

1       **Production of adsorbent for removal of propranolol hydrochloride: use of**  
2       **residues from *Bactris guineensis* fruit palm with economically exploitable**  
3                               **potential from the Colombian Caribbean**

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15

### **Abstract**

16           The production and consequently the consumption of the pulp of the fruit of the palm  
17 tree *Bactris guineensis* occurs extensively in Colombia. The majority of the fruit is formed by  
18 waste (peel and core), producing high residual biomass. Thus, it is necessary to find a practical  
19 utilization of these peels, making the production and consumption of the fruit of the palm tree  
20 *Bactris guineensis* highly sustainable. This study produced activated biochar chemically  
21 activated using ZnCl<sub>2</sub> and utilized it as an effective adsorbent. The high micropollutant uptake  
22 is because of the high porosity and good specific surface area ( $S_{\text{BET}} = 625 \text{ m}^2 \text{ g}^{-1}$ ). Under basic  
23 conditions, propranolol adsorption was favored for an adsorbent dosage of  $0.7 \text{ g L}^{-1}$ . The  
24 adsorbent showed fast kinetics, with the equilibrium influenced by the concentration.  
25 Avrami's model showed a satisfactory fit having a  $t_{0.95}$  ranging from 47.8 to 179.3 min.  
26 Equilibrium data were best adjusted to the Liu isotherm model. The values of  $Q_{\text{max}}$  increased  
27 with the temperature, reaching up to  $161.3 \text{ mg g}^{-1}$  ( $45^\circ\text{C}$ ). The thermodynamic data showed  
28  $\Delta G^\circ < 0$  for 298-328 K (adsorption process favorable)  $\Delta H^\circ = + 7.403 \text{ kJ mol}^{-1}$  (endothermic;  
29 magnitude compatible with physical adsorption), and  $\Delta S^\circ = +115.2 \text{ J K}^{-1} \text{ mol}^{-1}$  (releases of water  
30 molecules of the adsorbate before it being adsorbed in the carbon surface). The biochar  
31 chemically activated with ZnCl<sub>2</sub>, produced from the leftover peels of Colombian palm fruits,  
32 is therefore inferred to be a promising option as an adsorbent for the treatment of effluents  
33 containing the medication propranolol hydrochloride.

34 **Keywords:** Adsorption; Residue; Activated biochar, adsorption thermodynamics, nonlinear  
35 Van't Hoff equation.

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## 42 1. Introduction

43 Emerging micropollutants have attracted the scientific community's attention in recent  
44 years, as they are released in different sectors of society and can be detected in domestic,  
45 industrial, and, mainly, hospital effluents [1]. These residual compounds contaminate water  
46 resources and the soil, directly affecting the aquatic biota, the animals that consume this  
47 water, and even the plants. Therefore, in addition to techniques that remove these  
48 compounds, their long and medium-term effects must be studied [2,3]. Added to this, the  
49 United Nations (U.N.) has focused on sustainable development, which advocates the  
50 emergence of new environmental legislation policies on the global contamination of water  
51 resources, enabling studies on these ecological contaminants [1,4,5]. The class of drugs within  
52 emerging pollutants is a serious problem because while continuous discharges are released  
53 into the environment, they do not have environmental regulations [6–8]. It should be noted  
54 that even at low concentrations, these drugs may be quite hazardous to the aquatic biota,  
55 especially over an extended period [9–12].

56 The consumption of drugs used for hypertension has grown in recent years; propranolol  
57 hydrochloride ( $C_{16}H_{21}NO_2.HCl$ ) is widely used worldwide, where the human body does not  
58 absorb a large part eliminated in the urine [13]. Propranolol (PROP) is highly persistent in the  
59 environment and has a long duration after consumption, with 4-hydroxypropranolol as its  
60 main metabolite [14,15]. Conventional processes used in the treatment of effluents partially  
61 remove this contaminant [13,16], the remainder being discharged into water bodies, highly  
62 harmful to various organisms such as the green algae *S. vacuolatus* [17]. In Brazil, PROP has  
63 been detected in surface, drinking, and effluents from water and sewage treatment plants  
64 [18,19]. Due to this problem, several techniques have been studied, mainly in removing and  
65 degrading this compound [1,20–23]. Adsorption has the advantage of applying new  
66 adsorbents from plant residues, mainly for producing carbon-based materials [24–27].  
67 Normally, these carbonaceous materials, formed basically by carbon, have a good surface area  
68 and excellent pore development, some of the important characteristics of a good adsorbent  
69 [28,29].

70 The *Bactris guineensis* palm is an important fruit tree in the Colombian Caribbean  
71 extending to Central America. This fruit tree has great economic importance [30]. Popularly

72 known as corozo, its round and small fruits have a pulp with high nutritional value and can be  
73 consumed fresh and in the preparation of drinks, jellies, and even wines [31,32]. A single plant  
74 produces an average of 30 kg per year of fruit, reaching an annual productivity of 750 kg ha<sup>-1</sup>  
75 [30], generating large volumes of residual biomass corresponding to bark and seeds. In  
76 addition, studies have reported that dark-colored pulp has an antioxidant action [31,33].  
77 However, no studies reported residual biomass as a carbon precursor for preparing adsorbent  
78 material and possible application in removing emerging contaminants.

79 The activation process is one of the major steps to ensure that the adsorbent is able to  
80 remove or adsorb more molecules by creating pores and augmenting the textural proprieties  
81 [34]. Different activators can be used from salts, bases, and acids; among all the salts, the ZnCl<sub>2</sub>  
82 performs best, presenting a higher specific surface area and pore formation [35]. Therefore,  
83 enhancement of the textural proprieties is one of the most desired modifications that be done  
84 to the adsorption studies. In special, this modification technique tends to increase the  
85 adsorption capacity of the raw materials, allowing the molecules to diffuse more easily onto  
86 the pore and surface of the material [36].

87 Therefore, this use used the bark as the residual biomass of the *Bactris guineensis* fruit to  
88 prepare biochar chemically activated with zinc chloride (ZnCl<sub>2</sub>) and subsequent use as an  
89 adsorbent. The main objective is to bring a new application for this residual biomass since it  
90 presents a large volume and high annual consumption in Latin countries such as Colombia.  
91 Another point is the problem of emerging contaminants such as propranolol, which has a small  
92 variety of adsorbents aimed at its removal. First, the pristine biomass and biochar material  
93 were characterized using different characterization techniques. Then activated biochar was  
94 used to remove the drug for hypertension propranolol hydrochloride. Next, adsorbent dosage  
95 and pH studies were carried out. Then kinetic and isothermal studies were determined, where  
96 the experimental data were fitted to specific mathematical models. Last, the thermodynamic  
97 parameters of adsorption were estimated.

## 98 **2. Materials and methods**

### 99 *2.1 Chemical employed*

100 The chemicals and reagents (further described) were all obtained from Sigma-Aldrich-USA  
101 in analytical grade. In order to adjust the pH, 0.1 M of HCl and NaOH were used. For activation  
102 in the carbonization step, zinc chloride salt ( $\text{ZnCl}_2$ ) was used. The propranolol hydrochloride  
103 was used (chemical formula:  $\text{C}_6\text{H}_{21}\text{NO}_2\cdot\text{HCl}$ ; molecular weight:  $295.807 \text{ g mol}^{-1}$ ) as adsorbate  
104 [1]. In order to obtain different concentrations of PROP, a stock solution was prepared. In this  
105 case,  $1 \text{ g L}^{-1}$  of PROP was dissolved in methanol due to the low solubility of the drug; in the  
106 end, a  $1000 \text{ mg L}^{-1}$  contraction solution was generated. Working solutions with different  
107 concentrations were attained by diluting the stock solution with deionized water and  
108 adjusting the solutions' pH using 0.1M NaOH or HCl (Digimed pHmeter, DM 20, Brazil).

