Science and Technology Indonesia
e-ISSN:2580-4391 *p*-ISSN:2580-4405
Vol. 9, No. 4, October 2024

Research Paper

The Effects of Hydrothermal Temperatures on ZnO-Bentonite Composite Synthesis on Adsorption and Photodegradation of Methylene Blue Dye

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Abstract
This study explores the influence of hydrothermal temperatures on the synthesis of ZnO-Bentonite composites and their efficiency in the adsorption and photodegradation of Methylene Blue dye. ZnO nanoparticles were integrated into Na-Bentonite, with composites synthesized at hydrothermal temperatures of 100°C and 200°C. Various characterization techniques such as XRD, FTIR, UV-Vis DRS, TG-DTA and BET were utilized to analyze the structural and thermal properties. The results show that the composite synthesized at 200°C exhibits superior performance, with a maximum adsorption capacity of 120.48 mg/g at 50°C, significantly higher than the 49.26 mg/g achieved by the composite synthesized at 100°C. Moreover, the enhanced crystallinity and increased surface area, as evidenced by a 16 nm crystallite size at 100°C and 22 nm at 200°C, led to improved photocatalytic activity. The research concludes that higher hydrothermal temperatures improve both adsorption and photodegradation efficiency, making the composite synthesized at 200°C more effective for environmental applications.

Keywords
ZnO-Bentonite, Hydrothermal Synthesis, Adsorption, Photodegradation, Methylene Blue

Received: 11 July 2024, Accepted: 1 October 2024
https://doi.org/10.26554/sti.2024.9.4.1033-1041

1. INTRODUCTION

Bentonite, a naturally occurring clay, is widely recognized for its superior adsorption properties, making it an effective material for removing both metal contaminants and organic dyes from industrial wastewater. One of the most concerning dyes is Methylene Blue (MB), a cationic dye commonly used in industries such as textiles, paper, and leather. When present in high concentrations, dyes like MB and Congo Red (CR), representing cationic and anionic dyes respectively, pose significant environmental threats due to their toxicity and persistence (Oladoye, 2022). Cationic dyes, including MB, are particularly dangerous because their positive charge enables them to easily interact with negatively charged biological cells, increasing their potential toxicity to living organisms (Inyinbor, 2016). Consequently, the removal of these dyes from wastewater has become a crucial environmental concern.

Several methods are available for removing dyes and other organic compounds from wastewater, including chemical, physical, and biological treatments, as well as combinations of these techniques (Zhao, 2020). Among these, adsorption has been widely employed due to its efficiency and simplicity. Factors such as concentration, temperature, surface area, particle size, and contact time play critical roles in the adsorption process (Yang, 2021).

Additionally, photocatalysis has emerged as an effective complementary technique, particularly when using materials like ZnO, which can harness sunlight to degrade pollutants into less harmful substances. Photocatalysts are advantageous not only due to their degradative abilities but also because of their recyclability and potential for sunlight-driven processes, making them suitable for sustainable environmental applications (Kabra, 2020).

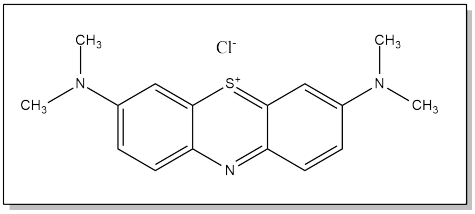

Figure 1. Chemical Structure of Methylene Blue

MB, with the chemical formula $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ and a molecular weight of 319.85 g/mol, is a carcinogenic and mutagenic substance that is difficult to degrade via conventional wastewater treatment methods (Gillman, 2021). Its strong affinity for water, combined with its chemical stability, makes it particularly resistant to biodegradation, thus posing significant challenges for wastewater management (Jiang, 2022). The incorporation of advanced materials like ZnO-modified bentonite has shown promise in overcoming these challenges. ZnO not only enhances the adsorption capacity of bentonite but also provides photocatalytic properties that accelerate the breakdown of organic contaminants such as MB (Sasikala et al., 2019).

The incorporation of ZnO into bentonite has been explored by various researchers due to its dual functionality in adsorption and photocatalytic applications. For instance, Sasikala et al. (2019) reported that ZnO-modified bentonite showed improved physical and chemical properties, including enhanced crystallinity and an increase in surface area. Nguyen et al. (2020) explored the hydrothermal synthesis of ZnO-bentonite composites and found that ZnO not only increases the surface area but also enhances the material's photocatalytic degradation efficiency, particularly under UV light. In comparison, our study focuses on the influence of hydrothermal temperature variation during synthesis, which has not been extensively explored in previous works. While previous studies concentrated on structural improvements and catalytic potential, this research provides new insights into how temperature affects the material's overall performance in both adsorption and photodegradation. Specifically, this study highlights the role of higher hydrothermal temperatures in enhancing surface area, pore structure, and crystallinity, which directly improves both the adsorption capacity and photodegradation efficiency.

