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Effect of Washing Temperature on Adsorption of Cationic Dyes by Raw Lignocellulosic Biomass

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Abstract: This study evaluated the potential of using raw *Maclura pomifera* and wild carob for the treatment of methylene blue (MB) and crystal violet (CV) as part of the search for new, abundant, and cost-effective natural materials applicable for wastewater treatment. Additionally, it explored the impact of washing water temperature on the adsorption performance of these raw organic materials. The physicochemical properties of the materials were characterized using BET, SEM/EDS, and FTIR analyses. The effects of various experimental parameters were investigated through batch adsorption experiments. The results demonstrated that the influence of washing water temperature was material-dependent. For *Maclura pomifera*, the maximum adsorption capacity of methylene blue and crystal violet decreased from 134.4 and 136.6 mg g⁻¹ for MPC to 67.1 and 90.5 mg g⁻¹ for MPH. In contrast, the adsorption capacities of wild carob biosorbents remained consistent, with the maximum amounts adsorbed for methylene blue and crystal violet by CC, CW, and CH being close, around 78.8 and 98.9 mg g⁻¹, respectively, indicating a minimal effect of washing temperature on this material. The adsorption of both dyes onto the adsorbents was positively affected by increasing the pH, contact time, and initial dye concentration and was negatively affected by increasing adsorbent dose or ionic strength. Adsorption isotherms and kinetics were modeled using various mathematical approaches. The kinetic data were accurately described by a pseudo-second-order model, with a significant contribution from intraparticle diffusion. The Sips and Redlich–Peterson models provided the best fit for the adsorption isotherms of both dyes on the biosorbents. These findings confirm that the selected biomaterials are excellent adsorbents for the removal of cationic dyes.

Keywords: biosorption; *Maclura pomifera*; wild carob; treatment; wastewater; methylene blue; crystal violet



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1. Introduction

Water is essential for the survival of humanity, as well as for all animal and plant species on Earth, and it is vital for the overall health of the environment. Indeed, all biological processes in the biosphere depend on the availability of water, and no other liquid can fulfill its role [1]. The rapid growth in population, along with increased urbanization, industrialization, and intensified agricultural practices, has led to a substantial rise in water consumption. This trend has also been accompanied by a corresponding increase in agricultural, industrial, and household waste, which contains detergents, cleaning agents,

and other contaminants, leading to the infiltration of harmful substances into groundwater reserves [2].

Dyes are among the pollutants that can pose serious problems. Most of dyes are synthetic, and they now represent a large group of chemical compounds [3]. The global production of synthetic dyes is estimated at 800,000 tonnes per year. Approximately 120,000 tonnes of these dyes are released annually during the fabric manufacturing and dyeing stages [4]. These compounds are known to be toxic, mainly due to their complex structures, non-biodegradability, and high molecular weight, which make them resistant to destruction by certain physico-chemical treatment methods [5–9]. Dyes cause short-term hazards such as eutrophication, under-oxygenation, color, turbidity, and odor, as well as long-term hazards including persistence, bioaccumulation, and diseases [2,10,11].

The treatment of water polluted by dyes has, therefore, become a priority in our modern world. Developing methods and optimizing existing processes to be both effective and inexpensive have been the focus of many studies [12]. Among the pollution control processes, adsorption remains a relatively common technique that is highly effective and easy to implement [13–15]. Commercial activated carbon is the most widely used adsorbent due to its high adsorption capacity, but it is expensive and requires regeneration [16–18]. Recently, significant research has been conducted to test adsorption on alternative natural materials, known as replacement materials. These natural materials are advantageous due to their biodegradability, low commercial value, non-toxic nature, and renewable origin [19–21].

Previous work has examined the feasibility of pollutant removal using a variety of biosorbents in their raw state, such as *orange peels* [22], *pine cones* [10], *cockle shells* [20,23], *artichoke leaves* [24], *Huai Flos chrysanthemum* [25], *sago waste* [26], and cones of *Pinus brutia* [27]. Other research has aimed to improve the retention capacity of these biosorbents through chemical treatments, for example, *coconut shells* [28] and *cupressus sempervirens* treated with sulfuric acid [16]; *Maclura pomifera* [2] and *durian leaves* [29] treated with sodium hydroxide; *bamboo* treated with sodium carbonate [30]; and *Sargassum* sp. treated with hydrochloric acid [31]. Additionally, some research has focused on the synthesis of activated carbon from economic precursors, such as chitosan-based carbons [32], *olive-stone*-based activated carbon [33], *wild-carob*-based activated carbon [6], and activated carbon prepared from *date stones*.

However, none of the previous studies have examined the impact of the wash water temperature on biosorbents used in their raw state—a parameter that could influence their performance. The washing conditions vary from one study to another without clear justification: some researchers have used hot water [34–36], while others have preferred water at room temperature [22,25,26].

In this study, we focused on valorizing two abundant solid wastes, wild carob and *Maclura pomifera*, by simultaneously examining the effect of washing water temperature (cold, warm, or hot) on the adsorption performance of these raw biosorbents for the removal of two cationic dyes, methylene blue and crystal violet, from aqueous solutions.

The physico-chemical properties of the biosorbents were characterized using a variety of techniques, including BET, SEM/EDS, FTIR, ATG, pH at zero charge, and surface function analysis using the Boehm method [37,38]. The impact of experimental parameters such as pH, contact time, initial dye concentration, adsorbent mass, ionic strength, and temperature was studied using a batch adsorption technique. Adsorption mechanisms were analyzed using three kinetic models (pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion models), and four theoretical isotherm models (Langmuir, Freundlich, Sips, and Redlich–Peterson) were tested to determine the most appropriate model for dye adsorption.

2. Materials and Methods

2.1. Preparation of the Biosorbents

To conduct various characterization and adsorption experiments, substantial quantities of wild carob (*Ceratonia siliqua*) and *Maclura pomifera* (Osage orange) were collected in Setif. The raw materials were washed with tap water to remove impurities, particularly soil sludge. They were then dried using solar energy in an oven at temperatures between 70 and 80 °C to prevent any alteration in the physico-chemical properties of the materials. After cooling, the materials were ground.

To demonstrate the effect of wash water temperature on the adsorption capacity of raw organic materials, wild carob and *Maclura pomifera* were washed under agitation with either cold distilled water at a room temperature of 60 °C or brought to boiling (100 °C). This washing process was repeated several times until the residual water was as clear as possible. The biomasses were then dried in an oven at 60 °C, ground, and sieved to retain the fraction between 250 and 500 µm. The powdered biomaterials were stored in hermetically sealed plastic containers and were used for analysis as well as for adsorption experiments.

Names of Materials Prepared

The materials prepared were as follows:

- CC: Carob washed in cold water;
- CW: Carob washed with warm water (60 °C);
- CH: Carob washed in hot water (100 °C);
- MPC: *Maclura pomifera* washed in cold water;
- MPW: *Maclura pomifera* washed in warm water;
- MPH: *Maclura pomifera* washed in hot water.

2.2. Characterization of the Biosorbents

The specific surface area and the various parameters of the porous structure were determined using a Micromeritics ASAP 2020 instrument (Micromeritics Inc., Norcross, GA, USA). The measurement was based on the physical adsorption of nitrogen on 100 mg of each material sample to be characterized, previously degassed under vacuum at 170 °C for 14 h, as well as on the thermodynamic characteristics of this phenomenon. The specific surface area (S_{BET}) was calculated using the BET equation, while the pore size distribution was determined using the density functional theory (DFT) method. The total pore volume (V_{tot}) was estimated as the liquid volume of nitrogen adsorbed at a relative pressure of 0.95. The micropore volume (V_{mic}), micropore surface area (S_{mic}), and external surface area (S_{ext}) were estimated using the t-plot method. The mean pore diameter (D_p) and adsorption energy (E_0) were determined by applying the Dubinin–Radushkevich model to the adsorption isotherm. Morphological and elemental analyses of the samples were carried out using an FEI Nova Nano SEM 450 SEM (Nova Nano SEM 450-FEG—source: FEI—Thermo Fisher Scientific, Hillsboro, OR, USA) equipped with an EDX detector (Quantax-200 system with X Flash 6/10 Si-drift detector: Bruker Corp., Billerica, MA, USA), by dispersing the adsorbent powder on a carbon adhesive pellet placed on a sample support. The surface functional groups of the samples were analyzed using a FTIR spectrometer (Cary 600; Agilent Technologies, Santa Clara, CA, USA) in a scanning range from 4000 to 400 cm^{-1} . Determination of total surface acidity and total surface basicity was performed using the Boehm method, which corresponds to the acid–base titration of surface functional groups. To determine the pH_{pzc} of the materials studied, distilled water was adjusted with HCl (0.1 M) or NaOH (0.1 M) to successive initial values between 2 and 11. The other parameters were kept constant (1 g L^{-1} of biosorbent, a stirring speed of 250 rpm, at room temperature (23 ± 2 °C) for 24 h).

2.3. Experimental Adsorption Protocol

The adsorption of the dyes, methylene blue (MB) and crystal violet (CV), on the different studied biosorbents was carried out in a batch process. A mass of 25 mg of

each adsorbent sample was suspended in 25 mL solutions of MB or CV at a well-defined initial concentration (25, 50, 100, 150, and 200 mg L⁻¹). The series of closed Erlenmeyer flasks (Jenway, Camlab, Cambridge, UK) was placed on a multi-stage stirring plate at room temperature at a speed of 250 rpm. The influence of initial pH on the adsorption of both dyes was studied by varying the pH between 2 and 11, with all other process parameters kept constant. The pH adjustments were made by adding small amounts of NaOH or HCl (0.1 M). The effect of the adsorbent dosage was investigated by varying the adsorbent-to-sorbate ratio between 0.25 and 2 g L⁻¹. Additionally, the impact of ionic strength on dye adsorption was assessed using NaCl solutions with concentrations ranging from 0 to 0.50 M. For the kinetic experiments, adsorption measurements were taken at specified time intervals (5, 10, 15, 20 min, etc.). In all other cases, a contact time of 24 h was applied to ensure that equilibrium was reached. After each adsorption experiment, the adsorbent was separated by centrifugation.

The initial and residual dye concentrations were analyzed using spectrophotometry at 665 nm for MB and 590 nm for CV. The quantity adsorbed was calculated using the following formula:

$$Q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

Q_t is the quantity adsorbed at time t (mg/g), C_0 is the initial concentration of the dye solution (mg/L), C_t is the concentration of the dye solution at time t (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g)

The quantity adsorbed can also be quantified by the removal yield (R). The dye removal yield is defined by

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

2.4. Kinetic and Isotherm Studies

Several kinetic models were employed to interpret the experimental data, providing essential information for the use of different materials in the field of adsorption. Our results were analyzed using three widely used models: pseudo-first-order [39], pseudo-second-order [40], and intraparticle diffusion [41] models. The main equations for these models are

$$Q_t = Q_e(1 - e^{-K_1 t}) \quad (3)$$

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t} \quad (4)$$

$$Q_t = K_{int} t^{0.5} + C \quad (5)$$

Q_e is the equilibrium adsorption capacity (mg g⁻¹); K_1 (min⁻¹), K_2 (g mg⁻¹ min⁻¹), and K_{int} (mg g⁻¹ min^{-0.5}) are the rate constants of the pseudo-first order, pseudo-second order, and intraparticle diffusion models, respectively. The value of C gives an idea of the thickness of the boundary layer.

To elucidate the retention mechanism and identify the isotherm that best represents the adsorption of MB and CV on different biosorbents, four theoretical models were tested on the experimental results: Langmuir [42], Freundlich [43], Sips [44], and Redlich–Peterson [45]. The equilibrium equations for these models are as follows:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

$$Q_e = \frac{Q_m (K_s C_e)^{m_s}}{1 + (K_s C_e)^{m_s}} \quad (8)$$

$$Q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \quad (9)$$

Q_m (mg g^{-1}) represents the maximum adsorbable quantity, K_L (L mg^{-1}) is the Langmuir equilibrium constant, and K_F (L g^{-1}) and n denote the adsorption capacity and intensity according to the Freundlich isotherm, respectively. K_S (L mg^{-1}) is the Sips constant; and K_R (L g^{-1}), α_R (L mg^{-1}), and β are the parameters of the Redlich–Peterson model.

2.5. Thermodynamic Analysis Methods

The calculation of certain thermodynamic parameters, such as the variation in the standard enthalpy of adsorption (ΔH°) (J mol^{-1}), the variation in entropy (ΔS°) ($\text{J mol}^{-1} \text{K}^{-1}$), and the variation in the standard free enthalpy (ΔG°) (J mol^{-1}), is essential in determining the nature of the elimination process. These parameters can be calculated using the following equations [16]:

$$\Delta G^\circ = -RT \ln(\rho K_C) \quad (10)$$

$$\ln(\rho K_C) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

$$K_C = \frac{Q_e}{C_e} \quad (12)$$

R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), K_C is the thermodynamic equilibrium constant (L g^{-1}), and ρ is the water density (g L^{-1}).

3. Results and Discussion

3.1. Characterization of Materials

3.1.1. Physical Characterization

Characterization by Gas Adsorption–Desorption

The nitrogen adsorption isotherms at 77 K for different biomasses (CC, CW, CH, MPC, MPW, and MPH) are shown in Figure 1, and the pore properties are detailed in Table 1. The adsorption and desorption isotherms for the various raw biosorbents changed gradually as the temperature of the wash water decreased for both materials. All biomasses exhibited type V isotherms, according to the IUPAC classification [46,47], which are characteristic of mesoporous adsorbents. These isotherms indicate low adsorbate/adsorbent interaction and the formation of multilayers at low pressure. For *Maclura pomifera*, the adsorption curves show that the volume of nitrogen adsorbed was significantly greater than that of wild carob, suggesting that *Maclura pomifera* has a more developed structure. This is confirmed by the results presented in Table 1, which show the significant differences in the textural properties of the two biosorbents.

Table 1. Textural characteristics of raw biosorbents by nitrogen gas adsorption.

Biomass	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{Mic} ($\text{m}^2 \text{g}^{-1}$)	S_{Ext} ($\text{m}^2 \text{g}^{-1}$)	V_{tot} (ccg^{-1})	V_{mic} (ccg^{-1})	$V_{\text{mic}}/V_{\text{tot}}$ (%)	D_p (nm)	E_0 (kJ mol^{-1})
MPC	237.3	166.2	71.1	0.347	0.089	24.42	6.13	4.25
MPW	234.0	157.0	77	0.332	0.081	34.37	6.35	4.10
MPH	182.4	129.8	52.6	0.215	0.074	28.60	6.34	4.10
CC	79.4	61.2	18.2	0.103	0.029	28.15	5.95	4.37
CW	46.2	32.6	13.6	0.069	0.018	26.12	6.19	4.20
CH	38.0	26.7	11.3	0.061	0.017	28.07	5.31	4.90

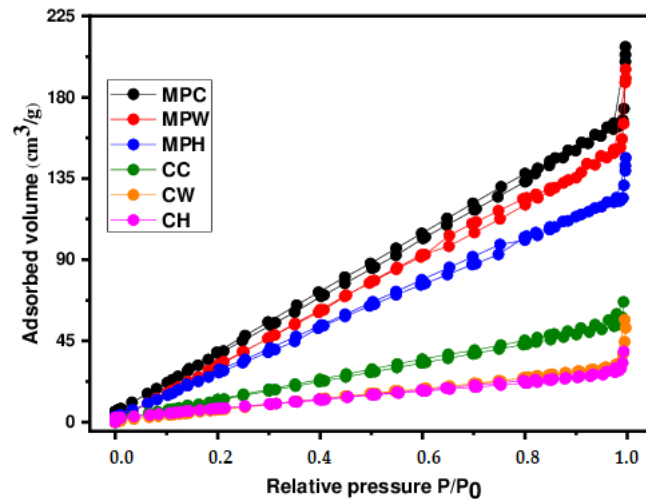


Figure 1. N₂ physisorption isotherms of raw biosorbents.

The results in Table 1 reveal considerable variability in the specific surface areas and associated pore volumes of the samples examined. The adsorbents derived from *Maclura pomifera* (MPC, MPW, and MPH) were more porous than those from carob (CC, CW, and CH). Notably, the temperature of the wash water negatively impacted the porosity of the biosorbents. This was likely due to structural degradation at higher temperatures. The data also confirmed the presence of highly developed mesoporosity in the different studied materials. The adsorption energy (E_0) was comparable across the different examined samples.

The BET specific surface area of our materials is significantly higher than that of many other biosorbents. Examples include pine cones [10], cockle shells [20], pine bark [48], and crab shell [49], which have specific surface areas of 55.8, 50.95, 26, and 13.4 m² g^{−1}, respectively.

Characterization by Scanning Electron Microscopy (SEM)

The microscopic scans of MPC, MPH, CC, and CH are shown in Figure 2, Figure 3, Figure 4, and Figure 5, respectively. Figures 4 and 5 show that, at different magnifications, wild carob possesses a conductive vessel structure perfectly wound into a cylindrical spring. Conversely, the SEM images of MPC and MPH display a smoother morphology, a relatively heterogeneous surface, and the presence of cavities. Observation of the pore structure indicated that washing with hot water affected the structure of the biosorbents. However, it should be noted that the obtained images show merely the surface cavities and the external openings of the macropores.