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## 110 *2.2 Precursor gathering, pyrolysis, and characterization*

111 The material gathered for pyrolysis and the characterization are specified in the  
112 Supplementary Material. In sum, the *Bactris guineenses* were obtained from a local producer  
113 in Barranquilla, Colombia. First, the fruit peel was separated, dried, and ground. After that,  
114 the powder was mixed with the activating agent ( $\text{ZnCl}_2$ ) and pyrolyzed using a quartz reactor  
115 at  $\text{N}_2$  atmosphere at 923.15 K. After that; the pyrolyzed material was washed with an HCl  
116 solution and dried. Finally, the source and pyrolyzed material were characterized through  
117 Fourier-transformed infrared spectroscopy, scanning electron microscopy, X-ray  
118 diffractometry, and  $\text{N}_2$  adsorption and desorption isotherms (only for the pyrolyzed material).

## 119 *2.3 Adsorption experiments with propranolol*

120 All samples were continuously stirred at 150 rpm utilizing a thermostatic stirrer. The  
121 PROP concentration was determined through spectrophotometry using a UV micro 1240  
122 (Shimadzu, Japan). The equipment was set to work at 255 nm, corresponding to the  
123 propranolol's maximum absorption wavelength. All assays were conducted in triplicates to  
124 guarantee the results' reliability; after each test, the samples were centrifuged at 5000 rpm  
125 for 15 min, separating the solid phase from the liquid phase; for details, see Supplementary  
126 material [37–42].

127

### 128 3. Results and Discussion

#### 129 3.1. Characterization results of the source and pyrolyzed material

130 During the pyrolysis step, a good part of the lignin and cellulose is converted into  
131 volatile material, influencing the final yield and increasing the specific surface area [43]. Due  
132 to this process, the final carbonaceous skeleton formed basically by carbon presented a yield  
133 close to 29 %. This result agrees with other research using  $\text{ZnCl}_2$  in proportions of 1:1. The  
134 biomasses used in this study were: jaboticaba residues [44], açaí residues [45], fruits of the  
135 invasive species *Hovenia dulcis* [46] and cassava peels [47]. When using KOH as an activating  
136 agent, the authors reported a yield close to 64% [48]. The biochar developed from *Bactris*  
137 *guineensis* residues obtained a satisfactory surface area of  $625 \text{ m}^2 \text{ g}^{-1}$  (Figure 1a). Figure 1b  
138 allows classifying the isotherms as type I (IUPAC); these structures correspond to micro and  
139 mesoporous materials [49,50]. The H4-type hysteresis slit is typical of structures with pores  
140 with diameters equal to those obtained in this study [50]. The results corroborate the  
141 developed carbonaceous material's pore volume ( $0.4223 \text{ cm}^3 \text{ g}^{-1}$ ). Analyzing the textural  
142 properties of the adsorbent is essential because they strongly influence the adsorption  
143 performance [51]. When observing structures composed of lignin and cellulose and  
144 carbonized with  $\text{ZnCl}_2$ , we observed similar characteristics to this study [52–54].

145 <Fig.1>

146 Figure 2 makes it possible to identify the main functional groups present on the surface  
147 of the materials. It is possible to observe that most groups remained after carbonization with  
148 a lower intensity. The band at  $3441 \text{ cm}^{-1}$  (biochar) and  $3445 \text{ cm}^{-1}$  (biomass), the O-H bonding  
149 occurs [55]. The bands at  $2922$  and  $2854 \text{ cm}^{-1}$  (BC) and  $2923$  and  $2855 \text{ cm}^{-1}$  (biomass) are  
150 assigned to asymmetric and symmetric C-H stretch bonds, respectively [56]. The band at the  
151  $1738 \text{ cm}^{-1}$  region is assigned to C=O bonds in ketones, and aldehydes are found in the biomass  
152 precursor [58]. However, in biochar, the disappearance of the C=O bond corroborates the loss  
153 of volatile material during pyrolysis [57].

154 The carboxylate stretching vibrations correspond to the band at  $1631 \text{ cm}^{-1}$  (biochar)  
155 and  $1641$  (biomass) [59]. The band at  $1451 \text{ cm}^{-1}$  in the biomass can be assigned to the C-H  
156 bending of lignocellulosic material or ring modes of aromatics in lignin [57,60]; this band

157 vanished in the biochar material. On the other hand, the bands at 1379  $\text{cm}^{-1}$  (carbon  
158 precursor) and 1383  $\text{cm}^{-1}$  (biochar) can be assigned to C-H bending [57,60]. The band at 1254  
159  $\text{cm}^{-1}$  (carbon precursor) is assigned to the C-O stretching of phenol present in lignin [29, 61].  
160 The bands at 1107  $\text{cm}^{-1}$  (carbon precursor) and 1153 and 1114  $\text{cm}^{-1}$  (biochar) are assigned to  
161 attributed to C-O-C of ether and C-C-O of esther stretching [29], and the peak at 1043  $\text{cm}^{-1}$   
162 (carbon precursor) is attributed to C-O stretching of phenolic groups or carboxylate [29; 61].  
163 ]. The band at 897  $\text{cm}^{-1}$  (carbon precursor) and 801  $\text{cm}^{-1}$  (biochar) are attributed to the C-H  
164 bending of aromatics [29]. The FTIR results of this work are similar to those obtained by  
165 Bouchelta et al. [58] by carbonizing date fruit waste.

166 <Fig.2>

167 Figure 3 corresponds to the XRD patterns of the source and pyrolyzed samples.  
168 Firstly, the long diffraction band between 15 and 30 corresponds to the presence of  
169 amorphous carbon [62]. This band undergoes changes after carbonization, where its width  
170 decreases and its intensity increases, which may be related to a more organized structure  
171 formed after the pyrolysis; however, the biochar material is still amorphous. Amorphous  
172 arrangements are usually disorganized and irregular. However, they have empty spaces in  
173 their organization, which can be occupied by adsorbate molecules, supporting the adsorption  
174 [24].

175 <Fig.3>

176 The high temperature employed together with the activation provided apparent  
177 morphological modifications to the surface of the materials (Fig. 4). Initially, the irregular  
178 particles of different sizes had a uniform and smooth surface (Fig. 4a). However, when they  
179 were carbonized, they started to contain numerous irregularities and protuberances (Fig. 4b).  
180 Materials formed by lignin and cellulose tend to have irregular and disorganized  
181 morphological structures, such as tree bark [63–66], fruit residues [44,67–70] and seeds of  
182 forest species [71–74]. These irregularities are alternately distributed and present cavities and  
183 empty spaces, which can be highly favorable for adsorption [46,70].

184 <Fig.4>

185 *3.2. Study of adsorbent dosage and pH*

186 The optimal BC dosage (Figure 5) was determined using 25 mg L<sup>-1</sup> of PROP. In the  
187 process of increased dosage from 0.5 to 1 g L<sup>-1</sup>, the capacity decreases from 75 to 51 mg g<sup>-1</sup>,  
188 while the removal shows the opposite behavior, increasing from 70 to 96%. The curves are  
189 crossed at 0.7 g L<sup>-1</sup> dosage, presenting a q value of 64 mg g<sup>-1</sup> and a removal percentage of 64  
190 %, which is fairly good. Therefore, 0.7 g L<sup>-1</sup> of BC was utilized for the next adsorption  
191 experiments. When using ionic liquid iron nanocomposite as an adsorbent in the removal of  
192 PROP, it was observed that increasing the dosage from 0.05 to 0.5 g L<sup>-1</sup> generated an increase  
193 in removal from 30 to 90 % [75].

