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ADSORPTION AND KINETICS OF METHYLENE BLUE ON MODIFIED LAPONITE

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Abstract: This investigation presents the findings on the adsorption and kinetics of methylene blue using a modified laponite-based adsorbent. The research demonstrated that methylene blue could be effectively adsorbed from aqueous solutions. The adsorption processes were analyzed based on Langmuir and Freundlich isotherm models, with the pseudo-second-order kinetic model showing the best fit to the data. Due to its high surface area and efficient ion-exchange capacity, the modified laponite can serve as an alternative adsorbent in water purification processes. The results highlight the potential of laponite for environmentally safe removal of dyes from industrial wastewater.

Keywords: Laponite, methylene blue, adsorption, kinetics.

Introduction. Worldwide, over 10,000 types of dyes are produced annually, exceeding 700,000 tons (7×10^5 tons), and are widely used in various industries such as textiles, paper, food, and pharmaceuticals. Effluents discharged from industrial facilities are often contaminated with colored compounds and toxic components, necessitating specialized treatment processes before being released into natural water bodies. However, due to the highly complex composition of these effluents, their effective treatment remains a challenging technological task. Wastewater may contain both organic and inorganic dye components as well as non-biodegradable compounds. Specifically, methylene blue (MB), a cationic dye containing nitrogen groups, exhibits high chemical stability and resistance to solar radiation. Consequently, the development and implementation of efficient methods for wastewater treatment remain pressing scientific and technological challenges [2-3].

Adsorption processes play a crucial role in various fields, particularly in environmental protection, chemical industries, biological systems, and technological operations. In recent years, significant research has been conducted on the efficient adsorption of anionic and cationic dyes and the investigation of their kinetic properties. The primary requirements for these processes include the use of economically viable and environmentally safe materials [4-6].

Laponite is a synthetic clay mineral structurally similar to natural hectorite. Both clays belong to the smectite group of phyllosilicates and are characterized by layered 2:1 crystal units. These structures consist of two tetrahedral silicon sheets sandwiching a central octahedral sheet of Mg^{2+} ions (Figure 1). Due to its high surface area, similar to other natural montmorillonites, laponite exhibits excellent adsorption properties. Its ability to adsorb cationic and anionic active substances makes it widely used for the efficient adsorption of pollutants, particularly dyes, from liquids.

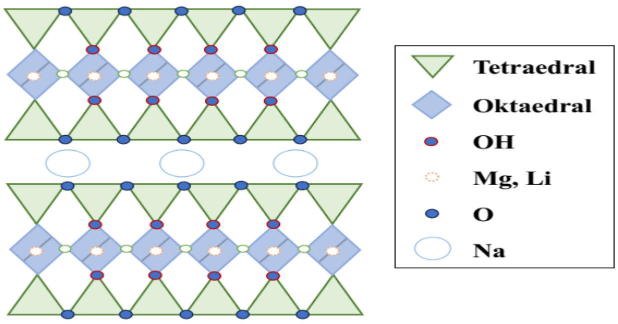
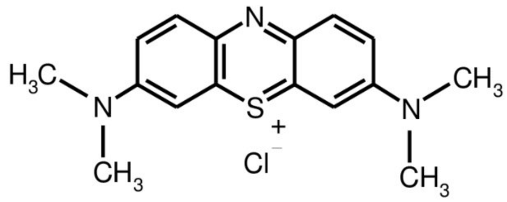


Figure 1. Structure of Laponite

Dyes are widely used in the chemical industry and pose significant environmental challenges due to their resistance to biodegradation. Cationic dyes, such as methylene blue, and anionic dyes, such as Congo red, are extensively utilized in the chemical, textile, and food industries. The release of these dyes into water bodies can pose threats to living organisms and harm ecological systems [7-8].

General name	Methylene blue
Chemical name	3,7-bis(Dimethlamino)-phenazathionium chloride tetramethylthionine chloride
Chemical formula	$C_{16}H_{18}ClN_3S$
Molecular weigth (g/mol)	319.85
Molecular diameter (nm)	0.80
λ_{max} (nm)	668
Chemical structure	

From this perspective, the necessity to improve technologies for dye removal from water through the use of efficient adsorbents such as modified laponite has become a pressing issue. The structure, ion-exchange capacity, and high dispersibility of laponite ensure its effectiveness in adsorbing dyes. The kinetics of the adsorption process, which relates to how quickly the adsorbent captures dyes over a given time, is critical to enhancing the efficiency of the adsorbent and expanding its practical applications.