In this study we synthesized ZnO columnar clay catalyst (Bentonite-ZnO) with hydrothermal temperature variation system and applied it as catalyst in Methylene Blue dye degradation through adsorption and photocatalysis procedures. The prepared materials were characterized using XRD, FTIR, UV-DRS, BET and TG-DTA analysis. Photocatalytic and flocculation factors studied include pH variation, exposure time variation, weight variation and reaction temperature variation.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instrumentation

Bentonite clay was obtained from West Java through a purification process. Pure-grade chemicals such as sodium chloride (NaCl), sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), hydrochloric acid (HCl), Methylene Blue (MB) dye, and distilled water were obtained from Merck and used directly without further purification. Instrumentation used includes an X-ray diffraction (XRD) D2 Phaser (Bruker Co., Germany), Fourier Transform Infrared (FTIR) 660D-ATR (JASCO Inc., Japan), Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) V-670 (JASCO Inc., Japan), and Thermogravimetric Differential Thermal Analyzer (TG-DTA) Thermoplus EVO 2 TG-DTA 8122 (Rigaku Co., Japan).

2.2 Bentonite Intercalation by Hydrothermal Modification

The cation exchange method was used to modify natural bentonite at room temperature (25°C). Saturated NaCl solution was used to dissolve 100 g of natural bentonite at a ratio of one to three times the bentonite weight. The mixture was then agitated for two hours. Subsequently, distilled water (twice the volume of the mixture) was added while continuously stirring for 10 minutes. The bentonite mixture obtained was precipitated and repeatedly treated with 333 mL of saturated NaCl, then mixed for another 2 hours. The mixture was washed three times with boiling distilled water. The precipitate was then dried in an oven at modified temperatures of 100°C and 200°C.

2.3 Synthesis of ZnO-Bentonite Composite

The design of the ZnO-Bentonite composite was carried out with a ratio of 1:2. A quantity of 10 grams of prepared bentonite was added to a solution containing 5 grams of hexahydrate zinc nitrate dissolved in 250 mL of distilled water. The solution was mixed on a magnetic stirrer until homogeneous. Then, 100 mL of 0.1 M NaOH solution was added to this solution with constant stirring for 1 hour. The mixture was then maintained at a temperature of 25°C for 5 hours. The resulting precipitate was separated from the supernatant by filtration and washed with alcohol. The solid was dried at a temperature of 200°C for 4 hours. Subsequently, the obtained bentonite and ZnO-bentonite composite were characterized using XRD, FT-IR, UV-Vis DRS, and TG-DTA.

2.4 Adsorption Studies

The impact of adsorption time was evaluated by varying the duration at intervals of 10, 20, 30, 40, 50, 60, 70, and 80 minutes. The adsorption process used 0.02 g of adsorbent in 20 mL of a 15 mg/L MB dye solution. The effect of pH on adsorption was examined by varying pH levels from 2 to 8. The influence of temperature and initial concentration on MB adsorption was investigated at different temperatures (30, 40, and 50 °C) and initial MB concentrations of 50, 65, 80, 95, 110, and 125 mg/L.

The adsorption kinetics for this experiment, as investigated by Wu et al. (2021), are represented by the pseudo-first order and pseudo-second order kinetic models, which are detailed in Equations (1) and (2), respectively:

$$ln(q_e - q_t) = lnq_e - tK_1 \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{1}{q_e} \quad (2)$$

In these equations, K_1 represents the rate constant for the pseudo-first order (min^{-1}), K_2 is the rate constant for the pseudo-second order ($g{\cdot}mg^{-1}{\cdot}min^{-1}$), t denotes time, and q_e and q_t are the adsorption capacities at equilibrium and at a specific time, respectively.