194 <Fig.5>

195 The effect of the pH of the solution was analyzed according to Figure 6. Initially,  
196 when the adsorbate solution pH is acidic (pH 3), the adsorption capacity is 30.6 mg g<sup>-1</sup>; when  
197 raising the pH to 6, the capacity drops to 26.8 mg g<sup>-1</sup>. From pH 6, the capacity increases until  
198 reaching the capacity of 33.56 mg g<sup>-1</sup> at pH 8. Then the capacity suffers a slight decrease up to  
199 pH 10. This behavior confirms that the incremental change of the solution pH, close to 8,  
200 favors the adsorption of the PROP. This result corroborates the study by Ali et al. [75], whereby  
201 by raising the pH from 3 to 11, the adsorption capacity of PROP rises to a pH close to 9 and  
202 then decreases again. PROP presents constant acidity being a secondary amine (pK<sub>a</sub>=9.5).  
203 Therefore, the charges of the β-blockers present in the solution are mostly positive, favoring  
204 adsorption at high pH. At pH > 8, the amine is released by hydrolysis and precipitated due to  
205 its low solubility, making adsorption above this value unfeasible [76]. Added to this, the point  
206 of zero charge of the adsorbent was 6.5, so when the pH is at this value, the charges on the  
207 surface are equal to zero. When the pH value is above 6.5, the surface is negatively charged;  
208 when the pH is below 6.5, the surface of the adsorbent is positively charged. Therefore,  
209 electrostatic repulsion occurs under acidic conditions, and electrostatic attraction occurs  
210 under basic conditions. In this study, pH 8 was fixed for further experiments.

211 <Fig.6>

### 212 3.3. Propranolol adsorption kinetics

213 By means of three concentrations, the performance of the carbonaceous material  
214 in the PROP uptake and the time to attain the equilibrium were analyzed according to the  
215 kinetic curves represented in Figure 7.



216 The experimental kinetic data were adjusted to the Pseudo-first-order (PFO),  
217 Pseudo-second-order (PSO), and Avrami fractional-order (AFO) models (see Table S1). The  
218 AFO presented the bested values of  $R^2_{adj}$ , followed by the PSO and PFO. This same tendency  
219 was obtained for the statistical parameter SD ( $\text{mg g}^{-1}$ ), with the lowest values reached by the  
220 AFO, followed by the PSO and PFO [77–80]. Also, to confirm the best kinetic model, the BIC  
221 analysis was carried out. The values of BIC for AFO were always lower than PFO and PSO.  
222 Therefore, the  $\Delta\text{BIC}$  of the two models can be conclusive for  $\Delta\text{BIC} < 2$  (the two models have  
223 no significant differences) or  $\Delta\text{BIC} \geq 10$  (indicates that the model with the lowest BIC is surely  
224 the best-fitted) [37,38]. On the other hand, for  $2 < \Delta\text{BIC} < 6$ , the model with a lower BIC value  
225 has a possibility of being the best-fitted model, or  $6 < \Delta\text{BIC} < 10$ , the model with a lower BIC  
226 value has a strong possibility of being the best-fitted model [37,38]. The  $\Delta\text{BIC}$  for PFO and  
227 Avrami were always higher than 10; therefore, PFO does not explain the kinetic results  
228 properly [37,38]. The  $\Delta\text{BIC}$  between PSO and Avrami was higher than 10 for  $C_0$  PROP of 50 and  
229 75  $\text{mg/L}$ , being AFO the best kinetic model [37,38]. However, for  $C_0$  25  $\text{mg L}^{-1}$  PROP, the  $\Delta\text{BIC}$   
230 between PSO and AFO was 7.063, with a high likelihood that the optimum kinetic model is the  
231 AFO. Therefore, AFO satisfactorily explains the kinetic data considering the set of the three  
232 concentrations of PROP [37,38].

233 Another important piece of information shown in Table S1 is the values of  $t_{1/2}$  and  
234  $t_{0.95}$  [38], which are defined as the time necessary to attain 50% and 95% of the maximum  
235 sorption capacity described by the model curve. Considering that AFO was the best-fitted  
236 kinetic model, it was observed that  $t_{1/2}$  for the uptake of PROP onto the BC ranged from 4.354  
237 min ( $C_0$  25  $\text{mg/L}$ ) to 15.02 min ( $C_0$  75  $\text{mg/L}$ ), and  $t_{0.95}$  for the uptake of PROP onto BC ranged  
238 from 47.82 ( $C_0$  25  $\text{mg/L}$ ) to 179.3 min ( $C_0$  75  $\text{mg/L}$ ). These results show that increased sorption  
239 capacity leads to increased time to attain equilibrium. Considering that the isotherms were  
240 performed with  $C_0$  up to 150  $\text{mg/L}$  of PROP, thus, it is advisable to employ a contact time of at  
241 least 240 min to perform the adsorption equilibrium experiments. Therefore, it is possible to  
242 conclude that the batch system may operate for around 15 min at a higher concentration  
243 before the need for regeneration.

244 When analyzing the kinetic behavior of PROP by other adsorbents in the literature,  
245 we observed that there are fast and slow kinetics cases. For example, when analyzing the  
246 adsorption of PROP on montmorillonite clay, the authors observed that about 96% of the drug

247 had already been removed in the first minute, confirming the high affinity of the adsorbent  
248 with the adsorbate [76]. Conversely, using Na-mica-4 and C18-mica-4, the authors took 24  
249 hours to achieve 97 % removal in river water samples synthetically contaminated with PROP  
250 [81]. Finally, when using granular activated carbon, the authors reported 88% and 68 %  
251 removal in 90 min [82] and 180 min [83], respectively.

252 <Fig.7>

### 253 3.4. Isothermal studies and estimation of thermodynamic parameters of adsorption

254 Isothermal studies were carried out at temperatures of 298, 308, 318, and 328 K, which  
255 resulted in the construction of four equilibrium curves (Fig. 8). These data help elucidate the  
256 interaction between BC and PROP and allow to calculate the parameters of thermodynamics  
257 of adsorption ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ). The curves were constructed by varying the concentration  
258 from 25 to 150 mg L<sup>-1</sup> of PROP. As a result, all curves show identical and favorable behavior  
259 for L-shaped adsorption [84].

260 <Fig.8>

261 The experimental equilibrium data fit the Langmuir, Freundlich, and Liu models (see  
262 Table S2). When analyzing the adjusted determination coefficients ( $R^2_{adj}$ ), it was verified that  
263 their values were closer to 1 using the Langmuir isotherm at the temperature of 298K. Liu for  
264 the temperature of 308 to 328 K. This statistical parameter was followed by SD, whose lowest  
265 values were obtained by the Langmuir model at 298 K, and Liu from 308 to 328 K. It was  
266 evident that the Freundlich isotherm model had the lowest values of  $R^2_{adj}$  and higher values  
267 of SD for all the temperatures, indicating that Freundlich isotherm model is not adequate to  
268 model the equilibrium data. Therefore, the BIC was utilized to verify what is the best isotherm  
269 model because it can be conclusive when  $\Delta BIC < 2$  (the difference between the two models is  
270 not statistically significant) or  $\Delta BIC \geq 10$  (indicates that the model with the lowest BIC is surely  
271 the best-fitted) [37,38]. At 298 K, the  $\Delta BIC$  between the Langmuir and Liu models was 1.606,  
272 indicating no relevant differences between the two isotherm models; both models can  
273 represent the equilibrium at 298 K. On the other hand, for 308, 318, and 328K, the  $\Delta BIC$   
274 between Liu and Langmuir were 70.70, 73.35, and 82.99, respectively, inferring that

275 undoubtedly, the Liu isotherm model is the best-fitted equilibrium model for representing the  
276 equilibrium data from 308 to 328 K. Considering that at 298 K, the differences of Liu and  
277 Langmuir were not significantly different, it could be stated that for the 298-328 K, the Liu  
278 model is the best equilibrium model to represent the experimental equilibrium data.

