

1 **Insight into adsorption mechanism of cationic dye onto biosorbents derived** 2 **from agricultural wastes**

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4 Hai Nguyen Tran^{a,b*}, Sheng-Jie You^{a*}, Tien Vinh Nguyen^c, and Huan-Ping Chao^{a,*}
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7 ^aDepartment of Environmental Engineering, Chung Yuan Christian University, Chungli 320,
8 Taiwan
9

10 ^bDepartment of Civil Engineering, Chung Yuan Christian University, Chungli 320, Taiwan
11

12 ^cFaculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway,
13 Sydney, Australia
14
15

16 **Abstract**

17 This study investigated the phenomenon and mechanism of adsorption of methylene green 5 (MG5)
18 on three pristine biosorbents: golden shower pod (GS), coconut shell (CC), and orange peel (OP).
19 The results showed that the biosorbents possessed low specific surface areas, but abundant
20 functional groups. Adsorption was strongly affected by the solution's pH and ionic strength. As
21 revealed in the kinetic study, equilibrium was rapidly established, requiring low activation energies;
22 a removal rate of 30%–87% was achieved within 1 min. The maximum Langmuir adsorption
23 capacities at 30 °C exhibited the following order: GS (106 mg/g) > OP (92 mg/g) > CC (59 mg/g).
24 Thermodynamic experiments suggested that the adsorption occurred spontaneously ($-\Delta G^\circ$) and
25 exothermically ($-\Delta H^\circ$). The primary adsorption mechanisms involved electrostatic attraction,
26 hydrogen bonding formations, and n - π interaction. Thermogravimetric analysis revealed that three
27 biopolymer components (i.e., hemicellulose, cellulose, and lignin) played controlling roles in the
28 adsorption process. Thus, these three agricultural residues can be considered potential low-cost
29 adsorbents for efficient dye adsorption applications.
30

31 **Keywords:** Biosorbent; cationic dye; adsorption mechanism; biopolymer; agricultural waste
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* Corresponding authors:

H.-N. Tran (trannguyenhai2512@gmail.com), S.-J. You (sjyou@cycu.edu.tw), and H.-P. Chao (hpchao@cycu.edu.tw)

34 **1. Introduction**

35 The presence of dyes and pigments in water bodies is enormously concerning for public
36 health. A variety of synthetic dyes are used in many industries, including leather, textile, paper,
37 rubber, dyestuff, cosmetics, plastics, pharmaceutical, printing, food, paint, pigment, petroleum,
38 pesticide and wood-preserving chemical industries. Notably, over 100,000 known commercial
39 dyes exist, and of the approximately 700,000 tons of dye produced each year, 10,000 tons are
40 subsequently discharged into wastewater streams (Raval et al., 2016). The uncontrolled and
41 untreated discharge of abundant colored wastewater into the water environment has attracted
42 substantial attention because dyes' toxic, carcinogenic, mutagenic, and allergenic properties
43 adversely affect aquatic organisms and human health.

44 Adsorption technology is considered the most economically favorable technique to remove
45 dyes among those available (i.e., membrane separation, oxidation, and irradiation) because of its
46 high removal efficiency, low operation cost, and ability to separate a wide range of contaminants
47 from industrial effluents. Various biosorbents derived from agricultural and industrial wastes have
48 been efficiently applied to remove different types of dyes in the literature, such as acid, cationic,
49 dispersive, direct, reactive, solvent, sulfur, and vat dyes (Annadurai et al., 2002; Gupta and Suhas,
50 2009; Contreras et al., 2012; Witek-Krowiak, 2013; Wang et al., 2014; Oladipo and Gazi, 2015;
51 Roosta et al., 2015; Sadaf et al., 2015; Jeyagowri and Yamuna, 2016; Tahir et al., 2017). Although
52 the removal efficiencies of biosorbents are lower than that of activated carbon, the industrial-scale
53 utilization of these materials is economically attractive (Contreras et al., 2012).

54 Natural lignocellulosic biomasses from agricultural residues can be regarded as low-cost
55 and renewable materials for the decolorization of wastewater effluents from the textile industry
56 because of the presence of biopolymers, such as polysaccharides, lignin, hemicelluloses, and

57 cellulose. These biopolymers include abundant oxygen-containing functional groups and are
58 potentially useful for the uptake of various contaminants from aqueous solutions. Methylene green
59 5 (MG5) is a cationic phenothiazine dye and heterocyclic aromatic chemical compound that can
60 be considered as a nitro derivative of methylene blue. In addition, MG5—commonly used in
61 various industries—shows considerable solubility in both polar organic media and water. However,
62 the factors contributing to the adsorption of MG5 on agricultural residues-derived biopolymers
63 have not been reported previously. In addition, the adsorption mechanisms of MG5 have not been
64 thoroughly described in the literature. Knowledge of these adsorption mechanisms is critical for
65 determining the amounts of MG5 adsorbed on different biosorbents.

66 In this study, three biosorbents (i.e., golden shower pod [GS], coconut shell [CS], and
67 orange peel [OP]) were used to investigate the uptake process of MG5 from an aqueous solution.
68 The biosorbents were selected based on their popularity and different properties, especially the
69 difference about the quantity of their biopolymer components (i.e., hemicellulose, cellulose, and
70 lignin). The batch adsorption experiments were performed under different operation conditions
71 (i.e., solution pH, ionic strength, contact time, initial concentration, temperature, and desorption
72 agent) to determine their effects on the adsorption process. The important contributions of the
73 tested biopolymers toward the total adsorption of MG5 were examined thoroughly by conducting
74 detailed comparisons of the changes in the biosorbents' properties after adsorption using various
75 techniques (i.e., thermogravimetric analysis [TGA], Fourier transform infrared [FT-IR]
76 spectroscopy, and Boehm titration).

77

78 **2. Materials and methods**

79 **2.1. Biosorbent preparation**

80 The GS, CC, and OP were obtained from a local market in Taiwan. The collected samples
81 were first washed with tap water at least three times and then with deionized distilled water to
82 remove water-soluble impurities and surface-adhered particles. Then, they were placed in an oven
83 at 105 °C for 48 h to remove excess water and moisture. The dried samples were ground and sieved
84 to obtain the desired particle sizes (0.106–0.250 mm). The samples were stored in tightly closed
85 brown glass bottles and used as potential biosorbents without any further treatment.

86 **2.2. Biosorbent analysis**

87 The biosorbent samples were degassed at 110 °C for 24 h in a vacuum oven before the
88 measurements. The textural properties were measured by collecting nitrogen adsorption–
89 desorption isotherms (Micromeritics ASAP 2020 sorptometer) at 77 K. The morphology of the
90 adsorbents was determined using scanning electron microscopy (SEM; Hitachi S-4800, Japan)
91 with an accelerating voltage of 3 kV. Before observation, the samples were coated with gold in E-
92 1010 Ion sputter. The thermal stability was measured by TGA (DuPont TA Q50, USA) under an
93 air atmosphere. The experiment was conducted from room temperature to 900 °C with a heating
94 rate of 10 °C/min. Proximate analysis was performed by following an international standard
95 procedure (ASTM).

96 The superficial chemistry of the biosorbent was elucidated using three techniques. Firstly,
97 the functional groups present on the adsorbent surface were detected using FT-IR (FT/IR-6600
98 JASCO). The spectra were scanned from 4,000 to 650 cm^{-1} . Secondly, the pH values of the
99 biosorbents at the point of zero charge (pH_{PZC}) were determined using “the drift method”. Recently,
100 Tran and coworkers (2017b) investigated the effects of operation conditions on the pH_{PZC} of

101 commercial activated-charcoal using “the drift method”. The results demonstrated that the point
102 of zero charge (9.81 ± 0.07) of charcoal was insignificantly dependent on the operation conditions
103 (i.e., CO₂, solid/liquid ratio, electrolyte type, electrolyte concentration, and contact time). Thirdly,
104 the quantities of acidic groups and basic sites on the adsorbent surface were determined through
105 Boehm titration, following the standardized protocol proposed by Goertzen and coworkers (2010).
106 The numbers of moles of adsorbent surface functionalities were determined from the equations
107 reported in our recent publication (Tran et al., 2017e).

108

109 **2.3. Dye adsorption study**

110 ***2.3.1 Batch adsorption experiment***

111 All of the MG5 solutions were serially diluted from an MG5 stock solution (1,000 mg/L).
112 The stock solution was prepared by dissolving a given amount of MG5 in deionized distilled water.
113 All chemicals used in this study were of analytical grade.

114 The effect of the pH on the dye adsorption capacity was measured by mixing 25-mL
115 solutions containing 300-mg/L MG5 with 0.1 g of each biosorbent using solutions with various
116 pH values. The initial pH value was adjusted from 2.0 to 10.0 ± 0.2 by adding 1-M NaOH or 1-M
117 HCl. Similarly, the influence of the ionic strength was examined by varying the NaCl
118 concentration from 0 to 0.5 M. The kinetic adsorption study was conducted using a series of 100-
119 mL Erlenmeyer flasks containing 50 mL of MG5 solution at 30 °C and 50 °C. Adsorption
120 isotherms were collected using MG5 concentrations ranging from approximately 100 to 1,000
121 mg/L at different temperatures. The thermodynamic parameters were estimated at three different
122 temperatures for various MG5 concentrations (approximately 100–1,000 mg/L). The MG5-
123 biosorbent mixtures were shaken using an orbital-shaking incubator (S300R-Firstek) at 150 rpm.

124 After predetermined intervals, the mixtures were separated using glass fiber filters. The MG5-
125 laden biosorbent was rinsed with deionized distilled water, dried, and stored for further
126 experiments (i.e., FT-IR, TGA, and desorption). The MG5 concentration in solution was
127 determined using ultraviolet-visible spectrophotometry (Genesys 10 UV-Vis; Thermo Scientific)
128 at the wavelengths of maximum absorption (Fig. 1). The amount of MG5 uptake at equilibrium,
129 q_e (mg/g), was calculated by the mass-balance equation.

$$q_e = \frac{(C_o - C_e)V_1}{m_1} \quad (1)$$

130 where C_o (mg/L) and C_e (mg/L) are the initial and equilibrium MG5 concentrations, respectively;
131 m_1 (g) is the mass of biosorbent used; and V_1 (L) is the volume of the MG5 solution. All batch
132 adsorption experiments were undertaken at a constant solid/liquid ratio of approximately 4.0 g/L.

133 **Figure 1**

134 The adsorption reversibility was determined by desorption experiments. A given mass of
135 MG5-loaded biosorbent (m_2) was desorbed using 0.025 L of various desorbing agents (V_2). The
136 amount of MG5 remaining on the biosorbent was estimated by the following mass-balance
137 relationship:

$$q_r = q_e - q_d = q_e - \frac{C_d V_2}{m_2} \quad (2)$$

138 where q_r (mg/g) is the mass of MG5 that remained adsorbed at the end of the desorption study, C_d
139 (mg/L) is the concentration of MG5 in the solution after desorption, and q_d (mg/g) is the mass of
140 MG5 desorbed if the adsorption was reversible.

