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Valorization of Cagaita (*Eugenia dysenterica*) Pulp through Torrefied Biomass Production for Methylene Blue Removal from Aqueous Solutions

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Abstract

A low-severity torrefaction route was employed to convert cagaita (*Eugenia dysenterica*) pulp into an efficient carbonaceous adsorbent for methylene blue (MB) removal from aqueous solutions. The torrefied biomass (TBCP), prepared at 250 °C for 1 h under air, exhibited a strong pH-dependent adsorption behavior, with the adsorption capacity increasing from 4.4 mg g⁻¹ at pH 2 to 20.7 mg g⁻¹ at pH 11. Kinetic studies revealed rapid MB uptake under alkaline conditions, well described by the pseudo-first-order model ($R^2 = 1.000$ at pH 11), while Elovich analysis highlighted surface heterogeneity effects at acidic and neutral pH. Thermodynamic evaluation at pH 7 confirmed a spontaneous ($\Delta G^\circ < 0$) and endothermic adsorption process ($\Delta H^\circ = +5.30$ kJ mol⁻¹) driven by entropy gain ($\Delta S^\circ = +110.6$ J mol⁻¹ K⁻¹). These results demonstrate that mild torrefaction is sufficient to generate an effective, low-cost adsorbent from fruit pulp waste, offering a sustainable alternative for dye-contaminated wastewater treatment.

1. Introduction

The discharge of synthetic dyes into aquatic environments represents a major environmental concern due to their persistence, visibility even at low concentrations, and potential toxic effects on aquatic ecosystems and human health [1,2]. The textile industry is the largest consumer of synthetic dyes, accounting for approximately 56% of the global dye production, and it is estimated that nearly 15% of these dyes are lost during industrial processes and discharged into wastewater streams [3]. As a consequence, a substantial fraction of dye-contaminated effluents is released into the environment without adequate treatment. It has been reported that only about 8% of textile wastewater undergoes proper treatment prior to discharge, while the textile sector is responsible for nearly 80% of the total colored effluent load released into aquatic systems [4]. This scenario results in severe environmental impacts, including reduced light penetration, disruption of aquatic photosynthesis, and increased ecotoxicological risks, even at low dye concentrations [4].

Among the various dyes employed industrially, methylene blue (MB; 3,7-bis(dimethylamino)phenothiazin-5-ium chloride; see Fig. 1) has been widely adopted as a model cationic dye in adsorption studies due to its high aqueous solubility, chemical stability, and straightforward detection by UV–Vis spectroscopic techniques [5].

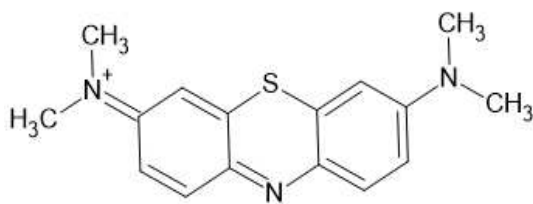


Figure 1. Chemical structure of methylene blue (MB^+), a cationic phenothiazine dye widely used as a model pollutant in adsorption studies. The structure was drawn using ChemSketch (ACD/Labs, freeware version).

Due to its pronounced toxicity and high solubility in water, methylene blue is regarded as one of the most hazardous pollutants [6]. In aquatic systems, its presence leads to increased turbidity, reduced light penetration, impairment of photosynthetic activity, and depletion of dissolved oxygen, ultimately causing adverse effects on aquatic life [6].

Among the various treatment methods for organic dyes, such as catalytic degradation, electrolysis, flocculation, and adsorption, the latter has gained considerable attention due to its low cost, operational simplicity, and high removal efficiency [7]. In this context, the use of biosorbents has emerged as a highly attractive alternative for the adsorption of textile dyes, particularly those derived from agricultural residues. Such materials are widely available, renewable, environmentally benign, and economically viable, while often requiring minimal processing prior to application. In addition, their lignocellulosic composition—rich in cellulose, hemicellulose, and lignin—provides abundant surface functional groups capable of interacting with cationic dye molecules, enabling effective dye removal from aqueous media [8].

In this context, the use of fruits native to the Brazilian Cerrado is of particular importance, given their wide availability and the still limited number of studies exploring their potential for environmental applications [5]. Biomaterials derived from Cerrado fruits are known to be rich in phenolic compounds and other bioactive constituents, which play a key role in adsorption processes. These compounds provide surface functional groups capable of interacting with organic pollutants, especially cationic dyes such as methylene blue, through electrostatic interactions and hydrogen bonding [5]. In addition, the presence of aromatic rings in lignin and phenolic structures favors π – π interactions with the aromatic framework of methylene blue, further enhancing adsorption Affinity [5].

Accordingly, the present study investigates the use of torrefied biomass derived from cagaita (*Eugenia dysenterica*) pulp (TBCP) as an adsorbent for methylene blue removal from aqueous solutions. Adsorption experiments were conducted to evaluate equilibrium behavior and to determine key adsorption parameters through isotherm modeling, complemented by kinetic studies to elucidate the adsorption mechanism. The raw pulp and the derived carbonaceous material were characterized by thermal analysis and Fourier-transform infrared spectroscopy (FTIR) in order to assess their thermal stability and surface functional groups, providing insight into structure–property relationships governing the adsorption process.

2. Experimental

2.1. Preparation and Characterization of torrefied biomass derived from cagaita (*Eugenia dysenterica*) pulp (TBCP)

Fully ripe fruits of *Eugenia dysenterica* DC (Fig. 2) were collected in 2024 in Sete Lagoas, Minas Gerais State, Brazil (19°28'36" S, 44°11'43" W), and transported to the Chemistry Laboratory of the Federal University of São João del-Rei (UFSJ). Fruit harvesting was conducted in accordance with Brazilian Law No. 12,727, dated October 17, 2012, which regulates the protection of native vegetation. The fruits were obtained from native (wild) plants occurring in Cerrado areas of the UFSJ campus.

