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1 **Advanced Green Peel Utilization for Efficient Methylene Blue Removal: Integrated**
2 **Analysis and Predictive Modeling**

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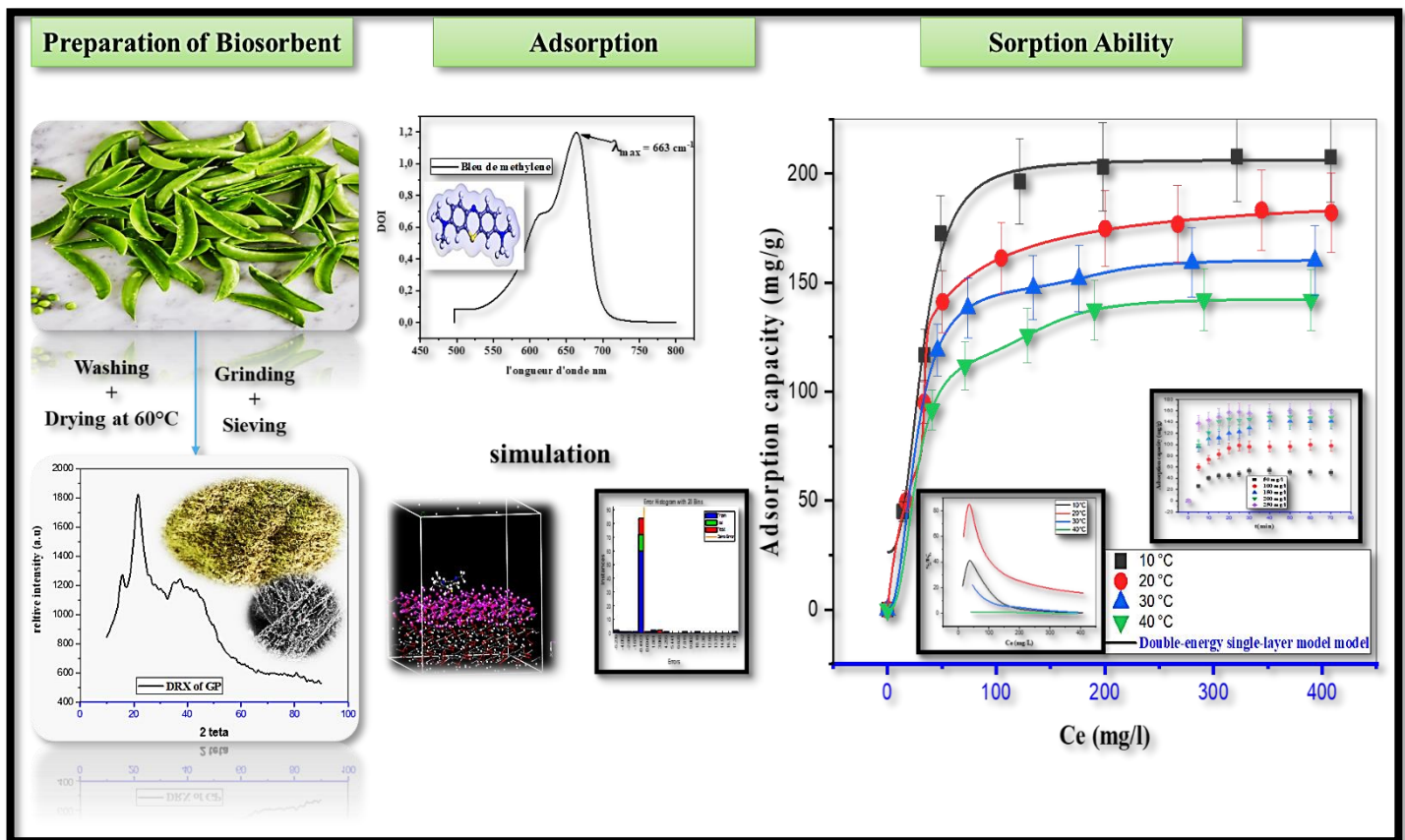
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23 **Abstract**

24 This study explores the adsorption of Methylene Blue (MB) onto Green Peel (GP) material,
25 utilizing advanced analytical techniques and modeling approaches. Fourier-transform infrared
26 spectroscopy (FT-IR) confirms GP's effectiveness as an adsorbent. The study systematically
27 examines the influence of key factors such as adsorbent dose, pH, MB concentration, and
28 temperature on adsorption efficiency. Among the isotherm models analyzed, the monolayer
29 with double energy (M2) model is identified as the most accurate for describing MB adsorption
30 onto GP. Steric parameters provide insights into the adsorption mechanism, revealing
31 temperature-dependent changes. Thermodynamic analysis indicates an exothermic adsorption
32 process, with a decrease in adsorption capacity at elevated temperatures. Density Function
33 Theory (DFT) analysis highlights the potential for electron transfer during adsorption,
34 contributing to a deeper understanding of the process. Molecular Dynamic Simulation (MDS)
35 uncovers stable adsorption configurations and reveals the significance of chemical interactions
36 and Van der Waals forces. Gaussian Process Regression with Lévy Flight Distribution
37 (GPR_LFD) demonstrates exceptional predictive accuracy, closely aligning experimental and
38 predicted MB uptake values. Optimal adsorption conditions (30 minutes contact time, 0.6 g
39 adsorbent dose, 400 mg/L initial MB concentration, pH 6.6, and 10°C) yield an adsorption
40 capacity of 207.90 mg/g. The integration of LFD optimization and GPR prediction through a
41 MATLAB interface further enhances the practical application of these findings. This
42 comprehensive investigation not only advances the understanding of MB adsorption onto GP
43 but also highlights GP's potential as an efficient, reusable adsorbent.

44 **Graphical Abstract:**



46

47 **Keywords:** Adsorption, Green peas, Methylene blue, density functional theory, Gaussian
 48 Process Regression, Lévy Flight Distribution.

49 1. Introduction

50 Industrial effluents from various industrial sectors, including textiles, dyeing, food processing,
 51 pharmaceuticals, paper manufacturing, leather production, and cosmetics, serve as a prominent
 52 source of environmental pollution and are notable generators of chromatic wastewater
 53 emissions [1–3]. Among these sectors, the dye industry plays a notably pivotal role in this
 54 environmental context. [4,5]. Dye compounds in water hinder sunlight penetration, disrupting
 55 aquatic plant photosynthesis and posing serious health risks due to their mutagenic,
 56 carcinogenic, and teratogenic properties, which can harm human kidneys, liver, reproductive
 57 system, and central nervous system [6–9]. Untreated wastewater containing dyes like

58 Methylene Blue, a chemically stable and water-soluble cationic dye, poses significant
59 environmental risks due to its persistence and widespread industrial use [10]. The release of
60 this dye into the environment causes serious health issues, including nausea, respiratory
61 problems, allergic reactions, cardiac arrhythmias, tissue necrosis, cognitive impairment, cancer
62 risks, and dysfunction in the brain, liver, and central nervous system [11,12]. Our previous
63 studies conclude that the biomass was ineffective in removing anionic azo dyes. The negatively
64 charged surface and open structure of the GP adsorbent likely contribute to its low adsorption
65 performance. Throughout the years, researchers have effectively devised a diverse array of
66 methodologies for the eradication of methylene blue in industrial effluent, including
67 electrochemical treatment, ion exchange, photocatalytic degradation [13], membrane filtration,
68 coagulation-flocculation [14,15], and Fenton process [16,17]. Among these techniques, the
69 adsorption method is an important process for improving the quality of water and protecting
70 the environment [4,18]. Due to its is an efficient, simple, regenerable, and eco-friendly method
71 for treating wastewater and reducing hazardous pollutants. [19,20].

72 Various adsorbents, including those made from agricultural and industrial byproducts, offer a
73 straightforward, cost-effective, and eco-friendly solution for dye removal. Using these raw
74 adsorbents helps reduce waste disposal costs and addresses environmental challenges.
75 Modifications are needed to enhance their practical use and improve their adsorption efficiency,
76 durability, and reusability [9]. Different modifying reagents, such as base solutions (sodium
77 hydroxide, calcium hydroxide, and sodium carbonate) and mineral and organic acids
78 (hydrochloric acid, sulphuric acid, nitric acid, tartaric acid, thioglycolic acid, citric acid, etc.),
79 are used in the chemical modification of adsorbents [21].

80 Researchers have conducted extensive examinations and assessments of prospective
81 biosorbents in order to successfully extract colors from water pollution.

82 In recent years, notable advancements have included the utilization of materials such as orange
83 peel [22], Ziziphus jujube [23], Pinus pinaster [24], almond shell [25], Acorus calamus [26],
84 green macroalgae [27], the prickly pear [28], corn cob [29], and other similar substances for
85 various successful applications in dye removal processes.

86 Despite advancements in adsorption methods, several limitations persist [30]. The limited
87 adsorption capacity of traditional adsorbents can be quickly exhausted, hindering their long-
88 term effectiveness [31]. Additionally, the efficiency of adsorption can be compromised by
89 inefficient processes, suboptimal conditions, and sometimes inadequate selectivity, leading to
90 the adsorption of non-targeted components [31]. The development of new, efficient adsorbents
91 remains a challenge, as does the optimization of operational conditions to ensure effective
92 adsorption in variable environments [30].

93 To address these existing challenges, researchers have adopted artificial intelligence (AI) and
94 optimization techniques using metaheuristic algorithms in the field of adsorption. Noteworthy
95 studies include the development of AI-based models for predicting vanadium adsorption onto
96 activated carbon nanocomposites [32], the application of AI modeling and genetic algorithm
97 optimization for the decolorization of bromo-cresol green dye using acid-functionalized rice
98 husk [33], and the utilization of deep learning and AI tools for modeling a pressure swing
99 adsorption unit [34]. Additionally, researchers have explored the use of activated carbon
100 derived from jujube pebbles for the adsorption of methylene blue, employing responsive surface
101 methods, machine learning techniques, thermodynamics and mechanism analysis, modeling of
102 kinetics and isotherms, and optimization [30]. Another study proposes a predictive model
103 combining K-Nearest Neighbor with the Gray Wolf Optimizer Algorithm (KNN_GWO) for
104 estimating the amount of phenol adsorption on powdered activated carbon [31]. Another study
105 utilized artificial intelligence, specifically Gaussian process regression (GPR) and particle
106 swarm optimization (PSO), to predict the adsorption capacity of MB dye and optimize the

107 treatment conditions of textile wastewater. These AI techniques are applied to enhance the
108 efficiency of the treatment process by providing accurate predictions and identifying optimal
109 operating conditions [35]. These approaches showcase the diverse applications of AI in
110 optimizing adsorption processes.

111 The use of AI has allowed for precise identification of optimal conditions to maximize
112 adsorption capacity, improve overall efficiency, and design selective adsorbents [30].
113 Moreover, AI has guided the virtual development of new adsorbent materials. Metaheuristic
114 algorithms have been leveraged to optimize operational parameters, effectively explore the
115 space of process operating conditions, dynamically regulate in response to load fluctuations,
116 and provide accurate predictions of adsorption performance [31].

117 In the context of this study, the utilization of green peel (GP) was meticulously investigated as
118 an adsorbent for the effective removal of methylene blue (MB) dye from solution-made water.

119 In the early stages, scanning electron microscopy (SEM) and Fourier-transform infrared
120 spectroscopy (FT-IR) were judiciously employed to confirm the dye adsorption process of GP.

121 Conversely, X-ray diffraction (XRD) was specifically utilized to elucidate the crystalline
122 structure of GP, offering crucial insights into the structural properties of the adsorbent material.

123 The Brunauer-Emmett-Teller (BET) theory is widely used to analyze the surface area and
124 porosity of materials

125 A systematic exploration of parameters influencing MB removal, including adsorbent mass,
126 pH, initial concentration, and temperature, was conducted. Detailed analysis of isotherm data,
127 accompanied by steric parameters, provided insights into the geometry and adsorption
128 mechanisms. Furthermore, a comprehensive investigation into the reactivity and stability of
129 MB and GP was undertaken, shedding light on potential electron transfer phenomena during
130 the adsorption process. In the context of MB adsorption onto cellulose-based materials like
131 green peel, diverse mechanisms contribute to the overall adsorption process. Notably,–MB

132 adsorption onto Green Peel (GP) involves multiple interactions, including electrostatic
133 attraction, van der Waals forces, hydrogen bonding, and, under certain conditions, covalent
134 bonding. Precipitation of MB onto GP occurs when concentrations exceed solubility,
135 contributing to overall adsorption. The significance of each mechanism depends on factors like
136 pH and temperature. GP's recyclability was confirmed using a 0.1 M ethanol solution,
137 demonstrating its potential for reuse after evaluating removal efficiency and adsorption
138 capacity. A dive into the stable adsorption configuration of MB on the GP surface through
139 molecular dynamics simulation was undertaken. Simultaneously, a model based on the
140 Gaussian process coupled with Levy flight distribution (GPR_LFD) was developed to predict
141 MB adsorption by GP. Furthermore, Levy flight distribution (LFD) was independently used to
142 identify optimal conditions for maximal MB removal. Finally, a user-friendly MATLAB
143 interface integrating LFD optimization and GPR_LFD prediction was designed to facilitate the
144 practical application of the obtained results.

145 Additionally, the study innovates by exploring the complex mechanisms of adsorption between
146 GP and MB, using kinetic and adsorption models, as well as techniques like molecular
147 mechanics and Density Functional Theory (DFT) simulation to provide critical insights into the
148 underlying interactions. The development of an advanced prediction model based on GPR_LFD
149 represents a major breakthrough, delivering highly precise estimates of GP's maximum
150 adsorption capacity. In this investigation, the research stands as a pioneering contribution to the
151 field of water treatment. By integrating innovative adsorbent materials, comprehensive
152 characterization techniques, and advanced simulation tools, significant strides have been made
153 in addressing water contamination issues caused by cationic dyes.

154 **2. MATERIAL AND METHODS**

155 **2.1. Adsorbate used**

156 To assess the adsorption capacity of the prepared biomass, a persistent and stable dye was
157 chosen. MB was selected due to its reputation for persistence in various environments.
158 Additionally, MB exhibits stability, ensuring the maintenance of its chemical and physical
159 properties under variable conditions. These characteristics have made MB an ideal candidate to
160 evaluate the adsorption efficiency of our biomass on a persistent contaminant. The
161 characteristics of MB are detailed in **Table S1**, with the molecular structure depicted in **Figure**
162 **S1**.

163 **2.2. Preparation of solution**

164 1 g of MB powder provided by the company SIGMA-ALDRICH was dispersed in 1 liter of
165 distillate water to produce 1 g/L colorant solution. Then, various solutions ranging from 100 to
166 600 mg/L were made using distillate water. These solutions were then applied to various
167 experiments.

168 A study of its visible UV spectrum at wavelengths between 200 and 800 nm, carried out using
169 a UV-1700 type spectrophotometer pharماسpec Shimadzu, made it possible to determine the
170 wavelength corresponding to the maximum absorbance, $\lambda_{\max} = 663$ nm.

171 **2.3. Adsorbent preparation**

172 GP were collected from residues of local green peas. After initial cleaning with distilled water
173 and drying at ambient temperature, the material was pulverized, rinsed, and dried overnight in
174 a furnace at 60°C to create natural biosorbents. Subsequently, preliminary trials were conducted
175 to select the optimal material among the natural biosorbent, the one activated by
176 orthophosphoric acid (GP-H₃PO₄), and the one activated by KOH (GP-KOH). Results indicated
177 that the natural biosorbent removed 80% of MB, while the activated biosorbents (GP-KOH and
178 GP-H₃PO₄) showed removal rates ranging from 69.17% to 28.14%. These outcomes prompted
179 the selection of natural biomass as the preferred adsorbent for further research.

2.4. Characterization of adsorbent

In the current investigation, a range of characterization techniques was applied and will be elaborated upon later in this study. In particular, infrared spectroscopy was employed to scrutinize the surface chemistry of various specimens, including raw GP and GP loaded with methyl blue (GP+MB). This analysis was carried out using a Fourier transform infrared spectrometer (FT-IR) of the SHIMADZU brand, specifically an IRAffinity-1S model, in conjunction with potassium bromide (KBr) discs, within a spectral range spanning from 4000 to 500 cm^{-1} .

X-ray diffraction (XRD) diagrams were constructed in a 2θ angle range spanning from 4 to 90 degrees, with an incremental step of 0.02 degrees and an acquisition time of 6.985 seconds per step. To probe the micromorphology of the untreated green peel, a Hitachi S-3000N Scanning Electron Microscope (SEM) was utilized for image capture at electron beam energies of 10 kV and magnifications of 30, 100, and 300.

The scanning electron microscope (SEM) is considered a highly valuable tool for the examination and analysis of microstructural morphology. SEM relies on electron-material interactions to generate high-resolution images of the sample's surface. This technique was employed to scrutinize the surface characteristics and morphological attributes of the green peel (GP) samples under investigation.

The specific surface area of GP was calculated by using the Brunauer–Emmett–Teller (BET) method based on the data of the N_2 adsorption–desorption isotherm.

The concept of the zero-point charge is a pivotal concept in physics, elucidating the circumstances surrounding the neutral electrical charge state of certain particles. This concept is founded on the fundamental premise that all matter inherently possesses an intrinsic level of energy, even in a state that may superficially appear at rest. This energy, recognized as "zero-

204 point" or "vacuum" energy, holds the potential to initiate interactions among particles, thereby
205 leading to the acquisition of a net electric charge.

206 In the pursuit of determining the point of zero charge (pHpzc), a method was employed wherein
207 50 mL of sodium chloride (NaCl) solution was placed within sealed vials. The pH levels of
208 these solutions were systematically adjusted across a range from 2 to 12 through the utilization
209 of either a 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) solution. Each
210 vial was supplemented with 15 mg of GP material. Subsequently, the suspensions underwent
211 agitation at ambient room temperature for an approximate duration of 24 hours, following
212 which the final pH values were ascertained.

213 **2.5. Effect of process variables on the adsorption process**

214 **2.5.1. The effect of biosorbent dose**

215 One key element in figuring out the biosorbent material's potential for biosorption is the fraction
216 of biosorbent in the solution. Adsorbent dosages of 0.2, 0.4, 0.6, 0.8, and 1 g/L were tested at
217 an initial dye concentration of 100 mg/L to examine the impact of the initial dosage of GP
218 biosorbent on the MB dye.

219 **2.5.2. Effect of initial pH**

220 Due to its ability to modify the surface characteristics of materials and affect the arrangement
221 of anions and cations, pH is crucial to adsorption. In order to investigate the impact of pH on
222 our experimental setup, a series of tests were conducted. namely, contacting a volume of 25 mL
223 of MB in 100 mL Erlenmeyer flasks with 15 mg of green pea material (GP) and an initial
224 concentration of 100 mg/L. These suspensions were initiated at distinct initial pH values
225 implied from [2, 4, 6, and 10] and maintained at room temperature. The mixtures were subjected
226 to agitation for 24 hours at a rate of 250 ppm. Following this, the suspensions underwent

227 centrifugation, and the ultimate concentration of filtrate was determined using ultraviolet (UV)
228 spectroscopy.

229 **2.6. Adsorption analysis**

230 **2.6.1. Adsorption kinetics**

231 Studying adsorption kinetics is a critical phase in the analysis of an adsorption method as it
232 facilitates the assessment of the duration necessary to reach adsorption equilibrium [36].

233 A range of distinct initial concentrations, represented by 50, 100, 150, 200, and 250 mg/L, were
234 employed in the formulation of solutions. For each of the above concentrations of MB, 0.015 g
235 of biosorbent material was introduced into 25 mL of a methyl blue solution in a 50 mL
236 volumetric flask under continuous stirring at a speed of 250 rpm. At specific time intervals,
237 samples were extracted for subsequent analysis using a Shimadzu Spectrophotometer UV-1700.
238 Kinetic modeling plays a crucial role in the design of adsorption systems, and the quantity of
239 adsorbate captured is computed using Equation (1) [37,38]

$$240 \quad Q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

241 Where C_o (mg.L^{-1}) is the first concentration of colorant, C_t (mg.L^{-1}) is the remaining
242 concentration of dye at the time t , V (mL) is the volume of the solution, and m (g) is the mass
243 of the adsorbent [39].

244 The dye clearance efficiency was determined using Eq. (2) [40]:

$$245 \quad R\% = \frac{C_o - C_e}{C_o} * 100 \quad (2)$$

246 **2.6.2. Kinetic modeling**

247 The kinetics of solute adsorption were characterized using an adsorption dynamics study, which
248 governed the rate of adsorption at the solid-solution interface. To fit the experimental data,

249 numerous kinetic models were used, including pseudo-first-order (PFO), pseudo-second-order
 250 (PSO), pseudo-nth-order (PNO) and Elovich models [41]. To identify the adsorption
 251 mechanism for design purposes, we used the intraparticle diffusion model [23,36], and the
 252 Fractional power kinetic model [42,43]

253 **Table.1.** Equation and parameters models for nonlinear regression of Kinetic adsorption.