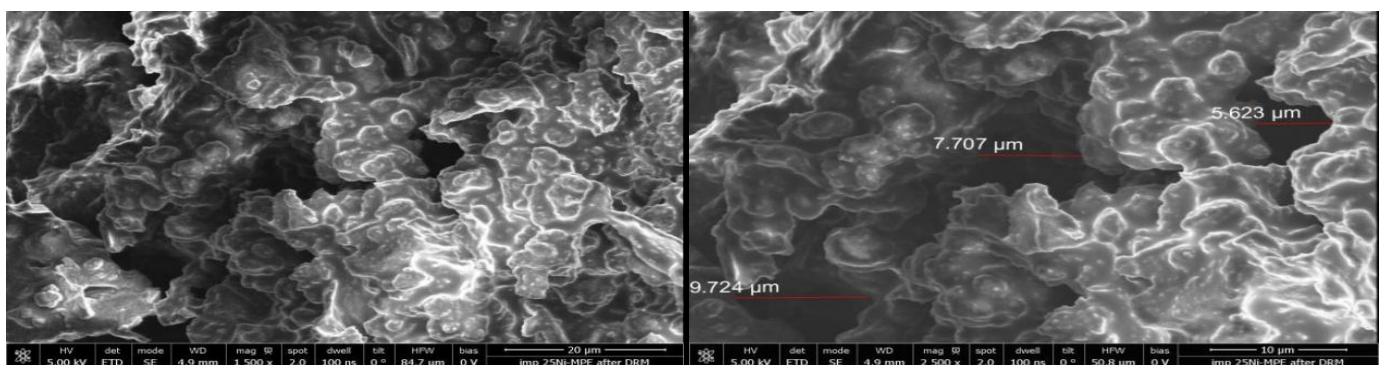


Figure 2. SEM image of MPC.

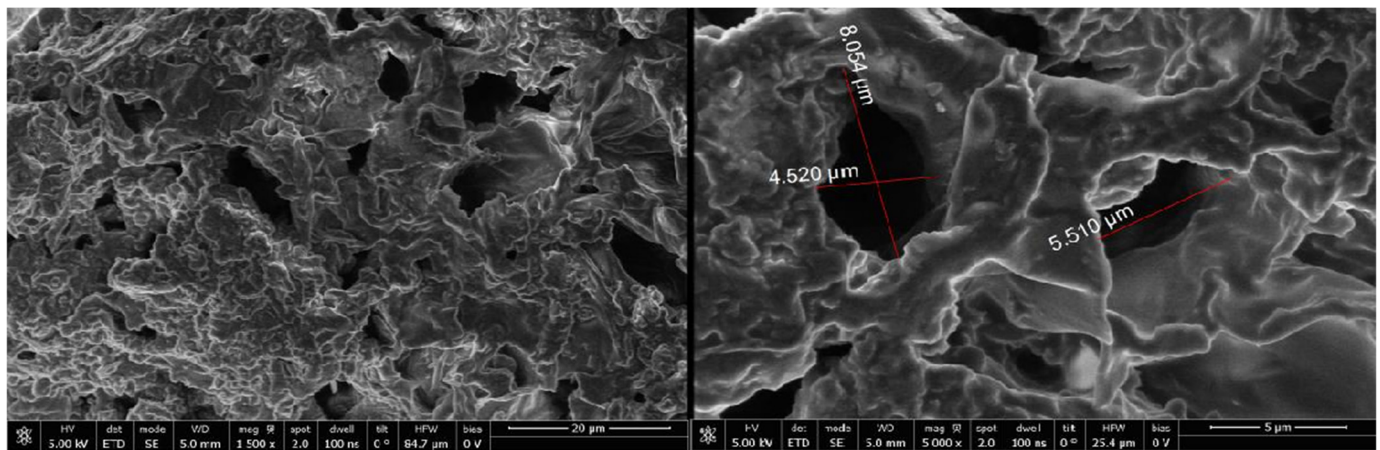


Figure 3. SEM image of the MPH.

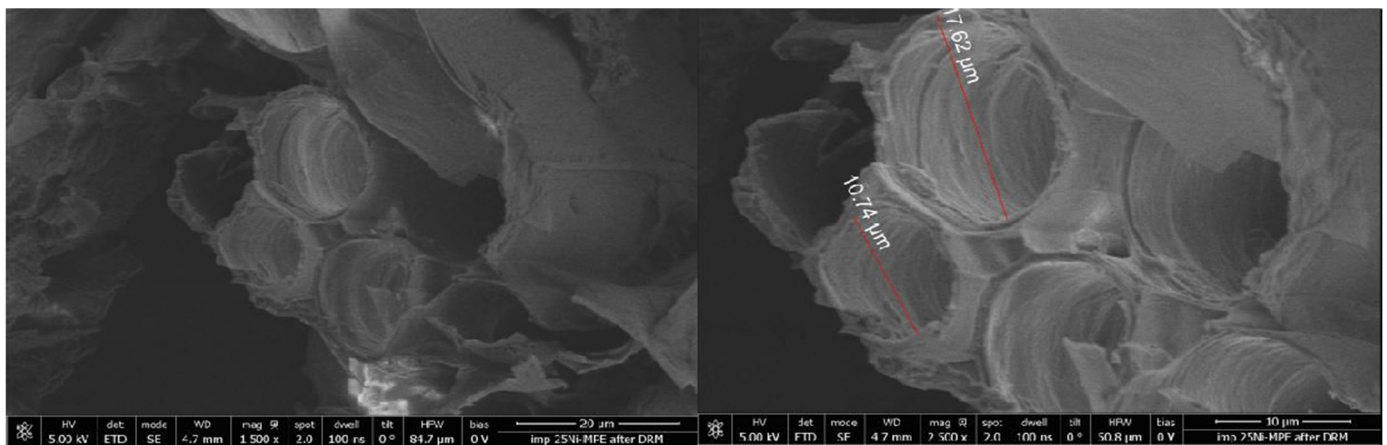


Figure 4. SEM image of CC.

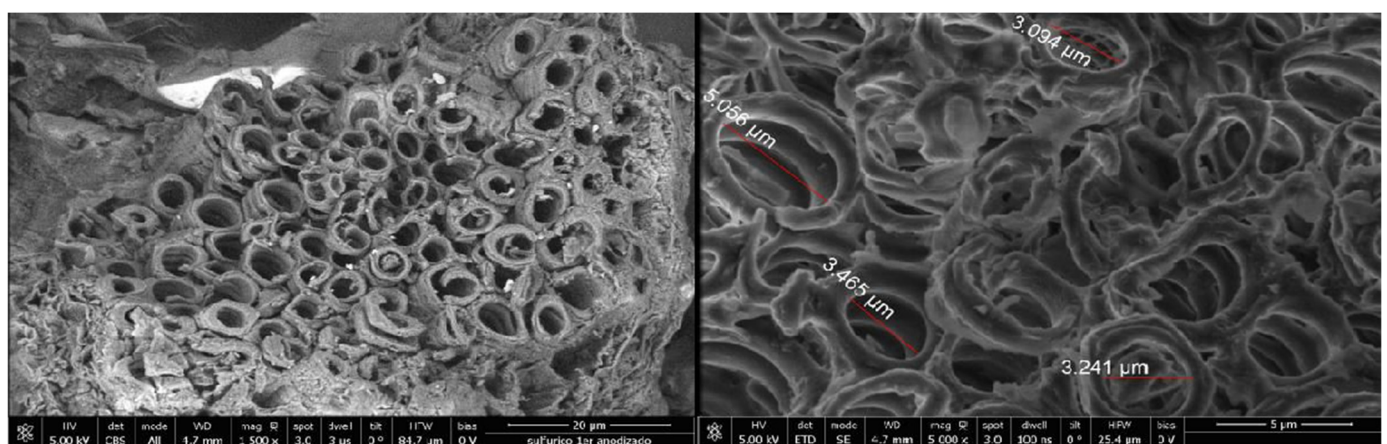


Figure 5. SEM image of CH.

3.1.2. Chemical Characterization

Elemental Analysis of the Materials

Table 2 presents the elemental composition of *Maclura pomifera* and wild carob washed with cold and hot water. These results show that the elemental composition of the adsorbents is typical of lignocellulosic material and is consistent with the findings often cited by other authors [50–52]. However, it should be noted that MPH and CH contain a higher proportion of carbon and a lower content of heteroatoms. This can be explained by the

elimination of soluble impurities at high temperatures. Various consequences may result from this change in the elemental composition of biosorbents, particularly in relation to their behavior in aqueous solution, such as the drop in the acidity of MPH and CH resulting from the reduction in oxygen content [53].

Table 2. Elemental composition of raw biosorbents.

Sample	Elemental Analysis (% by Mass)									
	C	O	Ca	S	Si	K	Al	N	Mg	P
MPC	45.4	40.2	1.5	1.0	-	0.9	4.1	5.2	0.7	1.0
MPH	62.4	36.1	0.6	0.4	-	-	0.5	-	-	-
CC	40.4	48.1	8.9	0.5	0.4	0.8	0.9	-	-	-
CH	52.6	47.2	-	0.2	-	-	-	-	-	-

pH at Zero Charge Point

The obtained pH_{PZC} values (Table 3) allowed for determining the acidic or basic nature of an adsorbent and, depending on the pH of the solution, its net surface charge [54–56].

Figure 6 shows a family of curves, indicating that all the supports had an acidic surface that decreased as the temperature of the wash water increased. These results are consistent with the previous findings from the elemental analysis.

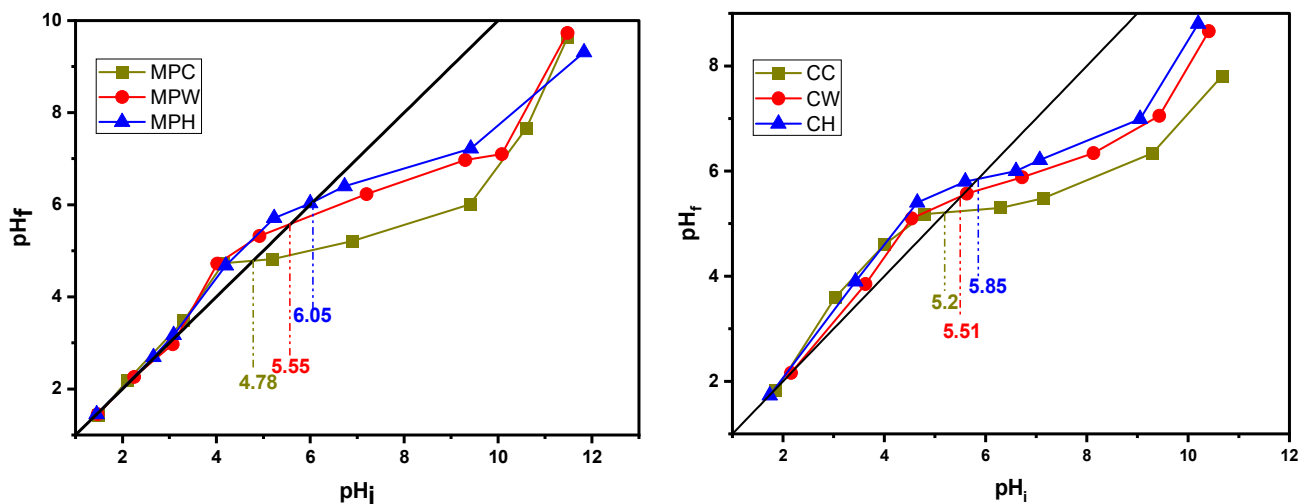


Figure 6. Isoelectric points of raw adsorbents ($m = 25$ mg, $V = 25$ mL, stirring speed = 250 rpm, and $t = 24$ h).

Table 3. Isoelectric points of raw adsorbents.

Adsorbent	MPC	MPW	MPH	CC	CW	CH
pH_{PZC}	4.78	5.55	6.05	5.20	5.51	5.85

Analysis of Surface Functions by the Boehm Method

The Boehm titration results (Table 4) revealed that all the materials had fewer basic groups compared to acidic groups, confirming their acidic nature. The surface chemistry of both materials was influenced by the temperature of the wash water. Specifically, there was decreases in both total acidity and total basicity, resulting in a reduction in the surface functional groups. The data indicate that the wild carob variety was acidic, though to a lesser extent than *Maclura pomifera*, with more acidic sites, suggesting a higher presence of oxygenated groups. These groups enhance the adsorption of cationic dyes. The findings are consistent with those reported in the literature [57].

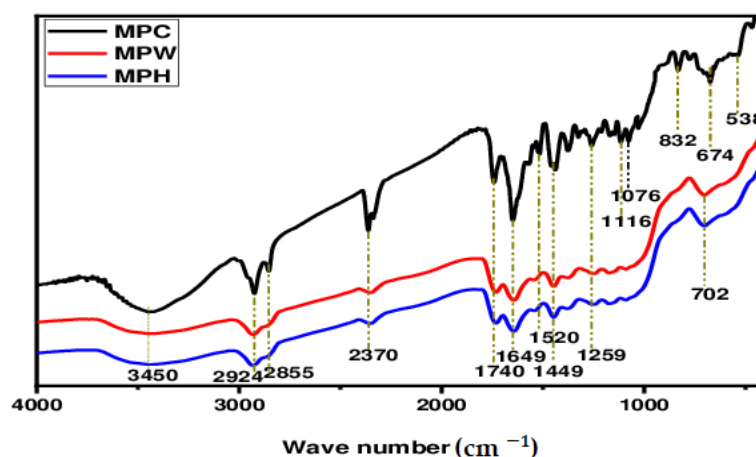
Table 4. Surface function content of raw samples.

Sample	MPC	MPW	MPH	CC	CW	CH
Total acidity (mmol g ⁻¹)	6.45	6.12	5.37	3.02	2.97	2.71
Total basicity (mmol g ⁻¹)	2.21	2.12	2.08	2.62	2.54	2.57

Analysis of Surface Functions by Fourier Transform Infrared Spectroscopy (FTIR)

To achieve a more comprehensive identification of the surface functions of the raw biosorbents and to highlight the impact of the wash water temperature on their surface chemistry, infrared spectroscopy was employed. The spectra for the materials washed with cold, warm, and hot water are presented in Figures 7 and 8. Table 5 summarizes the characteristic functional groups on the surfaces of the raw materials, including their nature and wavelength. From Figures 7 and 8, the following can be observed:

- The infrared spectra exhibit a similar peak distribution for both *Maclura pomifera* (MP) and wild carob (C) varieties.
- The spectra indicate that the active surface functional groups for both types of biosorbents are primarily -OH bonds from polymers and polysaccharides, as well as -CH₂ and -COOH bonds, which are known to play a significant role in dye adsorption.
- The spectra for each variety are nearly identical, with the primary difference being the relative intensity of the peaks.
- The intensities of the bands corresponding to O-H hydroxyl group vibrations (~3428 cm⁻¹) and C=O elongation vibrations (1740, 1649, and 1628 cm⁻¹) decrease with increasing wash water temperature for both materials. This trend aligns with the reduction in the acidity observed in the pH_{pzc} measurements and Boehm titrations. This decrease may be attributed to the breaking of certain chemical bonds at higher temperatures or to structural damage, which can limit the accessibility of specific surface chemical functions.

**Figure 7.** FTIR spectra of MPC, MPW, and MPH.

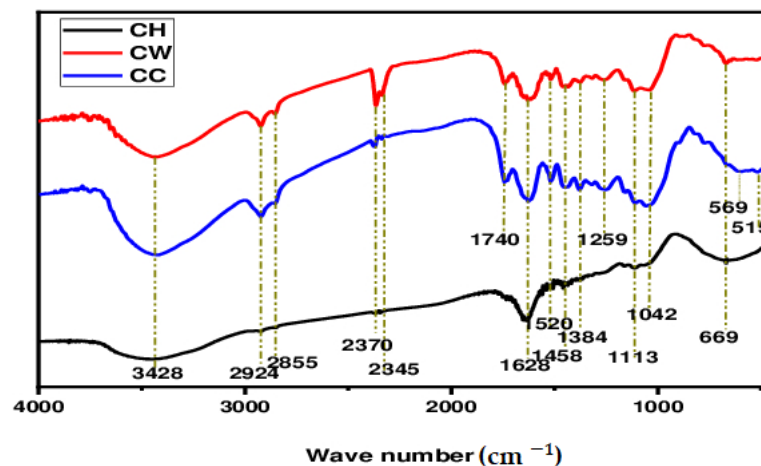


Figure 8. FTIR spectra of CC, CW, and CH.

Table 5. Surface functions of raw materials identified by infrared spectroscopy.

