

Adsorption of methylene blue dye using natural zeolite from sumbermanjing wetan malang

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Abstract. Industrial dye waste is difficult to decompose naturally and poses a significant environmental problem. Methylene blue (MB) is one of the most common dye pollutants, requiring effective removal methods such as adsorption. Adsorption is widely recognized as a simple and cost-effective approach for wastewater treatment. In this study, natural zeolite, a non-metallic mineral, was utilized as an adsorbent. However, due to its relatively low specific surface area, natural zeolite requires modification to increase its adsorption capacity. This research investigates the performance of alkali-activated natural zeolite obtained from Sumbermanjing Wetan, Malang, as a low-cost adsorbent for MB removal. The zeolite was chemically activated using a 2 M NaOH solution, and structural changes were analyzed using X-ray diffraction (XRD). Batch adsorption experiments were carried out to examine the effects of contact time, adsorbent dosage, initial dye concentration, and temperature on the adsorption process. The results show that MB adsorption onto the modified zeolite follows the Freundlich isotherm model and exhibits pseudo-second-order kinetic behavior. Thermodynamic analysis reveals that the adsorption process is spontaneous and exothermic, accompanied by a decrease in system entropy.

1 Introduction

The rapid growth of the textile, pharmaceutical, food, cosmetic, plastic, and paper industries has resulted in a substantial increase in the use of natural and synthetic dyes [1]. It is estimated that more than 100,000 commercial dyes are currently in use, with global synthetic dye production exceeding 7×10^5 tons per year [2,3]. These dyes are not only aesthetic additives but also persistent chemical pollutants that are often discharged into aquatic environments through industrial effluents, typically at concentrations ranging from 10 to 250 mg/L [4]. Among them, Methylene Blue (MB) is one of the most widely used cationic dyes.

Methylene Blue is commonly applied in the dyeing of cotton, silk, and paper products [7]. However, its presence in water bodies poses serious environmental concerns. Due to its complex aromatic structure, MB is highly resistant to natural degradation processes [8]. Furthermore, wastewater containing dyes is known to have carcinogenic and mutagenic properties, threatening aquatic ecosystems and human health through bioaccumulation [5,6]. Therefore, the treatment of dye-contaminated wastewater is urgently needed. Various treatment methods such as biodegradation, bioremediation, electrocoagulation, and photodegradation have been explored.

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However, many of these techniques are limited by high operational costs or the formation of toxic secondary byproducts. In contrast, adsorption has emerged as a preferred method due to its simplicity, efficiency, and cost-effectiveness. Adsorption involves the accumulation of adsorbate molecules on the surface of a solid adsorbent through physical or chemical interactions [9].

To improve the sustainability of adsorption-based treatment, increasing attention has been directed to mineral-based adsorbents, particularly natural zeolites. Zeolites are crystalline aluminosilicate minerals composed of interconnected TO_4 ($T = \text{Si}, \text{Al}$) tetrahedrons, forming a porous framework with a high surface area and ion-exchange capacity [9]. The abundance of zeolites in nature and their tunable physicochemical properties make them promising low-cost adsorbents for dye removal [10,11]. However, natural zeolites often contain impurities and clogged pores, which depend on their geological origin, including hydrothermal conditions, soil composition, and formation temperature [12]. Consequently, zeolites from different locations exhibit different mineralogical characteristics, requiring activation to improve pore accessibility and adsorption performance.

In this study, chemical activation using a 2 M NaOH solution was used to enhance the adsorption capacity of natural zeolites. Alkali treatment also enhances electrostatic interactions between the negatively charged zeolite surface and cationic dyes such as Methylene Blue [14], offering advantages over acid- or salt-based modification methods.

The uniqueness of this research lies in the utilization of a largely unexplored local resource: natural zeolite from Sumbermanjing Wetan, Malang Regency. This material has been identified as a mordenite-type zeolite [4] and is available in large quantities, with estimated reserves ranging from 800,000 to 1 million tons across an area of 16–33 hectares [15]. Despite its abundance, this zeolite deposit has not been extensively studied for organic dye removal. Previous studies have largely focused on its application for the adsorption of heavy metals (e.g., Cu, Pb, and Fe(III)) [13] or as a catalyst in the cracking of used cooking oil. Consequently, there is a significant lack of data regarding its performance in the removal of complex organic dyes such as Methylene Blue.

