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1 **Physical meaning of the parameters used in fractal**  
2 **kinetic and generalised adsorption models of**  
3 **Brouers-Sotolongo**

4  
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23

## 24 **Abstract**

25 The aim of the present study was to clarify the physical meaning of the parameters used in  
26 fractal kinetic and generalised isotherm models of Brouers-Sotolongo. For this purpose,  
27 adsorption of methylene blue (MB) and methyl orange (MO) onto four activated carbons  
28 (ACs) was carried out. These ACs were characterised in terms of composition, surface area,  
29 pore volumes and pore size distributions, carbon nanotexture and surface chemistry.  
30 Adsorption isotherms were carried out at 25°C, and at pH 2.5 and 8 for MO and MB,  
31 respectively, and fitted with Langmuir, Freundlich, Jovanovich, Hill-Sips (HS), Brouers-  
32 Sotolongo (BS), Brouers-Gaspard (BG) and General Brouers-Sotolongo (GBS) models.  
33 Adsorption kinetics were fitted by traditional pseudo-first and pseudo-second order models  
34 and compared to the Brouers-Sotolongo (BSf) fractal kinetic model. GBS and BSf were found  
35 to be the best models describing adsorption isotherms and kinetics, respectively. This finding  
36 suggests that MB and MO adsorption is probabilistic and closely correlated to the  
37 heterogeneous character of the adsorbent surface. Moreover, BSf and GBS parameters were  
38 correlated with surface area and amount of surface functional groups. In particular, higher  
39 surface area and amount of functional groups respectively decreased and increased the  
40 constants  $\tau_c$  and  $\alpha$  of the BSf stochastic model.

41

42

43

44 **Keywords:** Dyes adsorption; activated carbon; fractal kinetics; stochastic isotherm; surface  
45 heterogeneity; adsorption isotherms.

46

## 47 **1. Introduction**

48 Although water is an essential element to life on Earth, it is frequently contaminated by  
49 human activities, especially by those related to industries. Therefore, water depollution is an  
50 essential stage that should always be carried out by factories and chemical plants (Bello et al.  
51 2013). One of the methods used for pollutant removal is adsorption on highly porous  
52 materials, among them activated carbons (ACs). ACs are characterized by their well-  
53 developed textural properties and are indeed commonly used for air treatment (Choi et al.  
54 2016), biogas purification (Tian et al. 2009), gas storage (Sethia,Sayari 2016) and pollutants  
55 removal from water (Húmpola et al. 2016).

56 In order to understand the adsorption phenomena, different models can be applied for  
57 describing adsorption kinetics and isotherms data. For that purpose, stochastic isotherms and  
58 fractal kinetics have become increasingly employed (Sandro et al. 2009; Gaspard et al. 2006).  
59 Indeed, ACs can be considered as fractal materials due to their intricate porous network,  
60 developed during the activation process (Neimark 1992), and this has an influence on their  
61 adsorption properties. The adsorption process of a molecule dissolved in a solvent indeed  
62 takes place at the liquid-solid inter-phase with dimensional or topological constraints  
63 (Kopelman 1988). Thus, some physical properties of the adsorbate/adsorbent systems not only  
64 depend on the random behaviour of the mass distribution of adsorbent, but also on the fractal  
65 and stochastic character of its surface (Sokolowska et al. 2001).

66 Meilanov et al. (Meilanov et al. 2002) expressed the need of developing new studies of  
67 sorption kinetics based on fractals that would take the heterogeneity of adsorbents into  
68 account. This new approach was developed by Brouers and co-workers (Brouers,Sotolongo-  
69 Costa 2006; Brouers et al. 2005), who provided a new kinetic model called BSf including  
70 former models already applied to water treatment (Ben Hamissa et al. 2013) and to  
71 pharmacokinetics (Pereira 2010).

72 On the other hand, understanding adsorption isotherms, i.e., at equilibrium, remains a  
73 major way to predict the efficiency of some adsorbents for removing a given pollutant from  
74 water (Ncibi et al. 2008). Consequently, an abundant literature exists on the development of  
75 mathematical models and their suitability for describing adsorption phenomena. However,  
76 most of these models are empirical, are sometimes based on unrealistic assumptions and,  
77 finally, give little information on the physicochemical processes involved. For this reason,  
78 Brouers extended the empirical model of Langmuir in a more general one, called General  
79 Brouers-Sotolongo (GBS) model, based on a Burr distribution (Brouers 2014b).

80 Applying the aforementioned modern models presents many advantages compared to  
81 traditional ones. From the kinetics point of view, BSf allows determining valuable  
82 information with a very good accuracy such as adsorption capacity, fractal time exponent (see  
83 below for details), half-reaction time, and order of reaction. From the isotherms point of view,  
84 GBS allows determining the initial reaction kinetics at various concentrations of adsorbate,  
85 assessing the heterogeneity of ACs surface in terms of agglomeration and clustering of AC  
86 particles, or of fractal distribution of mesopores.

87 Herein, BSf and GBS models were used to describe adsorption kinetics and isotherms,  
88 respectively, of two dyes: methylene blue (MB) and methyl orange (MO), onto four ACs:  
89 F200, F300, Acticarbon® and Cecalite® (see below for description). These materials were  
90 also thoroughly characterised by elemental analysis, scanning electron microscopy (SEM), X-  
91 ray diffraction (XRD), Raman spectroscopy, thermogravimetry, mercury porosimetry, and  
92 adsorption-desorption of N<sub>2</sub> and CO<sub>2</sub> at -196°C and 0°C, respectively. Assessment of the  
93 surface functional groups of these ACs was obtained by a potentiometric titration technique.  
94 The initial pH,  $pH_{Initial}$ , and the pH of zero charge,  $pH_{PZC}$ , were also determined. We present  
95 correlations between the parameters of BSf and GBS models and the ACs' physicochemical

96 characteristics, namely porous texture and related parameters such as DFT surface area, and  
 97 their chemical characteristics such as nature and amount of surface functional groups.

98

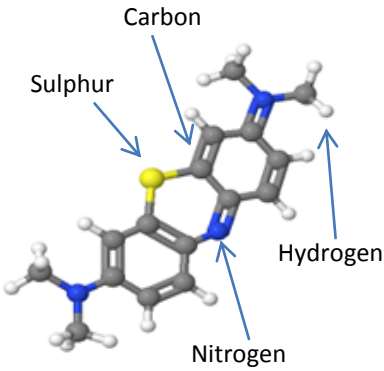
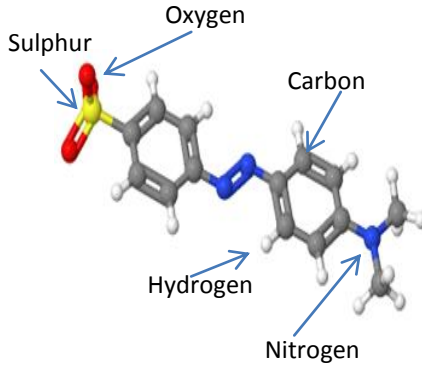
## 99 2. Materials and methods

### 100 2.1 Raw materials

101 Four commercial granular activated carbons (ACs) were used in this study. Filtrasorb 200  
 102 (F200) and Filtrasorb 300 (F300) from Calgon Corporation were obtained from a local textile  
 103 industry (Chimitex, Tunisia). Acticarbon® and Cecalite® were purchased from CECA  
 104 Company. All ACs were thoroughly washed with distilled water to remove surface impurities,  
 105 followed by drying at 80°C for 48h.

106

107 **Table 1:** Main characteristics of dyes used in the present work.

Dye	MB (Cationic dye)	MO (Anionic dye)
Molecular structure	 <p>Carbon Sulphur Nitrogen Hydrogen</p> <p><math>C_{16}H_{18}ClN_3S</math></p>	 <p>Sulphur Oxygen Carbon Hydrogen Nitrogen</p> <p><math>C_{14}H_{15}N_3O_3S</math></p>
Molecular weight ( $g \cdot mol^{-1}$ )	319.85	305.35
$\lambda$ (nm)	663	464

108

109 The basic dye, methylene blue (MB), and the acidic one, methyl orange (MO), both 85%  
 110 pure, were purchased from Sigma-Aldrich. Stock solutions were prepared by dissolving  
 111 accurately weighed amounts of MB and MO in distilled water to give a concentration of

112 1 g.L<sup>-1</sup>. The various solutions used in this study were then prepared by diluting the stock  
113 solution of either MB or MO with distilled water. **Table 1** shows the main characteristics of  
114 those dyes, such as their molecular structure and weight, their acidic or basic nature, and the  
115 optimum wavelength ( $\lambda$ ) used in UV-Vis experiments for their detection.

116

## 117 **2.2 Activated carbon characterisation**

118 The pore texture characterisation of ACs was carried out by adsorption-desorption studies  
119 of N<sub>2</sub> and CO<sub>2</sub> at -196°C and 0°C, respectively, in an ASAP 2020 manometric equipment  
120 (Micromeritics, USA). For each material, the BET model was applied to determine the  
121 apparent surface area,  $A_{BET}$  (m<sup>2</sup>.g<sup>-1</sup>), whereas the pore size distribution (PSD) was obtained by  
122 using two-dimensional (2D) version of the non-local density functional theory (NLDFT) with  
123 the Solution of Adsorption Integral Equation Using Splines (SAIEUS<sup>®</sup>) routine. SAIEUS<sup>®</sup>  
124 has the advantage of combining both CO<sub>2</sub> and N<sub>2</sub> adsorption data to get more accurate PSDs  
125 (Jagiello, Olivier 2013; Jagiello et al. 2015). The NLDFT method was also used to determine  
126 the surface area,  $S_{DFT}$  (m<sup>2</sup>.g<sup>-1</sup>), by integrating the PSD over the whole range of pore sizes  
127 (Centeno, Stoeckli 2010).

128 The total pore volume measurable by adsorption, or Gurvitch volume, was taken at the  
129 relative pressure of 0.97,  $V_{0.97}$  (cm<sup>3</sup>.g<sup>-1</sup>). The Dubinin-Raduskevich (DR) model (Dubinin 1981)  
130 was applied to obtain the microporous volume from the N<sub>2</sub> isotherm,  $V_{DR,N_2}$  (cm<sup>3</sup>.g<sup>-1</sup>) on one  
131 hand, and from the CO<sub>2</sub> isotherm,  $V_{DR,CO_2}$  (cm<sup>3</sup>.g<sup>-1</sup>) on the other hand. The average micropore  
132 volume,  $L_0$  (nm), was calculated from Stoeckli's equation (Stoeckli 1995):

$$133 \quad L_0 = \frac{10.8}{E_0 - 11.4} \quad (1)$$

134 where  $E_0$  (kJ.mol<sup>-1</sup>) is the adsorption energy calculated by the DR model. The micropore  
135 volume was also calculated by application of the 2D-NLDFT model,  $V_{\mu,NLDFT}$  (cm<sup>3</sup>.g<sup>-1</sup>). The  
136 mesopore volume,  $V_{mes}$  (cm<sup>3</sup>.g<sup>-1</sup>), was obtained from the difference  $V_{0.97} - V_{\mu,NLDFT}$ .

137 Meso- and macropore size distributions were also determined by mercury porosimetry  
138 using an Autopore IV apparatus (Micromeritics, USA). Mercury intrusion was performed in  
139 two steps at low (0.001-0.24 MPa) and at high (0.24-414 MPa) pressure. Application of  
140 Washburn's equation (Washburn 1921), equation (2), allowed calculating the pore size as a  
141 function of the mercury pressure. Assuming cylindrical pores of diameter  $d$ , it reads:

$$142 \quad d = -\frac{4 \sigma_{Hg} \cos\theta}{P} \quad (2)$$

143 where  $P$  is the pressure (MPa),  $\sigma_{Hg}$  is the surface tension of mercury ( $0.485 \text{ J.m}^{-2}$  at  $20^\circ\text{C}$ ),  
144 and  $\theta$  is the contact angle ( $140^\circ$ ). Pores as narrow as 3.7 nm could be probed at the highest  
145 available pressure, 400 MPa.