Equation number	Equation name	Equation formed	Parameters
(3)	pseudo-first-order (PFO)	$Q_t = Q_e (1 - e^{-k_1 t})$	Q_e (mg g ⁻¹) and Q_t (mg g ⁻¹) refer to the amount of dye adsorbed at equilibrium and at time t (min). respectively. k_1 (L min ⁻¹) is the equilibrium rate constant of the pseudo-first-order equation
(4)	pseudo-first-order (PSO)	$Q_t = \left(\frac{K_2 Q_e^2 t}{K_2 Q_e t + 1} \right)$	k_2 (L min ⁻¹) is the equilibrium rate constant of the pseudo-second-order equation
(5)	pseudo-nth-order (PNO)	$Q_t = Q_e - [(n-1)K_n t + Q_e^{(n-1)}]^{1/(1-n)}$	k_n is a constant and n is the biosorption reaction order.
(6)	Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	α is the constant of the initial sorption rate (mg/(g·min)). β is the constant of desorption (g/mg).
(7)	the intraparticle diffusion	$Q_t = K_{id} t^{0.5} + C$	k_{id} (mg.g ⁻¹ min ^{-0.5}) is the rate constant of intraparticle diffusion. C is the intercept.
(8)	Fractional power	$\ln Q_t = \ln K + \vartheta \ln t$	ϑ is the fractional power kinetic model constant. K is the fractional power kinetic model constant (mg g ⁻¹ h ⁻¹).

254

255 **2.7. Equilibrium modeling classical and advanced adsorption models**

256 Adsorption isotherms are pivotal in understanding the interactions between adsorbates and
 257 adsorbents, serving as indispensable tools for optimizing adsorbent utilization and providing
 258 crucial insights into determining adsorbent capacity. In our investigation, we acknowledge the
 259 significance of concentration gradients in propelling the adsorption process. Elevated
 260 concentration gradients enhance adsorption effectiveness by intensifying the driving force and
 261 facilitating mass transfer. This leads to more frequent collisions and quicker diffusion of MB
 262 molecules onto the surface of the adsorbent. However, it's important to note that high
 263 concentrations of MB may saturate adsorption sites and increase competition among molecules,
 264 consequently decreasing adsorption efficiency. Understanding these dynamics
 265 comprehensively is essential for maximizing the efficiency of adsorption systems and
 266 effectively addressing challenges posed by high dye concentrations in wastewater treatment.
 267 Our study offers crucial insights into enhancing adsorption mechanisms for efficient water
 268 filtration.

269 The adsorption isotherm experiments were carried out by contacting MB solutions at various
 270 concentrations (ranging from 50 to 800 mg/L) with 0.015 g adsorbent. These mixtures were
 271 stirred continuously at 250 rpm for 2 hours at three distinct temperatures (10, 20, and 30 °C).
 272 After reaching equilibrium, the solutions were separated, analyzed, and the adsorbed quantities
 273 were calculated using Eq (1).

274 Traditional isotherms data analysis, specifically the Langmuir, Freundlich, and Sips models,
 275 since the experimental data were fitted using three widely used conventional adsorption
 276 isotherm models. **Table 2** provides these models' fundamental formulations [40,44–47].

277 **Table.2.** shows the equations and parameters of such models.

Equation number	Equation name	Equation formed	Parameters
-----------------	---------------	-----------------	------------

			Q_e (mg g ⁻¹) is the amount of MB adsorbed per unit mass of adsorbent.
(9)	Langmuir	$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e}$	Q_m (mg.g ⁻¹) is the monolayer capacity of the adsorbent. C_e (mg.L ⁻¹) is the equilibrium dye concentration in the solution. K_L the Langmuir constant.
(10)	Freundlich	$Q_e = K_F C_e^{1/n}$	K_F and n^{-1} are empirical constants indicative of sorption capacity and sorption intensity, respectively.
(11)	Sips	$\frac{Q_e}{Q_m} = \frac{(K_S C_e)^m}{1 + (K_S C_e)^m}$	K_s is (L mg ⁻¹) the Sips constant m the exponent of the Sips model

278

279 Additionally, we evaluated the interactions between the examined dye, namely Methylene Blue
280 (MB), and the GP composite. This assessment involved the application of monolayer with
281 single energy (M1), monolayer with double energy (M2), and multilayer (M3) adsorption
282 models. In the context of these advanced statistical models, the subsequent calculations were
283 employed:

284 **Table.3.** The Advanced statistical physics models M1, M2 and M3 [48,49].

model	Equation	Parameters
Single-energy single-layer model eq(12)	$Q = \frac{Q_0}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n} = \frac{n \cdot N_m}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n}$	Q (mg.g ⁻¹): adsorbed quantity. n : number of ions per site. N_m (mg.g ⁻¹) : sites receptor density.
Double-energy single-layer model eq(13)	$Q = n \cdot N_m \cdot \frac{\left(\frac{C_e}{C_{1/2}}\right)^n + 2 \cdot \left(\frac{C_e}{C_{1/2}}\right)^{2n}}{1 + \left(\frac{C_e}{C_{1/2}}\right)^n + \left(\frac{C_e}{C_{1/2}}\right)^{2n}}$	Q_0 (mg.g ⁻¹); adsorbed quantity at saturation
Multilayer model eq (14)	$Q = n \cdot N_m \cdot \frac{F_1(C_e) + F_2(C_e) + F_3(C_e) + F_4(C_e)}{G(C_e)}$ with	$C_{1/2}$ (mg .L ⁻¹) : the concentration at half-saturation C_1 and C_2 (mg.L ⁻¹) : concentrations at half saturation for the first and the second active sites respectively.

$$F_1(C_e) = \frac{\left(-2 \cdot \left(\frac{C_e}{C_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{C_1}\right)^n\right)} + \frac{\left(\frac{C_e}{C_1}\right)^n \left(1 - \left(\frac{C_e}{C_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{C_1}\right)^n\right)^2}$$

$$F_2(C_e) = \frac{2 \cdot \left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(1 - \left(\frac{C_e}{C_2}\right)^{nN_2}\right)}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)}$$

$$F_3(C_e) = \frac{-\left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(\frac{C_e}{C_2}\right)^{nN_2} N_2}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)}$$

$$G(C) = \frac{\left(1 - \left(\frac{C_e}{C_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{C_1}\right)^n\right)} + \frac{\left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(1 - \left(\frac{C_e}{C_2}\right)^{nN_2}\right)}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)}$$

n_1 and n_2 : number of ions per site for the first and the second sites receptor respectively.

285

286 2.8. Precision of the kinetic model and adsorption isotherm

287 Nonlinear regression was carried out to identify the model parameters from experimental data.

288 In nonlinear regression, the model parameters are identified to minimize the sum of squared
289 model prediction errors.

290 In addition to the coefficient of determination (R^2), the normalized standard deviation
291 $\Delta Q(\%)$ defined in Eq(15) is also used to assess model performance[50].

$$292 \Delta Q(\%) = 100 \times \sqrt{\frac{\sum \left(\frac{Q_{t_{exp}} - Q_{t_{cal}}}{Q_{t_{exp}}}\right)^2}{n-1}} \quad (15)$$

293 Where the $Q_{t_{exp}}$ and $Q_{t_{cal}}$ refer to the experimental and calculated values from kinetic
294 adsorption and n is the number of data points.

295 The validity of the adsorption isotherm was also measured using the hybrid error function
296 (HYBRID), which is defined as [51]:

$$297 \quad HYBRID = \frac{100}{N-p} \sum_{i=1}^N \left[\frac{(Q_{t,exp} - Q_{t,cal})^2}{Q_{exp}} \right] \quad (16)$$

298 Where $Q_{t,exp}$ is the observation from the batch experimental, $Q_{t,cal}$ is the estimate from the
299 isotherm for corresponding Q_{exp} , N is the number of observations in the experimental isotherm
300 and p is the number of parameters in the regression model.

301 **2.9. The thermodynamic study**

302 The energy changes that take place during an adsorption process can be seen by using
303 thermodynamic parameters like Gibbs free (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), which can
304 also be used to investigate the impact of temperature. The following equations are used to
305 compute these parameters [52] :

$$306 \quad K = \frac{1000 * Q_e}{C_e} \quad (17)$$

$$307 \quad \Delta G = -RT \ln K \quad (18)$$

$$308 \quad \Delta G = \Delta H - \Delta S \quad (19)$$

309 In the above equations, K is the equilibrium constant; T (K) is the adsorption temperature; R
310 ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the universal gas constant. The ratio ' Q_e/C_e ' acts as the Langmuir
311 equilibrium constant at various temperatures. In general, ΔH° and ΔS° are calculated from the
312 slope and intercept of ΔG° versus T .

313 **2.10. Specifics of the Density Function Theory**

314 The characterization of the systems under investigation is substantially contingent on the
315 frontier molecular orbitals (FMOs), specifically the Highest Occupied Molecular Orbital
316 (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), which are determined

317 utilizing the Density Functional Theory (DFT) with the DMOI3 technique. The energies
318 associated with HOMO and LUMO play a pivotal role in quantum chemical computations, as
319 they furnish crucial insights into the microscopic interactions occurring within adsorption
320 systems. These parameters are integral to quantum chemistry simulations, and the computed
321 energy values for E_{HOMO} , E_{LUMO} , and E_o are presented in the formulae below [53].

322 The following formulas are employed to determine potential (μ), electronegativity (χ), global
323 hardness (η), global softness (S), global electrophilicity index (ω), softness (σ), and the
324 maximum amount of electronic charge (ΔN_{max}).

$$325 \quad \mu = E_{HOMO} + E_{LUMO} \quad (20)$$

$$326 \quad \chi = -\mu \quad (21)$$

$$327 \quad \eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (22)$$

$$328 \quad S = \frac{1}{2\eta} \quad (23)$$

$$329 \quad \omega = \frac{\chi^2}{2\eta} \quad (24)$$

$$330 \quad \sigma = \frac{1}{\eta} \quad (25)$$

$$331 \quad \Delta N_{max} = \frac{-\mu}{\eta} \quad (26)$$

332 **2.11. Description of Molecular Dynamic Simulation**

333 All molecular dynamic simulations (MDS) conducted in this study were executed utilizing the
334 BIOVIA MATERIALS STUDIO 2020 software. In these simulations, the GP (-1 0 0) surface
335 was employed as the substrate for investigating the adsorption of MB onto the GP surface. The
336 application of periodic boundary conditions defined a simulation box with dimensions of (27 Å
337 × 27 Å × 15 Å), encompassing the GP slab, the MB molecule, and a vacuum slab. Geometrical

338 refinement of the MB molecular structure and the GP (-1 0 0) surface was achieved by energy
339 minimization. Employing a time step of 0.1 femtoseconds (fs) and a simulation duration of 50
340 picoseconds (ps), the COMPASS force field model was applied under the NVT ensemble
341 during the course of the molecular dynamic simulations.

342 **2.12. Regenerative Characteristics**

343 In the desorption process, electron transfer between MB dye and the ethanol solvent is essential
344 for releasing MB molecules from the adsorption sites on the biosorbent. Effective electron
345 transport, facilitated by suitable electron sources or acceptors present in the system, promotes
346 increased desorption kinetics. This process can occur through redox reactions, where electron
347 donors donate electrons to the MB dye, aiding its detachment from the biosorbent surface, or
348 where electron acceptors take electrons from the MB dye, facilitating its release into the solvent.
349 Desorption experiments were conducted using a 0.1 M ethanol solution. Following each
350 adsorption cycle, the adsorbent material was immersed in 50 mL of 0.1 M ethanol solution for
351 1 hour and then dried at 60°C for 30 minutes. Post-adsorption, the concentration of MB in the
352 solution was measured to compute removal efficiency and adsorption capacity. The addition of
353 adequate electron donors or acceptors in the ethanol solution significantly enhances desorption
354 efficiency, resulting in more efficient removal of MB from the biosorbent material.

355 **2.13. Gaussian Process Regression coupled with Lévy flight distribution**

356 The seamless integration of Gaussian Process Regression (GPR) with the Lévy flight
357 distribution constitutes a refined statistical modeling approach aimed at delving deeply into the
358 intricate structure and inherent variability of the data. GPR, rooted in Gaussian stochastic
359 processes, operates under the assumption that observations stem from a multivariate normal
360 distribution [54,55], thereby establishing connections between each data point through a
361 covariance matrix [56]. This methodology adeptly captures both the general trend in the data

362 and the uncertainty associated with each prediction, proving particularly relevant in contexts
363 where relationships between variables are as diverse as they are nonlinear [30]. Key features of
364 GPR encompass the specification of covariance, often defined by a kernel, which articulates
365 the similarity between different observations [55]. The model is then meticulously adjusted to
366 maximize the likelihood of observed data while incorporating regularization to forestall any
367 undesirable overfitting [55].

368 Simultaneously, the Lévy flight distribution distinguishes itself with large amplitude jumps
369 between states, offering a dynamic alternative to the standard random walk traditionally
370 constrained in its jumps [57]. This characteristic is crucial for modeling rare events or
371 phenomena likely to exert significant impacts on the data, introducing an additional dimension
372 of robustness to the model [57]. Key aspects of the Lévy flight distribution include the
373 meticulous determination of the stability parameter, precisely governing the probability of large
374 amplitude jumps [57]. A higher stability index promotes more frequent and larger jumps,
375 reinforcing the model's ability to respond to data intricacies [57].

376 The synergistic union between Gaussian Process Regression and the Lévy flight distribution
377 aims to optimally leverage the intrinsic advantages of these two distinct approaches. The
378 resulting model capitalizes on the flexibility of GPR to model the underlying structure of the
379 data while integrating the unique capability of the Lévy flight distribution to capture rare events
380 and significant jumps. GPR ensures the provision of a comprehensive prediction enveloped in
381 confidence intervals, while the Lévy flight distribution introduces an unprecedented dimension
382 to finely capture unpredictable phenomena. The model adjustment process involves a
383 meticulous estimation of the parameters of the GPR kernel and the stability parameter of the
384 Lévy flight distribution, a crucial step to optimize model performance while guarding against
385 overfitting risks. Thus, this holistic approach provides a comprehensive solution for modeling
386 complex data, combining the agility of GPR to provide probabilistic predictions with the

387 distinctive power of the Lévy flight distribution to represent rare events and abrupt changes,
388 shaping a statistical modeling tool of great finesse.

389 Within this research endeavor, the integration of GPR with LFD, denoted as GPR_LFD, has
390 been utilized as a pivotal and sophisticated method for predicting the adsorbed quantities of
391 MB by GP. Utilizing parameters meticulously optimized in the preceding section, the predictive
392 model encompasses a comprehensive set of influential variables, including contact time (X1),
393 adsorbent mass (X2), MB concentration (X3), pH (X4), and Temperature (X5). After the
394 establishment of the database, a normalization process was applied to confine its values within
395 the interval [-1,1]. Subsequently, the dataset underwent a meticulous division, allocating 70%
396 for training, 15% for validation, and the remaining 15% for stringent testing to rigorously assess
397 the efficiency and generalization capability of the finest model.

398 During the intricate model creation phase, a thorough exploration and optimization process
399 encompassed ten distinctive kernel functions. This exhaustive set included, among others,
400 exponential, exponential squared, Matern32, Matern52, quadratic rational, ARD exponential,
401 ARD exponential squared, ARD Matern32, ARD Matern52, and ARD quadratic rational. The
402 optimization process was nuanced, involving the exploration of various basis functions such as
403 constant, linear, PureQuadratic, and zero, while simultaneously fine-tuning the parameters
404 (Kernel Scale [σ_M , σ_F], and σ) for each kernel function.

405 In this study, we present a novel contribution by introducing and implementing the GPR_LFD
406 approach, marking the first application of this innovative amalgamation of the Lévy Flight
407 Distribution algorithm with Gaussian Process Regression in adsorption. This distinctive
408 combination sets our research apart from earlier proposals and opens new avenues for
409 exploration in adsorption. It signifies a significant leap forward in the optimization of
410 hyperparameters for machine learning algorithms. This approach promises not only enhanced

411 results but also improved adaptability across diverse applications and datasets, underscoring its
412 potential as a robust and versatile modeling tool.

413 The integration of Lévy Flight Distribution (LFD) optimization and Gaussian Process
414 Regression (GPR) prediction within MATLAB culminates in a sophisticated framework that
415 yields multifaceted advantages across diverse domains [58]. Foremost, this amalgamation
416 engenders heightened optimization prowess by synergizing the exploratory efficiency of LFD
417 with the predictive accuracy of GPR [58]. By traversing the search space adeptly, LFD
418 optimally navigates complex landscapes, while GPR adeptly synthesizes insights from limited
419 data, culminating in refined optimization outcomes surpassing those achievable through
420 singular methodologies [58].

421 Moreover, the fusion of LFD and GPR manifests in the manifestation of robust predictive
422 models. GPR's capacity for discerning underlying patterns from sparse datasets harmonizes
423 seamlessly with LFD's ability to expedite model training and parameter refinement [58]. This
424 symbiosis empowers the construction of predictive models endowed with unparalleled accuracy
425 and adaptability, capable of elucidating system behaviors across varying contexts with
426 remarkable fidelity [58].

427 A salient consequence of this integration is the judicious allocation of resources. By leveraging
428 MATLAB's computational prowess, this amalgamated approach optimizes resource utilization,
429 mitigating time, computational, and experimental expenditures. Such efficiency not only
430 expedites decision-making processes but also augments cost-effectiveness, thereby fortifying
431 its appeal across sectors characterized by resource constraints [58].

432 Furthermore, the versatility of this integrated framework is unequivocal. Its applicability spans
433 myriad domains, from engineering and finance to healthcare and environmental science. Such
434 universality underscores its status as a potent toolset capable of addressing optimization and

435 prediction imperatives in multifarious contexts, thereby facilitating paradigm shifts and
436 catalyzing innovation across diverse disciplines.

437 In conclusion, the integration of LFD optimization and GPR prediction using MATLAB
438 represents a pinnacle in computational methodology, heralding a new era of optimization
439 efficacy, predictive precision, resource efficiency, and cross-disciplinary applicability. As the
440 frontier of computational science continues to evolve, this integrated framework stands as a
441 beacon of innovation, promising to illuminate pathways to transformative advancements across
442 the spectrum of human endeavor.

443 2.13.1. Statistical evaluation criteria

444 In the present study, the performance of each GPR model was evaluated using various model
445 performance measures including the Correlation Coefficient (R) and Root Mean Squared Error
446 (RMSE) [59–65]:

$$447 \quad R = \frac{\sum_{i=1}^N (y_{exp} - \bar{y}_{exp})(y_{pred} - \bar{y}_{pred})}{\sqrt{\sum_{i=1}^N (y_{exp} - \bar{y}_{exp})^2 \sum_{i=1}^N (y_{pred} - \bar{y}_{pred})^2}} \quad (27)$$

$$448 \quad RMSE = \sqrt{\left(\frac{1}{N}\right) \sum_{i=1}^N (y_{exp} - y_{pred})^2} \quad (28)$$

449 Where N is the number of data samples; y_{exp} and y_{pred} are the experimental and the predicted
450 values respectively; \bar{y}_{exp} and \bar{y}_{pred} are respectively the average values of the experimental and
451 the predicted values [66–70].

452 3. Results and discussion

453 3.1. Characterizations

454 **Figure S2** illustrates the diffraction pattern of GP, manifesting a distinct prominent peak at 2θ
455 = 22° attributed to the (0 0 2) crystallographic plane, alongside a minor peak at $2\theta = 15^\circ$
456 corresponding to the (1 0 1) plane [44,71]. The XRD spectrum shows that for the 2 theta analysis

457 range above 40° , there are no distinct diffraction peaks of crystalline cellulose. Instead, there
458 are mainly amorphous peaks. This implies that the predominant components of the native pulp
459 are non-cellulosic substances, such as hemicellulose and lignin [44,71]. These observations
460 collectively signify the characteristic structural features associated with cellulose I.

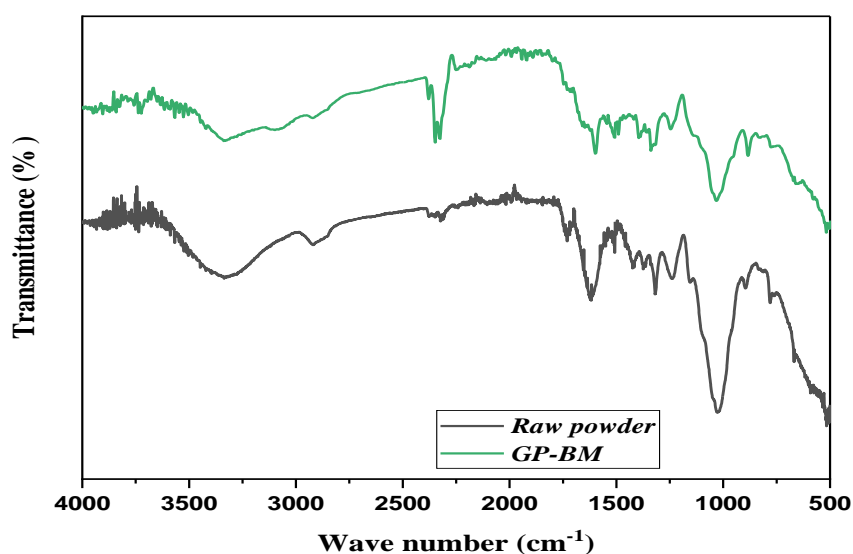
461 FT-IR characterization was employed to quantitatively appraise the functional categories that
462 are identifiable on the pure green peel (GP) samples. Both acid-activated (OP- H_3PO_4) and
463 alkali-activated (OP-KOH) samples were analyzed for comparative purposes. The outcomes,
464 as depicted in **Figure 1**, reveal the presence of distinct absorption bands. Notably, the surface
465 of GP exhibited a higher concentration of alcoholic and phenolic -OH functional groups in
466 comparison to cellulose, as evidenced by a broad absorption band at 3341 cm^{-1} [72]. Additional
467 spectral features included weak bands at 2924 cm^{-1} , indicative of hydrophobic CH_2
468 asymmetrical and symmetrical stretching vibrations, and a band at 1623 cm^{-1} , corresponding to
469 C=O and N-H functionalities, potentially associated with amide I groups [73]. Furthermore, the
470 band at 1320 cm^{-1} was attributed to the C-H group, and at 1030 cm^{-1} , stretching vibrations
471 corresponding to O-H and C-OH were identified, indicative of the presence of polysaccharides
472 within cell walls, such as arabinan and cellulose [74].

