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Hierarchical tannin-derived carbons as efficient tetracycline adsorbents

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22 **Abstract**

23 Mimosa tannin has been used to produce two different types of carbons materials:
24 hydrothermal carbon (HTC) on the one hand, and ordered mesoporous carbon (OMC) on the
25 other hand. Both were obtained after pyrolysis at 1173 K, resulting in materials with similar
26 BET areas, close to 580 m²/g, but very different pore size distributions (PSDs). HTC was
27 essentially microporous while OMC had a large fraction of mesopores. Tetracycline (TC)
28 adsorption on these carbons was studied at equilibrium but kinetics experiments were also
29 carried out at two different temperatures. The TC adsorption data were fitted by different
30 mathematical, classical models, and new kinetic models were introduced to take into account
31 their very different PSDs. While the two materials presented similar BET areas (A_{BET}), the
32 OMC had a TC adsorption capacity six times higher than that of the HTC. Adsorption kinetics
33 were also strongly affected by the PSD. The importance of having high accessible pore
34 volumes and not only high surface areas in order to have good performances in TC adsorption
35 has been evidenced not only with our materials but also in the light of the TC adsorption data
36 reported in the open literature. We proved that A_{BET} , while easy to calculate and always
37 reported, is not the best tool to assess the potential suitability of an adsorbent to the removal
38 of aqueous pollutants.

39

40 **Key words:** Kinetics modelling; Soft-templating; Tetracycline adsorption; Mesoporous
41 carbons; Tannin

42

43 1. INTRODUCTION

44 Antibiotics like tetracycline (TC) are frequently used to treat bacterial infections, as food
45 additives, and to keep the control of microbiological growth in industry [1]. In fact, TC is one
46 of the most used antibiotics, due its low price and broad spectrum of antimicrobial activity [2].
47 However, its massive use and inefficient management have led to substantial accumulations
48 in the environment [3]. The main problem lies in the ineffective absorption of TC by the body,
49 which means that 30 to 90% of the ingested TC is evacuated and ends up in wastewater,
50 which traditional treatments fail to eliminate [2,4,5]. As a consequence, antibiotics such as TC
51 are found in water bodies, which is dangerous because they are designed to have a biological
52 effect but also because their presence could increase the number of bacteria resistant to
53 antibiotics [6,7].

54 Several methods are applied to treat wastewater and remove antibiotics residues, such as
55 ozonation [8,9], electrocoagulation [10,11], biodegradation [12,13], membrane separation
56 [14,15], advanced oxidation process [16,17] and adsorption [18–20]. Adsorption is a very
57 competitive process that allows pharmaceutical compounds removal from aqueous solutions
58 due to its ease of use and low cost compared to other methods [21]. Nevertheless, in the
59 adsorption process, the critical parameter that makes it work well or not is the selection of the
60 adsorbent [22]. In this way, several adsorbents have been applied for the removal of
61 pharmaceutical compounds, such as zeolites [23], metal organic frameworks (MOFs) [24] and
62 activated carbons [25]. The latter are porous materials with highly developed pore texture,
63 large surface areas and a broad variety of functional groups [26,27]. Biomass such as algae
64 [28], rice crops byproducts [29–32], lignin [33], and others [25,34–37] have been used as
65 adsorbents to prevent water contamination from various types of pharmaceutical and personal
66 care products (PPCPs). Activated carbons can be produced by “physical” or “chemical”
67 routes, both methods increasing the surface area but requiring either a second step of

68 activation after pyrolysis (for physical activation) or extensive washing (for chemical
69 activation).

70 Different methodologies, such as hydrothermal carbonisation or templating have been
71 implemented to increase the heteroatoms content or the mesopore volume, respectively.
72 Hydrothermal carbonisation implies the treatment of precursors in aqueous solution at
73 moderate temperatures and under self-generated pressures [38,39]. Soft-templating [40] and
74 hard-templating [41,42] allow the production of micro-mesoporous carbons after pyrolysis of
75 a mesophase or a composite, respectively. In the case of hard-templating, the resultant carbon
76 is a negative replica of the template. In the case of soft-templating, an amphiphilic surfactant,
77 usually a triblock copolymer, is used in solution to form micelles that act as porogen in the
78 carbon precursor. A subsequent pyrolysis then eliminates the surfactant, producing
79 mesoporosity in the final carbon material. Soft-templating became popular because it is a less
80 expensive, simpler and greener method than hard-templating [43], for which silica or zeolite
81 is used as a template and must be removed after pyrolysis, using hazardous chemicals such as
82 HF [44].

83 Due to the low cost and high availability of carbon precursors, the application of porous
84 carbon materials to clean water streams containing TC has increased. The affinity of carbon
85 materials produced from several precursors and different methodologies have been tested.
86 Some biochars produced from ground coffee [45], loblolly pine [46] and others [47,48] have
87 shown TC adsorption capacities up to 593 mg g⁻¹. Hydrothermal carbons produced by
88 different precursors (e.g. American agave [25], orange peels [49] and others biomass [50,51]),
89 and templated carbon materials produced from various templates (e.g. silicas [52,53], zeolites
90 [54] and MOFs [55]) have been used to eliminate PPCPs. Some of these carbon materials [25]
91 exhibited tetracycline adsorption capacities above 50 mg g⁻¹.

92 Tannins are traditionally used in several industrial domains (e.g. leather [56], food [57,58],
93 medicine [59,60] and others [61,62]). However, in recent years, their use has been extended to
94 the manufacture of environment-friendly products (e.g. resins [63–65], foams [66–69] and
95 others [70–72]). They have also been applied to the production of ordered mesoporous
96 carbons (OMCs) and hydrothermal carbons (HTCs) [73], because the tannins in question here
97 are essentially based on flavonoid-type polyphenols, which have a good carbon yield after
98 crosslinking [74] and are easy to enrich with nitrogen [75]. Mimosa tannins (MT) in particular
99 have been used as precursors of OMCs and HTCs for several applications (e.g.
100 supercapacitors [74,76–78] and adsorbents [25]).

101 Mathematical modelling is a relevant tool to evaluate the adsorption efficiency and to
102 determine which phenomena play a role in the adsorption process [79]. Thus, depending on
103 the adsorbent characteristics (e.g. presence or absence of a hierarchical structure) or the
104 process conditions (e.g. temperature and stirring speed), the kinetics of the process can be
105 controlled by one or more phenomena simultaneously [80]. In the literature, there are different
106 models that consider a single phenomenon acting during adsorption (e.g. pseudo first [81] or
107 second order [82]), or two phenomena occurring in series (e.g. dual resistance models [19]).
108 However, there is a lack of models that consider the existence of different phenomena acting
109 simultaneously in a parallel way.

