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Kinetic Isotherm and Thermodynamic Modelling of Methylene Blue Adsorption Using Green Tea-Based Biosorbents

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ABSTRACT

The current research investigated how effectively two biosorbent materials made from green tea; dry powdered material (DPM) and charcoal powdered material (CPM), removed the methylene blue from aqueous solutions. Various experimental parameters were examined, including the pH, temperature, initial dye concentration, amount of adsorbent, and contact time. The results demonstrated that the maximum adsorption efficiency for both DPM and CPM occurred at pH 10. The adsorption equilibrium was rapidly attained for DPM and CPM, taking 10 and 15 min, respectively. The adsorption data was fitted with four isotherm models: Dubinin-Kaganer-Radushkevich (D-R) model, Freundlich, Temkin, and Langmuir models. The best correlation was found in Langmuir model (R^2 = 0.996 & 0.991). Maximum adsorption capacity values of 15.58 mg/g for DPM and 18.66 mg/g for CPM were found using the Langmuir equation. The adsorption kinetics followed a pseudo-second-order model. The thermodynamic results showed a standard enthalpy change (ΔH^o = 24.40 and 4.07 kJ/mol), standard entropy change (ΔS^o = 92.93 and 13.34 J/mol·K), and standard Gibbs free energy change (ΔG^o = –3.31 and 0.20 kJ/mol) for DPM and CPM, respectively. These findings indicate that the biosorption process is spontaneous and endothermic, as evidenced by the negative values of Gibbs free energy change ($\Delta G^o < 0$) and the positive values of enthalpy change ($\Delta H^o > 0$), respectively. The study demonstrates the efficient way in which dyes from wastewater can be removal by using biosorbents made from green tea.

Keywords: Mehtylene Blue, Biosorption, Isotherms models, Kinetic studies, Thermodynamic parameters

1. Introduction

Due to its well-known high water consumption, the textile industry is one of the largest water-intensive industries in the world economy [1]. For the purpose of producing 8000 kg of fabric per day, a standard-sized textile mill needs roughly 1.6 million liters of water [2,3]. Consequently, this enterprise generates substantial amounts of wastewater including hazardous substances such as surfactants, heavy metals as Cu (II), and dyes [4]. These substances' high toxicity, enduring presence in the environment, and propensity to accumulate in living things can all have a substantial effect on ecosystems. Therefore, it is imperative that these chemical species be eliminated from industrial effluents before they are released into natural water bodies [5-7].

There are numerous environmentally safe techniques for extracting dyes from aqueous solutions, such as membrane filtering, coagulation, chemical oxidation, and adsorption [8–16]. Adsorption is one of these techniques that has several advantages [17]. Its user-friendliness and ease of adaptation to different circumstances stem from its straightforward operation and implementation [18]. Furthermore, adsorption is highly effective in eliminating impurities, guaranteeing complete water purification. This approach is a good choice for large-scale applications because it is also reasonably priced. Moreover, the adsorption process's recyclable and sustainable nature are improved by the materials' frequent regeneration and reuse [19-20]. Adsorption is the method of choice for efficiently removing colors from water because of its many advantages, including its high efficiency, sustainability, economic feasibility, and ease of operation. Furthermore, research is constantly improving adsorbent materials and procedures, which raises the viability and efficacy of adsorption as a first line of treatment for wastewater containing phenol [21- 22].

An essential parameter for evaluating an adsorbent's efficacy is its adsorption capacity. Wastewater treatment has made use of a number of inexpensive alternative adsorbents made from biomass, industrial solid waste, agricultural byproducts, and solid waste from agriculture [23].

These adsorbents can be made from materials like rice husk, pinewood, wheat, sugarcane bagasse, orange peels, olive leaves, switchgrass, coffee and tea, and Ficus carica bast. Examples of these materials include clay, sludge, montmorillonite, flax fiber, zeolite, and biochar [24–38]. Wastewater containing dyes has been effectively treated by adsorption using these materials. However, because of its comparatively low adsorption capability, classic activated carbon is not widely used for pollution removal. Its limited surface functional groups, low adsorption selectivity, tiny specific surface area, and electrochemical characteristics are the reasons for this limitation.

The research investigated how well two green tea-derived biosorbent materials; dry material (DPM) and charcoal (CPM), removed methylene blue from aqueous solutions. The study's goals were to: (1) use adsorption models to confirm the adsorption rate and capacity; (2) evaluate the thermodynamic parameters that control the adsorption process; and (3) determine the factors that affect adsorption, such as contact time, adsorbent dose, initial dye concentration, pH, and temperature.

2. Materials and methods

2.1. Chemicals

Analytical-grade chemicals were all utilised, and no additional purification was necessary. Merck, Darmstadt, Germany provided the hydrochloric acid,

sodium hydroxide, and methylene blue dye. De-ionized water was used to make stock solutions of methylene blue, which were subsequently serially diluted to produce the working solutions.

2.2. Instrumentation

MB dye concentration was measured utilizing a UV-Visible spectrophotometer (6305 UV-Spectrophotometer from Jenway) both before and after adsorption. At 660 nm, the concentration of MB was measured. Using methylene blue concentrations from 1 to 10 ppm that were obtained from the stock solution, a calibration curve was made. A pH meter (3505 Jenway pH meter) was used to measure the pH. After that, the container containing the dye solution and adsorbent material mixture was put in a shaker bath with temperature control to reach the required temperature.

2.3. Preparation of adsorbent materials

The waste green tea leaves were taken from Libyan coffee shops in Misurata City. After that, they were cleaned with double-distilled water and dried in an oven set to 70 °C for a full day. After being allowed to dry, the leaves were pulverised using an electric grinder and screened to remove any particles larger than 125 µm. To get ready for the dry adsorbent material (DPM), this was done. After that, the resultant material was kept in separate containers for later research use [39].

The dry material was heated to 550 °C in a furnace for two hours in order to undergo pyrolysis and create charcoal powder (CHM). Following this procedure, the biochar was removed, ground into a fine powder, sifted, cleaned with double-distilled water, and then dried at 60 °C. For use in additional research, this finished product was stored [40].

