Adsorption of Methylene Blue on Nano-Crystal Cellulose of Oil Palm Trunk: Kinetic and Thermodynamic Studies

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Abstract: *The adsorption kinetic study of methylene blue using nano-crystal cellulose made from oil palm trunk was investigated. A sample of 0.08 g of nano-crystal cellulose was used to adsorb 300 mL of methylene blue solution, with a varied stirring speed at 100, 200, and 300 rpm. Meanwhile, the concentration of methylene blue was varied at 1, 2, and 3 mg/L. The experimental results showed that the range of adsorption rate constant was 0.0007–0.0130 m/min. For the thermodynamic study, adsorption temperature was varied at 303, 308, 313, and 318 K. The adsorption capacity values for such temperatures were 10.3389, 10.3802, 10.3614, and 10.3464 mg/g, respectively. It was found that ΔH° value of 0.00742 kJ/mol, ΔS° of 0.7758 kJ/mol K and ΔG° value of −242.81 kJ/mol. Based on the curve-fitting using the Henry, Langmuir, and Freundlich isotherm models, this adsorption tended to the Langmuir isotherm model, where the adsorption formed a monolayer covering the surface of the adsorbent. It was also found that the Langmuir affinity constant (K_L) value was 4.560 L/mg, and the maximum adsorption capacity (q_m) was 8.590 mg/g.*

Keywords: *nano-crystal cellulose; methylene blue; adsorption; oil palm trunk*

■ INTRODUCTION

The development of revolutionary technology 4.0 is the basis of the Indonesian government's thinking towards the "Making Indonesia 4.0" road map. One of the road maps is to develop several potential industrial sectors to develop the potential of Indonesia's industry, one of which is the textile industry [1].

The textile industry in Indonesia is integrated. Data from the central statistics agency shows that textile exports during January-August 2021 reached 160.854 tons, much higher than the same period in 2019 and 2020 of 152.474 tons and 147.982 tons, respectively. The development of the textile industry will be proportional to the increase in textile industry waste, especially liquid waste. Liquid waste that is difficult to process is textile dyes [2]. One of the dyes commonly used in the textile industry is methylene blue [3-4].

The existence of dye waste in the environment has become a significant world issue due to its damaging effect on aquatic life and ecosystems [5-6]. Disposal of dye waste without a prior degradation process can cause a health problem since dyes are toxic (or mutagenic) and carcinogenic [7-8]. Interestingly, the adsorption process is quite efficient in removing textile dyes from wastewater [9-12]. This study used nano-crystal cellulose as a biosorbent to adsorb methylene blue. The methylene blue is cationic, while nano-crystal cellulose is anionic, so there will be an electrostatic force between them. In this study, it is expected that nano-crystal cellulose has a larger surface area, increasing the adsorption sites of methylene blue [13].

Several studies have been done regarding the work function of nano-crystal cellulose as biosorbent for methylene blue, such as nano-crystal cellulose from oil palm empty fruit bunch (EFB) [9], from cotton [14], from sawdust [15], poly(acrylic acid)/nano-crystal cellulose modification to nanocomposites hydrogel [16], and cross-linked nano-crystal cellulose aerogels [17]. This study used oil palm trunks as raw materials for making the adsorbents.

Oil palm trunks have a reasonably high cellulose content of 40%. In addition to the high cellulose content, the availability of oil palm trunks in Indonesia is also relatively abundant. Indonesia has an area of 11 million hectares of oil palm. Every year 4% of the rehabilitated land area will produce oil palm trunk waste of around 100 million cubic meters. Until nowadays, the use of oil palm trunks in Indonesia has been carried out by Jamal Balfas at the Research and Development Center for Forestry Engineering and Forest Product Management (Balitbang Hutan) as plywood and solid wood [18]. The cellulose content and the abundant availability of materials are the main reasons for choosing materials that allow the success of cellulose-based biosorbent products.

The adsorption process is when one or more gas or liquid components are adsorbed on a solid surface [19]. The most common adsorption type in nano-crystal cellulose is physical and chemical adsorption. The adsorption mechanism of methylene blue by nano-crystal cellulose covers hydrogen bonding, ion-dipole interaction, and electrostatic interaction [13]. The authors have carried out previous research on the adsorption of nano-crystal cellulose. The authors analyzed the differences in NaOH concentrations in the alkaline treatment process on the results of the impurity of nano-crystal cellulose produced [20] and the effect on the adsorption of methylene blue, then continued with the characterization of samples of nano-crystal cellulose made from palm trunks [21]. The study focuses on the effect of stirring and the initial concentration of methylene blue on the adsorption rate to achieve an equilibrium using a fitted kinetics study of Langmuir isotherm model, Freundlich isotherm, and distribution coefficient. The isotherm study aims to conclude whether the adsorption runs physically or chemically based on the adsorbent and adsorbate mechanisms. It checks the value of the maximum adsorption capacity quantitatively. The thermodynamic study aims to determine whether the adsorption properties are spontaneous by finding the values of $\Delta H°$ and $\Delta S°$ to get the value of $\Delta G°$ of methylene blue adsorption using nano-crystal cellulose.