110 The present study aimed at comparing two different carbon materials produced from
111 mimosa tannins (MT), obtained by a first step of either hydrothermal treatment or soft-
112 templating, and followed by pyrolysis. No additional activation step has been applied. The
113 resultant textural and chemical properties of both kinds of adsorbents were very different,
114 and they have been studied to understand their performance in the adsorption of TC.
115 Depending on the material, the kinetics of TC adsorption were adequately predicted taking

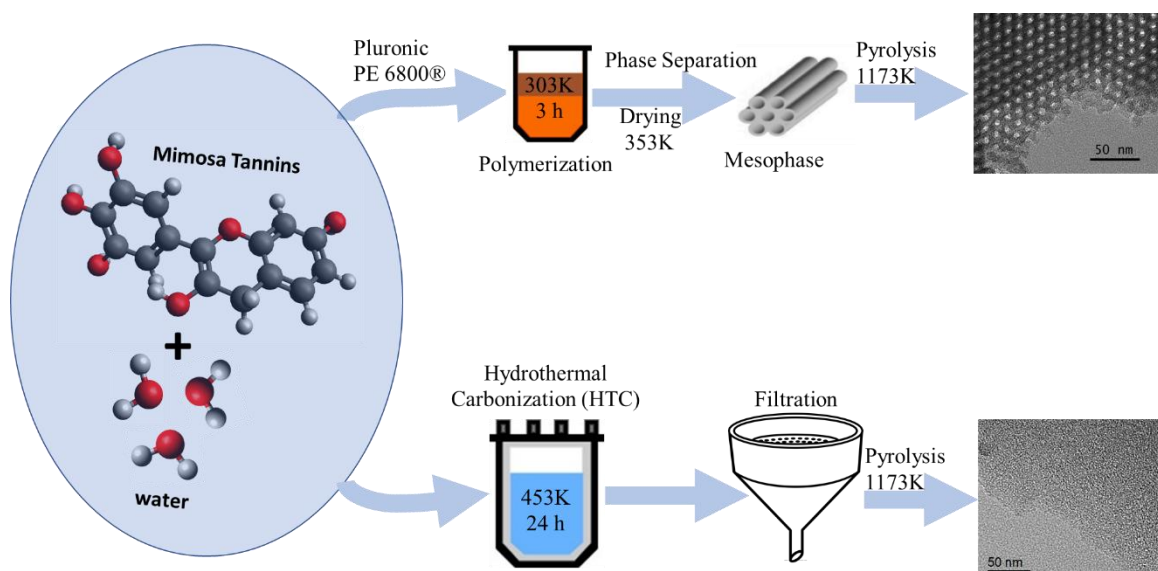
116 into account the diffusion resistance in micropores or a combined diffusion resistance in
117 micropores and mesopores.

118 **2. MATERIAL AND METHODS**

119 2.1. Materials preparation

120 Two kinds of carbon materials were prepared using mimosa tannin (MT) as carbon
121 precursor by applying hydrothermal carbonisation or soft-templating followed by pyrolysis.
122 The production methodologies of hydrothermal carbons (HTCs) were explained in detail by
123 Braghiroli et al [75] (see Fig. 1). In short, 4g of MT were dissolved in 40 mL of water. The
124 solution was poured in a Teflon-lined autoclave, which was hermetically closed and placed in
125 an oven at 453 K for 24 h. The recovered hydrochar was submitted to pyrolysis at 1173 K
126 under nitrogen atmosphere, using a constant heating rate of 1 K min⁻¹ up to the final
127 temperature, which was held for 1 hour. Finally, the sample was cooled under nitrogen
128 atmosphere.

129 Soft templating was performed using the surfactant Pluronic PE 6800® as pore-directing
130 agent. The method is similar to that reported by Sanchez-Sanchez et al [78] (see Fig. 1). In
131 short, 4g of MT were dissolved in 16 mL of water and 4g of Pluronic PE 6800® were
132 dissolved in other 16 mL of water. The two solutions were then poured together in a glass vial
133 and placed in a thermostatic bath at 303 K for 3 h. After this time, phase separation occurred.
134 The supernatant was separated and eliminated, and the solid fraction was dried in an oven at
135 333 K for 12 h, before subjecting it to pyrolysis. The mesophase was heated at 1 K min⁻¹ until
136 673 K, a temperature maintained for 4 h, followed by a second ramp of 2 K min⁻¹ until 1173
137 K, maintained for 1 h. Heating, pyrolysis and cooling were carried out under nitrogen
138 atmosphere.



139

140 **Figure 1.** Scheme of the synthesis of the tannin-based carbon materials.

141

142 2.2. Materials characterisation

143 The elemental composition of the HTC and OMC materials in terms of hydrogen, carbon,
 144 oxygen, nitrogen and sulphur contents (wt. %) was determined using a CHONS elemental
 145 analyser (Vario EL Cube, Elementar). Infrared spectra were obtained in the range of
 146 wavenumbers $600\text{-}4000\text{ cm}^{-1}$ using a Fourier-Transform Infrared (FTIR) spectrometer
 147 (Frontier Spotlight 400, Perkin-Elmer).

148 Small-angle X-ray diffraction (XRD) patterns were recorded with a Panalytical X'Pert Pro
 149 diffractometer. The latter was equipped with a Cu (K_{α} radiation) anticathode and a high-speed
 150 multichannel X'Celerator detector (scanning range $2\theta = 0.4 - 4^{\circ}$; step size = 0.01671° ; time
 151 per step size = 1.26 s), and was used in Bragg-Brentano configuration in reflection mode. The
 152 interplanar distance, d_{100} (nm), was calculated by applying Eq. (1):

$$153 \quad n \cdot \lambda = 2d_{100}\sin(\theta) \quad (1)$$

154 where n is a positive integer (we assume $n = 1$), λ is the wavelength (0.15418 nm) of the
 155 incident radiation, and θ is the Bragg angle.

156 The unit cell parameter (a , nm) of the carbon mesostructure was calculated by applying Eq.
157 (2):

$$158 \quad a = \frac{2}{\sqrt{3}} d_{100} \quad (2)$$

159 where d_{100} (nm) is the interplanar spacing obtained from XRD patterns.

160 The pH at which the net surface charge is zero, called point of zero charge (pH_{PZC}), is
161 affected by the nature and amount of functional groups existing on the surface of the materials.
162 Six 0.1 mol L⁻¹ aqueous solutions of NaNO₃ were prepared and the pH was adjusted using
163 either NaOH or HCl to values ranging from 2 and 12 by steps of two pH units. In each
164 solution, 25 mg of carbon were added and left under stirring for 24 h to obtain the pH at
165 equilibrium. The latter was measured and the difference between its value and the initial one
166 was plotted against the initial pH. The pH at which the curve goes through zero was taken as
167 the pH_{PZC} [83].

168 The textural properties of the two carbons were determined by adsorption of nitrogen and
169 carbon dioxide at 77 K and 273 K, respectively, using ASAP 2020 and ASAP 2040 automatic
170 adsorption devices (Micromeritics), respectively. The BET area, A_{BET} (m² g⁻¹), was calculated
171 by applying the BET (Brunauer-Emmet-Teller) method [84]. All the calculations were done
172 with the MicroActive® software provided by Micromeritics. The pore size distribution (PSD)
173 was determined by applying the non-local density functional theory (NLDFT), combining
174 both N₂ and CO₂ adsorption isotherms by the SAIEUS® software provided by Micromeritics.
175 We applied the 2D version of this theory, which takes into account heterogeneous surface
176 (2D_NLDFT-HS) [85,86]. The PSD results were used to calculate the following parameters:
177 the specific surface area, S_{NLDFT} (m² g⁻¹); the total pore volume V_T (cm³ g⁻¹); volume and
178 surface area of ultramicropores (pore size below 0.7 nm), $V_{\mu\mu}$ (cm³ g⁻¹) and $S_{\mu\mu}$ (m² g⁻¹),
179 respectively; volume and surface area of supermicropores (pore size between 0.7 and 2 nm)

180 $V_{s\mu}$ ($\text{cm}^3 \text{g}^{-1}$) and $S_{s\mu}$ ($\text{m}^2 \text{g}^{-1}$), respectively; volume and surface area of micropores (by
181 summing the super- and ultra-micropore volumes and areas), V_{μ} ($\text{cm}^3 \text{g}^{-1}$) and S_{μ} ($\text{m}^2 \text{g}^{-1}$),
182 respectively; and surface area of mesopores (by subtracting the micropore area from S_{NLDFT}),
183 S_m ($\text{m}^2 \text{g}^{-1}$).

184 The kinetics and equilibrium studies of tetracycline adsorption (CAS 60-54-8, 98% pure,
185 provided by Sigma Aldrich) were carried out in a batch system. The adsorption isotherms, at
186 288 and 308 K, were done as follow: 25 mL of tetracycline (TC) solutions at concentrations
187 ranging from 10 to 500 mg L^{-1} , at pH 6, were brought into contact with 25 mg of carbon in a
188 tightly closed flask under stirring for 24 h.

