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Utilization of Freeze-Dried κ-Carrageenan for Methylene Blue Adsorption

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Abstract

Methylene blue contamination in aquatic environments has become a global issue due to its widespread use in various industries. Methylene blue is a toxic, carcinogenic, and non-biodegradable dye. Adsorption can be employed as one method to mitigate this problem. The use of κ-carrageenan as an adsorbent offers an effective solution because κ-carrageenan is an abundant, easily obtainable, and economical biopolymer with promising adsorption performance. In this study, κ-carrageenan was cross-linked with K^+ to form a hydrogel, which was then freeze-dried to produce a macroporous κ-carrageenan adsorbent. Characterization using FTIR confirmed the successful preparation of the adsorbent and the adsorption of methylene blue. SEM images showed changes in surface morphology, indicating successful adsorption. The adsorption process was optimum at pH 5, an adsorbent mass of 0.1 gram, and a contact time of 3 hours. Adsorption followed a pseudo-second-order kinetic model and the Langmuir isotherm model, with a maximum adsorption capacity (q_{max}) of 128.7 mg/g at 328 K. Thermodynamic studies showed that the process was exothermic, became more disorder as a result of an increase in entropy, and occurred spontaneously. These results demonstrate that freeze-dried κ-carrageenan adsorbent has the potential for development in sustainable wastewater treatment technology.

Keywords: adsorption, freeze-dry, methylene blue, κ-carrageenan

1 Introduction

The use of synthetic dyes is increasing with the rapid growth of textiles, printing, food, cosmetic, and pharmaceutical industries. This increase is directly proportional to water pollution if waste is not properly managed. Globally, nearly 800,000 tons of synthetic dyes are used annually [1]. Industrial processes typically discharge 30-40% of this dye waste into aquatic environments [2]. Methylene blue is one of the most common basic dyes used in industries for coloring silk, wool, cotton, and paper. Methylene blue is a toxic, carcinogenic, and non-biodegradable dye. Continuous exposure can cause respiratory and psychological disorders, as well as blindness in living organisms [3–5].

Several methods can be used to mitigate methylene blue waste in water, including various enzymatic processes, photodegradation, electrochemical methods, coagulation, filtration, and adsorption [3,6]. In this case, adsorption is considered advantageous due to its simple process, low cost, and high efficiency. Polysaccharides such as alginate, cellulose, and carrageenan are attractive options for adsorbents raw materials, simply because they are abundant, biodegradable, and non-toxic [7–9].

κ-Carrageenan is a natural polysaccharide obtained from red algae. κ-Carrageenan chain consists of disaccharide as repeating units i.e. (1,3)-β-D-galactopyranose-4-sulfate and (1,4)-α-3,6-D-anhydrogalactopyranose [10]. The presences of ester sulfate groups ($-OSO_3^-$) as an anionic functional group making κ-carrageenan suitable as an adsorbent for separating cationic dyes such as methyl red, crystal violet, and methylene blue [11–13]. In addition, the use of refined food-grade κ-carrageenan as adsorbent's raw material has been previously demonstrated for Pb^{2+} [9] and methyl orange removal [14].

Chemical modification has been proven to increase the adsorption capacity of κ-carrageenan-based adsorbents. For methylene blue adsorption, Sharma et al. used an adsorbent synthesized from an itaconic acid solution with added κ-carrageenan, stirred and heated until a gel was formed. The gel was then cut into cylinders, washed with distilled water, and dried in an oven at 50 °C for 24 hours. The maximum adsorption capacity obtained was 2439.02 mg/g. The layered structure of the adsorbent resulted in a large surface area and functional groups suitable for swelling, which led to a very high adsorption capacity [12]. Duman et al. prepared an adsorbent from a mixture of agar and κ-carrageenan polysaccharides, mixed with distilled water at 70 °C. TEMED, APS, and TEGDE were then added to the solution. The reaction proceeded for three hours, followed by cooling to room temperature until the hydrogel formed. The maximum capacity obtained was 242.3 mg/g [15].

In line with green chemistry principles aimed at reducing chemical reagents, the physical technique of freeze-drying was employed to enhance the adsorbent's porosity and simplify the formulation. Although this method is energy-intensive, this approach successfully limits the need for additional synthetic monomers or chemical cross-linkers [16]. A freeze-dried hydrogel results in a dry porous adsorbent, which in turn has a high surface area. Therefore, this study uses freeze-dried κ-carrageenan cross-linked with K^+ for methylene blue removal. The adsorbent was characterized using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Adsorption optimization included parameters such as pH, adsorbent mass, contact time, initial adsorbate concentration, and temperature. To understand the adsorption process more deeply, this study also conducted kinetic, isotherm, and thermodynamic adsorption studies.