146 XRD measurements were performed by using the Cu  $K\alpha$  radiation generated by an X'Pert  
147 Pro diffractometer (Phillips, The Netherlands). The angle range used was  $8^\circ$ - $100^\circ$  with a scan  
148 step size of  $0.0334^\circ$ . Raman spectra were recorded in the range  $0$ - $3000 \text{ cm}^{-1}$  using a Labram  
149 HR800UV confocal Raman microscope (Horiba Jobin Yvon, Japan) equipped with a CCD  
150 detector cooled by Peltier effect. The morphology of the activated carbon was analysed by  
151 SEM with a FETQuanta 400 scanning electron microscope using an accelerating voltage of 3  
152 kV.

153 Carbon, hydrogen, nitrogen and sulphur contents were determined with a Vario EL Cube  
154 elemental analyser (Elementar, Germany). Oxygen was also directly determined with the  
155 same equipment in a second step. Thermogravimetric analysis (TGA) was performed with an  
156 SDT Q600 V8.3 Build 101 thermal analyser (TA Instruments, USA) at a heating rate of  
157  $10^\circ\text{C.min}^{-1}$  in an air flow of  $60 \text{ mL.min}^{-1}$ .

158 The pH at the point of zero charge, known as  $pH_{PZC}$ , is the pH at which the net charge of  
159 the surface is zero. The value of  $pH_{PZC}$  depends both on the nature and on the amount of  
160 functional groups at the surface. For determining it, 0.1 g of AC powder was put into contact  
161 with 20 mL of  $0.1 \text{ mol.L}^{-1}$  NaCl solution and stirred for 48 h. Then, the suspension was



162 filtered and the equilibrium pH was measured. To determine the initial pH of ACs,  $pH_{Initial}$ ,  
163 0.1 g of AC powder was placed in 20 mL of distilled water (initial pH 5.7 due to dissolved  
164 atmospheric carbon dioxide) and equilibrated during the night. Then, the pH of the suspension  
165 was measured at room temperature.

166 Potentiometric titration was used to identify and to quantify the functional groups on the  
167 AC surface. For that purpose, 0.1 g of AC was placed in 50 mL of  $NaNO_3$  solution (0.01  
168  $mol.L^{-1}$ ), used both as electrolyte and as suspension medium, to which 1 mL of HCl (0.1  
169  $mol.L^{-1}$ ) was added. Then the solution was stirred overnight under  $N_2$  saturation. The solution  
170 was then titrated with NaOH (0.1  $mol.L^{-1}$ ) under  $N_2$  saturation using a 905 Titrand automatic  
171 titrator (Metrohm, Switzerland) commanded with Tiamo<sup>®</sup> software V2.2. The  $pK_a$  distribution  
172 of the surface functional groups was calculated by determination of the proton binding  
173 function,  $f(pK_a)$ , and the total surface charge,  $Q$  ( $mmol.L^{-1}$ ), was obtained by applying the  
174 method of Jagiello (Jagiello 1994; Jagiello et al. 2000; Jagiello et al. 1995).

175

### 176 **2.3 Adsorption of MB and MO**

177 Adsorption studies were performed in batch experiments by adding 0.3 g of AC in 100 mL  
178 of MB and MO solutions at the desired concentration in the range 0.5 – 80  $mg.L^{-1}$ . The pH  
179 (2.5, 5 or 8) was adjusted by adding a small amount of either diluted HCl (0.1  $mol.L^{-1}$ ) or  
180 diluted NaOH (0.1  $mol.L^{-1}$ ) solution. The temperature (25, 35 or 50°C) was controlled with a  
181 thermostatic bath with an accuracy of  $\pm 1^\circ C$ . Suspensions of ACs in dye solutions were stirred  
182 with a magnetic device. Samples were investigated at different time intervals to measure dye  
183 removal and thus to perform kinetics studies. At each time increment, the residual dye  
184 concentration was determined by a Lambda 35 spectrophotometer (Perkin Elmer, USA) at a  
185 wavelength of 663 nm for MB and of 464 nm for MO (see again **Table 1**). The amount of  
186 adsorbed dye at equilibrium,  $q_e$  ( $mg.g^{-1}$ ), was calculated by application of equation (3):

187 
$$q_e = \frac{(C_0 - C_e) V}{m} \quad (3)$$

188 where  $C_0$  and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) are initial and equilibrium concentrations, respectively,  $V$  (L) is the  
189 volume of solution, and  $m$  (g) is the mass of AC in the suspension.

190 Thermodynamic parameters such as the variation of standard entropy,  $\Delta S^\circ$ , standard  
191 enthalpy,  $\Delta H^\circ$ , and standard free energy,  $\Delta G^\circ$ , were calculated as reported in Enaime et al.  
192 2017.

193

### 194 **2.3.1 Kinetic models**

195 The pseudo-first order (PFO) kinetic model, also known as Lagergren's model, is generally  
196 used to describe solid / liquid adsorption processes. This model assumes that the rate of solute  
197 uptake is proportional to the difference between the saturation concentration and the amount  
198 of adsorbed solute as a function of time. PFO model can be described by equation (4):

199 
$$q_t = q_{e,1} (1 - \exp(-k_1 t)) \quad (4)$$

200 where  $q_{e,1}$  is the amount of adsorbed dye at equilibrium ( $\text{mg}\cdot\text{g}^{-1}$ ),  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant  
201 of pseudo-first order adsorption, and  $t$  (min) is the time. The initial adsorption rate,  $h_1$  ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ )  
202 ( $\text{Miao et al. 2016; Lagergren 1898}$ ) is calculated by equation (5):

203 
$$h_1 = k_1 q_{e,1} \quad (5)$$

204 The pseudo-second-order model (PSO) kinetic model, also known as Ho and Mckay's  
205 model, is widely used for describing adsorption dynamics. In this model, the adsorption  
206 process, rather than the particle mass transfer process, is considered as the rate-limiting factor  
207 (Ho,McKay 1999). The PSO kinetic model can be written according to equation (6):

208 
$$q_t = \frac{q_{e,2}^2 k_2 t}{1 + q_{e,2} k_2 t} \quad (6)$$

209 where  $q_{e,2}$  is the amount of adsorbed dye at equilibrium ( $\text{mg.g}^{-1}$ ) and  $k_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) is the  
 210 rate constant of pseudo-second order adsorption.  $h_2$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) is the initial adsorption rate  
 211 (Ho,McKay 1998, 1999) and is calculated as follows:

$$212 \quad h_2 = k_2 q_{e,2}^2 \quad (7)$$

213 The equation of Brouers-Sotolongo (BS) takes into account the adsorption process  
 214 complexity (Brouers et al. 2004; Brouers 2014a), and has been recently used in various works  
 215 (Brouers,Sotolongo-Costa 2006; Gaspard et al. 2006; Ben Hamissa et al. 2013; Kesraoui et al.  
 216 2016). The BS equation reads:

$$217 \quad q_{n,\alpha}(t) = q_e \left[ 1 - \left( 1 + (n-1) \left( \frac{t}{\tau_{n,\alpha}} \right)^\alpha \right)^{\frac{-1}{(n-1)}} \right] \quad (8)$$

218 If we use the deformed  $n$ -exponential (Brouers,Sotolongo-Costa 2006)

$$219 \quad \text{Exp}_n(x) = [1 - (n-1)x]^{\frac{-1}{(n-1)}}, \quad (9)$$

220 the BSf model can therefore be written as shown in equation (10):

$$221 \quad q(t) = q_e \left[ 1 - \text{Exp}_n \left( - \left( \frac{t}{\tau_{n,\alpha}} \right)^\alpha \right) \right] \quad (10)$$

222 where  $\alpha$  is the fractal time exponent,  $n$  is a fractional (non-integer) reaction order, and  $q_{n,\alpha}(t)$   
 223 and  $q_{e,BS}$  are the adsorbed amounts at time  $t$  and at saturation, respectively.  $\tau_c$  is the  
 224 characteristic time of the complex kinetics, which depends on the initial concentration and on  
 225 the two exponents  $n$  and  $\alpha$ . When  $\alpha = 1$  and  $n = 1$ , the PFO equation is obtained, whereas  $\alpha =$   
 226  $1$  and  $n = 2$  leads to PSO. If  $\alpha \neq 1$  and  $n = 1$ , the Weibull distribution is obtained and reads:

$$227 \quad q_{1,\alpha}(t) = q_{e,W} \left[ 1 - \text{Exp} \left( - \left( \frac{t}{\tau_c} \right)^\alpha \right) \right]. \quad (11)$$

228 For  $\alpha \neq 1$  and  $n = 2$ , the Hill equation is obtained and reads:

$$229 \quad q_{2,\alpha}(t) = q_{e,H} \left[ 1 - \left( 1 + \left( \frac{t}{\tau_c} \right)^\alpha \right)^{-1} \right]. \quad (12)$$

230 The “half reaction” time  $\tau_{1/2}$ , given by equation (14), is the necessary time to adsorb half of  
 231 the initial concentration, and it can be derived from equation (13) using the deformed  
 232 logarithm (Brouers 2014a):

$$233 \quad \left[1 + (n - 1) \left(\frac{t}{\tau_c}\right)^\alpha\right]^{\frac{-1}{(n-1)}} = \frac{1}{2} \quad (13)$$

$$234 \quad \tau_{1/2} = \tau_c \left(\frac{2^{(n-1)} - 1}{n-1}\right)^{1/\alpha}. \quad (14)$$

235

### 236 2.3.2 Adsorption isotherm models

237 In the present paper, six models were used to study the adsorption isotherms: Langmuir  
 238 (Langmuir 1918), Freundlich (Freundlich 1906), Brouers-Sotolongo (BS) (Brouers 2014b),  
 239 Jovanovich (Jovanović 1969), Hill-Sips (HS) (Sips 1948) and General Brouers-Sotolongo  
 240 (GBS) (Brouers et al. 2005; Brouers 2014b). The first five models can be obtained by giving  
 241 well-defined values to the parameters  $a$  and  $c$  in the GBS equation:

$$242 \quad q_{e\ GBS} = q_{e\ max} \left(1 - \text{Exp}_c \left[-\left(\frac{C_e}{b}\right)^a\right]\right) = q_{e\ max} \left(1 - \left[1 + c \left(\frac{C_e}{b}\right)^a\right]^{-1/c}\right) \quad (15)$$

243 Thus, for  $c = 1$  and  $a = 1$ , the Langmuir isotherm is recovered:

$$244 \quad q_{eL} = q_{e\ maxL} \left(1 - \left[1 + \left(\frac{C_e}{b}\right)\right]^{-1}\right) = q_{e\ maxL} \frac{C_e}{b + C_e}. \quad (16)$$

245 For  $c = 0$ , we get the normal Brouers-Sotolongo (BS) isotherm:

$$246 \quad q_{e\ BS} = q_{e\ maxBS} \left(1 - \text{Exp} \left[-\left(\frac{C_e}{b}\right)^a\right]\right), \quad (17)$$

247 and at low concentration,  $C_e \ll b$ , one gets the Freundlich isotherm:

$$248 \quad q_{eF} = K_F C_e^a \quad (18)$$

249 For  $c = 0$  and  $a = 1$ , we find the Jovanovich isotherm:

$$250 \quad q_{eJ} = q_{e\ maxJ} \left(1 - \text{Exp} \left[-\left(\frac{C_e}{b}\right)\right]\right), \quad (19)$$

251 And finally, for  $c = 1$ , we get the HS isotherm:

252 
$$q_{eHS} = q_{e\max HS} \left( 1 - \left[ 1 + \left( \frac{C_e}{b} \right)^a \right]^{-1} \right). \quad (20)$$

253 It was shown that the constant  $c$  should range between 0 and 1 (Brouers, Al-Musawi 2015).  
 254 However, if the isotherm does not reach saturation, the constant  $c$  can be higher than 1 and  
 255 therefore the results have no physical meaning in a statistical approach. As it is difficult to  
 256 choose between HS and BS isotherm (i.e., between  $c = 0$  and 1), Brouers proposed to fit the  
 257 adsorption isotherms with  $c = 0.5$  (Brouers, Al-Musawi 2015), leading to what is known as the  
 258 Brouers-Gaspard (BG) isotherm, which reads:

259 
$$q_{eGBS} = q_{e\max} \left( 1 - \text{Exp}_{c=0.5} \left[ - \left( \frac{C_e}{b} \right)^a \right] \right) = q_{e\max} \left( 1 - \left[ 1 + \frac{1}{2} \left( \frac{C_e}{b} \right)^a \right]^{-2} \right). \quad (21)$$

260 The knowledge of constants  $a$ ,  $b$  and  $c$  allows determining  $C_e$  or a given percentage of  $C_e$ ; in  
 261 particular,  $Ce_{\frac{1}{2}}$  (50% of  $C_e$ ) was calculated with the following equations.

