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► To cite this version:

Angela Sanchez-Sanchez, Flavia L. Braghiroli, M.T. T Izquierdo, Julien Parmentier, Alain Celzard, et al.. Synthesis and properties of carbon microspheres based on tannin-sucrose mixtures treated in hydrothermal conditions. *Industrial Crops and Products*, 2020, 154, pp.112564. 10.1016/j.indcrop.2020.112564 . hal-03041960

HAL Id: hal-03041960

<https://hal.univ-lorraine.fr/hal-03041960>

Submitted on 5 Dec 2020

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23 Abstract

24 Sustainable carbon materials have been synthesised by use of inexpensive natural
25 precursors, tannin and sucrose, mixed in aqueous solution in various proportions (from 0:1 to
26 1:0), and then submitted to hydrothermal carbonisation (HTC) at various pH (from 2 to 8) and
27 temperatures (160, 180 or 200°C). The resultant hydrochars were finally pyrolysed at 900°C
28 under nitrogen flow to produce highly porous carbon materials with BET areas as high as 810
29 m²/g without activation. The effects of the initial tannin/sucrose weight ratios and of the HTC
30 conditions were investigated in terms of final particle size (from 1 to 10 µm), carbon yield
31 (from 30 to 45%), composition (C from 88 to 93 wt. %; O from 6 to 10 wt. %), surface
32 chemistry (C from 88 to 98 at. %; O from 2 to 12 at. %) and porous texture (NLDFT surface
33 areas and micropore volumes from 840 to 1420 m²/g and from 0.23 to 032 cm³/g,
34 respectively). All these parameters were discussed and correlated with the electrochemical
35 properties of the same materials. Special attention was paid to the separate roles of porosity
36 and surface chemistry, and on the reversibility of the electrochemical reactions.

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43 **Keywords:** Tannin; Sucrose; Hydrothermal Carbonisation; Sustainable Carbons;
44 Supercapacitor electrodes.

45

46 **1. Introduction**

47 Carbon materials are applied to several fields of paramount importance such as catalysis,
48 water and air depollution, and energy storage and conversion such as secondary batteries or
49 supercapacitors. The production of “sustainable carbon materials” from inexpensive carbon
50 sources including lignocellulosic biomass or other by-products contained in food/agricultural
51 waste, is of major importance nowadays. One way of achieving this target and producing
52 functionalised carbon materials is applying hydrothermal carbonisation (HTC) as a low-cost,
53 scalable, and industrially attractive first step of carbonisation prior to pyrolysis (Antonietti
54 and Titirici, 2010; Celzard et al., 2012; Hu et al., 2010). HTC maintains high oxygen content
55 and allows the functionalisation of the resultant materials without the need of additional
56 chemical reagents (Unur, 2013). The use of moderate temperature and pressure conditions are
57 fundamental for the onset of several reactions to which carbohydrates are submitted such as
58 hydrolysis, dehydration, condensation, aromatisation and polymerisation (Sevilla and Fuertes,
59 2009). An insoluble black solid that contains higher carbon content than in the original
60 material is obtained, and then a second-step of pyrolysis at 900°C can be applied for
61 increasing the electrical conductivity and improving the textural properties of the final
62 materials.

63 HTC has been applied to a broad range of carbohydrates and biomass: rice grains, oak
64 leaves, pine needles (Titirici et al., 2007), microalgae (Falco et al., 2012) and prawn shells
65 (White et al., 2009). Mimoso tannin has also been submitted to HTC. Mimoso tannin is a
66 phenolic material that has been used for the production of several materials such as
67 resins/adhesives (Pizzi, 1994), foams (Tondi et al., 2009; Letellier et al., 2017), gels
68 (Szcurek et al., 2011a, 2011b) and recently N-doped carbon materials (Braghioli et al.,
69 2012, 2015a). This is explained by the fact that such condensed (flavonoid) tannins are quite
70 reactive in the presence of aldehydes (e.g. formaldehyde), and another advantage is that they

71 can auto-condensate, especially when heated or in presence of strong mineral acids (Pizzi,
72 1983). Fig. 1 shows the main flavonoid structure of the robinetinidol unit (resorcinol A-ring
73 and pyrogallol B-ring) which constitutes approximately 70% of Mimosa tannin extract (Bate-
74 Smith, 1962; Pizzi, 1983; Hemingway et al., 1989; Pizzi, 1994).