The study of kinetics and thermodynamics, especially on the adsorption mechanism of nano-crystal cellulose made from oil palm stems, is still minimally studied. The results will be useful for optimizing products, operating conditions, and large-scale production processes.

■ FUNDAMENTALS

This subchapter explains the fundamental theory in detail in the proposed model used to describe the methylene blue adsorption process using nano-crystal cellulose.

Kinetics and Isotherm Studies

In methylene blue adsorption using nano-crystal cellulose, it can be assumed that the adsorbent granules are tiny, leading to fast diffusion of methylene blue from the adsorbent surface into the internal adsorbent pore. The concentration of methylene blue inside the pore is uniform; thus, the proposed mathematical model is as follows:

Mass balance of methylene blue in liquid materials

Rate of Mass in – Rate of Mass Out = Rate of Mass Accumulation

$$0 - k_c a(C_A - C_A^*)m = \frac{d}{dt}(VC_A) \tag{1}$$

$$\frac{dC_A}{dt} = -\frac{k_c am}{V}(C_A - C_A^*) \tag{2}$$

Mass balance of methylene blue in solid materials

Rate of Mass in – Rate of Mass Out = Rate of Mass Accumulation

$$k_c a(C_A - C_A^*)m - 0 = \frac{d}{dt}(m.X_A) \tag{3}$$

$$\frac{dX_A}{dt} = k_c a(C_A - C_A^*) \tag{4}$$

k_c is the rate of adsorption constant (m/min), a is the notation for the adsorbent specific surface area (m^2/g), m is the mass of the adsorbent used (g), V is the volume of solution (L), C_A^* is the adsorbate concentration in the liquid at equilibrium (mol/L), C_A is the concentration of adsorbate in the liquid (mol/L), $\frac{dC_A}{dt}$ is the distribution of adsorbate concentration in the liquid (mol/min), and $\frac{dX_A}{dt}$ is the distribution of the adsorbate concentration in the adsorbent (mol/min).

C_A^* is a number that cannot be measured, so the value of C_A^* will be substituted with some basic equilibrium equations. Here are some of the equations used.

Distribution coefficient

$$X_A = K_d \times C_A^* \qquad (5)$$

C_A^* is the adsorbate concentration in the liquid at equilibrium (mol/L) and X_A is the adsorbate concentration adsorbed on the surface of the adsorbent pore wall at equilibrium (mol/L), while K_d is the adsorption equilibrium constant.

Isotherm Langmuir

$$X_A = \frac{\beta C_A^*}{C_A^* + \alpha} \qquad (6)$$

X_A is the concentration of adsorbate adsorbed on the surface of the adsorbent pore wall at equilibrium (mol/L), α is q_m (mg/g), β is a constant of the Langmuir equation × q_m (mg/g), while C_A^* is the concentration of adsorbate in liquid at equilibrium pressure (mol/L).

Langmuir modeling describes the monolayer adsorption on the adsorbent surface. This model assumes that the adsorption rate is the same as the desorption rate [22]. This modelling used three assumptions: The adsorption energy is constant at all sites due to a homogeneous surface. The adsorption occurs at a specific (localized) site, the adsorption energy at all sites is the same, and each active site accommodates one adsorbate molecule only [23].

Isotherm Freundlich

$$X_A = K_f C_A^{*\beta} \qquad (7)$$

K_f is the Freundlich constant related to the adsorption capacity (mg/g) $(L/mg)^{-1/n}$, β is the Freundlich constant related to the heterogeneity factor or adsorption intensity, C_A^* is the concentration of adsorbate in the liquid at equilibrium (mol/L) and X_A is the concentration of adsorbate adsorbed on the surface of the adsorbent pore wall at equilibrium (mol/L). Freundlich modelling illustrates multilayer adsorption and heterogeneous adsorbent surfaces [23].