473 **Figure 2** indicates that the pH_{pzc} (point of zero charge) of the adsorbent was determined to be
474 5.5. This implies that the GP surface exhibited a positive charge when the solution's pH was
475 lower than 5.5 and a negative charge when the solution's pH exceeded 5.5.

476 Within this pH range, MB is found in both cationic (tri-protonated, or MBH_2^+) and
477 undissociated (MB°) forms. The cationic forms mono-protonated (MBH) and di-protonated
478 (MBH_2^+) occur for pH values higher than 6, with the latter form species predominating [75].
479 However, with pK_a values greater than 8.33, the nitrogen atom in the MB molecule's core cycle
480 is completely deprotonated, leaving the MB dye negatively charged (MB^-). Because our
481 biomaterial has a negative charge as a result (pH>5.5), we chose the cationic dye (MB).

482 **Figure 3** depicts the scanning electron microscope (SEM) analysis of the surface morphology
483 of GP biomass during the adsorption process of MB dye, conducted at varying magnifications
484 ranging from 100 to 5 μm and at an accelerating voltage of 5 kV. Furthermore, the raw green
485 peel exhibits a distinct structural characteristic. The SEM imagery reveals the presence of
486 abundant pores and an irregular surface structure within the fibers of the GP [76]. It is clearly
487 illustrated that the enhanced adsorption potential can be attributed to this specific surface
488 feature of the fiber material.

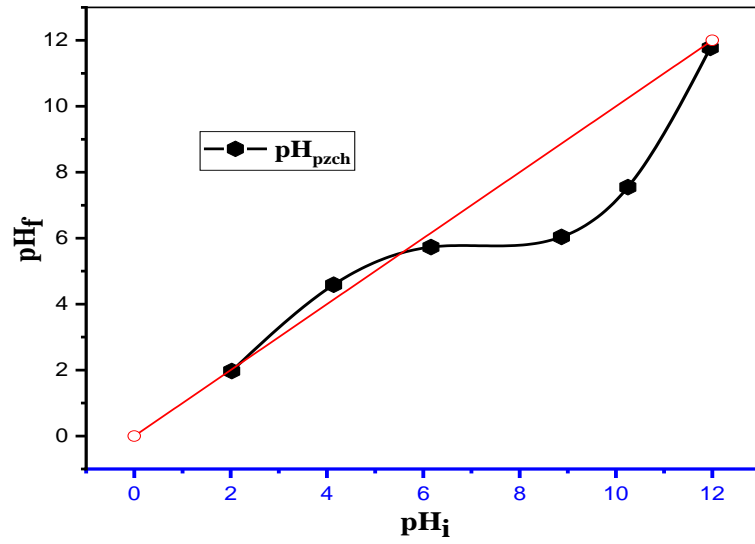
489 The BET characterization of Green Peel (GP) shows a surface area of 85.672 m^2/g ,
490 indicating a substantial amount of available surface for adsorption. This high surface area
491 suggests that GP has significant potential for adsorbing Methylene Blue (MB) or other
492 substances, reflecting its effectiveness as an adsorbent. The result points to GP's promising
493 performance in adsorption applications, although further analysis of its pore structure and
494 adsorption dynamics would provide additional insights.



495

496

Figure.1. FTIR characterization of biomass (raw and GP-BM).

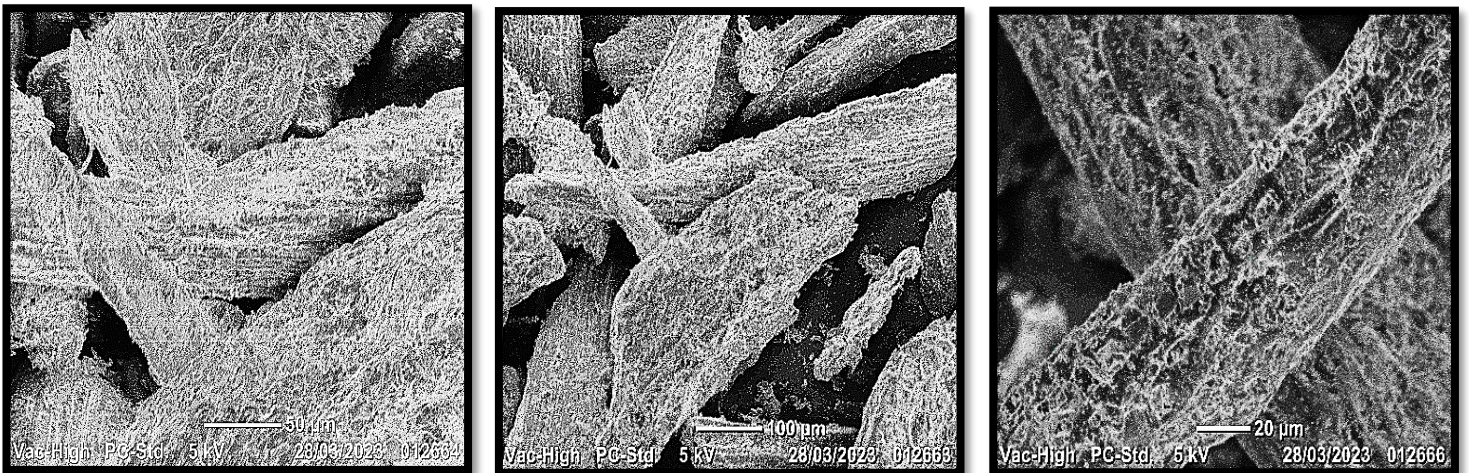


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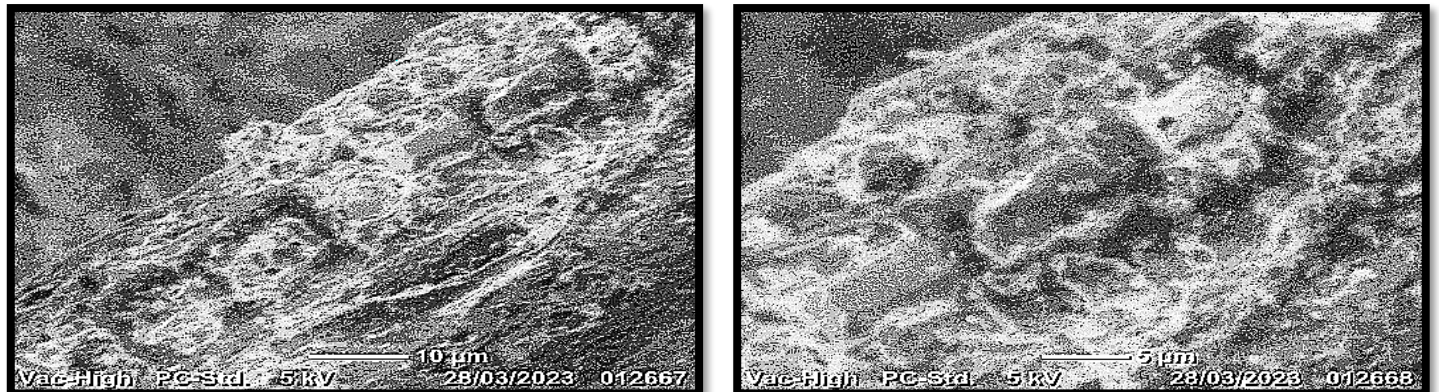
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Figure.2. Determination of the zero charge point of GP raw.

499



500



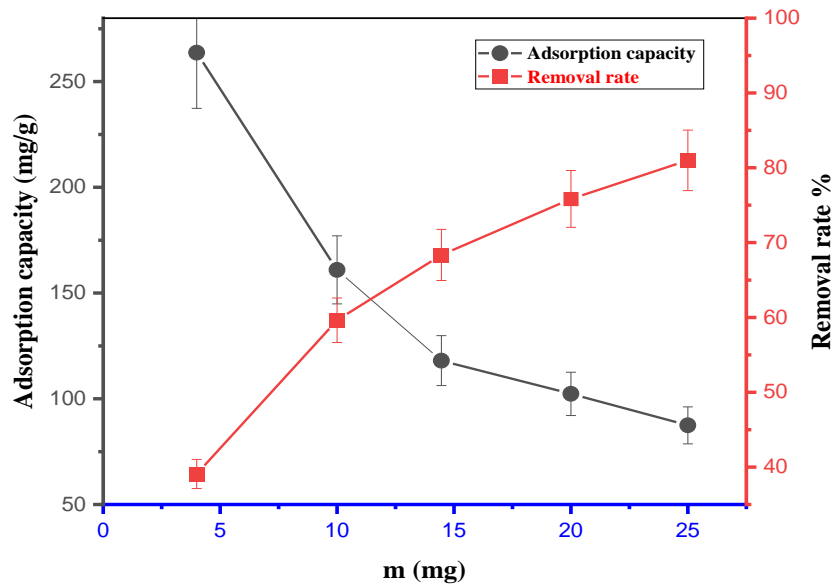
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Figure.3. SEM images of a GP raw.

502

3.2. Effect of adsorbent dose

503 **Figure 4** illustrates the impact of the mass of adsorbent on the binding of MB. It reveals a
 504 reduction in the adsorption capacity per unit mass of adsorbent as the adsorbent mass increases.
 505 This reduction is accompanied by an increase in the absorption rate, leading to enhanced
 506 pollutant removal. This phenomenon may be attributed to an increase in the available surface
 507 area and the number of active sites on the surface of GP material[26].



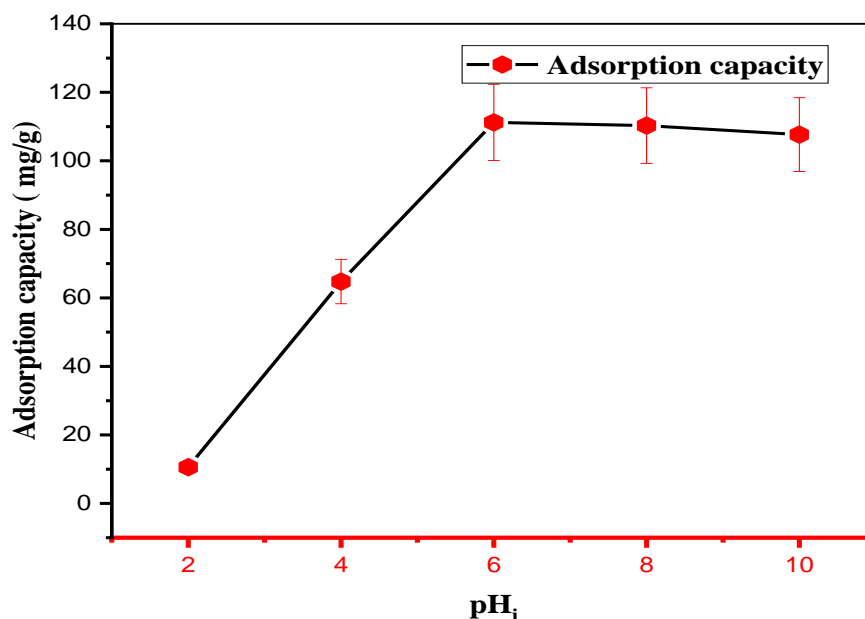
508

509 **Figure.4.** Effect of adsorbent dose on the adsorption of MB on GP (C_o : 100 mg. L⁻¹, Contact
 510 time: 30 min).

511 3.3. Effect of pH

512 **Figure 5** indicates how the pH of an aqueous solution affects the MB adsorption on GP material.
 513 The findings illustrate that under acidic conditions (pH < 6), the adsorption capacity of (GP)
 514 exhibits an augmentation from 10.6 to 111.22 mg/g. Conversely, under alkaline conditions (pH
 515 > 6), there is a reduction in adsorption capacity to 107.56 mg/g. At very low starting pH levels,
 516 there is relatively little MB absorption. This is brought on by the protonation of the adsorbate
 517 (MB) in an acidic environment and the competition with excess H⁺ ions and dye cations for
 518 active sites. Because of electrostatic attraction, there are fewer strongly charged sites and more
 519 less charged sites when the pH of the solution rises. The negatively charged adsorbent surface

520 at greater pH values changes the polarity of the adsorbent by forming an electric double layer,
521 resulting in dye adsorption [77].



522

523 **Figure.5.** Influence of pH on the adsorption of BM on GP (m_{GPb} : 0.015 g, C_o : 0.1 g/L,
524 Contact time: 30 min).

525 3.4. Removal Kinetics in Relation to Contact Duration

526 In **Figure S3**, the impact of contact duration on the adsorption capability of the biosorbent under
527 investigation is depicted for dye concentrations ranging from 50 to 250 mg/L. The dye solution
528 was allowed to come into contact with the biosorbents for 24 hours in order to calculate the
529 adsorption capacity at equilibrium, $Q_{e,exp}$, (**Table 1**). However, the data points shown in **Figure**
530 **S3** are only for the first 30 minutes because there were no noticeable changes in the adsorption
531 capacity of the biosorbent under study after that point. Due to the presence of multiple
532 functional groups on the surface of all biosorbents during the first stages of adsorption, which
533 led to highly attractive interactions between dye molecules and adsorbent, the adsorption
534 capacity of MB dye rose fast in the first 15 min. The concentration of adsorbed dye grew slowly
535 during prolonged contact durations, converging after 30 minutes to a value close to equilibrium.

536 The outcomes of the nonlinear regression of the PFO, PSO, and PNO equations are shown in
537 **Figure 6. Table 4** summarizes the parameters they were able to gather. At the beginning and
538 for the first five concentrations (50, 100, 150, 200, and 250 mg L⁻¹), respectively. The PFO-
539 derived curves are flatter than the experimental data from adsorption. They surpass the
540 experimental results for the latter step of adsorption, on the other hand. Given a little variation
541 in the beginning stage time, the same observation for the PSO-derived curves. Because of this,
542 there is another order n besides 1 and 2 that offers the least amount of variation throughout the
543 adsorption process [78]. The Elovich model's poor R² values (**Table 4**) showed that pore
544 diffusion was not the primary factor influencing MB adsorption onto GP.

545 The PNO-derived curves that deviate the least from the experimental data support this assertion,
546 and all of this was supported by **Table 4** normalized standard deviation ($\Delta Q\%$) and the
547 correlation coefficient R² values. The correlation coefficients of the pseudo-nth-order kinetic
548 model exhibit strong correlation coefficients and low average percentage error values. This
549 model performs better than the pseudo-first and pseudo-second-order equations and matches
550 the experimental data nicely. For concentrations of 50, 100, 150, 200, and 250 mg L⁻¹, the order
551 of the adsorption reaction n was discovered to be between 1.09, 1.41, 5.14, 1.26, and 2.98,
552 respectively.

553 The rate-controlling step is intraparticle diffusion, and the plot of (qt) vs (t^{1/2}) should be linear
554 and pass through the origin. The correlation coefficients in this study (0.978 <R²< 0.989) show
555 that the adsorption closely resembles the intra-particle diffusion model. However, the intercept
556 does not pass through the origin, indicating that intra-particle diffusion is not the rate-limiting
557 step. This shows that there are three unique zones, with the first being curved, the second being
558 linear, and the third being horizontal lines. The first area is swift and is a result of the outward
559 diffusion of MB molecules from their exterior surface. The diffusion of MB molecules in the
560 pores is regulated by intra-particle diffusion (inner diffusion) during the progressive adsorption

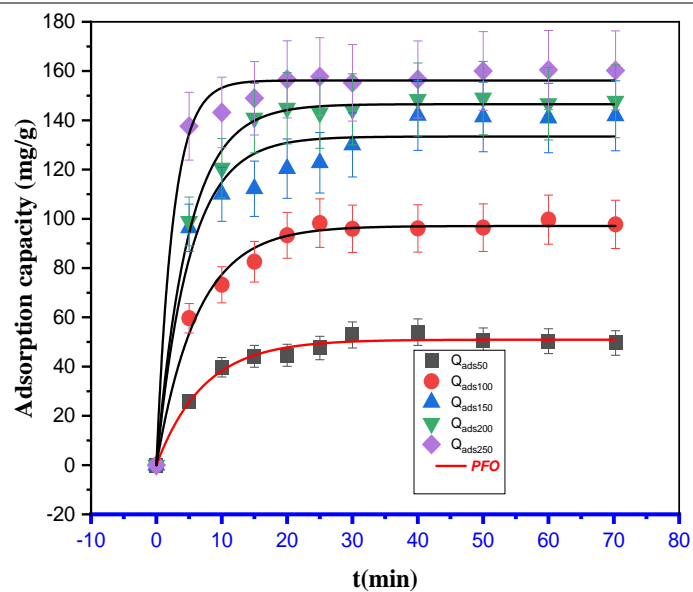
561 stage, which causes the second area. The intraparticle diffusion is beginning to slow down in
 562 the third area, which is the last equilibrium stage, as a result of the low concentration of MB in
 563 the solution. Further observations show that the boundary layer thickens as Co is increased from
 564 50 to 250 mg L⁻¹, which is explained by a decrease in the likelihood of external mass transfer
 565 and an increase in the likelihood of internal mass transfer.

566 Additionally, it was discovered that the intra-particle-diffusion rate constant, k_p , increased as
 567 the initial MB concentration increased, indicating that the boundary layer may have played a
 568 role in the growing driving force for the mass transfer between the solution and GP surface
 569 [79]. As shown by the positive and less than 1 value of v in the fractional power model, this
 570 model should explain the mechanism. However, the poor values of the correlation coefficient
 571 (R^2) along with the capacity calculated using this model are not close to the experimentally
 572 obtained value, indicating that this model is also not applicable (**Figure 6**).

