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Evaluating the Potential of Duck Egg Shell for Methylene Blue Adsorption in Medical Laboratory Wastewater

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ABSTRACT

It is important to develop an understanding of adsorbent performance in non-traditional wastewater streams like those from medical facilities. In this study, duck eggshell powder (DEP) was utilized for the removal of methylene blue (MB) and evaluated in medical laboratory wastewater. The effect of pH, initial MB concentration, contact time, and temperature on the adsorption process was investigated. The results showed that the optimum adsorption conditions were at pH 8, initial MB concentration of 80 $mg.L^{-1}$, contact time of 30 min, and temperature of 298 K. The adsorption process followed the Langmuir isotherm model and pseudo-second-order kinetic model, with a maximum uptake capacity of 5.991 $mg.g^{-1}$ and removal efficiency of 97.34%. The thermodynamic process of adsorption was non-spontaneous and endothermic. FT-IR, XRF, SEM-EDX, and BET analysis confirmed the interactions between MB and DEP before and after adsorption. The adsorption process occurred through electrostatic attraction, cation exchange, hydrogen bonding, and pore filling. This treatment was applied to medical laboratory wastewater with efficiency reaching 100% at optimum conditions (pH 8). The advantages of DEP are simple sample preparation, no need for additional precursors, and an abundant natural resource, thus providing an excellent opportunity for use as an adsorbent. Therefore, DEP has great potential as an effective adsorbent for removing MB dye from medical laboratory wastewater.

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INTRODUCTION

Water pollution is one of the most serious environmental issues faced by countries worldwide (Plessis, 2022). Contaminated water can serve as a source of various diseases and negatively impact aquatic ecosystems. One of the main contributors to water pollution is industrial waste, which contains various hazardous chemicals (Warren-vega & Campos-rodr, 2023), including heavy metals (Putra, Arman, et al., 2024), organic compounds (Shetty et al., 2023), and synthetic dyes (Dutta et al., 2024). These pollutants pose long-term risks to human health and other living organisms (Manisalidis et al., 2020). Among these pollutants, synthetic dyes such as methylene blue (MB) represent a significant threat to water quality. MB is widely used in the textile, pharmaceutical, and medical laboratory industries (Manisalidis et al., 2020). However,

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its persistence and non-biodegradability can severely degrade water quality. Furthermore, MB disrupts ecosystems by harming aquatic flora and fauna and reducing the quality of drinking water (Kishor et al., 2021; Silva, 2023).

Methylene blue (MB) is a cationic dye known for its high environmental stability and toxicity to aquatic organisms (Khan et al., 2022; Olusakin et al., 2022). Consumption of water containing high concentrations of MB can lead to health problems such as respiratory distress and tissue damage in both humans and animals (Schuijt et al., 2021). Various physical, chemical, and biological methods have been developed to remove MB from wastewater. However, most of these methods have limitations, such as high operational costs, the use of hazardous chemicals, or the generation of secondary waste requiring additional management (Tripathi et al., 2023). Therefore, there is an urgent need for environmentally friendly, cost-effective, and efficient methods to address MB contamination.

Adsorption has emerged as one of the most promising methods for addressing synthetic dye pollution. Adsorption involves the adherence of pollutant molecules onto the surface of an adsorbent material, offering high efficiency at relatively low costs (Putra et al., 2022; Sadegh & Mazloumbilandi, 2017). Previous studies have demonstrated that natural adsorbents, particularly eggshells, can effectively remove dyes from wastewater. Hevira et al. (2020) reported that chicken eggshells could adsorb MB with an efficiency of 94.5% in simulated solutions, as analyzed using FT-IR and SEM. Yusuff (2019) developed a composite of chicken eggshells and anthill clay, achieving an adsorption capacity of 303.03 $mg.g^{-1}$ at pH 8 based on the Langmuir isotherm model. While these results are promising, the studies were conducted solely in simulated conditions and did not evaluate the adsorbents' effectiveness in real wastewater scenarios.

In addition to chicken eggshells, studies suggest that duck eggshell powder (DEP) has significant potential as a natural adsorbent. Duck eggshells contain a higher calcium carbonate ($CaCO_3$) content than chicken eggshells, along with physical structures that enable more efficient adsorption (Juzsakova et al., 2023; Yirong & Vaurs, 2019). Hanifah et al. (2024) highlighted that duck eggshells possess chemical properties and pore structures that facilitate interactions with MB molecules. However, research on the use of duck eggshells as adsorbents remains limited. Furthermore, most previous studies have utilized eggshells in simulated laboratory solutions without assessing their effectiveness in complex wastewater, such as medical laboratory effluent. Such effluents often contain a mixture of hazardous chemicals, synthetic dyes, and pathogens, necessitating more effective and environmentally friendly treatment solutions.

This study aims to bridge this gap by evaluating the potential of duck eggshell powder (DEP) as a natural adsorbent for removing MB from medical laboratory wastewater. The research is conducted under real wastewater conditions and involves an in-depth analysis of adsorption parameters, including equilibrium, kinetics, and thermodynamics. DEP characterization was performed using FT-IR to analyze functional group changes, XRF to determine elemental composition, SEM-EDX to study surface morphology, and BET to measure specific surface area and pore size distribution. This approach not only explores the potential of DEP in medical wastewater treatment but also provides a more sustainable and practical solution for mitigating water pollution caused by synthetic dyes.

MATERIAL AND METHODS

Duck eggshell was used as an adsorbent, while Methylene Blue (MB) solution was used as the dye to be removed from the solution. In the adsorbent activation process, 0.01 M nitric acid (HNO_3) was used. In addition, there is the use of additional chemicals such as hydrochloric

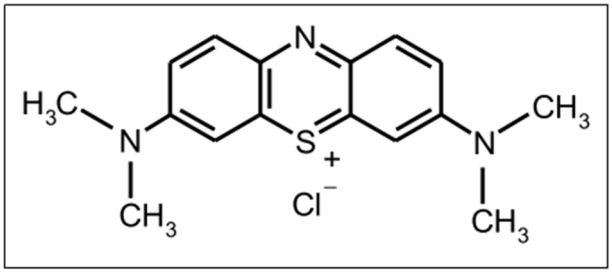

Fig. 1. Structure of Methylene Blue

acid (HCl) and sodium hydroxide (NaOH) to adjust the pH of the solution as needed, and all materials are produced by Merk with Pro Analyse (PA) purity level. Other materials used include ethanol, distilled water, and MB standard solution (Figure 1).