Under these conditions, no specific governmental license was required for the collection of non-timber forest products, since the harvesting was conducted on public land for non-commercial scientific research purposes. Permission for plant collection was granted by the responsible institutional authority of the Federal University of São João del-Rei (UFSJ), in compliance with Brazilian Law No. 12,651/2012 and Law No. 13,123/2015. Under these conditions, no specific governmental license was required for the collection of non-timber forest products, since the harvesting was conducted on public land for non-commercial scientific research purposes. Permission for plant collection was granted by the responsible institutional authority of the Federal University of São João del-Rei (UFSJ), in compliance with Brazilian Law No. 12,651/2012 and Law No. 13,123/2015.

Cagaita pulp (1 kg) was milled in a knife mill for 20 min and subjected to torrefaction at 250 °C for 1 h under air atmosphere. The resulting material was

washed with distilled water until the conductivity of the washing water decreased to $50 \mu\text{S cm}^{-1}$. All solutions were prepared using high-purity deionized water obtained from a Quimis deionization system to ensure consistency and purity. This preparation route was deliberately designed to minimize energy and resource consumption and did not involve any chemical treatments or high-energy inputs, such as thermal activation or specialized surface modifications.

Material characterization was performed using Fourier-transform infrared spectroscopy (FTIR/ATR). The analyses were carried out with an Agilent Cary 630 FTIR spectrophotometer (Agilent Technologies, USA) equipped with an attenuated total reflection (ATR) accessory to identify the surface functional groups of the biomass.

Thermal analysis was conducted at the Chemistry Department Laboratory of the Federal University of Minas Gerais (UFMG) using Mettler thermal analysis equipment. Approximately 40 mg of the biomass sample were placed in an aluminum crucible and heated from 25 to 800 °C at a heating rate of $10 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under a synthetic air atmosphere with a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$.

2.2. Batch Adsorption Experiments and Kinetic Studies of Methylene Blue Removal Using TBCP

Batch adsorption experiments were performed to investigate the adsorption behavior of methylene blue (MB). The adsorbent dosage was fixed at $1 \text{ g}\cdot\text{L}^{-1}$, and aqueous MB solutions with initial concentrations ranging from 10 to $100 \text{ mg}\cdot\text{L}^{-1}$ were employed. Adsorption experiments were carried out using a solution volume of 50 mL in a thermostatically controlled bath to ensure constant

temperature conditions. The residual concentration of methylene blue was determined by UV–Vis spectrophotometry at a wavelength of 663 nm.

To evaluate the thermodynamic parameters of adsorption, including the enthalpy (ΔH°) and entropy (ΔS°) changes, experiments were conducted at different temperatures (10, 25, and 60 °C). Kinetic adsorption studies were performed by monitoring the uptake of methylene blue as a function of contact time, allowing the assessment of adsorption kinetics and the applicability of kinetic models

The adsorption capacity of methylene blue at equilibrium, $q(\text{mg}\cdot\text{g}^{-1})$, was calculated using the mass balance equation given by Eq. (1), where $C_0(\text{mg}\cdot\text{L}^{-1})$ is the initial methylene blue concentration, $C(\text{mg}\cdot\text{L}^{-1})$ is the residual concentration after adsorption, $V(\text{L})$ is the volume of the solution, and $m(\text{g})$ is the mass of the adsorbent.

$$q = \frac{(C_0 - C) V}{m} \quad (\text{Eq. 1})$$

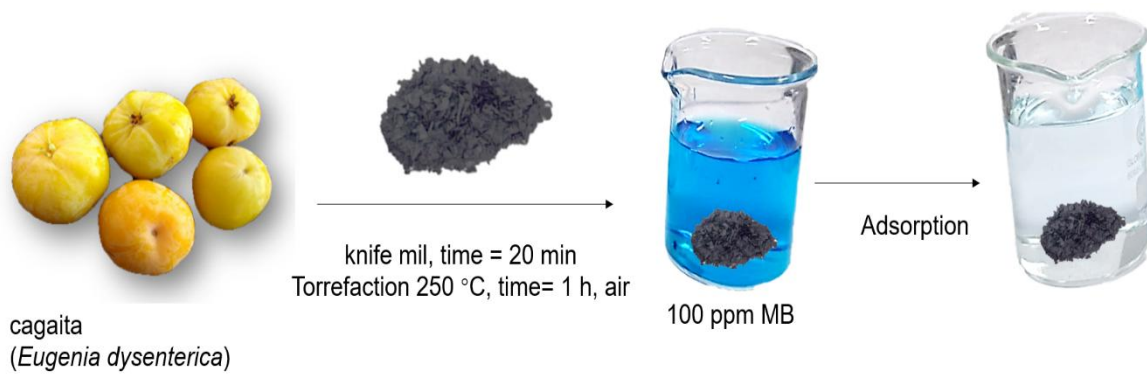


Figure 1. Schematic illustration of TBCP preparation and methylene blue adsorption.

3. Results

3.1. Thermogravimetric and differential thermal analysis (TG/DTA) of cagaita pulp

Figure 2 shows the thermogravimetric (TG) and differential thermal analysis (DTA) curves of cagaita pulp. A pronounced endothermic event at low temperatures (below 100 °C) is observed in the DTA curve and is attributed to the removal of free and bound water, which is consistent with the high moisture content typically found in fruit pulps [9–11]. In the temperature range between approximately 120 and 300 °C, the thermal signal remains relatively stable, indicating the gradual decomposition of low-molecular-weight organic compounds and the initial degradation of hemicellulosic components. A broad exothermic event is detected at higher temperatures (around 300–400 °C), which is associated with the intense thermal degradation of organic matter, including lignin decomposition and major structural transformations leading to the formation of highly carbonized residues [9]. At temperatures above 400 °C, no significant thermal events are observed, suggesting the presence of a thermally stable residue.

Overall, these results justify the selection of 250 °C as an appropriate temperature for TBCP production. At this temperature, the biomass has already undergone the main dehydration stage, as evidenced by the absence of significant endothermic events below 100 °C, and enters the torrefaction region of thermal conversion. Operating at 250 °C enables partial thermal modification of cagaita pulp, promoting dehydration, decarboxylation, and initial structural rearrangements, while avoiding the high-temperature regime associated with intense oxidative degradation, excessive mass loss, and extensive destruction of

oxygen-containing surface functional groups. The preservation of these functional groups is particularly relevant, as they play a crucial role in adsorption processes through electrostatic interactions and hydrogen bonding [12].