141 **2.3.2. Statistical analysis**

142 All experiments were conducted in triplicate, and the results are expressed as the
143 mean \pm standard deviation. Trial-and-error non-linear methods were performed using the Solver

144 add-in (Microsoft Excel) to compute the parameters of the isotherm and kinetic models. The
 145 coefficient of determination (R^2) of the non-linear optimization method was computed using Eq.
 146 3. To identify the best-fit model for the adsorption process, the chi-square (χ^2) and non-linear R^2
 147 values were determined (Tran, You et al. 2016a, Tran, You et al. 2017f, Tran, You et al. 2017d).
 148

$$R^2 = 1 - \frac{\sum (q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,mean})^2} = \frac{\sum (q_{e,cal} - q_{e,mean})^2}{\sum (q_{e,cal} - q_{e,mean})^2 + \sum (q_{e,cal} - q_{e,exp})^2} \quad (3)$$

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (4)$$

149 where $q_{e,exp}$ (mg/g) is the MG5 uptake at equilibrium obtained from Eq. 1, $q_{e,cal}$ (mg/g) is the MG5
 150 uptake determined from the model after using the Solver add-in, and $q_{e,mean}$ (mg/g) is the mean
 151 value of $q_{e,exp}$.

152 3. Results and discussion

153 3.1. Biosorbent characteristics

154 The basic properties of the biosorbents are listed in Table 1. Clearly, the biosorbents have
 155 low specific surface areas and total pore volumes, in agreement with their rough and heterogeneous
 156 morphologies shown in Figure 2. In addition, the biosorbents possess non-uniform sizes and shapes
 157 (Figure 2).

158 **Table 1**

159 **Figure 2**

160 Figure 3 and Table 2 present qualitative information on the functional groups (chemical
 161 bonds) available on the surfaces of the biosorbents and their spectroscopic assignments,
 162 respectively. The spectra of the three biomass samples are typical of lignocellulose material. The

163 intense bands at approximately 3400 cm^{-1} are assigned to the ($-\text{OH}$) stretching vibrations of the
164 hydroxyl groups in hemicellulose, cellulose, and lignin. The moderate peaks observed at roughly
165 2920 cm^{-1} are attributed to either asymmetric or symmetric $\text{C}-\text{H}$ stretching vibrations of the
166 methyl ($-\text{CH}_3-$) and methylene ($-\text{CH}_2-$) groups, as expected for hemicellulose, cellulose, and
167 lignin (Köseoğlu and Akmil-Başar, 2015). The presence of a carbon-carbon triple bond ($\text{C}\equiv\text{C}$) in
168 disubstituted alkynes is indicated by the peaks at approximately 2350 cm^{-1} . The presence of
169 carboxylic and lactonic groups ($\text{C}=\text{O}$) is evidenced by the well-defined bands at roughly 1470 cm^{-1} .
170 Similarly, the recognized bands at approximately 1620 cm^{-1} are ascribed to $\text{C}=\text{C}$ double bonds
171 in aromatic rings. The IR peaks near 1250 cm^{-1} are attributable to the $\text{C}-\text{O}-\text{C}$ stretching of aryl-
172 alkyl ether linkages in lignin (Yang et al., 2007). Notably, the characteristic peak of $\text{C}-\text{O}-\text{C}$ in the
173 spectrum of OP exhibited a very low intensity, indicating that the OP might contain less lignin
174 compounds than the woody samples (i.e., GS and CC). Finally, the $\text{C}-\text{O}$ stretching vibrations of
175 cellulose structure are responsible for the sharp bands at approximately 1050 cm^{-1} (Mujtaba et al.,
176 2016; Tran, You et al. 2017f).

177

178 **Figure 3**

179 **Table 2**

180 The pyrolytic characteristics of the examined biomass were determined using a
181 thermogravimetric analyzer, and they are presented in Figure 4 and Table 3. For the MG5-unloaded
182 biosorbent, four overlapping peaks corresponding to the maximum weight loss values are observed
183 in the thermogravimetric curves, except for that of OP. The weight loss temperatures (T_{max}) were
184 lower than $85\text{ }^\circ\text{C}$ because of the vaporization of moisture, and the thermal decomposition peaks at
185 T_{max} values of $237\text{--}299\text{ }^\circ\text{C}$, $327\text{--}341\text{ }^\circ\text{C}$, and $498\text{--}700\text{ }^\circ\text{C}$ were attributed to the thermal

186 degradation of hemicellulose, cellulose, and lignin, respectively. These results are consistent with
187 those of Yang and colleagues (2007). They noted that the pyrolysis of pure hemicellulose and
188 cellulose occurred at 220–315 °C ($T_{max} = 268$ °C) and 315–400 °C ($T_{max} = 335$ °C), whereas pure
189 lignin was more difficult to decompose (160–900 °C). The weight loss values of the three main
190 components of the tested biomasses exhibited the following order: lignin (37.9%) > cellulose
191 (30.1%) > hemicellulose (26.8%) for GS; lignin (33.2%) > hemicellulose (28.7%) > cellulose
192 (23.5%) > for CC; and cellulose (32.4%) > lignin (27.9%) > hemicellulose (19.5%) for OP. The
193 onset and endset values of the biosorbents, which were extrapolated based on the intersection of
194 two tangent lines of the TGA curves, provide additional useful information regarding the thermal
195 stability of these biomasses. The onset and endset of CC (244 and 641 °C) were higher than those
196 of GS (244 and 605 °C) and OP (188 and 337 °C), respectively, indicating that GS is more
197 thermally stable than the other tested biosorbents.

198 **Figure 4**

199 **Table 3**

200 **3.2. Effects of pH and ionic strength**

201 The surface charges of the biosorbents in solution were characterized by the point of zero
202 charge (PZC). The PZC was defined as the pH value at which the net (external and internal) surface
203 charges on an adsorbent are zero. Essentially, when the pH of a solution ($\text{pH}_{\text{solution}}$) exceeds the
204 pH_{PZC} , the adsorbent's surface becomes negatively charged because of the deprotonation of
205 oxygen-containing surface groups (i.e., $-\text{COOH}$ and $-\text{OH}$), favoring the adsorption of cationic
206 ions from the solution and vice versa. The pH_{PZC} values of the biosorbents were as follows: CC
207 ($\text{pH}_{\text{PZC}} = 6.5$) > OP (5.3) > GS (3.8). Thus, the acidic oxygen-containing functional groups

208 exhibited the following order: GS (8.74 mmol/g) > OP (6.90 mmol/g) > CC (4.21 mmol/g) (Figure
209 5a and Table 1).

210 The pH dependence of MG5 adsorption is presented in Figure 5b. Clearly, the adsorption
211 of MG5 by the biosorbent occurred when $\text{pH}_{\text{solution}} < \text{pH}_{\text{PZC}}$. Indeed, at a low pH (2.0), the
212 biosorbents were still able to adsorb MG5 molecules, although at this pH, the excess H^+ ions
213 present in the system showed strong competition with the cationic MG5 molecules for the active
214 adsorption sites. Notably, this was not observed for CC. This result might indicate that mechanisms
215 other than electrostatic attraction (i.e., hydrogen bonding or $n-\pi$ interactions) exist. The dye-
216 removal capacity is highly dependent on the pH_{PZC} of the biosorbent. The amount of dye adsorbed
217 increased substantially as the solution pH increased and plateaued when $\text{pH}_{\text{solution}} > \text{pH}_{\text{PZC}}$ (Figure
218 5b). An analogous result was found in the literature (Ncibi et al., 2009).

219 Figure 5c shows the influence of the ionic strength on the MG5 uptake. Clearly, the
220 adsorption capacities of the biosorbents were inhibited by the presence of univalent electrolyte in
221 the solution. The magnitude of the effect of the NaCl concentration on q_e (mg/g) varies widely
222 between adsorbents. For example, 0.05 M of Na^+ ions is sufficient to compete with MG5 ions for
223 the binding sites on the surfaces of GS and CC, whereas for OP, a concentration of 0.1 M is needed.
224 Therefore, the following conclusions can be drawn: (1) a screening effect (known as electrostatic
225 screening) exists between the positively charged biosorbent surface and MG5 molecules, and (2)
226 the electrostatic force plays a vital role in the adsorption mechanism.

227 **Figure 5**

228 **3.3. Adsorption kinetics**

229 The effect of the contact time on the uptake amount of MG5 at different temperatures is
230 described in Figure 6. The dye-removal rate increased continuously during the initial 10 min of

231 contact; subsequently, the removal rate decreased slightly and plateaued after approximately 30
 232 min for OP, 60 min for CC, and 120 min for GS. In addition, the amount of dye removed decreased
 233 at higher temperatures, suggesting that the adsorption process is favored at lower temperatures.
 234 The instantaneous adsorption phenomenon indicated that the biosorbents have strong affinities for
 235 the cationic dye molecules. The kinetics plays a significant role, facilitating scaling the process up
 236 to small reactor volumes to ensure efficiency and economy.

237 **Figure 6**

238 In this study, several kinetic models were applied to mathematically describe the intrinsic
 239 adsorption constants. The non-linearized forms of the pseudo-first-order (Lagergren, 1898) and
 240 pseudo-second-order (Blanchard et al., 1984) models are expressed in Eqs. 5–6. The Elovich
 241 model (Roginsky and Zeldovich, 1934) and intra-particle model (Weber and Morris, 1963) are
 242 presented in Eqs 7–8, respectively.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (6)$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \quad (7)$$

$$q_t = k_{ip} \sqrt{t} + C \quad (8)$$

243 where k_1 (1/min), k_2 (g/mg × min), α (mg/g × min), and k_{ip} (mg/g × min) are the rate constants of the
 244 pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models, respectively;
 245 q_e and q_t are the amounts of MG5 uptake per mass of the biosorbent at equilibrium and any time t
 246 (min), respectively; β (mg/g) is the desorption constant during any one experiment; and C (mg/g)

247 is a constant describing the thickness of the boundary layer. Higher values of C correspond to a
248 greater effect on the limiting boundary layer.