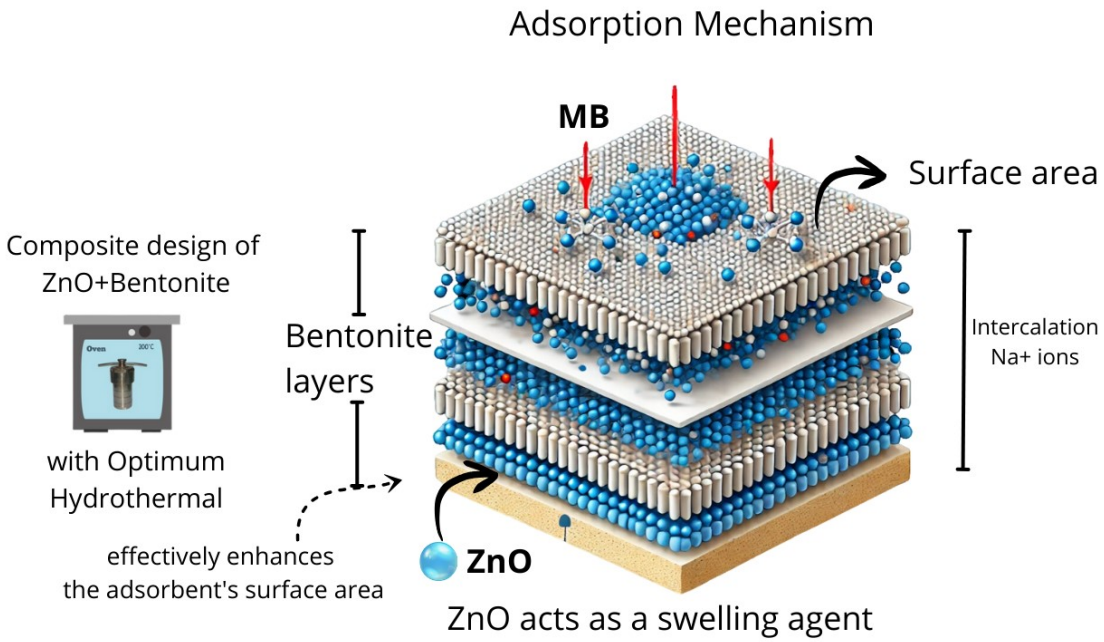

Figure 2. Adsorption Mechanism of ZnO-Bentonite

The Langmuir and Freundlich adsorption isotherms were analyzed to determine the adsorption characteristics of this experiment, following the equations provided by Sahnoun et al. (2018):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

$$lnq_e = lnK_F + \frac{lnC_e}{n} \quad (4)$$

In these equations q_e epresents the equilibrium adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium concentration after adsorption (mg/L), q_{max} denotes the maximum adsorption capacity (mg/g), K_L is the Langmuir adsorption constant (L/mg), Additionally, K_F and n are the Freundlich adsorption constants (L/g).

Thermodynamic parameters can be analyzed using the equations provided by Huang et al. (2017):

$$\Delta G = -RTlnK_d \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

Where ΔG is the value of free energy Gibbs (kJ/mol), ΔH is the enthalpy change of adsorption (kJ/mol), ΔS is adsorption entropy change (kJ/mol.K), R is the standard gas constant (8.324 kJ/mol), T is temperature reaction (K), and K_d is the equilibrium constant.

2.5 Analysis of Mechanism Adsorption

The adsorption of MB onto ZnO-Bentonite composites primarily involves electrostatic interactions between the cationic MB molecules and the negatively charged surface of the bentonite. The ZnO nanoparticles significantly contribute to the surface area enhancement, thereby providing additional adsorption sites for the dye (Figure 2). This process is favored at acidic conditions, particularly around pH 5, where the surface charge of bentonite becomes more negative, enhancing the electrostatic attraction between the composite and the cationic dye molecules (Zhu et al., 2020).

Intercalation of Na^+ into the bentonite layers further promotes ion-exchange capabilities, increasing the material's adsorption potential (Karthik and Meenakshi, 2019). ZnO also stabilizes the bentonite structure, preserving the composite's porosity and surface area, as observed in the BET surface analysis (Zhu et al., 2020). Moreover, ZnO's catalytic activity can also assist in the photodegradation of MB under UV irradiation, making it an ideal material for combined adsorption and photocatalytic applications (Karthik and Meenakshi, 2019).

The surface area and adsorption capacity of the ZnO-Bentonite composites were experimentally measured using BET (Brunauer-Emmett-Teller) surface area analysis. The results indicated a significant increase in surface area, particularly in the sample synthesized at 200°C, which correlates with its enhanced adsorption performance. Additionally, the adsorption kinetics were analyzed using pseudo-first-order and pseudo-second-order models. The pseudo-second-order model provided a better fit for the adsorption process, indicating that chemisorption predominantly controls the adsorption of MB molecules on the composite surface (Wu et al., 2021).

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The X-Ray Diffraction (XRD) patterns of natural bentonite, Bentonite-Na, and Bentonite-ZnO composites at different hydrothermal temperatures (Figure 3) demonstrate key changes in crystallinity and phase composition. The natural bentonite shows distinct peaks around 2θ = 6.18°, 19.8°, and 26.5°, corresponding to the layered structure of montmorillonite and quartz impurities.

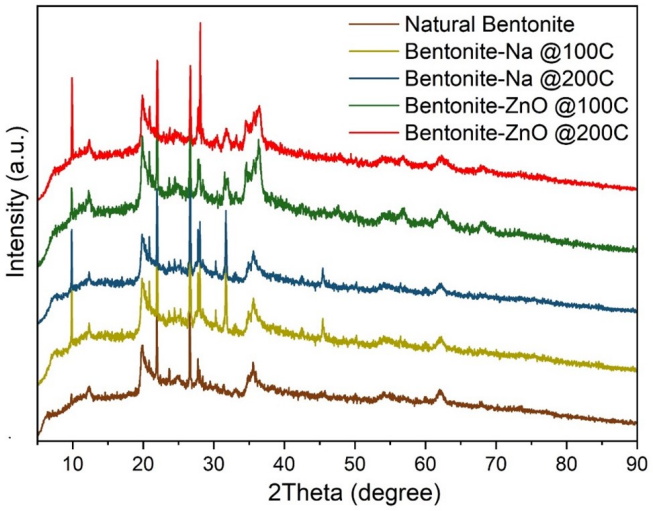

Figure 3. XRD Patterns of Natural Bentonite, Bentonite-Na and Bentonite-ZnO

Upon treatment to form Bentonite-Na, there is a noticeable increase in peak intensity at 2θ = 19.8°, indicating an enhancement in the crystallinity of the montmorillonite phase. The introduction of ZnO at 100°C results in additional peaks at 2θ = 31.8°, 34.4°, and 36.2°, which correspond to the hexagonal wurtzite structure of ZnO nanoparticles . These peaks become sharper and more defined in the Bentonite-ZnO composite synthesized at 200°C, suggesting improved crystallinity and particle size refinement due to the higher hydrothermal temperature.