262 In the GBS case, we have:

263 
$$Ce_{\frac{1}{2}} = b \left( \frac{2^c - 1}{c} \right)^{\frac{1}{a}}, \quad (22)$$

264 in BS case:

265 
$$Ce_{\frac{1}{2}} = b (\ln 2)^{\frac{1}{a}}, \quad (23)$$

266 in Jovanovich case:

267 
$$Ce_{\frac{1}{2}} = b \ln 2, \quad (24)$$

268 in HS and Langmuir case:

269 
$$Ce_{\frac{1}{2}} = b, \quad (25)$$

270 and finally in BG case:

271 
$$Ce_{\frac{1}{2}} = b (2\sqrt{2} - 2)^{\frac{1}{a}}. \quad (26)$$

272

273

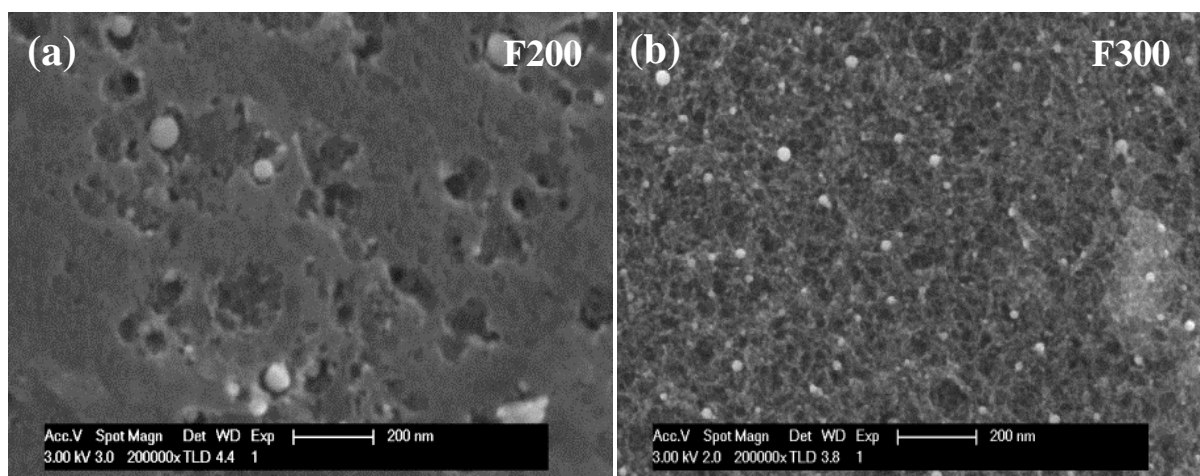
274 **3. Results and discussion**

275 **3.1 Physicochemical characteristics of ACs**

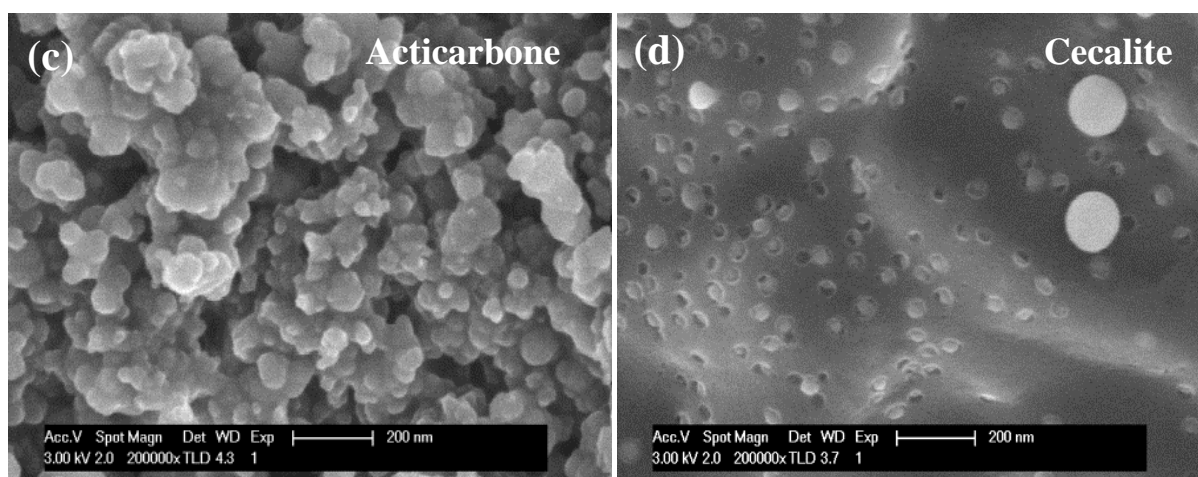
276 Physicochemical properties of all ACs in terms of elemental analysis, thermal stability in  
277 air flow, carbon nanotexture and crystalline structure are given in Supplementary Information.  
278 **Table SI 1** thus presents the C, H, O and N contents of all materials, whereas results of  
279 thermogravimetric, Raman and X-ray diffraction studies are given in **Fig. SI 1**, **Fig. SI 2**, and  
280 **Fig. SI 3**, respectively. The corresponding discussion is also provided in the Supplementary  
281 Information.

282 **Fig 1** shows the morphology of these ACs as seen by SEM. These images, obtained by  
283 using secondary electrons, demonstrate some important differences between materials in  
284 terms of grain morphology, surface roughness and open porosity. F200 (**Fig 1a**) has a  
285 heterogeneous surface with large pores of broad distribution of sizes. Regarding F300 (**Fig**  
286 **1b**), the pores are much smaller and the surface appears to be very rough. Acticarbon® (**Fig**  
287 **1c**) has a completely different morphology based on microspheres, somewhat similar to what  
288 is obtained by hydrothermal treatment of biomass (Braghiroli et al. 2015). Finally, Cecalite®  
289 (**Fig 1d**) presents a rather smooth surface with well-dispersed mesopores of rather equal sizes.

290



291



292  
 293 **Fig 1** SEM pictures of activated carbons used here: (a) F200, (b) F300, (c) Acticarbon®, and  
 294 (d) Cecalite®.

295  
 296 The adsorption-desorption isotherms of  $N_2$  and  $CO_2$  for the four activated carbons are  
 297 shown in **Fig 2a** and **Fig 2b**, respectively. **Fig 2c** shows the corresponding PSDs obtained by  
 298 application of the 2D-NLDFT method to both  $N_2$  and  $CO_2$  isotherms (Jagiello, Olivier 2013).  
 299  $N_2$  adsorption isotherm at  $-196^\circ C$  on Cecalite® was type Ia, characteristic of a microporous  
 300 material with adsorption occurring by primary filling of microspores at very low relative  
 301 pressure  $P/P_0$  (IUPAC 2015). The adsorption isotherms of F200 and F300 were type Ib,  
 302 characteristic of microporous materials with micropores wider than those of type Ia present in  
 303 Cecalite®. Cooperative filling as well as primary filling indeed takes place on a wider  $P/P_0$   
 304 range than for type Ia (IUPAC 2015). No horizontal plateau was clearly achieved, indicating  
 305 pore widening; these isotherms also showed a type H4 hysteresis loop, characteristic of slit-  
 306 shaped pores according to the IUPAC classification (IUPAC 2015). Finally, the  $N_2$  isotherm  
 307 on Acticarbon® was type IIb, with high adsorption at low  $P/P_0$ , and a well-developed  
 308 hysteresis loop, type H4, showing the simultaneous presence of micro and mesopores. The  
 309 hysteresis loop of Acticarbon® was more pronounced than that of F300, which means that  
 310 its mesoporous volume was more developed.

311

312 **Table 2:** Textural characteristics of the four activated carbons obtained by adsorption-  
 313 desorption of N<sub>2</sub> at -196°C and of CO<sub>2</sub> at 0°C, applying BET, DR and 2D-NLDFT methods.

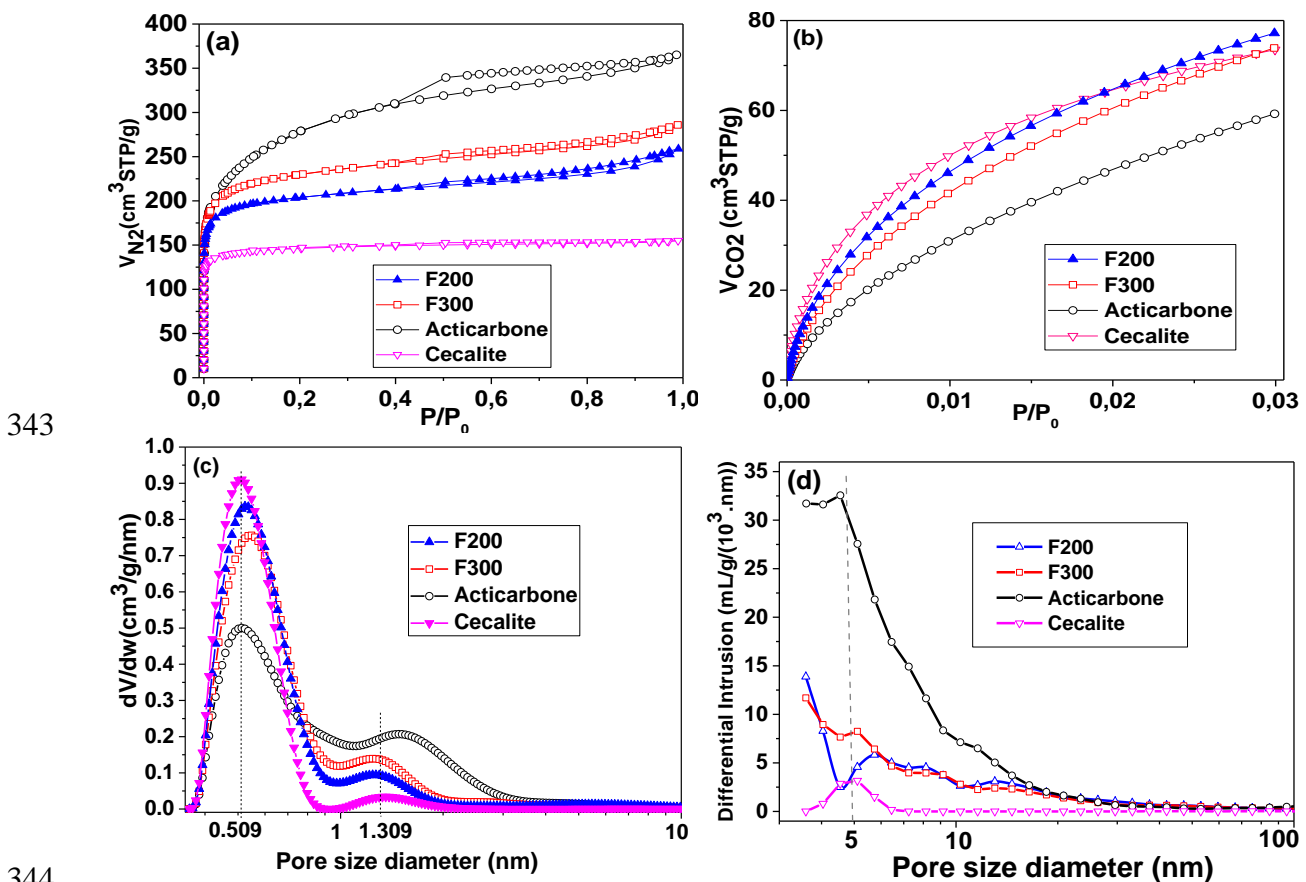
Materials	$A_{BET}$ (m <sup>2</sup> .g <sup>-1</sup> )	$S_{DFT}$ (m <sup>2</sup> .g <sup>-1</sup> )	$V_{DR, N_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{DR, CO_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{0.97}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{\mu, NLDFT}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (%)
F200	795	971	0.28	0.24	0.39	0.30	0.09	22
F300	884	1003	0.35	0.28	0.43	0.34	0.09	21
Acticarbone®	1014	967	0.35	0.18	0.56	0.38	0.16	29
Cecalite®	582	830	0.22	0.23	0.24	0.24	0.01	3