249 The activation energy of the sorption process (E_a ; kJ/mol) can be predicted using the
250 Arrhenius equation. Eq. 10 describes the activation energy estimated based on adsorption kinetics
251 experiments performed at two temperatures:

$$k = Ae^{-E_a/RT} \quad (9)$$

$$\ln k_{(323K)} - \ln k_{(303K)} = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right) \Leftrightarrow E_a = \frac{R \ln \frac{k_{(323K)}}{k_{(303K)}}}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (10)$$

252 where $k_{(323K)}$ and $k_{(303K)}$ are the rate constants of the kinetic model at 323 K and 303 K,
253 respectively; A is the pre-exponential factor (i.e., the frequency factor); R is the universal gas
254 constant ($8.314 \text{ kJ/mol} \times \text{K}$); and T is the absolute temperature in Kelvin.

255 Table 4 lists the relative kinetic parameters for dye adsorption at two temperatures.
256 According to the coefficient of determination (R^2), and chi-square (χ^2), it can be concluded that the
257 experimental data of adsorption kinetics were adequately described by the Elovich model ($R^2 =$
258 $0.955\text{--}0.994$ and $\chi^2 = 0.089\text{--}8.681$) than the others, such as the intra-particle diffusion model
259 ($0.739\text{--}0.911$ and $0.161\text{--}13.07$), the pseudo-second-order model ($0.475\text{--}0.963$ and $1.514\text{--}9.165$),
260 and the pseudo-first-order model ($0.258\text{--}0.874$ and $5.105\text{--}30.81$), respectively. The better fit of
261 experimental data with the Elovich model suggested that the surfaces of biosorbent are a
262 heterogeneous system, which is in accordance with the observation of their morphology in Figure
263 2.

264

265 As demonstrated in Table 4, the adsorption rates (i.e., k_1 , k_2 , and α) of the biosorbents
266 exhibited the following order: OP > CC > GS. This result is consistent with the order determined
267 for the removal percentages of MG5 at 1 min and 5 min of contact: 87% and 93% (OP) > 71% and
268 78 % (CC) > 30% and 52 % (GS), respectively. Equilibrium was established rapidly because (1)
269 the low activation energies (E_a) were required (Tran, You et al. 2017f), and (2) the adsorption
270 process only occurred in two steps associated with transport processes (Figure 6). In addition, the
271 negative values of E_a (from -62.23 to -3.52 kJ/mol) reflected the exothermic nature of the
272 adsorption process, and the low values of this parameter confirmed that physical adsorption
273 occurred via relatively weak attraction forces.

274 Notably, the rates (i.e., k_1 , k_2 , and α) of MG5 adsorption remarkably decreased with an
275 increase in temperatures, confirming that the adsorption process occurred with a slower speed
276 when the temperature of the solution increased.

277

278

Table 4

279

280 3.4. Adsorption isotherms

281 Although adsorption isotherms can contribute to elucidating adsorption mechanisms, it is
282 less helpful in this regard than kinetics and thermodynamics. However, collecting adsorption
283 isotherms is a useful strategy to both describe the relationship between the adsorbate concentration
284 in the solution (liquid phase) and the adsorbent (solid phase) at a constant temperature and design
285 adsorption systems. In this study, the Langmuir (Eq. 11), Freundlich (Eq. 12), and Dubinin-
286 Radushkevich (Eqs. 13–15) models were employed to describe both the adsorptive behavior of

287 cationic dye on different biosorbents. To minimize the respective error functions, the non-linear
 288 optimization technique was employed to calculate the adsorption parameters using these models.

$$q_e = \frac{Q_{\max}^0 K_L C_e}{1 + K_L C_e} \quad (11)$$

$$q_e = K_F C_e^n \quad (12)$$

$$q_e = q_{DR} e^{-K_{DR} \varepsilon^2} \quad (13)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (14)$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (15)$$

289 where q_e and C_e are obtained from Eq. 1; Q_{\max}^0 (mg/g) is the maximum saturated monolayer
 290 adsorption capacity of the adsorbent; K_L (L/mg) is the Langmuir constant related to the affinity
 291 between the adsorbent and adsorbate; K_F [(mg/g)/(mg/L)ⁿ] is the Freundlich constant, which
 292 characterizes the strength of adsorption; n (dimensionless; $0 < n < 1$) is a Freundlich intensity
 293 parameter that reflects the magnitude of the adsorption driving force or surface heterogeneity (the
 294 adsorption isotherm becomes linear for $n = 1$, favorable for $n < 1$, and unfavorable for $n > 1$; (Hai,
 295 2017)); q_{RD} (mg/g) is the adsorption capacity; K_{RD} (mol²/kJ²) is a constant related to the sorption
 296 energy; ε is the Polanyi potential; and E (kJ/mol) is the mean adsorption energy.

297 Hall and colleagues (1966) stated that the essential characteristics of the Langmuir
 298 isotherm model can be expressed in terms of a dimensionless constant separation factor or
 299 equilibrium parameter R_L , which is defined as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad (16)$$

300 where R_L is a constant separation factor (dimensionless), K_L is a Langmuir equilibrium constant,
301 and C_o is the initial MG5 concentration. The isotherm shape was used to predict whether the
302 adsorption system was favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible
303 ($R_L = 0$).

304 The MG5 adsorption isotherms for the biosorbents at different operation temperatures are
305 presented in Figure 7. Clearly, the region in which the experimental data relating to the adsorption
306 equilibrium are located is the Langmuir region, which is characterized by saturation at high
307 concentrations. The higher determination coefficient (R^2) and lower chi-square (χ^2) values of the
308 Langmuir model relative to those of the Freundlich model supports this hypothesis (Table 5). Thus,
309 the Langmuir model adequately described the equilibrium adsorption data.

310 According to the classification of adsorption isotherm shapes proposed by Giles and
311 coworkers (1974), the isotherm shapes of GS and CC (Figure 7) were classified as H-type (high
312 affinity); this type is characterized by extremely strong adsorption at low concentrations, followed
313 by a pseudo-plateau. In contrast, the isotherm shape of OP could be classified as L-type (Langmuir);
314 an initial concave region relative to the concentration axis characterizes this type. This result could
315 support the assumption that the CC and GS samples would exhibit different adsorption
316 mechanisms relative to the OP sample.

317

318 **Figure 7**

319 Table 5 lists the adsorption parameters obtained under the three temperatures tested. The
320 maximum monolayer adsorption capacities for MG5 were ranked as follows: GS (106 mg/g) > OP
321 (92 mg/g) > CC (59 mg/g). As shown in Figure 7, the adsorption efficiency is strongly affected by
322 the operation temperature. The uptake amount of MG5 decreased as the temperature increased,

323 indicating that the dye-adsorption process is exothermic. The decrease in the adsorption capacity
324 at higher temperatures is ascribed to the decrease of the adsorption energy E_a (Table 5).
325 Furthermore, the E_a values of the OP sample (0.018–0.031 kJ/mol) were substantially lower than
326 those of GS (0.18–0.87 kJ/mol) and CC (0.191–0.213 kJ/mol), demonstrating that GS and CC
327 might possess different adsorption mechanisms than OP.

328

329

Table 5

330

331 3.5. Adsorption thermodynamics

332 Thermodynamic studies are an indispensable component of predicting adsorption
333 mechanisms (e.g., physical and chemical). The thermodynamic parameters can be computed
334 according to the laws of thermodynamics using the following equations:

$$\Delta G^\circ = -RT \ln K_C \quad (17)$$

335 ΔG° , ΔH° , and ΔS° are related as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

336 The well-known van't Hoff equation is obtained by substituting Eq. 17 into Eq. 18

$$\ln K_C = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (19)$$

337 The Gibbs energy change (ΔG°) can be directly calculated from Eq. 17, whereas the
338 enthalpy change (ΔH°) and entropy change (ΔS°) were determined from the slope and intercept,
339 respectively, of a plot of $\ln K_C$ against $1/T$ (Eq. 19). The equilibrium constant (K_C) must be
340 dimensionless. In this study, the K_C derived from the Langmuir constant (K_L) was employed to

341 calculate the thermodynamic parameters (ΔG° , ΔH° , and ΔS°). Thus, K_C can be easily obtained as
342 a dimensionless parameter by multiplying K_L by 10^6 (the solution density, assuming that the
343 density of pure water is 1.0 g/mL) (Milonjić, 2009; Tran, You et al. 2016b; Tran, You et al. 2017d)

344 The thermodynamic parameters of the dye adsorption process are listed in Table 6. The
345 negative values of ΔG° at all investigated temperatures suggest that the adsorption phenomenon
346 occurred favorably and spontaneously. This conclusion is in good agreement with the hypotheses
347 relating to the separation factor ($0 < R_L < 1$) and Freundlich exponent n described in Section 3.4.
348 Meanwhile, the negative ΔH° reflects the exothermic nature of the adsorption process, which was
349 demonstrated by a decrease in the adsorption capacity (Figures 6–7) and the equilibrium constant
350 (Table 6) at higher temperatures. The $-\Delta H^\circ$ values also imply that energy is released as heat to the
351 surroundings via physisorption, chemisorption, or a mixture of both processes (comprehensive
352 adsorption). However, the low ΔH° magnitudes (from -28.33 to -4.15 kJ/mol) indicate that MG5
353 is removed via physisorption (Tran et al., 2016b). ΔS° exhibits the opposite trend relative to those
354 of $-\Delta H^\circ$ and ΔG° for the three biosorbents. The dye adsorption onto GS and CC is increasingly
355 random ($\Delta S^\circ > 0$), whereas that onto OP becomes less random ($\Delta S^\circ < 0$). This difference involves
356 the sign of the entropy change and may indicate that these materials exhibit different adsorption
357 mechanisms.

358

359 **Table 6**

360

361 **3.6. Adsorption reversibility**

362 To some extent, adsorption mechanisms can be elucidated based on desorption studies. The
363 adsorption reversibility was investigated using various desorbing agents, such as deionized water

364 (pH 2.0), 0.1-M HCl, methanol, and 0.1-M NaCl. If the dye adsorbed onto the adsorbents surface
365 is easily desorbed by NaCl or HCl, the adsorption mechanism must involve electrostatic attraction
366 between the negatively charged groups (i.e., $-\text{COO}^-$) on the surface of the biosorbent and the
367 cationic MG5 molecules. In contrast, the desorption of dye by methanol might correspond to other
368 types of interactions (i.e., hydrogen bonding or $n-\pi$ interactions). Based on Figure 8, which
369 presents the percentage values of MG5 desorption, the primary mechanisms for MG5 adsorption
370 are electrostatic interactions ($> 16\%$ for GS, 28% for CC, and $> 60\%$ for OP) and other interactions
371 involving the oxygen-containing functional groups on the biosorbent surface (approximately 76%
372 for GS, 62% for CC, and 34% for OP). Cation exchange could play a minor role in the adsorption
373 of the dye onto the adsorbents (below 10%). Based on the isotherm shapes and the results of the
374 kinetic study, the effects of the pH and ionic strength, the adsorption energy, thermodynamics, and
375 the desorption study, GS and CC likely have similar adsorption mechanisms.