2 Method

κ-Carrageenan powder (refined; food-grade) purchased from a local market, used as the primary material of adsorbent and KCl (Merck) as the cross-linking agent. Methylene blue powder (Merck) used as the adsorbate. To adjust the solution pH, HNO_3 (Merck) and NaOH (Merck) were used. In addition, KBr (Merck) was utilized as the medium for preparing pellets for FTIR characterization. All chemicals were used without prior purification.

2.1 Preparation of κ-Carrageenan Adsorbent

The adsorbent was prepared by first dissolving 1.25 g of κ-carrageenan in 40 mL of demineralized water at 90 °C and stirring the mixture until a homogeneous solution was obtained. A KCl solution, prepared by dissolving 0.1863 g of KCl in 10 mL of demineralized water, was then added to the κ-carrageenan solution. The mixture was cast into a silicone mold and left to harden, forming a hydrogel. The resulting hydrogel was cut into cubes of 0.5 cm × 0.5 cm × 0.5 cm. The hydrogel cubes were then soaked in 1 M KCl for 7 hours, followed by drying using an oven (60 °C for 12 hours), a fan (room temperature in open air for 24 hours), or freeze-drying (−10 °C at 15 Pa for 24 hours) until constant weight was achieved to produce the final adsorbent.

2.2 Adsorbent Characterization

Adsorbent surface morphology was studied using a JEOL JSM-6510 LA Scanning Electron Microscope. Functional groups were identified by FT-IR spectroscopy (Shimadzu Prestige-21), with samples prepared as KBr pellets and analyzed in the 4000–400 cm^{-1} range.

2.3 Adsorption Experiments

Adsorption experiments were conducted by contacting a 25 mL methylene blue solution with the adsorbent and shaking at 60 rpm. After contact, the remaining methylene blue solution was analyzed using a UV-Vis spectrophotometer (Agilent 8453) at 664 nm using quartz cuvette (10 mm width). The methylene blue calibration curve for this study was prepared for concentration range of 1 to 3.5 ppm, consistently yielding a high R^2 ≥ 0.99. Sample dilution was routinely performed to ensure that all measured solution concentrations fell within the linear range of this calibration curve. The adsorption parameters optimized in this study included pH, adsorbent mass, contact time, initial adsorbate concentration, and temperature. Adsorption kinetics, isotherms, and thermodynamics were investigated based on data obtained from experiments by varying the contact time, initial adsorbate concentration, and temperature. Calculations for the adsorption capacity (q, mg/g) and the adsorption percentage

(%adsorption, %) were performed using the following equations (**Eq. 1 and 2**):

$$q = \frac{C_i - C_f}{m_{ads}} \times V \quad \text{(Equation 1)}$$

$$\%\text{adsorption} = \frac{C_i - C_f}{C_f} \times 100\% \quad \text{(Equation 2)}$$

in these equations, C_i and C_f are the initial and final concentrations of methylene blue (mg/L), V is the methylene blue solution volume (L), and m_{ads} is the mass of the adsorbent (g).

3 Result and Discussion

3.1 Adsorbent Preparation

The formed κ-carrageenan hydrogel was cut into cubes with dimensions of 0.5 cm × 0.5 cm × 0.5 cm. The hydrogel cubes were then soaked in 1 M KCl for 7 hours, resulting in a firm white hydrogel. To confirm that freeze-drying is the best method, other drying methods were also performed, namely using a fan and an oven. As shown in **Fig. 1**, only the freeze-dried adsorbent was able to maintain its cubical shape, with its dimensions not changing significantly.