The overall XRD patterns also reveal a broadening of peaks for ZnO-bentonite synthesized at 100°C, indicating smaller crystal sizes. Scherrer's equation analysis yields crystallite sizes of ~16 nm at 100°C and ~22 nm at 200°C. This increase in crystallinity at 200°C suggests that higher temperatures promote more effective ZnO incorporation into the bentonite matrix, enhancing the material's structural stability and surface area, which is beneficial for adsorption and photocatalytic applications.

The thermal stability and decomposition behavior of natural bentonite, Bentonite-Na, and Bentonite-ZnO composites were evaluated using TG-DTA (Figure 4). The TG curve for natural bentonite shows a significant weight loss of 12% between 50°C and 200°C, attributable to the loss of adsorbed

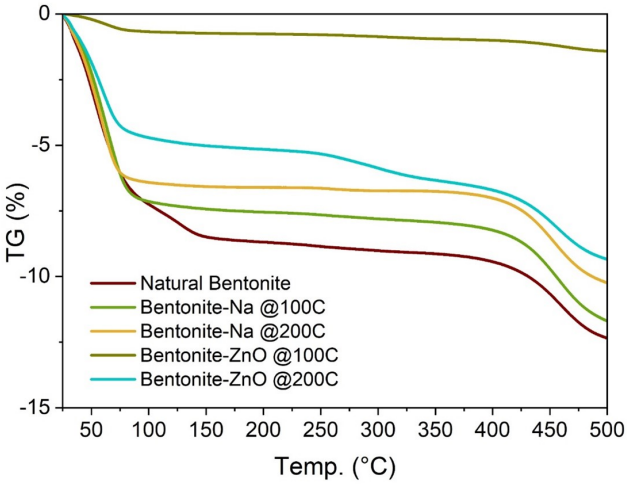

Figure 4. Thermogravimetric Differential Thermal Analyzer (TG-DTA)

water. Bentonite-Na exhibits a similar trend but with a lower total weight loss, indicating improved thermal stability due to the sodium activation.

For the Bentonite-ZnO composites, the TG curves demonstrate interesting behavior. The sample synthesized at 100°C shows a more gradual weight loss, amounting to ~8%, and appears more stable at higher temperatures (above 300°C) compared to the other samples. This can be attributed to the incomplete crystallization of ZnO, as confirmed by the XRD results, and the weaker interaction between ZnO and bentonite at lower hydrothermal temperatures. In contrast, the Bentonite-ZnO composite synthesized at 200°C exhibits a steeper weight loss, particularly between 100°C and 300°C, corresponding to the loss of adsorbed water and organic impurities. The overall weight loss for this sample is ~10%, which is slightly higher than the 100°C sample, suggesting that the structural changes at higher temperatures result in more significant water loss and thermal decomposition of residual organic compounds.

The DTA curves show a prominent exothermic peak around 300°C for the Bentonite-ZnO composite at 200°C, indicating the crystallization of ZnO, which supports the XRD findings. The improved thermal stability and lower weight loss at higher temperatures suggest that the ZnO-bentonite composite at 100°C has a more porous structure, which may enhance its adsorption capacity, while the 200°C sample benefits from better crystallinity, making it more effective for photocatalytic applications.

The distinctive vibrational bands corresponding to characteristic functional groups in bentonite and ZnO are displayed in the FTIR spectra of natural bentonite, Bentonite-Na, and Bentonite-ZnO composites synthesized at 100°C and 200°C (Figure 5). Numerous notable peaks are detected between 500 and 4000 cm^{-1}, suggesting crucial alterations in the material's structure as the hydrothermal temperature rises.