376 **Figure 8**

377 **3.7. Possible adsorption mechanisms**

378 Generally, the possible mechanisms of cationic dye adsorption onto biosorbents are as
379 follows: (1) electrostatic attraction, (2) hydrogen bonding, and (3) $n-\pi$ interactions (Tran et al.,
380 2017f). Notably, the specific surface areas of the analyzed biosorbents exhibited the following
381 order: GS ($5.72 \text{ m}^2/\text{g}$) $>$ CC ($3.16 \text{ m}^2/\text{g}$) $>$ OP ($2.08 \text{ m}^2/\text{g}$); in contrast, the maximum adsorption
382 capacities were as follows: GS (106 mg/g) $>$ OP (92 mg/g) $>$ CC (59 mg/g). Therefore, the specific
383 surface area is relatively less important for the adsorption capacities of these three biosorbents.

384 Weak electrostatic attractions can occur between the negatively charged sites on the surface
385 of OP and the cationic MG5 molecules in the solution. Clearly, when $\text{pH}_{\text{solution}} > \text{pH}_{\text{PZC}}$, the
386 oxygen-containing functional groups (i.e., carboxylic and phenolic groups) become ionized, and

387 thus, the pH of the solution decreases after adsorption (Figure 5d). The p*K*_a values of the
388 carboxylic (2.0–4.0) and phenolic (8.0–9.0) groups also play a role in explaining the biosorbents'
389 surface charges. Both the carboxylic and phenolic groups can undergo dissociation, and can
390 become predominantly negatively charged when the solution pH exceeds their p*K*_a values. The
391 pH of the solution used in this study was nearly 7.0, and at this pH value, the (–COOH) carboxylic
392 groups dissociate, forming negatively charged carboxylate (–COO[–]) groups. Thus, the carboxylic
393 groups directly account for the binding of MG5 onto the biosorbent surface (Figure 9a). This
394 finding is in agreement with the observed effects of the pH and ionic strength and the pH values
395 after adsorption and desorption.

396 Hydrogen bonding interactions can occur (1) between the surface hydrogens of the
397 hydroxyl groups (H-donors) on the adsorbent's surface and the appropriate atoms (i.e., nitrogen
398 and oxygen; H-acceptors) of MG5 (this phenomenon is also known as dipole–dipole hydrogen
399 bonding; Figure 9b) and (2) between the hydroxyl groups on the AC's surface and the aromatic
400 rings of MG5 (this phenomenon is also known as Yoshida hydrogen bonding; Figure 9c). The FT-
401 IR results demonstrated that the –OH groups at approximately 3400 cm^{–1} dramatically decreased
402 in intensity (Figure 3) and shifted toward slightly higher wavenumbers (Table 2), confirming the
403 existence of both dipole–dipole and Yoshida hydrogen bonding interactions (Blackburn, 2004).
404 However, OP exhibited the opposite behavior, showing an insignificant decrease in the intensity
405 of the peak at 3400 cm^{–1}. Therefore, the hydrogen bonding interactions contribute little to the
406 adsorption mechanisms of OP.

407 n- π interactions (or n- π electron donor-acceptor interactions) were originally proposed by
408 Mattson and colleagues (1969). In these interactions, the carbonyl oxygens on the surface of the
409 adsorbent act as electron donors, and the aromatic rings of MG5 act as electron acceptors (Figure

410 9d). The FT-IR spectra revealed that the C=O and C–O peaks shifted and decreased in intensity
411 after MG5 adsorption (Figure 3 and Table 2). The shifts of the C=O and C–O peaks after the
412 adsorption of this aromatic species is consistent with previously reported results (Xing et al., 1994;
413 Tran et al., 2017f; Tran et al., 2017g). As found for hydrogen bonding, n- π interactions did not
414 constitute a major mechanism for adsorption on OP, as evidenced by the slight decreases in the
415 intensities of the C=O and C–O peaks.

416 The changes in the TGA curves before and after MG5 adsorption provide additional
417 information about the adsorption mechanisms. The onset and endset points of the three biosorbents
418 shift toward higher values (Figure 4 and Table 3), confirming the successful adsorption of MG5
419 on the biosorbent surface. Moreover, derivative thermogravimetric analysis (DTG) data revealed
420 that the magnitudes of the three components (i.e., hemicellulose, cellulose, and lignin) decreased
421 remarkably after adsorption. Thus, these three components contribute to dye adsorption. However,
422 the extent of their contributions may depend strongly on their amounts.

423 Assuming that the percentages of the dye desorbed by (1) HCl and NaCl reflected the
424 electrostatic attraction and (2) methanol indicated the interactions of oxygen-containing functional
425 groups, the contributions of these different adsorption mechanisms for the three adsorbents could
426 be described as follows: hydrogen bonding and n- π interactions (76% and 62%) and electrostatic
427 attraction (17% and 28%) for GS and CC, respectively; and electrostatic attraction (74%) and
428 hydrogen bonding and n- π interactions (34%) for OP.

429 To identify the functional groups responsible for the adsorption, the dependence of the
430 MG5-adsorption capacity on the surface chemistry of the biosorbents were determined by
431 analyzing a plot of the Q^o_{max} from the Langmuir model (Table 5) versus the functional groups
432 (Table 1). The results indicated that, based on the extremely high linear regression coefficient (R^2

433 = 0.996), the acidic groups were involved in the dye-adsorption process, unlike the basic groups
434 ($R^2 = 0.566$). Among the acidic groups, the carboxylic groups played a more important role in the
435 adsorption of MG5 ($R^2 = 0.9803$) compared to the phenolic ($R^2 = 0.6116$) and lactonic ($R^2 = 0.4091$)
436 groups. Our recent study (Tran et al., 2017g) also demonstrated that the concentrations of total
437 acid groups (i.e., carboxylic and phenolic) on the hydrochar's surface determined the selective
438 adsorption order of the adsorbents: GSH > CCH > OPH.

439 The interactions responsible for the adsorption of MG5 molecules by the tested biosorbents
440 are summarized in Figure 9.

441 **Figure 9**

442 **3.8. Comparison**

443 Because few studies have measured the removal of MG5 from solution by biosorbents,
444 Table 7 compares the Q^o_{max} values determined in this study with previously reported Q^o_{max} values
445 for various cationic dyes using different types of biosorbents. Clearly, the selective trend of the
446 maximum adsorption capacity is inversely proportional to the molecular weight (M_w) of the dye.
447 According to Table 7, GS, CC, and OP are attractive alternatives for the removal of cationic dyes
448 from aqueous solutions.

449 **Table 7**

450 Furthermore, we also compared the S_{BET} and Q^o_{max} of MG5 adsorption onto the biosorbents
451 in this study with those of the other adsorbents in the previous literature (Table 8). These
452 adsorbents comprised hydrochar (Tran et al., 2017g), biochar (Tran et al., 2017c), non-spherical
453 activated carbon (Shiau and Pan, 2005; Tran et al., 2017b; Tran et al., 2017f), spherical activated
454 carbon (Huang et al., 2014; Tran et al., 2017a), silver nanoparticles-loaded activated carbon (Ag-
455 NP-AC) and zinc oxide nanorods-loaded activated carbon (ZnONR-AC) (Ghaedi et al., 2014),

456 mesoporous zeolite (MCM-41) (Lee et al., 2007), glucose hydrochar modified with 1%
457 triethylenetetramine (GH-TETA_{1%}) and activated carbon modified with 1% triethylenetetramine
458 (GAC1%) (Tran et al., 2017a), montmorillonite and activated clay (Shiau and Pan, 2005), titania
459 nanotube (Lin et al., 2010). The difference on the Q^o_{max} values between these adsorbents might
460 result from different primary adsorption mechanisms. For example, the MG5 adsorption
461 mechanisms for adsorption onto biosorbent and hydrochar were mainly regarded as electrostatic
462 attraction, while these for biochar and activated carbon were π - π interaction and pore filling.
463 Furthermore, the differences in the adsorbent's characteristics (i.e., textural properties and surface
464 chemistry) also caused the different the Q^o_{max} values.

465 Generally, in the same feedstock (i.e., golden shower pod as a typical example), the S_{BET}
466 values followed activated carbon > biochar > hydrochar > biosorbent and the density of oxygen-
467 contain functionalities followed biosorbent > hydrochar > activated carbon > biochar. In contrast,
468 the Q^o_{max} values exhibited the following order: activated carbon > biosorbent > hydrochar >
469 biochar. Therefore, to some extent, the density of oxygen-containing functionalities of an
470 adsorbent played a more critical role than its BET specific surface area. A comprehensive
471 comparison of the properties (i.e., textural, structural, morphological, physicochemical, crystal,
472 thermally stable properties, and surface chemistry) of activated carbons prepared from different
473 chemical activation methods and their precursors (i.e., biosorbent, hydrochar, and biochar) has
474 been reported in detail in our recent study (Tran et al., 2017e).

475

476

Table 8

477

478 4. Conclusions

479 The adsorption process was strongly dependent on the pH of the dye solution and the presence of
480 the electrolyte. The kinetic study confirmed that adsorption equilibrium was established rapidly
481 with low activation energies (from -48.6 to -7.23 kJ/mol), and that, removal rates of 30%–87%
482 and 52%–93% can be achieved within 1 min and 5 min of contact, respectively. The maximum
483 monolayer adsorption capacities were ranked as follows: GS (106 mg/g) > OP (92 mg/g) > CC (59
484 mg/g). The thermodynamic study suggested that the dye adsorption occurred spontaneously ($-\Delta G^\circ$)
485 and exothermically ($-\Delta H^\circ$). The primary adsorption mechanisms involved electrostatic interaction,
486 hydrogen bonding formations, and $n-\pi$ interaction. The carboxylic groups played a dominant role
487 in the adsorption process, and the three biopolymer components (i.e., hemicellulose, cellulose, and
488 lignin) contributed substantially. These three agricultural wastes could be low-cost, renewable
489 candidates for efficient dye adsorption.