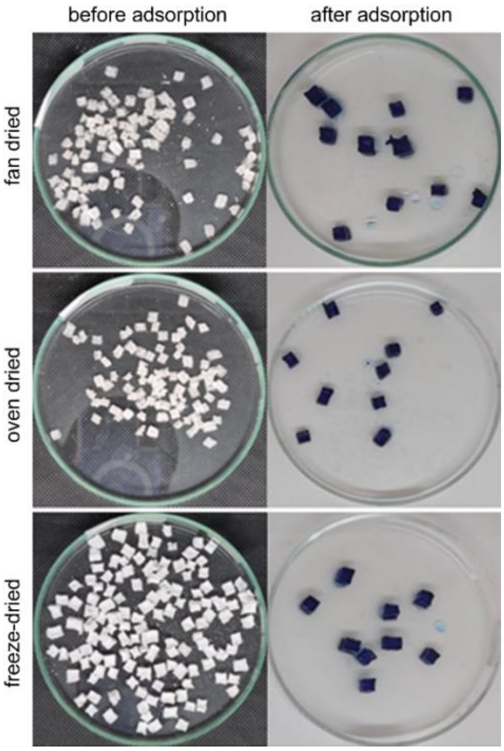

Figure 1. κ-Carrageenan adsorbents before and after methylene blue adsorption; prepared via different drying methods

Adsorbents dried with a fan or an oven did not retain their cubical shape; instead, they shrank slightly and tended to be flattened. This change in shape during fan and oven drying occurs because water slowly exits from the adsorbent's surface, allowing the structure to collapse slightly. The freeze-drying method removes water through a sublimation process, which does not significantly alter the adsorbent’s structure. This results in an adsorbent with large pores and a low density, which is an ideal characteristic for an adsorbent.

Fig. 1 also shows the change in adsorbent color from white to blue, indicating that the adsorption of methylene blue was successful. From the data presented in **Table 1**, it can be observed that the freeze-dried adsorbent exhibited the highest adsorption capacity and percentage. Considering the visual observation, the adsorption capacity, and the adsorption percentage, it can be concluded that the adsorbent prepared by the freeze-drying method offers significant advantages and is thus worthy of further and more systematic exploration.

Table 1. Effect of drying methods on the adsorption capacity and %adsorption of κ-carrageenan

Drying method	q (mg/g)	%adsorption (%)
Electric fan	3.83	15.70
Oven	2.13	8.71
Freeze-dry	8.23	34.18

Experiments: C_i = 50 ppm, m_{ads} = 0.05 g, and t = 30 minutes

3.2 *Adsorbent Characterization*

FTIR characterization was conducted to identify the functional groups in the material, which also served to verify the successful preparation of the adsorbent. κ-Carrageenan has four characteristic peaks: O-H bonds, S=O bonds from the ester sulfate group, C-O-C from α-3,6-D-anhydrogalactopyranose, and C-O-S from β-D-galactopyranose [17]. As shown in **Fig. 2**, characteristic peaks of the native κ-carrageenan powder were found at wavenumbers of 3446, 1041, 928, and 852 cm^{-1}, corresponding to the O-H, S=O, C-O-C, and C-O-S groups, respectively.

Overall, no new characteristic peaks appeared in the spectrum. However, a broadening of the O-H stretching peak was observed, suggesting a decrease in hydrogen bonding interactions and indicating a potential change in the cross-link density or molecular packing within the adsorbent structure. Specific shifts were noted in the adsorbent's spectrum, the O-H peak shifted from 3446 to 3419 cm^{-1}, and the S=O peak shifted from 1041 to 1027 cm^{-1}. These shifts are considered significant and denote a strong interaction between the functional groups of the adsorbent (i.e. O-H and S=O groups) and the cross-linking ion (K^+), which is vital for stabilizing the adsorbent structure. Therefore, it is suggested that electrostatic interaction occurred between the positively charged K^+ and the negatively charged ester sulfate group. Additionally, an ion-dipole interaction might also have taken place between K^+ and the O-H groups of κ-carrageenan.

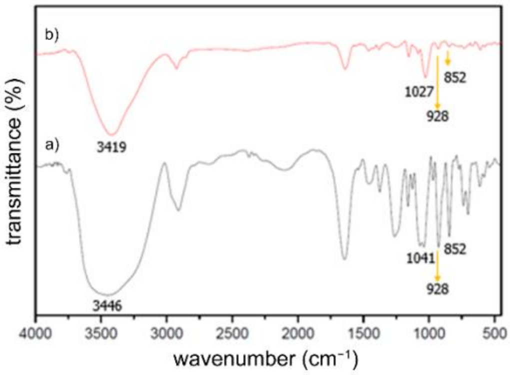

Figure 2. FTIR spectra of (a) κ-carrageenan and (b) freeze-dried κ-carrageenan

SEM characterization was performed to examine the surface morphology of the adsorbent before and after contact with methylene blue. The results of this characterization confirmed the successful adsorption of methylene blue.