This research is an experimental study conducted in the laboratory. The adsorption process uses a batch system with several stages as follows:

Adsorben preparation. The duck egg shells used in this study were collected from beverage stalls in Padang City, West Sumatra, Indonesia. Then, it was washed with water until clean, wind-dried for 2-3 days, ground until smooth, and sieved with a particle size of ≥75 μm. The duck egg shells were soaked with 0.01M HNO_3 in a ratio of 1:2 for 120 minutes, then washed and filtered until the pH was neutral, then sieved again to get the original particle size, and the duck egg shell powder (DEP) was ready for use (Hevira et al., 2020; Putra et al., 2022).

Characterization and adsorption process. The adsorption process in this study utilized duck eggshell powder (DEP) as an adsorbent to remove methylene blue (MB), which was selected as a representative cationic dye. Before adsorption, the pHpzc (point of zero charge) of DEP was determined to evaluate the surface charge characteristics of the adsorbent. Additionally, the characterization of DEP before and after adsorption was performed using various instrumental techniques. FT-IR (Bruker Alpha II) was employed to identify changes in functional groups due to adsorption, while XRF (Olympus Delta Premium) was used to determine the elemental composition of the adsorbent. SEM-EDX (FEI Quanta 200) was conducted to analyze the surface morphology and chemical distribution, and BET (Micromeritics ASAP 2020) was used to measure the specific surface area and pore size distribution of DEP. Adsorption experiments were conducted in batch mode, with operational parameters such as solution pH, initial MB concentration, and contact time being optimized to determine the best adsorption conditions. After the adsorption process, the residual MB concentration in the solution was measured using a UV-Vis Spectrophotometer (PerkinElmer Lambda 25). The data obtained from these experiments were used for adsorption isotherm, kinetics, and thermodynamic analyses to comprehensively understand the characteristics and mechanisms of the adsorption process, as outlined in the method by Hevira et al., (2020). DEP adsorption capacity was calculated based on the equation formulated in the following method (Azari et al., 2019; Putra & Fitri, 2021):

$$q = \frac{(Co - Ce)\,x\,V}{m} \tag{1}$$

$$\%\ R = \frac{(Co - Ce)}{Co}\ x\ 100\% \tag{2}$$

Where q is the sorption capacity ($mg.g^{-1}$), %R is the sorption efficiency (%), Co is the initial concentration of MB solution ($mg.L^{-1}$), Ce is the equilibrium concentration of the substance

remaining in the solution (mg.L^{-1}), V is the volume of solution (L), and m is the mass of adsorbent (g).

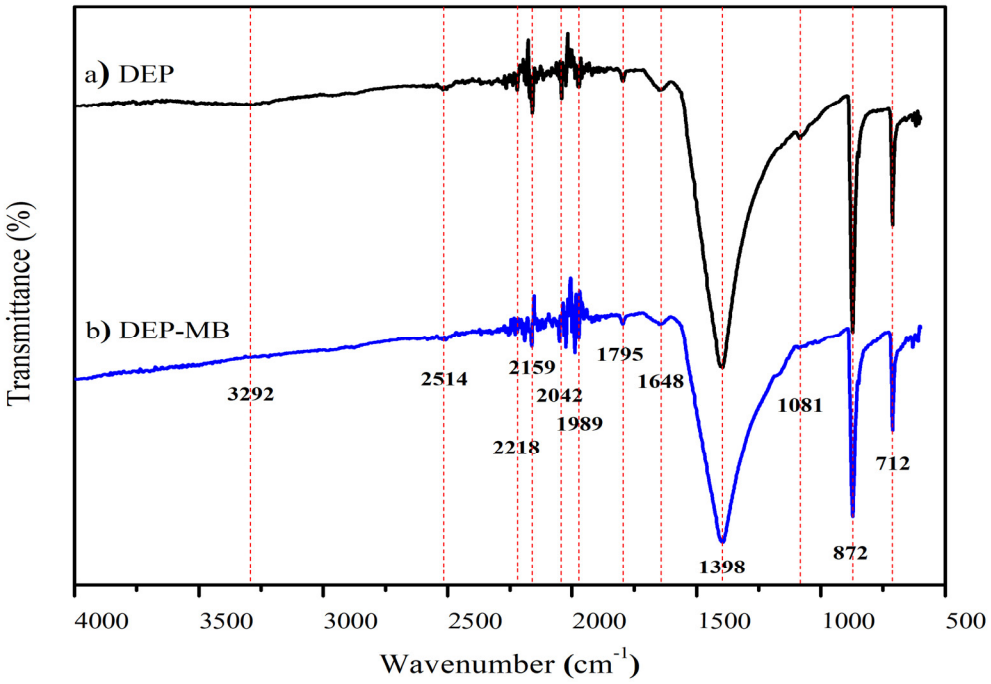

Fig. 2. FT-IR spectra, a) Before adsorption; b) After adsorption of MB

RESULTS AND DISCUSSION

Characterization of DEP adsorbent

FT-IR analysis of the interaction between DEP and MB revealed interesting findings that can be seen in Figure 2.

This analysis showed changes in the FT-IR spectra, indicating a shift in wave numbers reflecting changes in active functional groups during the MB sorption process. Comparison of the FT-IR spectra of the DEP adsorbent before and after MB sorption also showed significant differences. In the FT-IR spectrum of DEP before MB adsorption (Figure 2a), several absorption peaks were identified, including absorption peaks at wave numbers 3400-3600 cm^{-1} caused by hydroxyl functional groups (-OH), absorption peaks at wave numbers 1700-1800 cm^{-1} caused by carbonyl functional groups (C=O), and absorption peaks at wave numbers 1300-1400 cm^{-1} caused by alkane functional groups (-CH_3). Meanwhile, in the FT-IR spectrum after MB adsorption (Figure 2b), there is a shift in transmittance intensity in some of the absorption peaks mentioned above. There is also an absorption peak at wave number 2159 cm^{-1}, indicating aromatic functional groups (C=C). This absorption peak is more substantial in the FT-IR spectrum of DEP after MB adsorption. This difference can be explained by the interaction between aromatic functional groups of MB with polar functional groups on the DEP surface, such as hydroxyl groups (-OH) and carboxyl groups (COOH). When MB is adsorbed on DEP, an interaction occurs that increases the intensity of the absorption peak at wave number 2159 cm^{-1}. This reflects the adsorption process between MB and DEP, where the aromatic functional groups of MB interact with polar functional groups on the surface of DEP (Baalamurugan et al., 2020; Handayani et al., 2024).