Wave Number (cm ⁻¹)						FTIR Interpretation		
In This Study						In the Bibliography	Type of Vibration	References
MPC	MPW	MPH	CC	CW	CH			
3450	3450	3450	3428	3428	3428	3600–3300	Elongation vibrations of O-H hydroxyl groups (carboxylic acids, alcohols, phenols, cellulose, pectin, absorbed water, and lignin)	[58–60]
2924 2855	2924 2855	2924 2855	2924 2855	2924 2855	2924 2855	2920 2850	Asymmetrical and symmetrical C-haliphatic elongation vibration	[61]
2370	2370	2370	2370 2345	2370 2345	2370 2345	2350 2339	Elongation vibrations of the C≡C bond of the alkyne group	[62,63]
40	1740	1740	1740	1740	-	1743.5	C=O elongation vibrations (ketones, aldehydes, lactones, or carboxyl groups)	[64]
1649	1649	1649	-	-	-	1637	C=O elongation vibrations in cyclic amides	[65]
-	-	-	1628	1628	1628	1637–1606	Symmetric and asymmetric C=O elongation vibration in ionic carboxylic groups (COO-)	[51]
1520	1520	1520	1520	1520	1520	1600–1500	Elongation vibrations of C=C bonds in condensed aromatic rings	[66]
1449	1449	1449	1458	1458	1458	1458	Elongation vibrations of C=O in ether	[67]
-	-	-	1384	1384	1384	1384	Deformation vibrations of CH ₃ bond	[68]
1259, 1116, 1076	1259	1259	1259, 1113, 1042	1259, 1113, 1042	1113 1042	1350–900	C-O bond elongation vibrations in alcohols, phenols, acids, ethers, or esters	[59,60]
832,674	702	702	-	669	669	858–615	Deformation vibrations of C harmonics	[69]
538	-	-	569,515	-	-	500–600	Vibration of aromatic rings	[69]

3.2. Results of Methylene Blue and Crystal Violet Adsorption on Raw Materials

3.2.1. The Effect of Various Physico-Chemical Parameters

The Effect of pH

pH is an important factor in adsorption studies, as it can affect the structures of both the adsorbent and the adsorbate, as well as the adsorption mechanism. Therefore, it is crucial to know the adsorption efficiency at different pH values. The variation in the adsorption capacity of methylene blue (MB) and crystal violet (CV) by *Maclura pomifera* and wild carob is shown in Figures 9 and 10, respectively. The data presented in these figures indicate that the evolution of MB and CV adsorption with pH for the two varieties (MP and C) is very similar. The change in the surface charge was the main factor controlling the adsorption of MB and CV. It is noted that, for all six materials, there was a clear improvement in the adsorption capacity of the dyes with increasing pH, which then became substantially constant. Similar behavior has been observed in numerous studies [70–72]. This can be explained by the fact that when the pH is higher than the pH_{pzc}, the surface of the biosorbents is negatively charged, and the molecules of cationic dyes (MB and CV)

are positively charged [73]. Adsorption can be envisaged by the electrostatic interactions between the different charges of the adsorbents and dyes. At low pH, the sorbent surface is surrounded by H^+ ions, which reduce the interaction of the dye cations with the adsorbent sites. Conversely, at high pH, the H^+ concentration decreases, resulting in good interaction between the dye ions and the surface sites. Furthermore, the interaction of surface functional groups at varying pH values can be more complex than mere electrostatic attraction. This involves surface complexation, where pH influences adsorption through complexation reactions, shifting their equilibrium and altering adsorption efficiency. Additionally, variations in pH can modify the biosorbent's structure, affecting its porosity, surface area, and the accessibility of adsorption sites, thereby influencing adsorption mechanisms beyond electrostatic attraction.

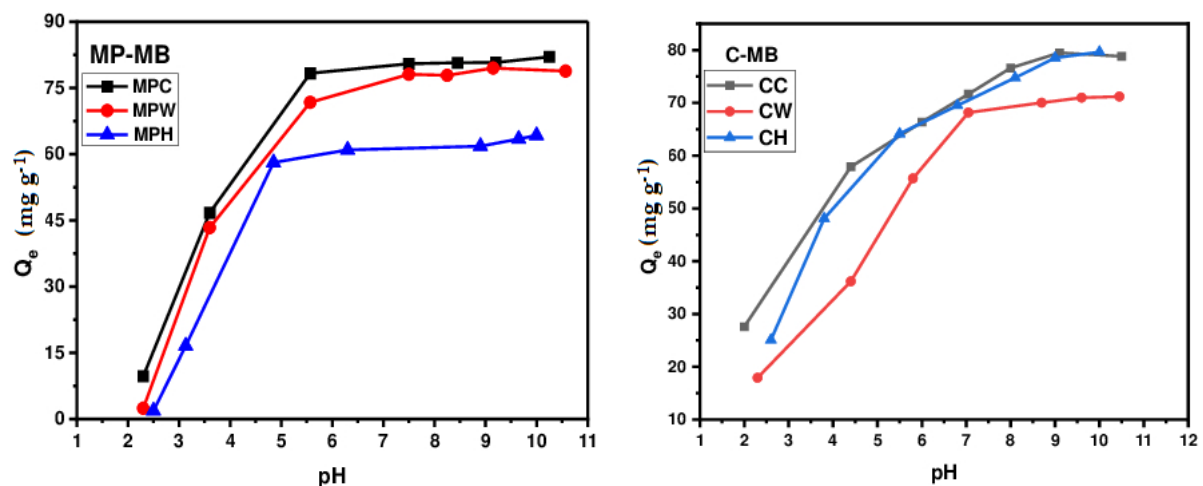


Figure 9. The effect of initial pH on the adsorption capacity of MB on *Maclura pomifera* and wild carob. $C_0 = 100\ mg\ L^{-1}$, $T = 23 \pm 2\ ^\circ C$, $V = 250\ rpm$, $r = 1\ g\ L^{-1}$.

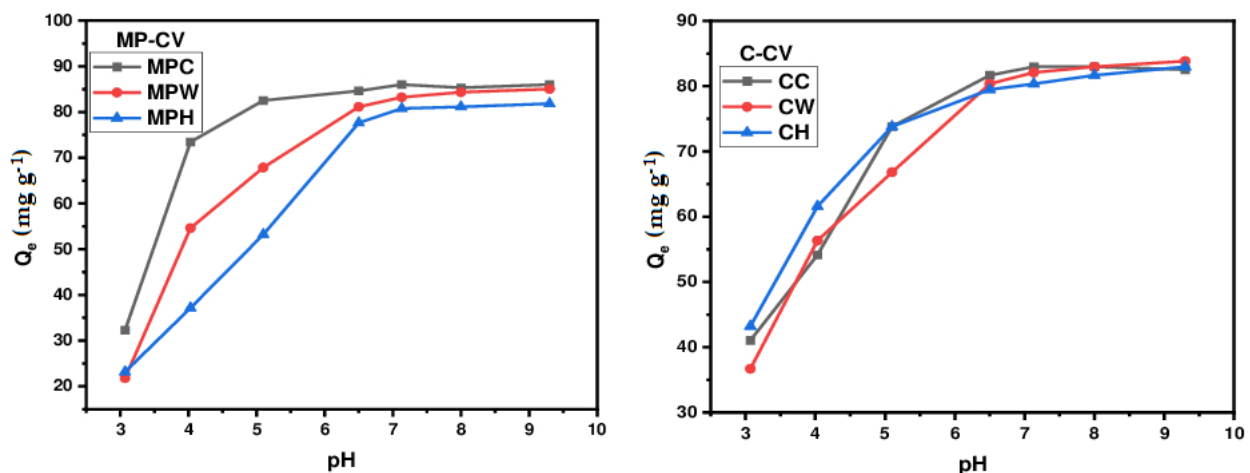


Figure 10. The effect of initial pH on the adsorption capacity of CV on *Maclura pomifera* and wild carob. $C_0 = 100\ mg\ L^{-1}$, $T = 23 \pm 2\ ^\circ C$, $V = 250\ rpm$, $r = 1\ g\ L^{-1}$.

Effect of Contact Time and Initial Dye Concentration

To compare the performance of the raw adsorbents and highlight the effect of the wash water temperature on the adsorption capacity of the biosorbents, the results of the kinetic study of MB and CV adsorption on the raw materials are shown in Figure 11. The kinetic study revealed that the two varieties (MP and C) exhibited similar behavior, although the adsorption kinetics of *Maclura pomifera* were faster than those of wild carob. The equilibrium time was reached after 60 min of contact for MB adsorption on MP, after 120 min for CV

adsorption on MP, and after 240 min for both MB and CV adsorption on C. These differences can be attributed to the structural and chemical properties of the adsorbents. For example, *Maclura pomifera* (MPC) has a larger specific surface area ($237.3 \text{ m}^2 \text{ g}^{-1}$) than wild carob (CC) at $79.4 \text{ m}^2 \text{ g}^{-1}$. A larger specific surface area, along with more developed porosity, means that there are more active sites available, which increase the rate of adsorption. Additionally, MPC contains more acidic surface functional groups (6.45 mmol g^{-1}) than CC (3.02 mmol g^{-1}), further contributing to the faster adsorption of cationic dyes. The quantities adsorbed by MPC were slightly higher than those by CC, specifically 80.1 mg/g and 72.1 mg/g for MB and 84.9 mg/g and 81.2 mg/g for CV. The adsorption capacities of MP and C were negatively affected by the increase in wash water temperature. These results are consistent with the predictions based on the physical and chemical properties of the materials.

Figures 12 and 13 show a study of the adsorption kinetics of the raw materials washed with cold water as a function of the initial concentrations of MB and CV. These adsorption kinetics show a commonly observed behavior for the adsorption of cationic dyes. All the curves show a rapid increase in the quantity adsorbed during the initial phase of the contact time, which then slows down, with each curve approaching an asymptote parallel to the time axis. The slope at the origin is almost infinite, indicating a very high affinity between the adsorbent and the adsorbate [71]. This behavior can be explained by the abundance of available sites on the adsorbent surface at the beginning of adsorption. Most of these sites are quickly occupied, and the remaining sites become increasingly difficult to access due to the repulsive forces between the molecules adsorbed on the biosorbent surface and those in the solution. Similar observations have been reported by other researchers [70,74]. The figures also show that the adsorbed amount increased with the initial concentration of MB and CV. This common result is generally explained by the fact that a higher initial concentration increases the driving force due to the concentration gradient, thereby enhancing retention. Additionally, a high initial concentration generates a large number of collisions between the dye ions and the adsorbent surface, improving the adsorption process [75]. Similar findings have also been reported by other researchers [76]. We also noted that the equilibrium time was more quickly reached for low concentrations, as concentrated dye solutions required more contact time to reach equilibrium due to the higher number of molecules to be adsorbed.

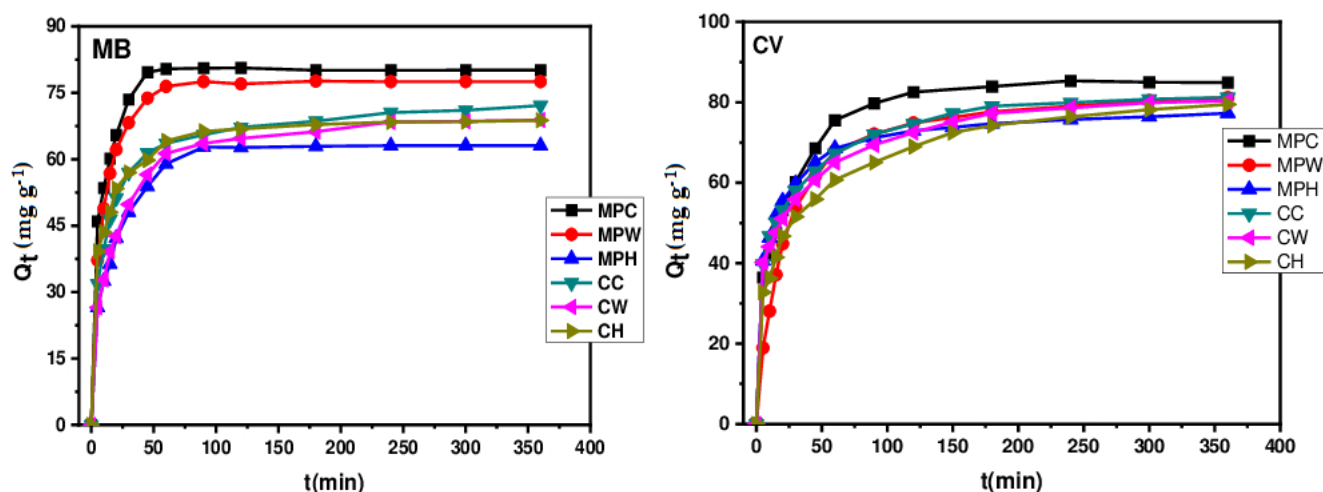


Figure 11. Adsorption kinetics of MB and CV on raw materials ($C_0 = 100 \text{ mg L}^{-1}$, natural pH, $T = 23 \pm 2 \text{ }^\circ\text{C}$, $V = 250 \text{ rpm}$, $r = 1 \text{ g L}^{-1}$).

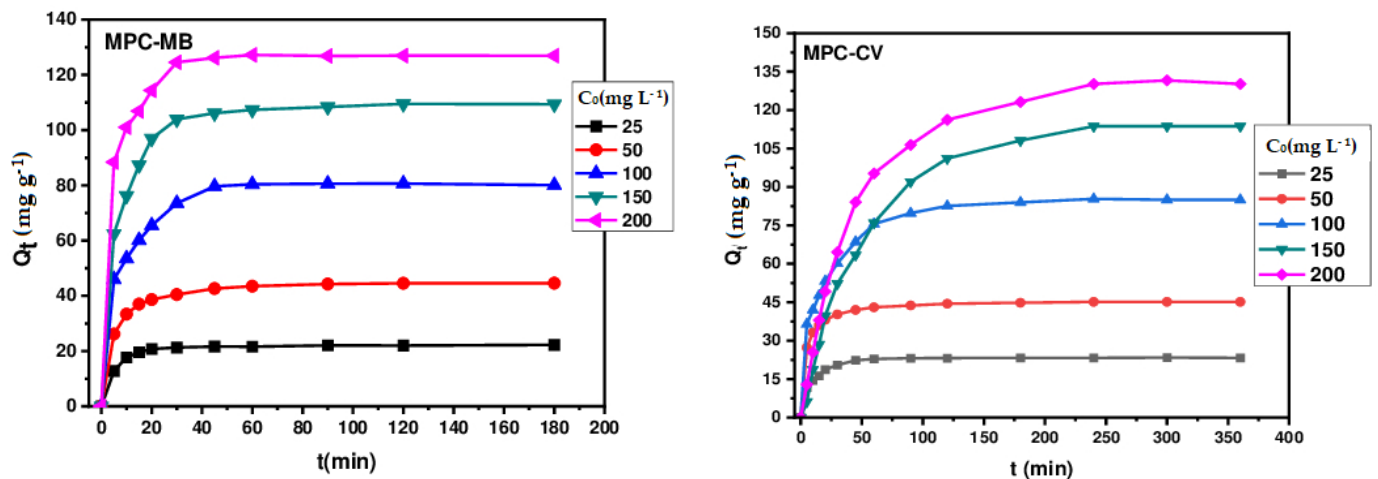


Figure 12. The effect of initial concentration on the elimination of MB and CV by MPC (natural pH, $T = 23 \pm 2$ °C, $V = 250$ rpm, $r = 1$ g L⁻¹).

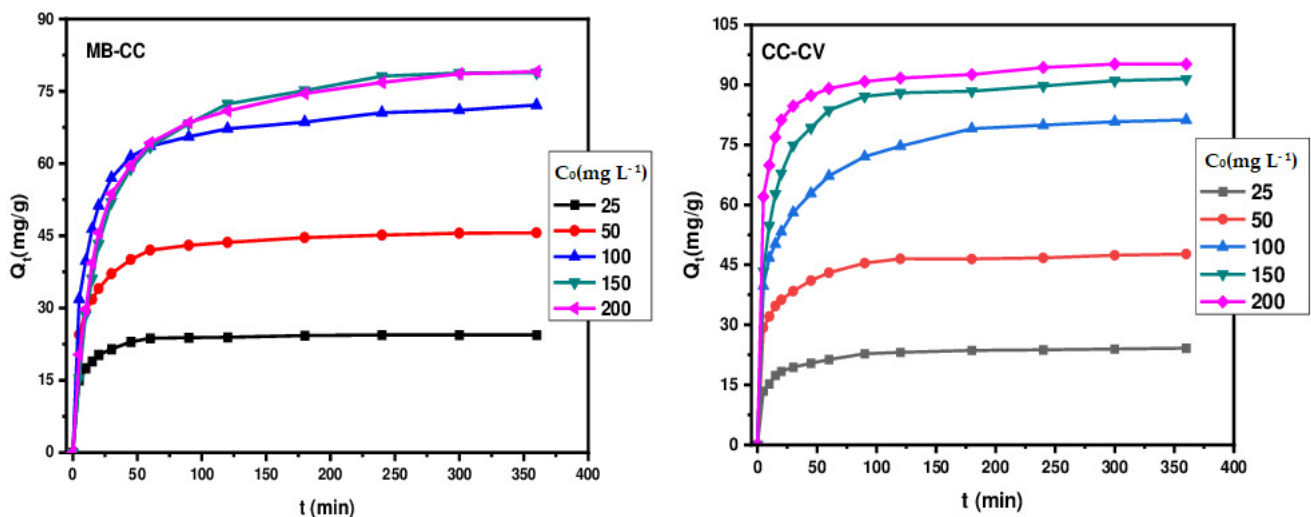


Figure 13. The effect of initial concentration on the elimination of MB and CV by CC (natural pH, $T = 23 \pm 2$ °C, $V = 250$ rpm, $r = 1$ g L⁻¹).

Effect of Adsorbent Mass

To study the influence of adsorbent mass, the solid/liquid ratio was varied, and the results are shown in Figure 14. The data indicated that the removal efficiency of MB by MPC and CC increased as the solid/liquid ratio increased. This is understandable, as increasing the biosorbent dose enhances the specific surface area and thus the number of adsorption sites [77,78], which consequently increases the amount of dye adsorbed. While the percentage of discoloration increases with a higher solid/liquid ratio, the amount adsorbed per unit mass (mg g⁻¹) decreases. Many researchers have attempted to explain this phenomenon. Vadivelan and Vasanth Kumar suggested that this decrease in Q_e is due to a split in the concentration gradient between the core of the solution and the surface of the adsorbent [79]. Ertas et al., on the other hand, attributed the decrease in the quantity adsorbed to the fact that an adsorbate particle at the same initial concentration (C_0) is shared by more adsorbent particles when the solid/liquid ratio increases. Each solid particle has fewer chances of binding the pollutant, thus reducing the adsorption capacity [80]. Another possible explanation for this phenomenon was provided by Ofomaja and Ho, who suggested that with an increase in the solid/liquid ratio, there is a possibility of particle agglomeration. This agglomeration results in a reduction in the specific surface

area of the adsorbent and the lengthening of the diffusion paths, which negatively impact the adsorption process [81].