189 The adsorption kinetics were determined at 288 and 308 K using 25 mg of carbon and 25
190 mL of TC solution at a concentration of 500 mg L^{-1} , at pH 6. Eight data points of
191 concentration as a function of contact time were recorded, the contact time varying between
192 15 min and 24 h.

193 The TC concentrations of the solutions were measured, after filtration with a Nylon®
194 membrane with a pore diameter of 0.25 μm , by UV-vis spectrometry at a wavelength of 358
195 nm (Lambda 35 Perkin Elmer).

196 2.3. Mathematical modelling of TC adsorption

197 2.3.1. Adsorption kinetics

198 The pseudo-first order (PFO) kinetics model was first proposed by Lagergren [81] and is
199 generally applied to liquid-phase adsorption [87]. The PFO model is represented by the
200 following equation:

$$201 \quad \frac{dq_t}{dt} = k_1(q_{eq} - q_t) \quad (3)$$

202 where q_t and q_{eq} (mg g^{-1}) are the amounts adsorbed at time t and at equilibrium, respectively,
203 and k_1 (h^{-1}) is the PFO constant.

204 The pseudo-second order (PSO) kinetics model is also largely used to describe adsorption
205 in the liquid phase [87]. This model was first proposed by Ho and McKay [82]. The PSO
206 model is described by the following equation:

$$207 \quad \frac{dq_t}{dt} = k_2(q_{eq} - q_t)^2 \quad (4)$$

208 where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the PSO rate constant.

209 The dual resistance model (DRM) considers that resistance to external mass transfer and
210 intraparticle diffusion simultaneously affect the adsorption kinetics. The resistance to external
211 mass transfer is generally associated with the existence of a layer of fluid around the
212 adsorbent, which could be represented as a liquid film where the solute diffuses from the
213 solution (C_t , mg L^{-1}) to the adsorbent surface (where the local concentration is C_s , mg L^{-1}).
214 Mathematically, this can be represented by a linear expression where the driving force is the
215 solute concentration gradient ($C_t - C_s$), according to:

$$216 \quad \frac{dq_t}{dt} = k_F(C_t - C_s) \quad (5)$$

217 where k_F ($\text{L g}^{-1} \text{h}^{-1}$) is the coefficient of mass transfer in the liquid film between the boundary
218 layer and the adsorbent surface.

219 The intraparticle diffusion of TC in the carbon micropores was evaluated by a linear
220 approximation of Fick's law by applying the following equation:

$$221 \quad \frac{dq_t}{dt} = Dif(q_{iso} - q_t) \quad (6)$$

222 where Dif (h^{-1}) is the coefficient of volumetric TC diffusivity in the carbon micropores and
223 q_{iso} (mg g^{-1}) is the equilibrium uptake predicted by the isotherm.

224 To take into account the existence of a hierarchical porosity, we proposed to evaluate the
 225 contribution of the mass transfer for each class of porosity. Therefore, a mathematical
 226 expression for the combined intraparticle diffusion, in which the PSD is taken in account, was
 227 proposed as follows:

$$228 \quad \frac{dq_t}{dt} = \sum_{i=1}^N Dif_i \left(\frac{S_i}{S_T} q_{iso} - q_i \right) \quad (7)$$

229 where N is the number of peaks found in the PSD, Dif_i (h^{-1}) is the average diffusivity of the
 230 pores at the peak i , S_i and S_T ($\text{m}^2 \text{g}^{-1}$) are respectively the area corresponding to the porosity of
 231 each peak i and the total surface area accessible to the TC molecules.

232 Since the models have different numbers of adjustable parameters, the adjusted coefficient
 233 of determination was applied to evaluate the performance of each kinetic model. The adjusted
 234 coefficient of determination is mathematical related to the traditional R^2 by the following
 235 equation [88]:

$$236 \quad R_{Adj}^2 = \frac{(1-R^2)(n_{dat}-1)}{n_{dat}-n_p-1} \quad (8)$$

237 where R^2 is the traditional coefficient of determination, and n_{dat} and n_p are respectively the
 238 numbers of experimental points and adjustable parameters.

239 2.3.2. Adsorption isotherms

240 Herein, we applied three isotherm adsorption models: Langmuir, Freundlich and Temkin.
 241 Langmuir's model [89] is mathematically represented by:

$$242 \quad q_{eq} = \frac{q_m \cdot b_L \cdot C_{eq}}{1 + b_L \cdot C_{eq}} \quad (9)$$

243 where C_{eq} (mg L^{-1}) is the liquid phase concentration at equilibrium, q_m (mg g^{-1}) is the
 244 maximum monolayer adsorption capacity and b_L (L mg^{-1}) is the Langmuir parameter, related
 245 to the free energy of adsorption.

246 The Freundlich model is mathematically represented by:

$$247 \quad q_{eq} = K_F C_{eq}^{\frac{1}{n_F}} \quad (10)$$

248 where K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n_F (dimensionless) are the parameters of the Freundlich model
249 related to the adsorption capacity and adsorption intensity, respectively. In addition, the
250 parameter $1/n_F$ defines if the isotherm is favourable and reversible (values between 0.1 and 1),
251 unfavourable (values above 1.0) or irreversible (values below 0.1) [90,91].

252 The Temkin model considers that the heat of adsorption decreases when the coverage
253 fraction increases, due to the adsorbate–adsorbent interaction [92]. The Temkin [93] models is
254 represented by:

$$255 \quad q_{eq} = B \cdot \ln(K_T \cdot C_{eq}) \quad (11)$$

256 where K_T (L mg^{-1}) is the Temkin isotherm constant and B (mg g^{-1}) is the constant related to
257 the heat of adsorption. Usually, B has a positive value, which is indicative of the endothermic
258 character of adsorption in the liquid phase.

259 The fits of the models to the experimental data were carried out employing as an objective
260 function the sum of the squared errors, Eq. (12), and applying the Nelder-Mead [94] method
261 available in the Maple® software.

$$262 \quad F_{OBJ} = \sum_{i=1}^{n_{dat}} (Y_{i,exp} - Y_{i,mod})^2 \quad (12)$$

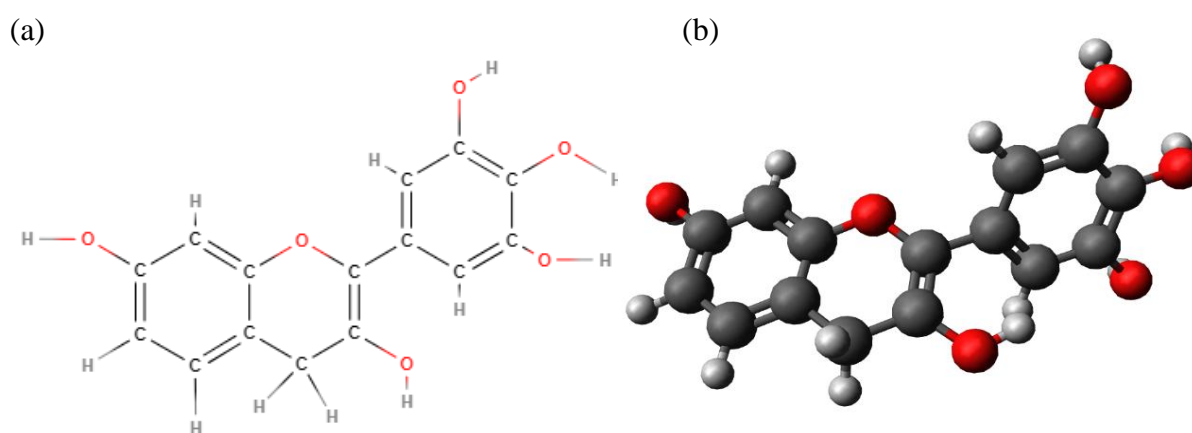
263 where F_{OBJ} is the objective function value, n_{dat} is again the number of experimental points and
264 $Y_{i,exp}$ and $Y_{i,mod}$ are the experimental and predicted values for the experimental point i ,
265 respectively.