Thermodynamic Study

This study used the entropy factor and Gibbs free energy to determine whether the process occurred spontaneously. The parameters of enthalpy (ΔH°), Gibbs energy (ΔG°), and entropy (ΔS°) can be found using the adsorption kinetics equation tested at different temperatures [24].

$$\Delta G^\circ = -RT \ln K_c \qquad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (9)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (10)$$

K_c is the adsorption equilibrium constant, T is the operating temperature (K), and R is the gas constant (8.314 J/mol K). The value of K_c is obtained from Eq. (11).

$$K_c = \frac{q_e}{C_e}\frac{m}{V} \qquad (11)$$

The value of q_e can be formulated by the Eq. (12)

$$q_e = \frac{C_o - C_e}{m} V \qquad (12)$$

■ EXPERIMENTAL SECTION

This research consists of four steps: preparation of nano-crystal cellulose, characterization of nano-crystal cellulose products, adsorption tests on methylene blue, and studies of kinetics and thermodynamics of the adsorption process, which refers to the previous research [25].

Materials

Nano-crystal cellulose, with oil palm trunk as raw material, has been prepared according to a method described in our previous research [20-21]. Briefly, the nano-crystal cellulose was synthesized by a sequential process of alkaline treatment, bleaching, hydrolysis, and sonication. Meanwhile, methylene blue (solid powder, Merck) was used as the parent material for the adsorbate solution in the adsorption test.

Instrumentation

The concentration of methylene blue on the adsorption test was measured using the PG Instruments

T60 UV-Vis Spectrophotometer at the wavelength 643 nm.

Procedure

Adsorption data were collected using a batch test. This test consists of two parts, kinetic studies, and thermodynamic studies.

Batch adsorption for kinetics studies

Firstly, adsorbent (0.08 g of nano-crystal cellulose) and methylene blue samples (300 mL of solution at concentrations 1, 2, and 3 mg/L) were prepared. The adsorbent was then put into an Erlenmeyer with methylene blue solution. The Erlenmeyer was stirred using a magnetic stirrer (varied at 100, 200, and 300 rpm). Every 20 min aliquot sample (5 mL) was taken to measure the value of the methylene blue concentration with a UV-Vis Spectrophotometer.

Batch adsorption for thermodynamic studies

For thermodynamic studies, 300 mL of 3 mg/L methylene blue solution was used as the liquid sample. A sample of nano-crystal cellulose (0.08 g) was used to adsorb the methylene blue. The adsorption was conducted for 2 h at varying temperatures (303, 308, 313, and 318 K). After adsorption, 5 mL of the sample was taken to analyze the final concentration of methylene blue using a UV-Vis Spectrophotometer.

■ RESULTS AND DISCUSSION

Result of Analysis and Characterization of Nano-Crystal Cellulose Product

Nano-crystal cellulose product as adsorbent has been characterized by several methods. Chesson analysis was used to determine its chemical composition. FTIR spectra have been conducted and it confirmed the loss and appearance of functional groups before and after adsorption. Meanwhile, SEM and TEM were carried out to analyze the morphology of the nano-crystal that have been made. The SEM and TEM results confirmed the shape of nano-crystal cellulose resembled needles. In addition, the XRD result indicated an increase in the degree of crystallization of the product. The BET method was used to determine the surface area with the result of the surface area is 77.369 m^2/g, and SAA confirm the size of the nano-crystal of cellulose that has been made with the size of the product ranging from 1.407 to 98.56 nm. These results have been discussed in our previous works [21,25].

Effects of Stirring Speed on Adsorption on Methylene Blue

The study adsorption was performed at room temperature, pH 9, with 300 mL solution and 0.08 g of adsorbent. The stirring variation was 100, 200, and 300 rpm. The stirring variation was also done at the variation of methylene blue of 1, 2, and 3 mg/L. The result of the adsorption process can be seen in Fig. 1.

The stirring can help the spread (mobility) of the adsorbent into the solution [26-28]. Thus, the faster the stirring, the higher the decolorization percentage in methylene blue. Besides, the faster the stirring, the smaller the resistance of the adsorbate to the adsorbent. Therefore, the faster the stirring, the smaller the final concentration [29].

Other factors that are dominant in the adsorption process are the internal surface area of the adsorbent, the distribution of pores, and the addition of active groups to the adsorbent [30]. Surface diffusivity is a function of surface loading [31]. The pore distribution will be proportional to the large surface area of the adsorbent. The greater the surface area, the greater the diffusivity of a compound and will increase the adsorption capacity. Specifically for cellulose nano-crystals, the dominant effect of an active group significantly affects the adsorption process, especially the addition of anionic groups to increase the electrostatic bond that occurs with methylene blue.