75 Figure 1

76 Various carbonaceous microspheres were obtained after tannin HTC, depending on
77 temperature, reaction time and tannin concentration, and their production was found to obey a
78 first-order kinetics with an activation energy of 91 kJ mol⁻¹ (Braghiroli et al., 2014). The
79 mechanism of microspheres formation proceeds by nucleation, leading to a high number of
80 small particles, followed by growth and coalescence, leading to bigger particles of lower
81 surface area. The hydrochar yield investigated as a function of pH was found to increase from
82 64.4 % at unmodified pH (around 4.2 for the aqueous tannin solution) to 86.7 % when the pH
83 was decreased to 1. The pH also influenced the morphology and the texture of the hydrochars,
84 those prepared at non-modified pH being powders, whereas those obtained at low pH being
85 stiff monoliths presenting a higher surface area, up to 800 m² g⁻¹ after pyrolysis at 900°C. But
86 in all cases, the micropore size distributions were the same (Braghiroli et al., 2015b).

87 Concerning sugars, Wang et al. (2001) submitted a sucrose solution (1.5 mol L⁻¹) to HTC
88 at 190°C during 5h to produce carbonaceous microspheres with an average diameter of 5 µm
89 and a BET area as high as 400 m² g⁻¹ after subsequent pyrolysis at 1000°C. Then, Sevilla and
90 Fuertes (2009) studied the hydrochars obtained after HTC of several saccharides in different
91 conditions of temperature (170-240°C) and reaction time (0.5-15h) concluding that they
92 presented a core-shell structure consisting of a hydrophobic core and a hydrophilic shell
93 containing reactive oxygenated functional groups. Next, Falco et al. (2012) observed the
94 effect of adding glucose to microalgae organisms submitted to HTC, and found that such

95 strategy allowed incorporating nitrogen in the final carbon matrix and also increasing the
96 carbon yield from 18 to 47.5%.

97 In the present study, we used condensed tannin combined with commercial sugar (sucrose)
98 to see the effects of such mixture on the preparation of carbon materials. Sucrose was selected
99 because it is a commercial product, readily available and not expensive but also for
100 comparison purposes with previous studies (Wang et al., 2001; Sevilla and Fuertes, 2009).
101 Various kinds of microspheres were seen by electron microscopy, depending on temperature,
102 pH, and sucrose / tannin ratio. After a subsequent thermal treatment at 900°C, the final carbon
103 materials presented developed textural properties especially at low pH. To understand better
104 the influence of the various chemical and structural characteristics of the present carbons,
105 some of them were tested as electrode materials and the reversibility of the oxygen groups'
106 reactions in acidic electrolyte was studied. Such electrochemical studies allowed separating
107 the roles of the materials' features, and suggesting how to improve further their capacitance if
108 we were to start developing supercapacitor electrodes.

109

110 **2. Materials and methods**

111 2.1 Raw materials

112 Mimosa tannin, kindly supplied by SilvaChimica, was used in this study. The extraction
113 process and the composition of the tannin extract was described elsewhere (Braghiroli et al., 2014).

114 2.2 Hydrothermal treatment

115 In a typical synthesis, 2.0 g of either tannin (T) alone, sucrose (S) alone, or tannin-sucrose
116 mixture, were dissolved in 16.0 g of water, put inside a glass vial and then into a Teflon-lined
117 autoclave for 24h installed in an oven preheated at 180°C. Different conditions of
118 hydrothermal carbonisation (HTC) were studied, using various fractions of sucrose: 0, 25, 50,

119 75 and 100 wt. %. The addition of sucrose changed the pH from 4.2 (100% T) to 8 (100% S).
120 The resultant materials were called HsStT180_u, s and t being the percentages of sucrose and
121 tannin, respectively, and u meaning unmodified pH. A second series of samples was prepared
122 by fixing the pH at 2 by use of pTSA. Those materials were labelled HsStT180_2. The HTC
123 temperatures were also varied, 160 or 200°C, and the corresponding samples were labelled
124 HsStT160_u or HsStT200_u for unmodified pH experiments.