The XRF analysis in Table 1 presents exciting findings related to the DEP adsorbent. This finding reveals that the main content in DEP is $CaCO_3$, with a composition of 98.202%. There are also other minerals in small amounts. The analysis also revealed changes in some elements in DEP before and after the adsorption process, suggesting an interaction between DEP and MB. $CaCO_3$ is the most dominant mineral in DEP. MB is a synthetic dye with a molecular structure consisting of two benzene groups connected by a methylene bridge. These benzene groups can bind to ions from minerals contained in DEP. MB can bind to calcium ions (Ca^{2+}) from $CaCO_3$, causing the concentration of $CaCO_3$ in DEP to decrease (Hevira, Rahmi, et al., 2020; Yusuff, 2019).

Figure 3, SEM analysis was conducted to assess the changes in morphology and chemical composition of the DEP adsorbent before and after the MB adsorption process. The results of SEM analysis at the initial stage before the adsorption process showed the surface characteristics of DEP with pores and irregular cavities (Figure 3a). The existence of these pores and cavities has a vital role as a place to adsorb MB. The formation of this surface occurs through the activation process using 0.01 M HNO_3, where unwanted particles dissolve in HNO_3, and consequently, the pores on the surface of the DEP adsorbent become more open and expansive. However, after going through the adsorption process, the surface morphology of the DEP adsorbent underwent significant changes. The surface that previously had pores and irregular cavities has become

Table 1. Inorganic composition of adsorbent before and after MB sorption

Element in compound	Adsorption MB	
	Before (%)	After (%)
CaO	98.202	96.995
P_2O_5	0.842	1.399
SO_3	0.302	0.797
Al_2O_3	0.337	0.301
MgO	0.283	0.157

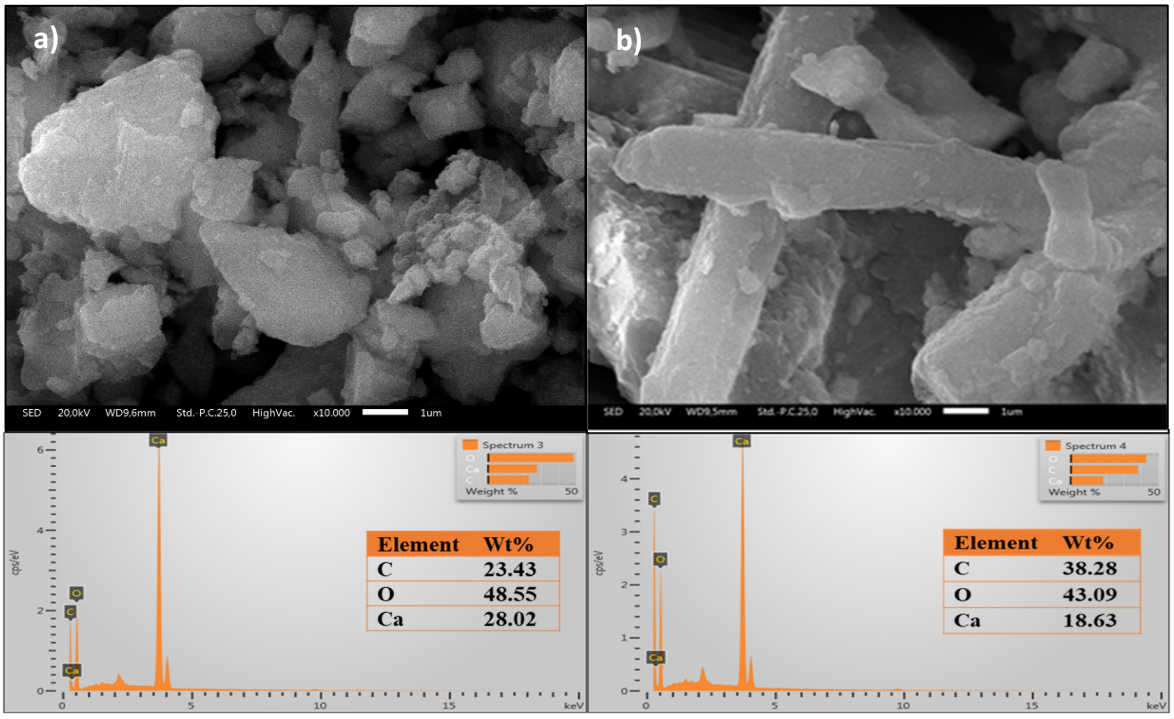

Fig. 3. Morphological image, a) Before adsorption; b) After MB adsorption, 10000x magnification

Table 2. The specific surface area of the adsorbent

Adsorbent	DEP	DEP-MB
BET surface area ($m^2.g^{-1}$)	0.6882	0.5494
Pore volume ($cm^3.g^{-1}$)	0.004141	0.003538

smoother and has no cavities (Figure 3b). This morphological change indicates that the MB adsorption process occurred on the DEP adsorbent surface, which was confirmed by the results of the visual SEM analysis. Overall, the difference in the morphology of the DEP adsorbent indicated the interaction that occurred between the adsorbent surface and the MB dye. The pores and cavities that initially served as adsorption sites became smoother and closed, indicating that MB had bound to the adsorbent surface (Baalamurugan et al., 2020; Hevira et al., 2020).

EDX analysis results revealed a significant transformation in the elemental composition of the DEP surface after MB adsorption. There was an increase in the mass of C on the adsorbent surface, while the mass of Ca decreased significantly. This decrease indicates the involvement of these active elements in the MB adsorption process. This indicates that MB has successfully bound to the DEP adsorbent surface. This data shows that MB is physically attached to the DEP structure after the adsorption process, accompanied by changes in the elements' characteristics. This finding not only strengthens our understanding of the adsorption mechanism of MB on DEP adsorbents but also provides a clearer picture of the interactions between MB and DEP adsorbents. Provides a clearer picture of the interactions that occur between the two.

BET analysis results on adsorbents to determine the specific surface area, pore volume, and pore size distribution of the adsorbent material (Mashkoor & Nasar, 2020), shown in Table 2 below:

Table 2 compares the physical properties of DEP before and after the MB adsorption process, revealing the changes in the adsorbent during the adsorption process. Previously, the surface area of DEP reached about 0.6882 $m^2.g^{-1}$, but after MB adsorption, it decreased to about 0.5494 $m^2.g^{-1}$. This change shows the effect of MB adsorption on the DEP surface structure, which may be related to the placement of MB molecules on the adsorbent surface. In addition to the change in surface area, the pore volume of DEP also decreased from 0.004141 $cm^3.g^{-1}$ before adsorption to 0.003538 $cm^3.g^{-1}$ after MB adsorption. This decrease in pore volume reflects the possible penetration of MB molecules into the adsorbent pores, filling the available space (Ayalew & Aragaw, 2020; Handayani et al., 2024). These data comprehensively show the changes in the physical properties of DEP during the MB adsorption process, including a decrease in surface area and reduced pore volume. These changes occurred due to the significant interaction between DEP and MB during the adsorption process, which significantly affected the pore structure of DEP.