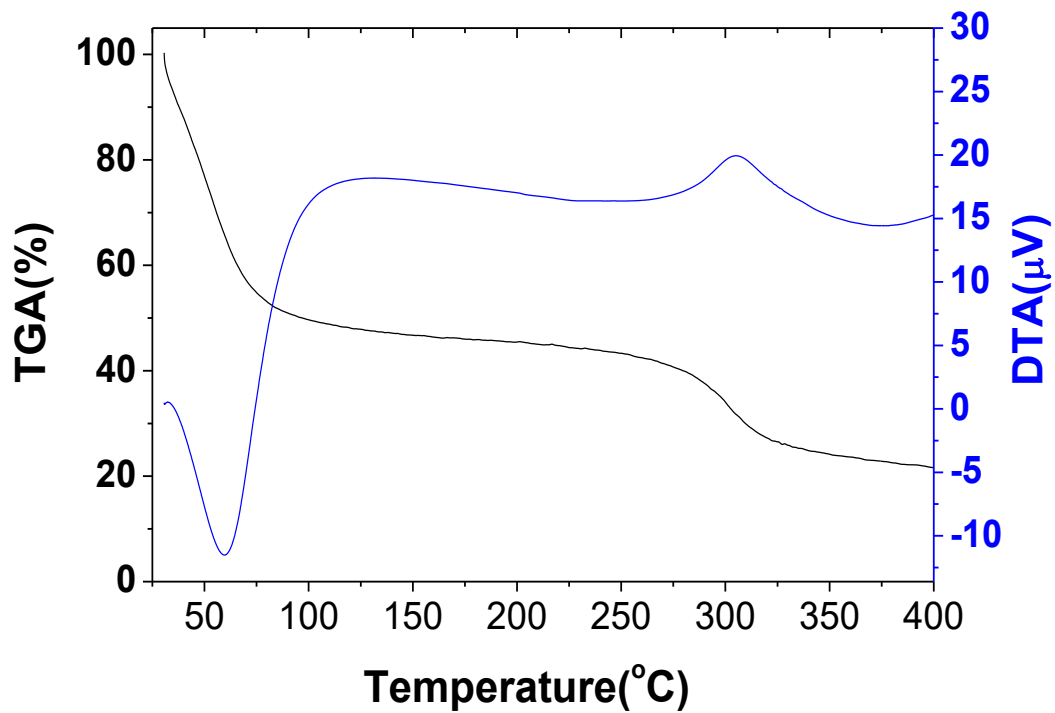


Figure 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of cagaita pulp, highlighting dehydration, organic matter decomposition, and carbonization regions.

3.2. FTIR analysis of cagaita pulp and TBCP

The FTIR spectra provide clear evidence of the chemical transformations associated with the conversion of cagaita pulp into TBCP by thermal treatment at 250 °C. The broad band centered around 3314 cm⁻¹, attributed to O–H stretching vibrations of hydroxyl groups involved in extensive hydrogen bonding, is markedly attenuated after thermal treatment, indicating dehydration and partial removal of oxygenated functionalities during the early stages of thermal modification.

The aliphatic C–H stretching bands at 2910 and 2835 cm⁻¹, characteristic of –CH₂ and –CH₃ groups in polysaccharides and other low-molecular-weight organic compounds, are prominent in the raw pulp but significantly reduced in the TBCP spectrum. This attenuation reflects the thermal decomposition of labile aliphatic structures and the progressive enrichment of thermally resistant carbon domains, a behavior commonly reported during biomass torrefaction and low-temperature thermal treatment of fruit-derived and lignocellulosic materials [12,13].

The band at 1715 cm⁻¹, associated with C=O stretching vibrations of carboxylic acids and ester groups, decreases substantially after thermal treatment, indicating dehydration and partial decarboxylation reactions that accompany the transformation of biomass into a more thermally stabilized carbonaceous structure, rather than full carbonization [14].

A key spectral feature supporting TBCP formation is observed in the shift of the band from 1617 cm⁻¹ in the raw pulp to 1565 cm⁻¹ in the TBCP. This change

is commonly associated with structural rearrangement and condensation of lignin-derived components, leading to an increased contribution of aromatic C=C skeletal vibrations and enhanced π – π conjugation. Similar shifts in this spectral region have been associated with structural rearrangement and increased aromatic character in thermally treated lignocellulosic materials [12–14]. In the present study, such changes are consistent with the early stages of aromatization expected under mild thermal treatment conditions. Additionally, the pronounced reduction of the band at approximately 1012 cm^{-1} , assigned to C–O stretching vibrations of cellulose and hemicellulose, confirms the partial degradation of carbohydrate structures and further supports the transformation of the lignocellulosic framework into TBCP.

Overall, the FTIR results demonstrate that thermal treatment at $250\text{ }^{\circ}\text{C}$ effectively promotes dehydration, partial decarboxylation, and initial aromatization of cagaita pulp, leading to the formation of a carbonaceous matrix characteristic of low-temperature torrefied biomass. Importantly, the preservation of residual oxygen-containing functional groups on the TBCP surface suggests the availability of active sites for adsorption, favoring electrostatic interactions, hydrogen bonding, and π – π interactions with cationic dyes such as methylene blue.

