However, at pH levels above 7, both the dye molecules and the catalyst surface become negatively charged, resulting in electrostatic repulsion that inhibits adsorption and reduces degradation efficiency [40]. Therefore, it hinders the methylene blue adsorption process.

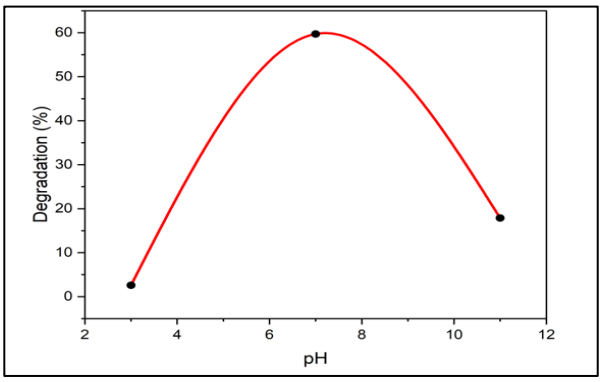


Figure 5. The effect of pH solution on the MB degradation percentage.

Isotherm Adsorption Study

Several adsorption isotherm parameters were obtained and are presented in **Table 1**. Among the three models evaluated, the Langmuir isotherm model, with an R^2 value of 0.7588 (**Figure 6**), demonstrated a better fit compared to the Freundlich (0.5797) and Temkin (0.6748) models. Therefore, the adsorption of methylene blue onto the surface of the HAp/ZnO nanocomposite is best described by the Langmuir isotherm model. This indicates that the adsorption process occurs in a monolayer on a homogeneous surface, where each active site on the adsorbent can accommodate only one adsorbate molecule, with no interactions occurring between adsorbate molecules [41]. The modeling results align with previous research, which also identified the Langmuir model as the most suitable for describing the adsorption isotherm of HAp/ZnO [42].

Table 1. Adsorption Isotherm Modeling Parameters.

Model	Parameter	Value
Langmuir	Q_0 (mg/g)	0.3353
	K_L (L/mg)	0.3645
	R^2	0.7588
Freundlich	K_F (L/mg)	2.4575
	n	-1.4219
	R^2	0.5797
Temkin	RT/b	-0.5018
	K_m (L/mg)	26.0145
	R^2	0.6748