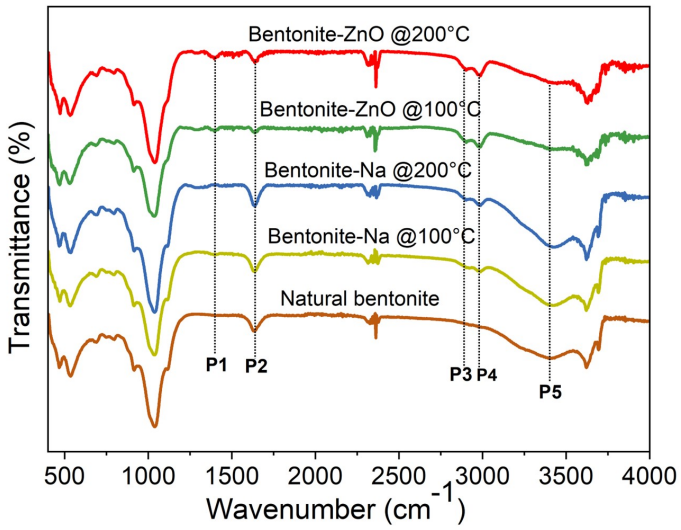

Figure 5. FT-IR Spectrums of Natural Bentonite, Bentonite-Na and Bentonite-ZnO

At region P1 (around 1000 cm^{-1}), corresponding to the stretching vibrations of Si−O−Si, a clear shift in peak position is observed. The Bentonite-Na sample synthesized at 200°C exhibits a sharp peak, indicative of enhanced structural reorganization, while the peak for Bentonite-ZnO at 200°C shows a similar trend but with reduced intensity due to the partial coverage of bentonite by ZnO nanoparticles. In the P2 region (around 1630 cm^{-1}), the H-O-H bending mode of water molecules is dominant. The Bentonite-ZnO samples exhibit a decrease in intensity, suggesting a lower degree of adsorbed water molecules at higher hydrothermal temperatures, which correlates well with the TG-DTA results.

In the P3–P4 regions (2900–3000 cm^{-1}), which correspond to the C−H stretching vibrations, a reduction in peak intensity with increasing hydrothermal temperature is noticeable, indicating the removal of organic impurities during the thermal treatment. Lastly, in the P5 region (3400 cm^{-1}), corresponding to the O−H stretching of hydroxyl groups, a distinct broad band is seen in natural and Bentonite-Na samples, while in Bentonite-ZnO, the band narrows, confirming the interaction of ZnO with bentonite, thus reducing the surface hydroxyl groups.

These findings align with similar trends observed in previous works where the incorporation of metal oxides such as ZnO into bentonite matrices resulted in significant changes in surface hydroxyl groups and structural organization of silicates under hydrothermal conditions. The analysis of the FTIR, XRD, and TG-DTA results reveals that hydrothermal synthesis at 200°C results in a more crystalline and thermally stable ZnO-bentonite composite, which is advantageous for photocatalytic degradation of Methylene Blue due to enhanced ZnO crystallinity. However, the sample synthesized at 100°C, with its more porous structure and higher thermal stability, may perform better in adsorption applications. These results are consistent with the work of previous studies on bentonite-ZnO composites and provide further insights into the role of hydrothermal temperature in tuning material properties.

The nitrogen adsorption-desorption isotherms provide insightful information on the surface characteristics of the materials analyzed, specifically the ZnO-Bentonite composite synthesized at hydrothermal conditions and compared with Na-Bentonite showed in Figure 6. Both samples exhibit type IV isotherms with hysteresis loops, a characteristic feature of mesoporous materials, suggesting a significant presence of mesopores within the structure. ZnO-Bentonite, however, demonstrates a notably higher nitrogen uptake, indicating an increase in surface area and porosity compared to Na-Bentonite, which directly affects the material's adsorption capacity and catalytic performance.

The loop hysteresis observed in ZnO-Bentonite begins at a lower relative pressure (P/P0), signifying a wider distribution of mesopores. This variation can be attributed to the introduction of ZnO nanoparticles into the bentonite matrix, creating new voids and enhancing porosity. The presence of mesopores enhances the ability of ZnO-Bentonite to accommodate larger molecules such as dyes during adsorption, potentially improving its utility in environmental remediation applications (Garcia et al., 2019; Liu, 2021).

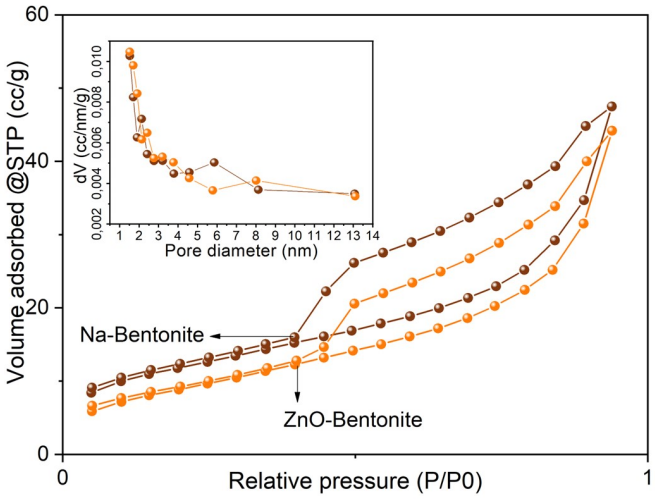

Figure 6. Nitrogen Adsorption-Desorption Isotherms Properties

In terms of pore size distribution, as shown in the inset figure, ZnO-Bentonite exhibits a broader range of pore diameters, extending from approximately 3 nm to 14 nm, with a peak centered around 4 nm. This broadening is likely due to the structural modification induced by the ZnO particles, which create a more heterogeneous pore network. Conversely, Na-Bentonite shows a narrower pore size distribution, emphasizing its more uniform mesopore structure, but less overall adsorption capacity (Patel, 2018; Tripathi, 2020).