Materials. Laponite is a synthetic mineral clay with the chemical formula: $Na_{0.7}Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4$. Its point of zero charge (pH_{PZC}) is 11, and its cation exchange capacity (CEC) is 0.55 meq/g. Laponite particles are disk-shaped, with a thickness of 1 nm and a diameter of 25 ± 2 nm [9].

The scanning electron microscopy (SEM) image of raw laponite confirms that the sample consists of large, plate-like aggregates with irregular shapes. The SEM analysis also indicates that these aggregates have a non-uniform structure (Figure 2).

In this study, all methylene blue (MB, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, molecular weight 373.9 g/mol) solutions were prepared by dissolving the required amount of MB in distilled water.

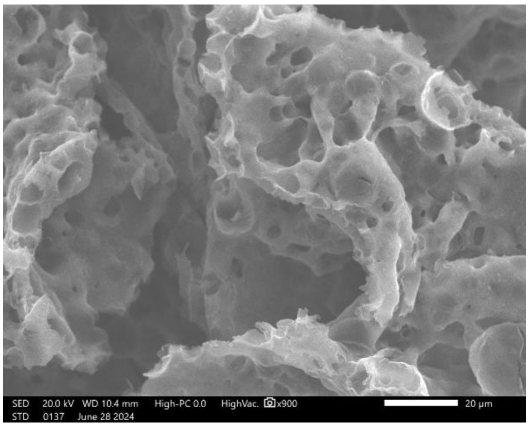


Figure 2. SEM image of raw laponite

Experiment. All adsorption experiments were conducted using 50 mg of a chromium-modified sample and 50 mL of MB solutions with initial concentrations (C_0) ranging from 5 to 20 mg/L in 100 mL glass containers at various temperatures. After reaching equilibrium, the suspensions were separated using a CenLee 20K centrifuge at 12,000 rpm to analyze the dye concentration [6]. The amount of MB adsorbed at equilibrium, q_e (mg/g), was calculated using the following equation:

$$q_e = V(C_0 - C_e)/m \qquad (1)$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g). The concentration of MB before and after adsorption was determined using a spectrophotometer at a maximum wavelength of $\lambda = 611$ nm.

Adsorption Isotherm. When the adsorption process reaches equilibrium, the adsorption isotherm plays a crucial role in describing how adsorbate molecules are distributed between the liquid and solid phases. The adsorption isotherms of MB on modified laponite at 298 K are presented in Figure 3. As seen in the figure, the adsorption amount increases with the rise in equilibrium MB concentration within the experimental concentration range. This is attributed to the increasing driving force resulting from the concentration gradient.

Under these conditions, higher MB concentrations in the solution lead to a greater number of active sites on the adsorbent being surrounded by MB ions, making the adsorption process more efficient. As a result, the q_e values increased with the rise in equilibrium MB concentration.

From Figure 3, it is evident that the adsorption capacity of MB on laponite at 298 K is 18.5 mg/g. Although the adsorption capacity of MB on modified laponite is not particularly high compared to other adsorbents, laponite stands out as a widely available and cost-effective synthetic material, making it a viable option for removing MB from solutions.