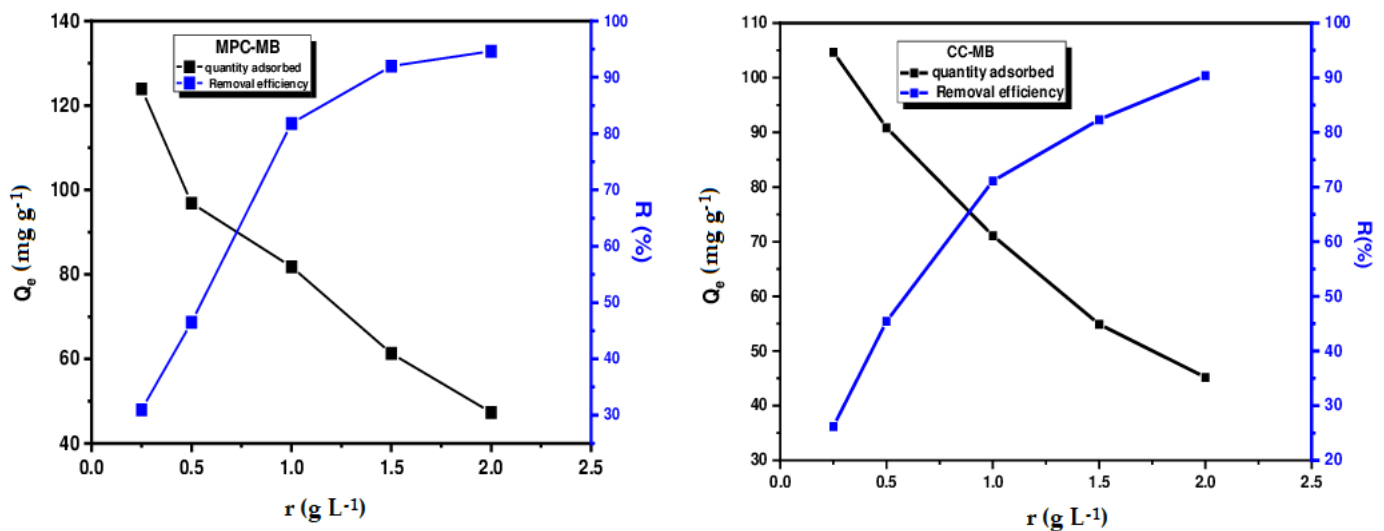


Figure 14. Effect of MPC and CC mass on MB adsorption ($C_0 = 100 \text{ mg L}^{-1}$, natural pH, $T = 23 \pm 2^\circ \text{C}$, $V = 250 \text{ rpm}$).

Effect of Ionic Strength

Textile industry waste contains numerous chemicals, including salts used in the stages preceding dyeing. The presence of these salts can significantly affect the adsorption of dyes during the treatment of such waste products. The curves in Figure 15 illustrate the impact of NaCl on the adsorption of MB by the raw materials. These curves show that for all raw materials, any increase in the quantity of dissolved salt led to a decrease in the quantity of dyes adsorbed. Newcombe and Drikas interpreted this decrease as a shielding effect caused by the salt ions against the electrostatic attraction between the negative surface of the adsorbent and the dye cations [82]. Janos et al. and Han et al. attributed this effect to competition between the dye cations and the salt cations [83,84]. Wang et al. added that the compression of the electrical double layer, caused by the increase in ionic strength, contributes to this phenomenon [85]. However, Chen et al. suggested an expansion of the electrical double layer when the ionic strength increased to explain the decrease in MB adsorption [86].

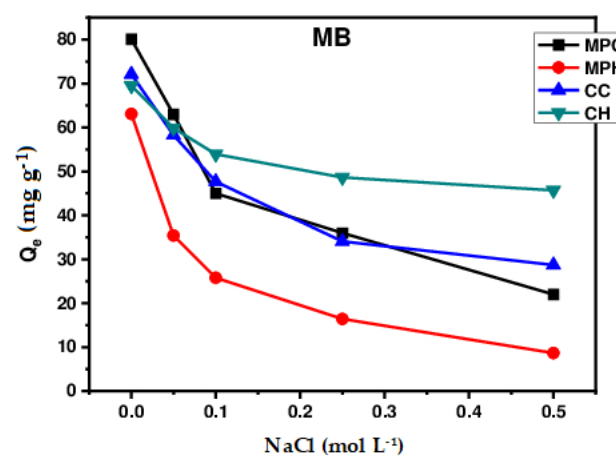


Figure 15. Effect of ionic strength on the adsorption of MB by raw materials ($C_0 = 100 \text{ mg L}^{-1}$, natural pH, $T = 23 \pm 2^\circ \text{C}$, $V = 250 \text{ rpm}$, $r = 1 \text{ g L}^{-1}$).

Effect of Temperature on the Adsorption Isotherm

The results of the adsorption isotherms for MB and CV on the raw materials are shown in Figure 16. For all the studied materials, the adsorption isotherms initially show a steeper inclination at lower concentrations, indicating the presence of many easily accessible sites [87]. Each curve eventually reaches a plateau, indicating that the sorbent is saturated at this level. This plateau can be influenced by the concentration of the biosorbent. By altering the amount of the utilized biosorbent, the number of active sites available for adsorption changes, which can affect the saturation point. According to Brunauer's classification of adsorption isotherms [46], these isotherms are of type I, demonstrating a high affinity between the dyes and the biosorbents. The maximum adsorption capacity of MB and CV varied depending on the nature of the biosorbents, being significantly higher for MPC than for CC (twice as high). The high adsorption capacity of *Maclura pomifera* (MPC) is logically linked to its developed structure and high content of basic functional groups compared to those of wild carob (CC). These characteristics enhance its ability to retain cationic dyes. Furthermore, the temperature of the wash water significantly affected the adsorption capacity of MP. The maximum adsorbed quantity of MB and CV decreased, respectively, from 133.4 and 136.6 mg g⁻¹ for MPC to 117.2 and 117.7 mg g⁻¹ for MPW and 67.1 and 90.5 mg g⁻¹ for MPH. This reduction could be attributed to the destruction of the structure or the breaking of certain chemical bonds at high temperatures. These findings are consistent with the textural and chemical properties of the materials. In contrast, the temperature of the wash water had no significant effect on the performance of the wild carob biosorbents. The maximum values of the equilibrium adsorption capacity for CC, CW, and CH were very close, indicating that the effect of wash water temperature depended on the nature of the used material.

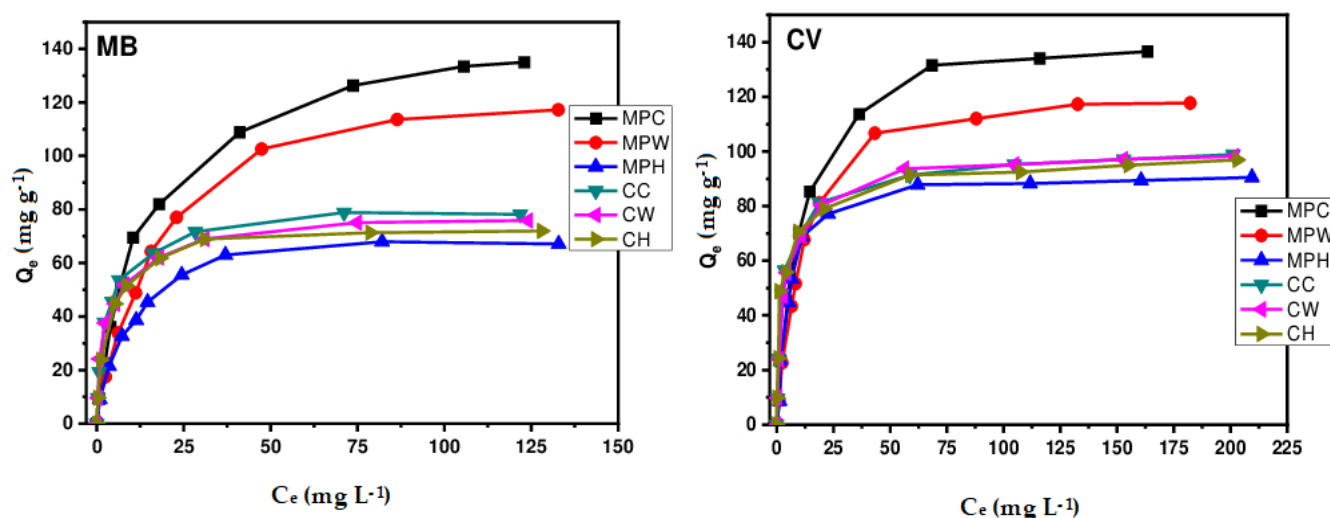


Figure 16. Adsorption isotherms for MB and CV on raw materials (natural pH, $T = 20\text{ }^{\circ}\text{C}$, $V = 250\text{ rpm}$, $r = 1\text{ g L}^{-1}$, $10 \leq C_0 \leq 300\text{ mg L}^{-1}$).

Figures 17–22 show the influence of temperature on the adsorption isotherms of MB and CV on raw MP and C. From these figures, we can see that for all the materials and for low initial concentrations, temperature had no influence on the quantity of MB and CV adsorbed. However, it did have a significant effect at high initial concentrations. Figures 17–19 show that MB and CV behaved differently. We observed that the quantity of MB adsorbed on MPC, MPW, and MPH decreased with increasing temperature, reflecting the exothermic nature of the adsorption. For CV, on the other hand, it increased with increasing temperature, in agreement with an endothermic process. Figures 20–22 show that temperature had a positive effect on the adsorption of both dyes by CC, CW, and CH. This indicated an endothermic nature of adsorption. The influence of temperature on the adsorption of cationic dyes has been examined in numerous studies, most of which noted a

positive effect of temperature on adsorption capacity [71,88,89]. This is due to the fact that increasing temperature facilitates the diffusion of adsorbate molecules through the outer boundary layer and into the pores of the adsorbent particles by reducing the viscosity of the solution [90].

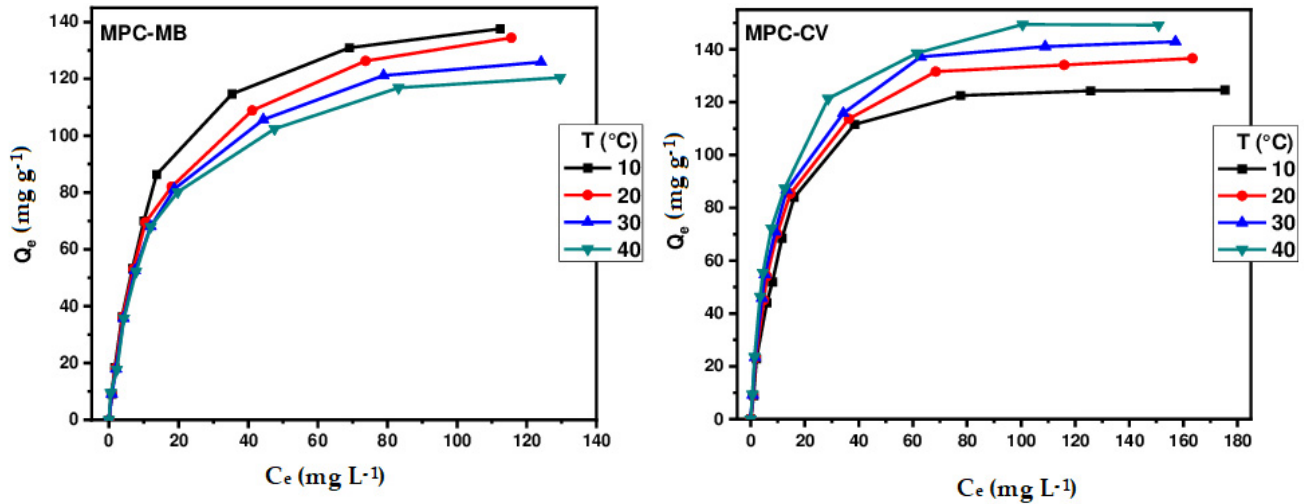


Figure 17. Adsorption isotherms for MB and CV on MPC (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

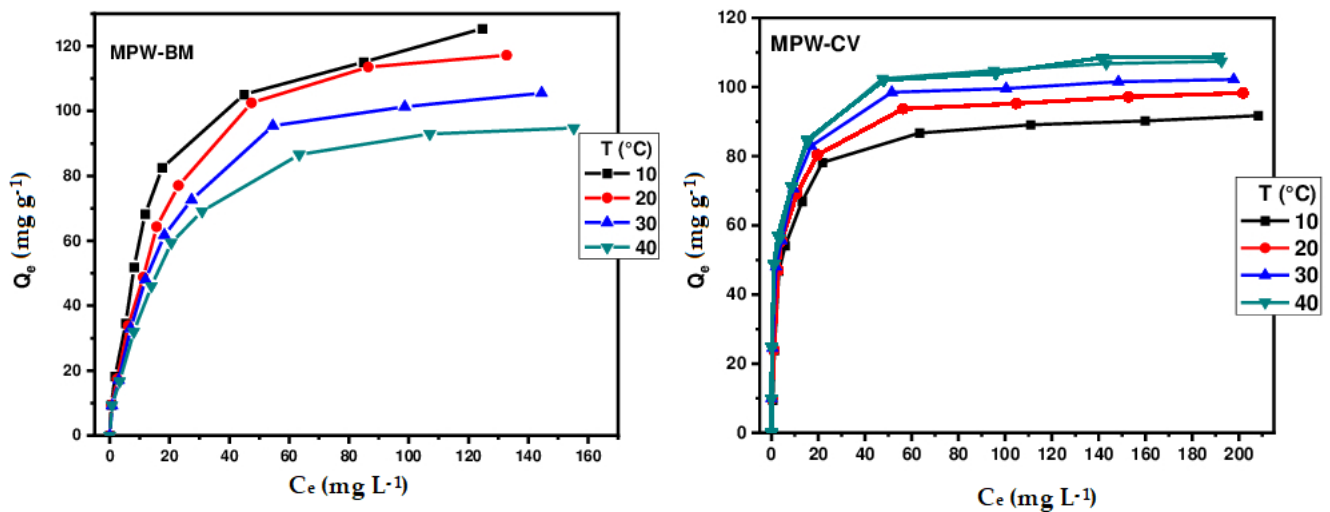


Figure 18. Adsorption isotherms for MB and CV on MPW (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

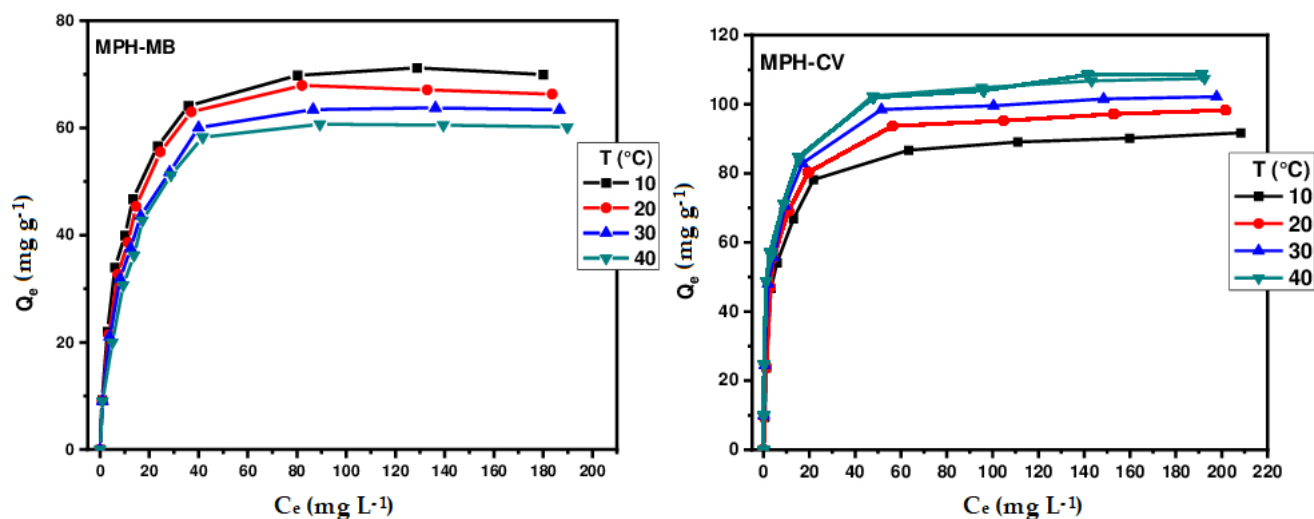


Figure 19. Adsorption isotherms for MB and CV on MPH (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