2.4. Biosorption procedure

Batch studies were carried out to examine how important factors including pH, contact time, adsorbent dose, beginning dye concentration, and temperature affected the adsorptive removal of methylene blue (MB). Every experimental run involved 150 rpm agitation of 50 mL of dye solution. The following ranges of parameters were tested: pH range (3–10), temperature range (25–50^{o}C), contact time (0–30 min), adsorbent dose (0.1–1.0), and dye concentration (5–200 ppm), until equilibrium was established. After the samples were removed, the remaining dye concentration in the aqueous solution was examined in order to calculate the kinetics, isotherm, and other thermodynamic adsorption parameters. One could change the pH of the solutions by adding HCl or 0.1 M NaOH. The following formula [41] was used to get the dye clearance percentage:

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

Where C_o and C_e are the starting and equilibrium dye concentrations, respectively, in milligrams per litre.

Equation [41] was used to determine the equilibrium adsorption capacity once the system achieved equilibrium concentration.

$$Q_e = \frac{(C_o - C_e) \times V}{M} \qquad (2)$$

Where V is the volume of solution (L), M is the mass of the adsorbent (g), and Q_e is the equilibrium adsorption capacity (mg/g).

2.5. Isotherms study

The methylene blue adsorption data on DPM and CPM was obtained, and as indicated in Table 1, the applicability of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms [42–44] was assessed.

2.6. Kinetics study

To determine which step of the adsorption process is rate-limiting, the kinetics of adsorption were examined in isolation. As shown in Table 1, two different kinetic models [45-46] were used to assess the effectiveness of

DPM and CPM as adsorbents for the removal of methylene blue. These models are known as pseudo-first-order and pseudo-second-order, respectively.

Table 1. Isotherms and kinetic models equations and parameters [42-46]

Isotherms Models

Eq. No.	Model	Linear equation	Parameters
3	Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{b\,Q_m\,C_e}$	Q_e: the adsorption capacity (mg/g) C_e (mg/L): concentration at equilibrium The Langmuir constant is b (L/mg) and the maximal adsorption capacity is Q_m (mg/g).
4	Freundlich	$\log Q_e = \log K_F + \frac{1}{n} \log C_e$	K_F (mg/g (L/mg)1/n): Freundlich adsorption constants n: Empirical constant characterizing the heterogeneity of the adsorbent surface
5	Temkin	$Q_e = B_T \ln K_T + B_T \ln C_e$	Temkin adsorption constant, B_T (J/mol) Temkin isotherm constant, K_T (L/mg)
6 & 7	D-R	$\log Q_e = \log Q_m - \beta\,\varepsilon^2$ $\varepsilon = RT\,\mathrm{Log}\,(1+\frac{1}{C_e})$	β: Dubinin-Radushkevich constant (mol^2/J^2) Polanyi potential ε (J/mol) and R (kJ/mol K) The constant of gas T (K): Temperature in absolute terms

Kinetic Models

Eq. No.	Model	Linear equation	Parameters
8	Pseudo-first-order	$\ln(Q_e - Q_t) = \ln(Q_e) - \frac{k_1}{2.303} \times t$	Q_t (mg/g): Adsorbed quantities at t time Q_e (mg/g): Adsorbed quantities at equilibrium k_1 (min^{-1}): The adsorption rate constant
9	Pseudo-second-order	$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e}$	The adsorption rate constant is k_2 (g/mg.min).

2.7. Thermodynamic parameters

An essential component of studies on adsorption is thermodynamics. The following equations (5) can be used to express the thermodynamic factors, such as entropy change (ΔS^o), enthalpy change (ΔH^o), and Gibbs free energy (ΔG^o), that affect the spontaneity and feasibility of the process:

$$\Delta G = \Delta H - T\,\Delta S \qquad (10)$$

$$\Delta G = -RT\,\mathrm{Ln}\,K_d \qquad (11)$$

To determine the apparent equilibrium constant of adsorption (Kc), the standard thermodynamic equilibrium constant should be calculated using activity instead of concentration:

$$K_d = \frac{Q_e}{C_e} \qquad (12)$$

The relationship between entropy, enthalpy, and K_d as illustrated below could be presented by the following equation:

$$\mathrm{Ln}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (13)$$

3. Results and Discussion

3.1. Effect of pH on biosorption

By changing the external charge of the adsorbent material, the pH variation in the solution has a considerable impact on the rate of adsorption. Experiments were carried out in a pH range of 3 to 10 to investigate the impact of pH on the adsorption of methylene blue (MB) onto dry adsorbent material (DPM) and charcoal powder (CPM), as illustrated in Fig. 1. The adsorption of the cationic MB dye was impeded by the greater concentration of H^+ ions on the adsorbent surface, which is probably why a reduced removal % was seen at pH values below 6. On the other hand, the cationic dye's adsorption rate was accelerated at higher pH levels due to the increasing concentration of anionic charges [47- 48].

Literature on zeta potential studies [49] supports these observations, indicating that the point of zero charge (pH_{PZC}) of the biochar is approximately 5.8. Thus, at pH levels above the pH_{PZC}, the adsorbent surface becomes more negatively charged, favoring the binding of the positively charged MB species.

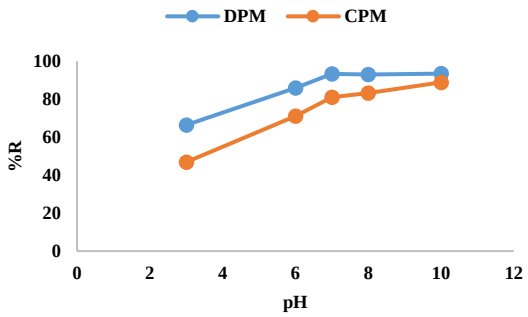


Fig. 1. Effect of pH on adsorption

3.2. Effect of adsorbent dose on biosorption

The adsorbent dose is a crucial factor influencing adsorption performance. To determine the optimal amount of adsorbent for methylene blue (MB) removal, the effect of varying adsorbent doses was studied at a constant MB concentration. Specifically, 50 mL of a 40 mg/L MB solution was treated with different adsorbent doses (100, 200, 400, 800, and 1000 mg), as illustrated in Fig. 2. Both adsorbents, dry powder material (DPM) and charcoal powder material (CPM), exhibited a similar trend in MB adsorption behavior under these conditions.