The pHpzc analysis aims to determine the pH at which the adsorbent surface's positive and negative charges are balanced. If the pH is lower than pHpzc, the adsorbent surface will be positively charged. Conversely, if the pH is higher than pHpzc, the adsorbent surface will tend to be negatively charged (Hevira et al., 2021; Putra, Fauzia, et al., 2024). The pHpzc value of DEP adsorbent is at pH 8, shown in Figure 4, where the surface has a neutral charge. pHpzc is important in the interaction with dyes such as MB because at pH below pHpzc, the surface will be positively charged, and at pH above pHpzc, it will be negatively charged (Hevira, Zilfa, et al., 2020). The study showed that the optimum pH of MB adsorption by the adsorbent was also at pH 8. This study revealed that pHpzc, close to the optimum pH of adsorption, allows optimum interaction between the adsorbent and MB. This provides important information about the influence of adsorbent surface charge on MB adsorption effectiveness. Information on pHpzc and its correlation with the adsorption optimum pH can be used to design more efficient

adsorption methods for the absorption of hazardous dyes (Jóźwiak et al., 2021; Munagapati et al., 2022).

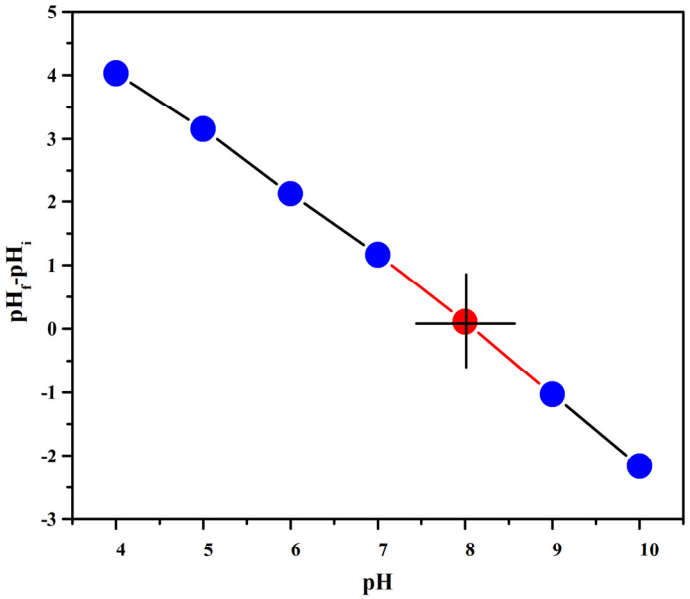

Fig. 4. pHpzc of DEP adsorbent

Equilibrium adsorption studies

The effect of pH on the adsorption capacity of MB, which is shown in Figure 5a using DEP, illustrates that the adsorbent surface shows a positive charge at low pH conditions. The presence of $CaCO_3$ in the adsorbent structure causes a slight increase in the basicity of the solution. At acidic pH conditions, excess H^+ ions in the solution can reduce the adsorption capacity of MB due to the competition of positive charges from MB and H^+ ions (Abdel-Khalek et al., 2017). At this condition, the positive charge on the DEP surface reaches an optimum point, facilitating a solid and effective interaction between the positively charged DEP and the negatively charged MB at alkaline pH. This resulted in a significant increase in adsorption capacity under these conditions. Previous studies have also reported this finding (Fadhil et al., 2019; Ngadi et al., 2013; Yusuff, 2019).

Figure 5b, variations in the initial MB concentration demonstrate that increasing the concentration from 10 to 80 mg.L^{-1} enhances the adsorption capacity of DEP. This can be attributed to the availability of more MB molecules to be adsorbed onto the surface of the adsorbent. This trend aligns with the findings of Gupta et al (2019), who reported that higher initial concentrations of cationic pollutants increase the concentration gradient between the solution and the adsorbent surface, thereby facilitating greater mass transfer. However, beyond a certain point, the adsorption capacity reaches saturation as all active sites on the adsorbent surface are utilized, as similarly observed in the study by Ayalew & Aragaw, (2020). In this study, DEP exhibited a maximum adsorption capacity of 5.99 mg.g^{-1} at an MB concentration of 80 mg.L^{-1}, which closely approaches the theoretical maximum adsorption capacity predicted by the Langmuir model.

Figure 5c, the effect of contact time on adsorption reveals that the adsorption capacity increases rapidly within the first 15 minutes, followed by a plateau after 30 minutes. This indicates that the adsorption of MB onto DEP occurs in two distinct stages: an initial rapid phase where active sites on the adsorbent surface are quickly occupied, followed by an equilibrium phase where the