314  
 315 **Fig 2d** shows the PSDs obtained by mercury porosimetry. The highest porosity, i.e., the  
 316 volume fraction of macropores and of mesopores available to mercury, corresponds to  
 317 Acticarbone®, around 54.3 %. The porosity measurable with this technique for the other ACs  
 318 was 39.7%, 35.3% and 38.0% for F200, F300 and Cecalite®, respectively. The mercury  
 319 intrusion-extrusion curves are given in **Fig SI 4** of the supplementary information, evidencing  
 320 the entrapment of mercury when the pressure was decreased. This finding suggests the  
 321 presence of a significant amount of ink bottle-shaped pores, but also that irreversible  
 322 compression may have occurred under pressure. More information is also given in **Table SI**  
 323 **2**, suggesting that all ACs are different either in terms of macro/mesopore size (e.g. when  
 324 F200 and Cecalite® are compared) or in terms of amounts of pores of similar sizes (e.g. when  
 325 F300 and Acticarbone® are compared).

326 reports the textural characteristics obtained from N<sub>2</sub> and CO<sub>2</sub> isotherms. The values of  
 327  $A_{BET}$  ranged from 582 m<sup>2</sup>.g<sup>-1</sup> for Cecalite® to 1014 m<sup>2</sup>.g<sup>-1</sup> for Acticarbone®.  $S_{DFT}$  values were  
 328 higher than those of  $A_{BET}$  for F200, F300 and Cecalite®, meaning that these ACs have an  
 329 important fraction of narrow microporosity in which only one single nitrogen monolayer can  
 330 be adsorbed. On the contrary,  $A_{BET}$  of Acticarbone® was higher than  $S_{DFT}$ . This means that the  
 331 pore texture is highly developed with wider micropores, wherein a supplementary nitrogen



332 molecule can be accommodated between two layers of  $N_2$  adsorbed onto the pore walls. The  
 333 volume of Dubinin-Raduskevich accessible to  $N_2$ ,  $V_{DR,N_2}$ , was always higher than  $V_{DR,CO_2}$   
 334 except for Cecalite®; this means that there is also an important fraction of micropores wider  
 335 than 1 nm because  $CO_2$  can probe pores narrower than 1 nm. In agreement with such finding,  
 336 the average micropore diameter,  $L_0$ , calculated by application of the DR model to the  $N_2$   
 337 isotherms, was indeed 0.7, 0.8, 1.1 and 0.6 nm for F200, F300, Acticarbone® and Cecalite®,  
 338 respectively. Acticarbone® had the highest fraction of mesoporosity (29 % of total volume  
 339 measurable by gas adsorption) while Cecalite® only had 3%. F200 and F300 had intermediate  
 340 and nearly identical mesoporous fractions of 22 and 21 %, respectively. The higher  
 341 supermicroporosity and mesoporosity of Acticarbone® is in good agreement with its higher  
 342 value of  $A_{BET}$  with respect to  $S_{DFT}$ .



345 **Fig 2** Adsorption-desorption isotherms of: (a)  $N_2$  at  $-196^\circ C$ , (b)  $CO_2$  at  $0^\circ C$ , and (c) PSDs  
 346 obtained from  $N_2$  and  $CO_2$  adsorption data; (d) PSDs obtained by mercury intrusion.

347

348 **Table 2:** Textural characteristics of the four activated carbons obtained by adsorption-  
 349 desorption of N<sub>2</sub> at -196°C and of CO<sub>2</sub> at 0°C, applying BET, DR and 2D-NLDFT methods.

Materials	$A_{BET}$ (m <sup>2</sup> .g <sup>-1</sup> )	$S_{DFT}$ (m <sup>2</sup> .g <sup>-1</sup> )	$V_{DR, N_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{DR, CO_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{0.97}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{\mu, NLDFT}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (%)
F200	795	971	0.28	0.24	0.39	0.30	0.09	22
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Acticarbone®	1014	967	0.35	0.18	0.56	0.38	0.16	29
Cecalite®	582	830	0.22	0.23	0.24	0.24	0.01	3

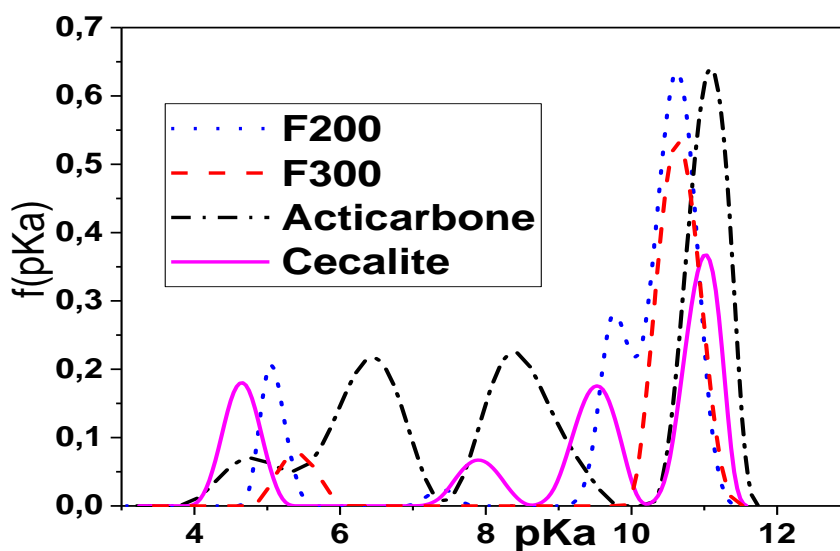
350

351 **Fig 2d** shows the PSDs obtained by mercury porosimetry. The highest porosity, i.e., the  
 352 volume fraction of macropores and of mesopores available to mercury, corresponds to  
 353 Acticarbone®, around 54.3 %. The porosity measurable with this technique for the other ACs  
 354 was 39.7%, 35.3% and 38.0% for F200, F300 and Cecalite®, respectively. The mercury  
 355 intrusion-extrusion curves are given in **Fig SI 4** of the supplementary information, evidencing  
 356 the entrapment of mercury when the pressure was decreased. This finding suggests the  
 357 presence of a significant amount of ink bottle-shaped pores, but also that irreversible  
 358 compression may have occurred under pressure. More information is also given in **Table SI**  
 359 **2**, suggesting that all ACs are different either in terms of macro/mesopore size (e.g. when  
 360 F200 and Cecalite® are compared) or in terms of amounts of pores of similar sizes (e.g. when  
 361 F300 and Acticarbone® are compared).

362

363 **Fig 3** shows the acidity distribution functions,  $f(pK_a)$ , of the four ACs. The resolution of  
 364 this method was demonstrated by using solutions of organic acids with known  $pK_a$  values  
 365 (Jagiello et al. 2000; Jagiello et al. 1995). At least four important functional groups were  
 366 evidenced, except for F300, which presented only two. Traditionally,  $pK_a = 3-8$  is the region

367 of carboxylic acids while  $pK_a = 8-10$  corresponds to the phenolic region (Bandosz et al. 1993;  
 368 Benaddi et al. 2000). The  $pK_a$  distribution curves showed the predominance of strongly basic  
 369 species such as hydroxyl functionalities (Zhang et al. 2015; Seredych et al. 2016). The amount  
 370 of very basic groups,  $pK_a > 10$ , accounts for nearly half of all functional groups of all ACs.  
 371 Therefore, all materials produced a pH slightly higher (1 to 1.4 pH unit) than that of the water  
 372 in which they were suspended, as shown by the values of  $pH_{Initial}$  presented in **Table SI 3**.  
 373 F200 and Acticarbone® had similar total amounts of surface groups, 1.145 and 1.150 mmol.g<sup>-1</sup>  
 374 <sup>1</sup>, respectively, and also a very similar  $pH_{PZC}$ , 7.20 and 7.36, respectively. F300 and Cecalite®  
 375 showed much less functional groups, 0.605 and 0.787 mmol.g<sup>-1</sup>, respectively, and slightly  
 376 higher  $pH_{PZC}$  of 8.03 and 7.75, respectively. **Table SI 3** also shows the results of the  
 377 potentiometric titration as well as  $pH_{PZC}$  and  $pH_{Initial}$  values for all ACs studied.



378  
 379 **Fig 3** Density of functional groups of all studied ACs.

380  
 381 **3.2 Adsorption of dyes**

382 In order to explain the adsorption kinetics and isotherms of MB and MO, the experimental  
 383 data were non-linearly fitted by using the *Levenberg Marquardt* iteration algorithm supplied  
 384 with OriginPro 2016 Software®. PFO, PSO and BSf models were used to fit the kinetic data.