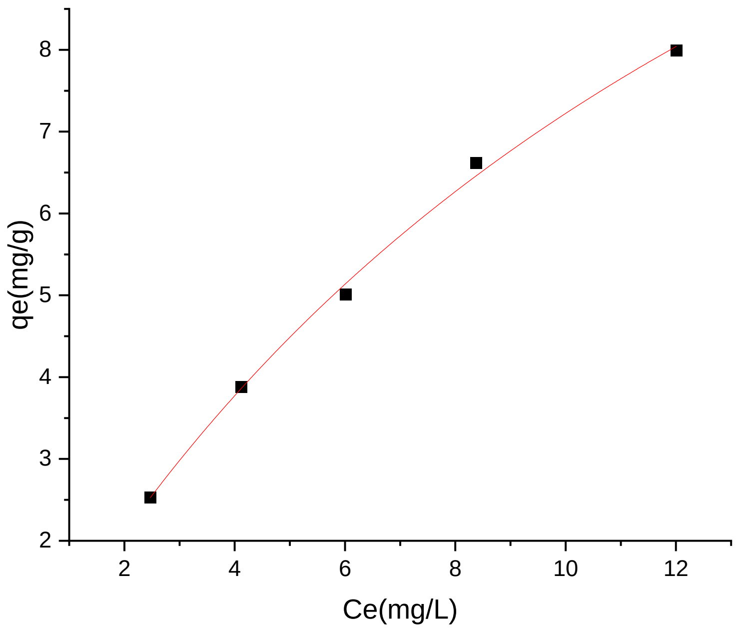


Figure 3. Adsorption Isotherm of MB on Laponite

Analyzing adsorption isotherm data and evaluating their fit with various models is a critical step in identifying a model that can be effectively applied for design purposes. Adsorption equilibrium is a dynamic concept that occurs when the rate of molecular adsorption onto the surface equals the rate of desorption from the surface.

Equilibrium adsorption isotherms are vital for designing adsorption systems, as their shape provides insight into the homogeneity or heterogeneity of the adsorbent surface. Furthermore, correlating equilibrium data with theoretical or empirical equations is essential for practical applications. The isotherm data were fitted using Langmuir and Freundlich models.

Langmuir Model. The Langmuir model is commonly used to describe the adsorption mechanism, assuming uniform adsorption energies across the surface. The maximum adsorption is determined by the saturation of a monolayer.

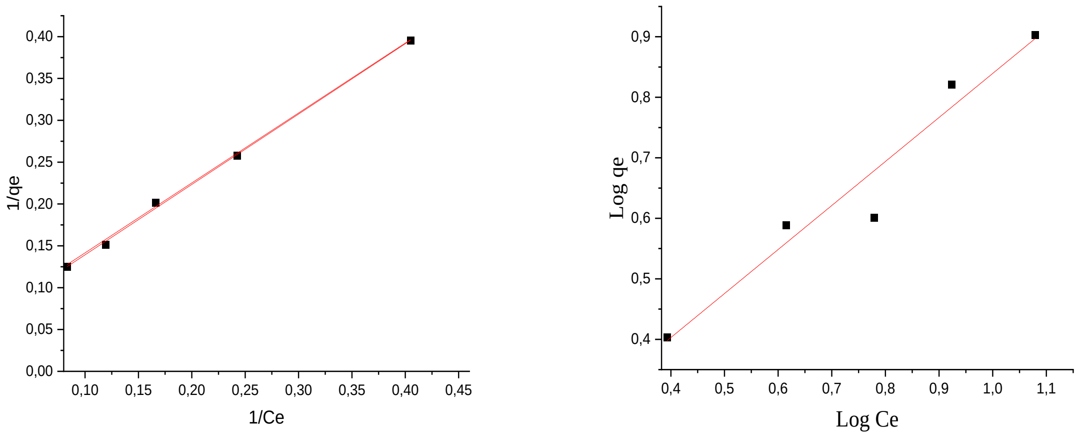
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e \times q_m \times b} \quad (2)$$

Here, qm represents the adsorption capacity (mg/g), and b is the Langmuir isotherm constant (L/mg). The efficiency of the adsorption process can be evaluated using the dimensionless separation factor R_L, calculated based on the *b* parameter.

A linear plot of $1/q_e$ versus $1/C_e$ results in a straight line (Figure 4a), where the slope corresponds to $1/q_m$. This linear relationship confirms that the adsorption of MB on laponite fits the Langmuir isotherm model.

$$R_L = \frac{1}{1 + b \times C_0} \quad (3)$$

If the R_L values were between 0 and 1, the adsorption process is favorable for the temperature range studied.



A) B)

Figure 4. Fit of MB adsorption isotherm to Langmuir (a) and Freundlich (b) models

Freundlich Model. The Freundlich adsorption isotherm describes the adsorption process on heterogeneous surfaces with multilayer adsorption. This linear model is defined by the following equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (4)$$

Here, q_e is the amount of MB adsorbed per unit mass of the adsorbent (mg/g), *Ce* is the equilibrium concentration of MB in the solution (mg/L), K represents the adsorption capacity, and *1/n* indicates the adsorption intensity.