The removal rate of MB increased as the adsorbent mass arose because there were more accessible adsorption sites and pores. After the adsorbent mass hit a particular threshold, the adsorption process started to approach equilibrium. At an initial MB concentration of 40 mg/L, the removal rate of MB reached saturation at an adsorbent mass of 1000 mg. The inability of the solution's MB dye molecules to completely occupy all of the adsorption sites at larger adsorbent doses led to surface equilibrium and a drop in the amount of adsorption capacity per unit mass of adsorbent [23,50].

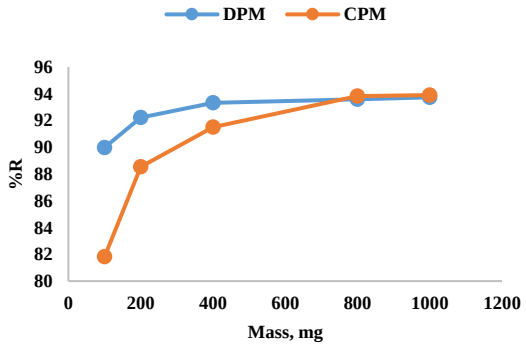


Fig. 2. Impact of adsorbent dose on adsorption

3.3. Effect of contact time on biosorption

In separate batches, spanning from 0 to 30 min, the effect of contact time on the elimination of methylene blue (MB) dye was investigated. The findings, which are displayed in Fig. 3, highlight how important contact time is to the adsorption process. For DPM and CPM, the adsorption was quick at first, reaching equilibrium in 10 and 15 min, respectively. For DPM and CPM, the maximum removal percentages were 92.8% and 83.3%, respectively, after 10 and 15 min. Following these intervals, the saturation of the adsorption process signified the attainment of equilibrium.

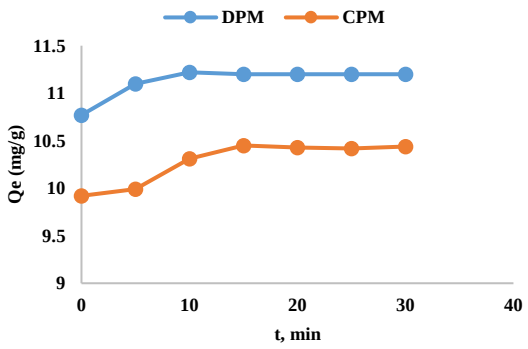


Fig. 3. Effect of contact time on adsorption

3.4. Effect of initial concentration on biosorption

Over a concentration range of 5–200 mg/L, the impact of dye concentration on the sorption of methylene blue (MB) onto DPM and CPM was examined (Fig. 4). Higher MB concentrations led to an increase in the equilibrium adsorption capacity, which rose from 1.31 mg/g to 57.90 mg/g for DPM and from 1.21 mg/g to 25.97 mg/g for CPM. No discernible variations in removal efficiency were seen above a certain dye concentration (Fig. 4). At larger dye concentrations, there is a stronger pushing force for mass transfer, which explains this occurrence. The adsorbent surface has vacant active spots at lower concentrations. Nevertheless, there are not enough active sites available for further dye adsorption above the ideal MB concentration [38,51].

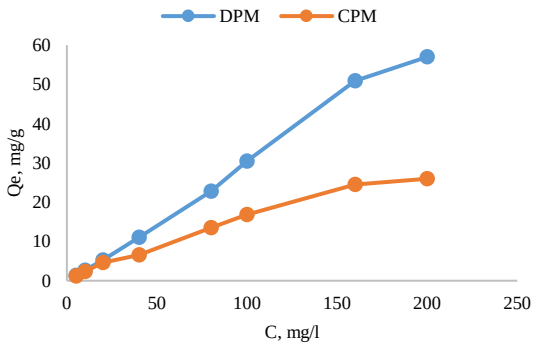


Fig .4. Initial concentration's impact on adsorption

3.5. Biosorption isotherms

Under certain conditions, both the equilibrium adsorption capacity and the equilibrium concentration of contaminants are analyzed using adsorption isotherms. These isotherms aid in determining adsorption capacity, adsorption behavior, and potential adsorption mechanisms. The adsorption isothermal behavior was described using four models: the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) models.

As illustrated in Fig. 5, the isotherm data were linearized using the Langmuir equation. Table 2 displays the parameters of the Langmuir isotherm. There is good agreement between the model parameters, as indicated by the high value of R^2. Furthermore, the strong correlation coefficient indicates that the Langmuir isotherm; which presupposes monolayer coverage and a uniform distribution of activity on the sorbent surface, is applicable. Fitting the Langmuir adsorption isothermal equation yielded the theoretical maximum adsorption capacities of MB onto DPM and CPM, which were 15.58 and 18.66 mg/g, respectively. DPM and CPM had highest experimental adsorption capabilities of 28.40 and 16.83 mg/g, respectively.

The Langmuir equation also allows for the calculation of the dimensionless separation factor (R_L). The R_L values were 0.041 and 0.067, implying that both DPM and CPM adsorbed MB favorably [53]. The same data were also fitted with the Freundlich equation, as Fig. 6 illustrates. R^2 values showed that the Freundlich equation and the experimental data agreed well, albeit marginally less so than the Langmuir model. Table 2 lists the pertinent Freundlich coefficients, which were determined using the isotherms.

Lower agreement was found when the Temkin and D-R isotherm models (Figs. 7 & 8) were fitted to the experimental data. R^2 values in this range suggest this. Overall, the Langmuir and Freundlich models and the

adsorption isotherm analysis results agreed well, with the Langmuir model exhibiting greater consistency.