As shown in Fig. 1, there was a significant decrease in the methylene blue concentration for the first 20 min. However, it tends to stagnant from 40 to 120 min, indicating a decrease in the effectiveness of the adsorption process. A single layer of adsorbate may be formed on the adsorbent surface. Once this layer is formed, the adsorption rate decreases. This monolayer indicated that one active site could only be occupied by one molecule [32]. The lower adsorption rate is due to a decrease in the number of vacant active sites on the adsorbent. It also indicates a reduced availability of active sites for further adsorption until it reaches equilibrium [33]. The conclusion that a single or double

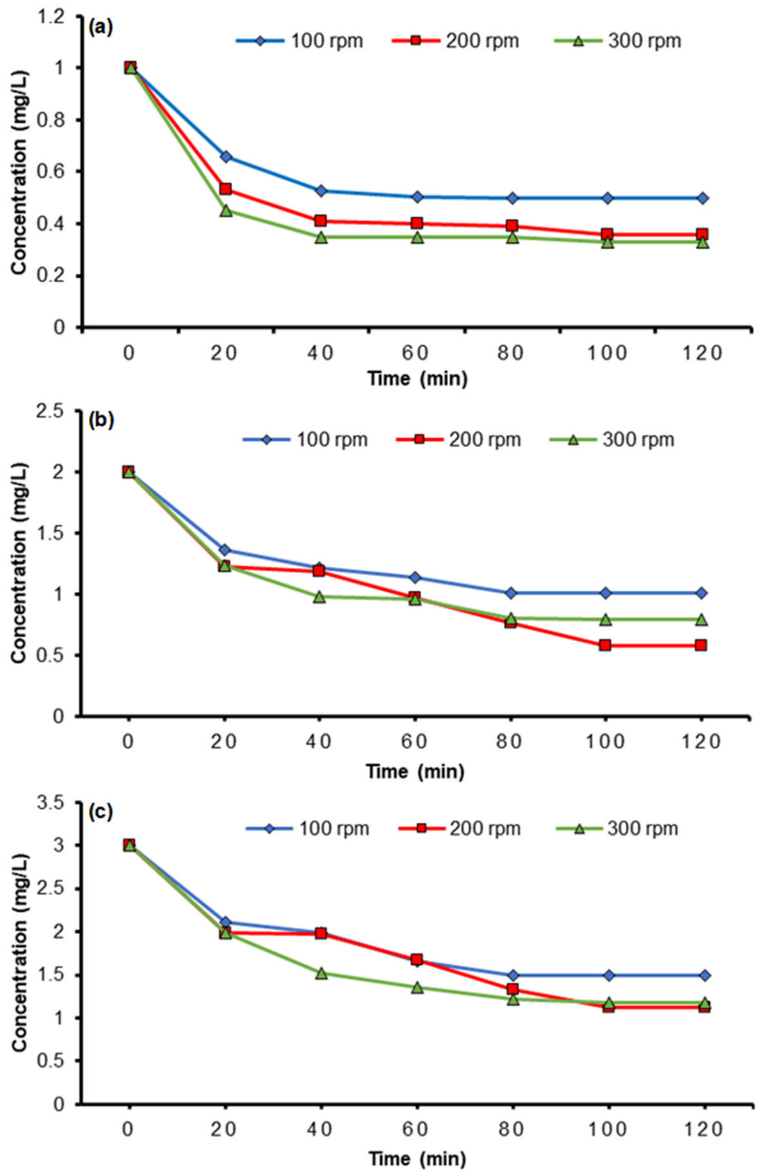

Fig 1. The study of adsorption of methylene blue at various concentrations (a) 1 mg/L, (b) 2 mg/L, and (c) 3 mg/L

layer is formed on the graph produced in the study whenever the short adsorption time produces a graphic pattern that reads saturated is possible to conclude that the layer on the adsorbent is a single layer. In contrast, for the double layer it can be concluded during the adsorption process experience a saturation point in an extended period.