3.2 pH Adsorption Effect

The pH of the solution plays a critical role in the adsorption process, particularly for cationic dyes like MB, due to the electrostatic interactions between the adsorbent surface and the dye molecules. From the provided data, ZnO-Bentonite composites synthesized at 100°C and 200°C demonstrate maximum adsorption at pH 5, which aligns with the expected behavior for cationic dye adsorption (Figure 7).

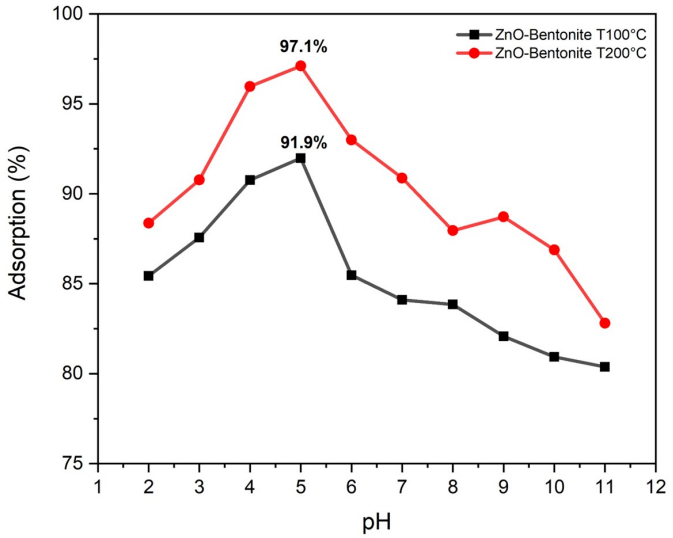

Figure 7. pH and Adsorption Performance

At acidic pH values, the surface of bentonite becomes protonated, and the electrostatic attraction between the positively charged MB molecules and the negatively charged bentonite surface is enhanced, leading to higher adsorption. The introduction of ZnO further enhances the adsorptive performance by increasing surface area and active sites, as confirmed by the BET surface area analysis (Zhu et al., 2020). As the pH increases beyond 5, the adsorption efficiency decreases, which can be attributed to the reduction in electrostatic attraction between the dye and the adsorbent. At higher pH values, the surface of ZnO-Bentonite may become negatively charged, resulting in electrostatic repulsion of the MB cationic dye, leading to reduced adsorption efficiency (Chen et al., 2019).

This behavior is consistent with findings from other studies, where adsorption of cationic dyes onto ZnO-Bentonite materials has been shown to be most effective under acidic to slightly neutral conditions (Wang et al., 2020).

3.3 Effect of Adsorption Time

The adsorption process over time is a crucial factor in determining the kinetics of adsorption, particularly for MB dye removal. The data provided shows that the adsorption increases rapidly during the initial phase before reaching equilibrium (Figure 8). This is expected as, in the early stages, more active sites are available for adsorption, which gradually become saturated over time.

The adsorption kinetics were analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. The results demonstrate that the PSO model provides a better fit for the data, as indicated by the higher R^2 values for both ZnO-Bentonite hydrothermal 100°C (T100) and hydrothermal 200°C (T200) composites. For the T100 sample, the calculated Q_e value of 1.071 mg/g and an R^2 value of 0.7494 for PFO suggests a poor fit, while the PSO model, with R^2 = 0.9888, provides a much better correlation. This indicates that the adsorption process is likely controlled by chemisorption, where chemical bonds form between the MB molecules and the active sites on the ZnO-Bentonite surface (Gupta and Saleh, 2020).

In comparison, the T200 sample also shows a better fit to the PSO model, with an R^2 value of 0.9888. The faster kinetics for the T200 sample are likely due to the enhanced surface area and pore volume from the higher hydrothermal synthesis temperature, which provides more active sites for adsorption (Gao et al., 2020).

The adsorption mechanism is a combination of physisorption (physical forces like van der Waals interactions) and chemisorption, where the latter dominates, particularly as the adsorbent surface becomes saturated (Nguyen et al., 2020).

3.4 Effect of Concentration and Adsorption Temperature

The thermodynamic analysis of ZnO-Bentonite composites was conducted at various concentrations and temperatures. As the concentration of Methylene Blue increases, the adsorption capacity also increases, reaching higher values at elevated temperatures. This is in line with the Langmuir and Freundlich isotherm models provided in the data (Table 1).

From the Langmuir isotherm analysis, the maximum adsorption capacity (Qmax) increases with temperature, suggesting an endothermic process, where higher temperatures favor adsorption. For example, at T = 50°C, the maximum adsorption capacity for the T-100°C sample is 49.26 mg/g, while for the T-200°C sample, the capacity reaches 120.48 mg/g, indicating a significant improvement in adsorption efficiency at higher temperatures (El-Khaiary, 2020).