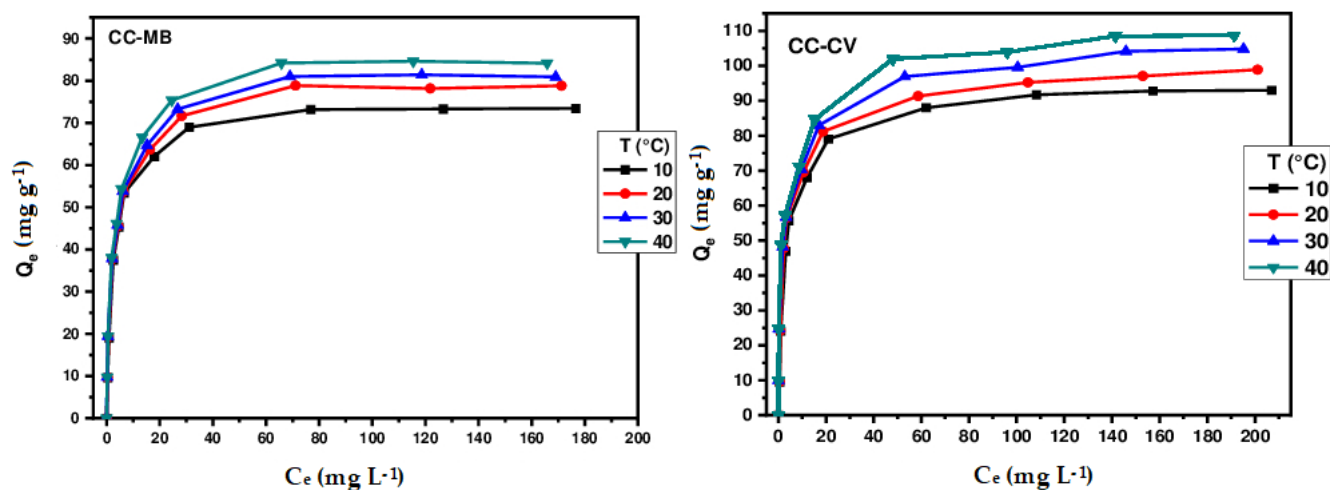


Figure 20. Adsorption isotherms for MB and CV on CC (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

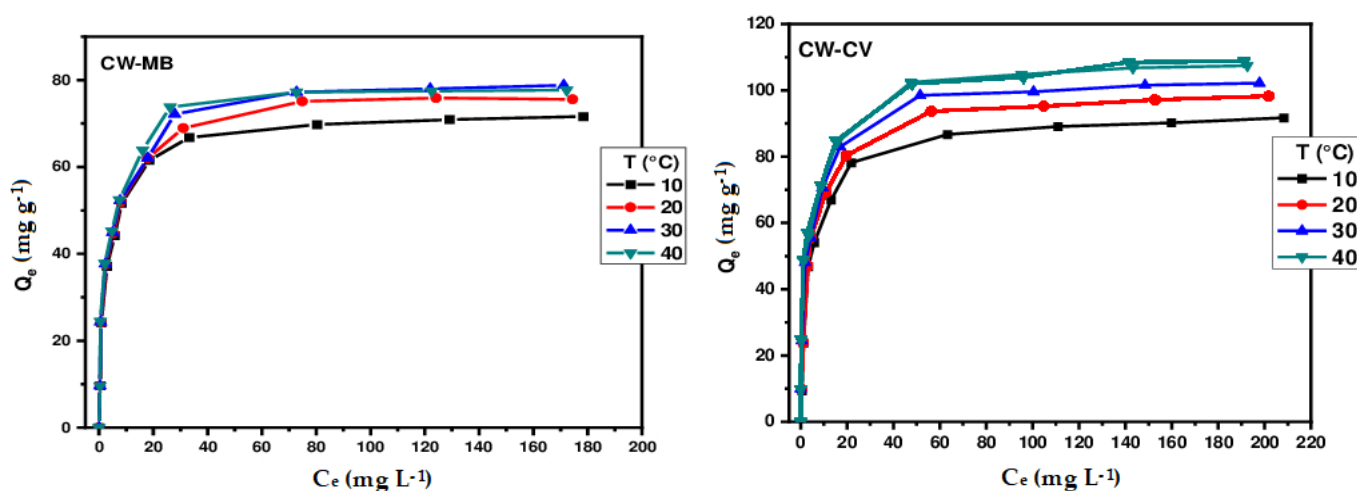


Figure 21. Adsorption isotherms for MB and CV on CW (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

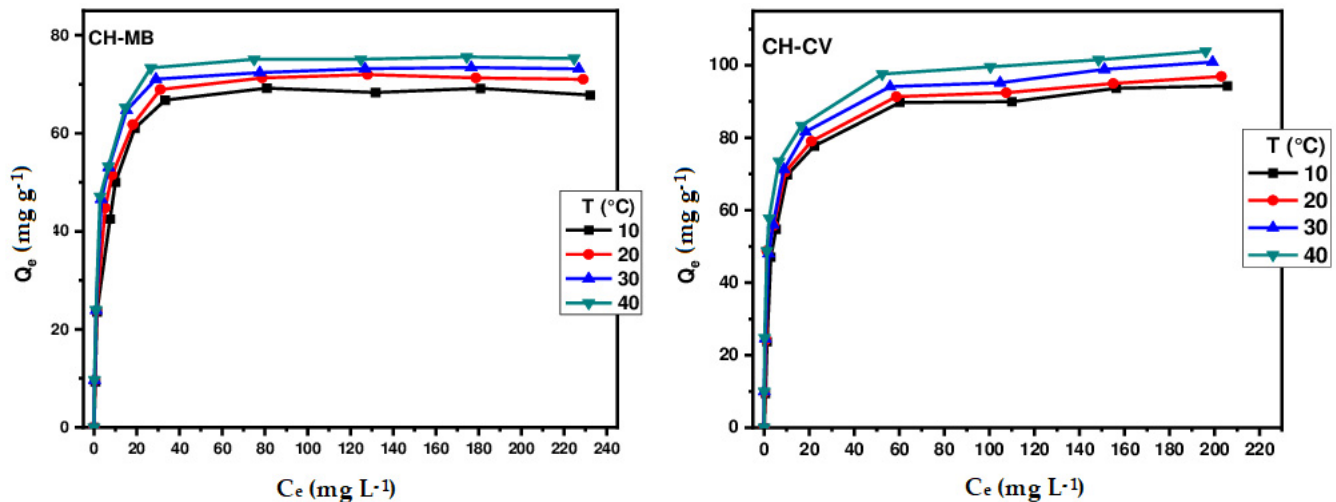


Figure 22. Adsorption isotherms for MB and CV on CH (natural pH, $V = 250$ rpm, $r = 1$ g L⁻¹, $10 \leq C_0 \leq 300$ mg L⁻¹).

3.2.2. Thermodynamic Analysis

Calculating certain thermodynamic parameters is essential for determining the nature of the retention process. The values of these parameters for the adsorption of MB and CV on raw biosorbents are presented in Table 6. The results show that the values of the variation in free enthalpy (ΔG°) were negative in all cases, indicating that the adsorption of MB and CV on the raw MP and C was spontaneous and favorable at any temperature [91].

The positive values of the standard entropy variation (ΔS°) suggest that the MB and CV molecules become less ordered at the solid/solution interface during the adsorption process [92,93]. The negative values of the standard enthalpy (ΔH°) for the adsorption of MB on MPC, MPW, and MPH confirmed that the adsorption process was exothermic and that lower temperatures favor adsorption. In contrast, for the other cases, ΔH° was positive, indicating that the adsorption process was endothermic and more favorable at higher temperatures [71]. The low absolute values of ΔH° for the different materials confirmed that the adsorbent–adsorbate interactions are physical in nature ($|\Delta H^\circ| \leq 40$ kJ mol⁻¹) [2].

Table 6. Thermodynamic parameters of MB and CV adsorption on raw materials.

Dye	Adsorbent	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				283K	293K	303K	313K
MB	MPC	−7.43	36.52	−17.76	−18.14	−18.48	−18.86
	MPW	−6.44	37.48	−17.02	−17.46	−17.80	−18.15
	MPH	−5.91	31.60	−14.86	−15.16	−15.49	−15.80
	CC	5.74	73.23	−14.97	−15.75	−16.45	−17.17
	CW	2.86	62.99	−14.95	−15.63	−16.25	−16.84
	CH	3.59	64.70	−14.71	−15.39	−16.02	−16.65
CV	MPC	9.60	95.44	−17.36	−18.42	−19.37	−20.22
	MPW	5.21	77.22	−16.64	−17.42	−18.18	−18.96
	MPH	4.76	71.77	−15.56	−16.25	−16.95	−17.73
	CC	6.04	77.32	−15.86	−16.60	−17.38	−18.18
	CW	7.61	82.55	−15.74	−16.59	−17.38	−18.23
	CH	4.64	72.08	−15.78	−16.46	−17.16	−17.95

3.2.3. Modeling Adsorption Kinetics

The nonlinear plots of the pseudo-first-order (PFO) and pseudo-second-order (PSO) models for the adsorption kinetics of MB and CV on MPC and CC are shown in Figures 23 and 24. The kinetic parameters obtained from these models are presented in Table 7. The most suitable model was evaluated based on the correlation coefficient (R^2) and the

comparison of the maximum quantity obtained from these models with the experimentally obtained values. Table 7 reveals that both adsorption kinetics models provided good fits across different concentrations, indicated by correlation coefficients (R^2) close to unity and minimal differences between the experimental equilibrium adsorption quantities ($Q_{e,exp}$) and those calculated using both models. However, the PSO model was more suitable for determining the adsorption kinetics of MB and CV on MPC and CC across the entire range of concentrations studied, as its R^2 correlation coefficients were higher than those of the PFO model.

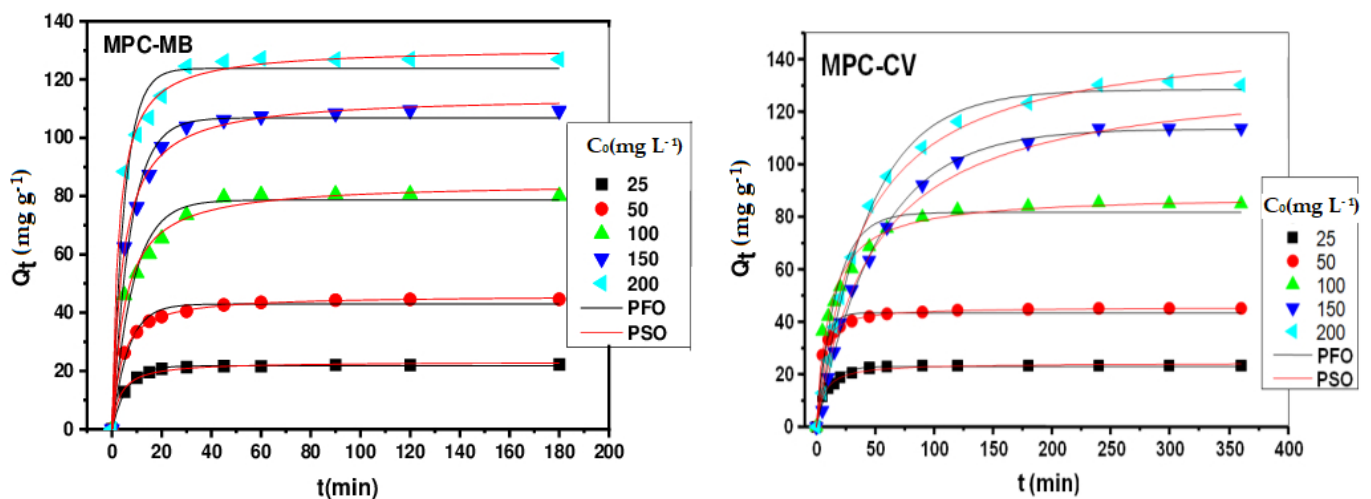


Figure 23. Nonlinear fit of the PFO and PSO models of MB and CV adsorption on MPC.

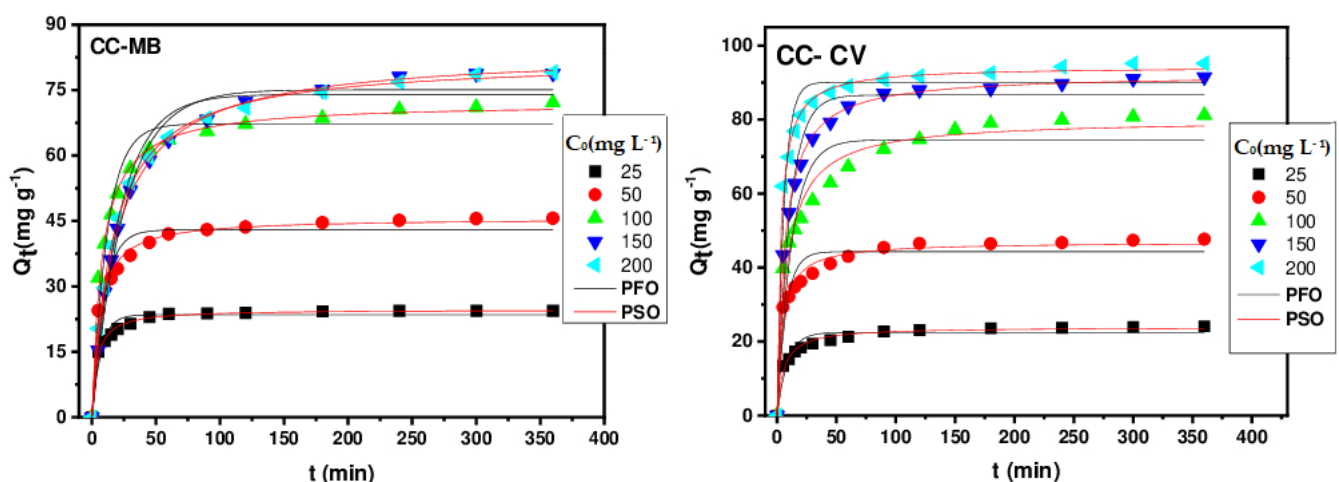


Figure 24. Nonlinear fit of the PFO and PSO models of MB and CV adsorption on CC.

The intraparticle diffusion model is commonly used to identify the mechanisms involved in adsorption. Generally, for this model to be applicable in describing adsorbate fixation phenomena, the plot of Q_t versus $t^{0.5}$ should be linear. Moreover, if this line passes through the origin, it indicates that intraparticle diffusion is solely responsible for the adsorption process, and the rate of intraparticle diffusion is the limiting step in the interaction [94]. However, in some cases, the model may exhibit a multilinear form, suggesting that the adsorption process is controlled by multiple steps [95,96]. For the adsorption of MB and CV by MPC and CC (Figures 25 and 26, respectively), two linear sections were observed, indicating that the adsorption of these dyes by the raw biosorbents is governed by two steps: the diffusion of the dyes into the solid phase, followed by an adsorption equilibrium where the actual binding occurs.

Table 7. Adsorption kinetics of MB and CV on MPC and CC.

Material	Dye	Pseudo-First-Order Model					Pseudo-Second-Order Model		
		C_0 (mg L ⁻¹)	$Q_{e.exp}$ (mg g ⁻¹)	Q_e (mg g ⁻¹)	K_1 (min ⁻¹)	R^2	Q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ min ⁻¹)	R^2
MPC	MB	25	22.24	21.77	0.169	0.998	23.11	0.013	0.991
		50	44.58	42.94	0.157	0.981	45.94	0.006	0.999
		100	80.09	78.65	0.119	0.962	84.65	0.002	0.989
		150	109.37	106.85	0.137	0.983	114.45	0.002	0.995
		200	126.91	123.83	0.200	0.972	130.83	0.003	0.995
	CV	25	23.25	22.89	0.098	0.975	24.20	0.007	0.992
		50	45.11	43.34	0.153	0.967	45.50	0.006	0.999
		100	84.92	81.59	0.059	0.940	88.16	0.001	0.982
		150	113.69	113.41	0.019	0.998	135.16	0.0002	0.993
		200	130.17	128.37	0.023	0.997	150.12	0.0002	0.995
CC	MB	25	24.40	23.50	0.145	0.957	24.68	0.011	0.995
		50	45.61	42.99	0.107	0.939	45.63	0.004	0.991
		100	72.13	67.27	0.083	0.958	72.06	0.002	0.996
		150	78.84	75.09	0.040	0.984	83.74	0.001	0.999
		200	79.08	74.01	0.046	0.976	81.89	0.001	0.999
	CV	25	24.16	22.47	0.115	0.927	23.87	0.008	0.986
		50	47.69	44.31	0.135	0.910	46.91	0.005	0.978
		100	81.22	74.53	0.080	0.890	80.02	0.002	0.968
		150	91.48	86.64	0.094	0.960	92.30	0.002	0.997
		200	95.20	90.12	0.175	0.959	94.35	0.003	0.996

The diffusion coefficients for the adsorption of MB and CV by the raw materials (Table 8) decreased significantly over time. This can be attributed to the fact that, in the initial phase, the high diffusion of these dyes within the adsorbent structure leads to a substantial reduction in the number of pores available for further diffusion. As a result, the movement of molecules within the pores, and subsequently solute diffusion, is hindered [97].

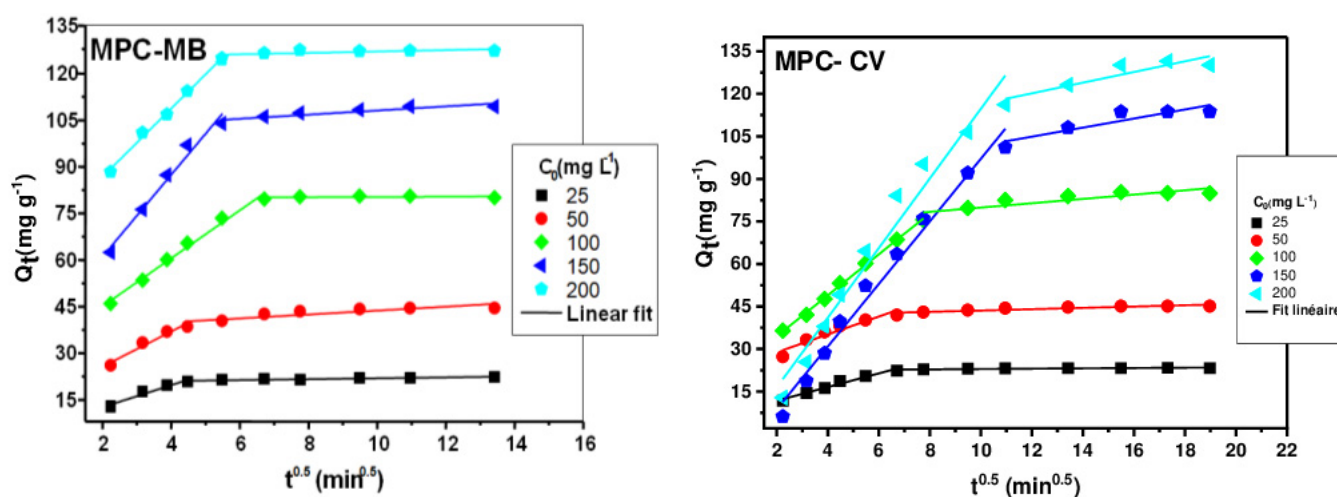


Figure 25. Intraparticle diffusion models for the adsorption of MB and CV on MPC.