490

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497

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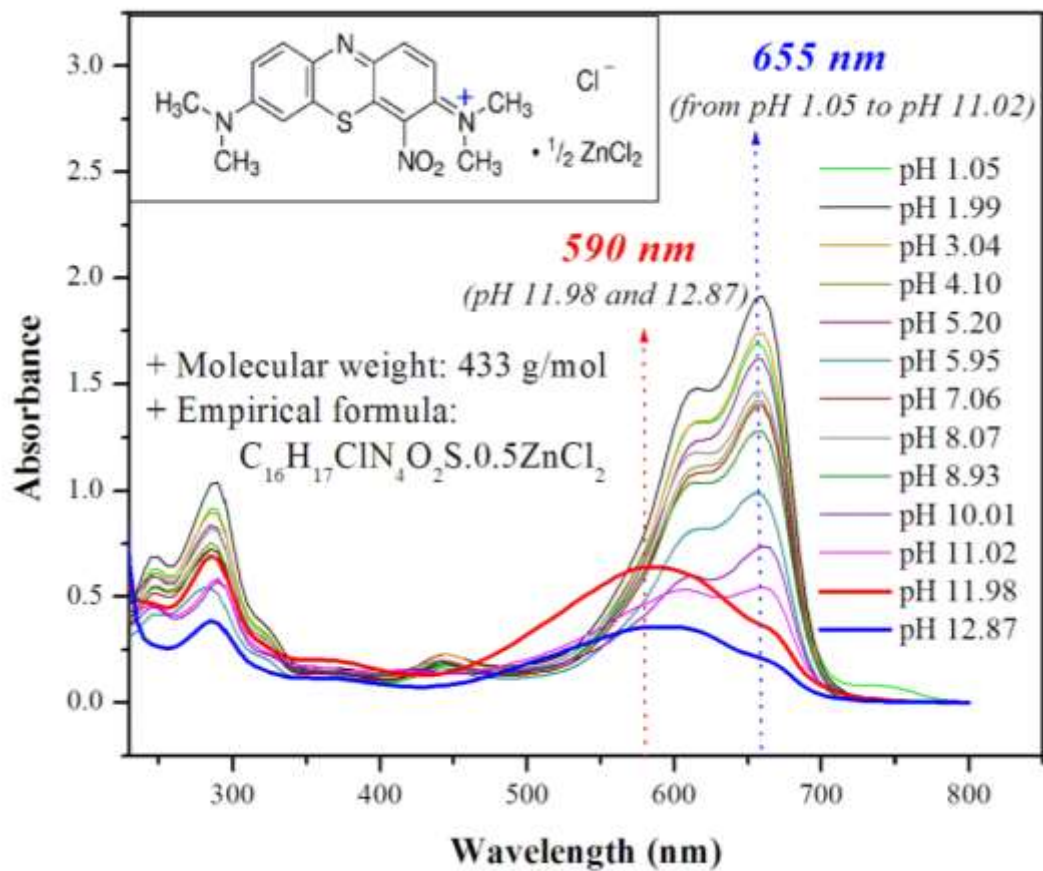
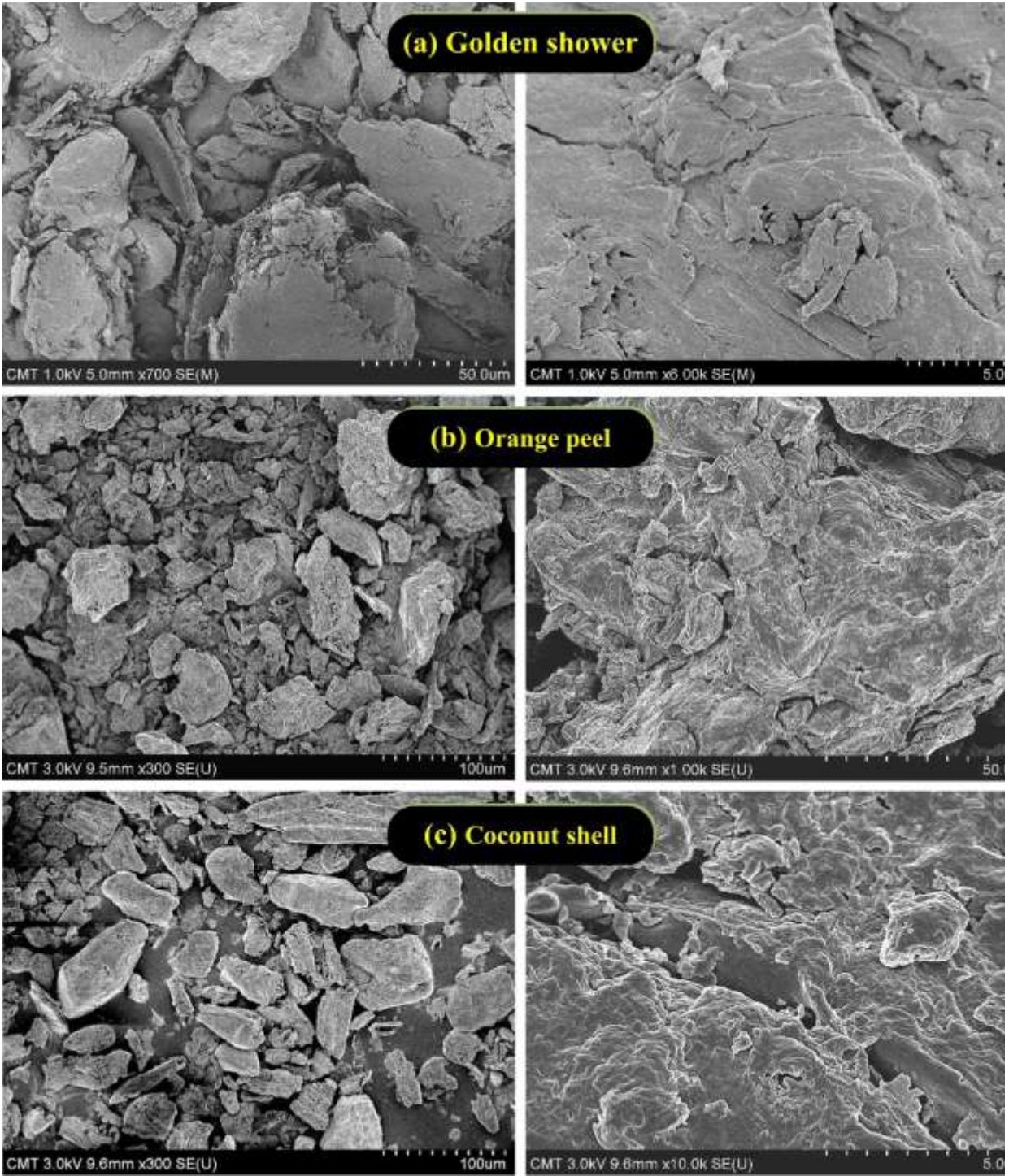


Figure 1. Effect of the pH of the MG5 solution on the λ_{max} value (Data published in our recent work; Tran et al., 2017f)

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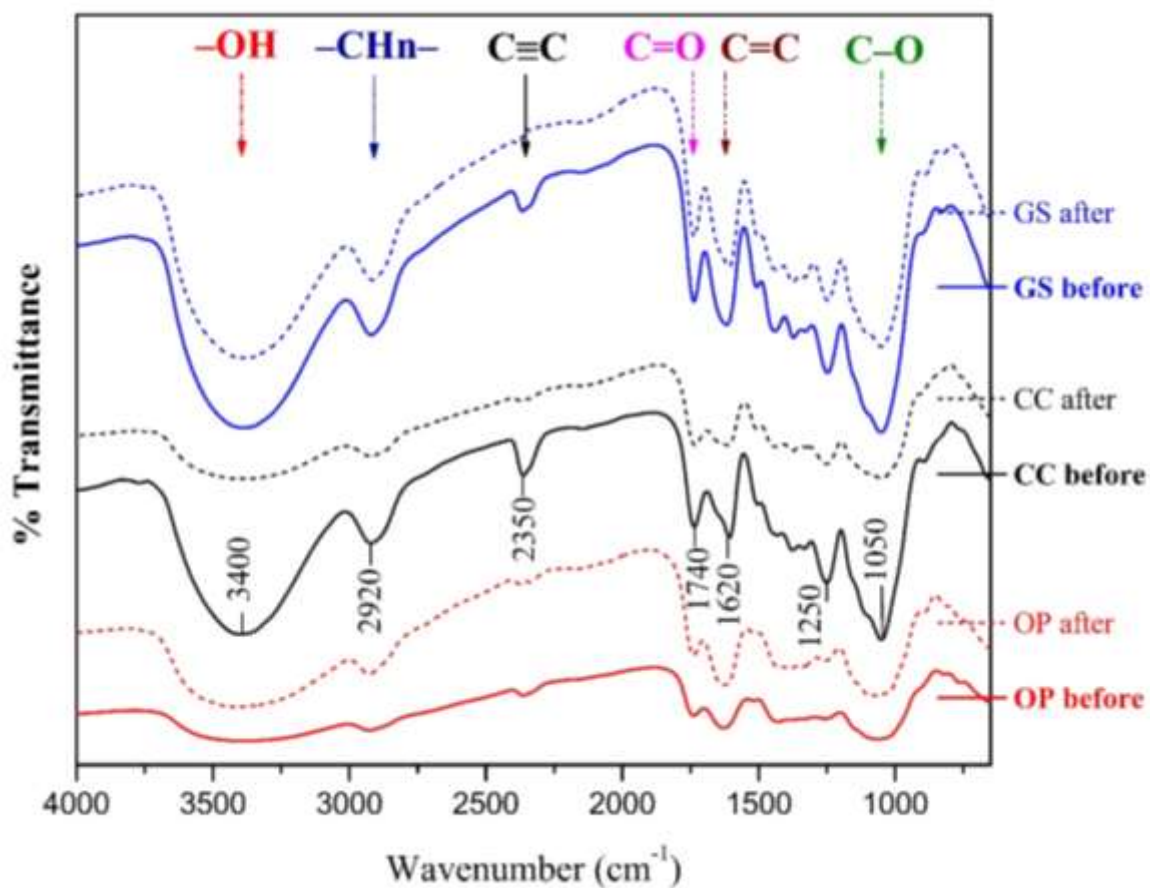


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Figure 2. SEM images of the pristine biosorbent samples