385 Langmuir, Freundlich, Jovanovich, HS, BS, BG and GBS models were used to fit the  
386 adsorption isotherms.

### 387 **3.2.1 Effect of pH, temperature and thermodynamic analysis on MB and MO adsorption**

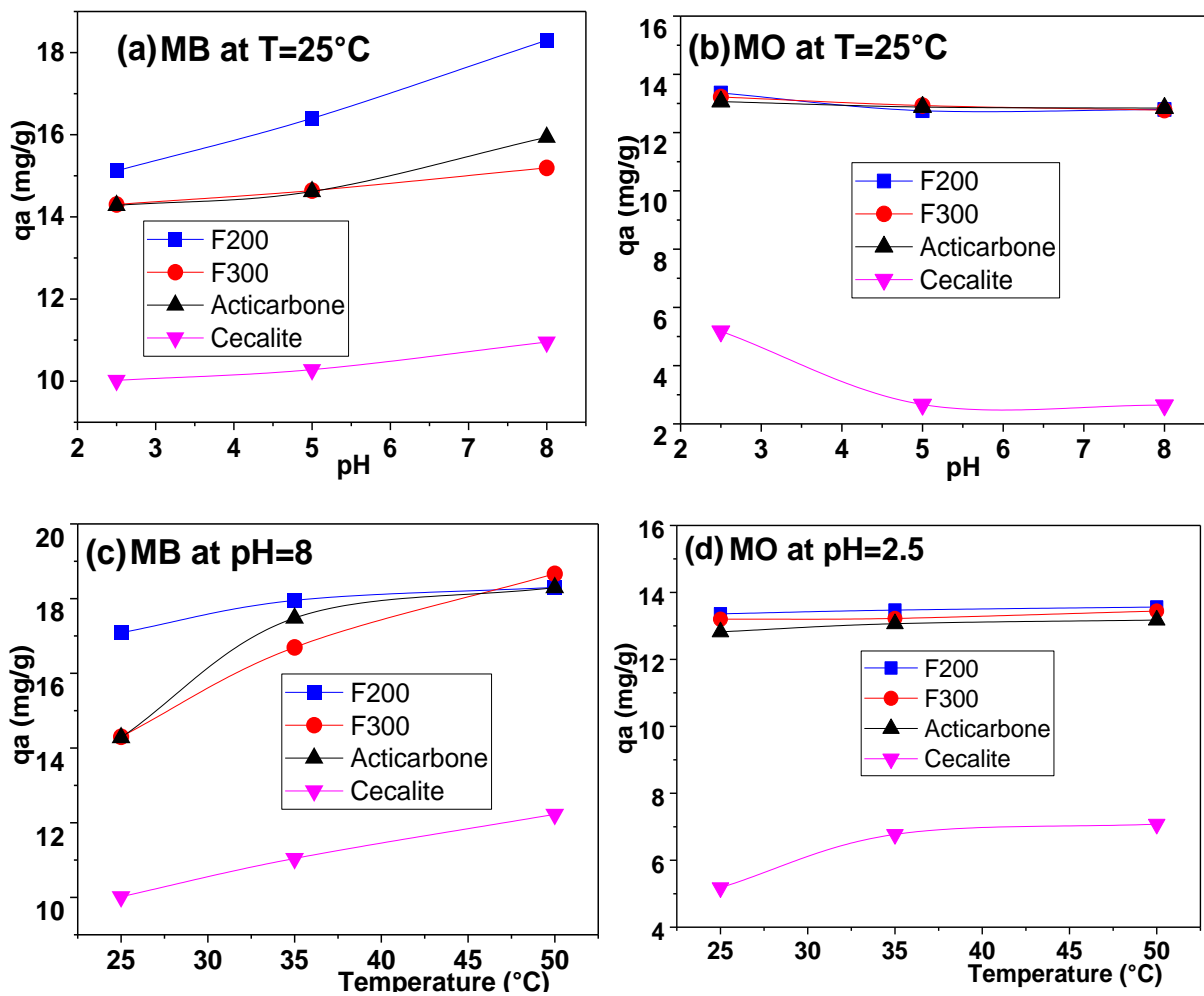
388 **Fig 4** shows the effect of pH and temperature on the removal of MB and MO by ACs. The  
389 removal efficiency was enhanced when the temperature increased from 25 to 50°C, indicating  
390 the endothermic character of the adsorption (Kesraoui et al. 2016). The removal efficiency  
391 also increased when the pH increased from 2.5 to 8 for MB adsorption, but decreased for MO  
392 adsorption. Rodríguez et al. found a similar result for the adsorption of MB and Orange II  
393 dyes on ACs (Rodríguez et al. 2009). This finding may be ascribed to the increase or decrease  
394 of repulsive and attractive forces between surface functional groups of ACs and anion of dyes  
395 used, which depend on  $pH_{PZC}$  values. The anionic dyes are indeed favourably adsorbed at  
396 acidic  $pH < pH_{PZC}$ , at which the surface is positively charged. On the contrary, cationic dyes  
397 are better adsorbed on anionic sites of the adsorbent surface when the latter is globally  
398 negatively charged for  $pH > pH_{PZC}$  (Kesraoui et al. 2016).

399 Thermodynamic parameters such as Gibbs free energy  $\Delta G^\circ$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ), enthalpy  $\Delta H^\circ$   
400 ( $\text{kJ}\cdot\text{mol}^{-1}$ ), and entropy  $\Delta S^\circ$  ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) were determined and are listed in

401  
402 **Table 3.** The positive value of  $\Delta H^\circ$  for MB and MO in the presence of all ACs indicates  
403 the endothermic nature of the adsorption process. The positive values of  $\Delta S^\circ$  correspond to an  
404 increase of disorder at the interface between dyes and the surface of all samples used  
405 (Bouhamed et al. 2016; Kesraoui et al. 2016), the absolute values reflecting the affinity of the  
406 adsorbents for those dyes. With only one exception, MO on Cecalite® at 25°C, the values of  
407  $\Delta G^\circ$  were always negative, showing the spontaneous nature of adsorption of MB and MO  
408 onto all ACs used (Acosta et al. 2016).  $\Delta G^\circ$  indeed varied from -10.70 to -19.51  $\text{kJ}\cdot\text{mol}^{-1}$ ,

409 suggesting the highly favourable adsorption of those molecules onto Acticarbone®, F300, and  
 410 F200. In contrast, adsorption was only slightly favourable on Cecalite®, which exhibited  
 411 absolute values of  $\Delta G^\circ$  one order of magnitude lower than those observed for the other ACs.  
 412 And especially, MO adsorption at pH 2.5 was even unfavourable at room temperature, as  
 413 shown by the positive value of  $\Delta G^\circ$  and the correspondingly lower values of  $\Delta H^\circ$  and  $\Delta S^\circ$   
 414 with respect to those of other activated carbons. A similar result was reported elsewhere  
 415 (Rodríguez et al. 2009).

416



417

418

419 **Fig 4** Effect of: (a, b) pH at 25°C and (c, d) temperature, on the adsorbed amount at  
 420 equilibrium of: (a, c) MB at pH 8, and (b, d) MO at pH 2.5, onto all ACs ( $C_0 = 40 \text{ mg.L}^{-1}$ )

421

422 **Table 3:** Thermodynamic parameters for the adsorption of MB and MO onto all activated  
 423 carbons samples at different temperatures and  $C_0 = 40 \text{ mg.L}^{-1}$ .

Samples	Dye	pH	$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )		
					25°C	35°C	50°C
F200	MB	8	49.40	212.50	-14.30	-15.60	-19.50
	MO	2.5	16.10	95.70	-12.50	-13.30	-14.90
F300	MB	8	16.60	100.70	-13.40	-14.30	-15.90
	MO	2.5	63.20	247.60	-10.70	-12.90	-16.80
Acticarbhone®	MB	8	20.10	112.80	-13.20	-15.10	-16.00
	MO	2.5	25.40	121.80	-11.20	-11.70	-14.20
Cecalite®	MB	8	11.10	40.80	-1.20	-1.30	-2.20
	MO	2.5	19.00	61.30	1.00	-0.20	-0.60

424

425

### 426 3.2.2 Kinetic models

427

428 **Table 4** shows the kinetic parameters obtained for initial dye concentrations equal to 10,  
429 40, 60, and 80 mg.L<sup>-1</sup> by application of the BSf model to the MB and MO adsorption data on  
430 Acticarbhone®. Equivalent data for the other 3 ACs are given in **Table SI 4**, **Table SI 5** and  
431 **Table SI 6** of the Supplementary Information. Fits were performed for values of  $n = 1$ , 1.5  
432 and 2. Although the determination parameter,  $R^2$ , was always very high, the best fit for MB  
433 adsorption was achieved with the reaction order fixed at  $n = 1$ . Similar results were obtained  
434 when MB was biosorbed on *Agave Americana* fibres (Ben Hamissa et al. 2013), and when  
435 Indigo Carmine dye was adsorbed on activated carbon (Kesraoui et al. 2016). Based on the  
436 determination coefficient, and given the fact that  $\alpha$  describes better the heterogeneity of the  
437 surface when its value doesn't exceed 1 (Brouers 2014a), the kinetics is also expected to be of  
438 order 1. For MO, excellent fits were also obtained with  $n = 1$  although the highest values of  
439  $R^2$  were obtained with  $n = 1.5$  or  $n = 2$  (see the data for the other ACs in **Table SI 4**, **Table SI**  
440 **5** and **Table SI 6** of the Supplementary Information).

441 Since, on average, excellent fits were found for all ACs with  $n = 1$ , which is the value  
442 leading most frequently to the highest determination coefficient, it was assumed that the

443 adsorption of MB and MO dyes on all ACs follows first-order kinetics. Fixing the reaction  
 444 order  $n = 1$  was indeed necessary to compare the BSf kinetics to other models.

445 **Fig 5** shows the experimental kinetic data and the calculated curves when  $n$  was fixed to 1  
 446 for MB and MO adsorption on Acticarbone®: a very good fit was obtained for all initial  
 447 concentrations from 5 to 80 mg.L<sup>-1</sup>, for both dyes. Equally good fits were obtained for the  
 448 other three ACs, and the corresponding results are given in **Fig SI 5**.

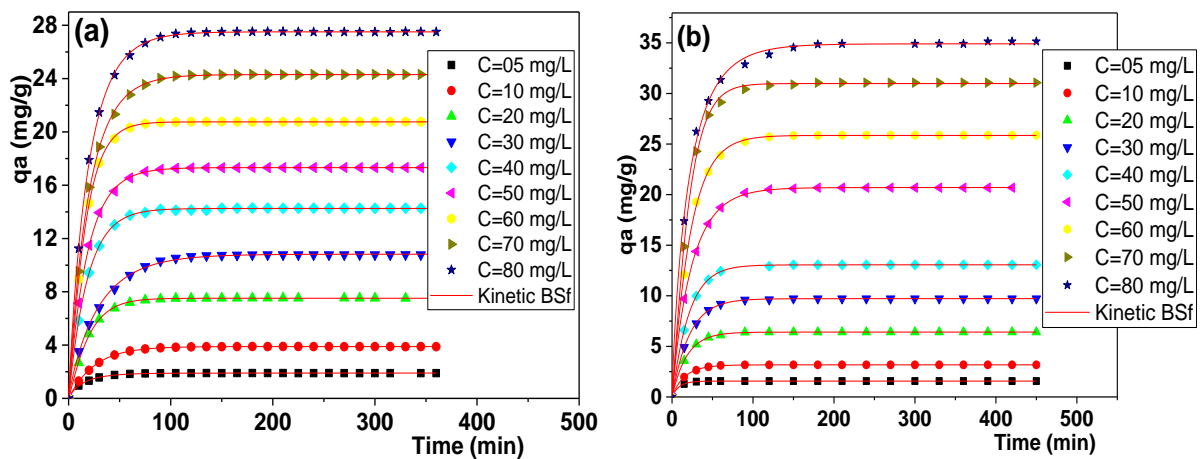
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450

451 **Table 4:** Effect of reaction order  $n$  on BSf kinetics parameters obtained by non-linear fit of  
 452 the adsorption of MB at pH 8 and MO at pH 2.5 on Acticarbone® at 25°C.

		Initial concentration of MB and MO (mg.L <sup>-1</sup> )											
		10			40			60			80		
		$\tau_c$	$\alpha$	$R^2$	$\tau_c$	$\alpha$	$R^2$	$\tau_c$	$\alpha$	$R^2$	$\tau_c$	$\alpha$	$R^2$
MB	$n = 1$	25.14	1.01	<u>1.00</u>	18.61	1.02	<u>1.00</u>	16.79	1.09	<u>1.00</u>	19.42	0.93	<u>1.00</u>
	$n = 1.5$	20.09	1.32	0.998	14.98	1.36	0.999	13.69	1.47	1.00	15.45	1.26	0.999
	$n = 2$	17.29	1.62	0.996	13.00	1.72	0.998	12.01	1.89	0.998	13.31	1.60	0.998
MO	$n = 1$	15.70	0.95	<u>1.00</u>	22.52	1.11	0.999	23.00	1.03	1.00	22.09	0.84	0.998
	$n = 1.5$	13.07	1.39	0.999	17.16	1.41	<u>1.00</u>	18.72	1.40	<u>1.00</u>	17.59	1.16	0.999
	$n = 2$	11.86	1.91	1.00	15.15	1.84	0.999	16.46	1.81	0.999	15.30	1.5	<u>1.00</u>

453



454

455 **Fig 5** BSf (1, $\alpha$ ) kinetics model applied to the adsorption of: (a) MB at pH 8 and (b) MO at pH  
 456 2.5, onto Acticarbone® for different initial concentrations at 25°C.