Effects of Initial Concentration on the Adsorption of Methylene Blue

Besides the stirring factor, the initial concentration of methylene blue also affects the mass transfer of methylene blue adsorption to nano-crystal cellulose [34-35]. Research on the effect of the initial concentration of adsorbate on various adsorbents has yielded uniform conclusions. Deepak and co-workers in their study on the adsorption of methylene blue using activated carbon adsorbent from *Ficus carica* bast mentioned that an increase in efficiency of methylene blue removal is proportional to the increase in the initial concentration of methylene blue [36]. Hence, a higher initial concentration gave a higher driving force to resolve the solid-liquid mass transfer resistance. Meanwhile, at a very low concentration, there will be a vacant active site on the surface of the adsorbent that is not occupied by the adsorbate molecule. It can be interpreted as a decrease in the adsorption capacity of the system. In addition, if an increase of initial concentration exceeds the optimum point, the active site on the surface of the adsorbent will decrease to slow down the adsorption process.

The graph of the methylene blue concentration variation on the adsorption capacity (mg/g) can be seen in Fig. 2. The figure shows the effect of the initial concentration of methylene blue with various stirring speeds on adsorption capacity. Generally, it can be concluded that the greater the initial concentration used, the higher the value of the adsorption capacity. This situation occurs with stirring speeds of 100, 200, and 300 rpm. The greater initial concentration gives a significant driving force to pass through the mass transfer resistance between the liquid (methylene blue) and the solid as nano-crystal cellulose [37]. At large concentrations of methylene blue, the amount of site nano-crystal cellulose may not be sufficient to absorb methylene blue molecules, causing a decrease in the percentage of color removal in the adsorption process.

The adsorption mechanism begins when methylene blue molecules reach the boundary layer and then diffuse to the adsorbent's surface. The molecules further diffuse to the interior of the adsorbent. As shown in Fig. 2, the phenomenon of methylene blue being adsorbed by the surface of the nano-crystal cellulose takes a relatively long time.

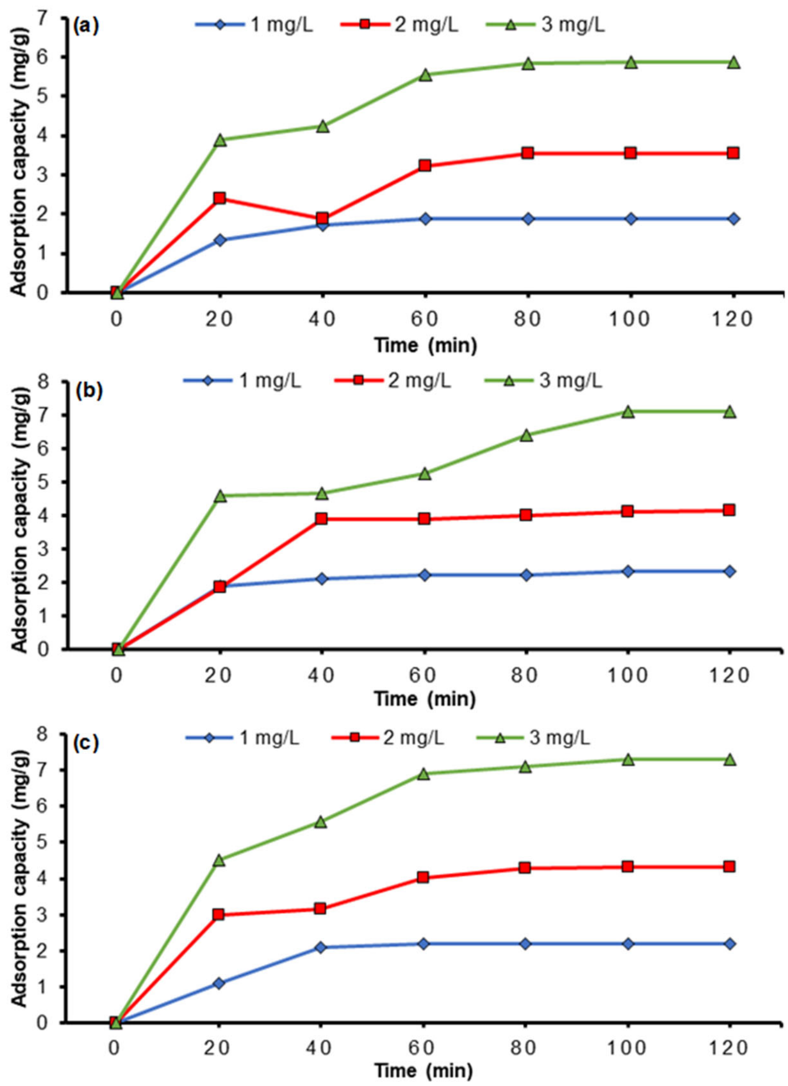

Fig 2. Adsorption capacity (a) 100 rpm, (b) 200 rpm, and (c) 300 rpm

Isotherms and Kinetics Studies

The kinetics study aims to identify the adsorption rate constant (k) value to achieve equilibrium [38]. The value of the adsorption rate constant (k_c) and the adsorption equilibrium constant was obtained using the Henry, Langmuir and Freundlich model equation approach. The results can be seen in Table 1. In addition, a comparison of simulation data of maximum adsorption capacity (q_m) and the experimental ones was presented in Table 2.