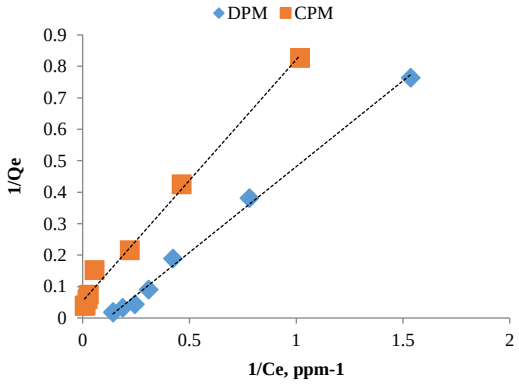


Fig. 5. Langmuir isotherms for MB adsorption

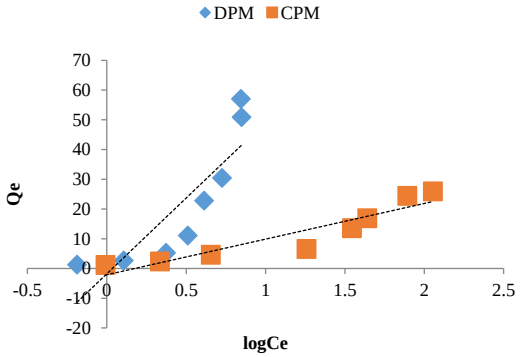


Fig. 7. Temkin isotherms for MB adsorption

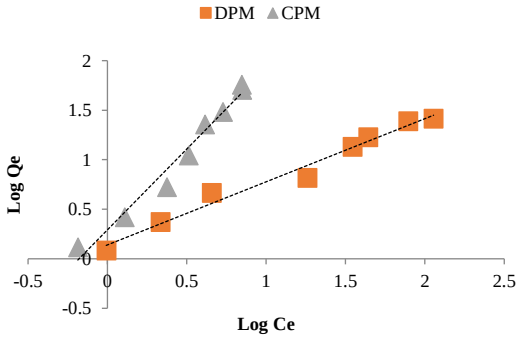


Fig. 6. Freundlich isotherms for MB adsorption

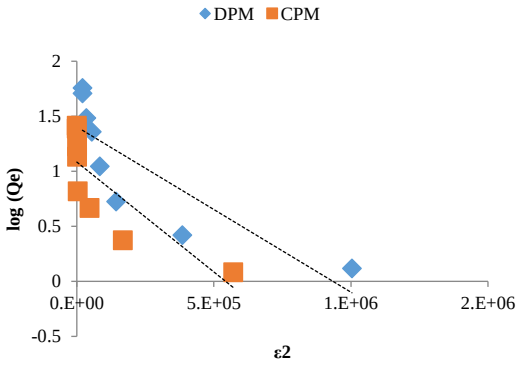


Fig. 8. D-R isotherms for MB adsorption

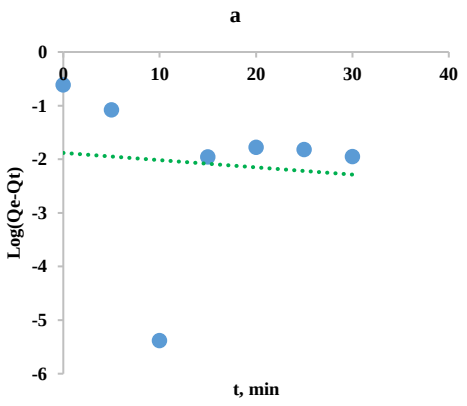
Table 2. Isotherms parameter values for various models in the adsorption of MB onto DPM & CPM

Langmuir	**Q_m (mg.g^{-1})**	**Q_m Experimental (mg.g^{-1})**	**b (L.mg^{-1})**	**R_L**	**R^2**
DPM	15.58	28.40	0.118	0.041	0.996
CPM	18.66	16.83	0.070	0.067	0.991
Freundlich		K_f ((mg/g)(mg/L)$^{1/n}$)	n (g.L^{-1})		R^2
DPM		1.38	1.57		0.979
CPM		1.96	0.61		0.973
Temkin		B_T	K_T		R^2

	$(J.mol^{-1})$	$(L.mg^{-1})$	
DPM	50.96	1.08	0.736
CPM	11.99	1.50	0.865
D-R	Q_m $(mg.g^{-1})$	β $(mol^2.J^{-2})$	R^2
DPM	25.32	$2x10^{-6}$	0.705
CPM	12.14	$2x10^{-6}$	0.664

3.6. Biosorption Kinetic

Pseudo-first- and second-order kinetic models were used to analyse the data for the adsorption of MB onto DPM and CPM. Table 3 provides a summary of the findings. The results presented in Figs. 9 and 10 demonstrate that the correlation coefficients for the pseudo-second-order kinetic model (1.000 and 0.999) were substantially higher than those for the pseudo-first-order model (0.009 and 0.370). Additionally, the calculated equilibrium adsorption capacities (Q_e) of 11.21 mg/g for DPM and 10.37 mg/g for CPM from the pseudo-second-order kinetics closely matched the experimental values (11.25 and 10.45 mg/g, respectively). This suggests that chemical interactions play a significant role in the adsorption process [52].