457

458 **Fig SI 6** shows the non-linear fit of the adsorption data kinetics of MB at pH 8 and of MO  
 459 at pH 2.5 onto Acticarbone® by the models listed in the experimental section (i.e., Pseudo-  
 460 first-order (PFO), Pseudo-second-order (PSO) and Brouers-Sotolongo fractal (BSf(1, $\alpha$ ))). The  
 461 corresponding kinetic models parameters are summarised in **Table 5**. For selecting the best  
 462 one, values of determination coefficients,  $R^2$ , and errors,  $\chi^2$ , were examined. For example, for  
 463 MO adsorption on F300 samples,  $R^2$  was found to be equal to 0.998, 0.992 and 1 for PFO,  
 464 PSO and BSf(1, $\alpha$ ), respectively, hence the Weibull equation ( $\alpha \neq 1$  and  $n = 1$ ) was the most  
 465 relevant one for fitting the kinetic data.

466

467 **Table 5:** Kinetic parameters obtained by fitting the experimental data with PFO, PSO and BSf  
 468 models ( $C_0 = 40 \text{ mg.L}^{-1}$  of MO at pH 2.5 and of MB at pH 8, at 25°C).

	MB				MO			
Samples	F200	F300	Acticarbone	Cecalite	F200	F300	Acticarbone	Cecalite
$q_{e,exp}$	18.30	14.30	14.28	10.02	13.36	13.22	13.06	5.18
PFO								
$q_{e,1}$	18.37	14.26	14.26	11.11	13.25	13.15	13.07	4.72
$k_1$	0.02	0.04	0.05	0.007	0.02	0.06	0.05	0.01
$R^2$	0.992	<u>0.999</u>	1	0.988	0.996	0.998	1	0.954
$\chi^2$	0.224	<u>0.009</u>	0.002	0.138	0.055	0.019	0.002	0.101
$h_1$	0.36	0.64	0.77	0.07	0.31	0.73	0.63	0.05
PSO								
$q_{e,2}$	21.35	15.31	15.13	15.27	14.73	13.74	13.74	5.70
$k_2$	0.001	0.005	0.006	0.001	0.002	0.008	0.006	0.002
$R^2$	0.974	0.979	0.976	0.999	0.995	0.992	0.981	0.982
$\chi^2$	0.728	0.243	0.253	0.114	0.082	0.091	0.220	0.038
$h_2$	0.50	1.10	1.40	0.09	0.47	1.45	1.17	0.07
BSf(1, $\alpha$ )								
$q_{e,BS}$	18.23	14.26	14.25	14.10	13.41	13.19	13.06	8.03



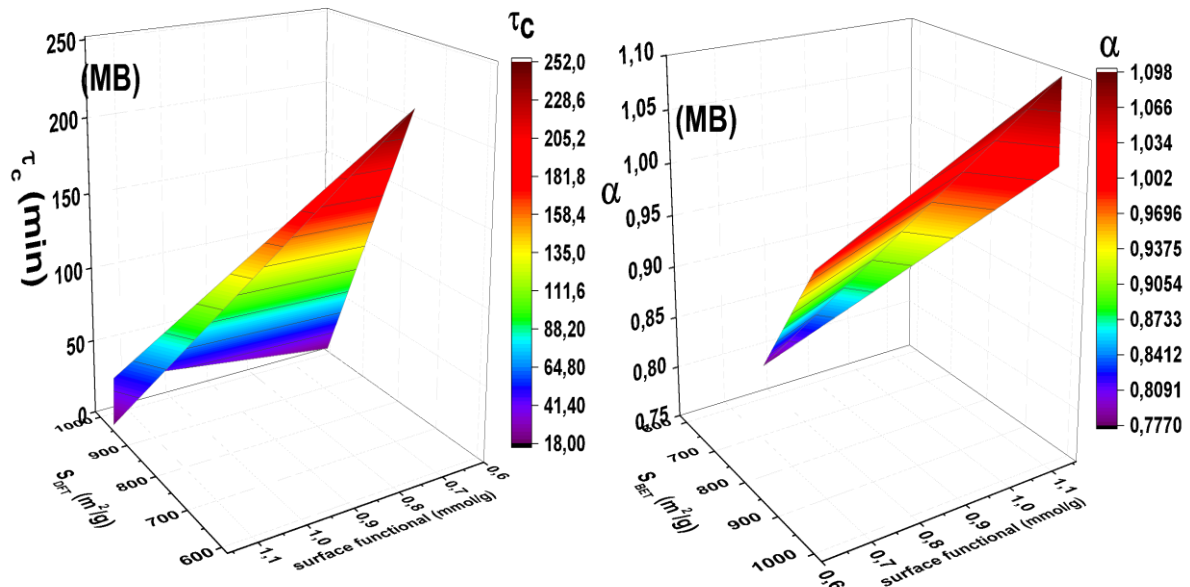
$\tau_c$	49.94	22.19	18.61	251.47	44.03	17.33	21.02	453.11
$\tau_{1/2}$	16.73	6.60	5.71	53.73	10.54	4.24	6.61	43.03
$\alpha$	1.10	0.99	1.02	0.78	0.84	0.85	1.04	0.51
$R^2$	<u>0.993</u>	0.999	<u>1</u>	<u>0.993</u>	<u>1</u>	<u>1</u>	<u>1</u>	<u>0.997</u>
$\chi^2$	<u>0.199</u>	0.010	<u>0.002</u>	<u>0.083</u>	<u>0.004</u>	<u>0.004</u>	<u>0.001</u>	<u>0.007</u>

469

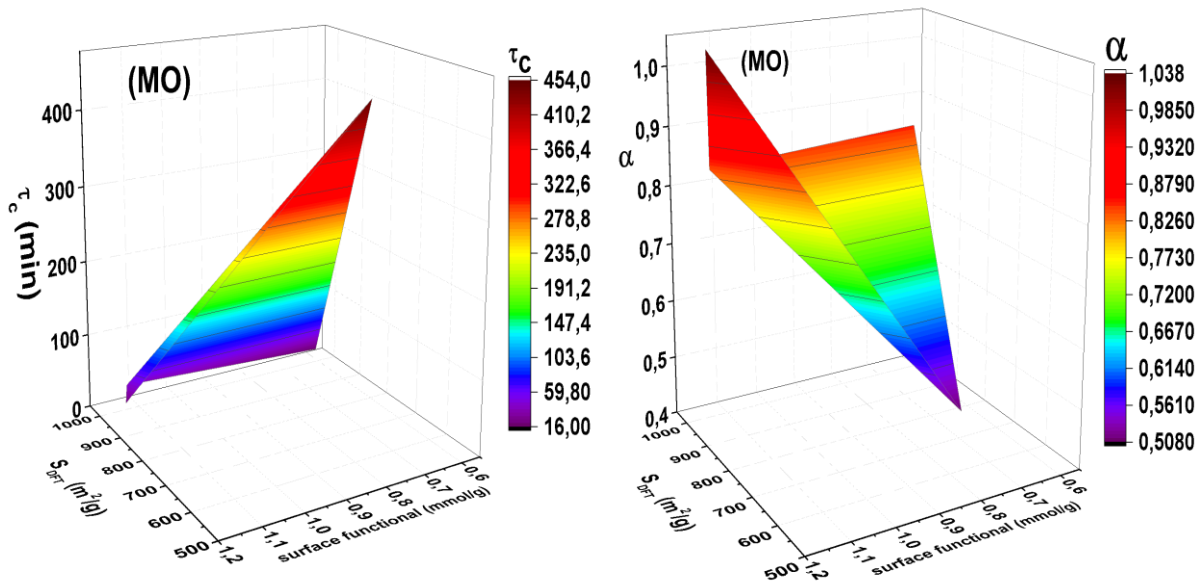
470 Relationships between fractal constants of BSf derived from the fits of this model to the  
471 adsorption data,  $\tau_c$  and  $\alpha$ , and their physicochemical properties of ACs,  $S_{DFT}$  and surface  
472 functional groups, were looked for. Gaspard et al. (Gaspard et al. 2006) already showed that  
473 BSf parameters are indeed correlated with the fractal dimension  $D$  for the adsorption of  
474 phenol and tannic acid onto three commercial ACs, and onto two ACs derived from *Vetiveria*  
475 *zizanioides*.

476 **Fig 6** shows the effect of  $S_{DFT}$  and surface functional groups on the BSf(1, $\alpha$ ) constants  $\tau_c$   
477 and  $\alpha$  for the adsorption of MB and MO dyes. Certain correlation between  $\alpha_{MB}$ ,  $\alpha_{MO}$  and  $S_{DFT}$   
478 and amount of functional groups can be seen. The constant  $\tau_c$  is also clearly correlated with  
479  $S_{DFT}$  and with the amount of functional groups. Constant  $\alpha$  is always inferior to 1 ( $0.51 < \alpha <$   
480  $0.99$ ) for the adsorption of MB onto F300 and Cecalite® and for the adsorption of MO onto  
481 F200, F300 and Cecalite®, clearly suggesting fractal adsorption. In contrast, for the  
482 adsorption of MB onto Acticarbon® and F200, and for the adsorption of MO onto  
483 Acticarbon®, the kinetic is not clearly fractal because the constant  $\alpha$  is higher than 1  
484 (Brouers et al. 2005; Ben Hamissa et al. 2013; Brouers 2014a).

485



486



487

488 **Fig 6** Effect of  $S_{DFT}$  and amount of surface functional groups on the BSf(1, $\alpha$ ) constants  $\tau_c$  and  
 489  $\alpha$  determined by adsorption of MB at pH 8 (top) and of MO at pH 2.5 (bottom) ( $C_0 = 40$   
 490  $\text{mg.L}^{-1}$ ,  $25^\circ\text{C}$ ).

491

492 On one hand, the increase of  $S_{DFT}$  makes the initial speed of the adsorption increase, and  
 493 consequently the characteristic time of adsorption  $\tau_c$  of MO and MB decreases. Therefore, the  
 494 time of half-reaction also decreases. On the other hand, the increase of the amount of surface  
 495 functional groups increases the characteristic time  $\tau_c$  towards an extremum before decreasing.

496 Despite the increase of the amount of surface functional groups from 0.60 to 0.79 mmol.g<sup>-1</sup>  
497 from F300 to Cecalite®, F300 being more porous than Cecalite®, the characteristic time  
498 increased from 22 to 251 min for MB adsorption, and from 17 to 452 min for MO adsorption.  
499 This shows that the effect of porosity is much more important than that of surface chemistry  
500 in agreement with previous studies (Brouers,Al-Musawi 2015; Jaramillo et al. 2012), and  
501 suggests that electrostatic interactions have a poor influence for retaining MB and MO at the  
502 surface of the ACs used. In other words, the surface functional groups have a significant  
503 impact on the kinetics of adsorption, but that of the nature of the porosity is even more  
504 important (Mailler et al. 2016).

505 The fractal constant  $\alpha$  increases with the specific surface area,  $S_{DFT}$ , due to the difference  
506 of porosity between the materials. This suggests that the fractal character of the surface  
507 increases due to its higher geometrical heterogeneity (Brouers,Al-Musawi 2015). Moreover,  
508 this result was also confirmed by the increase of  $\alpha$  with the number of functional surface  
509 groups, leading to chemical heterogeneity (Kesraoui et al. 2016). Finally, it can be noticed  
510 that the degree of fractality,  $\alpha$ , and the characteristic time,  $\tau_c$ , are inversely proportional to the  
511 number of functional groups.