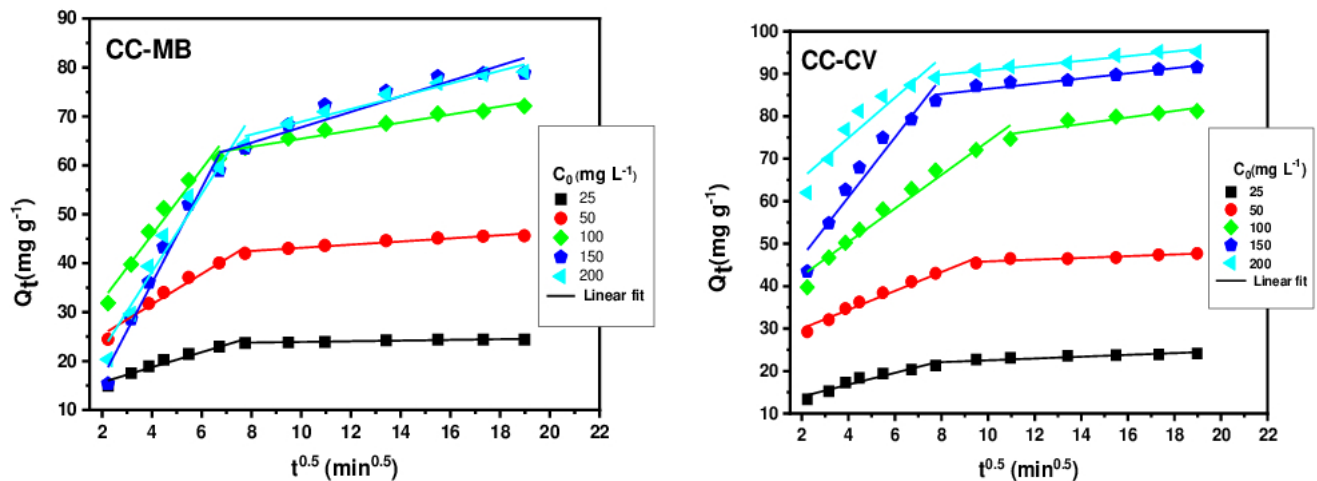


Figure 26. Intraparticle diffusion models for the adsorption of MB and CV on CC.

Table 8. Parameters of the intraparticle diffusion models of MB and CV adsorption on MPC and CC.

Material	Dye	C_0 (mg L ⁻¹)	Step 1			Step 2		
			K_1 (mg g ⁻¹ min ^{-0.5})	C (mg g ⁻¹)	R^2	K_2 (mg g ⁻¹ min ^{-0.5})	C (mg g ⁻¹)	R^2
MPC	MB	25	3.555	5.498	0.928	0.146	20.458	0.806
		50	5.653	14.375	0.942	0.630	37.424	0.708
		100	7.721	29.675	0.986	0.048	79.806	0.760
		150	13.191	34.679	0.969	0.665	101.472	0.785
		200	11.008	64.737	0.993	0.224	124.440	0.796
	CV	25	2.410	6.929	0.967	0.058	22.345	0.758
		50	3.148	22.544	0.887	0.233	41.236	0.789
		100	7.226	20.046	0.998	0.760	72.296	0.726
		150	11.042	−13.304	0.982	1.597	85.738	0.770
		200	12.282	−8.082	0.960	1.882	97.591	0.783
CC	MB	25	1.537	12.586	0.943	0.068	23.230	0.873
		50	3.106	19.169	0.966	0.322	39.929	0.939
		100	6.706	18.965	0.958	0.824	57.204	0.953
		150	9.726	−2.987	0.964	1.578	51.992	0.877
		200	8.000	6.171	0.950	1.305	55.848	0.950
	CV	25	1.395	11.208	0.920	0.213	20.397	0.782
		50	2.221	25.544	0.972	0.203	43.793	0.848
		100	3.960	34.510	0.964	0.768	67.434	0.806
		150	7.035	32.812	0.928	0.610	80.357	0.882
		200	4.751	55.871	0.865	0.551	85.354	0.959

3.2.4. Modeling the Adsorption Isotherms

The parameters obtained from isotherm modeling provide valuable insights into adsorption mechanisms, surface properties, and adsorbent–adsorbate affinities. The two most commonly used two-parameter models are the Langmuir and Freundlich models. However, for a more in-depth understanding of adsorption mechanisms, three-parameter models can also be implemented. Among these, the Sips model (Langmuir–Freundlich) and the Redlich–Peterson model are particularly notable. The applicability of these models can be evaluated based on the value of the R^2 correlation coefficient.

The graphical representation of each isotherm (Figures 27 and 28) and Table 9, which summarizes the correlation factors and constants for each model, show that all four models adequately represent the adsorption isotherms of MB and CV on MPC and CC, with

$R^2 > 0.9$. However, the Sips and Redlich–Peterson models, overall, provide the most accurate description of our experimental results across the entire studied temperature range.

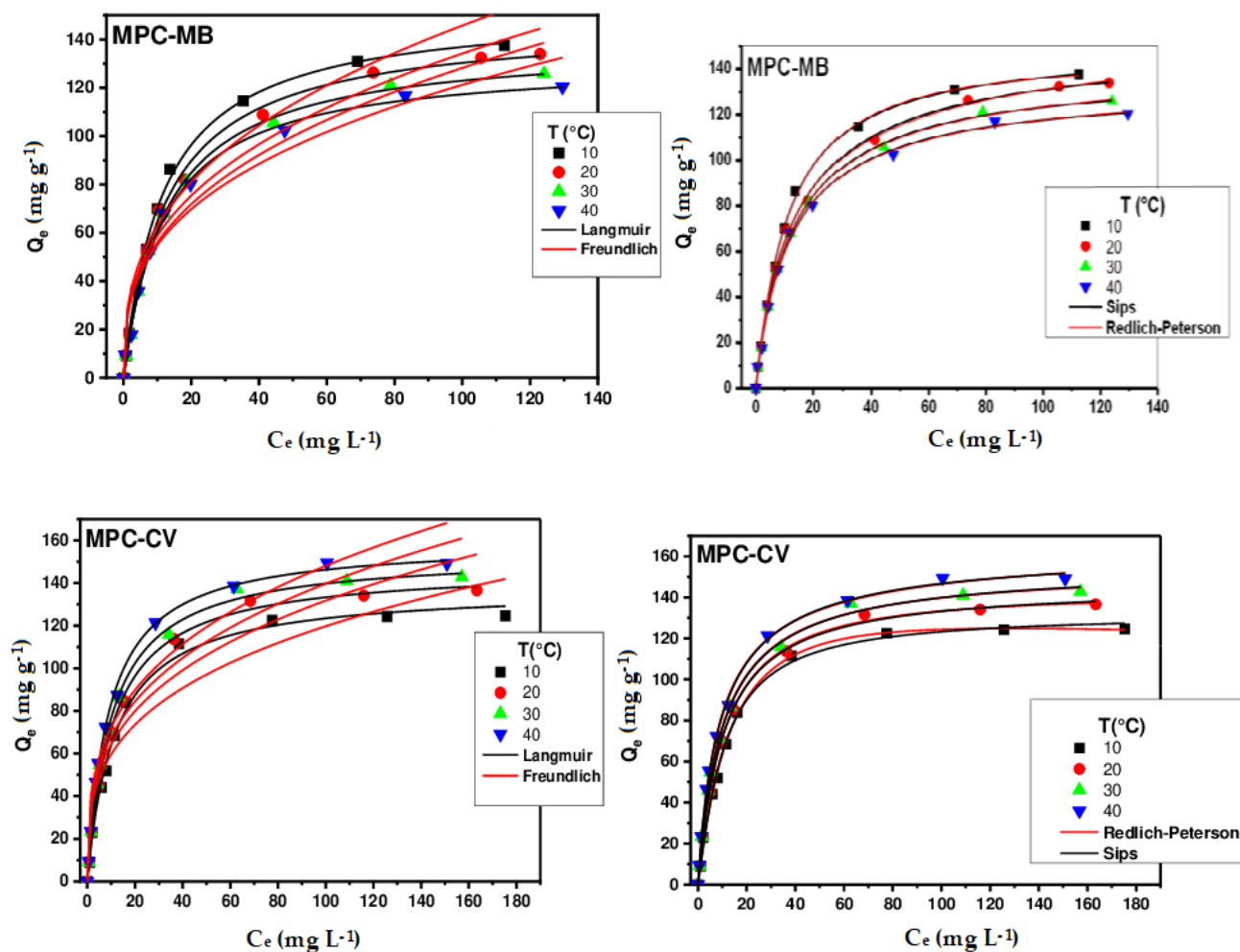


Figure 27. Non-linear modeling of the MB and CV isotherms on MPC.

Table 9. Results of MB and CV isotherm modeling on MPC and CC.

Materials	Dye	Temperature (°C)	Qe.exp (mg g ^{−1})	Langmuir			Freundlich			Sips			Redlich-Peterson				
				Q _m (mg g ^{−1})	K _L (L mg ^{−1})	R ²	K _F (mg g ^{−1}) (L mg ^{−1}) ^{1/n}	n	R ²	Q _m (mg g ^{−1})	K _S (L mg ^{−1})	m _s	R ²	K _R (L g ^{−1})	α _R (L mg ^{−1})	β	R ²
MPC	MB	10	137.61	153.01	0.085	0.999	27.21	2.74	0.938	149.05	0.091	1.07	0.999	12.19	0.067	1.04	0.999
		20	134.43	146.92	0.079	0.998	25.79	2.79	0.961	153.01	0.070	0.91	0.998	13.19	0.120	0.94	0.999
		30	125.87	138.50	0.079	0.999	24.46	2.78	0.949	140.66	0.076	0.97	0.999	11.58	0.095	0.97	0.999
		40	120.41	131.31	0.084	0.997	24.96	2.91	0.949	133.47	0.080	0.96	0.997	11.57	0.098	0.98	0.997
	CV	10	124.65	137.62	0.087	0.994	29.66	3.30	0.905	132.07	0.096	1.17	0.996	9.65	0.040	1.11	0.998
		20	136.59	147.46	0.094	0.999	31.46	3.22	0.926	146.04	0.097	1.03	0.999	13.20	0.080	1.02	0.999
		30	142.88	153.78	0.099	0.998	33.06	3.20	0.932	155.42	0.096	0.97	0.998	15.45	0.103	1.00	0.998
		40	149.16	159.56	0.110	0.998	35.42	3.22	0.936	163.62	0.102	0.93	0.998	18.62	0.131	0.98	0.998
CC	MB	10	73.43	74.46	0.371	0.998	30.66	5.21	0.884	75.31	0.362	0.94	0.998	29.69	0.428	0.98	0.998
		20	78.79	79.19	0.354	0.993	31.49	4.98	0.901	82.35	0.321	0.83	0.997	34.99	0.536	0.96	0.996
		30	80.93	81.48	0.358	0.989	32.50	4.96	0.913	86.70	0.307	0.76	0.997	41.74	0.674	0.94	0.995
		40	84.14	84.87	0.362	0.990	33.60	4.91	0.910	89.96	0.312	0.77	0.997	42.55	0.649	0.94	0.995
	CV	10	93.01	93.17	0.308	0.994	35.53	5.00	0.896	94.59	0.295	0.92	0.994	33.03	0.409	0.97	0.995
		20	98.88	96.76	0.363	0.990	37.59	5.03	0.901	99.08	0.335	0.88	0.990	42.85	0.540	0.96	0.993
		30	104.80	100.99	0.419	0.965	42.40	5.35	0.956	119.12	0.254	0.53	0.998	154.52	2.662	0.88	0.993
		40	108.73	103.85	0.524	0.950	45.81	5.55	0.963	130.18	0.229	0.46	0.995	218.24	3.655	0.88	0.988

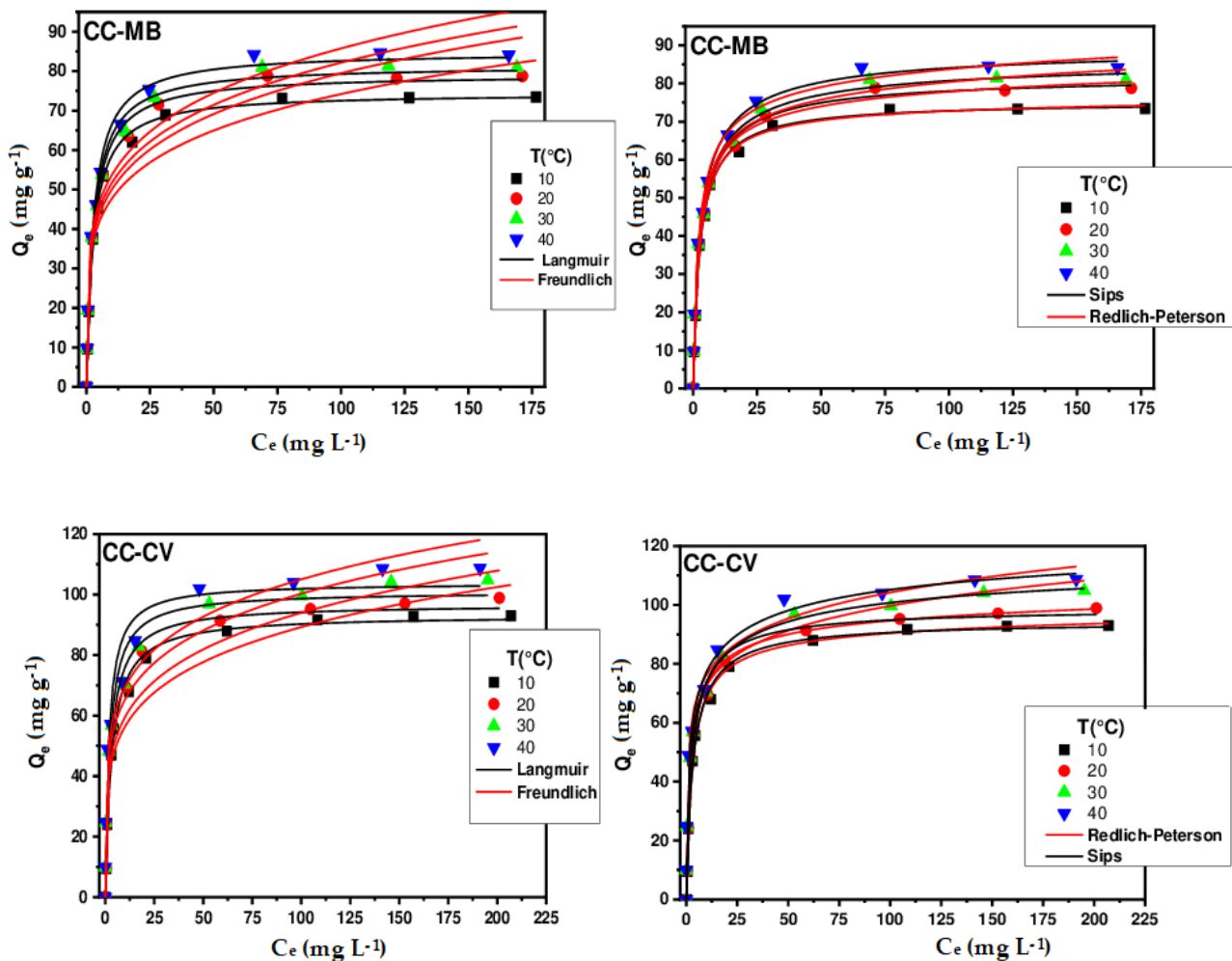


Figure 28. Non-linear modeling of the MB and CV isotherms on CC.

Table 10 shows the maximum adsorption capacities of MB and CV on some raw biosorbents, including our MPC and CC samples. The comparison demonstrates that our biomaterials have a higher adsorption capacity for MB and CV than several other reported adsorbents. Thus, the selected materials are excellent adsorbents for the removal of cationic dyes.

Table 10. The maximum adsorption capacities of MB and CV on some raw biosorbents, including our MPC and CC samples.

Adsorbent	Adsorbate	Adsorption Capacity (mg g ⁻¹)	Reference
Waste ash	MB	13.5	[98]
Macauba palm	MB	27.8	[99]
<i>Solanum elaeagnifolium</i> Cavanilles	MB	50.6	[100]
Watermelon seed hulls	MB	57.1	[101]
Peanut husk	MB	72.1	[102]
<i>Gelidium elegans</i>	MB	76.7	[100]
Sago waste	MB	83.5	[26]
Wild carob	MB	84.1	This study
Wood apple shell	MB	95.2	[103]
Cucumber peels	MB	111.1	[101]
<i>Maclura pomifera</i>	MB	137.6	This study

Table 10. Cont.