573 **Table.4.** Kinetic Parameters for nonlinear regression of BM Adsorption onto GP.

models	Parameters	50 mg.L ⁻¹	100 mg.L ⁻¹	150 mg.L ⁻¹	200 mg.L ⁻¹	250 mg.L ⁻¹
PFO	Q_{exp}	45.54	96.49	143.26	196.98	238.09
	Q_e	50.94	97.94	133.41	146.54	156.18
	K₁	0.138	0.159	0.197	0.205	0.394
	R²	0.989	0.988	0.948	0.994	0.990
	ΔQ%	0.140	0.002	0.047	0.692	1.183
PSO	Q_e	56.68	106.46	146.10	157.50	161.95
	K₂	0.003	0.002	0.002	0.002	0.006
	R²	0.976	0.989	0.983	0.992	0.997
	ΔQ%	0.598	0.106	0.003	0.433	1.022
PNO	Q_e	51.27	100.06	202.007	148.52	170.18
	K_n	0.004	0.005	1.09*10 ⁻¹⁰	0.007	4.42*10 ⁻⁵

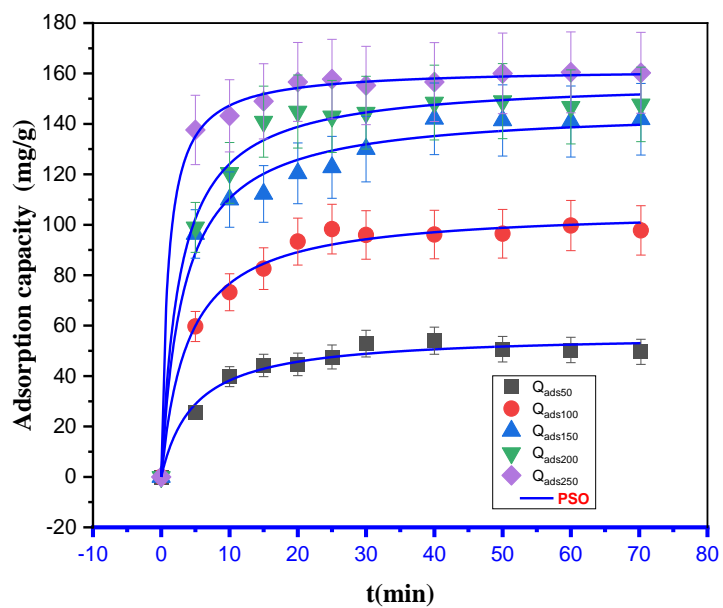
	n	1.09	1.41	5.14	1.26	2.98
	R²	0.986	0.992	0.992	0.996	0.998
	ΔQ%	0.158	0.013	1.681	0.641	0.813
Elovich	a	65.73	264.51	585.78	2352.44	1.751*10 ⁷
	B	0.114	0.058	0.052	0.058	0.112
	R²	0.945	0.971	0.993	0.973	0.997
Intraparticule	K_p	18.845	35.504	49.532	52.137	53.097
	C	2.723	7.655	11.763	17.894	29.727
	R²	0.914	0.932	0.959	0.899	0.838
Fictional power	K	3.11	3.907	4.35	4.482	4.844
	v	0.177	0.12	0.091	0.082	0.033
	R²	0.840	0.9	0.953	0.855	0.928



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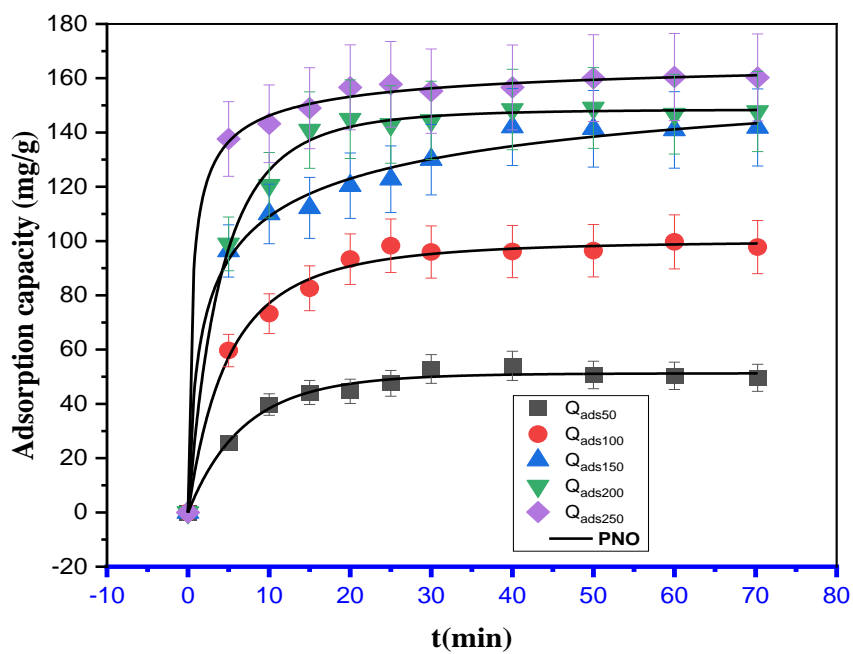
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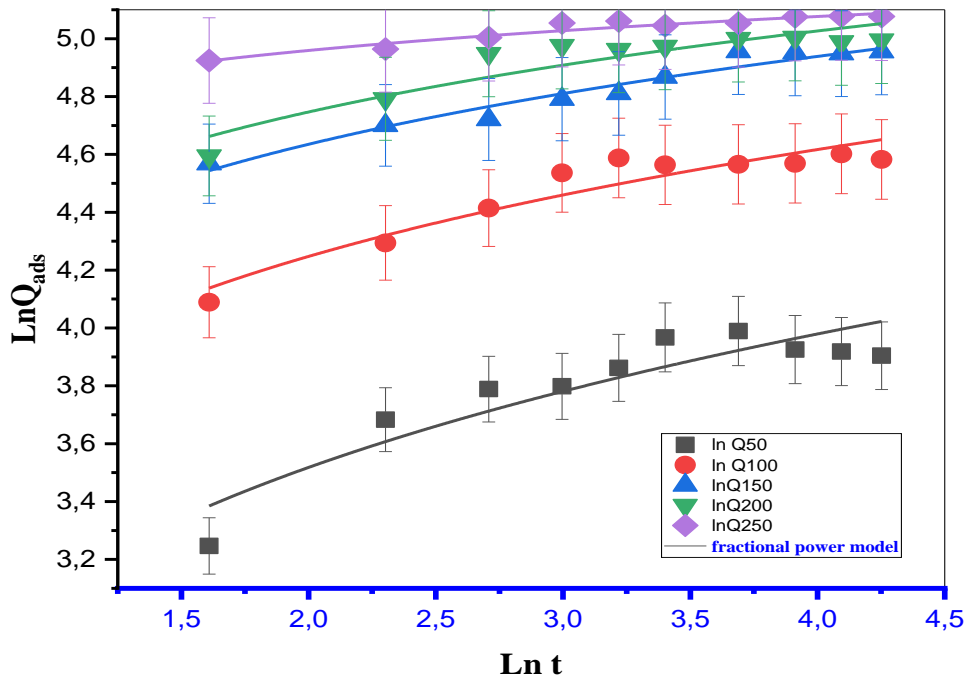
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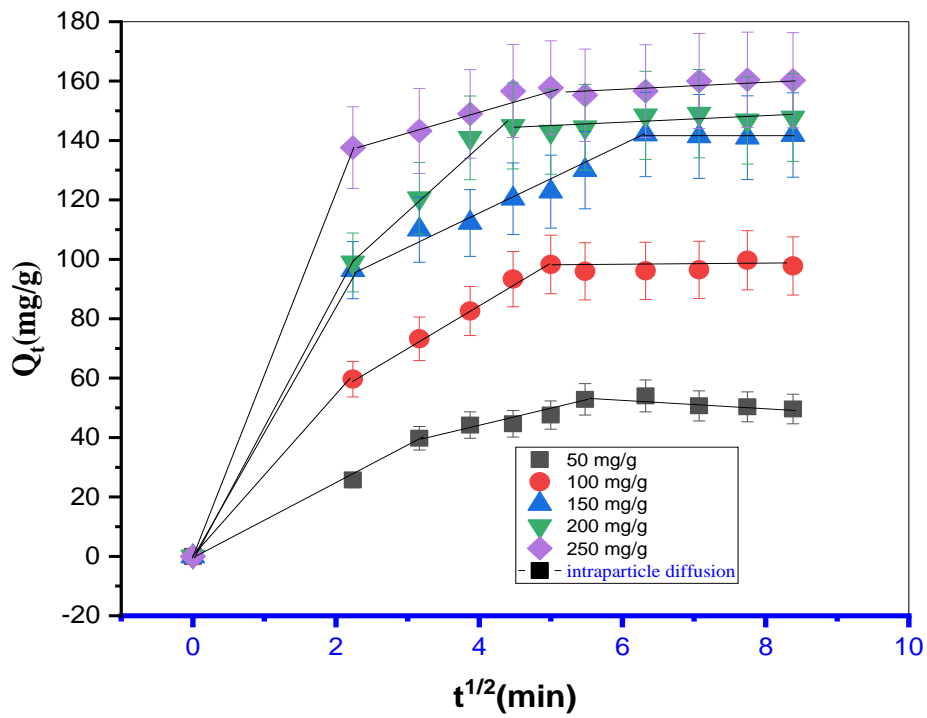
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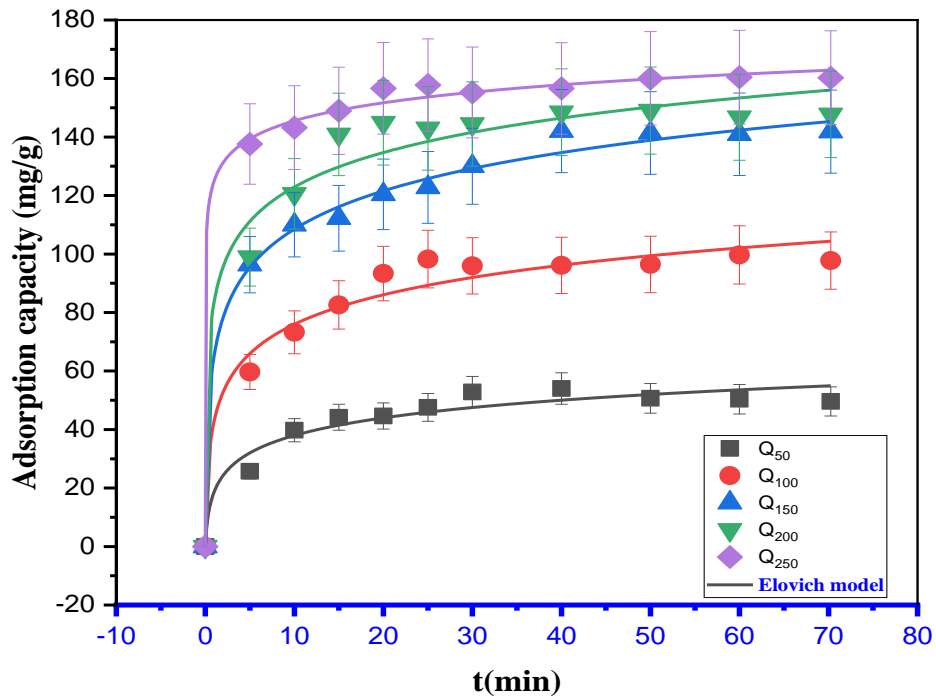
(d)



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(e)



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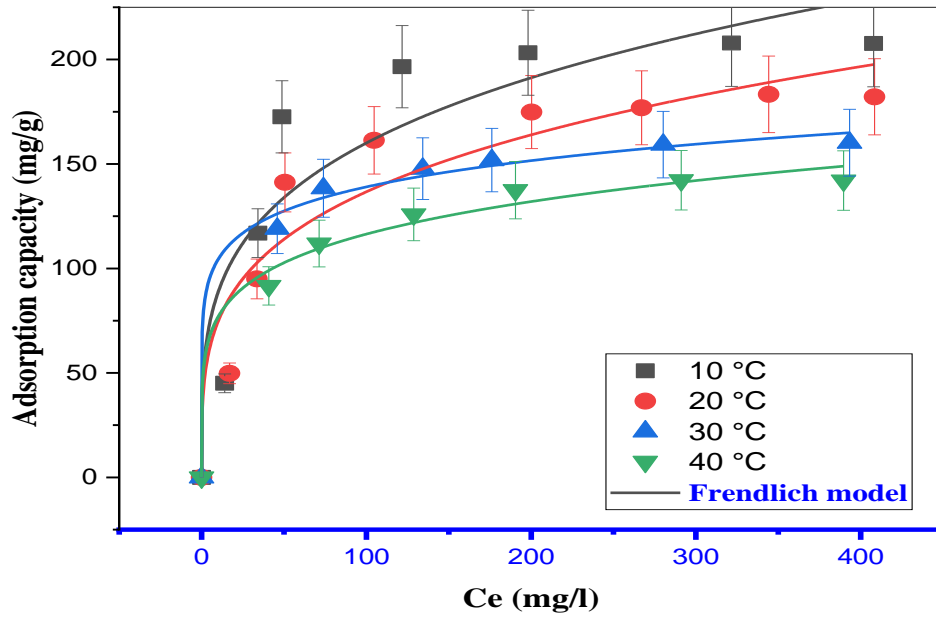
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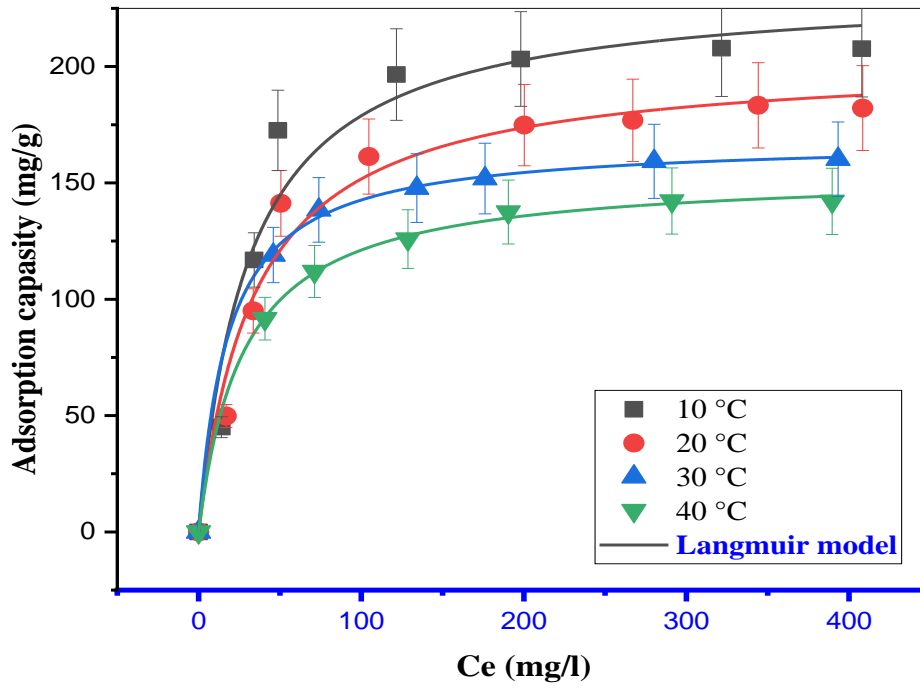
(f)

Figure.6. graph representative of Nonlinear simulation of the pseudo-first-order (a), pseudo-second-order (b), pseudo-nth-order (c), fractional power (d), intraparticle (e), and Elovich kinetic models (f). ($m = 30$ mg, $v = 50$ ml, stirring = 250 ppm, $T =$ ambient temperature).

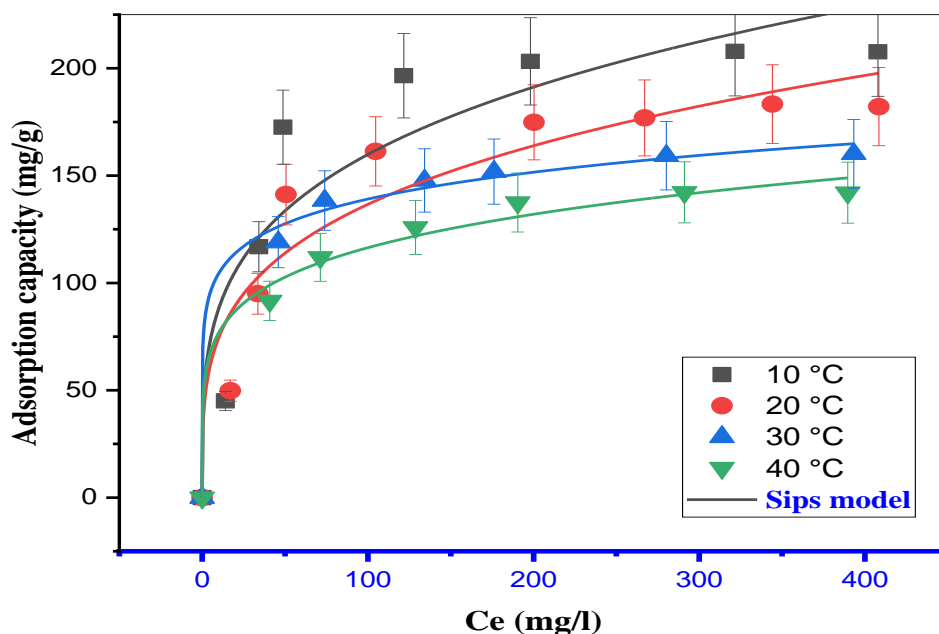
3.5. Adsorption isotherm study



591



592



593

594 **Figure.7.** Result of fitting isotherms data of MB adsorption onto GP with Langmuir,
595 Freundlich and Sips models. (m = 15 mg. v = 25 ml. stirring = 250 ppm. pH_{natural}).

596 The hybrid error function (HYBRID) and fitting parameters are displayed in **Table 5**. By
597 contrasting the (HYBRID) and R² scores for data fit. The high coefficients (R² > 0.99) and the
598 lower HYBRID levels demonstrate that the Langmuir model provides the best applicability to
599 the equilibrium adsorption data with a monolayer of MB attributed to a homogeneous
600 distribution of active sites on the surface of the GP. The maximum monolayer adsorption of
601 MB on GP was observed to be 207.33 mg/g at 10 °C, decreasing to 148.52 mg/g at 40 °C. This
602 reduction at higher temperatures is attributed to desorption, facilitated by the formation of more
603 hydrophobic bonds between the MB molecules in water. These bonds decrease the contact
604 between the molecules and the adsorbent surface [79], as molecules in water tend to detach
605 from the surface to which they adhere as temperature rises. This phenomenon occurs because,
606 with increased temperature, molecules in water exhibit a tendency to form stronger bonds with
607 each other, thereby diminishing their affinity for the surface. A high tendency for the adsorption
608 of the MB on the GP is indicated by values of 1/n for the Freundlich isotherm between 0 and 1,
609 whereas lower R² values imply that the model is inadequate for adjusting experimental data.

610 The three conventional models that were utilized to build the MB uptake dynamic are
 611 inadequate. The setup and regulation of the MB-GP interaction are therefore considered as
 612 requiring the help of theoretical treatment using sophisticated models.

613 **Table.5.** Different Isotherm model parameters for the adsorption of MB onto GP.

Models	Parameters	10 °C	20 °C	30 °C	40°C
Langmuir	Q_{exp}(mg • g⁻¹)	203.333	192.187	179.380	147.828
	Q _m (mg • g ⁻¹)	234.161	203.351	168.405	154.527
	K _L (L • mg ⁻¹)	0.032	0.029	0.055	0.036
	R²	0.997	0.997	0.999	0.999
	HYPRID	3.887	8.649	7.677	0.014
Freundlich	N	3.890	3.813	8.006	5.526
	K _F (mg•g ⁻¹)(L/mg) ^{1/n}	48.993	40.853	78.215	50.609
	R²	0.876	0.915	0.994	0.989
	HYPRID	19.850	1.055	11.734	1.066
	Sips	Q _m (mg•g ⁻¹)	126.71	115.05	99.60
	K _S (L•mg ⁻¹)	0.05276	0.09661	0.062117	1.4016
	M	1.05426	1.03999	1.1606	1.108
	R²	0.92913	0.90737	0.98158	0.91354
	HYPRID	481.237	516.00	519.374	658.377

614 3.6. Sophisticated statistical physics models

615 Our trial isotherm information was subjected to simulation applying ORIGIN software (version
 616 2018). In **Figure 8**, we determined the most suitable model or models for comprehending MB
 617 adsorption onto GP material by assessing the correlation coefficient R² as detailed in **Table 5**.
 618 The optimal model from advanced statistical physics for describing the MB adsorption onto the
 619 GP adsorbent was identified as the double-energy single-layer model.

620 3.6.1. Steric parameters

621 3.6.1.1 Parameter n

622 The adsorption geometry (vertical or horizontal) and uptake method (multi-docking or multi-
 623 interactions) of the studied dye MB on GP adsorbent may both be explained by the steric n
 624 parameter, where n is the number of dye molecules adsorbed per active site of the adsorbent

625 (GP). Based on the n parameter, three primary situations are often recognized when defining
626 the adsorption shape and mechanism: Si ($n > 1$) MB adsorption can occur in a vertical geometry
627 via a multi-interaction process, when ($n < 1$) MB adsorption takes place horizontally via a multi-
628 docking process (multiple GP functional groups can bind to a single molecule of the under-
629 studied dye), and when ($n=1$) this condition signifies the attachment of the adsorbed species to
630 an adsorption site in a non-parallel configuration, indicative of a mono-adsorbate process
631 leading to the formation of a monomer [80].

632 **Figure 9** shows the n values at four temperatures, 283, 293, 303, and 313 K, and the obtained
633 values of this parameter are given in **Table 6**. The n_1 values corresponding to the four
634 temperatures were found as 2.7, 3.058, 2.342 and 2.721, while the n_2 values are 0.452, 0.966,
635 7.411 and 5.126 at 283, 293, 303 and 313, respectively. The MB–GP interaction revealed a
636 vertical (non-parallel) arrangement with a multimolecular manner mechanism for the n_1 . In
637 addition, in the 2nd variable n_2 a vertical setting presented, a multimolecular mode for
638 temperatures 283 and 293, the adsorbed MB attitude was changed to horizontal placement, and
639 the molecule acquired a parallel (horizontal) orientation with a multi–docking mode by
640 increasing the solution temperature to 303 and 313 K.

641 3.6.1.2. **Parameter N_m**

642 The density of the receptor site N_m parameter functions as a steric indicator, specifying the
643 number of occupied adsorption sites within a unit mass of the adsorbent. Moreover, it denotes
644 the number of available adsorption sites for species adsorbed at the state of equilibrium [81].