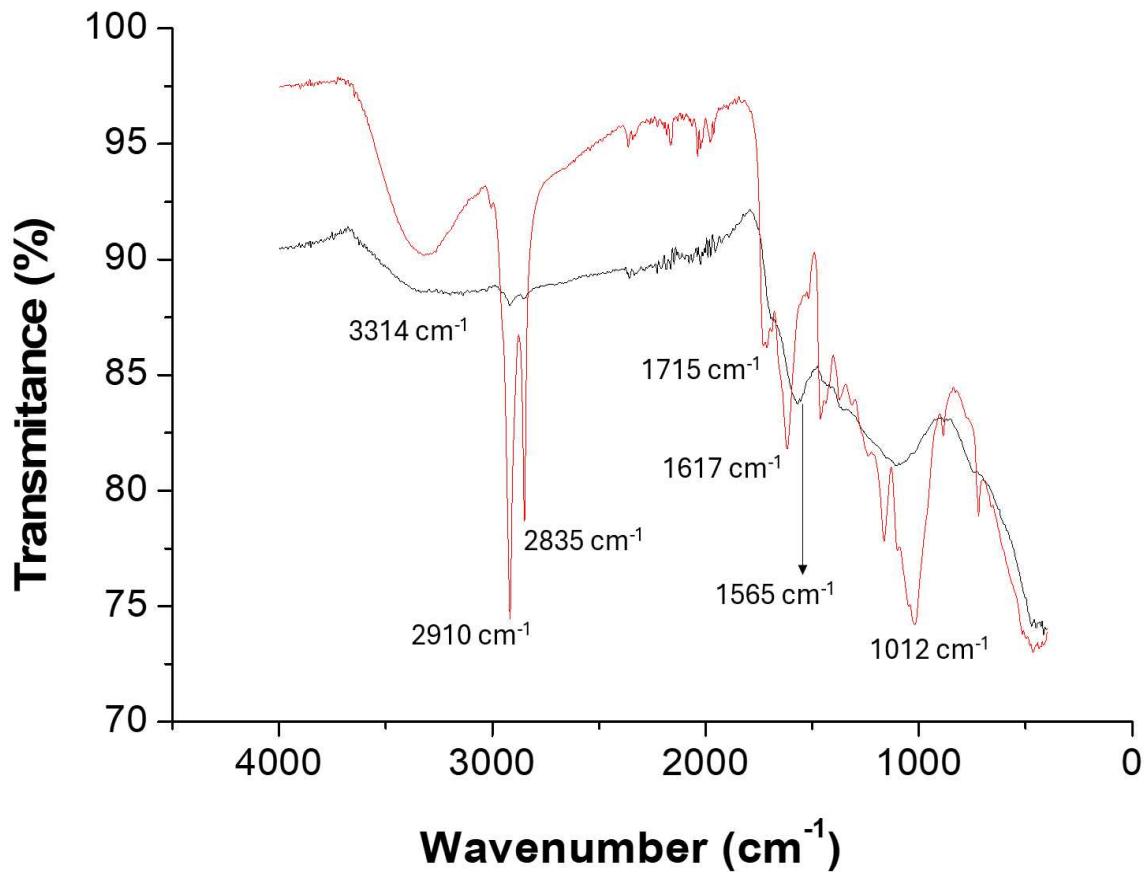


Figure 3. FTIR spectra of cagaita pulp (red) and TBCP produced at 250 °C (black), showing dehydration, loss of aliphatic groups, and increased aromatic character after carbonization.

3.3 Adsorption isotherms and thermodynamic parameters of methylene blue adsorption onto TBCP

The equilibrium adsorption of methylene blue (MB) onto TBCP was analyzed using the Langmuir (Eq. 2), Temkin (Eq. 3), and Freundlich (Eq. 4) isotherm models [15]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (\text{Eq. 2})$$

$$q_e = B \ln (A C_e) \quad (\text{Eq. 3})$$

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 4})$$

where q_e ($\text{mg} \cdot \text{g}^{-1}$) is the amount of MB adsorbed at equilibrium and C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium MB concentration. In the Langmuir model, $q_{\max}$ ($\text{mg} \cdot \text{g}^{-1}$) represents the maximum monolayer adsorption capacity and K_L ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir affinity constant. In the Temkin model, A ($\text{L} \cdot \text{mg}^{-1}$) is related to the initial adsorbate–adsorbent affinity, while $b_T = RTB^{-1}$ accounts for the decrease in adsorption energy with surface coverage. The Freundlich constants K_F and n describe adsorption capacity and surface heterogeneity, respectively [15].

Figure 4 presents the adsorption isotherms (q_e versus C_e) obtained at pH 7 for the TBCP produced at 250 °C for 1 h, together with the corresponding model fits. The isotherm parameters determined at pH 2, 7, and 11 are summarized in Table 1, highlighting the significant influence of solution pH on adsorption capacity, affinity, and energetic heterogeneity. Negative values of the Gibbs free energy change (ΔG°), calculated from the Langmuir equilibrium constant, confirm the spontaneous nature of MB adsorption, while the low values of the Temkin energy parameter (b_T) indicate that the process is predominantly governed by physisorption.

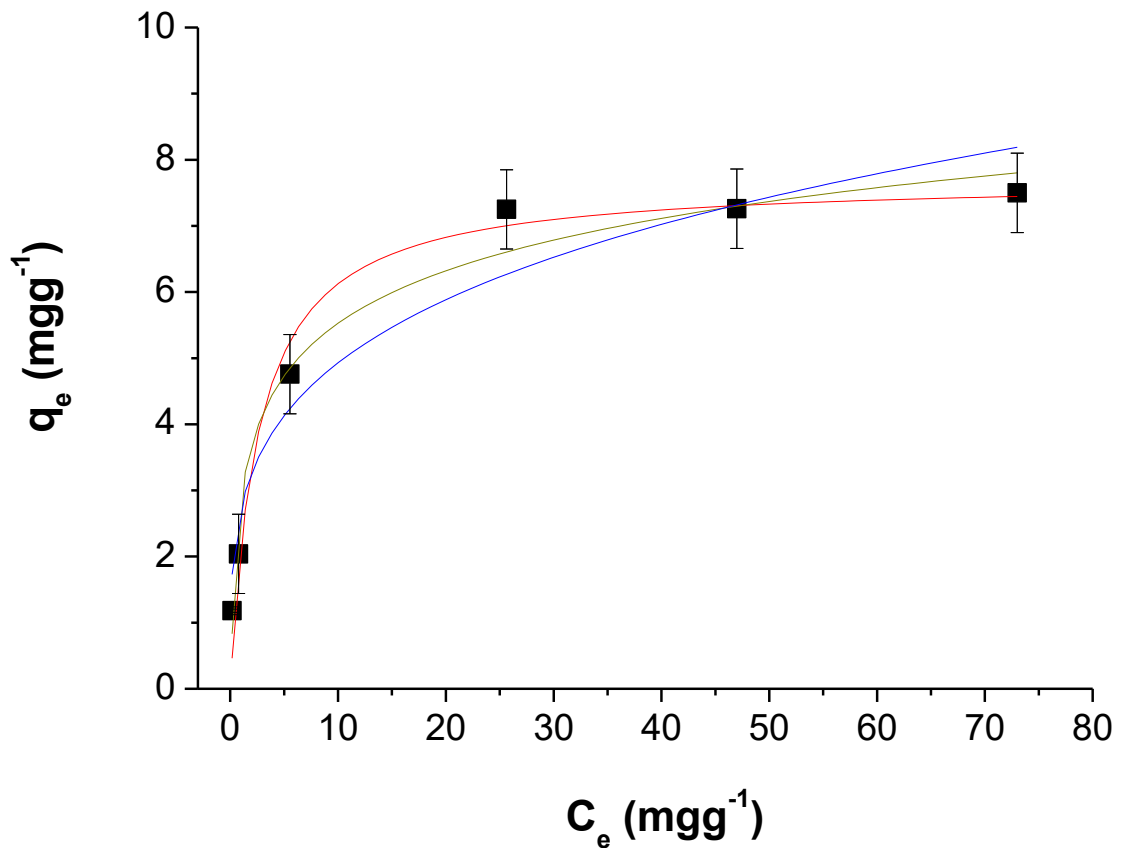
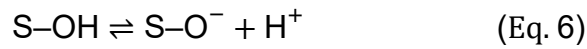