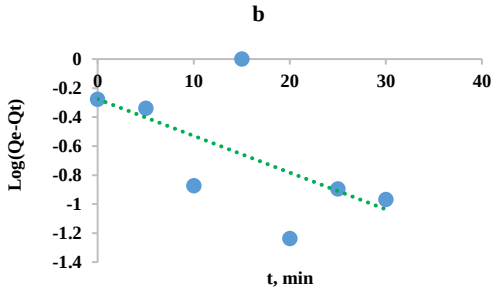


Fig. 9: Pseudo-first-order plot for MB adsorption onto: a) DPM, b) CPM

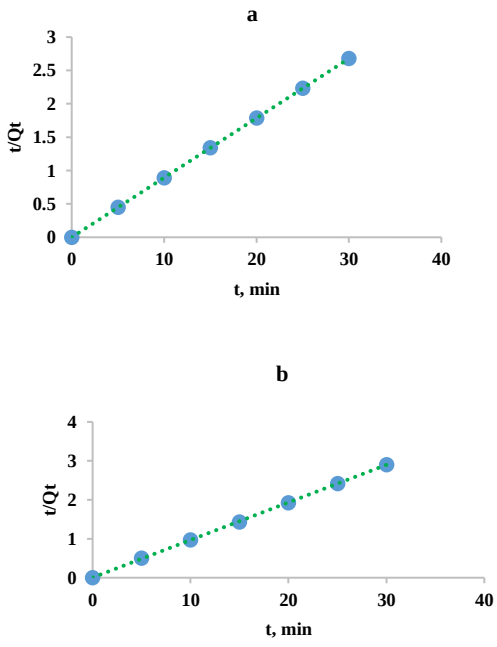


Fig. 10. MB adsorption pseudo-second-order plotted onto: a) DPM, b) CPM

Table 3. Kinetic parameter values of MB adsorption onto DPM and CPM

First order	Q_e (calculated) ($mg.g^{-1}$)	Q_e (experimentally) ($mg.g^{-1}$)	k_1 (min^{-1})	R^2
DPM	76.21	11.25	0.031	0.009
CPM	1.89	10.45	0.058	0.370
Second order	Q_e (calculated) ($mg.g^{-1}$)	Q_e (experimentally) ($mg.g^{-1}$)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
DPM	11.21	11.25	9.95	1.000
CPM	10.37	10.45	2.38	0.999

3.7. Effect of Temperature on Biosorption (Thermodynamic Studies)

Experiments were carried out at temperatures of 298, 303, 308, 313, 318, and 323 K to examine the impact of temperature on the adsorption of methylene blue (MB) by PDM and CPM. The effect of temperature on MB's adsorption onto both adsorbents is shown in Fig. 11. For both adsorbent materials, the equilibrium adsorption capacity of MB increased as the temperature rose. This implies that dye molecules' mobility increased with temperature, demonstrating the endothermic character of the adsorption process [54].

Thermodynamic variables are vital in determining the spontaneity and heat change that occur throughout the adsorption process. These parameters are free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These values were computed with the assumption that the activity coefficients are unity at low concentrations (10, 11, 12, 13). Fig. 12 displays the plots of 1/T against $\ln K_d$, from which equation 13 can be used to get ΔS and ΔH. Equation 10 can be used to find the value of ΔG. Table 4 lists the obtained thermodynamic parameters.

It has been noted that the ΔG° values for DPM and CPM are negative at higher temperatures and at all temperatures, respectively, suggesting that the adsorption process is spontaneous. The observation of a decrease in ΔG° as temperature rises indicates that adsorption is more effective at higher temperatures. The adsorption process for methylene blue is confirmed to be endothermic by the positive ΔH° value, which suggests a robust interaction between the adsorbent materials and methylene blue.

Methylene blue ions must first be partly stripped of their hydration shell, which requires energy input, before they can move through the solution and reach the adsorption sites. As a result, the positive ΔH° value suggests that adsorption rises as temperature drops. Furthermore, during the adsorption of MB onto both adsorbents, the positive ΔS° value indicates an increase in the degrees of freedom at the solid-liquid interface. This indicates the adsorbents' affinity for MB ions in aqueous solutions and could point to structural alterations in the adsorbents [54–56].

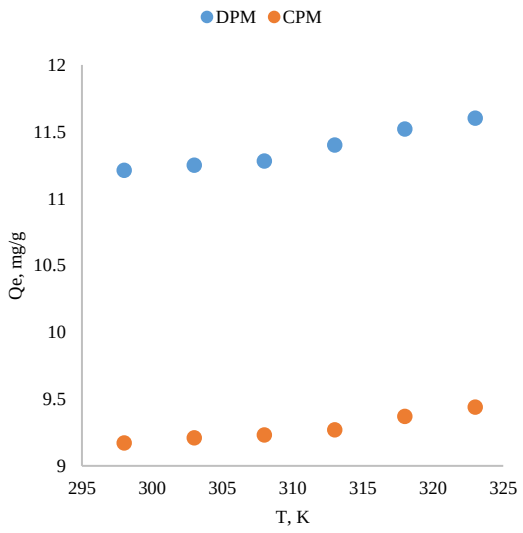


Fig. 11. Effect of temperature on adsorption

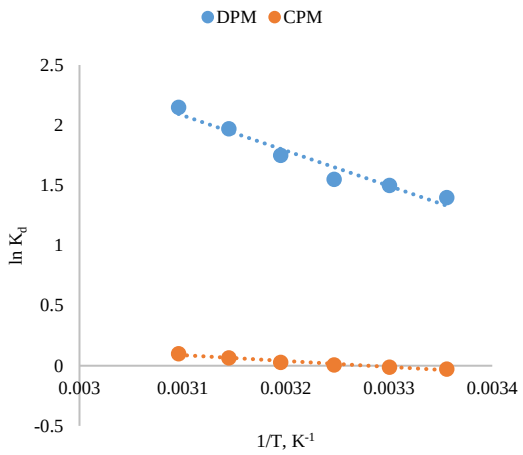


Fig. 12. Van't Hoff plots for the adsorption process

Table 4. Thermodynamic parameters of MB Dye Adsorption

Adsorbed surface	ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS° (J.K^{-1}mol^{-1})	R^2
DPM	-3.31	24.40	92.93	0.9501
CPM	0.20	4.07	13.34	0.9664

4.Conclusion

In the present investigation, dried waste plant material and charcoal made from green tea leaves were used as natural adsorbents to successfully remove methylene blue from aqueous solutions. Important factors that affected the adsorption yield were contact time, starting dye concentration, and adsorbent dosage. For the purpose of removing 40 mg/L of dye from the aqueous solution, the best amount of adsorbent under the evaluated experimental conditions was 0.1 g, and the necessary contact periods were 10 minutes for the dried material and 15 minutes for the charcoal material.