Therefore, this study aimed to evaluate the adsorption performance of NaOH-activated natural zeolite from Sumbermanjing Wetan for Methylene Blue removal. The effects of contact time, adsorbent dosage, initial dye concentration, and temperature were systematically investigated. The adsorption mechanism was analyzed using Langmuir and Freundlich isotherm models, pseudo-first-order and pseudo-second-order kinetic models, as well as thermodynamic parameters including enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°). Through this comprehensive evaluation, this study aimed to validate the effectiveness of this local zeolite as a sustainable and low-cost adsorbent for industrial wastewater treatment, while enriching the scientific understanding of Indonesia's natural mineral resources.

2 Materials and Methods

2.1 Materials

The materials used in this study were natural zeolite from Sumbermanjing Wetan, Malang Regency; distilled water; aquademin; NaOH p.a (Merck); methylene blue p.a (Merck); Whatman No. 41 filter paper, and universal indicator.

2.2 Chemical Activation of Sumbermanjing Wetan Natural Zeolite

A 10 g sample of natural zeolite obtained from Sumbermanjing Wetan was ground using a mortar and pestle and sieved through a 100-mesh screen to obtain a uniform particle size. The prepared zeolite was chemically activated by soaking it in a 2 M NaOH solution for 4 h to increase the

number of accessible active sites within the zeolite framework. After activation, the solid residue was separated using a Büchner funnel and thoroughly washed with deionized water until a neutral pH was achieved to remove any remaining alkaline species. The washed sample was afterward dried by thermal treatment at 100 °C for 120 min.

The crystalline structure of the activated zeolite was characterized using X-ray diffraction (XRD) to evaluate phase stability after alkali treatment.

2.3 Application of Natural Zeolite Adsorption on Methylene Blue Dye Liquid Waste

2.2.1 Determination of Maximum Wavelength of Methylene Blue

A methylene blue solution with a concentration of 3 ppm was placed in a cuvette, and its absorbance spectrum was recorded using a UV-Vis spectrophotometer over the wavelength range of 650–680 nm at 2 nm intervals. The wavelength corresponding to the highest absorbance was identified as the maximum absorption wavelength of the methylene blue solution.

2.2.2 Determination of Methylene Blue Standard Calibration Curve

Methylene blue solution with concentration variations of 3, 4, 5, and 6 ppm was measured for absorbance at the maximum wavelength. A standard calibration curve was constructed by plotting the absorbance value on the y-axis and against the corresponding of methylene blue concentrations on the x-axis. The resulting linear regression equation was used to determine the concentration of methylene blue in the adsorption samples.

2.2.3 Effect of Contact Time Variation on Methylene Blue Adsorption Capacity

A 25 mL solution of 10 ppm methylene blue was mixed with 0.1 gram adsorbent mass. The mixture was stirred using a shaker at 150 rpm with variations in contact time of 10, 20, 30, 40, 50, 60, and 80 minutes. Next, the mixture was filtered, and the filtrate obtained was measured for absorbance at the maximum wavelength using a UV-Vis spectrophotometer.

2.2.4 Effect of Adsorbent Mass Variation on Methylene Blue Adsorption Capacity

The amount of activated zeolite was varied (0.1, 0.15, 0.2, and 0.25 gram) in 25 mL of 10 ppm MB solution at the optimum contact time. The mixture was stirred using a shaker at 150 rpm.

2.2.5 Effect of Adsorbate Concentration Variation on Methylene Blue Adsorption Capacity

Methylene blue solution of as much as 25 mL with concentration variations of 10, 15, 20, and 25 ppm was put into 100 mL beaker glass respectively. The solution added 0.1 gram of natural zeolite and stirred using a stirrer at 150 rpm during the optimum contact time.

2.2.6 Effect of Temperature Variation on Methylene Blue Adsorption Capacity

Methylene blue solution with a concentration of 10, 15, 20 ppm as much as 25 mL was put into a 100 mL beaker glass. Then 0.1 gram of natural zeolite was added to the solution. The mixture

was stirred using a water bath shaker at 150 rpm at temperature variations of 25, 35, 45, 55, and 65°C during the optimum contact time.