279 Also, it was observed that for both Langmuir and Liu isotherm models, the values of  
280  $Q_{\max}$  increased with the temperature. Considering that the Liu isotherm model best described  
281 the equilibrium data, it could be stated that the  $Q_{\max}$  varied from 124.5 at 298 K to 161.3 mg  
282  $g^{-1}$  at 328 K. The increasing maximum sorption uptake with the temperature is due to the  
283 driving force gradient that increases with the adsorbate concentration [85]. To be more  
284 precise, the temperature increase can affect the mass transport mechanism by changing the  
285 external and internal mass transfer mechanism [36]. The external mass transfer depends on  
286 the film formed between the adsorbent and the aqueous phase, named the boundary layer.  
287 This layer can be affected by external forces such as velocity and temperature; thus, increasing  
288 the temperature diminishes the mass transfer resistance [86]. As the internal mass transfer is  
289 based on pore and surface diffusion, these phenomena are also a function of the textural  
290 properties and the experimental conditions. The temperature increase tends to increase pore  
291 diffusion, according to Willke-Chang [87], which also affects surface diffusion. Although  
292 studies analyzing the adsorption of PROP are few compared to other emerging pollutants,  
293 some studies confirm results similar to those obtained in this study. For example, when  
294 analyzing the adsorption of PROP in bentonite clay, the authors observed that the capacities  
295 increased from 0.298 to 0.426 mmol  $g^{-1}$  with the increase in temperature from 293 to 313 K  
296 [1].

297 When analyzing the maximum capacity obtained by the model (161.3 mg  $g^{-1}$ ) and  
298 comparing it with other reports, it is concluded that the residual peels of the carbonized  
299 *Bactris guineensis* fruits have a high potential for application concerning effluents containing  
300 PROP. When bentonite clay was employed as an adsorbent, a capacity of 0.468 mmol  $g^{-1}$  for  
301 the concentration of 0.05 to 3 mmol  $L^{-1}$  of PROP was observed [1]. The maximum capacity of  
302  $6.2 \times 10^5 \mu\text{mol } g^{-1}$  was obtained using Montmorillonite as an adsorbent, varying the  
303 concentration from 0.5 to 80 mg  $L^{-1}$  [76]. With nanocomposite, the capacity was 105.26  $\mu\text{g } g^{-1}$   
304 for a concentration of 10-70  $\mu\text{g } mL^{-1}$  [75]. Using corn husk biochar, the authors reported a  
305 capacity of 6.67  $\mu\text{mol } m^{-2}$  for a concentration of 0.800-30 mg  $L^{-1}$  [88]. Finally, a  $Q_{\max}$  of 287 mg

306  $\text{g}^{-1}$  was reported using p-doped mesoporous carbon with a concentration of  $100 \text{ mg L}^{-1}$  [89].  
307 A study on a fixed bed system with magnetic tire char reported a capacity of  $22.58 \text{ mg g}^{-1}$  [90].  
308 This means that the developed adsorbent can compete on par with other adsorbents in  
309 removing PROP and providing an application for the residue.

310

311 The thermodynamic parameters were obtained based on the equilibrium constants  
312 obtained from the equilibrium isotherms using the nonlinear Van't Hoff equation (Table S3)  
313 [37–42].

314 The  $K_e^0$  was obtained through the best-fit isotherm fitted in the 298–328 K interval (Liu)  
315 [37–42]. The thermodynamic parameters were obtained as described in the Supplementary  
316 Material [37–42]. The  $K_e^0$  values augmented from  $5.234 \cdot 10^4$  to  $6.886 \cdot 10^4$  as the temperature  
317 increased from 298 to 328 K, confirming that the adsorption process is endothermic.  
318 Conversely,  $\Delta G^0$  decreased from  $-26.92$  (298 K) to  $-30.38 \text{ kJ mol}^{-1}$  (328 K), indicating that the  
319 adsorption of PROP in the carbonaceous adsorbent was favorable and spontaneous. However,  
320  $\Delta H^0$  is positive ( $7.403 \text{ kJ mol}^{-1}$ ), indicating an endothermic process. The magnitude of  $\Delta H^0$  is  
321 compatible with the physical interactions of the PROP with BC. These interactions may be van  
322 der Waals forces,  $\pi$ - $\pi$  interactions [38]. Based on this study, the adsorption process is physical  
323 adsorption. Furthermore,  $\Delta S^0 + 115.2 \text{ J mol}^{-1} \text{ K}^{-1}$  suggests that the PROP was hydrated before  
324 being uptaken by the adsorbent, and releasing hydration waters increased the entropy when  
325 PROP molecules were adsorbed. In the literature, the study of the propranolol uptake from  
326 aqueous solutions in thermally treated bentonite clay also confirmed the behavior of an  
327 endothermic nature [1].

328

### 329 *3.5. Proposed reaction mechanism*

330 One can suggest an adsorption mechanism by taking into account the outcomes of the  
331 adsorbent's characterization, speciation, and standard enthalpy change's magnitude. First, the  
332 FT-IR results should be considered to propose a bare minimum adsorption surface. In this case,  
333 classical groups for activated biochar were found: C-H, C=O, OH (phenolic), and aromatic rings.  
334 Considering that the point of zero charge of the adsorption is 6.4, thus for solution  $\text{pH} > 6.4$ ,  
335 the adsorbent surface will be negatively charged (see Fig S.1). Another important factor is the

336 speciation of the adsorbate, in this case, the PROP, has two states one neutral and other  
337 protonated, due to the amine group (see Fig S.2). Last, the thermodynamic magnitude  $\Delta H^\circ$ ,  
338 indicates the nature of the bond, in this case being classified as physical interaction. Taking  
339 into consideration all the aspects of the system is possible to propose the mechanism,  
340 according to Figure 9. The PROP is expected to be adsorbed on the surface due to hydrogen  
341 bonds, Van de Waals interaction, or ion- $\pi$  interaction.

342 <Fig.9>

#### 343 4. Conclusion

344 Residual peels of the edible fruit *Bactris guineensis*, native to the Colombian Caribbean,  
345 were successfully charred with zinc chloride. For the literature, this study provides a new use  
346 for this residue, where carbonization with zinc chloride makes it possible to obtain an  
347 adsorbent with good textural characteristics and with great potential for adsorption in  
348 solutions contaminated with PROP. The adsorbent showed good superficial characteristics  
349 ( $S_{\text{BET}}=625 \text{ m}^2 \text{ g}^{-1}$ ;  $V_{\text{T}}= 4.223 \times 10^{-1} \text{ cm}^3 \text{ g}^{-1}$ ). The dosage of  $0.7 \text{ g L}^{-1}$  and the pH of 8 favored the  
350 adsorption of the drug on the activated charcoal surface. The system equilibrium was  
351 influenced by the concentration, being faster at the lowest concentration ( $25 \text{ mg L}^{-1}$ ) and  
352 longer at the highest concentration ( $75 \text{ mg L}^{-1}$ ). According to  $t_{0.95}$  obtained from the Avrami-  
353 fractional model, the time to attain 95% saturation ranged from 47.82 ( $25 \text{ mg L}^{-1}$ ) to 179.3 min  
354 ( $75 \text{ mg L}^{-1}$ ). Avrami's model represented the kinetic data well. The increase in temperature in  
355 the system confirmed a favoring of the adsorbate with the adsorbent. With the maximum  
356 capacity obtained ( $161.3 \text{ mg g}^{-1}$ ) at 328 K based on the Liu isotherm model. The  
357 thermodynamic parameters confirmed a physical and endothermic process ( $\Delta H^0 = 7.403 \text{ kJ}$   
358  $\text{mol}^{-1}$ ).