Table 1. Isotherm Parameters for MB Adsorption

Isotherm Type	Parameter	MB (298 K)
Langmuir	q_{max} (mg/g)	18.13
	K_L (L/mg)	0.065
	R_L	0.753
	R^2	0.9986
Freundlich	K_f	1.34
	1/n	0.7366
	R^2	0.9476

Adsorption Kinetics

The pseudo-first-order and pseudo-second-order models were selected as the most suitable for describing the adsorption of methylene blue onto laponite particles based on the linear regression correlation coefficient values, r^2.

Pseudo-First-Order Kinetic Model. This model is commonly used to describe the adsorption mechanism for various adsorbents. It can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

Here, k_1 is the pseudo-first-order adsorption rate constant (min^{-1}), while q_e and q_t represent the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium and at time *t*, respectively [10].

The relationship between the adsorption amount, qt (mg/g), and contact time is illustrated in Figure 4. It was observed that the adsorption process progressed rapidly during the initial 60 minutes, followed by a slower rate, eventually reaching a saturation point.

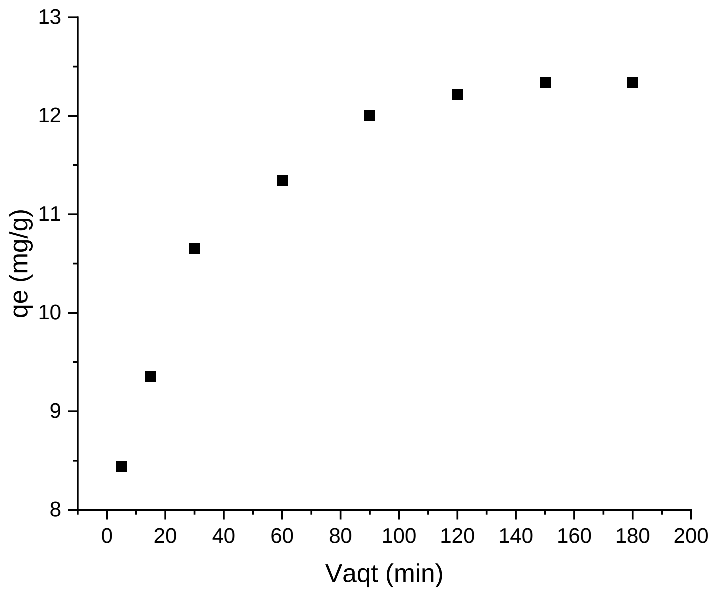


Figure 4. Adsorption of methylene blue on laponite as a function of contact time (adsorbent = 0.05 g, C0 = 20 mg/L, V = 0.05 L)

The calculated qe and k_f values, along with the corresponding linear regression correlation coefficient (R^2), are presented in Table 2. The results indicate that as the adsorption amount increased, the rate constant k_f also rose. This finding suggests that the pseudo-first-order model is not applicable for predicting the adsorption kinetics of methylene blue on laponite particles.

Pseudo-Second-Order Kinetic Model. This model is commonly used to describe adsorption processes in aqueous solutions. The linear form of the pseudo-second-order model equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

Here, k_2 is the pseudo-second-order adsorption rate constant (mg·min⁻¹), while q_e and q_t represent the amounts of adsorbate adsorbed per unit mass of the adsorbent at equilibrium and at time t, respectively [10].