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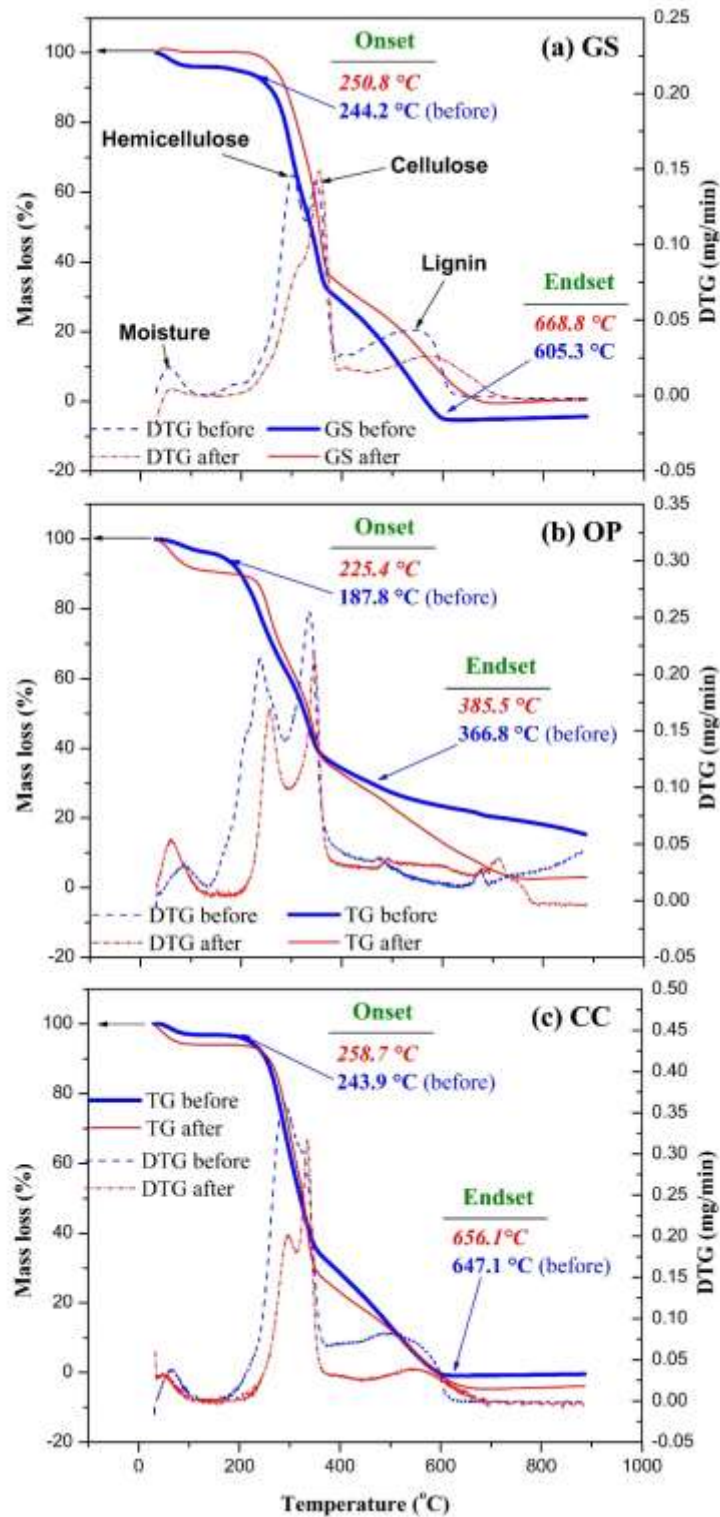


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625 **Figure 3.** FT-IR spectra of the biosorbents before and after MG5 adsorption

626

(without baseline correction)

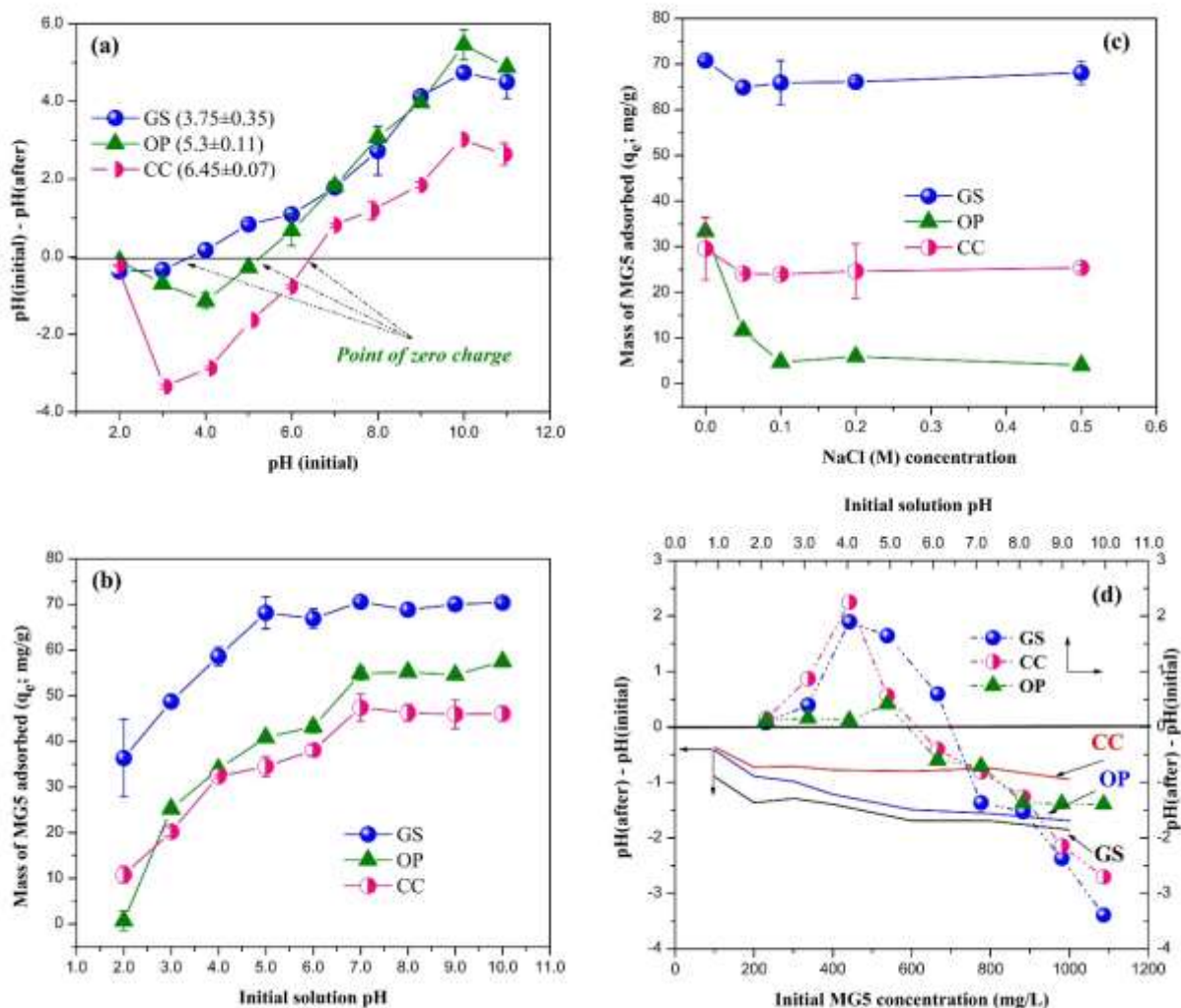


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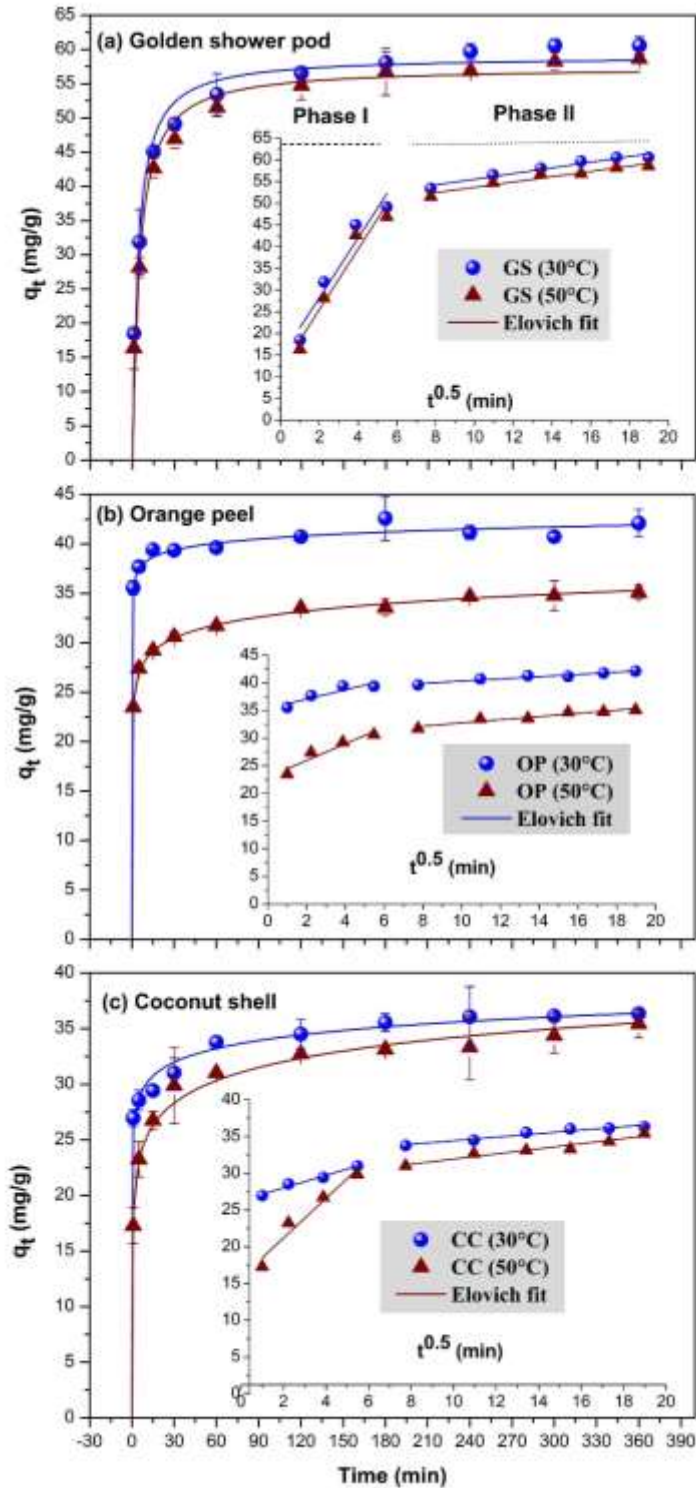
Figure 4. TGA of the biosorbents before and after MG5 adsorption