The pseudo-first-order and pseudo-second-order kinetic models, as well as the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models, were used to analyse the adsorption data. The pseudo-second-order kinetic model and the Langmuir isotherm model offered the best fit for both adsorbents, according to the correlation coefficients for the linear equations. Thermodynamic research demonstrated the spontaneous and endothermic nature of the adsorption process.

5. Acknowledgement

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6. Author contributions

Abdulfattah Mohamed Alkherraz: Conducted the experimental work, analyzed the data, and wrote the initial draft of the manuscript.

Khaled Muftah Elsherif: Designed the study, supervised the research process, and reviewed and edited the manuscript.

Aisha Hussien Madiry: Assisted with the experimental work, contributed to data analysis, and helped in reviewing the manuscript.

7. References

1. De Castro, M. L. F. A., Abad, M. L. B., Sumalinog, D. A. G., Abarca, R. R. M., Paoprasert, P., & de Luna, M. D. G. (2018). Adsorption of Methylene Blue dye and Cu(II) ions on EDTA-modified bentonite: Isotherm, kinetic and thermodynamic studies. Sustain. Environ. Res., 28(4), 197-205. https://doi.org/10.1016/j.serj.2018.04.001
2. Hu, Q. H., Qiao, S. Z., Haghseresht, F., Wilson, M. A., & Lu, G. Q. (2006). Adsorption study for removal of Basic Red dye using bentonite. Ind. Eng. Chem.

Res., 45(2), 733-738. https://doi.org/10.1021/ie050889y

3. Elsherif, K. M., & Yaghi, M. M. (2017). Membrane potential studies of parchment supported silver oxalate membrane. J. Mater. Environ. Sci., 8(1), 356-363.
4. El-Hashani, A., Elsherif, K. M., Edbey, K., Alfaqih, F., Alomammy, M., & Alomammy, S. (2018). Biosorption of Eriochrome Black T (EBT) onto waste tea powder: Equilibrium and kinetic studies. To Chem., 1(3), 263-275.
5. Alkherraz, A. M., Ali, A. K., El-Dali, A., & Elsherif, K. M. (2019). Biosorption study of Zn(II), Cu(II), Pb(II), and Cd(II) ions by palm leaves activated carbon. To Chem., 4, 8-17.
6. Elsherif, K. M., Saad, R. A. A., Ewlad-Ahmed, A. M., Treban, A. A., & Iqneebir, A. M. (2024). Adsorption of Cd(II) onto olive stones powder biosorbent: Isotherms and kinetic studies. Adv. J. Chem. Sect. A, 7(1), 59-74. https://doi.org/10.48309/ajca.2024.415865.1415
7. Haleem, A., Shafiq, A., Chen, S.-Q., & Nazar, M. A. (2023). Comprehensive review on adsorption, photocatalytic, and chemical degradation of dyes and nitro-compounds over different kinds of porous and composite materials. Molecules, 28, 1081. https://doi.org/10.3390/molecules28031081
8. El-Bery, H. M., Saleh, M., El-Gendy, R. A., Saleh, M. R., & Thabet, S. M. (2022). High adsorption capacity of phenol and methylene blue using activated carbon derived from lignocellulosic agriculture wastes. Sci. Rep., 12, 5499. https://doi.org/10.1038/s41598-022-09475-4
9. Elsherif, K. M., El-Hashani, A., El-Dali, A., & El-Kailany, R. (2014). Bi-ionic potential studies for thallium chromate parchment-supported membrane. Int. J. Res. Pharm. Chem., 4(2), 267-273.
10. Nasrullah, A., Bhat, A. H., Naeem, A., Isa, M. H., & Danish, M. (2018). High surface area mesoporous activated carbon-alginate beads for efficient removal of methylene blue. Int. J. Biol. Macromol., 107, 1792-1799. https://doi.org/10.1016/j.ijbiomac.2017.10.045
11. Elsherif, K. M., & Yaghi, M. M. (2017). Studies with model membrane: The effect of temperature on membrane potential. Mor. J. Chem., 5(1), 131-138. https://doi.org/10.48317/IMIST.PRSM/morjchem-v5i1.6324
12. Mohamed, F., Shaban, M., Zaki, S. K., Abd-Elsamie, M. S., Sayed, R., Zayed, M., Khalid, N., Saad, S., Omar, S., Ahmed, A. M., Gerges, A., Abd El-Mageed, H. R., & Soliman, N. K. (2022). Activated carbon derived from sugarcane and modified with natural zeolite for efficient adsorption of methylene blue dye: Experimentally and theoretically approaches. Sci. Rep., 12, 18031. https://doi.org/10.1038/s41598-022-22421-8
13. Elsherif, K. M., El-Hashani, A., El-Dali, A., & Saad, M. (2014). Ion-permeation rate of (1:1) electrolytes across parchment-supported silver chloride membrane. Int. J. Chem. Pharm. Sci., 2(6), 890-897.
14. Elsherif, K. M., El-Hashani, A., El-Dali, A., & Musa, M. (2014). Ion selectivity across parchment-supported silver chloride membrane in contact with multi-valent electrolytes. Int. J. Anal. Bioanal. Chem., 4(2), 58-62.
15. Bhatt, P., Joshi, S., Urper Bayram, G. M., Khati, P., & Simsek, H. (2023). Developments and application of chitosan-based adsorbents for wastewater treatments. Environ. Res., 226, 115530. https://doi.org/10.1016/j.envres.2023.115530
16. Elsherif, K. M., El-Hashani, A., & El-Dali, A. (2013). Potentiometric determination of fixed charge density and permselectivity for thallium chromate membrane. Ann. Chem. Res., 1(3), 15-25.
17. Kausar, A., Tul Zohra, S., Ijaz, S., Iqbal, M., Iqbal, J., Bibi, I., Nouren, S., El Messaoudi, N., & Nazir, A. (2023). Cellulose-based materials and their adsorptive removal efficiency for dyes: A review. Int. J. Biol. Macromol., 224, 1337-1355. https://doi.org/10.1016/j.ijbiomac.2022.10.220