Figure 4. Adsorption isotherms of methylene blue on TBCP produced at 250 °C for 1 h at pH 7, fitted with Langmuir, Temkin, and Freundlich models.

According to the Langmuir model, the maximum adsorption capacity of methylene blue increased from 4.37 mg g⁻¹ at pH 2 to 20.65 mg g⁻¹ at pH 11, indicating that alkaline conditions enhance the availability of active adsorption sites on the TBCP surface. In contrast, the Langmuir affinity constant decreased with increasing pH, suggesting that adsorption under acidic conditions is governed by a smaller number of highly energetic sites, whereas at higher pH values adsorption proceeds over a larger population of sites with lower average affinity. The high coefficients of determination ($R^2 > 0.96$) obtained at all pH values confirm that the Langmuir model adequately describes the adsorption behavior

across the investigated pH range. At alkaline pH, the deprotonation of surface carboxylic (Eq. 5) and hydroxyl (Eq. 6) functional groups leads to the formation of negatively charged sites on the TBCP surface. This process increases the number of electrostatically active adsorption sites and enhances the interaction with the cationic methylene blue molecules, contributing to the higher adsorption capacity observed under alkaline conditions [15]:



Negative Gibbs free energy (ΔG°) values were obtained at all investigated pH conditions, confirming the spontaneous nature of methylene blue adsorption onto the cagaita-derived TBCP. The magnitude of ΔG° decreased from $-32.07 \text{ kJ}\cdot\text{mol}^{-1}$ at pH 2 to $-26.33 \text{ kJ}\cdot\text{mol}^{-1}$ at pH 11, indicating that the adsorption driving force is stronger under acidic conditions and progressively weakens at higher pH. This behavior is consistent with the isotherm analyses and reflects a transition from adsorption on a limited number of high-energy sites at low pH—where hydrogen bonding interactions can contribute to an increased adsorption energy per site—to adsorption on a larger number of energetically weaker sites at neutral and alkaline pH. This interpretation is consistent with previous studies on heterogeneous carbon surfaces, which show that adsorption on a limited number of high-energy sites increases the average adsorption energy, even in physisorption-dominated systems [17].

According to the Freundlich model, all systems exhibited favorable adsorption behavior ($n > 1$), with a pronounced dependence on solution pH. At pH 2, the very high n value (15.13) indicates extremely favorable adsorption at

low dye concentrations, associated with a small number of highly energetic adsorption sites on the protonated TBCP surface. At neutral and alkaline pH, lower n values reflect a more moderate surface heterogeneity and a more gradual adsorption process, consistent with the trends observed in the Langmuir and Temkin analyses.

The Temkin model provided additional insight into the energetic aspects of methylene blue adsorption onto the TBCP. The Temkin energy parameter (b_t) exhibited a strong dependence on pH, reaching its highest value at pH 2 (9.45 $\text{kJ}\cdot\text{mol}^{-1}$), which indicates adsorption dominated by a small number of highly energetic sites under acidic conditions. At neutral and alkaline pH, significantly lower b_t values ($\sim 2 \text{ kJ}\cdot\text{mol}^{-1}$) were obtained, confirming that adsorption is governed predominantly by weak physical interactions. The Temkin constant A followed the same trend, reflecting a much stronger initial affinity at low pH.

Table 1. Isotherm parameters for methylene blue adsorption onto TBCP at different pH values.

pH	Langmuir	Temkin	Freundlich	ΔG° (kJ·mol ⁻¹)
2	$q_{\max} = 4.37 \text{ mgg}^{-1}$ $K_L = 1.30 \text{ Lmg}^{-1}$ $R^2 = 0.962$	$A = 2.48 \times 10^5 \text{ Lmg}^{-1}$ $b_T = 9.45 \text{ kJmol}^{-1}$ $R^2 = 0.99$	$K_F = 3.36 (\text{mgg}^{-1})(\text{Lmg}^{-1})^{1/n}$ $n = 15.13$ $R^2 = 0.99$	-32.07
7	$q_{\max} = 7.71 \text{ mgg}^{-1}$ $K_L = 0.38 \text{ Lmg}^{-1}$ $R^2 = 0.977$	$A = 12.52 \text{ Lmg}^{-1}$ $b_T = 2.17 \text{ kJmol}^{-1}$ $R^2 = 0.97$	$K_F = 2.73 (\text{mgg}^{-1})(\text{Lmg}^{-1})^{1/n}$ $n = 3.91$ $R^2 = 0.94$	-29.06
11	$q_{\max} = 20.65 \text{ mgg}^{-1}$ $K_L = 0.12 \text{ Lmg}^{-1}$ $R^2 = 0.974$	$A = 7.12 \text{ Lmg}^{-1}$ $b_T = 2.05 \text{ kJmol}^{-1}$ $R^2 = 0.99$	$K_F = 3.57 (\text{mgg}^{-1})(\text{Lmg}^{-1})^{1/n}$ $n = 6.00$ $R^2 = 0.97$	-26.33

Table 2. Maximum adsorption capacities ($q_{\max}$) for methylene blue on biomass-derived carbon materials.