3 Results and Discussion

3.1 Chemical Activation of Natural Zeolite Sumbermanjing Wetan

The activation process of natural zeolite from Sumbermanjing Wetan was conducted using 2 M NaOH for 4 hours. Physically, the treated zeolite shifted from a brownish-white (Fig. 2) to a brighter white color (Fig. 1), which indicates the successful removal of certain surface impurities.

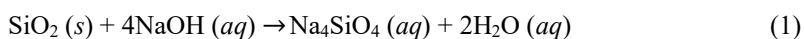


Fig. 1. Natural Zeolite After Activation



Fig. 2. Natural Zeolite Before Activation

The addition of NaOH base can cause an increase in the adsorption capacity of zeolites due to the opening of the active sites surface of zeolites due to a decrease in the Si / Al ratio, besides that the addition of NaOH is intended to remove free SiO₂ and other impurities on the surface of natural zeolites that can close the pores of natural zeolites. A zeolite has a negative charge even in acidic conditions, this is due to the occurrence of cation substitution in the lattice, lattice imperfections, and disconnection of the Si-O-Si bond. The addition of NaOH Na⁺ ions will play a role in dissolving Si and forming sodium silicate which causes the zeolite structure to become more negative. The addition of bases can make zeolites more polar than the addition of acids and cause zeolites to be hydrophilic. The reaction between NaOH and free SiO₂ in zeolite is shown in Equation 1.



Natural zeolite which has a primary structure of SiO₄ and AlO₄ tetrahedral connected by oxygen ions. When SiO₂ reacts with NaOH it will form sodium orthosilicate (Na₄SiO₄). This compound can be dissolved by washing it using distilled water. Therefore the step after soaking with 2 M NaOH is washing with distilled water until the pH of the zeolite is the same as the pH of distilled water. Based on SDS data on the thermo fisher scientific safety data sheet with CAS number 1347-30-5 states that sodium orthosilicate compounds can dissolve in water. Zeolites that have been washed with distilled water and reached the same pH as the pH of the next distilled water are baked for 120 minutes at 100 °C.

3.2 Successful Activation of Natural Zeolite Seen Using XRD (X-ray diffraction)

The XRD diffractograms (Fig. 4) were utilized to observe the effect of this activation on the crystalline framework. The results confirm that the natural zeolite from Sumbermanjing Wetan maintains a mordenite structure, as evidenced by the primary peaks at 29.42° and 34.52°, which align with the International Zeolite Association standards.

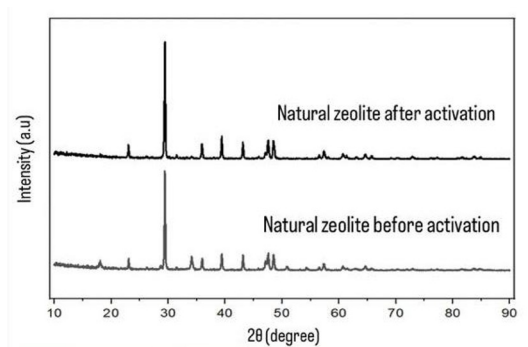


Fig. 4. XRD diffractograms of Natural Zeolite After and Before Activation

A key difference observed after activation is the decrease in intensity or disappearance of peaks in the 2θ : 10-20° range. Crystallographically, this change is likely attributed to the removal of mineral impurities or the partial dissolution of amorphous volcanic glass during the alkaline treatment. While this indicates a "cleaning" of the zeolite channels to make the active sites more accessible, it is acknowledged that XRD alone provides a qualitative assessment of the structure.

3.3 Application of Natural Zeolite Adsorption on Methylene Blue Dye stuff Liquid Effluent

3.4.1 Determination of Maximum Wavelength of Methylene Blue

To ensure the highest sensitivity for the subsequent adsorption measurements, the optical characteristics of the Methylene Blue (MB) solution were evaluated via UV-Vis spectrophotometry. A 3 ppm MB solution was scanned within the visible spectrum (650–680 nm) at a 2 nm resolution to identify the wavelength of maximum absorbance. As shown in Fig. 5, the absorption maximum was identified at 666 nm, which is consistent with the characteristic electronic transitions of the MB chromophore in an aqueous environment. This λ_{\max} was established as the fixed wavelength for all subsequent batch adsorption experiments to minimize measurement error and provide a reliable basis for the Beer-Lambert law application during concentration quantification.