266

267 3. RESULTS AND DISCUSSION

268 3.1 Materials composition, structural and textural properties

269 Table 1 shows the elemental composition of raw mimosa tannin (MT) and the two carbon
270 materials derived from MT. The C, H, O and N contents of the latter are close to those already
271 reported in previous studies [39,48,73,95]. Moreover, the ultimate analysis of MT is also in
272 good agreement with the elemental composition of the main flavonoid unit contained in
273 mimosa tannin (Fig. 2).



274
275 **Figure 2.** (a) 2D (a) and (b) 3D molecular structure of the main flavonoid unit contained in
276 mimosa tannin[96].

277 After pyrolysis, there is a carbon enrichment due to heteroatoms evolution by dehydration
278 [97], crosslinking and aromatisation reactions, producing tars and gases [98]. The oxygen
279 content of the carbon produced after hydrothermal treatment (HTC), 11.90 wt.%, is much
280 higher than that of the carbon produced by soft templating (OMC), 3.45 wt.%. This high
281 oxygen content in HTC might lead to a decrease in the TC adsorption capacity [99], since the
282 oxygen content is correlated with the decrease in electron-rich sites in the carbon sheets of the
283 adsorbent, which have high affinity for aromatic compounds [100]. Both carbons show low H,
284 N and S contents, all less than 1.00 wt. %, although HTC has a higher amount of heteroatoms.

285

286

287 **Table 1.** Elemental analysis of mimosa tannin and derived carbons.

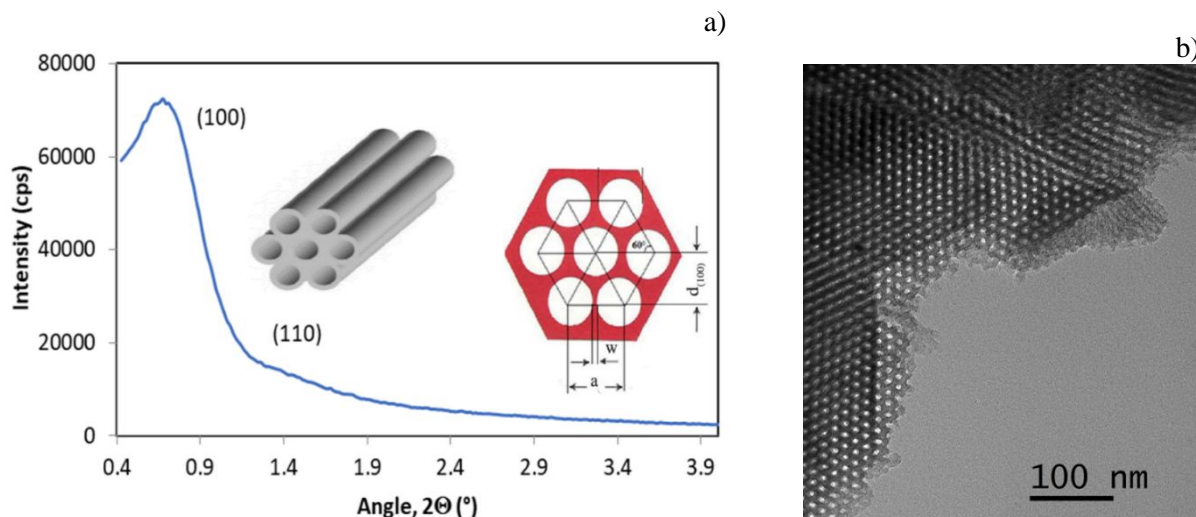
Sample	C (wt. %)	N (wt. %)	H (wt. %)	S (wt. %)	O (wt. %)
Raw mimosa tannin	55.40	0.75	5.00	0.00	38.85
HTC	86.50	0.70	0.90	0.00	11.90
OMC	95.98	0.13	0.44	0.00	3.45

288 Fig. SI 1 shows the FTIR spectra of HTC and OMC. The peak located around 3400 cm^{-1} is
 289 normally related to the presence of hydroxyl groups or to water chemisorbed on the surface,
 290 since this wavenumber is attributed to the stretching vibration of O-H group [101,102]. The
 291 peaks observed around 1610 and 1010 cm^{-1} are due to the presence of C=C and C-O groups,
 292 respectively [102]. The two carbons did not show any of the peaks presents in the FTIR
 293 spectrum of their precursor, supporting the low amount of functional groups and hence the
 294 poorly developed surface chemistry. This will be supported by the measurements of pH_{PZC} .

295 The small-angle XRD spectrum of OMC presents one well-resolved band at $2\theta = 0.67^\circ$,
 296 and a shoulder at $2\theta = 1.46^\circ$ (Fig. 3.a). These two values of 2θ correspond to the (100) and
 297 (110) reflections, respectively, and this indicates that the carbon has an ordered mesoporous
 298 structure belonging to the $P6mm$ space group [103,104]. The interplanar spacing, d_{100} , and the
 299 unit cell parameter, a , calculated for the ordered mesoporous carbon are 13.04 and 15.06 nm,
 300 respectively. The scheme given in Fig. 3.a shows the ordered structure of the OMC and its
 301 structural parameters d_{100} and a . In addition, Fig. 3.b shows the TEM image of the OMC (SI 3
 302 shows that of the HTC), where it is possible to see the hexagonal order of the mesopores. The
 303 SEM images of the two carbon materials are shown in Fig. SI 4. Fig. SI 4.a shows the typical
 304 microspheres produced when tannin is subjected to hydrothermal treatment [38,39], while the
 305 OMC showed a more glassy appearance, with holes and sharp edges, see Fig. SI 4.b.

306 TC has three acid functional groups [2] (see Fig. 4.a and 4.b) and thus TC exists under
 307 different forms of speciation in aqueous solution, depending on the pH, due to protonation-