Material	Experimental condition	$q_{\max}$	Reference
Melia azedarach fruit-derived biochar	Pyrolysis under N_2 (700 °C, 1 h); acid washing (0.1 mol L ⁻¹ HCl); drying at 105 °C; sieved < 74 µm	11,11 mgg ⁻¹ pH = 4.6 T = 20°C	[18]
Rice husk-derived activated carbon (benchmark)	Pyrolysis under N_2 (450 °C, 1 h); chemical activation (ZnCl ₂ , 650 °C, 2 h); HCl washing; drying at 110 °C; sieved ~150 µm	9.83 mgg ⁻¹ T = 30 °C	[19]
Caryocar brasiliense (pequi) almond-derived biochar	Pyrolysis under inert atmosphere at 500 °C; no chemical activation; ground and sieved	42.7 mgg ⁻¹ pH ≈ 7 T = 25 °C	[20]
Torrefied barley straw	Torrefaction at 200–240 °C for 20–60 min under controlled atmosphere	11.6 mgg ⁻¹	[21]
Cagaita pulp-derived thermally treated	Torrefaction at 250 °C, 1 h, air; washed to 50 µS cm ⁻¹	20.65 mgg ⁻¹ pH = 11 T = 25°C	(<i>this study</i>)

3.4 Thermodynamic analysis

The thermodynamic study was conducted at pH 7, since under alkaline conditions methylene blue may undergo degradation at elevated temperatures. Figure 5 shows the variation of the standard Gibbs free energy change (ΔG°) as a function of temperature for methylene blue adsorption. The thermodynamic parameters were determined using the Gibbs–Helmholtz relationship (Eq. 7):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{Eq. 7})$$

where T is the absolute temperature (K). Linear regression of ΔG° versus temperature yielded a standard enthalpy change of $\Delta H^\circ = +5.30 \pm 3.30 \text{ kJ mol}^{-1}$ and a standard entropy change of $\Delta S^\circ = +110.6 \pm 10.6 \text{ J mol}^{-1} \text{ K}^{-1}$.

The positive value of ΔH° indicates that the adsorption process is endothermic, although the relatively low enthalpy change suggests that the process is governed mainly by weak physical interactions. The positive ΔS° reflects an increase in interfacial disorder during adsorption, which can be attributed to the release of water molecules from the adsorbent surface and from the hydration shell of methylene blue molecules. The negative ΔG° values observed over the investigated temperature range confirm the spontaneous nature of the adsorption process, with spontaneity being increasingly favored at higher temperatures due to the dominant entropic contribution.

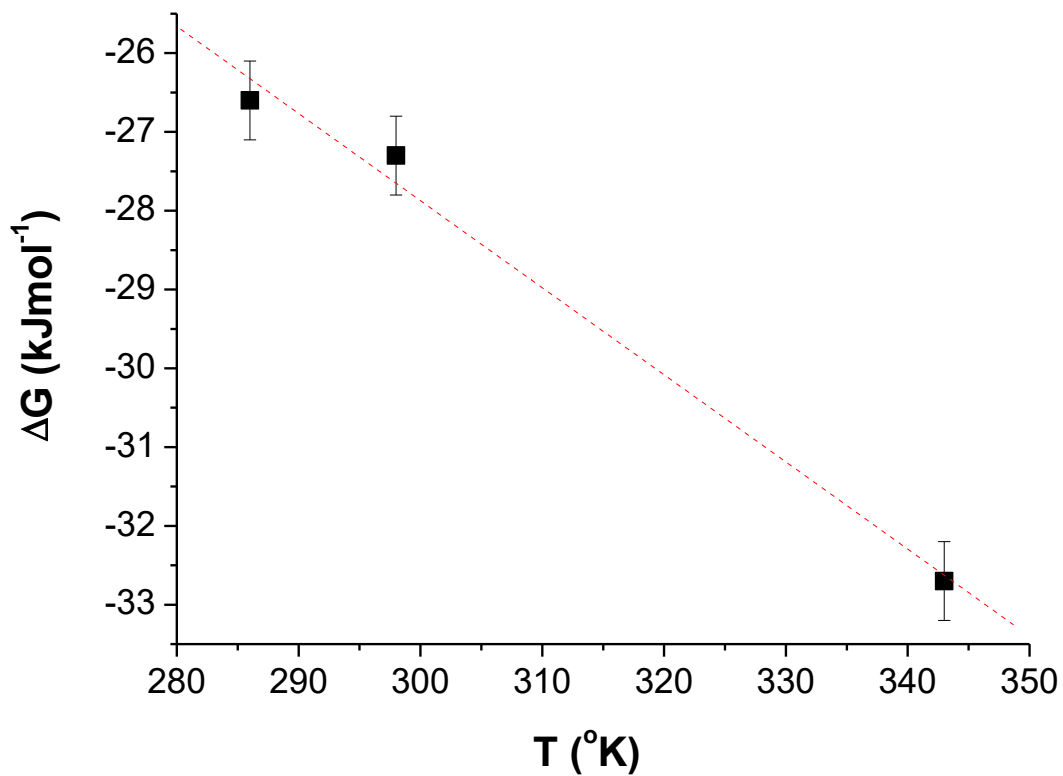


Figure 5 .Temperature dependence of ΔG° for methylene blue adsorption at pH 7 on on TBCP.

Figure 6 presents a schematic illustration of the main mechanisms involved in the adsorption of methylene blue (MB^+) onto TBCP under different pH conditions. Under alkaline conditions ($\text{pH} = 11$), the surface carboxylic groups of TBCP are predominantly deprotonated ($-\text{COO}^-$), favoring electrostatic attraction between the negatively charged surface and the cationic dye MB^+ , which represents the dominant adsorption mechanism under these conditions.