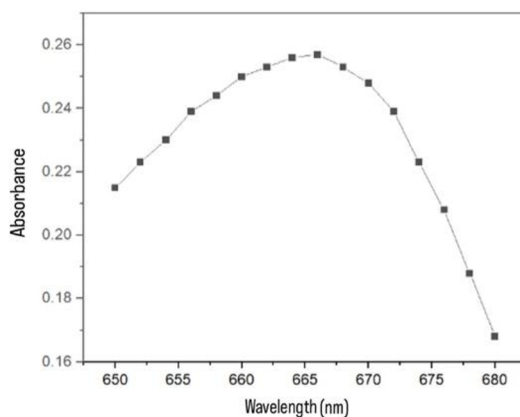


Figure 5. Absorbance Curve of Methylene Blue at Wavelength 650-680 nm

3.4.2 Determination of Methylene Blue Standard Calibration Curve

To ensure high sensitivity and accurate quantification for the subsequent adsorption studies, the optical properties of the Methylene Blue (MB) solution were characterized using UV-Vis spectrophotometry. A 3 ppm MB solution was scanned within a visible spectrum range of 650–680 nm at a 2 nm interval to identify the absorption maxima (λ_{max}). The results identified the λ_{max} at 666 nm, this fixed wavelength was established as the operational standard for all subsequent batch adsorption measurements. Utilizing this specific wavelength ensures adherence to the Beer-Lambert law, providing a reliable basis for calculating dye concentration changes throughout the experimental variations in adsorbent mass, time, and temperature.

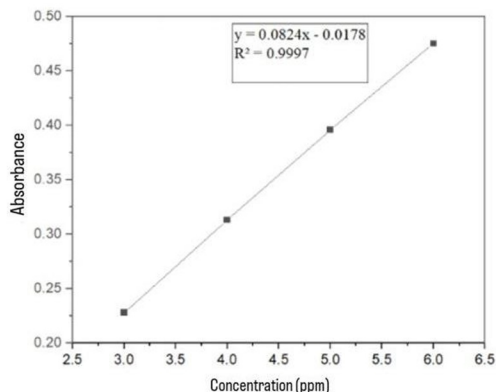


Fig. 6. Methylene Blue Standard Calibration Curve

3.4.3 Effect of Contact Time Variation on Methylene Blue Adsorption Capacity

The effect of contact time on the adsorption capacity of Methylene Blue (MB) was investigated to determine the optimal duration for reaching equilibrium. As illustrated in Fig. 7, the adsorption capacity initially increases significantly with time, reaching an optimum value of 1.614 mg/g at 60 minutes.

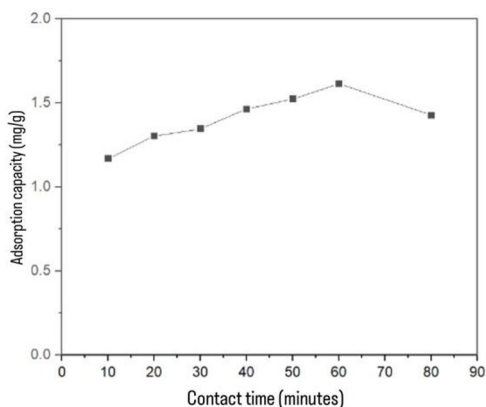


Fig. 7. Effect Curve of Contact Time on Methylene Blue Adsorption Capacity

During the initial 60 minutes, the rapid increase in capacity is attributed to the high availability of vacant active sites on the surface of the natural zeolite. At this stage, the concentration gradient between the bulk solution and the adsorbent surface is at its maximum, facilitating frequent and effective interactions between the cationic MB molecules and the negative surface charges of the zeolite framework. However, the slight decline in adsorption capacity observed at the 80-minute

interval requires a deeper analytical interpretation beyond a simple reduction in interaction. Upon reaching the 60-minute mark, the system approaches a state of dynamic equilibrium where the majority of accessible active sites have become saturated. The decrease observed thereafter is likely due to the saturation of the adsorbent surface, where the repulsion between already adsorbed cationic dye molecules and those remaining in the solution prevents further attachment. Furthermore, in a batch system, prolonged stirring after equilibrium may lead to a minor desorption effect as the system balances the forces of attraction and repulsion. Therefore, 60 minutes was established as the optimum contact time for all subsequent experimental variations.