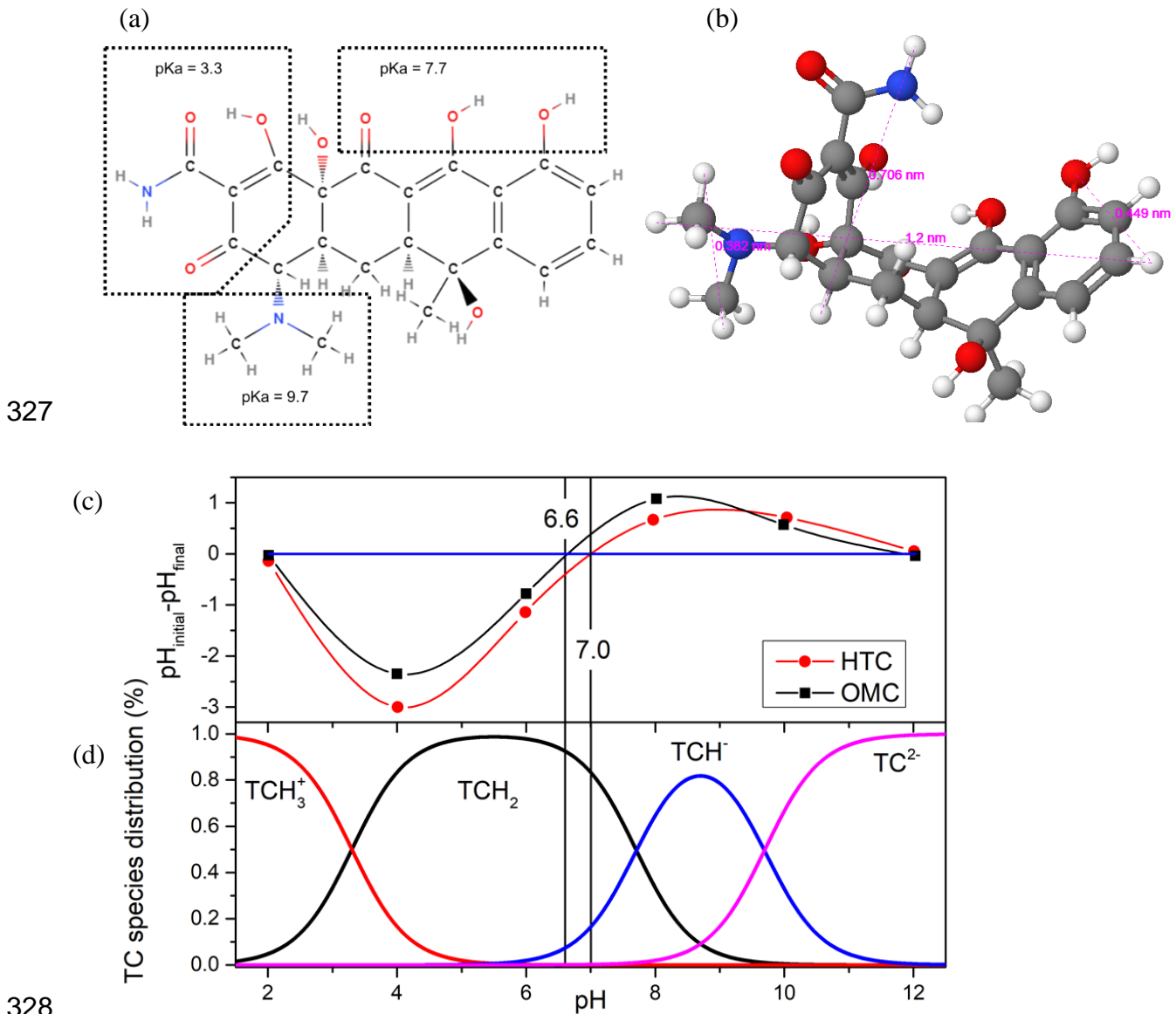
308 deprotonation reactions. Fig. 4.d shows the four possible species: H_3TC^+ , H_2TC^0 , HTC^{-1} and
309 TC^{-2} [105]. Thus, at pH 6, at which the equilibrium and kinetics experiments have been
310 carried out, TC exists mainly in zwitterionic form (i.e., neutral species).



311
312 **Figure 3.** a) Small-angle XRD pattern of the OMC. The insets present a view of the
313 hexagonally ordered mesoporous channels and a cross-section of the structure, showing the
314 structural parameters d_{100} and a . The thickness of the mesopore wall, w , is also shown. b)
315 TEM image of the tannin-based OMC.

316 The values of pH_{PZC} of HTC and OMC are very similar, 7.0 and 6.6, respectively. At pH
317 below pH_{PZC} , the surface is positively charged due to an excess of H^+ ions, and on the
318 contrary, at pH above pH_{PZC} , the surface of the carbon is negatively charged due to an excess
319 of OH^- ions.

320 By analysing the results of pH_{PZC} (Fig. 4.c) with the TC speciation diagram (Fig. 4.d), it is
321 possible to identify a narrow region where there are differences in charges between the
322 adsorbate and the adsorbent surface. Due to this, the electrostatic interaction and the hydrogen
323 bonds should not have a significant influence on the adsorption mechanism. Therefore, the π -
324 π electron donor-acceptor interaction between the polarised aromatic rings on the carbon
325 surface and the TC molecule remains the main explanation for the adsorption mechanism
326 [99,106,107].



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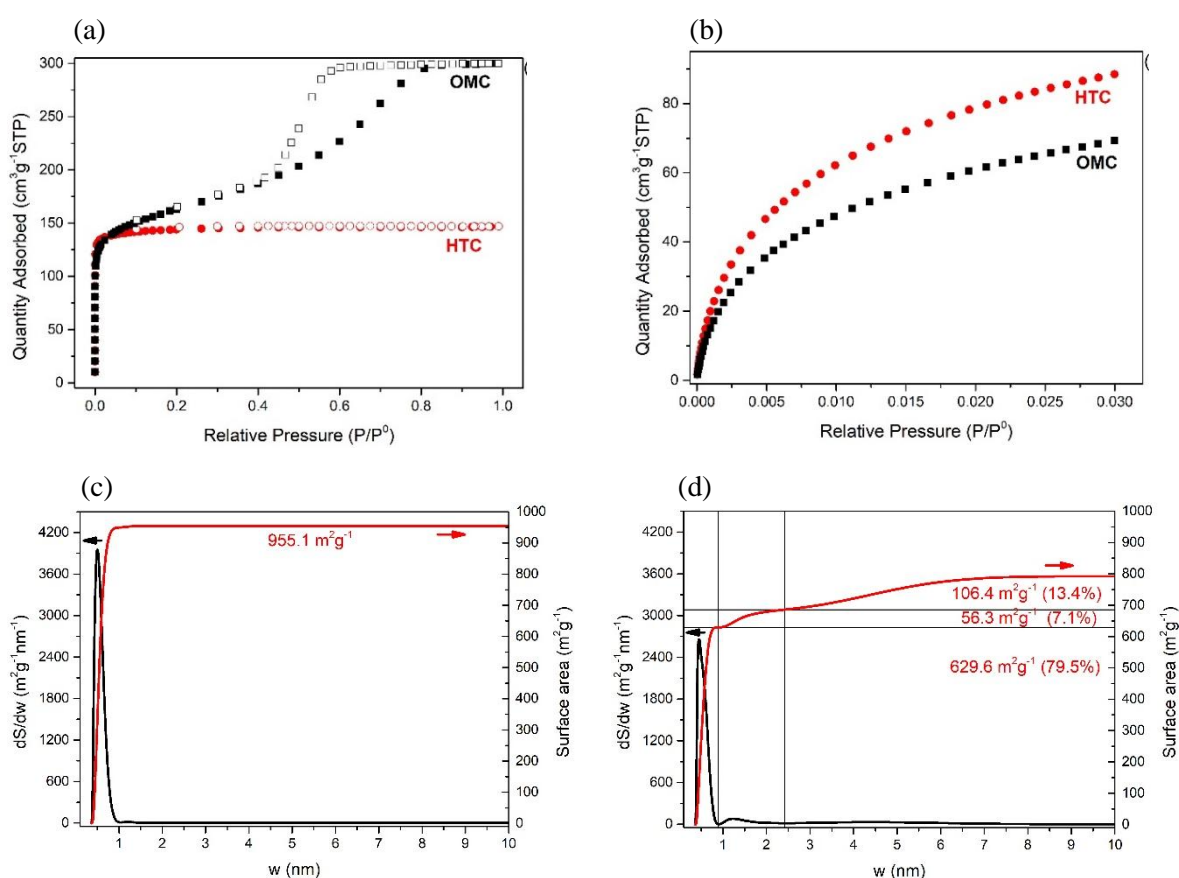
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Fig. 5.a and 5.b show the N_2 and CO_2 adsorption-desorption isotherms at 77 K and 273 K, respectively, for the two adsorbents. Both N_2 isotherms present a strong increase in the uptake at low pressure, indicating the presence of micropores, characteristic of tannin-derived carbons. The N_2 isotherm of HTC can be classified as type I(a), characteristic of a purely microporous carbon with a very narrow pore size distribution [108]. In contrast, the N_2 isotherm of OMC is a combination of types I (a) and IV(a). Therefore, HTC has only micropores while OMC has micropores and mesopores. This is clearly seen in Fig. 5.c and 5.d, where the PSD per surface area (dS/dw) as well as the cumulated S_{NLDFT} are shown for HTC

339 and OMC, respectively. In Fig. SI 2, the PSD per volume (dV/dw) and the cumulated volumes
 340 are presented, exhibiting the same features as in Fig. 5.c and 5.d. HTC presents a single PSD
 341 peak centred at 0.6 nm, more than 99% of the S_{NLDFT} value being due to pores narrower than 1
 342 nm. OMC presents a tri-modal PSD, with contributions to the cumulated S_{NLDFT} of 79, 7 and
 343 13% for pore diameters narrower than 0.9 nm, between 0.9 and 2.4 nm, and wider than 2.4
 344 nm, respectively (see again Fig. 5.d). Similar results have been reported in the literature for
 345 other hydrothermal carbons [25,109] and other ordered mesoporous carbons [110–112].