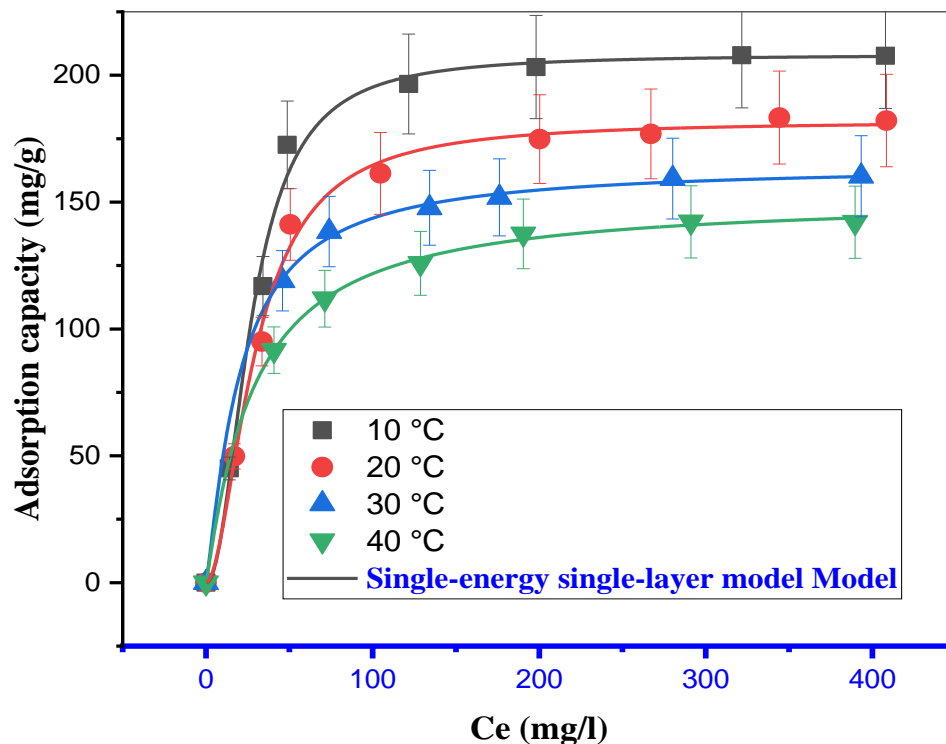
645 In **Figure 9**, the temperature-dependent variation in receptor site density (N_m) is depicted. The
646 densities of the GP receptor sites, specifically N_{m1} and N_{m2} , exhibited a decreasing trend with
647 the temperature rise. This phenomenon is correlated with an elevation in the quantity of

648 captured molecules (n_1 and n_2 per site), indicative of a heightened tendency toward aggregation
649 as the temperature rises.

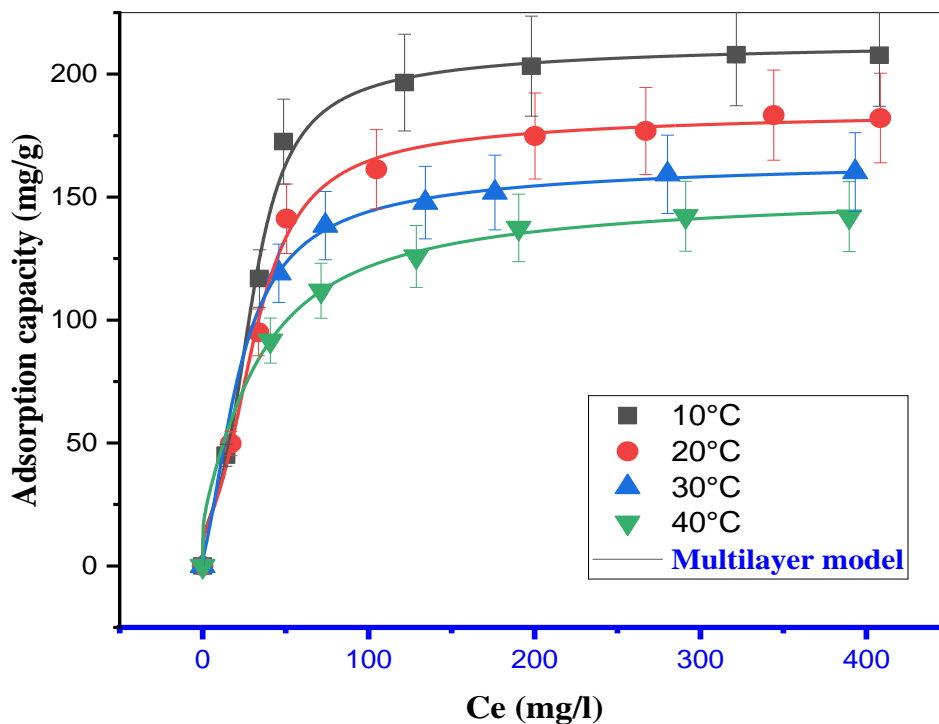
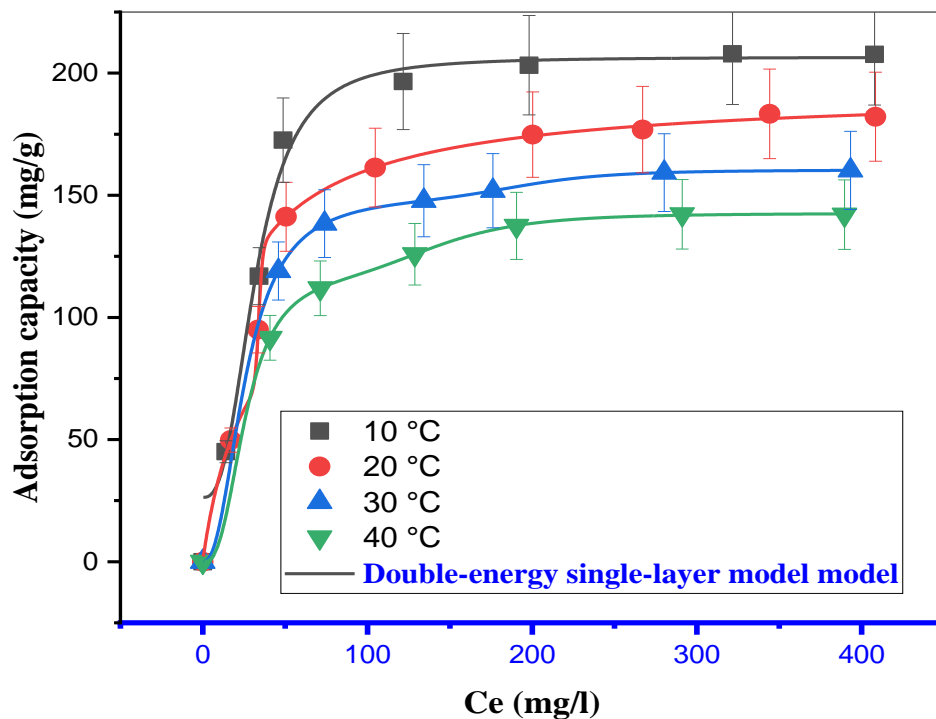
650 3.6.1.3. Parameter Q_{sat}

651 The saturation adsorption quantity, Q_{sat} , serves as a steric parameter interdependent with other
652 steric factors ($Q_{sat,i}=N_{mi}*n_i$). In accordance with the most appropriate statistical physics model,
653 Q_{sat} can be expressed in terms of the number of species adsorbed per adsorption site, the density
654 of adsorption sites, and/or the formation of layers. This metric enables an assessment of the
655 effectiveness of the adsorbent utilized in the adsorption process [82].

656 In **Figure 9**, the temperature-dependent variation of the overall saturation adsorption quantity
657 was graphically represented. The total adsorbed amount at saturation exhibited a notable
658 sensitivity to temperature fluctuations. Specifically, an elevation in temperature led to a
659 decrease in the adsorbed quantity, attributable to the exothermic nature of the adsorption
660 process a characteristic feature in conventional adsorption phenomena.



661



664 **Figure.8.** The outcome of fitting isotherm data pertaining to the adsorption of MB onto a GP
 665 adsorbent with M1, M2, and M3 models (m = 15 mg. v = 25 ml. stirring = 250 ppm. pH=6.6).

666

667

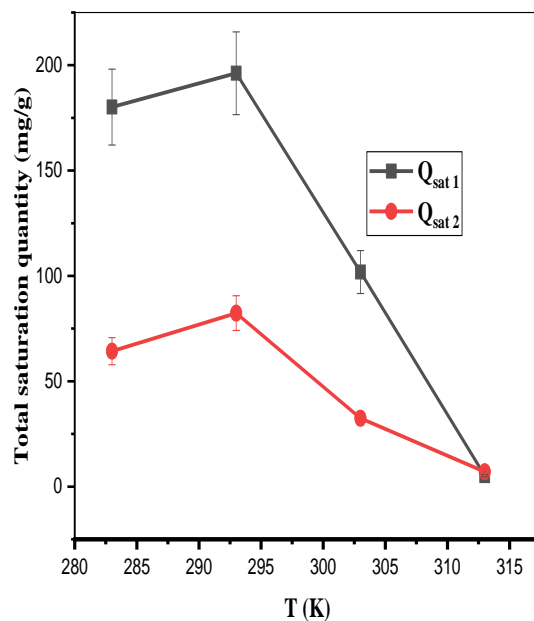
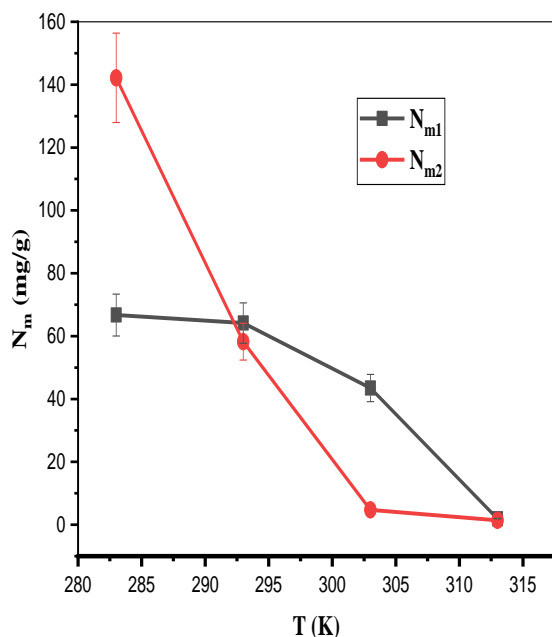
Table.6. The determined parameter values for advanced models in the context of the

668

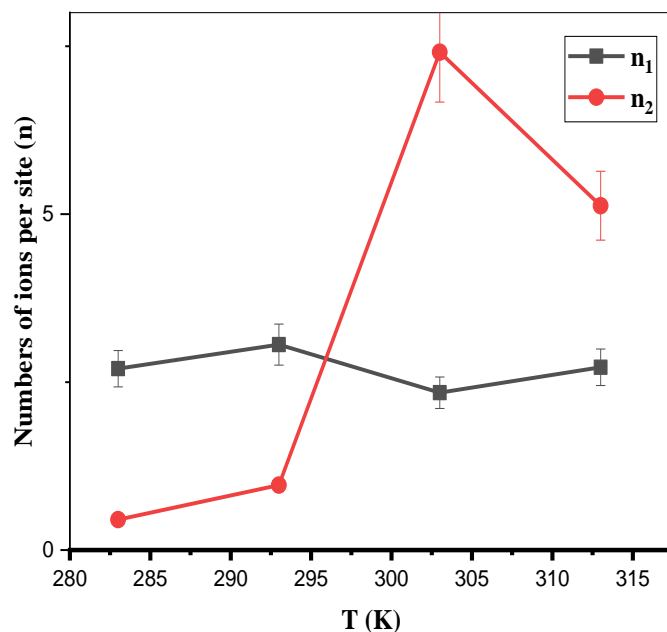
adsorption process of MB onto GP biomass.

Models	Parametrs	T = 283 K	T = 293 K	T = 303 K	313 K
M1	n	2.102	1.844	1.209	1.101
	N_m	98.981	98.642	135.976	137.628
	$C_{1/2}$	27.381	29.598	20.277	27.866
	R²	0.993	0.995	0.999	0.999
M2	n_1	2.700	3.058	2.342	2.721
	n_2	0.452	0.966	7.411	5.126
	N_{m1}	66.716	64.158	43.494	1.861
	N_{m2}	142.174	58.234	4.727	1.377
	C_1	32.101	34.024	25.945	25.944
	C_2	6.569×10^{-16}	30.487	195.439	143.787
	R²	0.995	0.999	1	0.999
M3	n	0.178	0.164	0.095	0.117
	N_{m1}	36.423	33.872	30.501	23.634
	N_{m2}	32.784	33.399	58.987	56.983
	C_1	1.151×10^{-32}	3.737×10^{-34}	4.91×10^{11}	6.848×10^{-35}
	C_2	30.957	33.193	18.847	34.896
	R²	0.995	0.996	0.999	0.999

669



670



671
 672 **Figure.9.** Changes in Nm, n, and Qsat with temperature during the adsorption process of MB-
 673 GP.

674 **3.7. Thermodynamic**

675 From **Table S2**, it is clear that the sorption of MB onto GP is exothermic, as shown by the
 676 negative value of H, supporting the findings on the temperature impact, which shows that the
 677 adsorption capacity falls as temperature rises. From 10 to 40 °C, ΔG° is positive and augmented,
 678 indicating that adsorption is viable at higher temperatures. At the solid-liquid interface during
 679 adsorption, the positive entropy ΔS° indicates an increase in randomness as indicated in **Table**
 680 **S2**.

681 The application of the advanced Double-energy single-layer model (M2) enables the
 682 computation of thermodynamic parameters, encompassing entropy, Gibbs free energy, and
 683 internal energy [83,84].

684 **Table.7.** The function of entropy, free enthalpy, and internal energy as related to the M2 model.

685

Function	Equation	Number
Entropy	$\frac{S_a}{K_B} = N_1 \left[\ln \left(1 + \left(\frac{C_e}{C_1} \right)^{n_1 m} \right) + \frac{n_1 \ln \left(\frac{C_1}{C_e} \right)}{1 + \left(\frac{C_1}{C_e} \right)^{n_1 m}} \right] + N_2 \left[\ln \left(1 + \left(\frac{C_e}{C_2} \right)^{n_2} \right) + \frac{n_2 \ln \left(\frac{C_2}{C_e} \right)}{1 + \left(\frac{C_2}{C_e} \right)^{n_2}} \right]$	(29)
Gibbs free enthalpy	$G = K_B T \ln \left(\frac{C_e}{Z_v} \right) \left[\frac{Q_{sat1}}{1 + \left(\frac{C_1}{C_e} \right)^{n_1 m}} + \frac{Q_{sat2}}{1 + \left(\frac{C_2}{C_e} \right)^{n_2 m}} \right]$ $Z_v = \frac{Z_{gtr}}{V} = \left(\frac{2\pi m K_B T}{h^2} \right)^{3/2}$	(30)
Internal energy	$E_{int} = K_B T \left[N_{1s} \frac{\ln \left(\frac{C_e}{Z_v} \right) + n_{1m} \ln \left(\frac{C_1}{C_e} \right)}{1 + \left(\frac{C_1}{C_e} \right)^{n_{1m}}} + N_{2s} \frac{\ln \left(\frac{C_e}{Z_v} \right) + n_2 m \ln \left(\frac{C_2}{C_e} \right)}{1 + \left(\frac{C_2}{C_e} \right)^{n_2 m}} \right]$	(31)

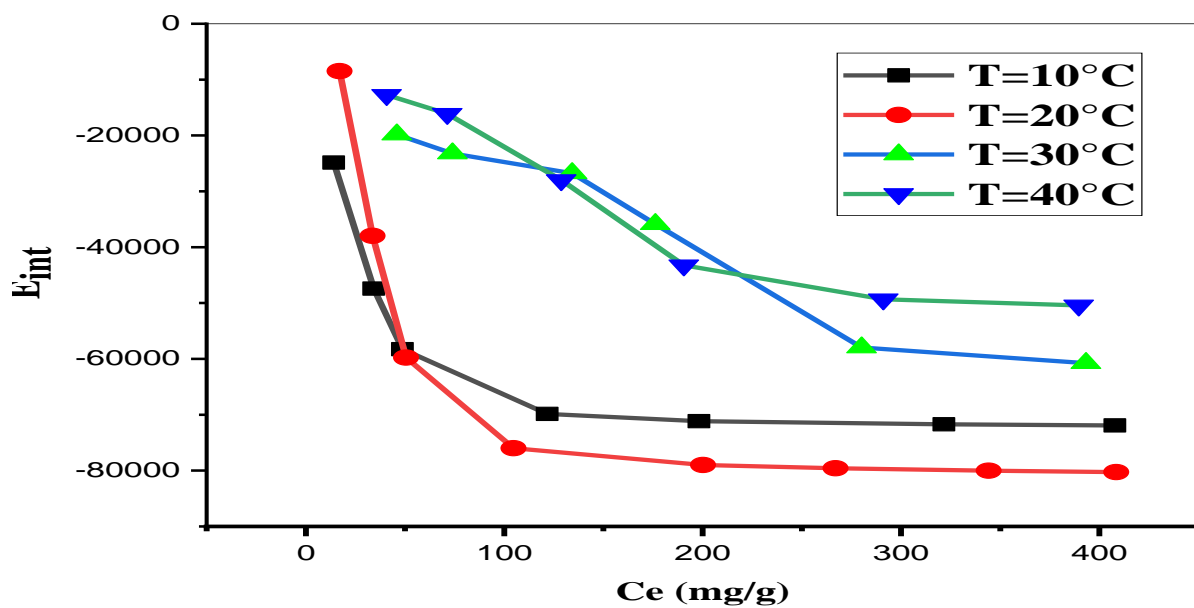
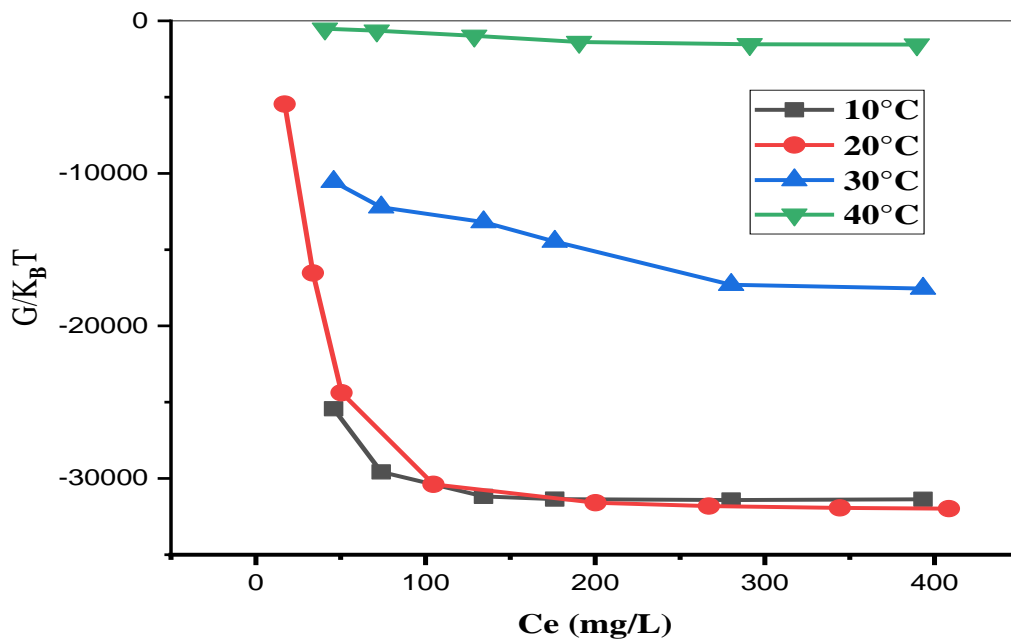
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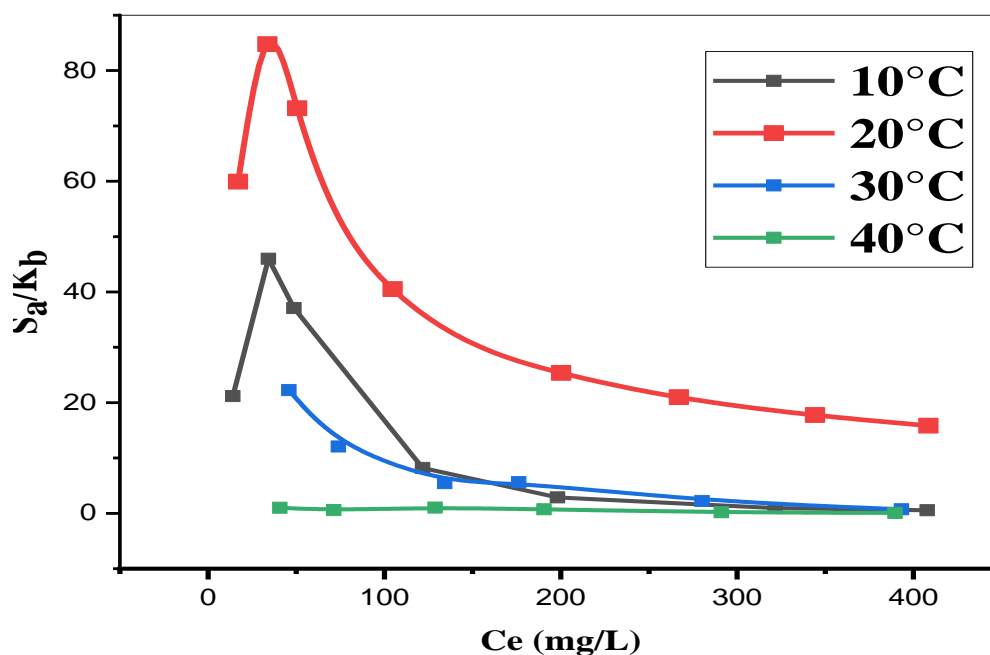
687 The computation of the Gibbs free enthalpy involves the utilization of **Equation (34)** as
688 outlined in **Table 7**, relying on the M2. Subsequently, the Gibbs free enthalpy is graphically
689 represented against adsorbate concentrations across diverse temperatures for the GP adsorbent,
690 as illustrated in **Figure 10**. The observation in **Figure 10** indicates the negativity of the Gibbs
691 free energy, signifying the spontaneous nature of the adsorption process. Furthermore, an
692 increase in temperature is correlated with a diminishing free enthalpy, indicating a
693 consequential reduction in the viability of the adsorption process [85].