3.4.4 Effect of Adsorbent Mass Variation on Methylene Blue Adsorption Capacity

The variation of adsorbent mass (0.1, 0.15, 0.2, and 0.25 g) was conducted to determine its effect on the removal of Methylene Blue (MB). As illustrated in Fig. 8, a clear decrease in the adsorption capacity q_e was observed as the adsorbent mass increased. While a mass of 0.1 g yielded a maximum capacity of 1.5024 mg/g, increasing the mass to 0.25 g resulted in a significantly lower q_e .

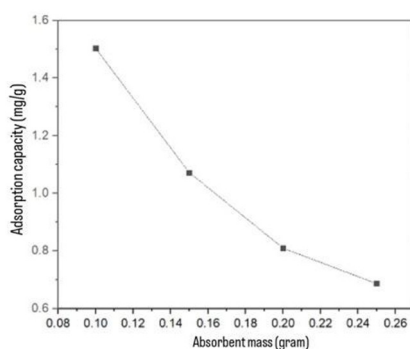


Fig. 8. The curve of the effect of adsorbent mass on methylene blue adsorption capacity

This phenomenon requires a more precise analytical interpretation. The decrease in q_e with increasing mass is primarily due to mass normalization. In the calculation of q_e , the mass of the adsorbent (m) is the denominator ($q_e = \frac{(C_0 - C_e)V}{m}$). As the mass increases, the total amount of dye removed may not increase proportionally because the initial dye concentration is fixed. Consequently, the amount of dye adsorbed per unit of mass decreases, leading to a reduction in q_e values.

Furthermore, the "weakness" often observed at higher dosages is not necessarily due to a change in bonding strength, but rather the under-saturation of active sites. At high adsorbent doses, the total number of available active sites exceeds the number of dye molecules in the solution. This leaves many sites vacant, effectively "diluting" the capacity measured per gram. Additionally, overlapping or aggregation of zeolite particles at higher dosages can shield some surface areas, preventing the MB molecules from reaching all active sites. Therefore, 0.1 g was confirmed as the optimum adsorbent dose for this system.

3.4.5 Effect of Adsorbate Concentration Variation on Methylene Blue Adsorption Capacity

The influence of initial dye concentration on the adsorption capacity of Methylene Blue (MB) was evaluated across a range of 10 to 25 ppm. As illustrated in Fig. 9, the adsorption capacity q_e exhibits a linear increase directly proportional to the initial concentration of the adsorbate.

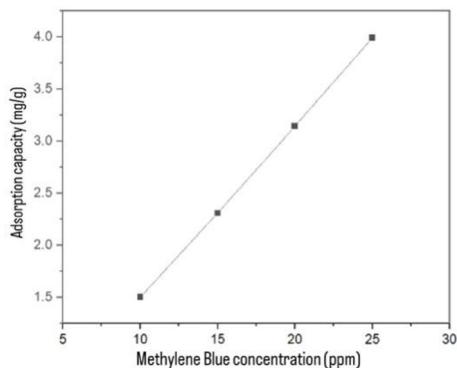


Fig. 9. The curve of the Effect of Adsorbate Concentration on Methylene Blue Adsorption Capacity

This phenomenon is fundamentally driven by the concentration gradient between the bulk solution and the solid adsorbent surface. Analytically, a higher initial concentration provides a more potent driving force for mass transfer, overcoming the resistance to the migration of MB molecules from the liquid phase to the active sites of the zeolite.

Specifically, at higher concentrations, the number of MB ions surrounding the zeolite particles increases, resulting in more frequent collisions and effective interactions with the aluminosilicate framework. This intensified competition for the available surface area ensures that a greater proportion of active sites are utilized, thereby maximizing the adsorption capacity. This relationship between concentration and capacity provides the essential data required to determine the adsorption isotherm model for this system.