The Freundlich model shows that the adsorption of MB onto ZnO-Bentonite is also affected by surface heterogeneity, as indicated by the Freundlich constant (n) values. The T-200°C sample displays better adsorption efficiency at higher temperatures, as evidenced by higher values of K_F, suggesting stronger adsorption at elevated temperatures (Litefti et al., 2019).

Thermodynamically (Table 2), the ΔH° values indicate that the adsorption process is endothermic, and the ΔS° values suggest an increase in randomness at the solid-liquid interface. The negative ΔG° values across different temperatures confirm that the adsorption process is spontaneous for both the T-100°C and T-200°C samples (Wang et al., 2020).

Table 1. Methylene Blue Adsorption Isotherm Parameters on ZnO-Bentonite Composite

Adsorbent	T (°C)	Langmuir			Freundlich		
		Q_{max}	K_L	R^2	n	K_F	R^2
T-100°C	30	103.093	0.178	0.169	4.941	44.875	0.032
	40	135.135	0.247	0.894	3.233	45.342	0.432
	50	49.261	0.812	0.834	2.734	141.612	0.545
T-200°C	30	103.093	0.255	0.474	1428.571	74.388	0.000001
	40	39.526	0.416	0.752	3.917	117.409	0.211
	50	120.482	0.344	0.625	5.741	59.621	0.126

Table 2. Thermodynamic Adsorption Data of ZnO-Bentonite Composite

Adsorbent	Concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)		
				303 K	313 K	323 K
T-100°C	50	11.11083	0.049916	-4.014	-4.513	-5.012
	65	6.449087	0.003211	5.476	5.444	5.412
	80	32.53767	0.086715	6.263	5.396	4.529
	95	29.43987	0.119173	-6.670	-7.861	-9.053
	110	95.48629	0.329958	-4.491	-7.790	-11.090
	125	55.88172	0.197998	-4.112	-6.092	-8.072
T-200°C	50	16.392	0.065	-3.33501	-3.986	-4.637
	65	66.571	0.231	-3.46868	-5.780	-8.092
	80	19.866	0.092	-7.86189	-8.777	-9.692
	95	3.914	0.040	-8.08159	-8.477	-8.873
	110	12.395	0.063	-6.813	-7.447	-8.081
	125	10.294	0.050	-4.879	-5.380	-5.880

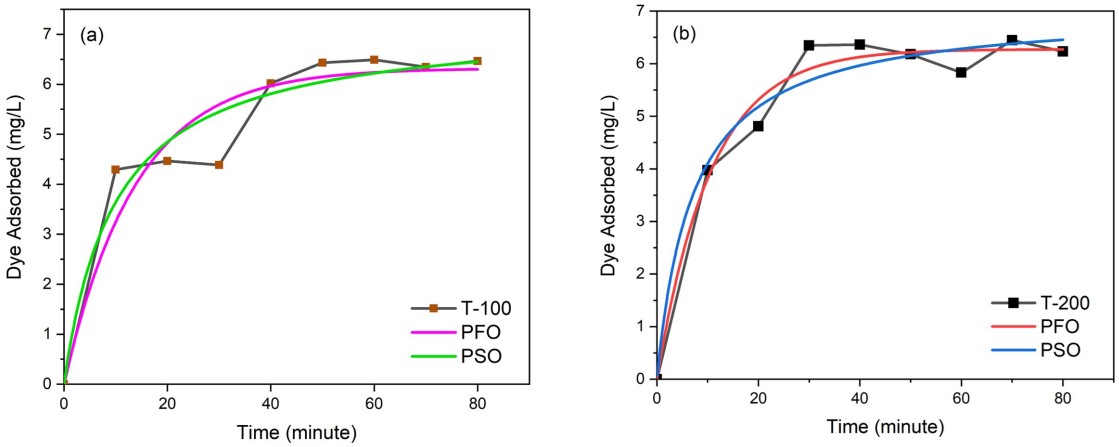

Figure 8. Adsorption kinetics through time variation

3.5 Effect of Adsorbent Dosage on Photodegradation

The effect of adsorbent dosage on the photodegradation of Methylene Blue (MB) using ZnO-Bentonite composites is significant, as shown in Figure 9. As the dosage of the ZnO-Bentonite composite increases, the photodegradation efficiency improves, up to a certain optimal level. This trend can be explained by the availability of more active sites for the adsorption and subsequent degradation of MB molecules as the dosage increases.