Adsorbent	Adsorbate	Adsorption Capacity (mg g ⁻¹)	Reference
Waste coir pith	CV	2.56	[104]
Sugarcane dust	CV	13.9	[105]
<i>Coniferous pinus</i> bark	CV	32.8	[106]
Kaolinite clay	CV	44.2	[107]
Almond skin waste	CV	85.5	[108]
Coffee waste	CV	125.0	[109]
Wild carob	CV	108.7	This study
Wood apple shell	CV	129.9	[103]
<i>Maclura pomifera</i>	CV	149.2	This study
Royal palm leaf sheath	CV	344.8	[110]

4. Conclusions

This study investigated the adsorption of methylene blue (MB) and crystal violet (CV) onto raw *Maclura pomifera* and wild carob washed with cold, warm, or hot water. The physicochemical characterization of the raw biomass revealed that the temperature of the washing water negatively impacts the texture of the biosorbents, reduced their acidic nature, and diminishes the intensity of active functional groups on the surface of both materials. The results show that the maximum adsorption capacity for MB and CV is dependent on the type of biosorbent, with *Maclura pomifera* exhibiting a higher capacity than wild carob. The wash water temperature adversely affects the adsorption performance of *Maclura pomifera*, while it has no significant effect on the adsorption capacity of wild carob, indicating that the impact of washing water temperature is material-specific.

The adsorption of MB and CV on raw biosorbents is positively influenced by increasing pH, contact time, or initial dye concentration and is negatively affected by increasing adsorbent dose or ionic strength. The thermodynamic analysis revealed that the biosorption process of MB and CV on raw biosorbents is physical, favorable, and spontaneous. It is exothermic in the case of MB adsorption on *Maclura pomifera* washed with cold, warm, and hot water, while it is endothermic in other cases. The dye adsorption kinetics for wild carob are slower compared to those of *Maclura pomifera*. Equilibrium was achieved after 240 min of contact for both MB and CV adsorption on wild carob, after 120 min for CV adsorption on *Maclura pomifera*, and after 60 min for MB adsorption on *Maclura pomifera*. The analysis of the kinetic data indicated that intraparticle diffusion is not the rate-limiting step in the adsorption of MB and CV on MPC and CC; it occurs concurrently with second-order kinetics. The Sips and Redlich–Peterson models were found to be the most reliable in describing the adsorption isotherms for MB and CV on MPC and CC across the different studied temperatures.

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References

1. Kumar, R.; Singh, C.K.; Kamesh; Misra, S.; Singh, B.P.; Bhardwaj, A.K.; Chandra, K.K. Water Biodiversity: Ecosystem Services, Threats, and Conservation. In *Biodiversity and Bioeconomy*; Elsevier: Amsterdam, The Netherlands, 2024; pp. 347–380. [\[CrossRef\]](#)
2. Bounaas, M.; Bouguettoucha, A.; Chebli, D.; Reffas, A.; Gatica, J.M.; Amrane, A. Batch Adsorption of Synthetic Dye by Maclura Pomifera, a New Eco-Friendly Waste Biomass: Experimental Studies and Modeling. *Int. J. Chem. React. Eng.* **2019**, *17*, 20180063. [\[CrossRef\]](#)
3. Lairini, S.; El Mahtal, K.; Miyah, Y.; Tanji, K.; Guissi, S.; Boumchita, S.; Zerrouq, F. The Adsorption of Crystal Violet from Aqueous Solution by Using Potato Peels (*Solanum tuberosum*): Equilibrium and Kinetic Studies. *J. Mater. Environ. Sci.* **2017**, *8*, 3252–3261.
4. Mansour, H.B.; Barillier, D.; Corrolier, D.; Ghedira, K.; Leila, C.G.; Mosrati, R. In Vitro Study of Dna Damage Induced by Acid Orange 52 and Its Biodegradation Derivatives. *Environ. Toxicol. Chem.* **2009**, *28*, 489–495. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Khalfaoui, A.; Bouchareb, E.M.; Derbal, K.; Boukhaloua, S.; Chahbouni, B.; Bouchareb, R. Uptake of Methyl Red Dye from Aqueous Solution Using Activated Carbons Prepared from Moringa Oleifera Shells. *Clean. Chem. Eng.* **2022**, *4*, 100069. [\[CrossRef\]](#)
6. Bounaas, M.; Bouguettoucha, A.; Chebli, D.; Gatica, J.M.; Vidal, H. Role of the Wild Carob as Biosorbent and as Precursor of a New High-Surface-Area Activated Carbon for the Adsorption of Methylene Blue. *Arab. J. Sci. Eng.* **2021**, *46*, 325–341. [\[CrossRef\]](#)
7. Güzel, F.; Saygılı, H.; Saygılı, G.A.; Koyuncu, F. Decolorisation of Aqueous Crystal Violet Solution by a New Nanoporous Carbon: Equilibrium and Kinetic Approach. *J. Ind. Eng. Chem.* **2014**, *20*, 3375–3386. [\[CrossRef\]](#)
8. Khan, T.A.; Sharma, S.; Ali, I. Adsorption of Rhodamine B Dye from Aqueous Solution onto Acid Activated Mango (*Mangifera indica*) Leaf Powder: Equilibrium, Kinetic and Thermodynamic Studies. *J. Toxicol. Environ. Health Sci.* **2011**, *3*, 286–297.
9. Benalia, A.; Derbal, K.; Baatache, O.; Lehcili, C.; Khalfaoui, A.; Pizzi, A. Removal of Dyes from Water Using Aluminum-Based Water Treatment Sludge as a Low-Cost Coagulant: Use of Response. *Water* **2024**, *16*, 1400. [\[CrossRef\]](#)
10. Baatache, O.; Derbal, K.; Benalia, A.; Aberkane, I.; Guizah, Q.E.; Khalfaoui, A.; Pizzi, A. Valorization of Pine Cones (*Pinus nigras*) for Industrial Wastewater Treatment and Crystal Violet Removal: A Sustainable Approach Based on Bio-Coagulants and a Bio-Adsorbent. *Water* **2024**, *16*, 260. [\[CrossRef\]](#)
11. Cheruiyot, G.K.; Wanyonyi, W.C.; Kiplimo, J.J.; Maina, E.N. Adsorption of Toxic Crystal Violet Dye Using Coffee Husks: Equilibrium, Kinetics and Thermodynamics Study. *Sci. Afr.* **2019**, *5*, e00116. [\[CrossRef\]](#)
12. Khalfaoui, A.; Bendjamaa, I.; Bensid, T.; Meniai, A.H.; Derbal, K. Effect of Calcination on Orange Peels Characteristics: Application of an Industrial Dye Adsorption. *Chem. Eng. Trans.* **2014**, *38*, 361–366. [\[CrossRef\]](#)
13. Goci, M.C.; Leudjo Taka, A.; Martin, L.; Klink, M.J. Chitosan-Based Polymer Nanocomposites for Environmental Remediation of Mercury Pollution. *Polymers* **2023**, *15*, 482. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Mane, V.S.; Vijay Babu, P.V. Kinetic and Equilibrium Studies on the Removal of Congo Red from Aqueous Solution Using Eucalyptus Wood (*Eucalyptus globulus*) Saw Dust. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 81–88. [\[CrossRef\]](#)
15. Aydin, H.; Baysal, G.; Bulut, Y. Utilization of Walnut Shells (*Juglans regia*) as an Adsorbent for the Removal of Acid Dyes. *Desalin. Water Treat.* **2009**, *2*, 139–147. [\[CrossRef\]](#)
16. Bounaas, M.; Bouguettoucha, A.; Chebli, D.; Reffas, A.; Harizi, I.; Rouabah, F.; Amrane, A. High Efficiency of Methylene Blue Removal Using a Novel Low-Cost Acid Treated Forest Wastes, *Cupressus sempervirens* Cones: Experimental Results and Modeling. *Part. Sci. Technol.* **2019**, *37*, 504–513. [\[CrossRef\]](#)
17. Saygılı, H.; Güzel, F.; Önal, Y. Conversion of Grape Industrial Processing Waste to Activated Carbon Sorbent and Its Performance in Cationic and Anionic Dyes Adsorption. *J. Clean. Prod.* **2015**, *93*, 84–93. [\[CrossRef\]](#)
18. Liu, C.H.; Wu, J.S.; Chiu, H.C.; Suen, S.Y.; Chu, K.H. Removal of Anionic Reactive Dyes from Water Using Anion Exchange Membranes as Adsorbents. *Water Res.* **2007**, *41*, 1491–1500. [\[CrossRef\]](#)
19. Aragaw, T.A.; Alene, A.N. A Comparative Study of Acidic, Basic, and Reactive Dyes Adsorption from Aqueous Solution onto Kaolin Adsorbent: Effect of Operating Parameters, Isotherms, Kinetics, and Thermodynamics. *Emerg. Contam.* **2022**, *8*, 59–74. [\[CrossRef\]](#)
20. Laggoun, Z.; Khalfaoui, A.; Benalia, A.; Ghomrani, A.F.; Bouchareb, R.; Mahfouf, A.; Pizzi, A.; Panico, A.; Derbal, K. Applied Sciences Application of Response Surface Design for Optimization of Direct Red Dye Biosorption onto Cockles. *Appl. Sci.* **2023**, *13*, 12333. [\[CrossRef\]](#)
21. Gündüz, F.; Bayrak, B. Biosorption of Malachite Green from an Aqueous Solution Using Pomegranate Peel: Equilibrium Modelling, Kinetic and Thermodynamic Studies. *J. Mol. Liq.* **2017**, *243*, 790–798. [\[CrossRef\]](#)
22. Khalfaoui, A.; Benalia, A.; Selama, Z.; Hammoud, A.; Derbal, K.; Panico, A.; Pizzi, A. Removal of Chromium (VI) from Water Using Orange Peel as the Biosorbent: Experimental, Modeling, and Kinetic Studies on Adsorption Isotherms and Chemical Structure. *Water* **2024**, *16*, 742. [\[CrossRef\]](#)
23. Nayeem, A.; Mizi, F.; Ali, M.F.; Shariffuddin, J.H. Utilization of Cockle Shell Powder as an Adsorbent to Remove Phosphorus-Containing Wastewater. *Environ. Res.* **2023**, *216*, 114514. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Khalfaoui, A.; Khelifi, M.N.; Khelfaoui, A.; Benalia, A.; Derbal, K. The Adsorptive Removal of Bengal Rose by Artichoke Leaves: Optimization by Full Factorials Design. *Water* **2022**, *14*, 2251. [\[CrossRef\]](#)

25. Zhang, Y.; Wan, H.; Zhao, J.; Li, J. Biosorption of Anionic and Cationic Dyes via Raw and Chitosan Oligosaccharide-Modified Huai Flos Chrysanthemum at Different Temperatures. *RSC Adv.* **2019**, *9*, 11202–11211. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Amode, J.O.; Santos, J.H.; Alam, Z.M.; Mirza, A.H.; Mei, C.C. Adsorption of Methylene Blue from Aqueous Solution Using Untreated and Treated (*Metroxylon* spp.) Waste Adsorbent: Equilibrium and Kinetics Studies. *Int. J. Ind. Chem.* **2016**, *7*, 333–345. [\[CrossRef\]](#)
27. Bouguettoucha, A.; Chebli, D.; Mekhalef, T.; Noui, A.; Amrane, A. The Use of a Forest Waste Biomass, Cone of *Pinus Brutia* for the Removal of an Anionic Azo Dye Congo Red from Aqueous Medium. *Desalin. Water Treat.* **2015**, *55*, 1956–1965. [\[CrossRef\]](#)
28. Jawad, A.H.; Abdulhameed, A.S.; Mastuli, M.S. Acid-Fractionalized Biomass Material for Methylene Blue Dye Removal: A Comprehensive Adsorption and Mechanism Study. *J. Taibah Univ. Sci.* **2020**, *14*, 305–313. [\[CrossRef\]](#)
29. Hussin, Z.M.; Talib, N.; Hussin, N.M.; Hanafiah, M.A.K.M.; Khalir, W.K.A.W.M. Methylene Blue Adsorption onto NaOH Modified Durian Leaf Powder: Isotherm and Kinetic Studies. *Am. J. Environ. Eng.* **2015**, *5*, 38–43. [\[CrossRef\]](#)
30. Laskar, N.; Kumar, U. Adsorption of Crystal Violet from Wastewater by Modified Bambusa Tulda. *KSCE J. Civ. Eng.* **2018**, *22*, 2755–2763. [\[CrossRef\]](#)
31. Mahmood, Z.; Zahra, S.; Iqbal, M.; Raza, M.A.; Nasir, S. Comparative Study of Natural and Modified Biomass of *Sargassum* sp. for Removal of Cd²⁺ and Zn²⁺ from Wastewater. *Appl. Water Sci.* **2017**, *7*, 3469–3481. [\[CrossRef\]](#)
32. Abdullah, N.H.; Borhan, A.; Saadon, S.Z.A.H. Biosorption of Wastewater Pollutants by Chitosan-Based Porous Carbons: A Sustainable Approach for Advanced Wastewater Treatment. *Bioresour. Technol. Rep.* **2024**, *25*, 101705. [\[CrossRef\]](#)
33. Regadera-Macías, A.M.; Morales-Torres, S.; Pastrana-Martínez, L.M.; Maldonado-Hódar, F.J. Optimizing Filters of Activated Carbons Obtained from Biomass Residues for Ethylene Removal in Agro-Food Industry Devices. *Environ. Res.* **2024**, *248*, 118247. [\[CrossRef\]](#)
34. Benyoucef, S.; Harrache, D.; Djaroud, S.; Sail, K.; Gallart-Mateu, D.; de la Guardia, M. Preparation and Characterization of Novel Microstructure Cellulosic Sawdust Material: Application as Potential Adsorbent for Wastewater Treatment. *Cellulose* **2020**, *27*, 8169–8180. [\[CrossRef\]](#)
35. Shrestha, B.; Kour, J.; Ghimire, K.N. Adsorptive Removal of Heavy Metals from Aqueous Solution with Environmental Friendly Material—Exhausted Tea Leaves. *Adv. Chem. Eng. Sci.* **2016**, *6*, 525–540. [\[CrossRef\]](#)
36. Shrestha, B.; Homagai, P.; Pokhrel, M.; Ghimire, K. Adsorptive Removal of Toxic Metal from Aqueous Solution by Using a Biowaste-Used Tea Leaves. *Nepal. J. Sci. Technol.* **2013**, *13*, 109–114. [\[CrossRef\]](#)
37. Reffas, A.; Bouguettoucha, A.; Chebli, D.; Amrane, A. Adsorption of Ethyl Violet Dye in Aqueous Solution by Forest Wastes, Wild Carob. *Desalin. Water Treat.* **2016**, *57*, 9859–9870. [\[CrossRef\]](#)
38. Al-Ghouti, M.A.; Al-Degs, Y.S. New Adsorbents Based on Microemulsion Modified Diatomite and Activated Carbon for Removing Organic and Inorganic Pollutants from Waste Lubricants. *Chem. Eng. J.* **2011**, *173*, 115–128. [\[CrossRef\]](#)
39. Lagergren, S.K. About the Theory of So-Called Adsorption of Soluble Substances. *K. Sven. Vetenskapsakademiens Handl. Band* **1898**, *24*, 1–39.
40. Ho, Y.S.; Mckay, G. Pseudo-Second Order Model for Sorption Processes. *Process Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
41. Weber, W.J.; Morris, J.C. Kinetics of Adsorption on Carbon from Solution. *J. Sanit. Eng. Div.* **1963**, *89*, 31–59. [\[CrossRef\]](#)
42. Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [\[CrossRef\]](#)
43. Freundlich, H.M.F. Over the Adsorption in Solution. *J. Phys. Chem.* **1906**, *57*, 385–471.
44. Dotto, G.L.; Vieira, M.L.G.; Esquerdo, V.M.; Pinto, L.A.A. Equilibrium and Thermodynamics of Azo Dyes Biosorption onto *Spirulina Platensis*. *Braz. J. Chem. Eng.* **2013**, *30*, 13–21. [\[CrossRef\]](#)
45. Redlich, O.; Peterson, D.L. A Useful Adsorption Isotherm. *J. Phys. Chem.* **1959**, *63*, 1024. [\[CrossRef\]](#)
46. Brunauer, S.; Deming, L.S.; Deming, W.E.; Teller, E. On a Theory of the van Der Waals Adsorption of Gases. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732. [\[CrossRef\]](#)
47. Brunauer, S.; Emmett, P.H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319. [\[CrossRef\]](#)
48. Jang, A.; Seo, Y.; Bishop, P.L. The Removal of Heavy Metals in Urban Runoff by Sorption on Mulch. *Environ. Pollut.* **2005**, *133*, 117–127. [\[CrossRef\]](#)
49. An, H.K.; Park, B.Y.; Kim, D.S. Crab Shell for the Removal of Heavy Metals from Aqueous Solution. *Water Res.* **2001**, *35*, 3551–3556. [\[CrossRef\]](#)
50. Ozdemir, I.; Şahin, M.; Orhan, R.; Erdem, M. Preparation and Characterization of Activated Carbon from Grape Stalk by Zinc Chloride Activation. *Fuel Process. Technol.* **2014**, *125*, 200–206. [\[CrossRef\]](#)
51. Djilani, C.; Zaghdoudi, R.; Modarressi, A.; Rogalski, M.; Djazi, F.; Lallam, A. Elimination of Organic Micropollutants by Adsorption on Activated Carbon Prepared from Agricultural Waste. *Chem. Eng. J.* **2012**, *189–190*, 203–212. [\[CrossRef\]](#)
52. Aydin, H.; Baysal, G. Adsorption of Acid Dyes in Aqueous Solutions by Shells of Bittim (*Pistacia khinjuk* Stocks). *Desalination* **2006**, *196*, 248–259. [\[CrossRef\]](#)
53. Reffas, A. Étude de L’Adsorption de Colorants Organiques (Rouge Nylosan et Bleu de Méthylène) sur des Charbons Actifs Préparés à Partir du Marc de Café. Ph.D. Thesis, University of Mentouri-Constantine, Constantine, Algeria, 2010.