18. Alkherraz, A. M., Ali, A. K., & Elsherif, K. M. (2020). Removal of Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions by adsorption onto olive branches activated carbon: Equilibrium and thermodynamic studies. Chem. Int., 6(1), 11-20. https://doi.org/10.5281/zenodo.2579465
19. Elsherif, K. M., El-Dali, A., Alkarewi, A. A., Ewlad-Ahmed, A. M., & Treban, A. (2021). Adsorption of crystal violet dye onto olive leaves powder: Equilibrium and kinetic studies. Chem. Int., 7(2), 79-89. https://doi.org/10.5281/zenodo.4441851
20. Hashmi, Z., Jatoi, A. S., Nadeem, S., Anjum, A., Imam, S. M., & Jangda, H. (2024). Comparative analysis of conventional to biomass-derived adsorbent for wastewater treatment: A review. Biomass Conv. Bioref., 14, 45–76. https://doi.org/10.1007/s13399-022-02443-y
21. Elsherif, K. M., El-Hashani, A., & Haider, I. (2018). Biosorption of Fe(III) onto coffee and tea powder: Equilibrium and kinetic study. Asian J. Green Chem., 2, 380-394. https://doi.org/10.22034/ajgc.2018.65163
22. Alkherraz, A., Ali, A., & Elsherif, K. (2020). Equilibrium and thermodynamic studies of Pb(II), Zn(II), Cu(II) and Cd(II) adsorption onto mesembryanthemum activated carbon. Journal of Medicinal and Chemical Sciences, 3(1), 1-10. https://doi.org/10.26655/JMCHEMSCI.2020.1.1
23. Kuang, Y., Zhang, X., & Zhou, S. (2020). Adsorption of methylene blue in water onto activated carbon by surfactant modification. Water, 12, 587. https://doi.org/10.3390/w12020587
24. Elsherif, K. M., Ewlad-Ahmed, A. M., & Treban, A. (2017). Removal of Fe(III), Cu(II), and Co(II) from aqueous solutions by orange peels powder: Equilibrium study. World J. Biochem. Mol. Biol., 2(6), 46-51.
25. Xiang, Y., Gao, M., Shen, T., Cao, G., Zhao, B., & Guo, S. (2019). Comparative study of three novel organo-clays modified with imidazolium-based gemini surfactant on adsorption for bromophenol blue. J. Mol. Liq., 286, 110928. https://doi.org/10.1016/j.molliq.2019.110928
26. Elsherif, K. M., Ewlad-Ahmed, A. M. S., & Treban, A. A. S. (2017). Biosorption studies of Fe(III), Cu(II), and Co(II) from aqueous solutions by olive leaves powder. Appl. J. Environ. Eng. Sci., 3(4), 341-352. https://doi.org/10.48422/IMIST.PRSM/ajees-v3i4.9806
27. Fan, S., Wang, Y., Wang, Z., Tang, J., & Li, X. (2017). Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: Adsorption kinetics, equilibrium, thermodynamics and mechanism. J. Environ. Chem. Eng., 5, 601-611. https://doi.org/10.1016/j.jece.2016.12.019
28. Elsherif, K. M., El-Hashani, A., & El-Dali, A. (2013). Effect of temperature on membrane potential and evaluation of thermodynamic parameters of parchment supported silver thiosulphate. Der Chem. Sin., 4(6), 13-21.
29. Wang, G., Wang, S., Sun, Z., Zheng, S., & Xi, Y. (2017). Structures of nonionic surfactant modified montmorillonites and their enhanced adsorption capacities towards a cationic organic dye. Appl. Clay Sci., 148, 1-10. https://doi.org/10.1016/j.clay.2017.08.001
30. Elsherif, K. M., Haider, I., & El-Hashani, A. (2019). Adsorption of Co(II) ions from aqueous solution onto tea and coffee powder: Equilibrium and kinetic studies. J. Fundam. Appl. Sci., 11(1), 65-81
31. Wang, W., Huang, G., An, C., Zhao, S., Chen, X., & Zhang, P. (2018). Adsorption of anionic azo dyes from aqueous solution on cationic gemini surfactant-modified flax shives: Synchrotron infrared, optimization and modeling studies. J. Clean. Prod., 172, 1986-1997. https://doi.org/10.1016/j.jclepro.2017.11.227
32. Elsherif, K. M., El-Dali, A., Ewlad-Ahmed, A. M., Treban, A. A., Alqadhi, H., & Alkarewi, S. (2022). Kinetics and isotherms studies of safranin adsorption

onto two surfaces prepared from orange peels. Mor. J. Chem., 10(4), 639-651. https://doi.org/10.48317/IMIST.PRSM/morjchem-v11i1.32137