694 The assessment of internal energy serves as a comprehensive means to evaluate all
695 energy contributions to the MB adsorption system [48,84]. The general expression for internal
696 energy is represented by **Equation (35)**. The depicted values for this thermodynamic parameter
697 in the examined adsorption system are presented in **Figure 10**. Notably, all recorded internal
698 energy values manifest as negative, indicative of the spontaneous occurrence of the Methylene
699 Blue adsorption systems and the concurrent release of energy.

700 The entropy variation for M2 model given by **Equation (33)**, exhibits two distinct
701 behaviors discernible in terms of concentration. At lower concentrations ($C_{1/2} > C$), there is an
702 observed increase in entropy, indicating a rise in molecular disorder. This implies that MB

703 molecules undergo random movement across the biosorbent (GP) surfaces, facilitated by the
 704 abundant active sites provided by GP at low concentrations, enhancing the adsorption process.
 705 Conversely, at higher concentrations ($C_{1/2} < C$), an opposite phenomenon is evident. The
 706 elevation in concentration results in a reduction of entropy. This decline is attributed to a
 707 plausible decrease in the number of receptor sites available on GP for adsorption as the
 708 concentration increases [84,85].





711

712 **Figure.10.** Evolution of entropy, free enthalpy, and internal energy as a function of
 713 concentration during the absorption of MB by GP adsorbent at distinct temperatures.

714 **3.8. Density Function Theory (DFT) study**

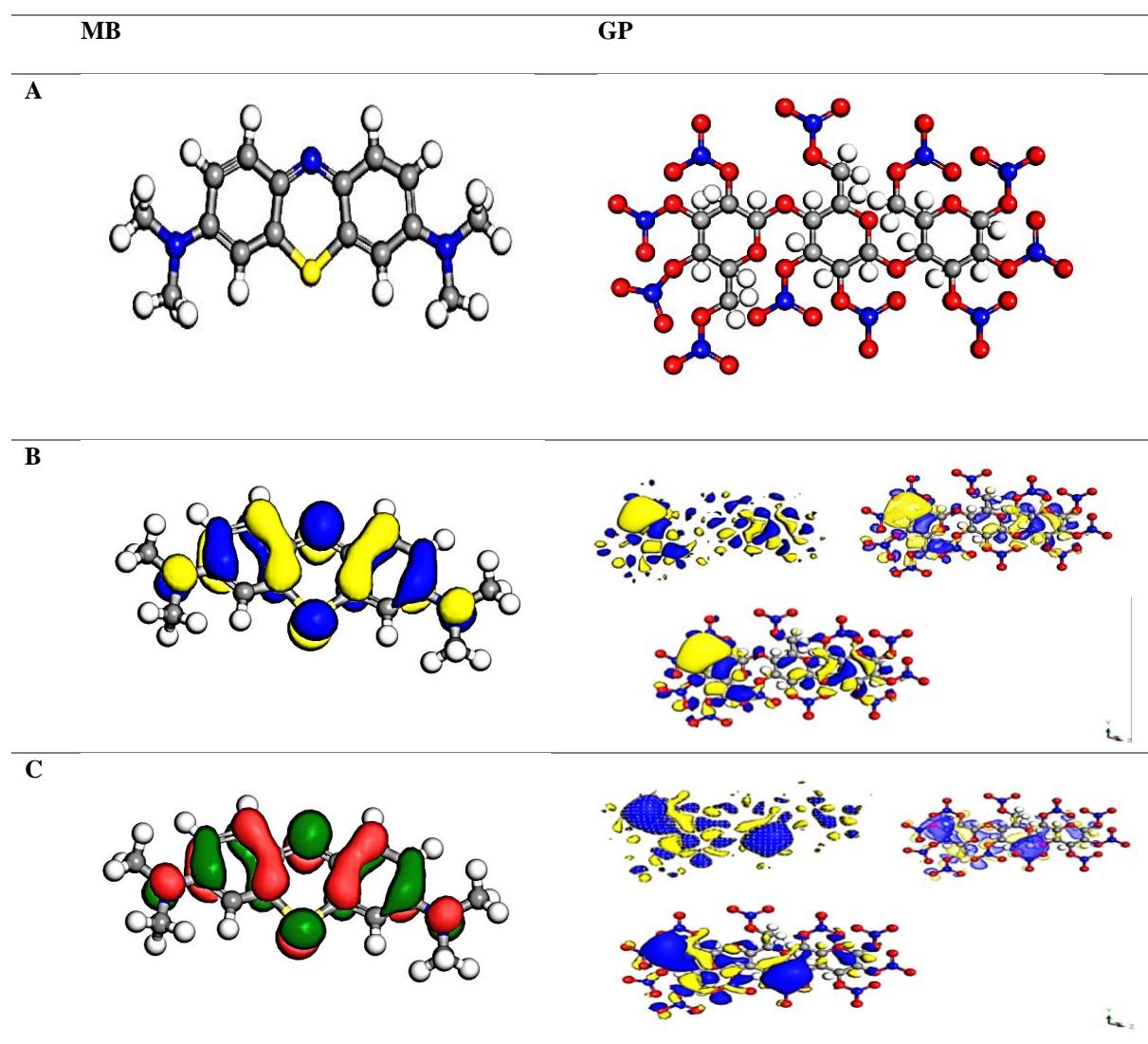
Quantum chemical parameters	MB	GP
E_{Tot} (ev)	-1181.86	-4104.31
E_{HOMO} (ev)	-3.870	0.423
E_{LUMO} (ev)	-2.684	0.268
ΔE^{Gap} (ev)	1.186	-0.155
η (ev)	-0.593	0.07751
X (ev)	6.554	-0.691
S (ev)	-0.843	6.4516
ω (ev)	-36.218	3.0805
σ (ev)	-1.686	12.903
ΔN_{max} (ev)	-11.05	-8.916

715

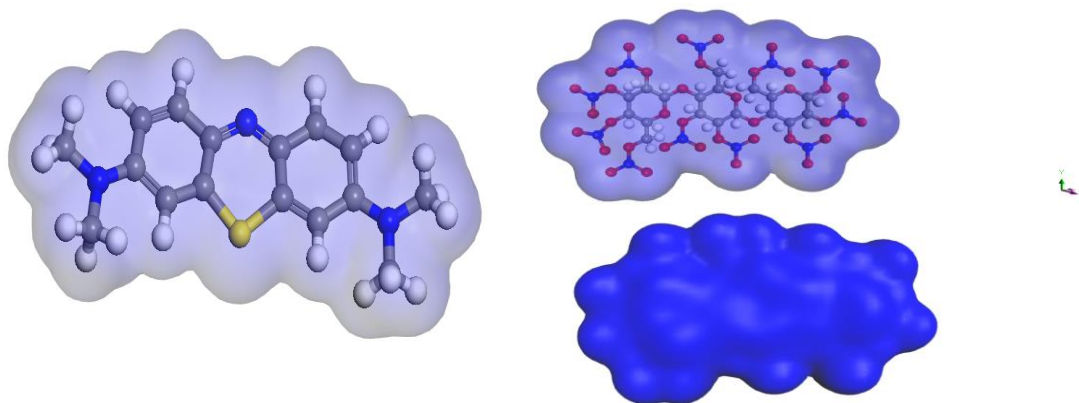
716 As widely recognized, the propensity of a molecule to undergo electron loss is frequently
 717 associated with its highest occupied molecular orbital energy (E_{HOMO}), whereas the molecule's
 718 capacity to accept electrons, as well as its lowest unoccupied molecular orbital energy (E_{LUMO}),
 719 are closely tied to its electron affinity [47,53].

720 Furthermore, a diminutive energy gap (E_{GAP}) signifies heightened reactivity within the
721 molecule, thereby enhancing the efficacy of MB adsorption onto the GP surface, thereby
722 manifesting a notably stable adsorption process.

723 The concept of global hardness encapsulates a molecule's resistance to deformations or
724 polarization when subjected to minor perturbations in chemical reactions. In general, molecules
725 characterized by low global hardness values and elevated global softness values exhibit greater
726 ease in adhering to suitable surfaces. The capacity of molecules to attract electrons is also
727 demonstrated by the electrophilicity index, which can rise with falling values.



d



728

729 **Figure.11.** (a) Optimized molecular structure, (b) HOMO, (c) LUMO and (d) electron
730 density.

731 3.9. Molecular Dynamic Simulation study

732 A pivotal approach for elucidating the intricate interactions between MB molecules and the
733 adsorbent (GP) surface involves leveraging molecular dynamic simulations (MDS). The MDS-
734 based investigation reveals that the equilibrium configuration of MB adsorption onto the GP (-
735 1 0 0) surface, as illustrated in **Figure 12**, corresponds to the most thermodynamically stable
736 state. **Figure 12** depicts the parallel adsorption mode of MB molecules on the GP (-1 0 0)
737 surface, which underscores the strong intermolecular contacts between MB and the GP surface
738 atoms. The chemical adsorption of MB onto the GP surface can be attributed to the contribution
739 of electron-rich atoms, specifically sulfur, nitrogen, and oxygen, as inferred from a
740 comprehensive analysis of the molecular structures of both MB and GP. Furthermore, Van der
741 Waals dispersion is crucial in enabling and facilitating the capture of MB molecules onto the
742 cellulose surface, which aligns with the outcomes obtained during the isoelectric point
743 characterization, confirming physical adsorption. The computational assessment of various
744 adsorption energy parameters for MB onto the GP surface is concisely presented in **Table 8**.
745 The observed negative adsorption energy value (-75.821 kcal/mol) underscores the fact that the
746 adsorption procedure is spontaneous. The notably elevated binding energy value (37.117

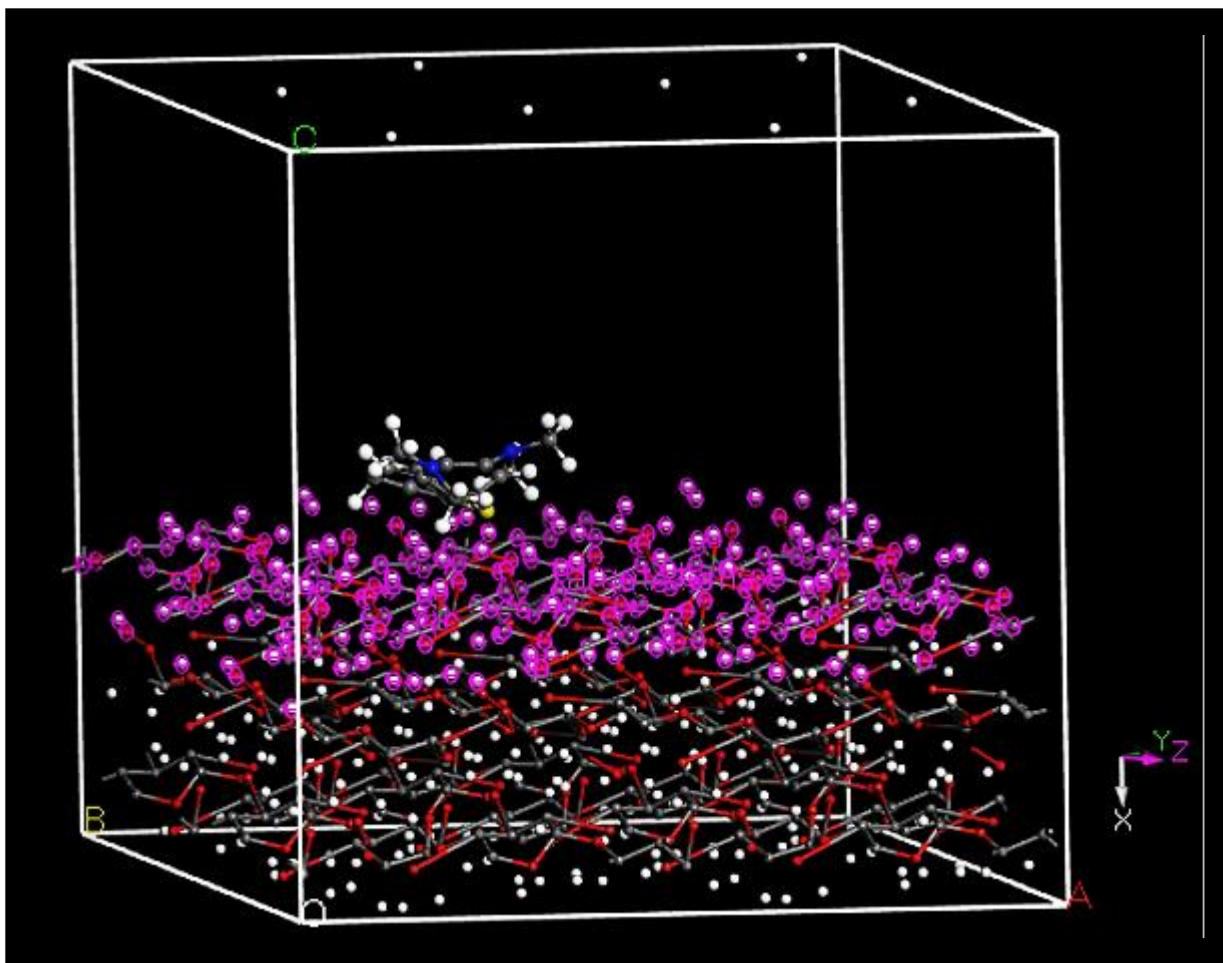
747 kcal/mol) can be attributed to a superior and highly stable adsorption process. It is noteworthy
748 that the deformation energy associated with the molecular rearrangements induced by MB
749 adsorption implies a reduction in the stability of both the MB molecules and the GP surface.

750 In summary, molecular dynamic simulations serve as a pivotal tool for gaining a comprehensive
751 understanding of the complex interplay between MB molecules and the GP surface [86]. The
752 adsorption process is primarily governed by chemical interactions involving electron-rich
753 atoms, and it is further enhanced by Van der Waals forces, culminating in a stable adsorption
754 configuration. Thermodynamic analysis, as succinctly conveyed in **Table S2**, underscores the
755 spontaneity and favorability of the adsorption process, with the deformation energy indicating
756 the stability implications arising from MB-induced conformational changes.

757 **Table.8.** Energies derived from computational calculations pertaining to the adsorption of MB
758 molecules onto the GP surface.

Adsorption energy, Kcal/mol	Rigid adsorption energy, Kcal/mol	Deformation energy, Kcal/mol	BM: d Fad/dNi	Total energy, Kcal/mol
-75.821	-85.69	9.868	-75.821	-143.212

759



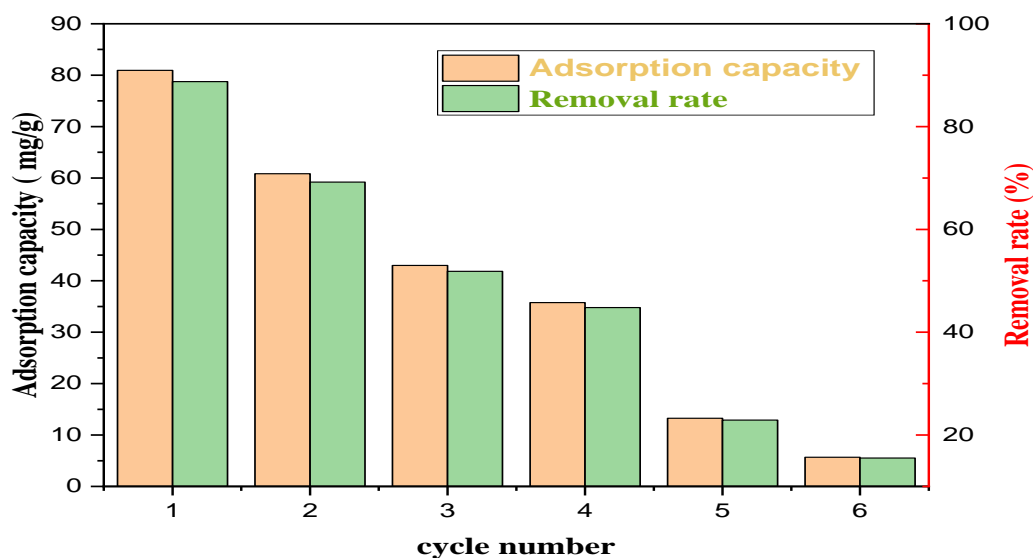
760

761 **Figure.12.** The arrangement of MB's equilibrium adsorption onto the GP surface.

762 **3.10. Regenerative Characteristics**

763 The recyclable properties of the adsorbent material played a pivotal role in the assessment of
 764 its applicability. The regenerative performance of GP in the context of MB adsorption is
 765 depicted in **Figure 13**. It is obvious that both have the ability for adsorption and desorption
 766 efficiency exhibited a diminishing trend with an increasing number of usage cycles. During the
 767 first four cycles, GP retained substantial adsorption efficacy, demonstrating adsorption
 768 capacities (mg/g) and removal rates (%) of 80.92, 60.84, 43, and 35.75 mg/g for cycles 1 to 4
 769 respectively, constituting 78.75%, 59.20%, 41.84%, and 34.78% of the initial values.
 770 Nonetheless, after five cycles, the adsorption capacity of the adsorbent decreased to 13.26 mg/g.
 771 This decline is related to the incomplete desorption of MB from the adsorption sites, when MB

772 molecules are not fully released from these sites, they continue to occupy space on the
 773 biosorbent surface, limiting its capacity to adsorb more MB molecules, resulting in a decrease
 774 in the adsorption capability of the GP. Consequently, the optimal usage cycle for GP was
 775 determined to be five cycles.



776

777 **Figure.13.** Assessment of the Durability and Reusability of GP for MB Adsorption.

778 Experimental Parameters: MB Solution (100 mg/L), T= Room Temperature, GP Mass= 50
 779 mg, Time: 1 hour.

780 **3.11. Gaussian Process Regression coupled with Lévy flight distribution**

781 After optimizing ten kernel functions using the LFD algorithm in conjunction with the base
 782 function, the most effective kernel function was selected based on statistical criteria. **Table 9**
 783 presents the outcomes of this selection process, offering details on the best model, its
 784 corresponding parameters (kernel scale and sigma), and performance assessments using
 785 statistical metrics (R and RMSE) across three distinct phases (training, validation, and all data).
 786 The table also includes information on kernel settings, the preferred kernel function, resulting
 787 basis functions, the count of Lévy flights employed, and the number of iterations required to
 788 achieve the best model.

Table.9. Performances of the GPR-LFD model.

LFD	Max_iteration=50 SearchAgents_no=100											
	Kernel function	Basis Function	Kernel Scale		Sigma	Quantity	R			RMSE		
			Sigma M	SigmaF			Train	Val	ALL	Train	Val	ALL
GPR_DA	ARD- Exponential	PureQuadratic	11.9415 25.4642 22.5696 28.4045 89.6149	134.7677	0.5744	65	1.0000	0.9980	0.9990	0.0142	3.1874	2.5390

790

791 The results obtained following the optimization of kernel functions and basis functions
792 highlight the superiority of the model using the ARD exponential kernel with the PureQuadratic
793 basis compared to other kernels listed in **Table 9**. It is important to note that the parameters of
794 the LFD were set to Max_iteration=50 and SearchAgents_no=100.

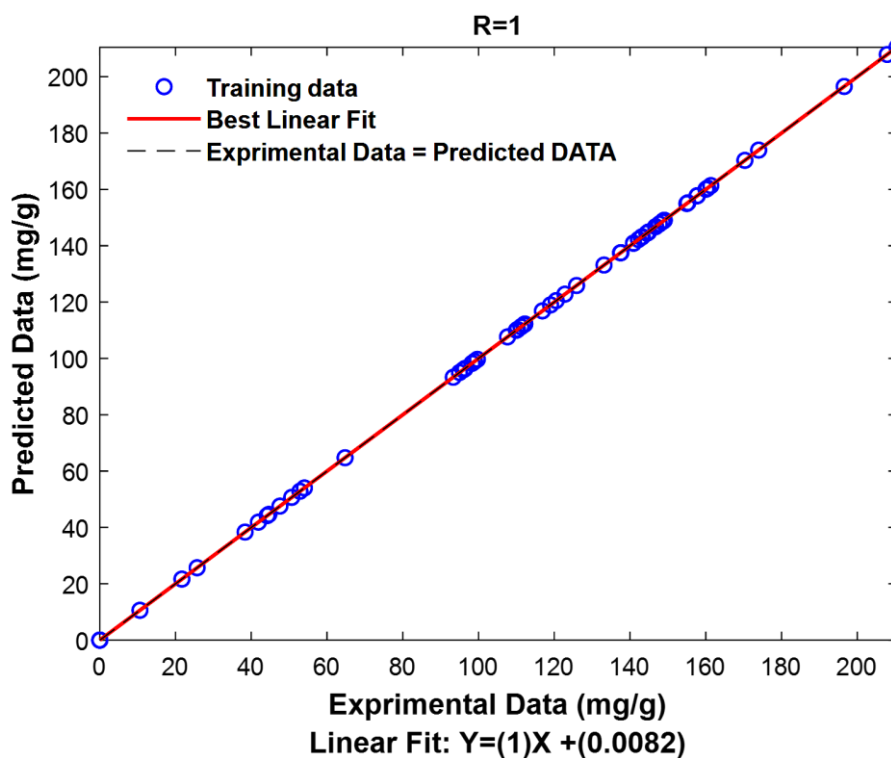
795 In terms of performance metrics, the correlation coefficients demonstrate an exceptional fit of
796 the model to the data. The correlation coefficient for the training set reaches a perfect value of
797 1.0000, indicating an optimal correlation. For the validation set, the high correlation coefficient
798 of 0.9980 emphasizes a robust agreement with the validation data. The overall correlation
799 coefficient, which stands at 0.9990, attests to an outstanding overall performance of the model.