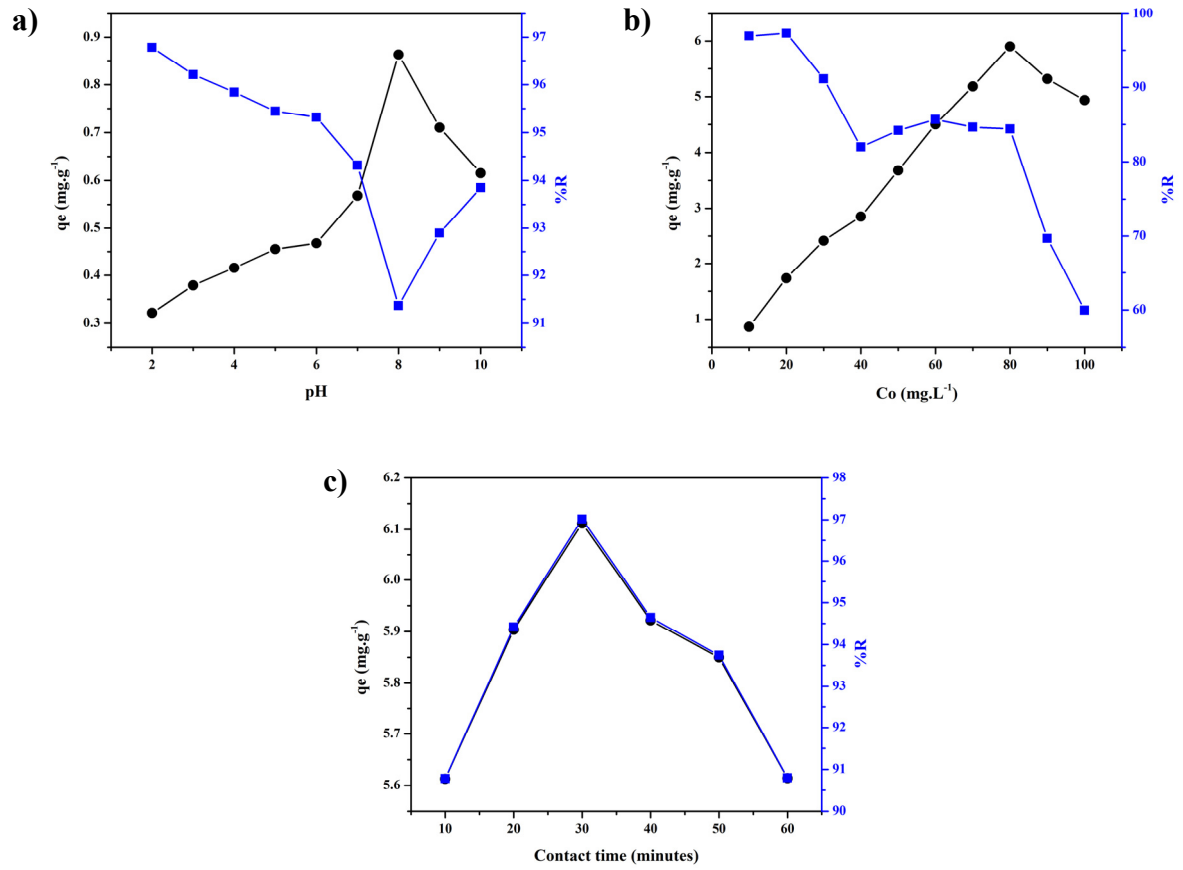

Fig. 5. a) Variation of solution pH; b) Variation of initial concentration of MB solution; c) Contact time of MB adsorption

diffusion of MB molecules into the adsorbent's pores becomes the rate-controlling step. This phenomenon is consistent with the findings of Mashkoor & Nasar, (2020), who reported that the optimal contact time is often determined by the diffusion of pollutants into the microporous structure of the adsorbent. Similarly, Handayani et al., (2023), observed a comparable pattern in the adsorption of synthetic dyes using biomaterials, with optimal contact times ranging from 20 to 30 minutes.

Study of adsorption isotherms and kinetics

It is crucial to study adsorption isotherms to determine the type of adsorbate layer formed on the adsorbent surface, obtain information about the maximum adsorption capacity, and predict the adsorption mechanism (Gupta et al., 2019). In this study, the adsorption isotherm models analyzed include Freundlich, Langmuir, and Temkin. The presence of R^2 values close to 1 in an isotherm model indicates that the model tends to be closest to the actual adsorption process. Details of the linear equations of the isotherm models can be found in Table 3.

Where qe is the adsorption capacity of adsorption capacity ($mg.g^{-1}$), K_f ($(L.mg^{-1})^{1/n}$), and n ($L.mg^{-1}$) is the Freundlich isotherm constant, Ce is the solute concentration in solution ($mol.L^{-1}$), qm is the monolayer adsorption capacity ($mg.g^{-1}$). KL is the Langmuir adsorption constant ($L.mg^{-1}$), β is Temkin's constant, indicating the heat of adsorption ($J.mol^{-1}$), and k_T is the equilibrium binding constant, related to the maximum binding energy ($L.g^{-1}$) (Putri et al., 2020).

The results of the analysis of the three isotherm models are shown in Figure 6 and Table 4. The

Table 3. Ishoterm model for analyzing adsorption experimental data

Ishoterm Model	Equation	Plots	Reference
Freundlich	$\text{Log qe} = \log K_f + \frac{1}{n} \log \text{Ce}$	Log Ce vs Log qe	(Putri et al., 2020)
Langmuir	$\frac{\text{Ce}}{\text{qe}} = \frac{1}{K_L\, \text{qm}} + \frac{\text{Ce}}{\text{qm}}$	Ce vs $\frac{Ce}{qe}$	
Temkin	$\text{qe} = \beta \ln k_T + \beta \ln \text{Ce}$	ln Ce vs qe	

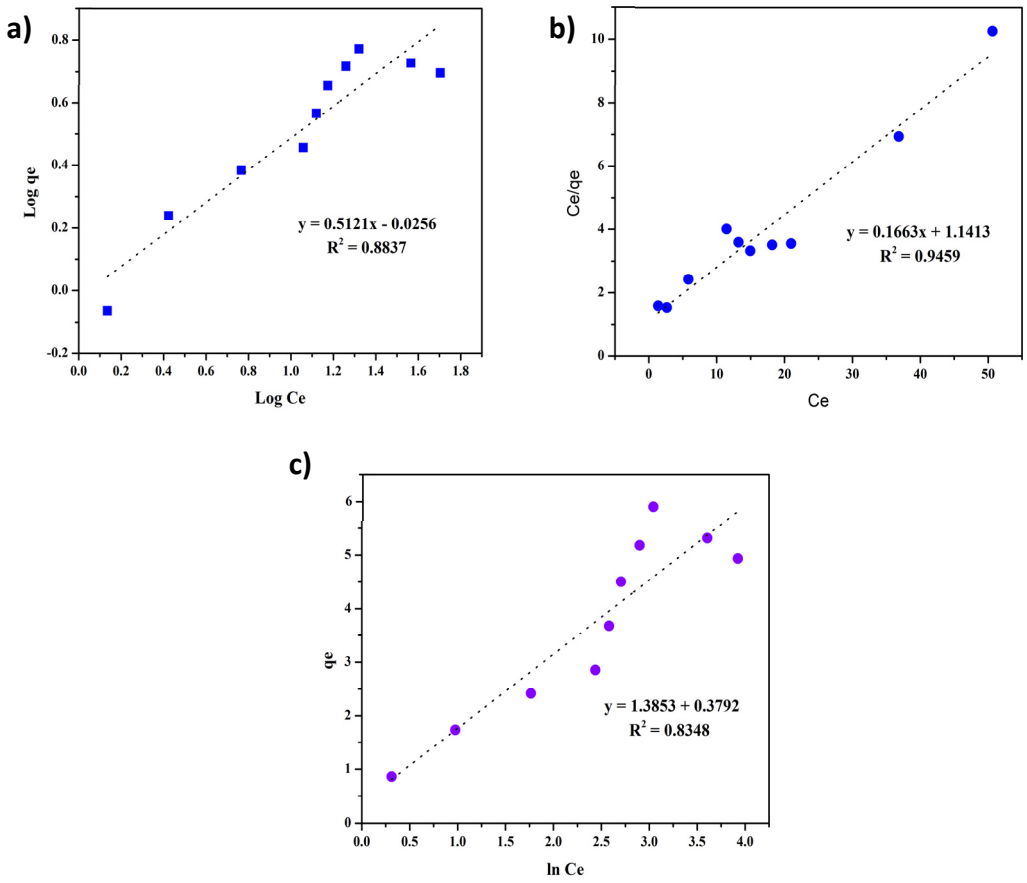

Fig. 6. Linear isotherm curves: a) Freunlich; b) Langmuir; c) Temkin.