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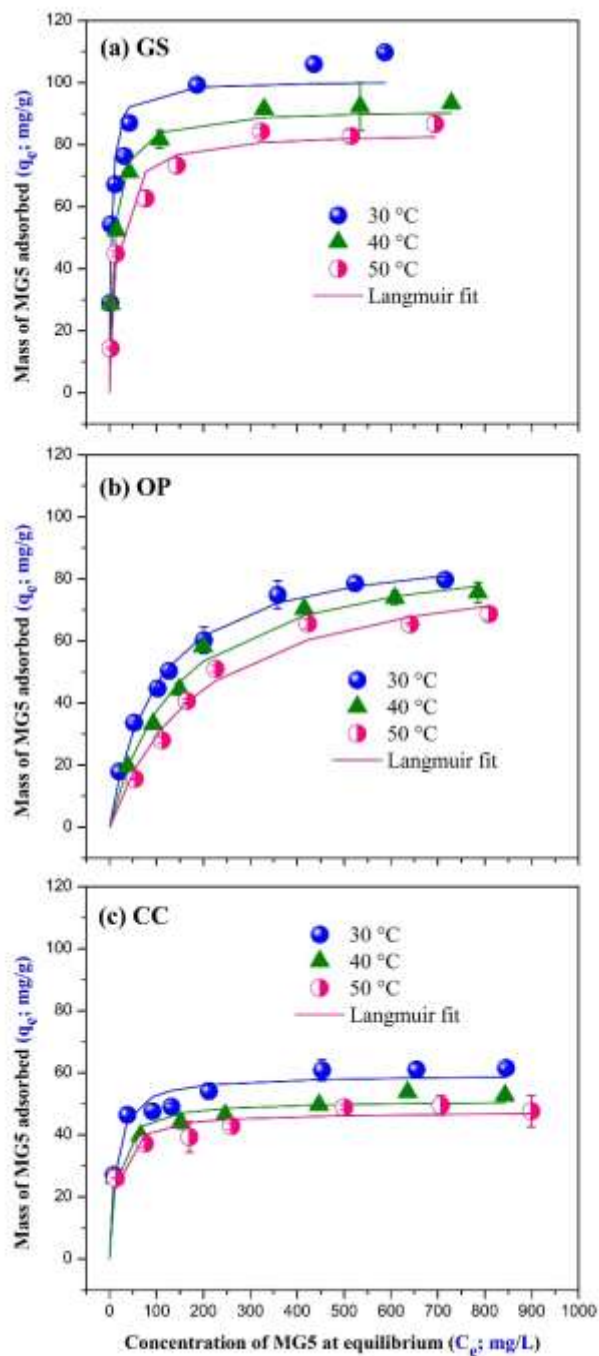
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 631 **Figure 5.** (a) The PZC values of the biosorbents, (b) the dependence of the
 632 adsorption capacity on the pH, (c) the effect of the ionic strength on the
 633 adsorption capacity, and (d) the pH values after adsorption
 634 (Experimental conditions: $t = 24$ h, $C_0 = 300$ mg/L, $m/V = 4.0$ g/L; 0 M NaCl for
 635 the experiments of the dependence of the adsorption capacity on the pH and initial
 636 solution pH 7.0 for the experiments of the effect of the ionic strength).

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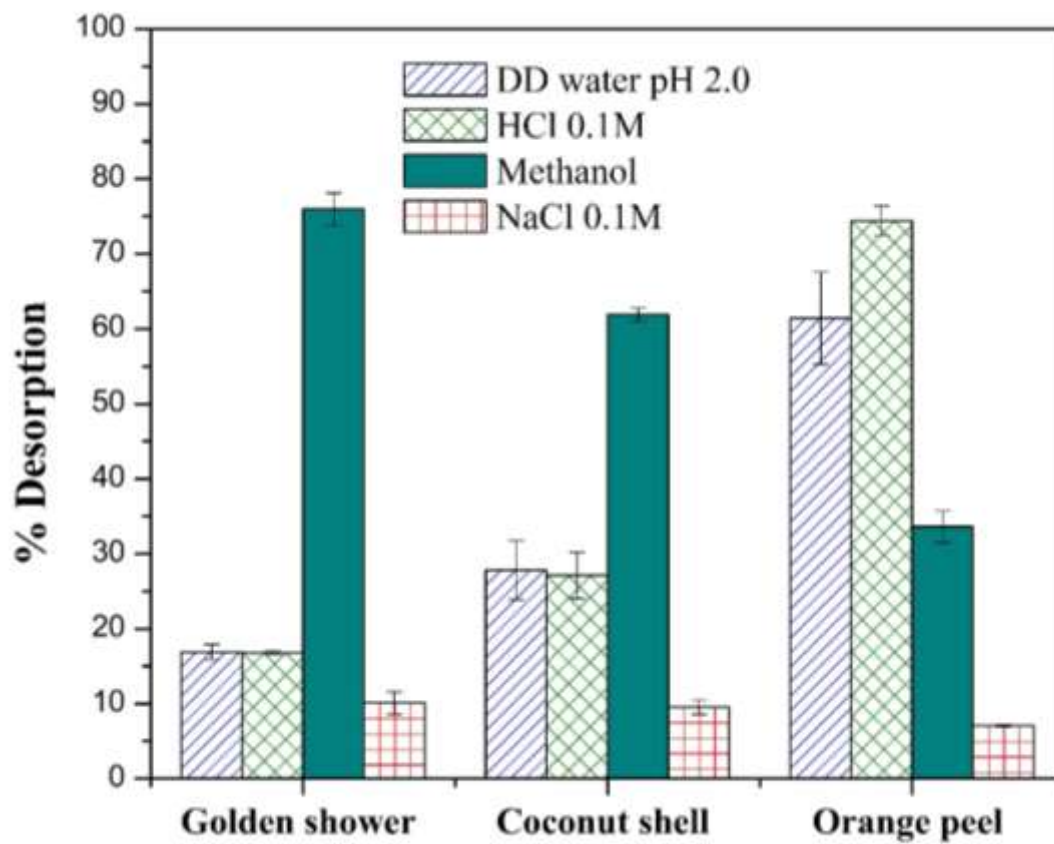
638 **Figure 6.** MG5 adsorption kinetics at different temperatures and intra-particle
 639 diffusion plots for MG5 adsorption (figures inside)

640 (Experimental conditions: pH 7.0, 0 M NaCl, $m/V = 4.0$ g/L, and $C_0 = 330$ mg/L)



641
 642 **Figure 7.** MG5 adsorption isotherms at different temperatures
 643 (Experimental conditions: pH 7.0, 0 M NaCl, m/V = 4.0 g/L, $t = 24$ h, and $C_o =$
 644 100–1,000 mg/L)

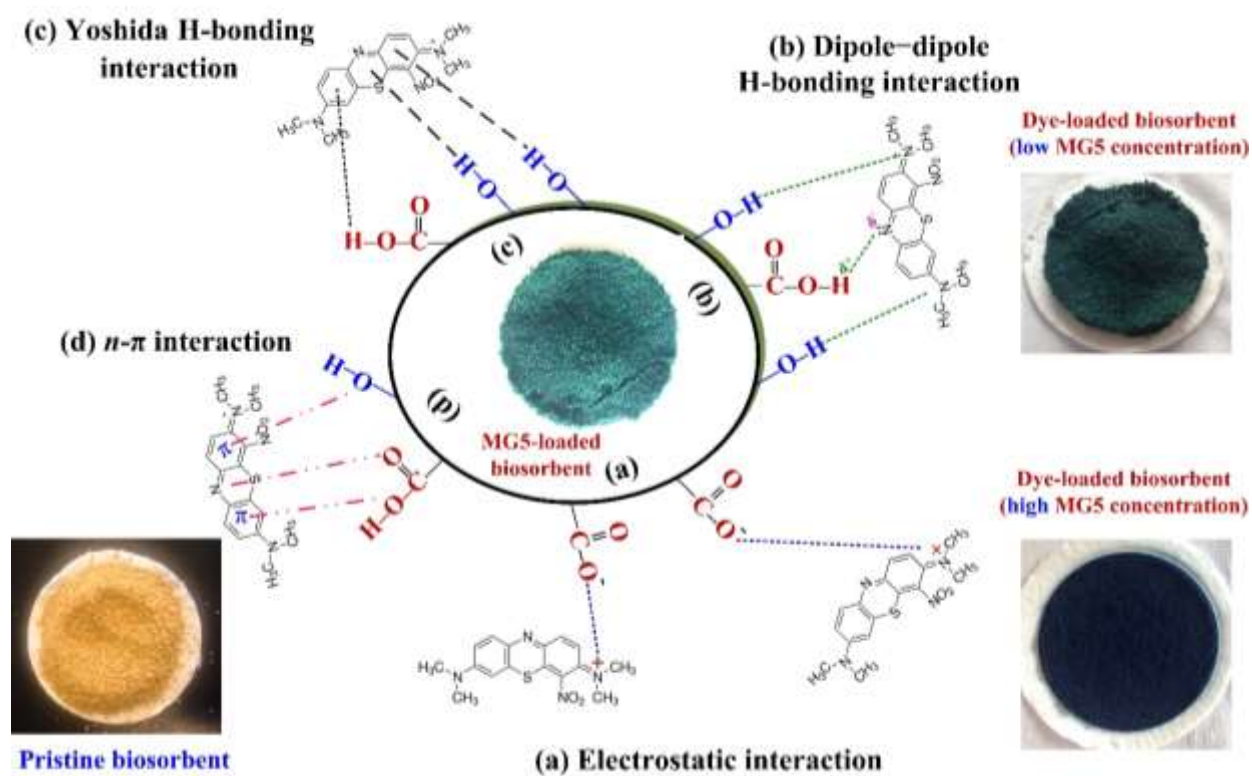
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Figure 8. Percentage of MG5 desorbed using various desorbing agents

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649

650 **Figure 9.** Proposed MG5-adsorption mechanisms for different biosorbents

651

652

653 **Table 1.** Basic characteristics of the pristine biosorbent samples

	Unit	GS	CC	OP
1. Textural properties				
S _{BET}	m ² /g	5.727	3.167	2.086
S _{Langmuir}	m ² /g	16.78	8.093	7.185
S _{External}	m ² /g	14.54	6.367	4.339
V _{total} × 10 ⁻³	cm ³ /g	9.962	4.135	4.237
2. Physicochemical properties				
Hardness	%	49.1±2.01	58.5±2.51	39.7±1.15
Bulk density	g/cm ³	0.66±0.02	0.65±0.20	0.61±0.05
pH _{1:20}	–	5.43±0.33	6.5±0.25	4.69±0.18
3. Ultimate analysis				
C	wt%	53.39	55.50	54.34
H	wt%	6.14	6.273	5.91
N	wt%	0.84	0.44	1.14
O ^a	wt%	39.63	37.79	38.61
4. Proximate analysis				
Moisture	wt%	5.80±0.28	8.09±1.59	8.54±1.98
Total ash	wt%	1.17±0.30	1.67±0.15	3.49±0.99
Volatile	wt%	76.2±0.53	73.0±3.34	74.3±2.95
Fixed carbon ^a	wt%	16.8±0.78	17.2±1.91	13.6±2.18
5. Boehm titration results				
Total acidic groups	mmol/g	8.74±0.21	4.21±0.25	6.90±0.38
+ Phenolic	mmol/g	0.37±0.38	2.15±0.95	1.97±0.18
+ Lactonic	mmol/g	1.75±0.21	0.96±0.15	0.85±0.49
+ Carboxylic	mmol/g	6.16±0.14	1.10±0.25	4.07±0.66
Total basic groups	mmol/g	0.12±0.30	2.25±0.55	2.14±0.63

654 ^aCalculated by difference; means ± standard deviation; pH_{1:20} means approximately 1.0 g
655 adsorbent per 20 mL of distilled deionized water (4h of contact time); data for GS published in
656 our previous study (Tran et al., 2017e).