800 Regarding the RMSE, measuring the difference between predicted and actual values, the results
801 are equally remarkable. The RMSE for the training set is 0.0142, indicating high accuracy in
802 predicting training data. For the validation set, the RMSE remains remarkably low at 3.1874,
803 confirming the robustness of the model in predicting validation data. The overall RMSE,
804 established at 2.5390, reflects a satisfactory overall performance of the model across all data.

805 The optimized model with the ARD exponential kernel and Pure Quadratic basis stands out for
806 its excellent fit to the data, characterized by high correlation coefficients and exceptionally low

807 prediction errors, both for the training and validation sets. These results underscore the
808 reliability and precision of the model in predicting the adsorbed quantities of MB by GP,
809 reinforcing its significant potential for advanced predictive applications.

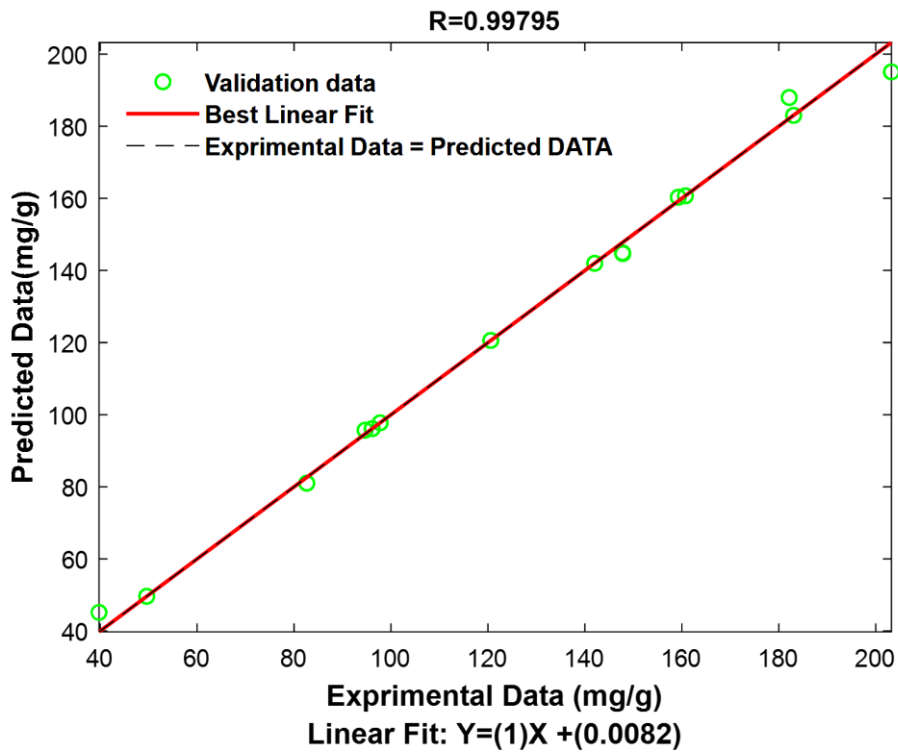
810 These results are visually presented in **Figure 14**, providing a graphical representation of the
811 findings.



812

813

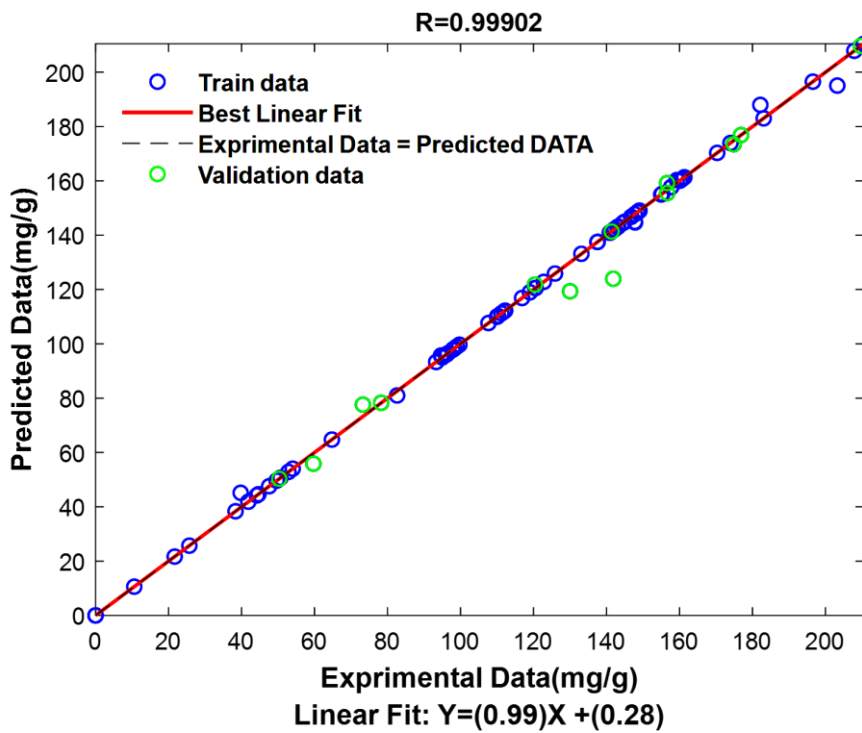
(a)



814

815

(b)



816

817

(c)

818 **Figure.14.** Relationship between the experimental and the GPR_LFD model predicted values:

819

(a) training Data, (b) validation Data, and (c) All Data

820 **3.11.1. Performance of GPR_LFD model tested**

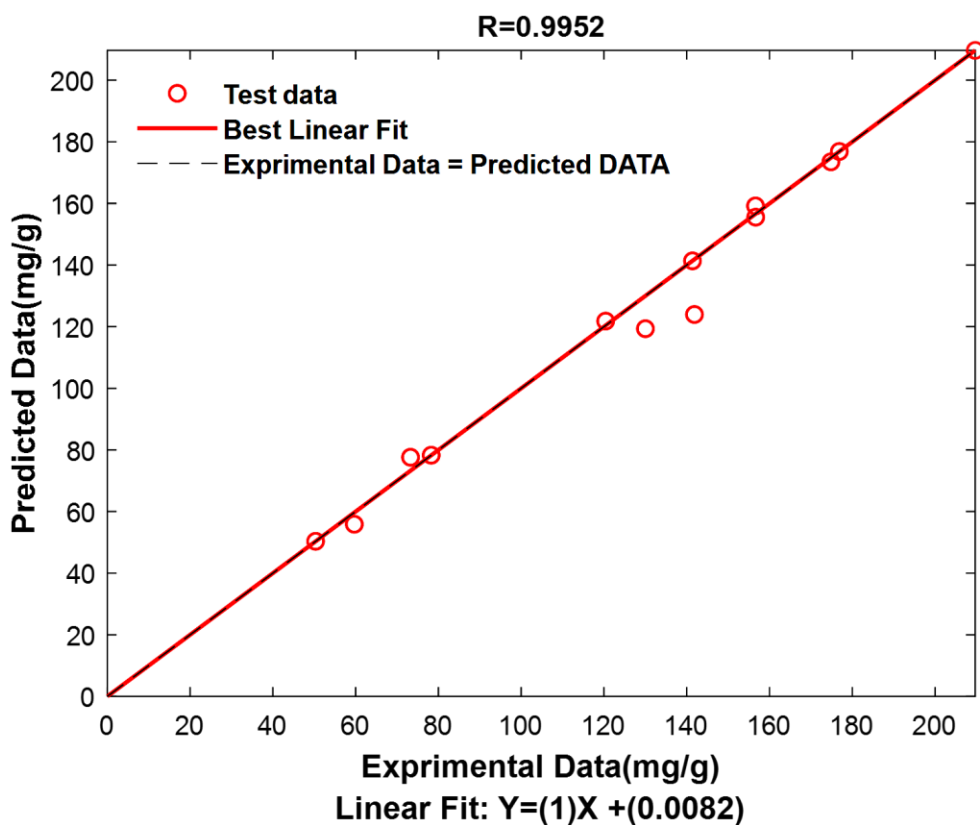
821 In the initial phase of data partitioning, a deliberate reservation of 15% from the database was
822 specifically earmarked for assessing the GPR_LFD model's top performance achieved through
823 interpolation. The outcomes of this thorough evaluation have been meticulously documented in
824 **Table 10**, providing a comprehensive presentation of statistical coefficients and their
825 corresponding errors.

826 **Table.10.** Model test performance of GPR_LFD.

R	RMSE
0.9952	3.8513

827 The results from **Table 10** reveal the outstanding performance of the GPR_LFD model during
828 its evaluation of the test data. A remarkably high correlation coefficient of 0.9952 attests to a
829 robust positive correlation between the model predictions and the actual values. Furthermore,
830 the low RMSE of 3.8513 indicates notable accuracy, with model predictions exhibiting an
831 average error margin of approximately 3.85 units compared to the actual values. These findings
832 confirm the GPR_LFD model's ability to accurately and reliably capture underlying
833 relationships in the data, underscoring its relevance and efficacy in the context of interpolating
834 test data.

835 To provide a visual representation of these performances, experimental values and predicted
836 values have been graphically represented in **Figure 15**.



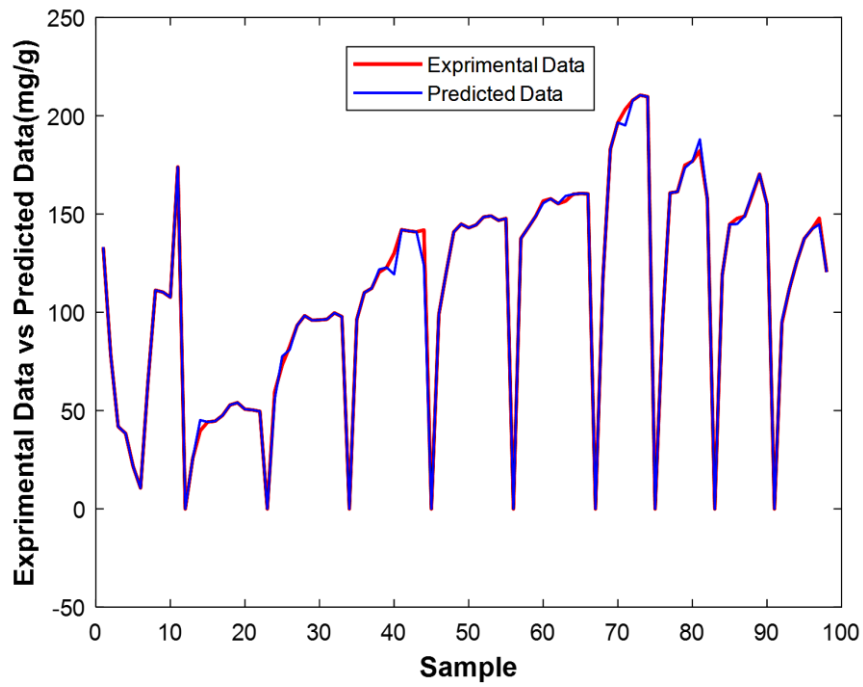
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838 **Figure.15.** Comparison between experimental and predicted values to assess performance OF
 839 GPR_LFD.

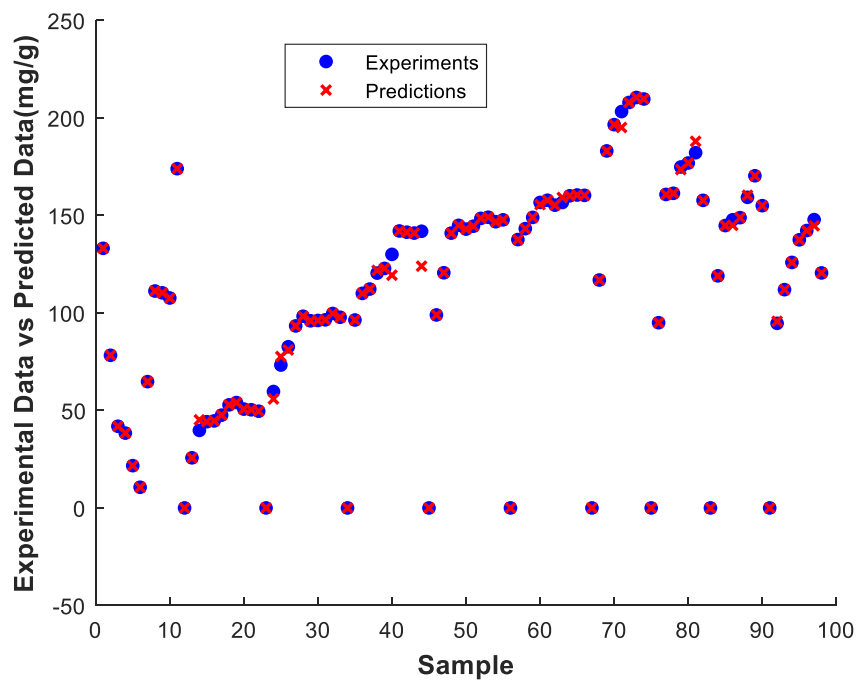
840 **3.11.2. Residues study**

841 In this section, a rigorous and comprehensive evaluation was conducted to thoroughly assess
 842 the performance and efficacy of the selected model [66,87]. This in-depth assessment
 843 encompassed both the application of the residual method and an error histogram, spanning
 844 various critical phases, including training, validation, and testing [61,65]. Following this, a
 845 meticulous comparative analysis was performed by superimposing experimental values onto
 846 predicted ones, covering all data points across the training, validation, and testing datasets,
 847 vividly depicted in **Figure 16(a)**. Furthermore, an extensive error quantification involved a
 848 scrupulous examination of the disparities between experimental and predicted values for the
 849 entire dataset, including data from the training, validation, and testing sets, adhering to

850 established methodologies. The outcomes of this thorough error assessment were thoughtfully
851 visualized in **Figure 16(b)**, employing advanced residual analysis techniques.



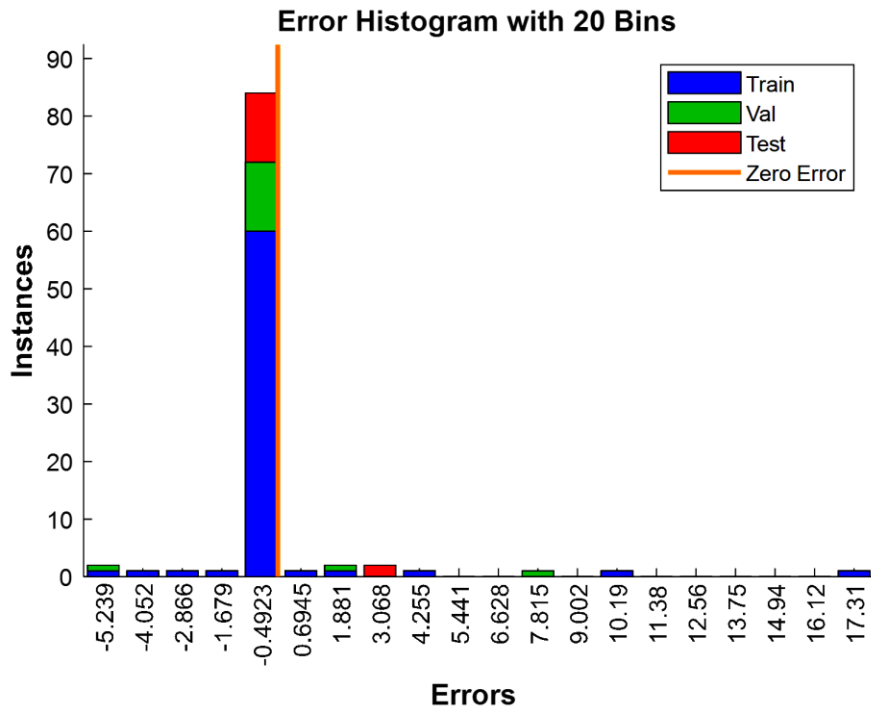
852



853

854

(a)



855

856

(b)

857 **Figure.16.** Residuals relating to the models established by the different techniques according
 858 to the estimated values: (a) Relationship between experimental data and the predicted data of
 859 samples, and (b) Instances distribution of errors.

860 The findings depicted in **Figure 16a** gracefully emphasize a substantial agreement between
 861 experimental and predicted values, providing compelling validation of the model's
 862 effectiveness. Moreover, **Figure 16b** offers additional persuasive evidence of the model's
 863 efficiency, with 84 out of 98 experimental values closely aligning with their predicted
 864 counterparts, resulting in only minor deviations. Notably, the residual errors for the remaining
 865 14 cases were exceptionally minimal, further highlighting the model's outstanding performance.
 866 These comprehensive observations unequivocally establish the model's robustness and
 867 precision, leaving no room for doubt about its capabilities.

868 **3.12. Optimization and Validation of the optimum conditions**

869 The optimization of independent parameters for maximizing MB uptake was carried out using
 870 the Lévy flight distribution method [57]. The accuracy of the optimization results was then
 871 rigorously validated through laboratory experiments. The comparative analysis in **Table 11**
 872 intricately presents predicted values alongside experimental results, offering a comprehensive
 873 view of the corresponding errors between the two datasets.

874 Where: $\text{Error} = \text{Experimental response} - \text{Predicted response}$ (32)

875 **Table.11.** Comparison between actual and predicted responses at optimum
 876 conditions.

GPR_LFD	
• $X_1 = 30 \text{ min. } X_2 = 0.6 \text{ g. } X_3 = 400 \text{ mg/L, } X_4 = 6.6 \text{ and } X_5 = 10^\circ\text{C}$	
MB uptake (mg/g). experimental values	207.90
MB uptake (mg/g). predicted values	207.89
Error (mg/g)	0.008

877

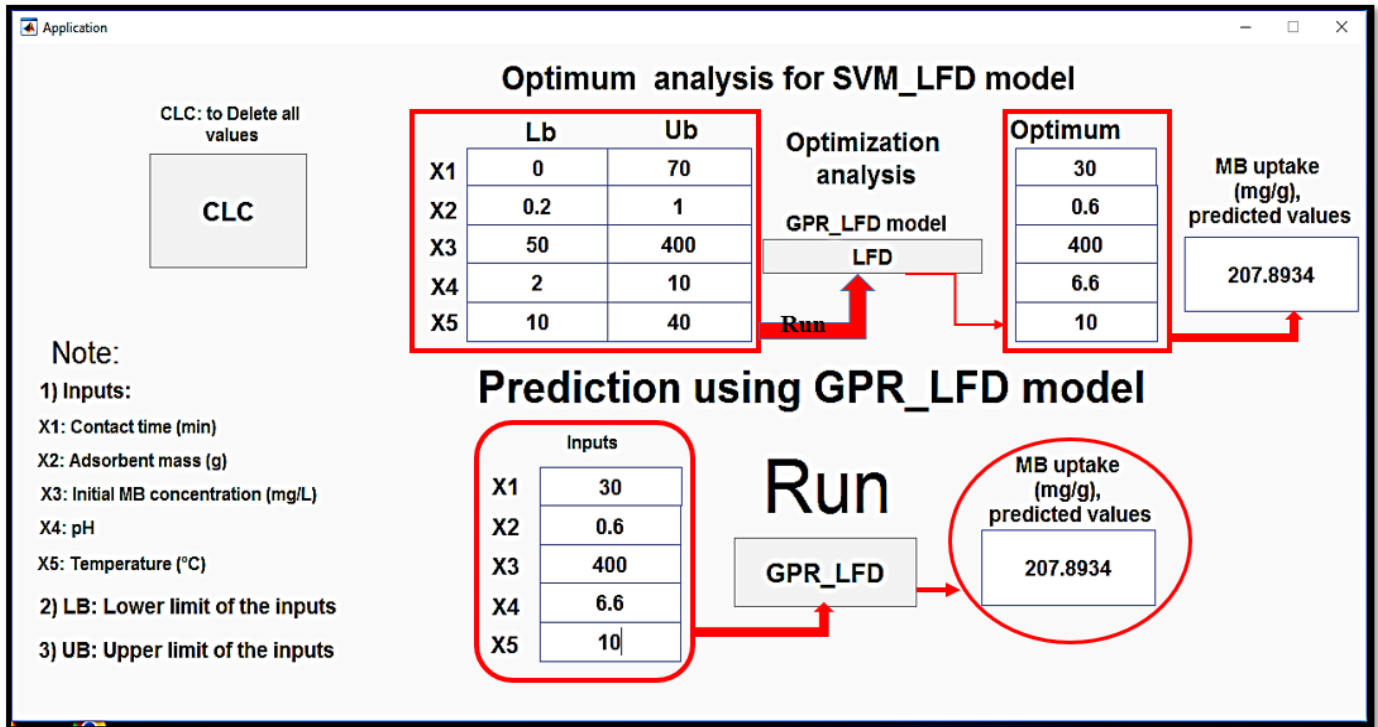
878 The results prominently showcase a compelling alignment between the observed outcomes and
 879 the predictions derived from the GPR_LFD model in the domain of MB adsorption. Under the
 880 precisely defined optimal conditions—characterized by a 30-minute contact time, 0.600 g of
 881 adsorbent mass, an initial MB concentration of 400 mg/L, a pH level of 6.6, and a temperature
 882 of 10°C, the experimental MB adsorption rate reached an impressive 207.90 mg/g. Remarkably,
 883 the model-predicted value closely mirrored this at 207.89 mg/g, with a minute discrepancy of
 884 only 0.008 mg/g. This nuanced precision in the concordance between predicted and observed
 885 values vividly underscores the LFD algorithm's exceptional efficacy in orchestrating
 886 optimization with remarkable finesse.