359 Therefore, applying the residual biomass generated by the *Bactris guineensis* palm fruit  
360 production chain as biomass for producing activated biochar has great potential. Its use as an  
361 adsorbent in solutions containing propranolol hydrochloride can be used successfully and  
362 efficiently. Future perspectives are to develop new coals with this biomass, applying possible  
363 new activating agents. Analyzing the adsorption capacity of these new biochars with other  
364 emerging pollutants is also possible. A pilot study in a fixed bed column is highly necessary for

365 possible large-scale applications. Therefore, the analysis of the adsorbent through continuous  
366 systems must also be studied. With this, parameters such as the amount of adsorbent mass,  
367 flow rates, and concentrations must be analyzed. After analyzing and defining the studies in  
368 continuous systems, it is necessary to overcome the barrier between the scientific society and  
369 society, in this case, the industries. At first, when the skin is left over from consumption along  
370 with other remains of the same species, it would be interesting to create collection points in  
371 large markets in the largest cities. In addition, the entire industrial process that generates the  
372 waste must be willing to supply this waste. Thus, the residues from two sources should be  
373 sent to a processing industry, where rotary kilns with the activating agent are used to generate  
374 activated carbon. Finally, it is necessary to create charcoal pellets to ensure material  
375 resistance and possible application in other industrial processes and water treatment.

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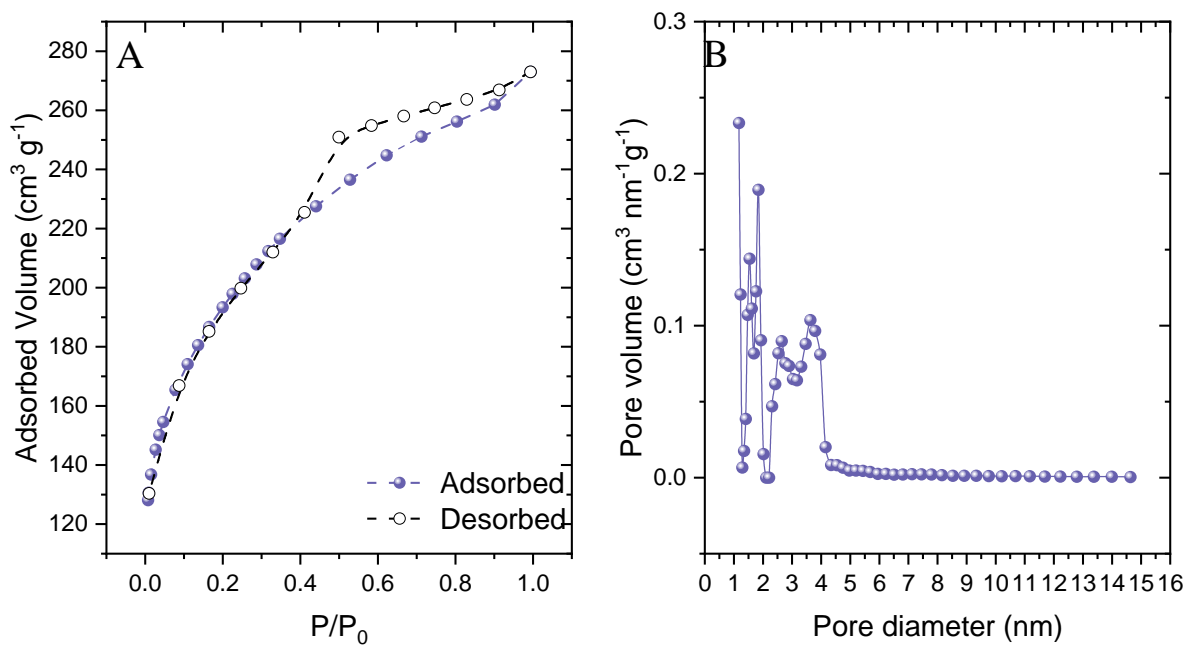
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Fig. 1. N<sub>2</sub> adsorption-desorption isotherms (a) and desorption pore size distribution (b).

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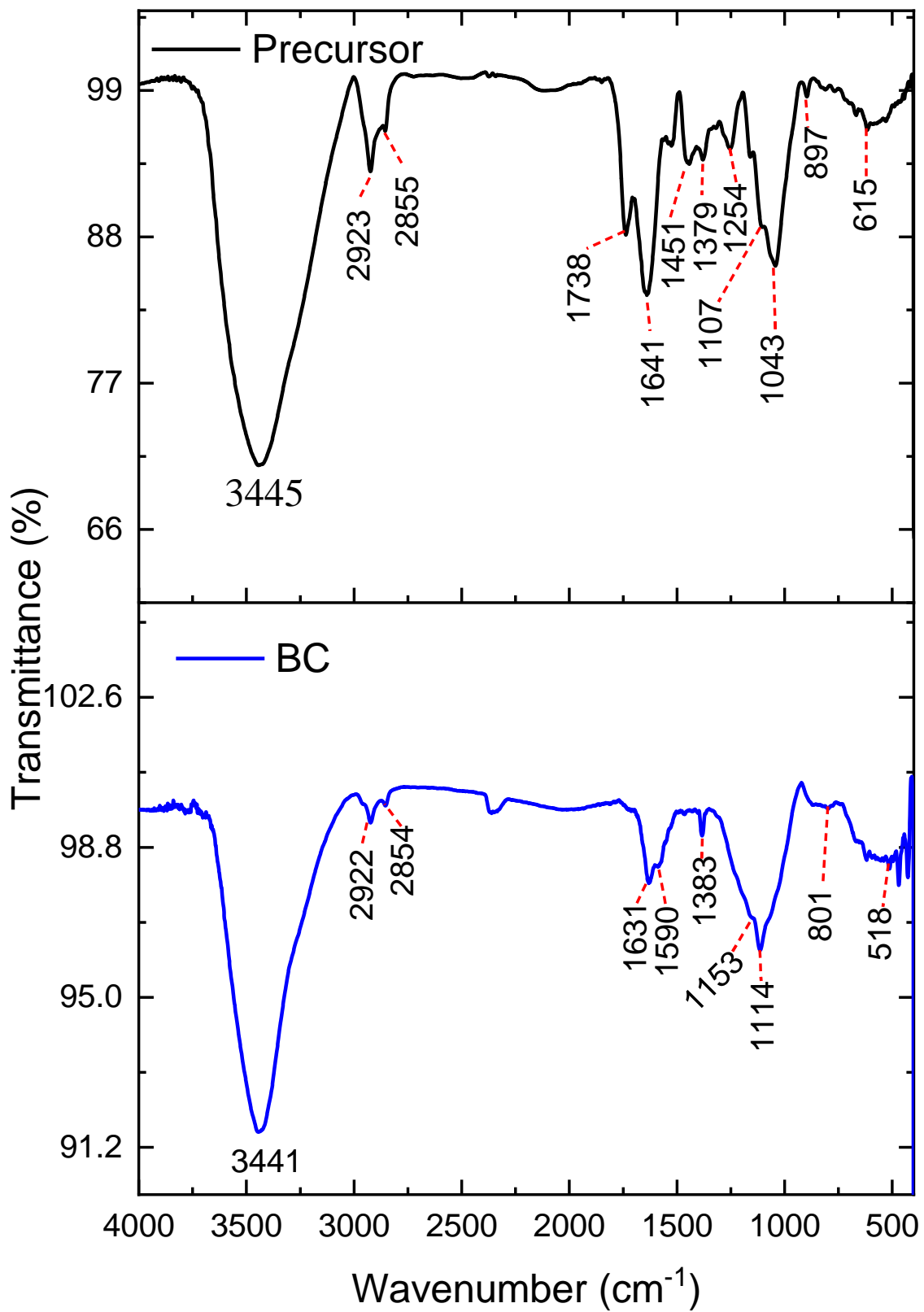


Fig. 2. FT-IR spectra precursor and BC.