346 **Figure 5.** (a) N₂ and (b) CO₂ adsorption/desorption isotherms, where full and empty symbols
 347 correspond to adsorption and desorption data, respectively; Pore size distributions and
 348 cumulated surface areas S_{NLDFT} of (c) HTC and (d) OMC.

349 Table 2 shows the textural properties of HTC and OMC. Both carbons have close values of
 350 A_{BET} , but HTC has a higher S_{NLDFT} , 955 m² g⁻¹ compared to 792 m² g⁻¹ for OMC. This is due
 351 to the micropore content of HTC, 0.27 cm³ g⁻¹ (100% of the total pore volume V_{T}), higher

352 than that of OMC, $0.20 \text{ cm}^3 \text{ g}^{-1}$ (44% of V_T), whereas the average micropore size remains the
 353 same for both HTC and OMC: 0.6 nm. Nevertheless, OMC presents a pore volume almost
 354 twice that of HTC, which is mainly due to mesopores, which represent 56.5% of V_T . The
 355 surface area due to mesopores in the OMC is, however, only $113 \text{ m}^2 \text{ g}^{-1}$.

356 **Table 2.** Textural properties of the carbon materials.

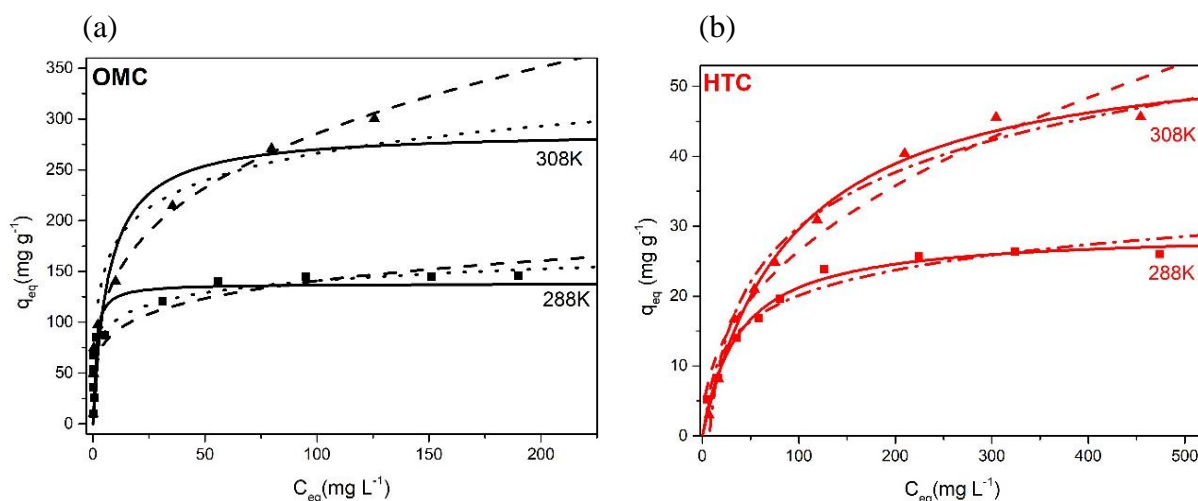
Material	A_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_{NLDFT} ($\text{m}^2 \text{ g}^{-1}$)	S_{m}^* ($\text{m}^2 \text{ g}^{-1}$)	S_{μ}^* ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{s}\mu}^*$ ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{u}\mu}^*$ ($\text{m}^2 \text{ g}^{-1}$)	V_T ($\text{cm}^3 \text{ g}^{-1}$)	V_{meso}^* ($\text{cm}^3 \text{ g}^{-1}$)	V_{μ}^* ($\text{cm}^3 \text{ g}^{-1}$)	$V_{\text{s}\mu}^*$ ($\text{cm}^3 \text{ g}^{-1}$)	$V_{\text{u}\mu}^*$ ($\text{cm}^3 \text{ g}^{-1}$)
HTC	580	955	0.0 (0%)	955 (100%)	92.5 (10%)	862.5 (90%)	0.27	0.0 (0%)	0.27 (100%)	0.04 (15%)	0.23 (85%)
OMC	592	792	113 (14%)	679 (86%)	83.2 (11%)	596.2 (75%)	0.46	0.28 (56%)	0.20 (44%)	0.05 (11%)	0.16 (33%)

357 * The percentages given in brackets correspond to the contributions of the various pore volumes and surfaces to
 358 the total pore volume and surface, respectively V_T and S_{NLDFT} .

359

360 3.2. Tetracycline adsorption

361 Fig. 6 shows the TC adsorption isotherms at two different temperatures, 288 K and 308 K,
 362 together with the fits using Langmuir, Freundlich and Temkin adsorption models.



363 **Figure 6.** Tetracycline adsorption isotherm on OMC (black) and HTC (red) at 288K (■) and
 364 308K (▲), and their fits by Langmuir (—), Freundlich (--) and Temkin (---) models.

365 The TC adsorption capacity increases with temperature for both carbons. We can also
 366 observe that the Freundlich model fits better the TC adsorption isotherms of OMC while the
 367 Langmuir model fits better those of HTC. This might be due to the fact that the experimental
 368 TC isotherms on HTC and the OMC are type I(a) and mixed types Ia and II, respectively
 369 [108].

370 Table 3 shows the isotherm parameters obtained and the determination coefficients
 371 obtained by fitting the models to the experimental data. The TC adsorption capacities of OMC
 372 are around 6 times higher than those of HTC. This behaviour cannot be attributed to the
 373 surface chemistry, which is quite similar as indicated above, nor to A_{BET} or S_{NLDFT} . The only
 374 significant difference between the two carbon materials is their mesopore volume.

375

376 **Table 3.** Estimated parameter values from the fits of the TC isotherms.