Table 4. Isotherm parameters of MB adsorption

Parameters	Value
Freundlich	
K_F ($(L.mg^{-1})^{1/n}$)	0.943
1/n	0.512
R^2	0.884
Langmuir	
q_m ($mg.g^{-1}$)	6.013
K_L ($L.mg^{-1}$)	6.863
R_L	0.002
R^2	0.946
Temkin	
β ($J.mol^{-1}$)	1.385
KT ($L.g^{-1}$)	3.999
R^2	0.835

order of the adsorption process tends to follow the Langmuir > Freundlich > Temkin isotherm model. The Langmuir isotherm model gives good results, as evidenced by the R^2 value close to 1, indicating a better match between the experimental data and the model used in this study.

Langmuir isotherm model can provide information about the maximum adsorption capacity and bonding strength between adsorbent and adsorbate. From the research data, it is assumed that the adsorption of MB using DEP occurs on a homogeneous surface, where the adsorption energy is the same at each adsorption site. This model also assumes that adsorption occurs in a single layer or monolayer adsorption (Cusioli et al., 2020; Putri et al., 2020).

The kinetics study of MB adsorption with DEP is crucial because it can provide information about the adsorption capacity and rate constants of the adsorbent. Several kinetics models were analyzed in MB adsorption using DEP. These models are expressed in formulations, as shown in Table 5.

Where qt is the amount of methylene blue adsorbed at time t ($mg.g^{-1}$), qe is the amount of methylene blue adsorbed at equilibrium ($mg.g^{-1}$), and k_2 is the rate constant of the pseudo-second-order model ($g.mg^{-1}.min^{-1}$).

The adsorption kinetics data of MB using DEP tended to follow a pseudo-second-order model. The calculated qe value (qe = 5.659 $mg.g^{-1}$) of DEP was observed to agree with the experimental qe value (qe = 5.991 $mg.g^{-1}$). Therefore, this indicates that the pseudo-second-order equation is suitable for describing the kinetics of MB adsorption on DEP under equilibrium conditions. In addition, the correlation coefficient (R^2) value of this model can be used to evaluate the fit of the experimental data, with $R^2 \geq 1$, where this model assumes the adsorption rate is proportional to the square of the number of vacant sites on the adsorbent surface and the adsorbate concentration (Chen et al., 2019). In Figure 7 and Table 6, it can be seen that the DEP pseudo-second-order kinetic model is significantly higher ($R^2 = 0.996$), approaching $R^2 \geq 1$, than the pseudo-first-order kinetic model ($R^2 = 0.027$). The fit of the kinetic model data to the pseudo-second-order equation indicates that MB sorption using DEP occurs through a chemisorption process, and the reaction rate is directly proportional to the number of active sites available on the adsorbent surface (Dahlan et al., 2019; Polat & Bursali, 2021).

Adsorption thermodynamics

The thermodynamics of adsorption is essential to study because it can provide information about the stability and spontaneity of the adsorption process and can determine whether the adsorption process is thermodynamically favorable and requires energy. In addition, adsorption thermodynamics can provide information on the maximum adsorption capacity and bonding strength between adsorbent and adsorbate (Mbarki et al., 2018).

Thermodynamic parameters in this study, such as standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were obtained from Langmuir Isotherm plots relating to the effect of adsorption temperature on MB adsorption capacity, this process was carried out by varying the adsorption temperature from 298, 308, and 318 K, at various MB concentrations from 10-50 $mg.L^{-1}$. The following equation can calculate the thermodynamic parameters of adsorption (R. Ahmad & Ejaz, 2024; Handayani et al., 2023; Harrache et al., 2019).

$$Ke = \frac{q_e}{C_e} \tag{3}$$

$$\Delta G^o = -RT\ ln\ Ke \tag{4}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{5}$$

From the results obtained, the standard Gibbs free energy (ΔG°) is positive, enthalpy (ΔH°) is positive, and entropy (ΔS°) is negative. A positive ΔG° value indicates that the adsorption process is thermodynamically unfavorable, while a positive ΔH° value indicates that the adsorption

Table 5. Kinetic model for analyzing adsorption experimental data

Kinetics Model	Equation	Plots	Reference
Pseudo-first-order	$q_t = q_e(1 - e^{-k_1 t})$	t vs ln (q_e-q_t)	(Kumar, 2006)
Pseudo-second-order	$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t}$	t vs t/q_t	
Intraparticle Diffusion	$q_t = K_{diff}\, t^{0.5} + C$	$t^{0.5}$ vs q_t	(Chen et al., 2019)
Elovich	$q_t = \left(\frac{1}{\beta}\right) In\,(\alpha\beta) + \left(\frac{1}{\beta}\right) In\, t$	In t vs q_t	