Table 1 indicates that stirring speed does not affect the value of the constant adsorption rate (k_c). The k_c value has no significant differences at 100, 200, and 300 rpm. This trend was observed for all three models. Furthermore, the proposed models have an SSE (sum square of errors) value of approximately 0. The three models can be considered suitable for the phenomenon of methylene blue adsorption using nano-crystal cellulose. Among the three models, The SSE value in the Freundlich model is the smallest. However, the q_m data of the Freundlich model (Table 2) were inconsistent with the experimental data. The Henry model's q_m data also differed significantly from the experimental ones. Overall, Table 2 suggested that the fittest model of the MB adsorption was the Langmuir model, in which the adsorption capacity tends to increase when the initial concentration of methylene blue is higher [33,39].

The Langmuir isotherm model is an adsorption kinetics model commonly used to describe complex adsorption mechanisms. This model adequately describes the adsorption of methylene blue by nano-crystal cellulose. The adsorption mechanism relies not only on the adsorbent's pores but on the presence of hydrogen bonds and Van der Waals interactions that occur to achieve stability. In this adsorption mechanism,

Table 1. Adsorption rate constants (k_c) at the stirring speeds of 100, 200, and 300 rpm on varied concentrations of methylene blue (1, 2 and 3 mg/L)

MB concentration	Stirring speed (rpm)	Henry model			Langmuir model			Freundlich model		
		k_c	K_d	SSE	k_c	K_L	SSE	k_c	K_f	SSE
1 mg/L	100	0.0013	4.4870	0.0040	0.0007	3.056	0.0206	0.0016	11.78	0.0006
	200	0.0019	8.3402	0.0009	0.0930	2.662	0.0419	0.0089	9.265	0.0432
	300	0.0028	7.8611	0.0036	0.0100	2.743	0.0174	0.0028	8.628	0.0036
2 mg/L	100	0.0012	4.2190	0.0117	0.0012	3.362	0.0139	0.0018	6.668	0.0106
	200	0.0026	6.2668	0.3127	0.0102	1.000	0.5250	0.0013	11.66	0.1444
	300	0.0029	4.9792	0.2157	0.0102	1.000	0.5250	0.0012	13.54	0.039
3 mg/L	100	0.0021	3.7576	0.0371	0.0009	2.782	0.1122	0.0007	8.122	0.018
	200	0.0015	4.3399	0.1850	0.0014	4.369	0.1791	0.0014	3.585	0.018
	300	0.0026	5.1870	0.2492	0.0130	4.560	0.0231	0.0016	6.446	0.018

Table 2. Maximum adsorption capacity data (q_m) at the stirring speeds of 100, 200, and 300 rpm on varied concentrations of methylene blue (1, 2 and 3 mg/L)

MB concentration	Stirring speed (rpm)	Henry model	Langmuir model	Freundlich model	Experimental data
1 mg/L	100	1.9163	7.8620	9.4240	7.0254
	200	2.6250	8.3540	7.4120	7.0438
	300	2.6250	8.3990	6.9024	7.0596
2 mg/L	100	6.3750	5.2130	5.3344	7.3914
	200	6.3750	8.9470	9.3280	7.7127
	300	6.3750	8.8760	10.8320	7.7258
3 mg/L	100	10.1250	7.6070	6.4976	7.8865
	200	10.1250	5.9100	2.8680	7.9418
	300	10.1250	8.5900	5.1568	8.0155

the hydrogen bond is characterized by the presence of hydrogen from the nano-crystal cellulose hydroxyl group, which binds the nitrogen element of methylene blue. The Van der Waals force is characterized by dipole ion interactions and electrostatic interactions.

The Langmuir isotherm model is a suitable model to describe the chemical adsorption mechanism. It is indicated by the visible adsorption mechanism, namely the monolayer [40]. This monolayer surface illustrates that the adsorption is carried out by an active site, and one active site can be occupied by one molecule only [41].