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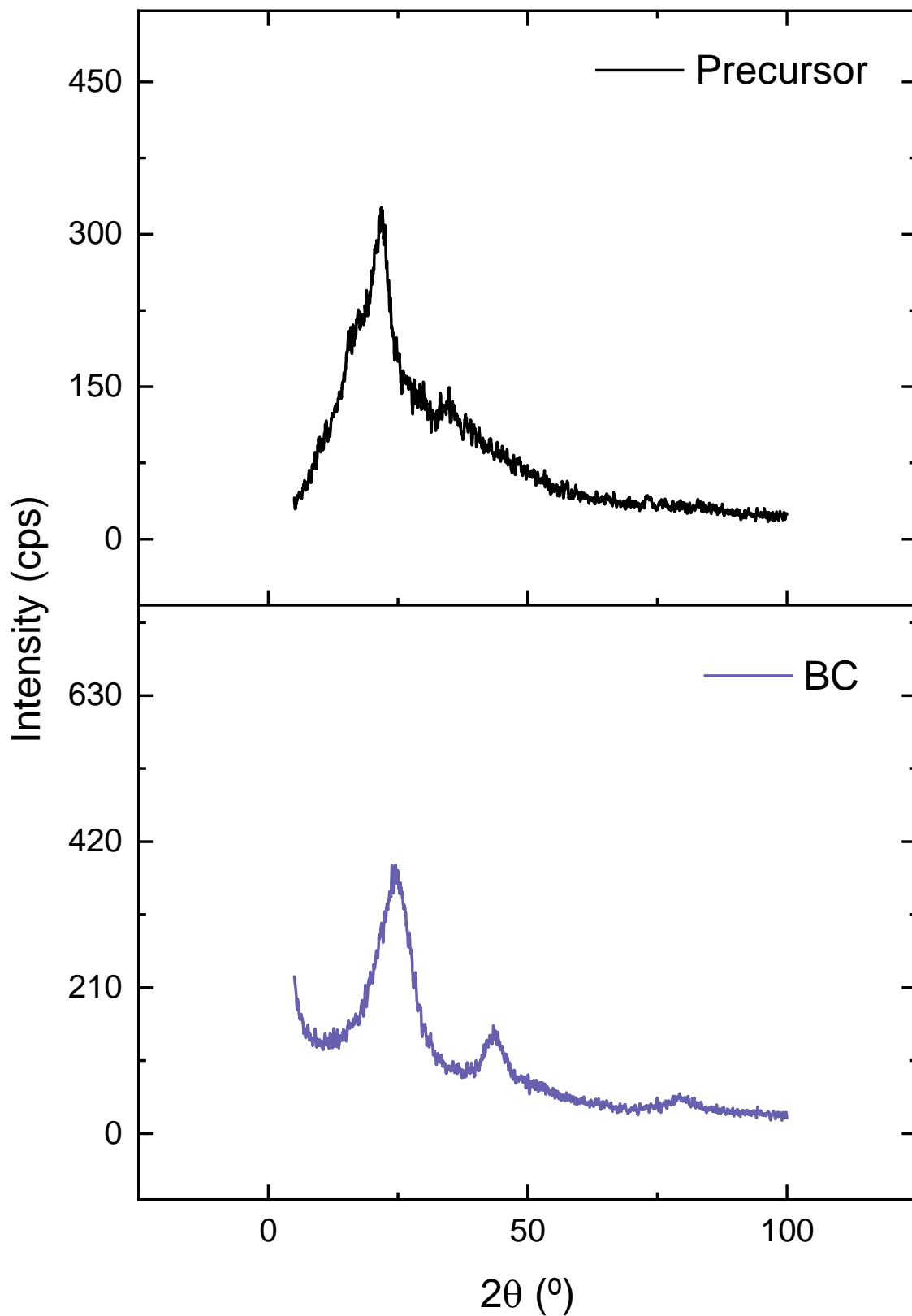


Fig. 3. XRD patterns for precursor and BC.

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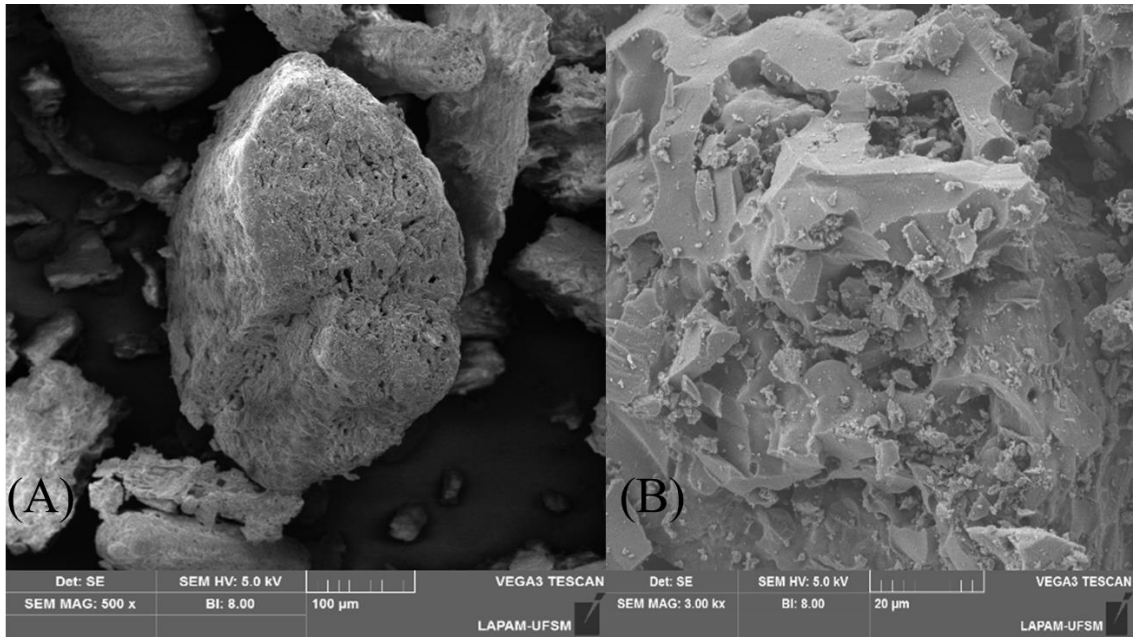
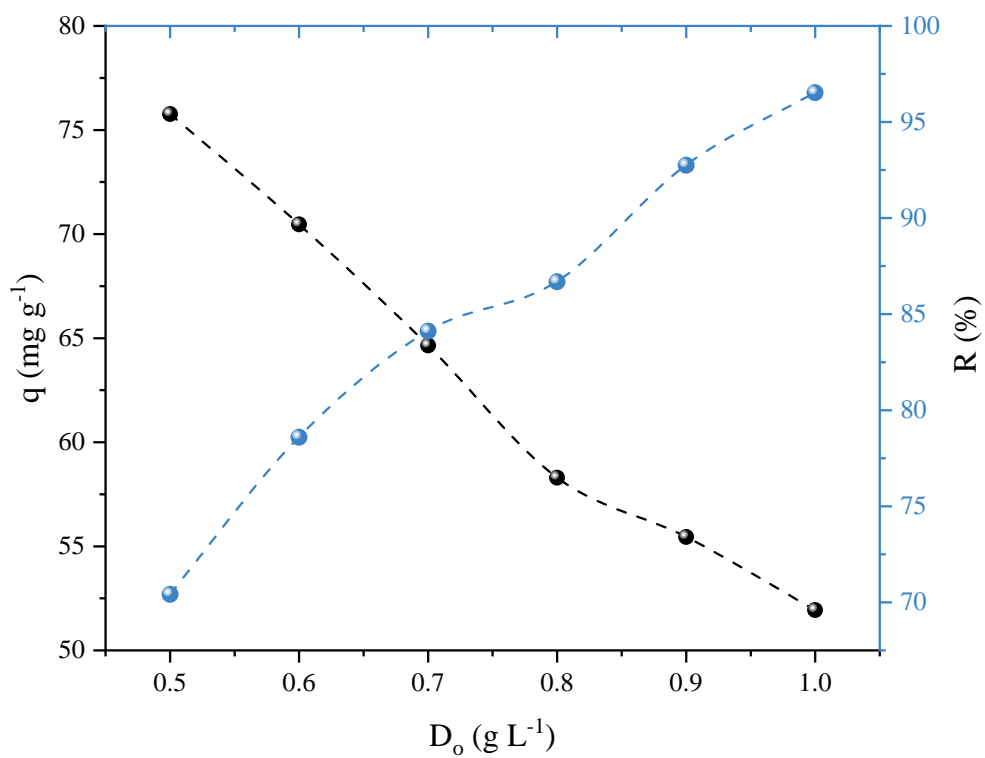