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660 **Table 2.** FTIR spectral characteristics (cm^{-1}) of the biosorbents before and after MG5 adsorption
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Samples	Functional groups			
	O–H	C=C	C=O	C–O
Pristine GS	3389	1738	1678	1052
MG5-loaded GS	3390	1736	1608	1050
Pristine CC	3392	1734	1613	1050
MG5-loaded CC	3395	1737	1606	1050
Pristine OP	3393	1739	1630	1065
MG5-loaded OP	3397	1739	1625	1073

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664 **Table 3.** T_{\max} values and mass loss percentages of the main components of the biosorbents before
 665 and after the adsorption of MG5

DTG peak	T_{\max} (°C)/mass loss (%)						Definition
	Before MG5 adsorption			After MG5 adsorption			
	GS	CC	OP	GS	CC	OP	
1	54/1.39	61/1.02	87/2.01	57/0.21	53/3.06	61/3.66	Moisture
2	299/26.8	289/28.7	237/19.5	320/25.8	299/27.0	256/17.8	Hemicellulose
3	351/30.1	327/23.5	333/32.4	356/26.0	335/28.2	346/34.6	Cellulose
4	–	–	490/18.1	–	–	492/20.1	CaO
5	548/37.9	498/33.2	700/27.9	583/37.8	540/34.7	711/23.4	Lignin

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667 **Table 4.** Corresponding adsorption kinetic parameters for MG5 adsorption by GS, CC, and OP

	GS		OP		CC	
	30 °C	50 °C	30 °C	50 °C	30 °C	50 °C
$q_{e,exp}$	60.30	56.89	41.58	34.54	35.03	32.07
<i>Pseudo-first-order model</i>						
$q_{e,cal}$	59.39	54.76	40.30	32.32	33.49	31.45
k_1	0.162	0.131	2.822	1.283	1.632	0.612
R^2	0.844	0.874	0.540	0.488	0.258	0.577
χ^2	30.81	25.94	5.105	7.336	9.247	13.85
<i>Pseudo-second-order model</i>						
$q_{e,cal}$	59.02	57.45	40.69	33.03	34.08	32.72
$k_2 (\times 10^{-3})$	4.412	3.695	151.7	60.66	85.64	23.66
R^2	0.953	0.963	0.653	0.716	0.475	0.833
χ^2	9.165	7.640	1.514	4.062	6.551	5.468
<i>Elovich model</i>						
$\alpha (\times 10^3)$	0.154	0.100	2108	456.6	4.065	1.682
β	0.141	0.138	0.982	0.518	0.564	0.345
R^2	0.961	0.957	0.967	0.994	0.955	0.976
χ^2	7.723	8.681	0.133	0.089	0.556	0.776
<i>Intra-particle diffusion model</i>						
K_{ip}	1.863	1.897	0.285	0.536	0.519	0.779
C	31.39	28.79	37.14	26.25	27.84	22.19
R^2	0.741	0.739	0.833	0.847	0.911	0.784
χ^2	11.85	13.07	0.161	0.687	0.307	2.508
<i>Activation energy</i>						
$Ea(k_1)$	-8.64		-32.07		-39.90	
$Ea(k_2)$	-7.22		-37.29		-52.33	
$Ea(\alpha)$	-17.45		-62.23		-35.23	
$Ea(k_{ip})$	-3.52		-14.12		-9.23	

668 **Note:** the units of kinetic parameters are q_e (mg/g), β (mg/g), k_1 (1/min), k_2 (g/mg×min), k_{ip}
669 (mg/g×min), α (g/mg×min), Ea (kJ/mol). The kinetic parameters were determined by non-linear
670 method, expected for the intra-particle diffusion model.

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672 **Table 5.** Relative adsorption isotherm parameters for MG5 adsorption

Units	Golden shower pod (GS)			Orange peel (OP)			Coconut shell (CC)			
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	
Langmuir parameters										
Q_{\max}^o	mg/g	105.6	91.35	84.16	92.35	91.96	88.88	59.47	51.1	47.5
K_L	L/mg	0.132	0.106	0.072	0.010	0.007	0.005	0.079	0.076	0.071
R^2	–	0.966	0.973	0.971	0.993	0.991	0.969	0.916	0.915	0.824
χ^2	–	4.67	3.88	2.17	0.71	0.9	1.95	1.66	1.10	1.63
Freundlich parameters										
K_F	(mg/g)/ (mg/L) ⁿ	40.4	34.8	23.4	9.05	6.89	4.56	22.1	20.1	19.3
n	–	0.164	0.159	0.210	0.344	0.371	0.417	0.160	0.149	0.142
R^2	–	0.915	0.881	0.925	0.956	0.967	0.905	0.951	0.960	0.954
χ^2	–	12.3	6.77	11.5	3.99	5.05	10.7	1.24	0.57	0.95
Dubinin-Radushkevich parameters										
Q_{DR}	mg/g	87.4	81.0	78.5	72.7	73.6	67.5	55.0	48.0	44.4
K_{DR}	mol ² /kJ ²	0.74	1.76	15.36	498.21	1191.70	1593.91	10.96	13.13	13.67
E	kJ/mol	0.822	0.532	0.180	0.032	0.020	0.018	0.214	0.195	0.191
R^2	–	0.770	0.703	0.867	0.783	0.845	0.907	0.748	0.764	0.702
Separation factor										
R_L	$\times 10^{-3}$	7.2–60.3	8.6–74.1	13–126	88–508	116–550	155–629	11.4–97	12–101	13–106

673 *Note: the parameters from the selected models were determined using non-linear method.*

674 **Table 6.** Adsorption thermodynamics parameters for MG5 adsorption

T (K)	van't Hoff equation	K _C	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol × K)
Golden shower pod (GS)					
303	y = 2956x+2.07 R ² = 0.969	131900	-29.72	-24.57	17.21
313		105900	-30.12		
323		72000	-30.05		
Orange peel (OP)					
303	y = 3407x - 2.03 R ² = 0.999	10022	-23.22	-28.33	-18.32
313		6933	-23.03		
323		5000	-22.88		
Coconut shell (CC)					
303	y = 499x + 9.63 R ² = 0.991	79100	-28.43	-4.151	80.10
313		75652	-29.25		
323		71423	-30.03		

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679 **Table 7.** Comparison of the cationic dye maximum capacities (Q_{max}^o) of the biosorbents studied
 680 here and those of other biosorbents reported in the literature

Biosorbent	Dye	Mw (g/mol)	Q_{max}^o (mmol/g)	Reference
<i>Cinnamomum camphora</i>	MG	365	0.424	Wang et al. (2014)
<i>Simarouba glauca</i>	MG	365	0.342	Jeyagowri and Yamuna (2016)
Orange peel	BB41	483	0.326	Contreras et al. (2012)
Chitosan aniline composite with PH	CV	408	0.257	Tahir et al. (2017)
Starch composite with PH	CV	408	0.248	Tahir et al. (2017)
Golden shower	MG	433	0.244	This study
Chitosan pyrrole composite with PH	CV	408	0.229	Tahir et al. (2017)
Polyaniline composite with PH	CV	408	0.221	Tahir et al. (2017)
Polypyrrole composite with PH	CV	408	0.218	Tahir et al. (2017)
Orange peel	MG5	433	0.213	This study
Pine sawdust	MG	365	0.196	Witek-Krowiak (2013)
Coconut shell	MG5	433	0.137	This study
Brewer's spent grains	BB41	483	0.067	Contreras et al. (2012)
Banana peel	MB	320	0.065	Annadurai et al. (2002)
Orange peel	MB	320	0.058	Annadurai et al. (2002)
Banana peel	MV	256	0.048	Annadurai et al. (2002)
Orange peel	MV	256	0.045	Annadurai et al. (2002)
Banana peel	RB	479	0.043	Annadurai et al. (2002)
Orange peel	RB	479	0.030	Annadurai et al. (2002)

681 *Note: MG5 (methylene green 5); MG (Malachite green); MB (Methylene blue); MV (Methyl violet); RB*
682 *(Rhodamine B); BB41 (Basic Blue 41); CV (Crystal Violet); and PH (peanut hull)*

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685 **Table 8.** Comparison of the maximum capacities (Q_{max}^o) of MG5 adsorption by the biosorbents
 686 studied here and those of other adsorbents reported in the literature

Adsorbent	S_{BET} (m^2/g)	pH	T ($^{\circ}C$)	Q_{max}^o (mg/g)	Reference
Biosorbent					
Golden shower	5.727	7.0	30	106	<i>This study</i>
Coconut shell	3.167	7.0	30	59.5	<i>This study</i>
Orange peel	2.086	7.0	30	92.4	<i>This study</i>
Hydrochar					
Golden shower	14.7	7.0	30	59.6	Tran et al. (2017g)
Coconut shell	6.65	7.0	30	32.7	Tran et al. (2017g)
Orange peel	6.99	7.0	30	15.6	Tran et al. (2017g)
Commercial glucose	7.08	5.0	25	13.9	Tran et al. 2017a)
Biochar					
Golden shower	604	7.0	30	45.5	Tran et al. (2017c)
Coconut shell	536	7.0	30	41.5	Tran et al. (2017c)
Orange peel	565	7.0	30	35.2	Tran et al. (2017c)
Activated carbon					
Golden shower	812–1,413	7.0	30	253–531	Tran et al. (2017f)
Orange peel	1,025	7.0	30	330	Tran et al. (2017f)
Commercial glucose	335	5.0	25	175	Tran et al. (2017a)
Commercial AC	768	5.0	25	178	Huang et al. (2014)
Commercial xylose	1,386	5.0	25	417	Huang et al. (2014)
Commercial sucrose	1,494	5.0	25	299	Huang et al. (2014)
Commercial glucose	1,612	5.0	25	444	Huang et al. (2014)
Norit RB4C	1,026	7.0	30	543	Tran et al. (2017b)
Activated carbon	946	3.0	25	272	Shiau and Pan (2005)
Others					
Ag-NP-AC	NA	7.0	25	167	Ghaedi et al. (2014)
ZnONR-AC	NA	7.0	25	200	Ghaedi et al. 2014)
MCM-41	1,004	4.0	25	137	Lee et al. (2007)
GH-TETA _{1%}	NA	5.0	25	67.6	Tran, et al. (2017a)
GAC _{1%}	233	5.0	25	101	Tran, et al. (2017a)
Montmorillonite	165	3.0	25	128	Shiau and Pan (2005)
Activated clay	278	3.0	25	271	Shiau and Pan (2005)
Titania nanotube	292	4.0	25	292	Lin et al. (2010)

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