3.4.6 Effect of Temperature Variation on Methylene Blue Adsorption Capacity

The effect of temperature on the adsorption capacity of Methylene Blue (MB) was evaluated across a range from 25°C to 65°C. As illustrated in Fig. 10, the adsorption capacity q_e decreases progressively as the temperature rises. This inverse relationship between temperature and capacity is a characteristic indicator that the adsorption of MB onto the activated natural zeolite is an exothermic process.

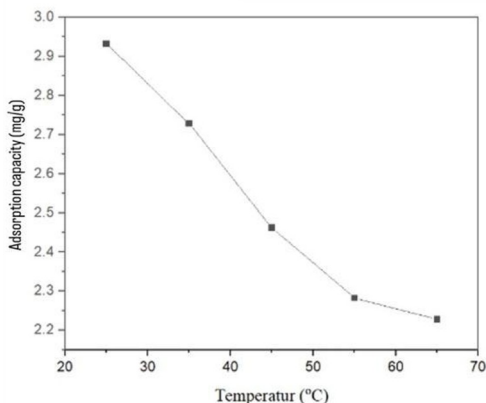


Fig. 10. Temperature Effect Curve on Methylene Blue Adsorption Capacity

The reduction in capacity at higher temperatures can be scientifically justified by the increased mobilization and kinetic energy of the dye ions. As thermal energy enters the system, the mobility of the Methylene Blue molecules increases significantly, which enhances their ability to escape the attractive forces of the zeolite's active sites. This increased molecular motion leads to a higher

rate of desorption, where dye molecules that were previously bound to the aluminosilicate surface are released back into the aqueous solution.

Furthermore, the weakening of the adsorption capacity at elevated temperatures suggests that the physical bonds formed between the cationic dye and the negative surface of the zeolite are sensitive to thermal disruption. Because the process is exothermic, the addition of heat essentially shifts the equilibrium toward the desorbed state, confirming that the system is most stable and efficient at lower temperatures. Consequently, the maximum adsorption was achieved at 25°C, establishing that room temperature conditions provide the optimal environment for maximizing the interaction between the adsorbate and the adsorbent's active sites.

3.5 Kinetics, Isotherm, and Thermodynamics Study of Methylene Blue Adsorption by Natural Zeolite

3.5.1 Kinetics of Methylene Blue Adsorption

The kinetic behavior of Methylene Blue (MB) adsorption onto activated natural zeolite was evaluated using both pseudo-first-order and pseudo-second-order models to understand the rate-controlling steps of the process. Based on the experimental data shown in Table 1, the pseudo-second-order model provides a superior statistical fit, yielding a correlation coefficient ($R^2 = 0.9927$) that is notably higher than that of the pseudo-first-order model ($R^2 = 0.9621$).

Table 1. Adsorption Kinetics Model Result Data

q_e (mg/g)	Pseudo First-Order			Pseudo Second-Order		
	q_e cal (mg/g)	k_1 (min^{-1})	R^2	q_e cal (mg/g)	k_2 (g/mg.min)	R^2
1,614	0,7095	0,0389	0,9621	1,7455	0,7838	0,9927

While the high R^2 value for the pseudo-second-order model suggests that the adsorption rate is dependent on the available capacity of the adsorbent, it is important to note that a mathematical fit does not definitively confirm a specific chemical mechanism. Although several studies frequently associate the pseudo-second-order model with chemisorption involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate, this interpretation remains theoretical in the absence of spectroscopic evidence. In this system, the model fitting primarily indicates that the rate-limiting step may involve the interaction between the cationic MB molecules and the negative surface of the aluminosilicate framework. However, the overall adsorption process is likely a complex combination of surface attachment and intraparticle diffusion. Therefore, the pseudo-second-order model serves as an effective mathematical tool to describe the adsorption rate and predict the equilibrium capacity q_e , but it should not be viewed as conclusive proof of the molecular-level bonding mechanism between the MB chromophore and the zeolite's active sites.

3.5.2 Thermodynamics of Methylene Blue Adsorption

The energy changes associated with the adsorption process were quantified through the determination of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). As summarized in Table 2, the calculated values for ΔG° are negative across all studied temperatures, indicating that the adsorption of Methylene Blue onto the activated natural zeolite is a thermodynamically spontaneous process. Furthermore, the increasingly negative value of ΔG° at lower temperatures suggests that the spontaneity of the system is favored at lower temperatures..