In contrast, under acidic conditions ($\text{pH} = 2$), protonation of the carboxylic groups ($-\text{COOH}$) significantly weakens electrostatic interactions. In this case, methylene blue adsorption is mainly governed by π - π stacking interactions

between the aromatic system of the dye and the carbonaceous matrix of TBCP, as well as by hydrogen bonding interactions of the π -H type, involving surface oxygen-containing functional groups. Overall, the figure highlights the pH-dependent shift in the adsorption mechanism, with electrostatic interactions prevailing in alkaline media and π - π stacking and hydrogen bonding dominating under acidic conditions.

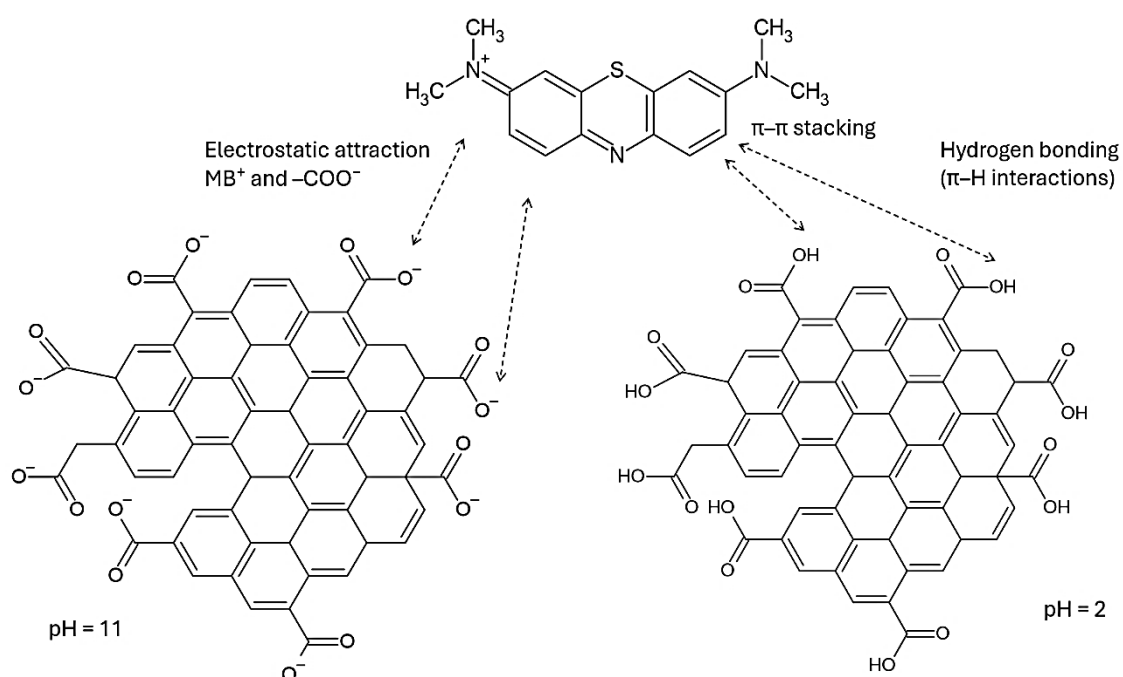


Figure 6. Schematic representation of the adsorption mechanisms of methylene blue (MB⁺) onto TBCP at different pH conditions, highlighting electrostatic attraction at pH 11 and π - π stacking and hydrogen bonding interactions at pH 2.

3.5. Adsorption kinetics of methylene blue

To describe the adsorption kinetics of methylene blue onto TBCP, the experimental data were fitted using the pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich kinetic models, which are commonly applied to heterogeneous adsorption systems.

The pseudo-first-order (PFO) model is expressed as Eq. 8, where q_t (mg g⁻¹) is the amount of adsorbed dye at time t , q_e (mg g⁻¹) is the equilibrium adsorption capacity, and k_1 (min⁻¹) is the PFO rate constant. The pseudo-second-order (PSO) model is given by Eq. 9, where k_2 (g mg⁻¹ min⁻¹) is the PSO rate constant.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (Eq. 8)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (Eq. 9)$$

The Elovich model, typically associated with adsorption on energetically heterogeneous surfaces, is described by (Eq. 10), where a (mg g⁻¹ min⁻¹) represents the initial adsorption rate and b (g mg⁻¹) is related to the extent of surface heterogeneity and activation energy for adsorption.

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (Eq. 10)$$

Figure 7 shows the adsorption kinetics of methylene blue onto TBCP at different pH values using an initial dye concentration of 100 mg L^{-1} . A pronounced dependence of both adsorption rate and adsorption capacity on solution pH is observed. For clarity, only the pseudo-first-order (PFO) kinetic model is presented in the figure, as it provides the most consistent overall description of the experimental kinetic data across the investigated pH range. The suitability of the PFO model is supported by its high correlation coefficients and its ability to capture the pH-dependent trends in adsorption rate and equilibrium uptake (Table 4). The fitting results obtained using the Elovich and pseudo-second-order (PSO) models, which provide additional mechanistic insights into surface heterogeneity and adsorption rate-controlling steps, are summarized in Tables 3 and 5, respectively.

In the Elovich model at pH 2, the low value of a combined with a high b value indicates slow initial adsorption on a highly heterogeneous surface, consistent with adsorption governed by π – π interactions and hydrogen bonding. At neutral pH, the increase in a and the decrease in b suggest a partial reduction in surface heterogeneity and the coexistence of multiple interaction mechanisms. In contrast, at pH 11, the very high a value and the poorer Elovich fit indicate that adsorption is no longer controlled by surface heterogeneity, but rather by strong electrostatic attraction, rendering the Elovich model less representative under alkaline conditions.

In addition to the Elovich model, the adsorption kinetics were also analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO) models. Under alkaline conditions (pH 11), the PFO model provided an excellent fit to the experimental data ($R^2 = 1.000$), reflecting fast adsorption kinetics dominated by

electrostatic attraction between methylene blue and the deprotonated TBCP surface. At neutral pH (pH 7), both PFO and PSO models yielded high correlation coefficients, indicating a mixed kinetic regime. In contrast, at acidic pH (pH 2), the lower rate constants and weaker fits of PFO and PSO compared to Elovich suggest that adsorption is not governed by a single rate-limiting step, but rather by adsorption on energetically heterogeneous sites.