The Langmuir isotherm model for the methylene blue adsorption process using nano-crystal cellulose was also confirmed in several studies, such as the adsorption of methylene blue from nano-crystal cellulose made by the TEMPO [42] method. In addition, the model was also appropriate for the adsorption of nano-crystal cellulose on various organic dyes, such as methylene blue, methyl orange, rhodamine B, and crystal violet. The adsorption of methylene blue adsorption using nano-crystal cellulose-alginate hydrogel on a fixed-bed column also followed the model [43].

Based on the isotherm study, the layer of nano-crystal cellulose produced is a monolayer. To maximize the removal of methylene blue from a solution by using cellulose nano-crystal based on the layer formed, another

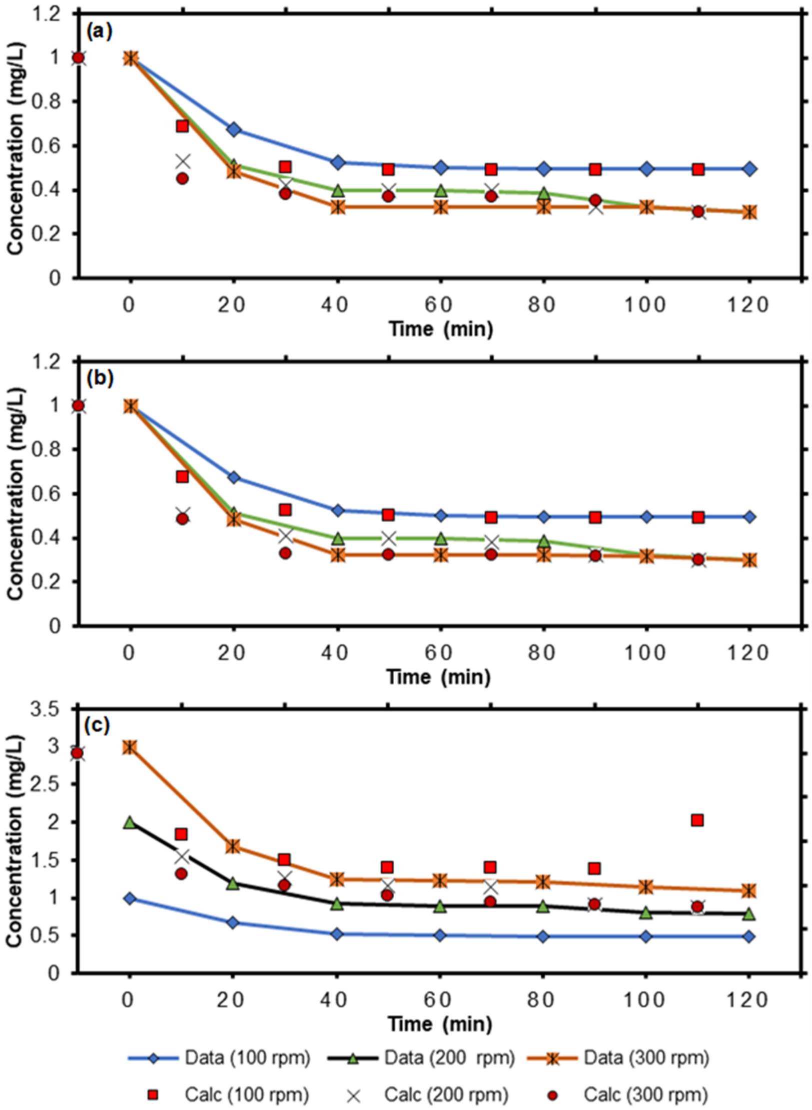

Fig 3. Fitting results (a) Henry model, (b) Langmuir model, (c) Freundlich model

active group, which is anionic, can help the binding of methylene blue (which is cationic). In chemical adsorption, the k value on surface interactions tends to be low. It indicates that the limiting step in the methylene blue adsorption mechanism using nano-crystal cellulose does not depend on diffusion but on surface interactions. The results of fitting each model to the sample with the lowest SSE can be seen in Fig. 3.

Thermodynamic Study

The parameters used for thermodynamic studies are changes in standard enthalpy (ΔH°), entropy (ΔS°), and standard free energy (ΔG°) resulting from the transfer of moles of solute from solution to the solid-liquid surface. Thermodynamic studies were carried out on 3 mg/L of methylene blue with a stirring speed of 300 rpm at a pH of 9.

The thermodynamic study was tested at various temperatures to determine the value of Gibbs energy produced by the adsorption process, and the results can be seen in Table 3.