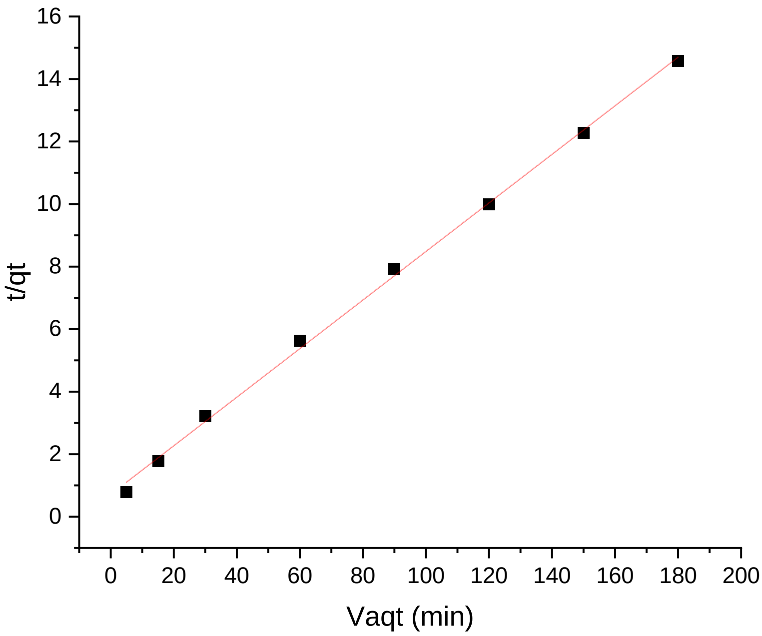


Figure 5. Adsorption of methylene blue on laponite as a function of contact time (adsorbent = 0.05 g, C_0 = 20 mg/L, V = 0.05 L)

The calculated q_e and k_2 values, along with the corresponding linear regression correlation coefficient (R^2), are summarized in Table 2 (Figure 5). The high correlation coefficients ($R^2 > 0.99$) of the pseudo-second-order kinetic model confirm the applicability of this equation and indicate that the adsorption process of methylene blue on laponite follows second-order kinetics.

Table 2. Kinetic parameters for the adsorption of methylene blue on laponite

Pseudo-First-Order	$q_{e,}$ (mg/g)	5.64
	K_1	0.000072
	R^2	0.9657
Pseudo-Second-Order	q_e (mg/g)	12,87333
	K_2	0.00847
	R^2	0,9984

Conclusion. The studies demonstrated that the modified laponite sample is effective in adsorbing methylene blue from aqueous solutions. The adsorption amount increases with the initial dye concentration and contact time but decreases with an increase in the adsorbent dosage. Kinetic analyses showed that the process conforms to pseudo-second-order kinetics. Modified laponite can be proposed as an efficient alternative adsorbent for wastewater treatment.

References:

1. S.Sivamani, G.B. Leena, Removal of Dyes from Wastewater using Adsorption - A Review. *International Journal of BioSciences and Technology*. **2**, 47–51 (2009).

2. Srivastava, A., Shukla, S., Jangid, N. K., Srivastava, M. & Vishwakarma, R. in *Research Anthology on Emerging Techniques in Environmental Remediation* 493–507 (IGI Global, 2022). doi:10.4018/978-1-6684-3714-8.ch026.

3. Mahdavinia, G. R., Soleymani, M., Sabzi, M., Azimi, H., & Atlasi, Z. (2017). Novel magnetic polyvinyl alcohol/laponite RD nanocomposite hydrogels for efficient removal of methylene blue. Journal of Environmental Chemical Engineering, 5(3), 2617–2630. https://doi.org/10.1016/j.jece.2017.05.017

4. N. Mamataliev, A. Abdikamalova, I. Eshmetov, A. Kalbaev, Adsorption activity of pillared clays with respect to vapors of organic adsorbates. Journal of Chemical Technology and Metallurgy. 58, 1028–1036 (2023).

5. R. Zhu, Q. Chen, Q. Zhou, Y. Xi, J. Zhu, H. He, Adsorbents based on montmorillonite for contaminant removal from water: A review, Applied Clay Science, 123, 2016, 239-258.

6. N. Mamataliev, A. Kalbaev, I. Eshmetov, S. Kuldasheva, in AIP Conference Proceedings (American Institute of Physics, 2024), vol. 3045.

7. 1. Y. Yao, F. Xu, M. Chen, Z. Xu, Z. Zhu, Adsorption behavior of methylene blue on carbon nanotubes. *Bioresource Technology*. **101**, 3040–3046 (2010).

8. W. Wang *et al.*, Synthesis of chitosan cross-linked 3D network-structured hydrogel for methylene blue removal. *International Journal of Biological Macromolecules*. **141**, 98–107 (2019).

9. Chimene, D., Alge, D. L. & Gaharwar, A. K. 2015 Two-dimensional nanomaterials for biomedical applications: emerging trends and future prospects. Advanced Materials 27, 7261–7284.

10. Braik, S., Amor, T. B., Michelin, L., Rigolet, S., Bonne, M., Lebeau, B., & Hafiane, A. (2022). Natural water defluoridation by adsorption on Laponite clay. *Water Science and Technology*, *85*(6), 1701–1719.

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