### 512 **3.2.3 Adsorption isotherms**

513 A stochastic analysis of physicochemical reactions in complex systems  
514 (Stanislavsky,Weron 2013) showed that the exponent  $c$  is related to clustering or  
515 agglomeration at the surface of the adsorbent (i.e., the constant  $c$  gives an idea of the degree  
516 of heterogeneity of the adsorbent since its value is inversely proportional to the surface  
517 heterogeneity). **Table 6** shows the effect of changing the constant  $c$  in the GBS model on the  
518 quality of the fits, seen through the resultant changes of determination coefficient,  $R^2$ . The fits  
519 were performed with  $c = 0, 0.5$  and  $1$  (i.e., correspond to BS, BG and HS isotherm models,  
520 respectively), and the best ones were obtained with the BS model ( $c = 0$ ) for the adsorption of

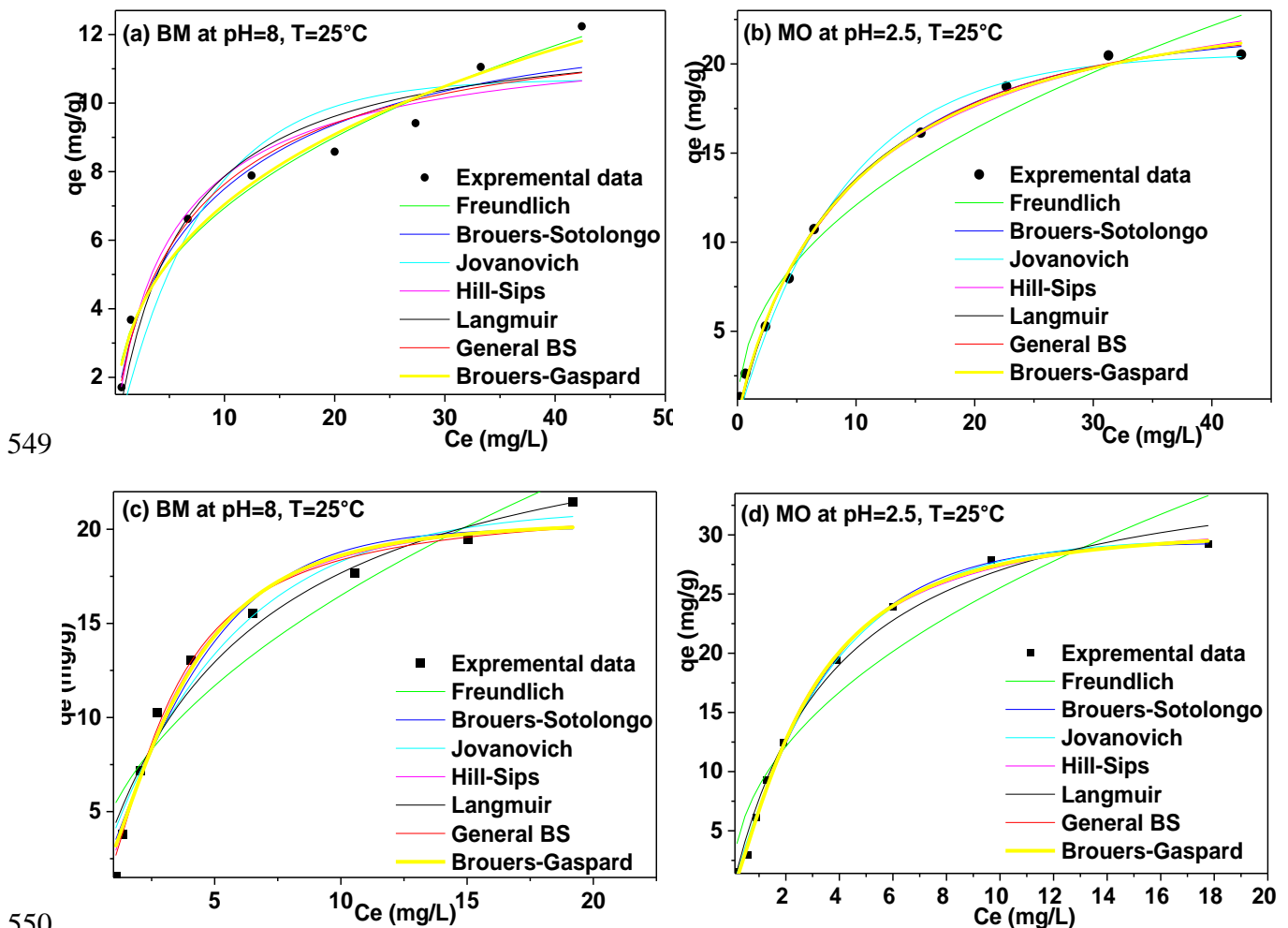
521 MB on all ACs except F300, best described by HS model ( $c = 1$ ). Similar results were  
 522 obtained when  $Pb^{2+}$  was biosorbed onto algal biomass (Brouers,Al-Musawi 2015). The  
 523 isotherms of MO adsorption onto F200 and Acticarbon® were best described by BG  
 524 isotherm ( $c = 0.5$ ). MB and MO adsorption isotherms onto F300 were very well described by  
 525 the HS model, indicating a poorly heterogeneous surface. In contrast, MB and MO isotherms  
 526 adsorption onto Cecalite® were best fitted by the BS model, indicating the high heterogeneity  
 527 of the surface. Generally, MB and MO adsorption isotherms onto all samples were adequately  
 528 described by HS, BG and BS models, indicating the presence of active sites with  
 529 heterogeneous sorption interactions (Brouers,Al-Musawi 2015).

530 **Table 6:** Effect of constant  $c$  of GBS isotherm model obtained by non-linear fit of adsorption  
 531 data of MB at pH 8 and MO at pH 2.5 onto all ACs at 25°C.

GBS		$R^2$			
		F200	F300	Acticarbon®	Cecalite®
MB	$c = 0$	<u>0.998</u>	0.961	<u>0.983</u>	<u>0.970</u>
	$c = 0.5$	0.997	0.976	0.971	0.969
	$c = 1$	0.996	<u>0.983</u>	0.979	0.970
MO	$c = 0$	0.998	0.989	0.997	<u>0.997</u>
	$c = 0.5$	<u>0.998</u>	0.993	<u>0.998</u>	0.995
	$c = 1$	0.998	<u>0.995</u>	0.997	0.994

532  
 533 In order to compare the stochastic isotherm models to more classical models, and to avoid  
 534 deciding between BS and HS models whose fits are equally good, the BG model was used  
 535 (Brouers,Al-Musawi 2015) (i.e., with the constant  $c$  fixed at 0.5). **Fig 7** shows the fit of the  
 536 adsorption data of MB at pH 8 and MO at pH 2.5 on Cecalite® and Acticarbon® by the  
 537 models listed in the experimental section (i.e., Freundlich, Langmuir, Jovanovich, BS, HS,  
 538 and BG). The corresponding models parameters and the  $R^2$  values are listed in **Table 7** and in  
 539 **Table SI 7**. Based on  $R^2$ , Freundlich, Jovanovich and Langmuir models (**Table SI 7**) were not

540 appropriate for fitting MB and MO adsorption isotherms. HS and BG models seemed to be  
 541 more adequate, but the BS model gave the best fits for all pH and temperatures tested (see  
 542 **Table 7**). Brouers and Al-Musawi (Brouers,Al-Musawi 2015) explained that this finding is  
 543 related to the presence of active sites on a physically and chemically heterogeneous surface.  
 544 Chemical heterogeneity is the result of different functional groups such as carbonyls,  
 545 carboxyls, phenols, lactones, amines, aldehydes, as well as delocalised electrons determining  
 546 the more or less acidic / basic nature of ACs, as seen from the potentiometric titration  
 547 technique (Jagiello 1994). Geometrical heterogeneity is due to pores of different sizes and  
 548 morphologies (Jagiello,Olivier 2013).



551 **Fig 7** Non-linear fits of isotherm data at 25°C by several isotherm models for the adsorption  
 552 of: (a, c) MB at pH 8, and (b, d) MO at pH 2.5 on (a, b) Cecalite® and (c, d) Acticarbon®.

553

554 A correlation was looked for between the constants  $a$  and  $b$ , derived from a stochastic  
555 model of GBS isotherm adsorption in the case  $c = 0.5$  (i.e., BG model), and  $S_{DFT}$  and amount  
556 of surface functional groups. Constants  $a$  and  $b$  were calculated by fitting the isotherm data of  
557 MB and MO adsorption on all ACs. **Fig 8** shows the effect of  $S_{DFT}$  and surface functional  
558 groups on the BG constants  $a$  and  $b$  for the adsorption of MB and MO dyes. Correlations were  
559 indeed observed: the constant  $a$  initially decreased with the amount of functional groups then  
560 increased, clearly proving that the reaction of adsorption was initially fast. It can be concluded  
561 that there is a close relationship between the exponent  $a$  and the fractal character of the  
562 surface due to its heterogeneity (Ben Hamissa et al. 2007). When the surface heterogeneity  
563 decreased, the exponent constant  $a$  increased.

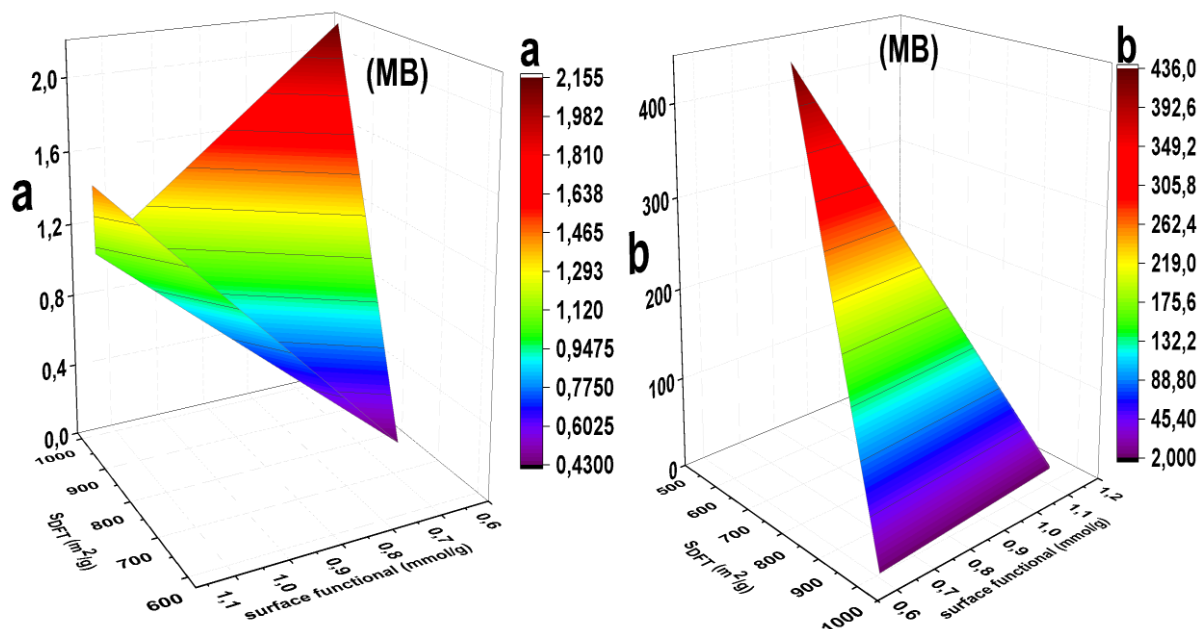
564

565 **Table 7:** Isotherm parameters of Brouers-Sotolongo, Hill-Sips and Brouers-Gaspard models  
566 fitted to the adsorption data of MB and MO at pH 8 and 2.5, respectively, and at 25°C.