The study was conducted at 303, 308, 313, and 318 K and presented in Table 3. The increased temperature from 303 to 308 K indicates an increase in the adsorption capacity from 10.3389 mg/g to 10.3802 mg/g. Based on the data presented, the temperature increase causes an increase in the adsorption capacity due to the swelling of the internal structure of the nano-crystal cellulose, which allows methylene blue to penetrate further [44]. However, when the temperature was increased to 313 and 318 K, there was a slight decrease in the adsorption capacity. An increase in temperature can reduce the surface area value of nano-crystal cellulose [45]. Decreasing the adsorbent area reduces the adsorption site for methylene blue. According to Tang et al. [46], the greater operating temperature of the adsorption test can reduce the pore width and decrease the diffusion of methylene blue tested on flakes-shaped nano-crystal cellulose. Besides, the hydroxyl groups in the cellulose crystal nanostructures are bound in hydrogen bonds at higher temperatures due to the larger capillary force so that the cellulose crystal nano molecules are close to each other.

The higher the temperature, the lower the final absorbed concentration of methylene blue. The lower the final adsorbed methylene blue concentration, the higher the adsorption capacity (mg/g). It indicates that the nature of the adsorption process is endothermic. A higher operating temperature causes an increase in the adsorption capacity by diffusing the intraparticle of methylene blue molecules into the adsorbent pores. Based on the Table 3, when the temperature was increased to 313 and 318 K, the value of the adsorption capacity decreased as a result of the weakening of the hydrogen and hydroxyl bonds in nano-crystals cellulose due to increased molecular motion. Exothermic conditions by increasing the operating temperature in this study are quite possible to optimize the adsorption process. However, the operating temperature must be controlled to avoid the agglomeration of nano-crystal cellulose, leading to an increase in nano-crystalline cellulose's particle size. The obtained data became the basis for creating the graph with ln K_c as the y-axis and 1/T as the x-axis (see Fig. 4).

Based on the calculation, the value of ΔH° is 0.00742 kJ/mol. It confirms that the adsorption process is endothermic. The value of ΔS° is 0.7758 kJ/mol K, and based on the enthalpy and entropy values, the ΔG° value reaches −242.81 kJ/mol. It shows the feasibility of the

Table 3. Calculation of thermodynamic studies

Temperature (K)	C_e (mg/L)	q_e (mg/g)	K_c
303	0.311	10.3389	5.541
308	0.300	10.3802	5.767
313	0.305	10.3614	5.661
318	0.309	10.3464	1.724

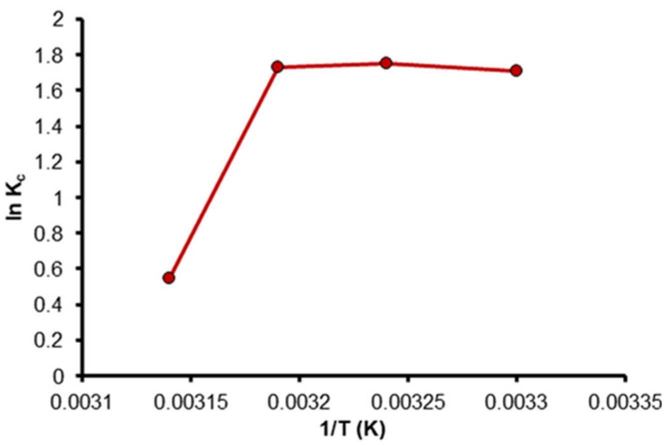

Fig 4. Graph ln K_c vs 1/T

process and the spontaneous process of methylene blue adsorption by nano-crystal cellulose [47].

Based on the experimental results, an important parameter that can maximize the adsorption of methylene blue in a solution is to set the agitator rotation at a higher rpm, and operate at a temperature of 313 K. Raising the temperature above the standard temperature, in this case, can help stretch the internal structure of nano-crystal cellulose. Conditions can be optimized by increasing the surface area of the adsorbent by reducing the size of the cellulose nano-crystals produced. The larger the surface area of the adsorbent, the more adsorbate can be adsorbed on the pore structure, and also attached to the nano-crystal cellulose bonds, which have more active functional groups.

■ CONCLUSION

The kinetic study showed that the surface interaction was the limiting step in the methylene blue adsorption mechanism. Meanwhile, the thermodynamic study concluded that the adsorption process was spontaneous and endothermic. The appropriate model for the adsorption is the Langmuir isotherm model. Overall, methylene blue adsorption using nano-crystal cellulose followed the chemical adsorption type.

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■ AUTHOR CONTRIBUTIONS

The first author and also as the corresponding author served as a researcher and carried out data collection. The second and third authors served as writers, conducting revisions and final assessments of the data and written reports.

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