Fig. 4. SEM images of precursor material (A) and activated biochar (B).

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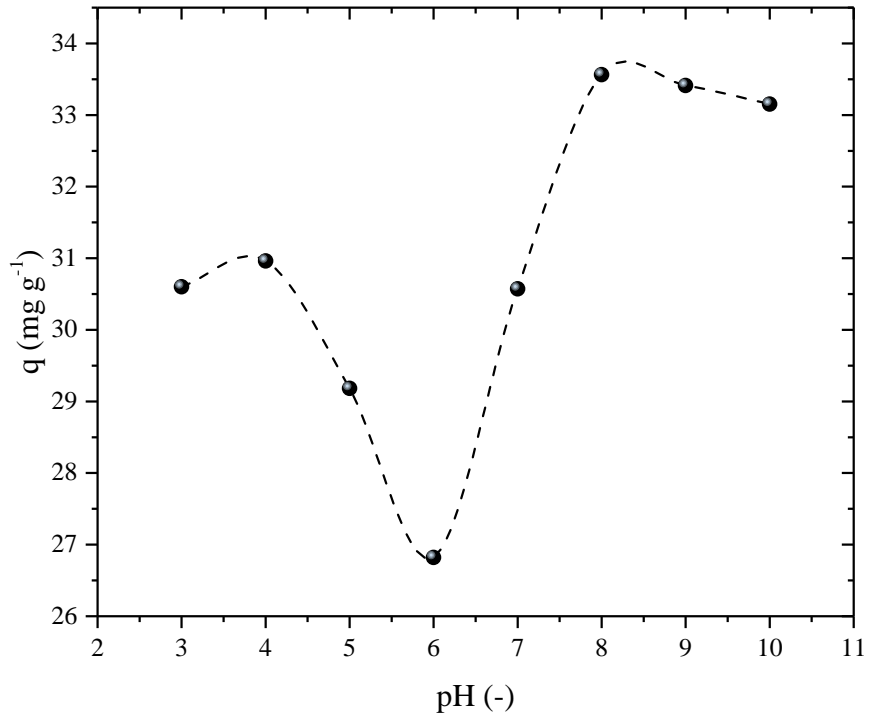


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743 **Fig.5.** Biochar adsorbent dosage on PROP uptake. Conditions:  $C_0 = 25 \text{ mg L}^{-1}$ , adsorbate volume 50 mL,  
 744 natural solution pH,  $t = 120 \text{ min}$ , 298 K.

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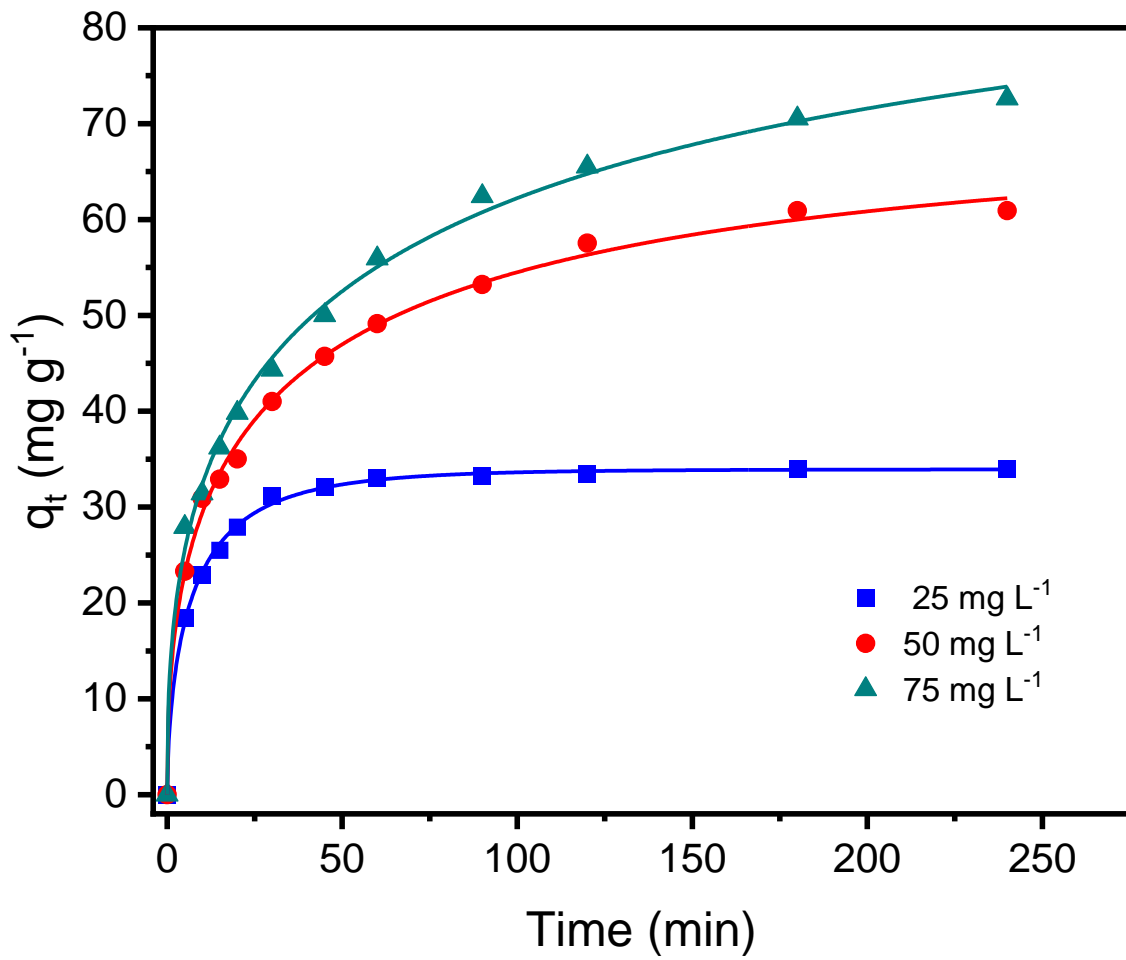
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748 **Fig.6.** Effect of pH on PROP uptake. Conditions: adsorbate solution 50 mL,  $C_0 = 25 \text{ mg L}^{-1}$ , adsorbent  
749 dosage  $0.7 \text{ g L}^{-1}$ , contact time 120 min, 298 K.