33. Hailu, S. L., Nair, B. U., Mesfin, R. A., Diaz, I., & Tessema, M. (2017). Preparation and characterization of cationic surfactant modified zeolite adsorbent material for adsorption of organic and inorganic industrial pollutants. J. Environ. Chem. Eng., 5, 3319-3329. https://doi.org/10.1016/j.jece.2017.06.039
34. Elsherif, K. M., & Yaghi, M. M. (2016). Studies with model membrane: Determination of fixed charge density of silver sulfite membrane. Am. J. Polym. Sci. Technol., 2(2), 28-33.
35. Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., Wang, H., & Peng, X. (2015). Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. Fuel, 155, 77-85. https://doi.org/10.1016/j.fuel.2015.04.019
36. Elsherif, K. M., El-Hashani, A., & El-Dali, A. (2013). Potentiometric determination of fixed charge density and permselectivity for silver thiosulphate membrane. J. Appl. Chem., 2(6), 1543-1551.
37. Mubarik, S., Saeed, A., Athar, M. M., & Iqbal, M. (2016). Characterization and mechanism of the adsorptive removal of 2,4,6-trichlorophenol by biochar prepared from sugarcane bagasse. J. Ind. Eng. Chem., 33, 115-121. https://doi.org/10.1016/j.jiec.2015.09.029
38. Pathania, D., Sharma, S., & Singh, P. (2017). Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. Arab. J. Chem., 10, S1445-S1451. https://doi.org/10.1016/j.arabjc.201
39. Elsherif, K. M., El-Hashani, A., & Haider, I., (2018), Equilibrium and kinetic studies of Cu (II) biosorption onto waste tea and coffee powder (WTCP). Iran. J. Anal. Chem., 5(2), 31-38. https://doi.org/20.1001.1.23832207.2018.5.2.5.4
40. Alkherraz, A. M., Elsherif, K. M., El-Dali, A., Blayblo, N. A., & Sasi, M., (2022), Thermodynamic, equilibrium, and kinetic studies of safranin adsorption onto Carpobrotus edulis. Asian J. Nanosci. Mater., 5(2), 118-131. https://doi.org/10.26655/AJNANOMAT.2022.2.4
41. Alkherraz, A. M., Elsherif, K. M., Madiry, A. H., & Sasi, M. S., (2024), Evaluating the efficiency of red tea leaves residues in adsorption of methylene blue dye from liquid wastes: isotherms, kinetics, and thermodynamics studies. Arab. J. Sci. Res., 5(1), 2. https://doi.org/10.5339/ajsr.2024.2
42. Derakhshan, Z., Baghapour, M. A., Ranjbar, M., & Faramarzian, M., (2013), Adsorption of methylene blue dye from aqueous solutions by modified pumice stone: Kinetics and equilibrium studies. Health Scope, 2(3), 136-144. https://doi.org/10.17795/jhealthscope-12492
43. Turp, S. M., Turp, G. A., Ekinci, N., & Özdemir, S., (2020), Enhanced adsorption of methylene blue from textile wastewater by using natural and artificial zeolite. Water Sci. Technol., 82(3), https://doi.org/10.2166/wst.2020.358
44. Cheruiyot, G. K., Wanyonyi, W. C., Kiplimo, J. J., & Maina, E. N., (2019), Adsorption of toxic crystal violet dye using coffee husks: Equilibrium, kinetics and thermodynamics study. Sci. Afr., 5, e00116. https://doi.org/10.1016/j.sciaf.2019.e00116
45. Deng, H., Yang, L., Tao, G., & Dai, J., (2009), Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation--application in methylene blue adsorption from aqueous solution. J Hazard Mater., 166(2-3), 1514–1521. https://doi.org/10.1016/j.jhazmat.2008.12.080
46. Ghoohestani, E., Samari, F., Homaei, A., & Yosuefinejad, S., (2024), A facile strategy for preparation of Fe3O4 magnetic nanoparticles using Cordia myxa leaf extract and investigating its

adsorption activity in dye removal. Sci Rep., 14(1), 84. https://doi.org/10.1038/s41598-023-50550-1

47. Sahu, S., Pahi, S., Tripathy, S., Singha, S. K., Behera, A., Sahu, U. K., & Patel, R. K., (2020), Adsorption of methylene blue on chemically modified lychee seed biochar: Dynamic, equilibrium, and thermodynamic study. J. Mol. Liq., 315, 113743. https://doi.org/10.1016/j.molliq.2020.113743
48. Sen, T. K., Afroze, S., & Ang, H. M., (2011), Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of Pinus radiata. Water Air Soil Pollut., 218, 499–515. https://doi.org/10.1007/s11270-010-0663-y
49. Hasfalina, C. B. M., Akinbile, C. O., & Jun, C. X., (2015), Coconut husk adsorbent for the removal of methylene blue dye from wastewater. BioRes., 10(2), 2859-2872. https://doi.org/10.15376/biores.10.2.2859-2872
50. Mouni, L., Belkhiri, L., Bollinger, J. C., Bouzaza, A., Assadi, A., Tirri, A., Dahmoune, F., Madani, K., & Reminie, H., (2018), Removal of methylene blue from aqueous solutions by adsorption on kaolin: Kinetic and equilibrium studies. Appl. Clay Sci., 153, 38–45. https://doi.org/10.1016/j.clay.2017.11.034
51. Iqbal, J., Watto, F.H., Watto, M.H.S., Malik, R., Tirmizi, S.A., Imran, M., & Ghangro, A.B., (2011), Adsorption of acid yellow dye on flakes of chitosan prepared from fishery waste. Arab. J. Chem., 4, 389–395. https://doi.org/10.1016/j.arabjc.2010.07.007
52. Han, Q., Wang, J., Goodman, B. A., Xie, J., & Liu, Z., (2020), High adsorption of methylene blue by activated carbon prepared from phosphoric acid treated eucalyptus residue. Powder Technol., 366, 239–248. https://doi.org/10.1016/j.powtec.2020.02.013
53. Gemici, B. T., Ozel, H. U., & Ozel, H. B., (2021), Removal of methylene blue onto forest wastes: Adsorption isotherms, kinetics and thermodynamic analysis. Environ. Technol. Innov., 22, 101501. https://doi.org/10.1016/j.eti.2021.101501
54. Shahryari, Z., Goharrizi, A. S., & Azadi, M., (2010), Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. Int. J. Water Resour. Environ. Eng., 2(2), 016-028.
55. Sah, M.K., Edbey, K., El-Hashani, A., Almshety, S., Mauro, L., Alomar, T.S., AlMasoud, N., & Bhattarai, A., (2022), Exploring the biosorption of methylene blue dye onto agricultural products: A critical review. Separations, 9(256). https://doi.org/10.3390/separations9090256
56. Ghosh, D., & Bhattacharyya, K.G., (2002), Adsorption of methylene blue on kaolinite. Appl. Clay Sci., 20, 295–300. https://doi.org/10.1016/S0169-1317(01)00081-3