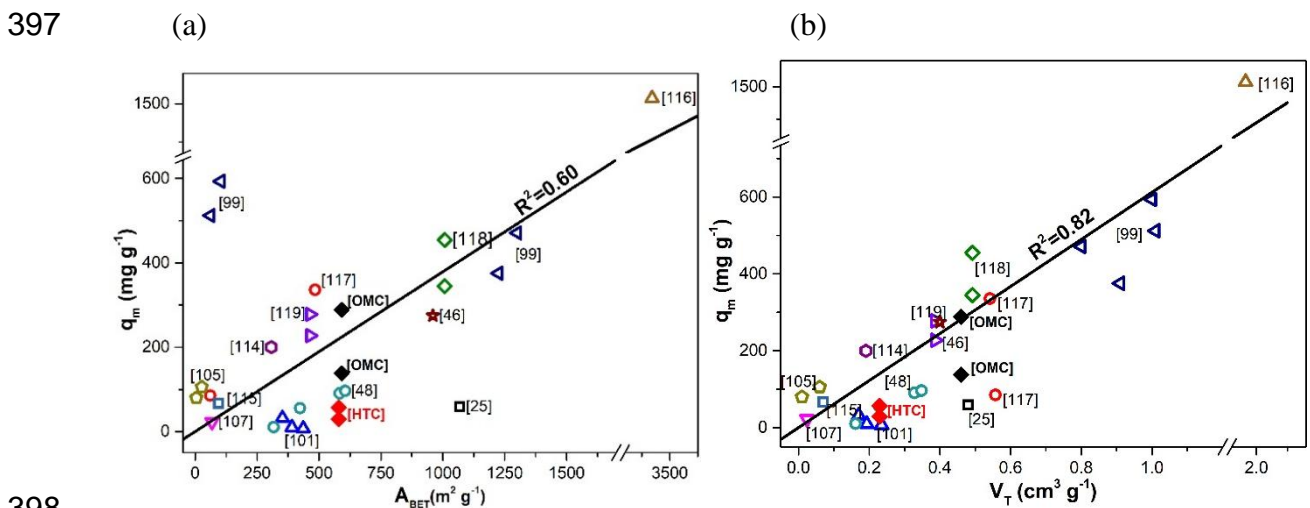
T (K)	Langmuir			Freundlich			Temkin		
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R ²	B (mg g ⁻¹)	K_T (L mg ⁻¹)	R ²
OMC									
288	137.9	0.894	0.82	58.4	5.239	0.86	17.0	38.9	0.87
308	288.5	0.146	0.90	72.6	3.363	0.99	38.7	9.8	0.96
HTC									
288	29.2	0.027	0.98	5.04	3.48	0.90	5.26	0.46	0.96
308	56.9	0.011	0.99	3.57	2.30	0.93	11.30	0.14	0.98

377

378 As expected for liquid-phase adsorption, the Langmuir monolayer adsorption capacity (q_m)
 379 increases with temperature, whereas the adsorption constant (b) decreases. The $1/n$ parameter
 380 of the Freundlich model was in all cases in the range corresponding to the favourable and
 381 reversible isotherm ($0.1 < 1/n < 1.0$). The parameter B of the Temkin isotherm model
 382 increases with the temperature according to the mathematical relationship $B = RT/b_T$ [113],

383 where b_T is a factor related to adsorbent-adsorbate interactions. The Temkin adsorption
 384 constant (K_T) follows the same temperature behaviour as that of Langmuir.

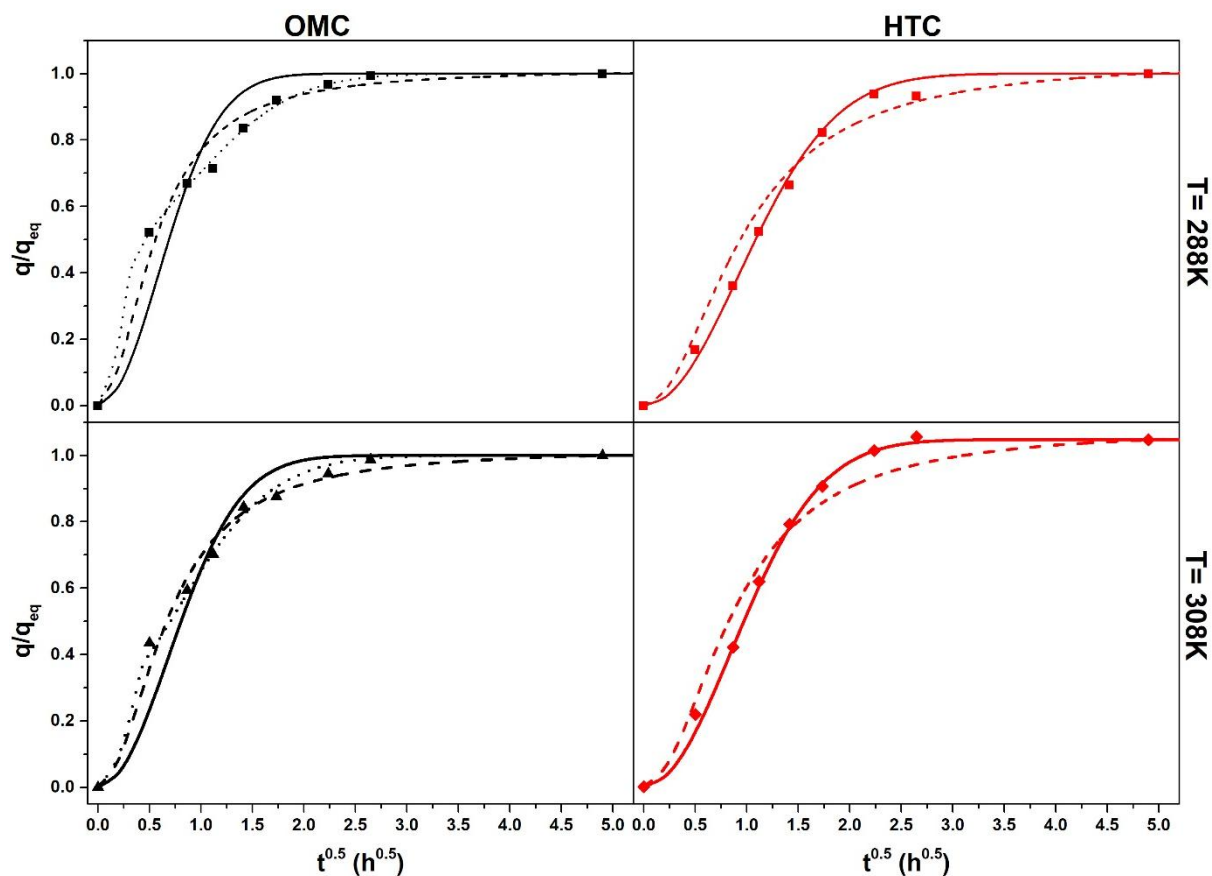
385 Fig. 7 shows the maximum TC adsorption capacities obtained in this study as well as those
 386 reported in the literature for other carbons [25,46,48,99,101,105,107,114–119], as a function
 387 of either A_{BET} or V_T . The determination coefficient when using A_{BET} is much lower, $R^2 = 0.60$,
 388 than that obtained when using V_T , $R^2 = 0.82$. This poor relationship with A_{BET} is because the
 389 value of A_{BET} mainly corresponds to the contribution of micropores (pore diameter < 2 nm),
 390 which sometimes are not fully accessible to the TC molecules. Moreover, as shown in Fig. 4.b,
 391 the size of the TC molecule varies from 0.38 to 1.2 nm, depending on its orientation. The
 392 better correlation of q_m with V_T could be related to the fact that mesopores and macropores,
 393 which are fully accessible to the TC molecule, have a higher impact on the value of V_T . Event
 394 like that, the correlation between q_m and V_T is not excellent. A much better correlation should
 395 be obtained using the mesopore volumes instead of V_T . Unfortunately, these data are not
 396 always available in the open literature.



399 **Figure 7.** Relationship between the maximum TC adsorption capacity and (a) the BET
 400 surface area A_{BET} , or (b) the total pore volume V_T .

401 Fig. 8 shows the TC uptake at 288 K and 308 K for the two carbon adsorbents as a function
 402 of time. The equilibrium was reached after 9 h for both HTC and OMC. The TC adsorption

403 kinetics on HTC is adequately fitted by the PFO kinetic model. However, the behaviour of TC
 404 adsorption kinetics on the OMC is somewhat different but in a good agreement with the
 405 results already reported in a previous study [101], where the adsorption of TC on a
 406 mesoporous carbon was studied. Taking into account the existence of three different diffusion
 407 rates controlling the adsorption kinetics in the OMC, i.e., applying Eq. (7) with $N = 3$ and
 408 assuming that the mass transfer at the mesoporous peak is only governed by external diffusion,
 409 the kinetic model proposed takes the form of a Triple Dual Resistance Model (TDRM). This
 410 model was able to describe the experimental data with a good accuracy ($R^2 > 0.99$) for both
 411 temperatures, see below.