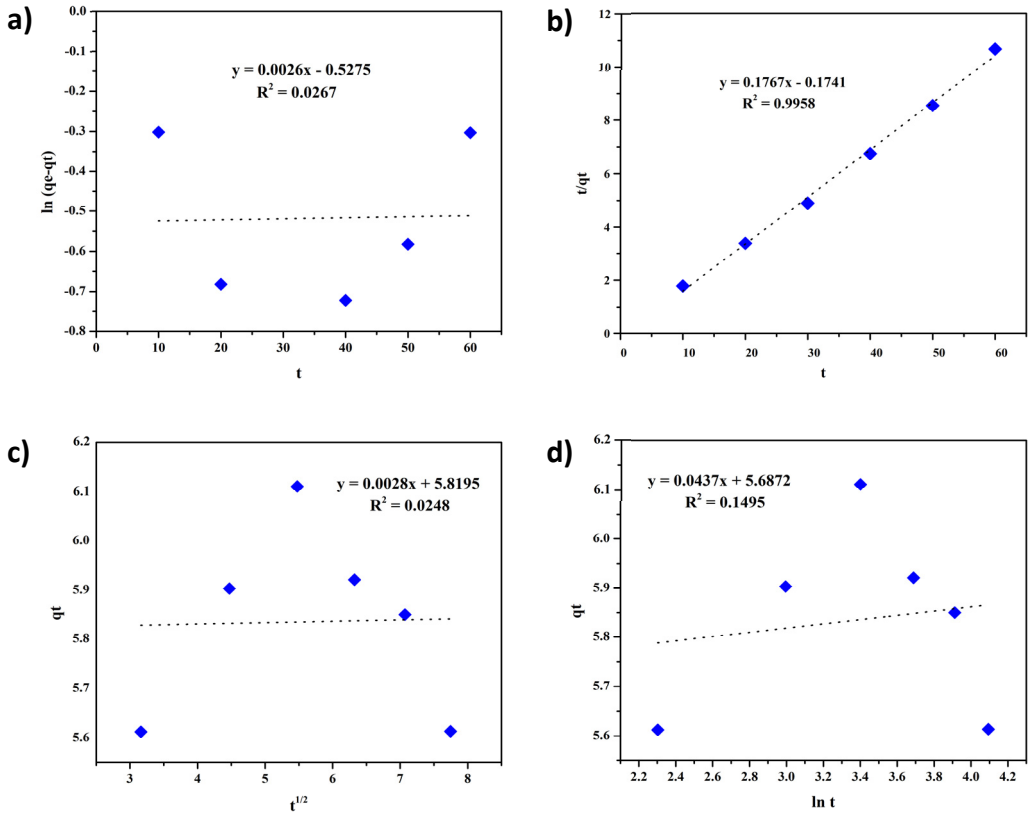

Fig. 7. Linear kinetics curves: a) Pseudo First Order; b) Pseudo Second Order; c) Intraparticle Diffusion; d) Elovich

Table 6. Kinetics parameters of MB adsorption

Kinetics Model	Value
qe (exp) (mg.g^{-1})	5.991
Pseudo-first-order	
k_1 (1.min^{-1})	0.003
qe (calc) (mg.g^{-1})	0.408
R^2	0.027
Pseudo-second-order	
k_2 (g.mg^{-1}.min^{-1})	0.179
qe (calc) (mg.g^{-1})	5.659
R^2	0.996
Intraparticle Diffusion	
K_{diff} (mg.g^{-1}.(min$^{1/2}$)$^{-1}$)	0.003
C (mg.g^{-1})	5.819
R^2	0.025
Elovich	
β (g.mg^{-1})	22.883
α (mg.min.g^{-1})	295.066
R^2	0.149

Table 7. Thermodynamic parameters of MB adsorption

Parameters	Temperature (K)			Result
	298	308	318	
ΔG° (kJ.mol^{-1})	10.800	11.453	12.106	Non-spontaneous
ΔH° (kJ.mol^{-1})		8.658		Endothermic
ΔS° (kJ.mol^{-1}.K^{-1})		-0.065		Disorder decreases

Table 8. Comparison of MB sorption capacity with some other adsorbents

Adsorbent	Dye	pH	Particle Size (μm)	q (mg.g^{-1})	% Removal	Reference
Duck Eggshell Powder	MB	8	≤ 75	5.99	97.34	This Study
Chicken Eggshell with its Membrane	MB	6	≤ 425	13.51	94.5	(Hevira, Rahmi, et al., 2020)
	IC	6		10.64	85.5	
Eggshell	MB	7.2	-	91.07	95.89	(Fadhil et al., 2019)
Composite Chicken Eggshell - Anthill Clay	MB	8	250-177	303.03	99.9	(Yusuff, 2019)
Eggshell - Treated Palm Oil Fuel Ash	MB	6	-	23.81	76.52	(Hasan et al., 2019)
		6.5		23.26	75.56	
Burned Coal Eggshell	MB	7	-	-	92.79	(Kamal et al., 2015)
					74.76	
Eggshell Powder	MB	10	-	57.03	78.98	(Ngadi et al., 2013)

process requires energy to occur (M. A. Ahmad et al., 2019; Zhai et al., 2019). In addition, a negative entropy value (ΔS°) indicates that the adsorption process causes rearrangement on the adsorbent surface. The negative value of entropy change means that during adsorption, the homogeneity of the adsorbent surface increases, and there is no significant change in the internal structure of the adsorbent (Iwuozor et al., 2021; Zein et al., 2022). Therefore, from this research data, it can be assumed that the MB adsorption process using DEP is not spontaneous, requires energy, and has a low level of randomness. The data can be seen in Table 7.

Comparison with the literature

DEP showed better adsorption ability, with a 5,991 mg.g^{-1} capacity and removal efficiency of 97.34% at all optimum conditions, including pH, initial MB concentration, contact time, and temperature. From Table 8, it can be concluded that DEP has a much higher MB adsorption capacity than other adsorbents. The advantages of DEP lie in its ease of preparation without the need for particular precursors and the great potential of abundant natural resources as adsorbents. This approach aligns with the concept of "Zero Waste and Green Environment," signifying an environmentally friendly solution in dealing with pollution by synthetic dyes and bringing positive implications to environmental protection.

Application to medical laboratory waste

The ability of DEP to adsorb MB in wastewater may differ from that of simulated dye solutions. Therefore, this study used wastewater from the Syedza Saintika University medical laboratory containing synthetic dyes. As shown in Table 9, the adsorption results at the optimum pH (pH 8) showed a removal percentage of 100% compared to the natural pH of medical laboratory wastewater (pH = 5.8) with a removal percentage of 77.87%. At pH 8, the presence of OH^- ions in the solution causes deprotonation so that the adsorbent surface is negatively charged and can form electrostatic interactions with positively charged MB so that the % removal becomes optimum. This proves that pH is important in adsorption (Handayani et al., 2024; Hevira et al., 2020). Although applied to medical laboratory waste with low pH, the absorption capacity of MB using DEP is categorized as better than the % removal of adsorbents with close pH. This

can be seen from the comparative study in Table 9.