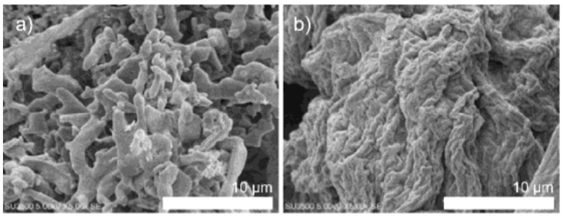

Figure 3. SEM images of freeze-dried κ-carrageenan adsorbent at 5000× magnification (a) before, and (b) after adsorption of methylene blue

In **Fig. 3**, a clear difference is observed between the two surfaces: the originally porous surface became covered. This occurred because the interaction between the adsorbent and methylene blue led to the formation of a layer of methylene blue on the adsorbent's surface, thus altering its surface morphology [18]. Similar observation was obtained compared to the adsorption of methylene blue onto carrageenan and itaconic acid-based adsorbent [12].

3.3 *Effect of pH*

The effect of pH was investigated because both the adsorbate and the adsorbent surface have different charges at various pH levels. A series of experiments was conducted with an initial methylene blue concentration of 50 ppm, an adsorbent mass of 0.05 g, a contact time of 30 minutes, and a pH range of 1-8.

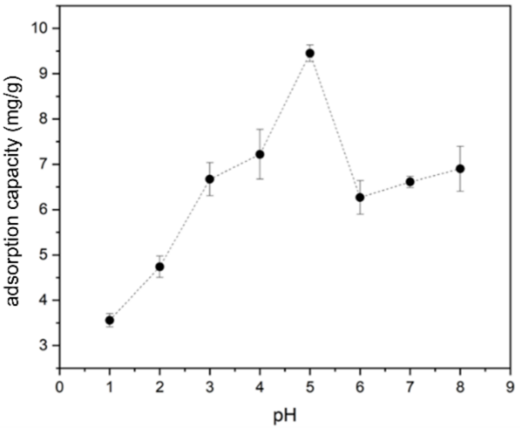

Figure 4. Effect of pH on methylene blue adsorption on freeze-dried κ-carrageenan

Fig. 4 shows that the adsorption capacity increased from pH 1 to 5, then decreased at pH 6, and remained relatively constant from pH 6 to 8. These results are consistent with the changes in the properties of both the adsorbent and the adsorbate at different pH values. The optimal pH for adsorption was found to be 5, at which methylene blue has a charge of +2 [19].

The surface charge of κ-carrageenan also depends on the solution's pH. With a pK_a of 2.8, the sulfate ester groups of κ-carrageenan become deprotonated when the pH is greater than 2.8, making the adsorbent negatively charged. Therefore, this adsorption process is expected to rely on the electrostatic interaction between the negatively charged adsorbent surface and the positively charged methylene blue.

3.4 *Effect of Adsorbent Mass*

In the adsorbent mass optimization study, experiments were conducted with an initial adsorbate concentration of 50 ppm, at pH 5, for 30 minutes, using adsorbent masses ranging from

0.025 to 0.2 g. As shown in **Fig. 5**, the adsorption capacity decreased as the adsorbent mass increased. This trend generally occurs because the adsorption capacity value is normalized by the mass of the adsorbent used.

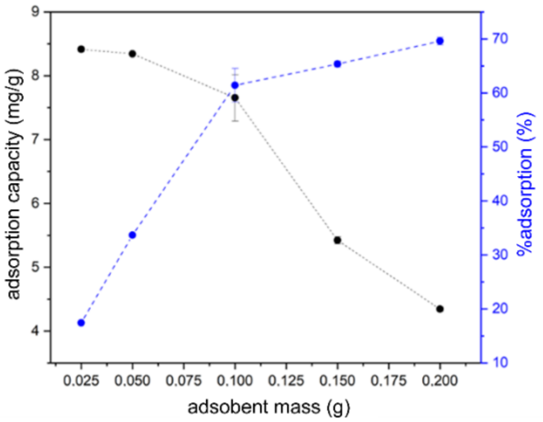

Figure 5. Effect of adsorbent mass on methylene blue adsorption on freeze-dried κ-carrageenan

In contrast, the %adsorption increased with increasing adsorbent mass. A higher quantity of adsorbent provides more active sites for adsorption. The adsorption percentage rose sharply from 0.025 g to 0.1 g, after which it remained relatively constant. This constant value suggests that the active sites of the adsorbent had been optimally filled with methylene blue. Therefore, an adsorbent mass of 0.1 g was selected as the optimum mass for subsequent experiments.