412
 413 **Figure 8.** Tetracycline adsorption kinetics on the OMC (black, left) and the HTC (red, right)
 414 at 288 K (top) and 308 K (bottom), and the corresponding fits using PFO (—), PSO (--) and
 415 TDRM (···) models.

416

417 Table 4 shows the parameters and determination factors obtained using PFO and PSO
 418 kinetic models to fit the experimental data. Although both models are capable of describing
 419 the TC adsorption kinetics, PFO model best fits the TC adsorption kinetics on HTC, which
 420 may indicate that adsorption is controlled by diffusion into the narrowest pores. PSO best fits
 421 the TC adsorption kinetics on OMC, suggesting that external diffusion controls the adsorption
 422 rate. Experimental adsorption and modelling results are shown in Fig. 8 (PSO, PFO and
 423 TDRM) and Figure SI 5 (other kinetic models).

424 **Table 4.** Parameters and determination factors obtained by fitting classical adsorption kinetics
 425 models to TC adsorption on HTC and OMC.

T (K)	PFO				PSO			
	HTC		OMC		HTC		OMC	
	K_1 (h ⁻¹)	R_{ADj}^2	K_1 (h ⁻¹)	R_{ADj}^2	K_2 (g mg ⁻¹ h ⁻¹)	R_{ADj}^2	K_2 (g mg ⁻¹ h ⁻¹)	R_{ADj}^2
288	0.59	0.99	1.46	0.89	0.039	0.97	0.023	0.98
308	0.69	1.00	1.07	0.95	0.026	0.97	0.008	0.99

426 Table 5 shows the parameters obtained by taking into account the contribution of each
 427 range of porosity. The traditional dual resistance model (DRM), described by equations (5)
 428 and (6), is better adapted to the TC adsorption data on HTC than other conventional models
 429 (PFO, PSO) are. However, a triple dual resistance model becomes a better alternative for
 430 describing the TC adsorption kinetics on OMC.

431

432 **Table 5.** Parameters and determination factors obtained by fitting dual resistance kinetics
 433 models to TC adsorption on HTC and OMC.

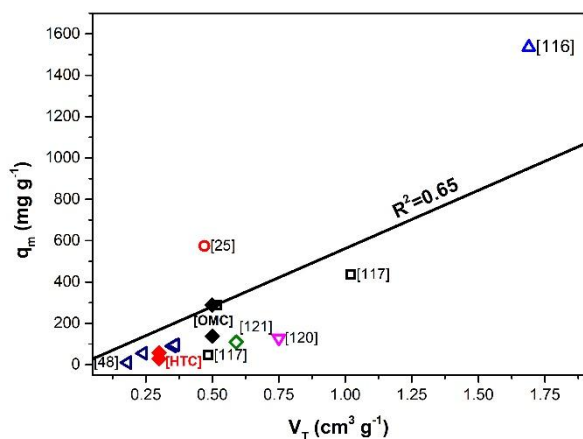
T (K)	DRM			TDRM				
	K_f (L g ⁻¹ h ⁻¹)	Dif (h ⁻¹)	R_{ADj}^2	K_f (L g ⁻¹ h ⁻¹)	Dif_1 (h ⁻¹)	Dif_2 (h ⁻¹)	S (m ² g ⁻¹)	R_{ADj}^2
HTC								
288	0.998	0.590	0.99	-	-	-	-	-
308	0.998	0.712	1.00	-	-	-	-	-
OMC								
288	1.16	1.11	0.85	1.35	8.47	0.56	329.9	1.00
308	1.16	1.11	0.94	1.35	15.3	0.67	482.9	1.00

434 The TDRM allowed us estimating the surface area accessible in the OMC (see Table 5),
 435 and the exclusion pore size diameter, i.e., the pore diameter below which the TC molecule
 436 cannot access. Such exclusion diameter was calculated from the accessible surface area and
 437 the cumulative surface curve shown in Fig. 5.d). The calculation of the latter led to values of
 438 0.54 and 0.59 nm at 308 K and 288 K, respectively. By applying these pore diameters to the
 439 PSD of the HTC, it was possible to obtain an estimate of the surface area accessible to TC.

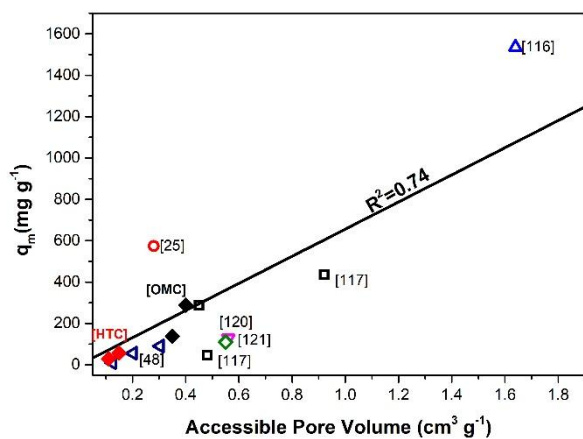
440 Fig. 9 shows q_m as a function of the theoretical accessible pore volume (APV), obtained
 441 from the exclusion pore diameter and the cumulative pore volume shown in Fig. SI 2, and
 442 from the total pore volume (V_T) for the two materials of this study and some others from the
 443 open literature [25,48,116,117]. There are less points than in Fig. 7 because PSDs were not
 444 always available and they are necessary to calculate the APV. q_m follows a linear trend as a
 445 function of the V_T ($R^2 = 0.65$) although the determination factor when representing q_m as a
 446 function of APV ($R^2 = 0.74$) is much better, since the TDRM allows having different APVs at
 447 different temperatures for the same adsorbent and discard the pore volume fraction that is not
 448 accessible to TC. Therefore, we showed that TDRM provides a tool for understanding how
 449 temperature, through changes in the properties of diffusion and fluid dynamics, affect the

450 maximum amount adsorbed. Moreover, we demonstrated that A_{BET} , although it is easy to
 451 calculate and reported by everyone, is not the best tool to evaluate the potential suitability of
 452 an adsorbent to remove pollutants in water phase. In this study, we showed, step by step, that
 453 V_T is better than A_{BET} and APV still better than V_T .

454 (a) (b)



455



456

457 **Figure 9.** Correlation between the maximum tetracycline adsorption capacity and (a) total and
 458 (b) accessible pore volumes.

459

460 4. CONCLUSION

461 Two different carbons were produced by a first step of either hydrothermal treatment or
 462 soft templating, to obtain purely microporous (HTC) or micro-mesoporous (OMC) carbon
 463 materials, respectively, after pyrolysis at 1173 K. The BET area (A_{BET}) was very similar for

464 the two carbons, but the latter had distinct pore size distribution and total pore volume (V_T).
465 The OMC indeed had an almost two times higher V_T , of which 56.5% were mesopores.

466 Tetracycline (TC) adsorption increased with temperature and the OMC had an adsorption
467 capacity three times higher than the HTC. This difference was attributed to the accessible
468 surface and not to the A_{BET} or the surface chemistry, which are very similar.

469 The kinetics of TC adsorption on OMC was controlled by a combined diffusion in two
470 ranges of micropores and in mesopores, while on HTC it was adequately fitted by a model
471 taking into account the diffusional resistance in the micropores. Moreover, these models
472 allowed estimating the pore size accessible to the TC molecules, and calculate the accessible
473 surface areas and pore volumes (APV). The applied kinetic approach gave an explanation
474 about the better TC adsorption performance of the OMC compared to HTC.

475 We have undoubtedly shown that A_{BET} , while easy to calculate and reported by everyone,
476 is not the best tool to assess the potential suitability of an adsorbent to the removal of TC on
477 carbon materials (e.g. OMC and HTC). V_T is better than A_{BET} and, APV even better than V_T
478 because APV is the accessible pore volume of adsorbent to a given pollutant.

479

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484

485

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