Table 9. Application of MB adsorption conditions on medical laboratory waste

Conditions	pH	Co ($mg.L^{-1}$)	Ce ($mg.L^{-1}$)	qe ($mg.g^{-1}$)	% R
Real	5.8	76.78	16.99	5.98	77.87
Optimum	8	76.78	0	7.68	100

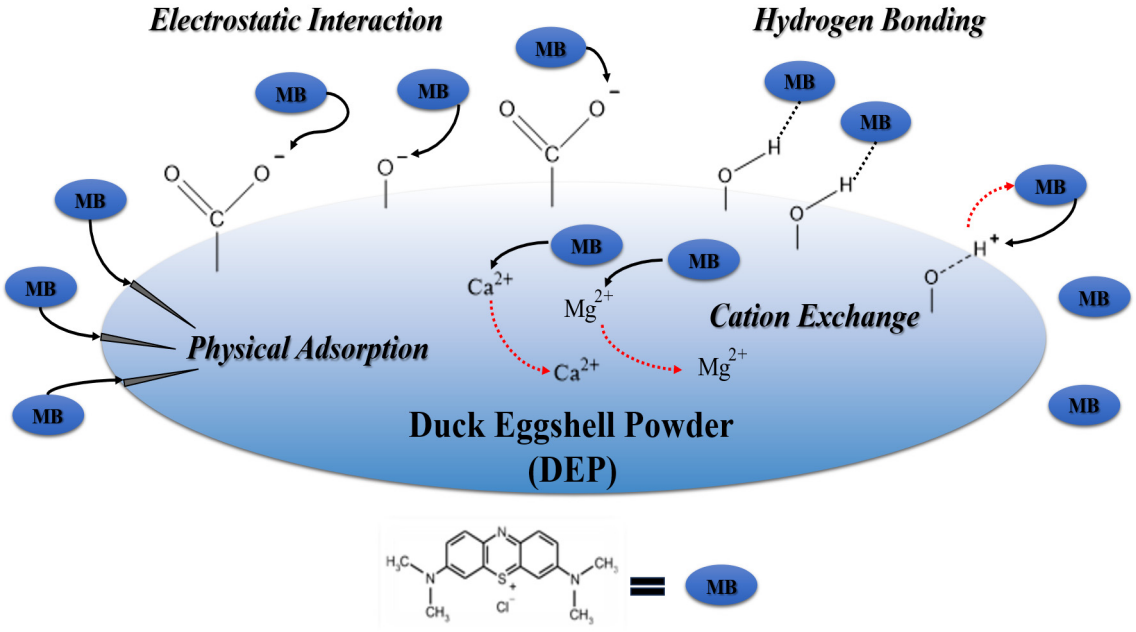

Fig. 8. Predicted adsorption mechanism of MB

Mechanism of Methylene Blue Removal

From the results of characterization and equilibrium studies, isotherms, kinetics, and thermodynamics that have been carried out, supporting data are obtained to predict the adsorption mechanism that occurs in MB sorption with DEP. The MB sorption process using DEP involves various interaction mechanisms, including: 1) Physical adsorption occurs when MB molecules are adsorbed on the DEP surface through van der Waals and hydrophobic force interactions. 2) Chemical adsorption occurs through hydrogen bonding between functional groups on the MB molecule and the DEP surface. 3) Electrostatic interaction occurs through ionic and polar covalent bonds between the positively charged MB molecules and the negatively charged DEP surface. 4) Cation exchange between cations found on DEP and positive ions from MB. The predicted mechanism is evidenced by the results of XRF analysis (Table 2), revealing the presence of calcium carbonate ($CaCO_3$) in DEP, which contributes to ion exchange and surface complexation processes.

Furthermore, this mechanism illustrates that various complex interactions between the hydrophobic properties, functional groups, and charges on the MB molecule, as well as the DEP surface, play a role in the sorption process (Hevira et al., 2020; Zein et al., 2022). This suggests that MB sorption on DEP involves one type of interaction and a combination of physical and chemical interactions (Figure 8). Thus, a comprehensive understanding of this sorption mechanism provides deeper insight into the adsorbent and MB dye interactions.

CONCLUSION

This study shows that duck eggshell powder (DEP) is an effective adsorbent for removing methylene blue (MB) from medical laboratory wastewater. Under optimal conditions, pH 8, initial MB concentration of 80 $mg.L^{-1}$, contact time of 30 min, and temperature of 298 K, the maximum adsorption capacity was reached at 5.99 $mg.g^{-1}$ with removal efficiency up to 97.34%. Isotherm studies showed that MB adsorption followed the Langmuir model, indicating monolayer adsorption on the DEP homogeneous surface, with a coefficient of determination $R^2 = 0.946$. In addition, the kinetics study revealed that the adsorption of MB on DEP follows a pseudo-second-order model, indicating that the process is predominantly influenced by the chemical reaction between MB and active sites on the DEP surface. Characterization using FT-IR, SEM-EDX, and BET confirmed the changes in surface structure, pore distribution, and the presence of active functional groups on DEP before and after adsorption. The results also showed that DEP can be used for medical wastewater treatment with removal efficiency reaching 100% at pH 8. However, thermodynamic studies showed that the adsorption process is non-spontaneous and endothermic, so temperature and other operational settings need to be considered for practical applications. For future research, it is recommended to test the effectiveness of DEP on complex medical laboratory waste, which contains various contaminants such as heavy metals and other organic compounds. In addition, physical or chemical modifications to DEP can be developed to increase its adsorption capacity. Research related to the regeneration and reusability of DEP also needs to be conducted to ensure the sustainability of its use in waste treatment. Implementation on an industrial scale by considering energy efficiency and integration with other waste treatment technologies is also important to be explored. In addition, it is necessary to assess the environmental impact of DEP use, including post-adsorption residue management.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript. In addition, the authors have completely observed the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

ABBREVIATIONS

%R	: Sorption Efficiency
Al_2O_3	: Aluminum Oxide
BET	: Brunauer-Emmett-Teller (Surface Area Analysis Method)

Ca : Calcium
Ca^{2+} : Calcium Ion
CaO : Calcium Oxide
Ce : Equilibrium Concentration ($mg.L^{-1}$)
Co : Initial Concentration ($mg.L^{-1}$)
DEP : Duck Eggshell Powder
EDX : Energy Dispersive X-ray Spectroscopy
FT-IR : Fourier Transform Infrared Spectroscopy
HCl : Hydrochloric Acid
HNO_3 : Nitric Acid
m : Mass of Adsorbent (g)
MB : Methylene Blue
MgO : Magnesium Oxide
NaOH : Sodium Hydroxide
P_2O_5 : Diphosphorus Pentoxide
PA : Pro Analyse
R^2 : Coefficient of Determination
SEM : Scanning Electron Microscopy
SO_3 : Sulfur Trioxide
V : Volume of Solution (L)
XRF : X-ray Fluorescence
$\Delta G°$: Gibbs Free Energy
$\Delta H°$: Enthalpy Change
$\Delta S°$: Entropy Change

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