3.5 *Effect of Contact Time*

The effect of contact time was studied by conducting adsorption experiments with an initial adsorbate concentration of 50 ppm, at pH 5, with an adsorbent mass of 0.1 g, for a duration of 15-480 minutes. As presented in **Fig. 6**, the adsorption capacity increased with increasing contact time. However, after 180 minutes, the adsorption capacity became relatively constant, indicating that adsorption equilibrium was reached at a contact time of 180 minutes. Once the adsorption equilibrium state was achieved, the active sites on the adsorbent were optimally occupied, so the amount of adsorbed material no longer increased.

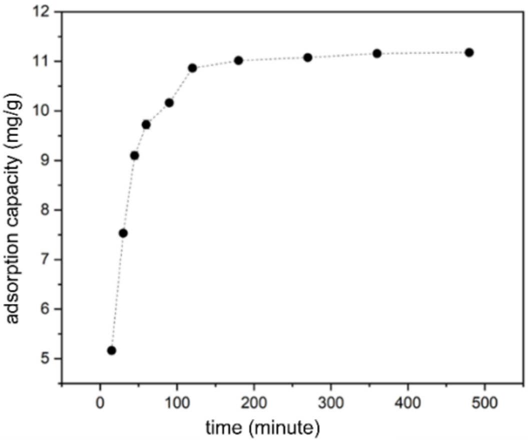

Figure 6. Effect of contact time on methylene blue adsorption on freeze-dried κ-carrageenan

3.6 *Adsorption Kinetic*

Adsorption kinetics were investigated using data from the contact time variation experiments. The pseudo-first-first-order (Equation 3) and pseudo-second-order (Equation 4) kinetic linear models were applied to analyze the experimental data.

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \qquad \text{(Equation 3)}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 (Q_e)^2} + \frac{1}{Q_e} t \qquad \text{(Equation 4)}$$

in these equations, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and specific time, respectively. The k_1 (min^{-1}) and k_2 ($g/mg.min^{-1}$) represents the rate constants for pseudo-first-order and pseudo-second-order adsorption. **Fig. 7** shows the adsorption kinetics models.

As shown in Table 2, the pseudo-first-order kinetic model had a lower correlation coefficient (R^2) of 0.9591 compared to the pseudo-second-order model's R^2 of 0.9985. Furthermore, the pseudo-first-order model's residual sum of squares (RSS) value was 8.1209, which is larger than the value of 4.9198 obtained for the pseudo-second-order model. Since a higher R^2 value and a lower RSS value indicate a better fit, it can be concluded

Table 2. Adsorption kinetic parameters for adsorption of methylene blue on freeze-dried κ-carrageenan

Pseudo-first-order				Pseudo-second-order			
k_1 (min^{-1})	q_e (mg/g)	R^2	RSS	k_2 ($g.mg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	RSS
0.0319	9.28	0.9591	8.1209	0.0046	12.23	0.9985	4.9198

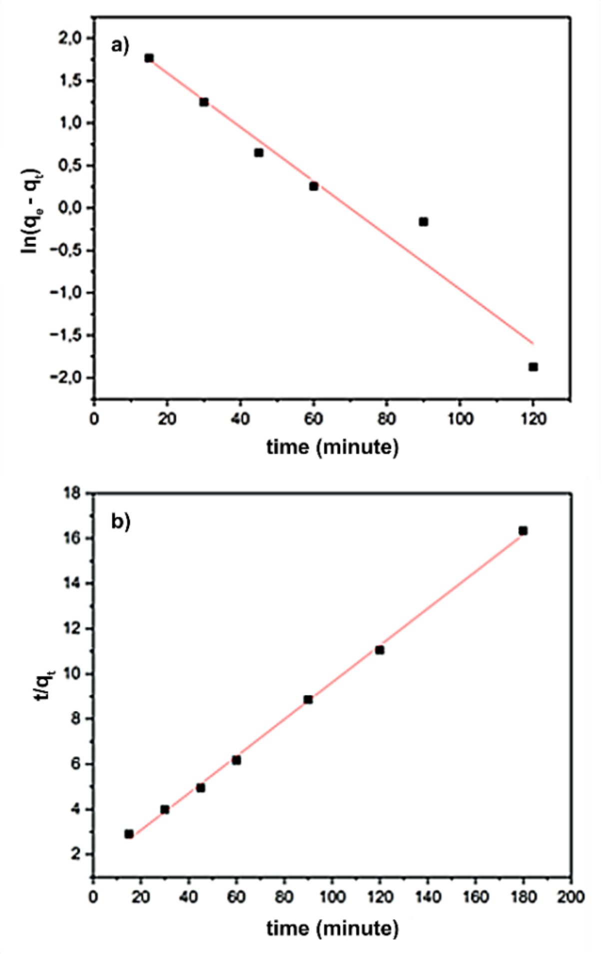

Figure 7. Adsorption kinetics of (a) pseudo-first-order and (b) pseudo-second-order for methylene blue adsorption on freeze-dried κ-carrageenan