54. Benalia, A.; Atime, L.; Baatache, O.; Khalfaoui, A.; Fadia, A. Removal of Lead in Water by Coagulation Flocculation Process Using Cactus-Based Natural Coagulant: Optimization and Modeling by Response Surface Methodology (RSM). *Environ. Monit. Assess.* **2024**, *196*, 244. [[CrossRef](#)] [[PubMed](#)]
55. Khalfaoui, A.; Benalia, A.; Laggoun, Z.; Bouchareb, R.; Zaaamta, I.; Melloul, R.; Menasria, A.; Merouani, S.; Antonio Pizzi, K.D. Effective Synthesis and Application of Artichoke and Orange Peels-Based Bio-Sorbents for Ketoprofen Removal from Wastewater: Process Optimization Using Factorial Methodology. *Desalin. Water Treat.* **2024**, *317*, 100197. [[CrossRef](#)]
56. Benalia, A.; Baatache, O.; Derbal, K.; Khalfaoui, A.; Amrouci, Z.; Pizzi, A.; Panico, A. The Use of Central Composite Design (CCD) to Optimize and Model the Coagulation-Flocculation Process Using a Natural Coagulant: Application in Jar Test and Semi-Industrial Scale. *J. Water Process Eng.* **2024**, *57*, 104704. [[CrossRef](#)]
57. Altenor, S.; Carene, B.; Emmanuel, E.; Lambert, J.; Ehrhardt, J.J.; Gaspard, S. Adsorption Studies of Methylene Blue and Phenol onto Vetiver Roots Activated Carbon Prepared by Chemical Activation. *J. Hazard. Mater.* **2009**, *165*, 1029–1039. [[CrossRef](#)]
58. Liang, S.; Guo, X.; Feng, N.; Tian, Q. Isotherms, Kinetics and Thermodynamic Studies of Adsorption of Cu²⁺ from Aqueous Solutions by Mg²⁺/K⁺ Type Orange Peel Adsorbents. *J. Hazard. Mater.* **2010**, *174*, 756–762. [[CrossRef](#)]
59. Liou, T.H. Development of Mesoporous Structure and High Adsorption Capacity of Biomass-Based Activated Carbon by Phosphoric Acid and Zinc Chloride Activation. *Chem. Eng. J.* **2010**, *158*, 129–142. [[CrossRef](#)]
60. Durán-Valle, C.J.; Gómez-Corzo, M.; Pastor-Villegas, J.; Gómez-Serrano, V. Study of Cherry Stones as Raw Material in Preparation of Carbonaceous Adsorbents. *J. Anal. Appl. Pyrolysis* **2005**, *73*, 59–67. [[CrossRef](#)]
61. Park, S.H.; McClain, S.; Tian, Z.R.; Suib, S.L.; Karwacki, C. Surface and Bulk Measurements of Metals Deposited on Activated Carbon. *Chem. Mater.* **1997**, *9*, 176–183. [[CrossRef](#)]
62. Daoud, M.; Benturki, O.; Kecira, Z.; Girods, P.; Donnot, A. Removal of Reactive Dye (BEZAKTIV Red S-MAX) from Aqueous Solution by Adsorption onto Activated Carbons Prepared from Date Palm Rachis and Jujube Stones. *J. Mol. Liq.* **2017**, *243*, 799–809. [[CrossRef](#)]
63. Njoku, V.O.; Hameed, B.H. Preparation and Characterization of Activated Carbon from Corn cob by Chemical Activation with H₃PO₄ for 2,4-Dichlorophenoxyacetic Acid Adsorption. *Chem. Eng. J.* **2011**, *173*, 391–399. [[CrossRef](#)]
64. Benalia, A.; Derbal, K. Etude Expérimentale et Modélisation du Processus de la Coagulation Flocculation: Application Aux Eaux Destinée a la Consommation. Master's Thesis, University of Constantine 3, El Khroub, Algeria, 2015.
65. Baatache, O.; Derbal, K.; Benalia, A.; Khalfaoui, A.; Bouchareb, R.; Panico, A.; Pizzi, A. Use of Pine Cone as Bio-Coagulant for Heavy Metal Removal from Industrial Wastewater: Use of Box—Behnken Design. *Ind. Crop. Prod.* **2024**, *210*, 118185. [[CrossRef](#)]
66. Moreno-Castilla, C.; Carrasco-Marín, F.; Mueden, A. The Creation of Acid Carbon Surfaces by Treatment with (NH₄)₂S₂O₈. *Carbon* **1997**, *35*, 1619–1626. [[CrossRef](#)]
67. Socrates, G. *Infrared and Raman Characteristic Group Frequencies*, 3rd ed.; Wiley: Hoboken, NJ, USA, 2001; ISBN 978-0-470-09307-8.
68. Ahmad, A.L.; Loh, M.M.; Aziz, J.A. Preparation and Characterization of Activated Carbon from Oil Palm Wood and Its Evaluation on Methylene Blue Adsorption. *Dye. Pigment.* **2007**, *75*, 263–272. [[CrossRef](#)]
69. Cengiz, G.; Aytar, P.; Şam, M.; Çabuk, A. Removal of Reactive Dyes using Magnetically Separable *Trametes versicolor* Cells as a New Composite Biosorbent. *Sep. Sci. Technol.* **2014**, *49*, 1860–1871. [[CrossRef](#)]
70. Marrakchi, F.; Ahmed, M.J.; Khanday, W.A.; Asif, M.; Hameed, B.H. Mesoporous-Activated Carbon Prepared from Chitosan Flakes via Single-Step Sodium Hydroxide Activation for the Adsorption of Methylene Blue. *Int. J. Biol. Macromol.* **2017**, *98*, 233–239. [[CrossRef](#)]
71. Bentahar, Y. Caractérisation Physico-Chimique des Argiles Marocaines: Application à L'adsorption de L'arsenic et des Colorants Cationiques en Solution Aqueuse. Ph.D. Thesis, University of Nice-Sophia Antipolis, Nice, France, 2016.
72. Deng, H.; Yang, L.; Tao, G.; Dai, J. 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.* **2009**, *166*, 1514–1521. [[CrossRef](#)]
73. Wang, S.; Zhu, Z.H.; Coomes, A.; Haghseresht, F.; Lu, G.Q. The Physical and Surface Chemical Characteristics of Activated Carbons and the Adsorption of Methylene Blue from Wastewater. *J. Colloid Interface Sci.* **2005**, *284*, 440–446. [[CrossRef](#)]
74. Albarelli, J.Q.; Rabelo, R.B.; Santos, D.T.; Beppu, M.M.; Meireles, M.A.A. Effects of Supercritical Carbon Dioxide on Waste Banana Peels for Heavy Metal Removal. *J. Supercrit. Fluids* **2011**, *58*, 343–351. [[CrossRef](#)]
75. Khanday, W.A.; Marrakchi, F.; Asif, M.; Hameed, B.H. Mesoporous Zeolite-activated Carbon Composite from Oil Palm Ash as an Effective Adsorbent for Methylene Blue. *J. Taiwan Inst. Chem. Eng.* **2017**, *70*, 32–41. [[CrossRef](#)]
76. Auta, M.; Hameed, B.H. Chitosan-Clay Composite as Highly Effective and Low-Cost Adsorbent for Batch and Fixed-Bed Adsorption of Methylene Blue. *Chem. Eng. J.* **2014**, *237*, 352–361. [[CrossRef](#)]
77. Senthil Kumar, P.; Sivarajanee, R.; Vinothini, U.; Raghavi, M.; Rajasekar, K.; Ramakrishnan, K. Adsorption of Dye onto Raw and Surface Modified Tamarind Seeds: Isotherms, Process Design, Kinetics and Mechanism. *Desalin. Water Treat.* **2014**, *52*, 2620–2633. [[CrossRef](#)]
78. Hameed, B.H. Evaluation of Papaya Seeds as a Novel Non-Conventional Low-Cost Adsorbent for Removal of Methylene Blue. *J. Hazard. Mater.* **2009**, *162*, 939–944. [[CrossRef](#)]
79. Vadivelan, V.; Vasanth Kumar, K. Equilibrium, Kinetics, Mechanism, and Process Design for the Sorption of Methylene Blue onto Rice Husk. *J. Colloid Interface Sci.* **2005**, *286*, 90–100. [[CrossRef](#)] [[PubMed](#)]

80. Ertas, M.; Acemioğlu, B.; Alma, M.H.; Usta, M. Removal of Methylene Blue from Aqueous Solution Using Cotton Stalk, Cotton Waste and Cotton Dust. *J. Hazard. Mater.* **2010**, *183*, 421–427. [[CrossRef](#)] [[PubMed](#)]
81. Ofomaja, A.E.; Ho, Y.S. Equilibrium Sorption of Anionic Dye from Aqueous Solution by Palm Kernel Fibre as Sorbent. *Dye. Pigment.* **2007**, *74*, 60–66. [[CrossRef](#)]
82. Newcombe, G.; Drikas, M. Adsorption of NOM onto Activated Carbon: Electrostatic and Non-Electrostatic Effects. *Carbon* **1997**, *35*, 1239–1250. [[CrossRef](#)]
83. Janoš, P.; Coskun, S.; Pilařová, V.; Rejnek, J. Removal of Basic (Methylene Blue) and Acid (Egacid Orange) Dyes from Waters by Sorption on Chemically Treated Wood Shavings. *Bioresour. Technol.* **2009**, *100*, 1450–1453. [[CrossRef](#)]
84. Han, R.; Zou, W.; Yu, W.; Cheng, S.; Wang, Y.; Shi, J. Biosorption of Methylene Blue from Aqueous Solution by Fallen Phoenix Tree's Leaves. *J. Hazard. Mater.* **2007**, *141*, 156–162. [[CrossRef](#)]
85. Wang, X.S.; Zhou, Y.; Jiang, Y.; Sun, C. The Removal of Basic Dyes from Aqueous Solutions Using Agricultural By-Products. *J. Hazard. Mater.* **2008**, *157*, 374–385. [[CrossRef](#)]
86. Chen, H.; Zhao, J.; Dai, G. Silkworm Exuviae-A New Non-Conventional and Low-Cost Adsorbent for Removal of Methylene Blue from Aqueous Solutions. *J. Hazard. Mater.* **2011**, *186*, 1320–1327. [[CrossRef](#)]
87. Pavan, F.A.; Camacho, E.S.; Lima, E.C.; Dotto, G.L.; Branco, V.T.A.; Dias, S.L.P. Formosa Papaya Seed Powder (FPSP): Preparation, Characterization and Application as an Alternative Adsorbent for the Removal of Crystal Violet from Aqueous Phase. *J. Environ. Chem. Eng.* **2014**, *2*, 230–238. [[CrossRef](#)]
88. Smahi, Z. Essais de Valorisation D'un Déchet Cellulosique: Tiges de Chardons Dans L'élimination D'un Colorant Basique à Partir de Solutions Aqueuses Synthétiques. Ph.D. Thesis, University Abu-Bakr Belkaïd, Tlemcen, Algeria, 2017.
89. Doğan, M.; Özdemir, Y.; Alkan, M. Adsorption Kinetics and Mechanism of Cationic Methyl Violet and Methylene Blue Dyes onto Sepiolite. *Dye. Pigment.* **2007**, *75*, 701–713. [[CrossRef](#)]
90. Doğan, M.; Alkan, M.; Demirbaş, Ö.; Özdemir, Y.; Özmetin, C. Adsorption Kinetics of Maxilon Blue GRL onto Sepiolite from Aqueous Solutions. *Chem. Eng. J.* **2006**, *124*, 89–101. [[CrossRef](#)]
91. Choumane, F.Z. Elimination des Métaux Lourds et Pesticides en Solution Aqueuse par des Matrices Argileuses. Ph.D. Thesis, University Abu-Bakr Belkaïd, Tlemcen, Algeria, 2015.
92. Nasuha, N.; Hameed, B.H. Adsorption of Methylene Blue from Aqueous Solution onto NaOH-Modified Rejected Tea. *Chem. Eng. J.* **2011**, *166*, 783–786. [[CrossRef](#)]
93. Çolak, F.; Atar, N.; Olgun, A. Biosorption of Acidic Dyes from Aqueous Solution by *Paenibacillus Macerans*: Kinetic, Thermodynamic and Equilibrium Studies. *Chem. Eng. J.* **2009**, *150*, 122–130. [[CrossRef](#)]
94. Ely, A. Synthèse et Propriétés de Biosorbants à Base D'argiles Encapsulées dans des Alginates: Application au Traitement des Eaux. Ph.D. Thesis, University of Limoges France, Limoges, France, 2010.
95. Dawood, S.; Sen, T.K. Removal of Anionic Dye Congo Red from Aqueous Solution by Raw Pine and Acid-Treated Pine Cone Powder as Adsorbent: Equilibrium, Thermodynamic, Kinetics, Mechanism and Process Design. *Water Res.* **2012**, *46*, 1933–1946. [[CrossRef](#)]
96. Dotto, G.L.; Pinto, L.A.A. Adsorption of Food Dyes Acid Blue 9 and Food Yellow 3 onto Chitosan: Stirring Rate Effect in Kinetics and Mechanism. *J. Hazard. Mater.* **2011**, *187*, 164–170. [[CrossRef](#)]
97. Gil, A.; Assis, F.C.C.; Albeniz, S.; Korili, S.A. Removal of Dyes from Wastewaters by Adsorption on Pillared Clays. *Chem. Eng. J.* **2011**, *168*, 1032–1040. [[CrossRef](#)]
98. Alene, A.N.; Abate, G.Y.; Habte, A.T. Bioadsorption of Basic Blue Dye from Aqueous Solution onto Raw and Modified Waste Ash as Economical Alternative Bioadsorbent. *J. Chem.* **2020**, *2020*, 8746035. [[CrossRef](#)]
99. Vieira, S.S.; Magriotis, Z.M.; Santos, N.A.V.; das Gracas Cardoso, M.; Saczk, A.A. Macauba palm (*Acrocomia aculeata*) Cake from Biodiesel Processing: An Efficient and Low Cost Substrate for the Adsorption of Dyes. *Chem. Eng. J.* **2012**, *183*, 152–161. [[CrossRef](#)]
100. Kasbaji, M.; Mennani, M.; Boussetta, A.; Grimi, N.; Barba, F.J.; Mbarki, M.; Moubarik, A. Bio-Adsorption Performances of Methylene Blue (MB) Dye on Terrestrial and Marine Natural Fibers: Effect of Physicochemical Properties, Kinetic Models and Thermodynamic Parameters. *Sep. Sci. Technol.* **2023**, *58*, 221–240. [[CrossRef](#)]
101. Akkaya, G.; Güzel, F. Application of Some Domestic Wastes as New Low-Cost Biosorbents for Removal of Methylene Blue: Kinetic and Equilibrium Studies. *Chem. Eng. Commun.* **2014**, *201*, 557–578. [[CrossRef](#)]
102. Song, J.; Zou, W.; Bian, Y.; Su, F.; Han, R. Adsorption Characteristics of Methylene Blue by Peanut Husk in Batch and Column Modes. *Desalination* **2011**, *265*, 119–125. [[CrossRef](#)]
103. Jain, S.; Jayaram, R.V. Removal of Basic Dyes from Aqueous Solution by Low-Cost Adsorbent: Wood Apple Shell (*Feronia acidissima*). *Desalination* **2010**, *250*, 921–927. [[CrossRef](#)]
104. Namasivayam, C.; Dinesh Kumar, M.; Selvi, K.; Ashruffunissa Begum, R.; Vanathi, T.; Yamuna, R.T. "Waste" Coir Pith—A Potential Biomass for the Treatment of Dyeing Wastewaters. *Biomass Bioenergy* **2001**, *21*, 477–483. [[CrossRef](#)]
105. Ho, Y.S.; Chiu, W.T.; Wang, C.C. Regression Analysis for the Sorption Isotherms of Basic Dyes on Sugarcane Dust. *Bioresour. Technol.* **2005**, *96*, 1285–1291. [[CrossRef](#)]
106. Ahmad, R. Studies on Adsorption of Crystal Violet Dye from Aqueous Solution onto Coniferous Pinus Bark Powder (CPBP). *J. Hazard. Mater.* **2009**, *171*, 767–773. [[CrossRef](#)] [[PubMed](#)]
107. Boukhemkhem, A.; Aissa-Ouaissi-Sekkouti, B.; Bedia, J.; Belver, C.; Molina, C.B. Adsorption of Crystal Violet on Kaolinite Clay: Kinetic and Equilibrium Study Using Non-Linear Models. *Clay Miner.* **2022**, *57*, 41–50. [[CrossRef](#)]

108. Atmani, F.; Bensmaili, A.; Mezenner, N.Y. Synthetic Textile Effluent Removal by Skin Almonds Waste. *J. Environ. Sci. Technol.* **2009**, *2*, 153–169. [[CrossRef](#)]
109. Lafi, R.; ben Fradj, A.; Hafiane, A.; Hameed, B.H. Coffee Waste as Potential Adsorbent for the Removal of Basic Dyes from Aqueous Solution. *Korean J. Chem. Eng.* **2014**, *31*, 2198–2206. [[CrossRef](#)]
110. Sen, N.; Shefa, N.R.; Reza, K.; Shawon, S.M.A.Z.; Rahman, M.W. Adsorption of Crystal Violet Dye from Synthetic Wastewater by Ball-Milled Royal Palm Leaf Sheath. *Sci. Rep.* **2024**, *14*, 5349. [[CrossRef](#)] [[PubMed](#)]

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