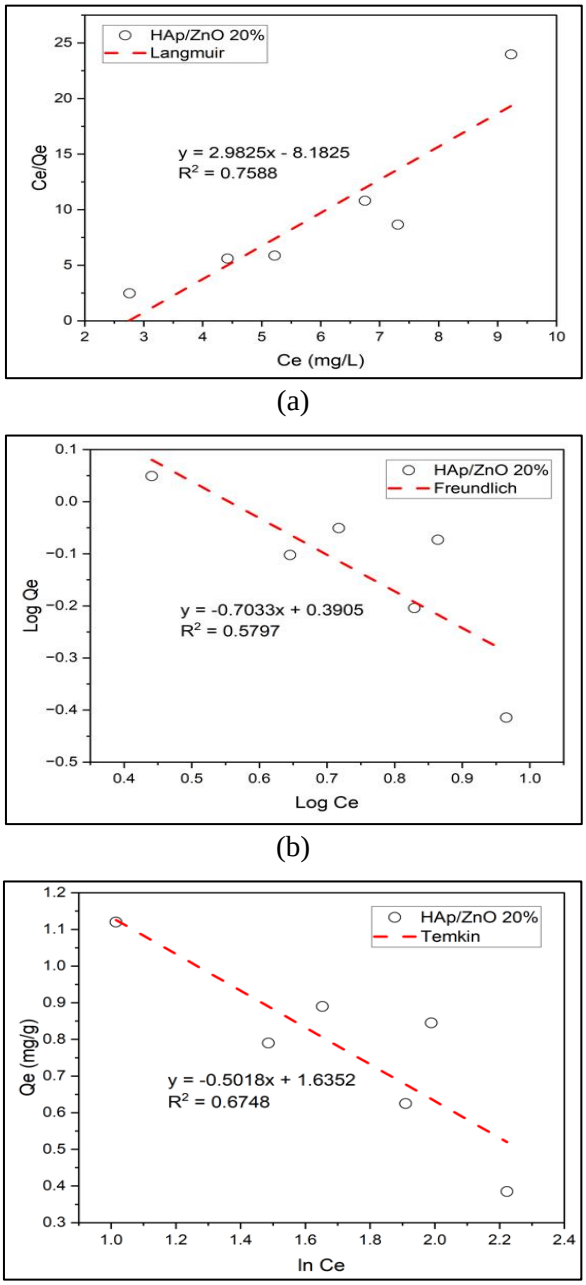


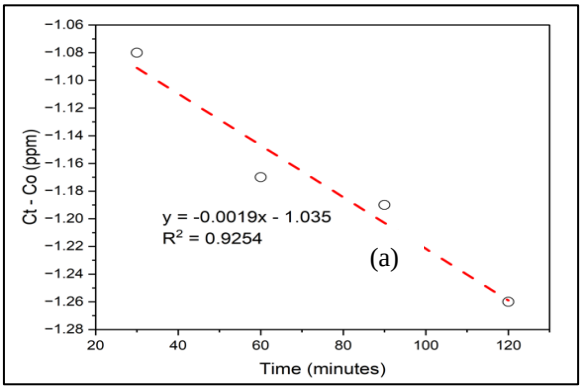
Figure 6. Plots of adsorption modeling (a) Langmuir, (b) Freundlich, and (c) Temkin.

Photodegradation Reaction Kinetics Study

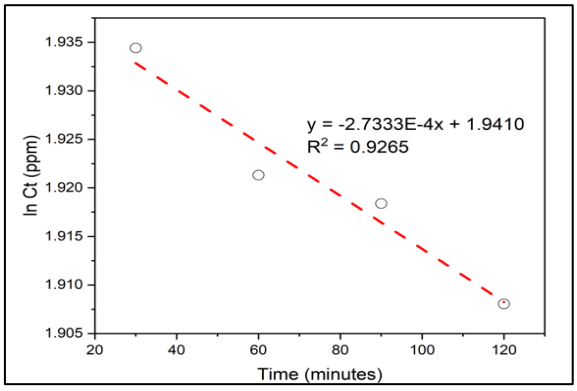
The reaction kinetics study was conducted to analyze the photodegradation behavior of methylene blue in the presence of the HAp/ZnO nanocomposite and to determine the degradation rate. The results of this study are presented in **Figure 7**.

One of the key parameters in the graph is the R^2 value, which is 0.9275. This indicates that the photocatalytic degradation of methylene blue follows pseudo-second-order reaction kinetics. Plotting $1/C_t$ (final concentration) against time (t)

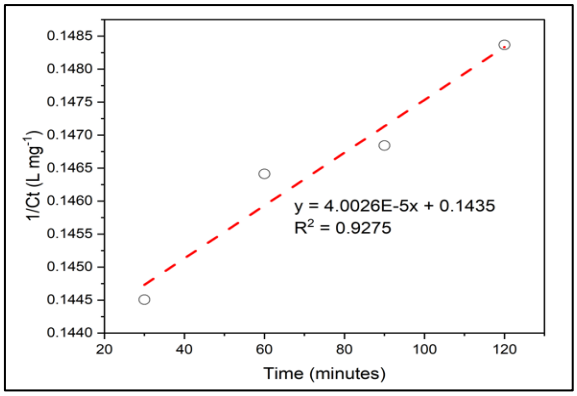
resulted in a linear curve, confirming the second-order reaction model. Additionally, the reaction kinetics were analyzed using pseudo-zero-order and pseudo-first-order models. The slope of the graph [43] represents the reaction rate constant, which was determined to be 4.0026×10^5 L/mol·min. A higher reaction rate constant signifies a faster degradation process [43]. The findings of this study align with those reported by Kusumawati, where the reaction kinetics of hydroxyapatite-activated carbon also followed a pseudo-second-order model, with a rate constant of 1×10^5 L/mol·min [44].



(a)



(b)



(c)

Figure 7. Plots of (a) pseudo-zeroth order, (b) pseudo-first order, and (c) pseudo-second order.

CONCLUSION

The results demonstrated that the HAp/ZnO nanocomposite effectively degraded methylene blue in water through photocatalysis. The optimal degradation occurred under specific conditions: a photon exposure time of 120 minutes, a pH of 7, a catalyst weight of 20 mg, and an initial methylene blue concentration of 5 ppm. Adsorption isotherm modeling indicated that the interaction between the HAp/ZnO nanocomposite and methylene blue followed the Langmuir isotherm model, with an R^2 value of 0.7588 and a maximum adsorption capacity of 0.3353 mg/g. Furthermore, the degradation process followed pseudo-second-order kinetics, highlighting the effectiveness and reliability of the HAp/ZnO nanocomposite as a photocatalyst.

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