However, beyond a certain dosage level, the rate of improvement slows down, likely due to agglomeration of excess ZnO particles, which reduces the surface area and active sites available for the interaction with MB molecules. This phenomenon is common in adsorption and photocatalysis systems, where the excessive amount of adsorbent may result in reduced light penetration, causing a shielding effect that lowers the efficiency

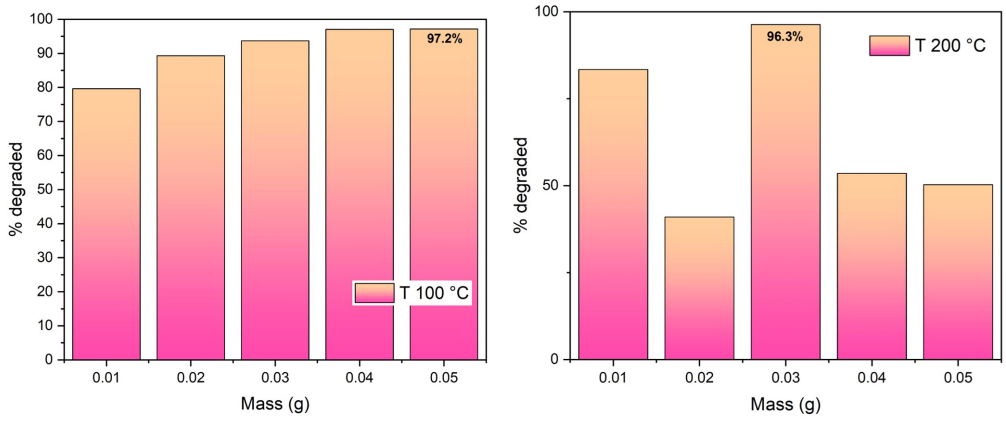

Figure 9. Effect of Adsorbent Dosage

of photocatalysis (Zhao, 2020).

The increase in degradation efficiency with adsorbent dosage aligns with previous studies on ZnO composites. Studies have shown that an increase in ZnO-Bentonite dosage leads to higher photocatalytic activity due to the increased number of catalytic sites. However, the presence of too much ZnO can lead to particle aggregation, reducing the overall efficiency by limiting the active surface area available for photocatalysis (Litefti et al., 2019).

3.6 Effect of Time on Photodegradation

The photodegradation efficiency of MB by ZnO-Bentonite composites as a function of time shows a clear trend where degradation increases rapidly at the beginning and then levels off as the reaction approaches equilibrium (Figure 10). In the initial stages, a large number of MB molecules are adsorbed onto the ZnO-Bentonite surface, where they are rapidly degraded by the photogenerated reactive oxygen species (ROS) produced under UV light.

As the time progresses, the degradation rate slows down as fewer MB molecules remain in the solution, and most of the available active sites on the ZnO-Bentonite surface have been occupied. The leveling off of the degradation curve indicates that the system has reached a steady-state where further degradation is limited by the availability of MB molecules in the solution and the saturation of the adsorbent surface.

The photodegradation process follows a pseudo-first-order kinetics model, which is consistent with previous findings where the rate of degradation of organic pollutants like MB decreases over time due to the consumption of readily available dye molecules and saturation of the catalyst surface (Zhang et al., 2017).

The combination of adsorption and photocatalysis in ZnO-Bentonite composites enhances the overall efficiency of dye removal. Initially, MB molecules are adsorbed onto the bentonite surface, and subsequently, the ZnO nanoparticles generate ROS upon UV light irradiation, breaking down the dye molecules into smaller, less harmful compounds. This dual action ensures efficient removal of MB from the solution.

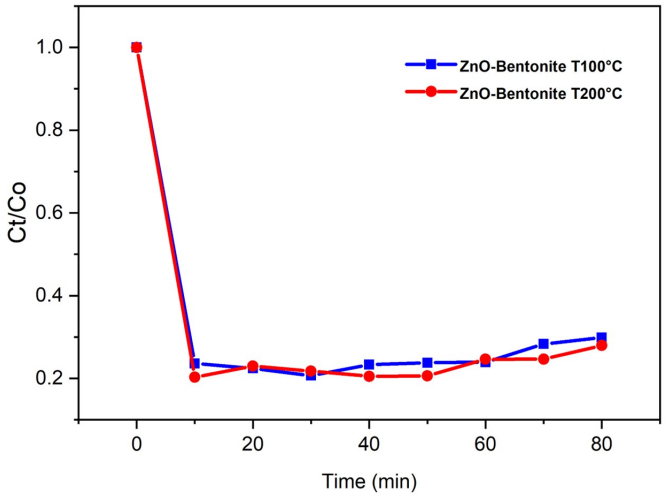

Figure 10. Effect of Contact Duration

4. CONCLUSIONS

This study demonstrates that hydrothermal temperatures significantly impact the synthesis and performance of ZnO-Bentonite composites for Methylene Blue dye removal. Specifically, the composite synthesized at 200°C achieved an adsorption capacity of 120.48 mg/g, outperforming the 49.26 mg/g capacity of the composite at 100°C. Higher temperatures improved crystallinity and surface area, leading to faster adsorption kinetics, with equilibrium reached 20 minutes earlier. The enhanced photocatalytic activity at 200°C is linked to improved ZnO crystallization, resulting in increased reactive oxygen species (ROS) generation under UV light. These findings underscore the importance of optimizing synthesis conditions to develop effective materials for environmental remediation, particularly in dye removal and wastewater treatment.

5. ACKNOWLEDGMENT

This research is fully supported by the Research Center of Inorganic Materials and Coordination Complexes, Sriwijaya University, Palembang, 30662, Indonesia.

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