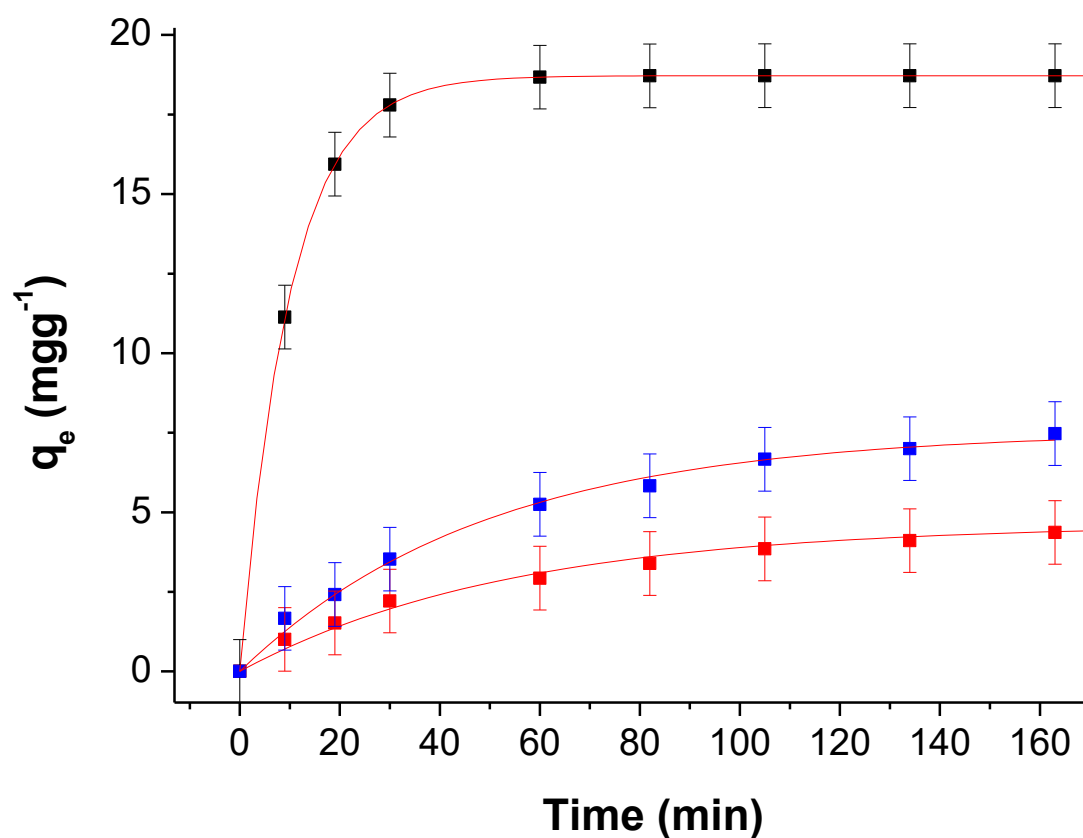


Figure 7. Adsorption kinetics of methylene blue onto TBCP at different pH values (2, 7, and 11) using an initial dye concentration of 100 mgL⁻¹. Solid lines represent the pseudo-first-order (PFO) model fits to the experimental data.

Table 3. Elovich kinetic parameters for methylene blue adsorption onto TBCP at different pH values using an initial MB concentration of 100 mg L⁻¹.

pH	a (mg g ⁻¹ min ⁻¹)	b (g mg ⁻¹)	R ²
2	0.1496 ± 0.0078	0.6385 ± 0.0198	0.998
7	0.2333 ± 0.0183	0.3497 ± 0.0194	0.997
11	226.26 ± 376.29	0.510 ± 0.106	0.956

Table 4. Elovich kinetic parameters for methylene blue adsorption onto TBCP at different pH values using an initial MB concentration of 100 mg L⁻¹.

pH	q _e (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²
2	4.62 ± 0.14	0.0185 ± 0.0018	0.986
7	7.55 ± 0.20	0.0203 ± 0.0015	0.995
11	18.72	0.1004	1.000

Table 5. Elovich kinetic parameters for methylene blue adsorption onto TBCP at different pH values using an initial MB concentration of 100 mg L⁻¹.

pH	q _e (mg g ⁻¹)	k ₂ (gmg ⁻¹ min ⁻¹)	R ²
2	5.84 ± 0.16	0.00316 ± 0.00034	0.996

7	9.91 ± 0.27	0.00186 ± 0.00018	0.998
11	19.72 ± 0.32	0.00928 ± 0.00138	0.988

4. Conclusion

Torrefied biomass derived from cagaita (*Eugenia dysenterica*) pulp (TBCP), produced at 250 °C for 1 h under air, proved to be an effective low-cost adsorbent for methylene blue removal from aqueous solutions. The maximum adsorption capacity reached 20.65 mg g⁻¹ at pH 11, which is comparable to or higher than several biomass-derived carbons prepared under more energy-intensive conditions.

Adsorption was strongly pH-dependent, increasing from 4.37 mg g⁻¹ at pH 2 to 20.65 mg g⁻¹ at pH 11, reflecting the key role of surface deprotonation and electrostatic attraction under alkaline conditions. Thermodynamic analysis at pH 7 revealed a spontaneous ($\Delta G^\circ < 0$) and endothermic process ($\Delta H^\circ = +5.30$ kJ mol⁻¹), driven mainly by entropy gain ($\Delta S^\circ = +110.6$ J mol⁻¹ K⁻¹), consistent with physisorption.

Kinetic studies showed fast adsorption under alkaline conditions, with excellent agreement with the pseudo-first-order model ($R^2 = 1.000$ at pH 11), while Elovich analysis highlighted the role of surface heterogeneity under acidic and neutral conditions.

Overall, the results demonstrate that mild torrefaction is sufficient to produce an efficient carbonaceous adsorbent, combining low processing severity, competitive adsorption capacity, and favorable kinetic and thermodynamic

behavior, reinforcing the potential of cagaita pulp residues for sustainable wastewater treatment applications.

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