that the pseudo-second-order kinetic model provides a better description of the methylene blue adsorption kinetics. The pseudo-second-order kinetic model was found to provide the best fit for the adsorption data. However, relying solely on this model is often insufficient to definitively distinguish between physisorption and chemisorption. To achieve more conclusive adsorption classification, we therefore utilized the enthalpy change (ΔH) obtained from the thermodynamic analysis. The work of Duman i.e. the adsorption of methylene blue on agar/κ-carrageenan composite also fits with the pseudo-second-order kinetic model [15]. The experimental equilibrium adsorption capacity (q_e) used for the kinetics study was 11.02 mg/g (at a contact time of 180 minutes). This value is not significantly different from the theoretical q_e for the pseudo-second-order kinetic model, which was 12.23 mg/g.

3.7 Adsorption Isotherm

The adsorption isotherm study was conducted using data from experiments that varied the initial adsorbate (methylene blue) concentration. These experiments were performed with methylene blue solution at pH 5, an adsorbent mass of 0.1 g, and a contact time of 3 hours. The initial methylene blue concentrations ranged from 25 to 800 ppm. As shown in **Fig. 8**, the adsorption capacity increased with an increasing initial adsorbate concentration. This is because more methylene blue molecules were available to be adsorbed until the available active sites on the adsorbent became saturated. In contrast, the adsorption percentage decreased with a rise in the initial adsorbate concentration. This occurred because, as the initial concentration increased, the amount of methylene blue remaining in the solution also increased, thus lowering the overall percentage of removal.

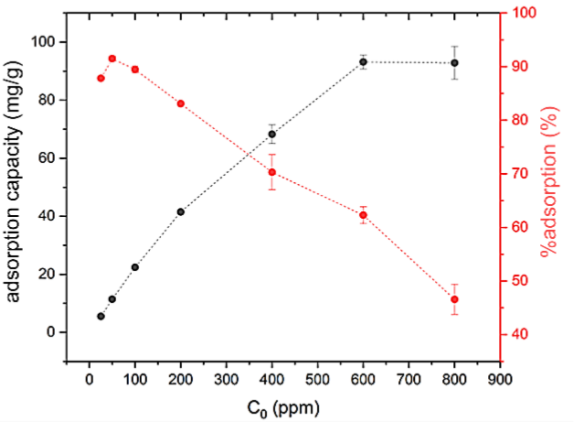

Figure 8. Effect of initial methylene blue concentration on methylene blue adsorption on freeze-dried κ-carrageenan

Data obtained from the initial adsorbate concentration variation experiments were plotted based on the linear equations of the Langmuir (Equation 5) and Freundlich (Equation 6) adsorption isotherm models. **Fig. 9** shows the linear fitting curves of the adsorption isotherm models.

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right) C_e + \frac{1}{q_{max} K_L} \qquad \text{(Equation 5)}$$

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right) \log(C_e) \quad \text{(Equation 6)}$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_e (mg/L) is the equilibrium concentration of methylene blue, K_L is the Langmuir isotherm constant, and q_{max} (mg/g) is the maximum adsorption capacity. As for the Freundlich model, K_F is the Freundlich isotherm constant, and 1/n is a measure of the adsorption intensity.