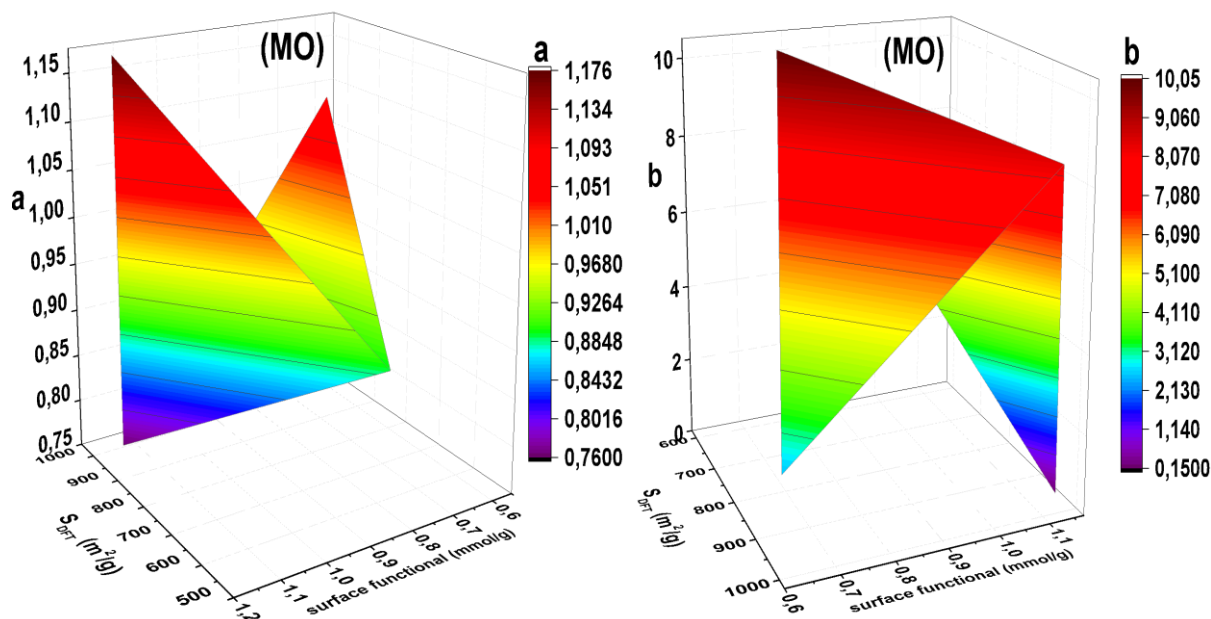
Dyes	MB				MO			
Samples	F200	F300	Acticarbone	Cecalite	F200	F300	Acticarbone	Cecalite
Brouers-Sotolongo								
$q_{e\ max}$	29.42	22.82	20.07	12.31	36.79	29.23	29.37	21.97
$a$	0.99	1.80	1.20	0.61	0.73	0.95	1.05	0.82
$b$	2.39	2.66	4.28	11.08	7.89	2.96	3.56	10.70
$Ce_{1/2}$	0.71	1.36	1.57	1.55	1.51	0.84	1.13	2.49
$\chi^2$	0.18	2.43	1.93	0.55	0.26	1.20	0.41	0.20
$R^2$	<u>0.998</u>	0.973	0.971	0.963	0.998	0.992	0.997	<u>0.998</u>
Hill-Sips								
$q_{e\ max}$	35.04	23.96	21.11	12.39	48.86	32.35	31.99	26.78
$a$	1.14	2.49	1.69	0.87	0.79	1.20	1.34	0.93
$b$	2.15	2.19	3.16	5.29	8.95	2.24	2.69	9.96
$Ce_{1/2}$	2.15	2.19	3.16	5.29	8.9	2.24	2.69	9.96
$\chi^2$	0.39	1.13	1.11	0.80	0.21	0.61	0.40	0.36
$R^2$	0.997	<u>0.987</u>	<u>0.983</u>	0.946	<u>0.999</u>	<u>0.996</u>	0.997	0.995
Brouers-Gaspard								
$q_{e\ max}$	32.09	23.37	20.54	41.48	42.82	30.67	30.80	24.24
$a$	1.08	2.15	1.46	0.43	0.76	1.09	1.17	0.89
$b$	2.22	2.37	3.56	434.33	8.36	2.50	3.03	10.03

$Ce_{1/2}$	1.86	2.17	3.13	280.36	6.53	2.10	2.58	8.12
$\chi^2$	0.29	1.58	1.40	0.40	0.23	0.80	0.20	0.30
$R^2$	0.997	0.976	0.971	0.969	<u>0.998</u>	0.993	<u>0.998</u>	0.995

567



568



569

570 **Fig 8** Effect of  $S_{DFT}$  and amount of surface functional groups on the GBS ( $c = 0.5$ ) constants  $a$   
 571 and  $b$  determined from adsorption at 25°C of MB at pH 8 and of MO at pH 2.5.

572

573 Higher porosity of ACs increased the adsorption capacity and made the reaction faster, as  
 574 observed by the increase of the constant  $a$ . Such increase is the result of geometrical

575 heterogeneity, which is due to differences of pores sizes and shapes, and to cracks and pits  
 576 (Ncibi et al. 2008; Francois, Francisco 2016; Altendor et al. 2012). The constant  $a$  of BG  
 577 mentioned in **Table 7** and the rate constants of initial kinetics of adsorption,  $h_1$  and  $h_2$  (**Table**  
 578 **5**), increase with the porosity of ACs (

579 **Table 2:** Textural characteristics of the four activated carbons obtained by adsorption-  
 580 desorption of N<sub>2</sub> at -196°C and of CO<sub>2</sub> at 0°C, applying BET, DR and 2D-NLDFT methods.

Materials	$A_{BET}$ (m <sup>2</sup> .g <sup>-1</sup> )	$S_{DFT}$ (m <sup>2</sup> .g <sup>-1</sup> )	$V_{DR, N_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{DR, CO_2}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{0.97}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{\mu, NLDFT}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (cm <sup>3</sup> .g <sup>-1</sup> )	$V_{mes}$ (%)
F200	795	971	0.28	0.24	0.39	0.30	0.09	22
F300	884	1003	0.35	0.28	0.43	0.34	0.09	21
Acticarbone®	1014	967	0.35	0.18	0.56	0.38	0.16	29
Cecalite®	582	830	0.22	0.23	0.24	0.24	0.01	3

581

582 **Fig 2d** shows the PSDs obtained by mercury porosimetry. The highest porosity, i.e., the  
 583 volume fraction of macropores and of mesopores available to mercury, corresponds to  
 584 Acticarbone®, around 54.3 %. The porosity measurable with this technique for the other ACs  
 585 was 39.7%, 35.3% and 38.0% for F200, F300 and Cecalite®, respectively. The mercury  
 586 intrusion-extrusion curves are given in **Fig SI 4** of the supplementary information, evidencing  
 587 the entrapment of mercury when the pressure was decreased. This finding suggests the  
 588 presence of a significant amount of ink bottle-shaped pores, but also that irreversible  
 589 compression may have occurred under pressure. More information is also given in **Table SI**  
 590 **2**, suggesting that all ACs are different either in terms of macro/mesopore size (e.g. when  
 591 F200 and Cecalite® are compared) or in terms of amounts of pores of similar sizes (e.g. when  
 592 F300 and Acticarbone® are compared).



593 ). However, when  $a < 1$ , a slow initial sorption kinetics is observed and all sites don't have  
594 the same energy as assumed by Langmuir (Langmuir 1918), whereas when  $a > 1$ , a fast initial  
595 sorption kinetics occurs and there is probably more than one molecule sorbed by active site. It  
596 can be concluded that the exponent  $a$  expresses the fractal properties of a heterogeneous  
597 system and of its related adsorption mechanisms (Brouers 2014a; Kesraoui et al. 2016;  
598 Brouers,Al-Musawi 2015; Francois,Francisco 2016).

599 Regarding the constant  $b$ , **Fig 8** shows that the increase of the porosity from Cecalite® to  
600 Acticarbone® decreased the constant  $b$  from 10.05 to 0.15 mg/L for MO, and from 436.00 to  
601 2.00 mg.L<sup>-1</sup> for MB. However, there is no clear effect of the amount of functional surface  
602 groups on the constant  $b$ , making difficult to establish whether porosity has a predominant  
603 role over surface functions in that case (Jaramillo et al. 2012; Brouers,Al-Musawi 2015).

604

#### 605 **4. Conclusions**

606 In the present study, four micro/mesoporous activated carbons (ACs: Acticarbone® and  
607 Cecalite® from CECA Company, and F300 and F200 from Calgon Corporation) were  
608 thoroughly characterised. From the many different techniques that were used, the main  
609 porous, structural, nanotextural and physicochemical features of those materials could be  
610 accurately determined.

611 Their adsorption properties with respect to methylene blue (MB) and methyl orange (MO)  
612 were investigated at different pH and temperatures. For all ACs, both MB and MO uptakes  
613 increased with temperature. However, due to the different cationic / anionic natures of those  
614 dyes, the adsorption of MB increased with pH, whereas that of MO decreased with pH.

615 The thermodynamics studies revealed that the adsorption process is spontaneous and  
616 endothermic, and the kinetic studies showed that, in all cases, the Brouers-Sotolongo fractal

617 kinetic model (BSf) was the best for describing the adsorption process. Although changing the  
618 reaction order  $n$  had a low impact on the quality of the fits, suggesting that this parameter is  
619 not very important, the best results were most of the time obtained with  $n = 1$ . The fractal time  
620 parameter  $\alpha$  of the BSf kinetic model increased with both surface area and amount of surface  
621 functional groups of the AC, due to the correspondingly increased geometrical and chemical  
622 heterogeneity.

623 The adsorption isotherm studies showed that both Brouers-Sotolongo (BS) and Hill-Sips  
624 (HS) models fitted the experimental data quite well. For comparing those stochastic models  
625 with more classical ones, and as it was difficult to decide between BS and HS isotherms, we  
626 fixed the parameter  $c = 0.5$ , thus corresponding to the Brouers-Gaspard (BG) equation. It was  
627 seen that the constant  $a$  of the model decreased with the amount of surface functional groups,  
628 but increased with the surface area. Now,  $a < 1$  suggests a slow initial sorption and that all the  
629 sites do not have the same energy, whereas  $a > 1$  corresponds to a fast initial sorption and to  
630 more than one molecule sorbed by active site. The behaviour experimentally observed for  $a$   
631 thus indicates that the latter is a measure of the scaling (fractal) properties of the AC surface.  
632 The parameter  $c$  of the same model is related to the agglomeration and clustering of AC  
633 particles, or to the fractal distribution of mesopores. The constants of the BG isotherm could  
634 also be correlated with physicochemical characteristic of the ACs.

635 To sum up, the stochastic and fractal models of Brouers-Sotolongo, which are non-  
636 empirical complex models established from a probabilistic calculation, are the most adequate  
637 to describe the adsorption of dyes on ACs, and provide a meaningful physicochemical  
638 explanation of the different adjustable parameters. However, more investigations based on  
639 microscopy observations are needed to confirm the relationships between the constant  $c$  and  
640 agglomeration of AC particles or fractal distribution of pores. Another point to be studied is  
641 the determination of the adsorption energy distributions. These objectives will be fulfilled in

642 the near future, as well as the search for possible correlations between pH and temperature  
643 and the stochastic parameters.

#### 644 **Supplementary information**

645 SI includes results and discussion on ACs characterisation by elemental analysis,  
646 thermogravimetric analysis in air, Raman spectroscopy, XRD, potentiometric titration and  
647 intrusion-extrusion of mercury.

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654 funds.

655

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816 **Figure captions**

817 Fig 1 SEM pictures of activated carbons used here: (a) F200, (b) F300, (c) Acticarbone®, and  
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819 Fig 2 Adsorption-desorption isotherms of: (a) N<sub>2</sub> at -196°C, (b) CO<sub>2</sub> at 0°C, and (c) PSDs  
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827 Fig 6 Effect of  $S_{DFT}$  and amount of surface functional groups on the BSf(1,α) constants  $\tau_c$  and  
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