887 These findings not only affirm the reliability of the GPR_LFD model but also underscore the
888 algorithm's inherent ability to guide the optimization process with precision. The LFD
889 algorithm's seamless convergence on optimal conditions, resulting in such close
890 correspondence between experimental and predicted values, attests to its robustness and
891 efficiency in navigating intricate parameter spaces. This detailed congruence further instills
892 confidence in the model's capacity to capture complex patterns and optimize outcomes
893 accurately, solidifying its value as a powerful tool in the realm of MB adsorption studies.

894 **3.13. Interface for optimization and prediction**

895 At the forefront of advancements in computational tools for environmental research, an
896 innovative MATLAB application has been meticulously engineered to harness the formidable
897 capabilities of the LFD algorithm. This application serves a dual purpose by not only optimizing
898 process conditions but also predicting MB uptake with precision, employing the sophisticated
899 GPR_LFD model. A hallmark of user-friendliness, this cutting-edge tool seamlessly integrates
900 the computational prowess of MATLAB with the intricate workings of the LFD algorithm.
901 Users can effortlessly input a spectrum of experimental parameters, including contact time,
902 adsorbent mass to initial MB concentration, pH, and temperature. This dynamic interface
903 empowers the LFD algorithm to dynamically optimize these conditions, refining them to their
904 optimal configurations. Beyond this, the application utilizes the GPR_LFD model to predict
905 MB uptake with a high degree of accuracy, facilitating a comprehensive understanding of
906 adsorption behavior under various scenarios. What sets this application apart is not only its
907 functionality but also its intuitive user interface, allowing researchers and practitioners to
908 explore diverse scenarios effortlessly. The real-time visualization of how different parameters
909 impact MB adsorption enhances its usability. This innovative MATLAB application emerges
910 as a powerful, efficient, and user-centric tool, embodying the seamless integration of LFD

911 optimization and GPR_LFD prediction, making it indispensable for researchers in the dynamic
 912 field of MB adsorption studies.
 913



914 **Figure.17.** MATLAB Interface for optimization analysis (LFD) and prediction of MB uptake
 915 using GPR_LFD.

916 3.14. Comparison with Published Results: A Comparative Analysis

917 The **Table 12** provides a comparison of the maximum adsorption capacities of various
 918 adsorbents, expressed in milligrams per gram (mg/g). Among the listed adsorbents, the
 919 biocomposite film derived from cellulose demonstrates a maximum adsorption capacity of
 920 146.81 mg/g. This highlights the adsorption capabilities of this material, indicating its potential
 921 for water contaminant removal. The tea-derived activated material (AST) shows a slightly
 922 lower adsorption capacity, at 104.2 mg/g. Although this value is lower than that of the
 923 biocomposite film of cellulose, it remains significant, suggesting the effectiveness of AST as
 924 an adsorbent. On the other hand, the sludge-rice husk biochar exhibits a more modest adsorption

925 capacity, at 22.59 mg/g. However, it still serves as a potentially useful adsorbent, especially
 926 considering its biological origin and availability. The jute stick biomass stands out with an
 927 impressive adsorption capacity of 198.86 mg/g, making it one of the most efficient adsorbents
 928 on the list. This high adsorption capacity underscores the effectiveness of jute stick biomass for
 929 water contaminant removal. The banana stem-activated carbon shows an adsorption capacity
 930 of 64.66 mg/g, making it a reasonable choice for various water purification applications,
 931 although it is less efficient than jute stick biomass. Macore fruit shells exhibit the lowest
 932 adsorption capacity among the listed adsorbents, with a value of 10.61 mg/g. While this is the
 933 lowest value listed, it remains significant in certain application contexts. Lastly, the "GP"
 934 developed in this study stands out with a remarkable adsorption capacity of 207.89 mg/g, the
 935 highest among all the mentioned adsorbents. This high value suggests that the "GP" could be a
 936 highly effective adsorbent for water contaminant removal, offering new prospects for treating
 937 contaminated water.

938 **Table.12.** Comparative Assessment of Adsorption Capacities for MB Dye among Various
 939 Adsorbents.

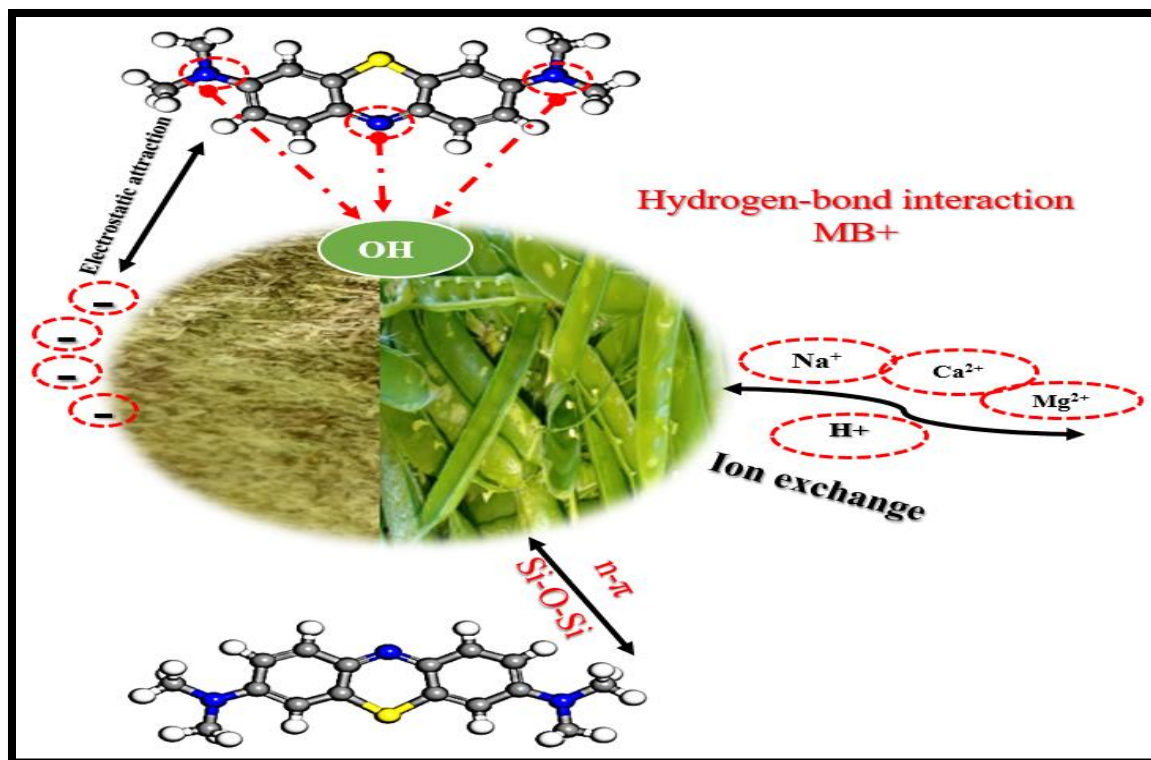
Adsorbent name	Capacity maximum (mg/g)	Reference
Biocomposite film derived from cellulose	146.81	[88]
Tea-derived activated material (AST)	104.2	[89]
Sludge-rice husk biochar	22.59	[90]
Jute stick biomass	198.86	[91]
Banana stem-activated carbon	64.66	[92]
Macore fruit shells	10.61	[93]
GP	207.89	This work

940
 941 In conclusion, the data from the table reveal that the "GP" exhibits the highest adsorption
 942 capacity among all listed adsorbents. This remarkable performance suggests that the "GP" could

943 be an extremely effective adsorbent for treating contaminated water, thereby providing new
944 opportunities to enhance water purification technologies. These findings underscore the
945 importance of research on advanced materials such as the "GP" in seeking sustainable solutions
946 to challenges related to access to clean water.

947 **3.15. Proposal for an adsorption mechanism**

948 **Figure 18** provides a visual representation of the interactions involved in the adsorption process
949 of cationic methylene blue dye onto the biosorbent. Understanding the mechanism behind the
950 adsorption of organic compounds onto the adsorbent requires a comprehensive analysis,
951 typically involving a comparison of the FTIR spectra of the adsorbent before and after the
952 adsorption process. This analysis is often supplemented by studies conducted under various
953 conditions such as pH, temperature, and initial dye concentration, as well as desorption
954 experiments. These investigations, combined with FTIR analysis and MDS results, allow
955 researchers to propose the primary adsorption mechanisms. The identified mechanisms
956 typically include electrostatic attraction, dipole-dipole interactions, Yoshida hydrogen bonding
957 formations, and $n-\pi$ interactions. Specifically, the primary adsorption process for various
958 aromatic contaminants on carbonaceous materials is often attributed to the $n-\pi$ electron
959 interaction. In this process, the aromatic rings of pollutant molecules act as electron acceptors,
960 while carbonyl oxygen ions on the biochar surface serve as electron donors. Through spectral
961 analysis, researchers observe a significant reduction in the intensity of the band at 1623 cm^{-1} ,
962 associated with C=O functional groups, after adsorption, indicating the involvement of $n-\pi$
963 interactions in the adsorption process. Hydrogen bonding interactions also play a crucial role in
964 adsorption and can be classified into two types. Firstly, dipole-dipole hydrogen bonds
965 frequently form between appropriate atoms (e.g., oxygen or nitrogen) of the aromatic
966 adsorbates and surface hydrogen atoms of hydroxyl groups on the carbonaceous material.
967 Secondly, Yoshida hydrogen bonding connections typically occur between the aromatic rings
968 of adsorbate molecules and the surface hydroxyl groups of the carbonaceous material. Spectral
969 analysis post-adsorption shows a slight decrease in the intensity of bands associated with C-O
970 and -OH groups, suggesting the presence of dipole-dipole and Yoshida hydrogen bonding
971 interactions. Overall, understanding these complex interactions is essential for elucidating the
972 adsorption mechanisms and optimizing the adsorption process for efficient removal of
973 contaminants from water sources.



974

975

Figure.18. Adsorption mechanism of MB onto GP absorbent.

976

3.16. Cost Analysis for natural GP biosorbent Synthesis

977

The Energy and Cost Estimate section provides a meticulous breakdown of the financial aspects

978

associated with the production of natural green pea peels (GP) biosorbent. This analysis aims

979

to offer a comprehensive prediction of the anticipated production costs involved in generating

980

one kilogram of GP biosorbent. **Table 13** in the section presents a detailed cost estimation of

981

the various stages involved in the production process. The first item listed is the "Cost of peels

982

collection," which is intriguingly noted as 0.00 USD. This indicates that there are no direct

983

expenses incurred in collecting the pea peels, suggesting that they are obtained as a byproduct,

984

potentially from food processing industries or agricultural activities. This approach not only

985

minimizes production costs but also underscores the sustainability of utilizing agricultural

986

waste for value-added purposes. Moving on, the "Cost of drying of adsorbent" is also listed as

987

0.00 USD, with a note specifying that the drying process utilizes natural sunlight. By leveraging

988

solar energy for drying, the production process avoids the need for energy-intensive methods,

989 significantly reducing operational expenses. This environmentally friendly approach not only
 990 contributes to cost-effectiveness but also aligns with sustainable practices. The final cost item
 991 in **Table 13** is "Milling and sieving," which incurs a total cost of 100 w. The cost is expressed
 992 in terms of power consumption, with 1 kW/h equivalent to 0.035 USD in Algeria. This cost
 993 likely represents the electricity consumption associated with milling and sieving equipment
 994 used to process the pea peels into the desired biosorbent form. Despite this expense, the overall
 995 cost remains relatively low, further enhancing the economic viability of the production process.

996 In summary, the cost estimation provided in **Table 13** offers valuable insights into the financial
 997 aspects of GP biosorbent production. The absence of expenses for peels collection and drying,
 998 coupled with the utilization of solar energy and relatively low milling and sieving costs,
 999 highlights the cost-effectiveness and sustainability of the production process. This
 1000 comprehensive cost analysis serves as a valuable tool for decision-makers and stakeholders,
 1001 facilitating informed decisions regarding resource allocation and investment in GP biosorbent
 1002 production for efficient and environmentally friendly water treatment solutions. According to
 1003 these results, a comparison of its costs with current studies is presented in **Table S3**.

1004 **Table.13.** cost estimation of GP biosorbent.

unit	Total cost
Cost of peels collection	0.00 USD
Cost of drying of adsorbent	0.00 USD (dried using the sun)
Milling and sieving	100 w (1KW/h = 0.035 USD in Algeria)

1005

1006 **4. Conclusion**

1007 This research presents a comprehensive exploration of the Methylene Blue (MB) adsorption
 1008 dynamics onto Green Peel (GP), employing diverse methodologies from statistical physics

1009 models to Molecular Dynamic Simulation (MDS). The study firmly establishes GP's suitability
1010 for adsorption, substantiated by analyses like X-ray diffraction (XRD) and Fourier-transform
1011 infrared spectroscopy (FT-IR), The Brunauer-Emmett-Teller (BET), providing a robust
1012 foundation for subsequent investigations. By dissecting influential factors in MB removal such
1013 as adsorbent mass, pH, concentration, and temperature, the research furnishes crucial insights
1014 into the nuances of the adsorption process.

1015 Isotherm data analysis identifies the double-energy single-layer model as the most fitting,
1016 supported by comprehensive correlation coefficient evaluation. Steric parameters reveal
1017 intricate adsorption geometry and mechanisms, with temperature-dependent variations
1018 shedding light on captivating shifts in orientation and modes. Thermodynamic scrutiny exposes
1019 the exothermic nature of MB adsorption onto GP, coupled with a noticeable decline in
1020 adsorption capacity at elevated temperatures. Density Function Theory (DFT) studies deepen
1021 our understanding of the interaction, reactivity, and stability of both MB and GP systems. These
1022 studies emphasize the potential for electron transfer during adsorption. In the desorption
1023 process, electron transfer between the MB dye and the ethanol solvent plays a crucial role in
1024 facilitating the release of MB molecules from the adsorption sites on the biosorbent. When a
1025 suitable electron acceptor or donor is present in the system, it provides a pathway for electron
1026 transfer to occur more efficiently. This can happen through various mechanisms, such as redox
1027 reactions, where the electron donor transfers electrons to the MB dye, promoting its desorption
1028 from the biosorbent surface. Conversely, electron acceptors can accept electrons from the MB
1029 dye, facilitating its release into the solvent. Overall, the presence of suitable electron donors or
1030 acceptors enhances the kinetics of the desorption process, leading to more effective removal of
1031 MB from the biosorbent material. On the other hand, while regenerative properties underscore
1032 GP's recyclability, albeit with diminishing efficiency over successive usage cycles, Molecular
1033 Dynamics Simulation (MDS) unveils the stable adsorption configuration of MB onto the GP

1034 surface. This approach elucidates the intricate interplay of chemical interactions and Van der
1035 Waals forces. Density Function Theory (DFT) studies deepen our understanding of the
1036 interaction, reactivity, and stability of both MB and GP systems. These studies emphasize the
1037 potential for electron transfer during adsorption. In the desorption process, electron transfer
1038 between the MB dye and the ethanol solvent plays a crucial role in facilitating the release of
1039 MB molecules from the adsorption sites on the biosorbent. On the other hand, while
1040 regenerative properties underscore GP's recyclability, albeit with diminishing efficiency over
1041 successive usage cycles, Molecular Dynamics Simulation (MDS) unveils the stable adsorption
1042 configuration of MB onto the GP surface. This approach elucidates the intricate interplay of
1043 chemical interactions and Van der Waals forces. Harnessing Gaussian Process Regression
1044 coupled with Lévy flight distribution (GPR_LFD), the study optimizes kernel functions,
1045 pinpointing the ARD exponential kernel and PureQuadratic basis as optimal choices. Rigorous
1046 model testing attests to its precision, reliability, and exceptional alignment with the data.
1047 Experimental validation under optimized parameters (30-minute contact time, 0.600 g
1048 adsorbent mass, initial MB concentration of 400 mg/L, pH 6.6, and 10°C) yields a striking
1049 congruence between experimental and predicted MB uptake values, reaching an impressive
1050 207.90 mg/g. A user-friendly MATLAB interface integrates LFD optimization and GPR
1051 prediction for practical application. In essence, this research bridges empirical observations
1052 with advanced modeling techniques, advancing our understanding of MB adsorption onto GP
1053 and emphasizing GP's substantial potential as an effective adsorbent. The study not only
1054 contributes to scientific understanding but also hints at future applications in environmental
1055 remediation and wastewater treatment, showcasing the synergy between empirical investigation
1056 and computational modeling in unraveling complex phenomena.

1057 **Nomenclature**

1058 C the intercept of Intraparticle diffusion function

1059	C_0	initial concentration of MB ($\text{mg}\cdot\text{L}^{-1}$)
1060	C_e	final concentration of MB in the solution
1061	C_t	concentration of MB at time t ($\text{mg}\cdot\text{L}^{-1}$)
1062	$C_{1/2}$	the concentration at half-saturation ($\text{mg}\cdot\text{L}^{-1}$)
1063	C_1	concentrations at half saturation for the first active site ($\text{mg}\cdot\text{L}^{-1}$)
1064	C_2	concentrations at half saturation for the second active site ($\text{mg}\cdot\text{L}^{-1}$)
1065	E_{int}	System internal energy ($\text{J}\cdot\text{mol}^{-1}$)
1066	F	fraction of MB adsorbed at time t
1067	G	Gibbs free enthalpy ($\text{J}\cdot\text{mol}^{-1}$)
1068	GP	Green pea
1069	h	Planck constant ($\text{J}\cdot\text{s}^{-1}$)
1070	K_B	Boltzmann constant ($\text{J}\cdot\text{K}$)
1071	k_1	equilibrium rate constant of PFO equation ($\text{L}\cdot\text{min}^{-1}$)
1072	k_2	equilibrium rate constant of PSO equation ($\text{L}\cdot\text{min}^{-1}$)
1073	K_F	Freundlich constant ($\text{g}\cdot\text{L}\cdot\text{mg}$)
1074	K_{id}	the rate constant of intraparticle diffusion($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$)
1075	K_L	Langmuir constant ($\text{L}\cdot\text{mg}^{-1}$)
1076	k_n	equilibrium rate constant of PNO equation ($\text{L}\cdot\text{min}^{-1}$)
1077	K_s	Sips constant ($\text{L}\cdot\text{mg}^{-1}$)
1078	M	mass of the mixture (g)
1079	m_s	the exponent of the Sips model
1080	MB	methylene blue
1081	n	number of ions per site
1082	n_1	number of ions per site for the first site receptor
1083	n_2	number of ions per site for the second site receptor
1084	n_f	Freundlich (R-P) constant
1085	n_o	biosorption reaction order N number of experimental points performed
1086	N_m	sites receptor density($\text{mg}\cdot\text{g}^{-1}$)
1087	PFO	pseudo-first-order,
1088	PSO	pseudo-second-order

1089	PNO	pseudo-nth-order
1090	Q _e	amount of dye adsorbed at equilibrium (mg•g ⁻¹)
1091	Q _t	quantity adsorbed at time t (mg•g ⁻¹)
1092	R	the correlation coefficient
1093	RMSE	Root Mean Squared Error
1094	S _a	Entropy (J•mol•K ⁻¹) t time (min)
1095	T	temperature (°C or °K)
1096	V	volume of the mixture (L)
1097	Z _v	Translation partition function per unit volume
1098	Z _{gtr}	translation partition function
1099	β	the constant of desorption (g/mg).
1100	α	the constant of initial sorption rate (mg/(g•min))
1101	ϑ	the fractional power kinetic model constant.

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