Table 2. Adsorption Thermodynamics Study Result Data

T(K)	1/T(K)	C ₀ (ppm)	C _e (ppm)	K _c	lnK _c	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/K.mol)
318	0,0031	20	10,155	1,969	0,677	-1791,91	-3956,05	-6,8665
328	0,0030	20	10,871	1,839	-1662,46			
338	0,0029	20	11,09	1,803	0,589	-1657,102		

The calculated enthalpy change (ΔH°) for the system is negative, confirming the exothermic nature of the interaction. However, it is important to acknowledge that the absolute value of ΔH° is relatively small (40 kJ/mol). While this low energy value is close to the range of experimental uncertainty, it provides a strong indication that the process is governed by physical forces rather than strong chemical bonding. Specifically, the energy released during the attachment of MB molecules to the zeolite surface is consistent with the magnitude of van der Waals forces. Regarding the entropy of the system, the negative value of ΔS° indicates a decrease in the degree of randomness at the solid-liquid interface during the adsorption process. This suggests that the MB molecules become more ordered as they transition from the free-moving aqueous phase to being localized on the active sites of the aluminosilicate framework.

Based on these thermodynamic indicators specifically the low magnitude of the exothermic heat of adsorption and the reversibility of the system at low temperatures, the adsorption mechanism is reasonably characterized as physisorption.

3.5.3 Methylene Blue Adsorption Isotherm

The relationship between equilibrium adsorption capacity and the equilibrium concentration of Methylene Blue (MB) was analyzed using the Langmuir and Freundlich isotherm models. Based on the statistical parameters presented in Table 3, the Freundlich model showed a correlation coefficient (R^2) closer to one than the Langmuir model. These results indicate that the Freundlich isotherm more accurately describes the adsorption behavior of MB on active natural zeolite from Sumbermanjing Wetan.

An analytical review of the Langmuir parameters, specifically the equilibrium capacity (Q_0) and the Langmuir constant (b_L), revealed negative values. From a crystallographic and thermodynamic perspective, negative constants in a Langmuir model are physically meaningless, as they imply a negative adsorption capacity or negative energy of adsorption. This outcome represents a model failure, suggesting that the fundamental assumptions of the Langmuir isotherm—specifically that adsorption occurs on a homogeneous surface with a fixed number of identical active sites forming a monolayer—do not apply to this natural zeolite system.

Table 3. Results Data of Both Adsorption Isotherm Models

Suhu	Langmuir Isotherm			Freundlich Isotherm		
	R ²	Q _o (mg/g)	b _L	R ²	n	k _f
45	0.9651	-8.764	-0.0220	0.9993	0.8704	0.1658
55	0.9994	-1.954	-0.0500	0.9980	0.5787	0.0364
65	0.9960	-2.354	-0.0429	0.9996	0.6252	0.0452

The superior fit of the Freundlich model suggests that the aluminosilicate surface of the zeolite is likely heterogeneous, possessing active sites with varying energy levels. While a better fit with the Freundlich model is often associated with multilayer adsorption, it is important to state this conclusion with scientific caution. Mathematical fitting alone does not definitively prove the formation of multiple layers of MB molecules; rather, it indicates that the energetic distribution of the zeolite surface is non-uniform. Consequently, the adsorption process is best characterized as a heterogeneous surface interaction, where the initial dye molecules preferentially occupy the highest-energy sites before spreading to lower-energy regions of the zeolite framework.

4 Conclusion

The optimal adsorption conditions were identified as a 60-minute contact time and an adsorbent mass of 0.1 g. The observed decrease in capacity (q_c) with higher dosages is analytically attributed to mass normalization rather than a reduction in site interaction. Adsorption capacity increased linearly with initial concentration, driven by an enhanced mass transfer driving force. The process is characterized as a spontaneous, exothermic physisorption mechanism, indicated by the decline in capacity at higher temperatures due to increased dye mobility and thermal desorption. Kinetics followed the pseudo-second-order model ($R^2 = 0.9927$), while equilibrium data favored the Freundlich isotherm. The failure of the Langmuir model, marked by physically meaningless negative parameters, confirms that the zeolite surface is energetically heterogeneous.

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