Table 3. Adsorption isotherm parameters for adsorption of methylene blue on freeze-dried κ-carrageenan

Langmuir				**Freundlich**			
q_{max} (mg/g)	K_L	R^2	RSS	K_F	n	R^2	RSS
102.7	0.0263	0.9969	0.4392	6.9936	2.1858	0.9960	0.6581

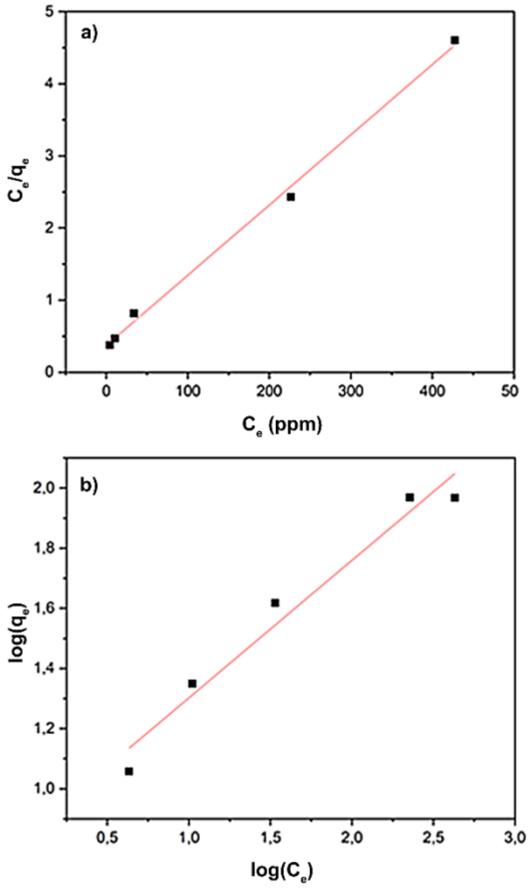

Figure 9. (a) Langmuir and (b) Freundlich adsorption isotherm for methylene blue adsorption on freeze-dried κ-carrageenan

As shown in **Table 3**, the Langmuir adsorption isotherm model has a higher correlation coefficient (R^2) of 0.9904 compared to the Freundlich model, which has an R^2 of 0.9490. Furthermore, the residual sum of squares (RSS) was also calculated for both models; the Langmuir model has a smaller RSS value of 0.4392, which is significantly lower than the 0.6581 value for the Freundlich model. Although high coefficients of determination (R^2) were obtained from the linearized models, we acknowledge that in some cases, using linear regression to fit the data might bias the residual errors and potentially affect the accuracy of the isotherm parameters when compared to non-linear approaches.

Given these results, it can be concluded that the Langmuir model provides a better fit for the experimental data than the Freundlich model. Similar results were also observed on the adsorption of methylene blue onto agar/κ-carrageenan composite [15]. Langmuir isotherm indicates that the adsorption process follows a monolayer mechanism, where the adsorbent forms a single layer of adsorbate on its surface and the adsorbate cannot adsorb other adsorbate molecules. This behavior is likely due to the cationic nature of methylene blue, which causes electrostatic repulsion between molecules and prevents the formation of a multilayer adsorbate.

Table 4. R_L data for adsorption of methylene blue on freeze-dried κ-carrageenan at 308 K

C_i (ppm)	**R_L**
25	0.6033
50	0.4320
100	0.2755
200	0.1597
400	0.0868
600	0.0596
800	0.0454

To assess the feasibility and favorability of the adsorption process, according to the Langmuir model, the dimensionless separation factor (R_L) was determined for every initial adsorbate concentration using Equation 7, as follows:

$$R_L = \frac{1}{1+K_L C_i} \qquad \text{(Equation 7)}$$

Table 4 demonstrates that the calculated R_L values across all experimental initial concentrations C_i

consistently fell within the range of $0 < R_L < 1$. This result confirms that the adsorption process is favorable under the employed experimental conditions.

3.8 Adsorption Thermodynamics

The adsorption thermodynamics study was conducted by performing adsorption experiments at various temperatures. These experiments were performed with an adsorbate solution at pH 5, an adsorbent mass of 0.1 g, and a contact time of 3 hours. The temperature varied at 308, 318, and 328 K to determine the effect of energy on the adsorption capacity.

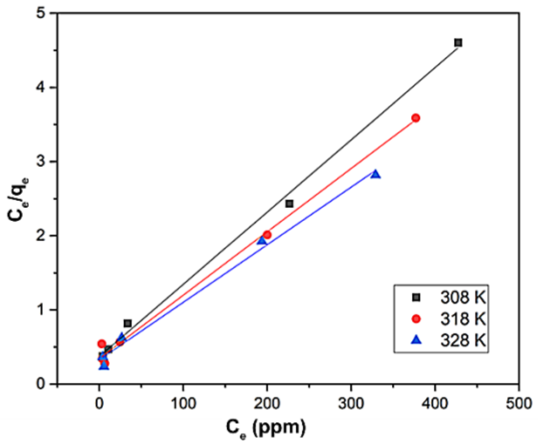

Figure 10. Langmuir adsorption isotherm for methylene blue adsorption on freeze-dried κ-carrageenan at 308, 318, and 328 K

The data obtained from the temperature variation experiments were plotted according to the linear equation of the Langmuir isotherm model (Equation 5). **Fig. 10** shows the linear fitting results for the Langmuir adsorption isotherm at these temperatures.