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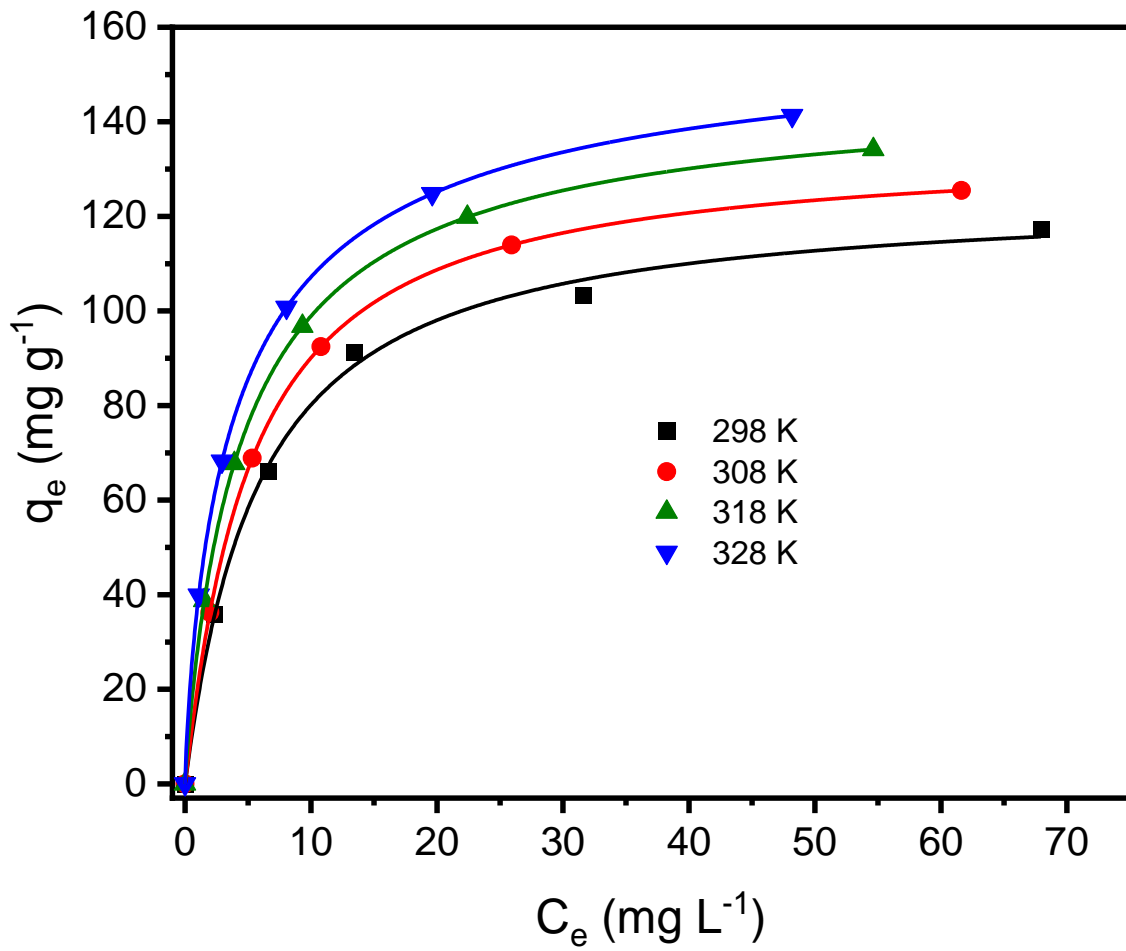
754 Fig. 7. Avrami fraction order kinetic model for the uptake of PROP onto activated biochar. Conditions:  
755 adsorbent dosage 0.7 g L<sup>-1</sup>, initial pH = 8, adsorbent volume 25 mL, initial PROP concentration 25 mg L<sup>-1</sup>.  
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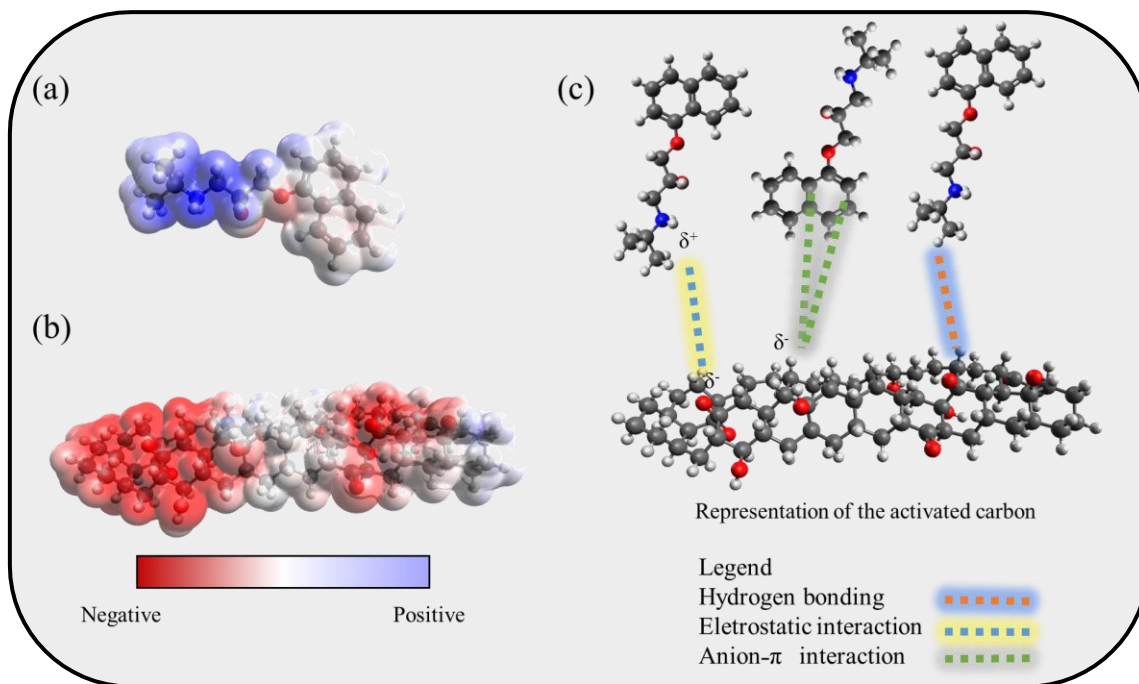
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762 Fig.8. Liu equilibrium curves for the uptake of PROP on activated biochar at different temperatures.

763 Conditions: initial PROP pH 8, adsorbent dosage 0.7 g L<sup>-1</sup>, contact time 300 min.

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767 **Fig.9.** Proposed adsorption mechanism of PROP onto the adsorbent

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