Table 5. Langmuir adsorption isotherm parameters at 308, 318, and 328 K

T (K)	R^2	q_{max} (mg/g)	K_L
308	0.9969	102.7	0.0263
318	0.9946	117.1	0.0247
328	0.9926	128.7	0.0239

Table 5 shows the Langmuir adsorption isotherm parameters at various temperatures. In the current work, the obtained q_{max} of 128.7 mg/g at 328 K is considered reasonable for a physically cross-linked biopolymer adsorbent. In comparison, while some κ-carrageenan derivatives reported in the literature exhibit significantly higher capacities (e.g., 2439 mg/g by Sharma et al. [12]and 242.3 mg/g by Duman et al. [15]), it is crucial to note that these materials often involve complex chemical modification. The lower capacity observed in this study is primarily attributed to our simpler and more cost-effective preparation method, which relies on the use of K^+ as crosslinker and freeze-drying process without such chemical reaction. This approach highlights our research contribution by focusing on simplicity, potential scalability, and sustainable, low-cost adsorbent development rather than raw performance maximization.

The obtained Langmuir isotherm constants K_L were converted into the dimensionless thermodynamic equilibrium constant K_c using the following Equation 8:

$$K_c = K_L \times 55{,}5 \times MM \times 1000 \qquad \text{(Equation 8)}$$

where MM is the molar mass of the adsorbate (methylene blue), and 55.5 is the number of moles of water per Liter.

Afterwards, the equilibrium constants were used to determine the thermodynamic parameters according to the Van't Hoff equation:

$$\ln(K_c) = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \qquad \text{(Equation 9)}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). To determine the enthalpy change (ΔH) and entropy change (ΔS), a linear plot of ln K_c versus 1/T was constructed based on the Van 't Hoff equation (Equation 8). Afterwards, the Gibbs free energy change (ΔG) was calculated using Equation 10:

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Equation 10)}$$

The obtained thermodynamic parameters are presented in **Table 6**. In this study, the enthalpy change was found to be -3.99 kJ/mol. The negative value of the enthalpy change (ΔH) indicates that the adsorption process is exothermic. Since the typical enthalpy change for physisorption ranges from 2.1–20.9 kJ/mol and for chemisorption is 80–200 kJ/mol [20], our calculated value falls within the physisorption range. Therefore, the adsorption of methylene blue is a type of physisorption, likely dominated by dipole-dipole and dispersion interactions [21].

Table 6. Adsorption thermodynamics parameters for methylene blue adsorption

T (K)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)
308	-3.99	96.81	-33.82
318			-34.78
328			-35.75

The positive value of the entropy change (ΔS) suggests that the system becomes more disordered during adsorption. This increase in disorder might be attributed to the release and reorganization of water molecules and counter-ions from the surfaces of the adsorbent and adsorbate upon adsorption. The negative Gibbs free energy change (ΔG) indicates that the adsorption process is spontaneous across the tested temperature range. This spontaneity implies that the adsorbate readily interacts with the active sites on the adsorbent [22]. Furthermore, the ΔG values become more negative as the temperature increases. While this negative trend confirms that the process remains spontaneous at higher temperatures, the decrease in the Langmuir constant (K_L) with rising temperature confirms that the adsorption are favored at lower temperatures, consistent with the exothermic nature of the process.

4 Conclusion

The freeze-dried κ-carrageenan adsorbent was successfully prepared using K^+ as a cross-linker, resulting in a porous material. The successful synthesis was verified through FTIR analysis, while effective methylene blue adsorption was confirmed by SEM analysis, which showed a change in the adsorbent's morphology. Adsorption was optimized at a pH of 5, with an adsorbent mass of 0.1 g, and a contact time of 3 hours, achieving a maximum capacity of 128.70 mg/g. The adsorption kinetics were best described by a pseudo-second-order model, and the isotherm data fit the Langmuir model. Thermodynamic studies further revealed the process to be both spontaneous and exothermic. Collectively, these results demonstrate the potential of freeze-dried κ-carrageenan as a promising, low-cost material with a simple preparation method for methylene blue removal from aqueous systems.

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