125 In all cases, the filtrates were recovered, washed with water, and then dried in a vacuum
126 oven at 80°C. Pyrolysis was carried out under nitrogen flow in a tubular furnace heated at 1°C
127 min⁻¹ up to 900°C, and this temperature was hold for 3h. Pristine tannin (OS100T) was also
128 carbonised in the same conditions and labelled C0S100T. In order to distinguish carbon
129 materials from hydrochars, we added a 'C' at the beginning of the label; for instance, the
130 sample H100T180_2 became CH100T180_2 after pyrolysis at 900°C.

131 2.3 Materials characterisation

132 Scanning electron microscopy (SEM) observations were carried out with a FEI-Quanta 400
133 apparatus for investigating the morphology of the samples, which were metallised beforehand.
134 A series of images was taken for each sample, and only one was provided here as an example.
135 The purpose was to evaluate the morphology of the samples and to observe general trends in
136 the particle size, depending on the preparation conditions.

137 Pore texture parameters were obtained by krypton adsorption at -196°C for organic, or
138 non-porous samples obtained after HTC, and by nitrogen adsorption at -196°C for pyrolysed
139 materials, using a ASAP 2020 automatic apparatus (Micromeritics) in both cases. CO₂
140 adsorption at 0°C was also carried out on pyrolysed samples using a Micromeritics ASAP
141 2420 apparatus. The following parameters were determined: NLDFT surface area, S_{NLDFT} (m²
142 g⁻¹); BET area, A_{BET} (m² g⁻¹); total pore volume, $V_{0.97}$ (cm³ g⁻¹); micropore volumes, $V_{DR,N2}$

143 and V_{DR,CO_2} ($\text{cm}^3 \text{g}^{-1}$), from the N_2 or CO_2 adsorption isotherms; micropore volume, $V_{\mu,NLDFT}$
144 ($\text{cm}^3 \text{g}^{-1}$), by applying the 2D- NLDFT-HS to both CO_2 and N_2 adsorption isotherms; and
145 mesopore volume, V_{mes} ($\text{cm}^3 \text{g}^{-1}$), calculated as the difference $V_{0.97} - V_{DR,N_2}$. The pore size
146 distributions (PSDs) were calculated by applying the 2D-NLDFT-HS method to both CO_2 and
147 N_2 adsorption isotherms. More details are given elsewhere (Schaefer et al., 2016).

148 Ultimate analyses of samples were carried out in a CHONS elemental analyser (Vario El
149 cube, Elementar) as reported elsewhere (Celzard et al., 2019). Temperature-Programmed
150 Desorption (TPD) experiments were performed with a custom-built set-up, consisting of a
151 tubular quartz reactor placed inside an electric furnace. In a typical experiment, the sample
152 was heated up to 1100°C in Ar atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The amounts of
153 CO and CO_2 were determined as reported elsewhere (Tellez-Juárez et al., 2014).

154 X-ray photoelectron spectroscopy (XPS) results were recorded with an ESCAPlus
155 OMICROM system equipped with a hemispherical electron energy analyser. Measurements
156 were carried out as reported elsewhere (Sanchez-Sanchez et al., 2018).

157 Electrochemical characterisation was performed with a Biologic VMP3 multi-potentiostat.
158 The carbon electrodes were prepared by spreading onto a graphite foil a paste ($\sim 15 \text{ mg cm}^{-2}$)
159 made of the carbon material mixed with polytetrafluoroethylene (PTFE) binder and carbon
160 black in the weight percent ratio of 85:10:5. The resulting electrodes were then pressed at 5
161 MPa and impregnated by $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ electrolyte during 48 hours. Cyclic voltammetry
162 (CV) tests were carried out at different scan rates between 0.5 and 100 mV s^{-1} and within the
163 potential window of 0 – 0.8 V in a three-electrode cell, using a platinum gauze as the counter
164 electrode and a saturated calomel electrode (SCE) as the reference one. The specific
165 capacitance ($C, \text{F g}^{-1}$) was calculated from the CV curves according to Eq. (1):

$$166 \quad C = (\int I dV) / (s \Delta V m) \quad (1)$$

167 where I (A) is the current, s (V s^{-1}) is the scan rate, ΔV (V) is the potential window and m (g)
168 is the mass of carbon in the electrode.

169 3. Results and discussion

170 3.1 Carbon yields and morphologies

171 To study the effects of the pH on the tannin / sucrose solution submitted to HTC, the same
172 weight (1 g) of sucrose and tannin was used. Table 1 shows the main characteristics of these
173 hydrochars (H50S50T) at different pH ranging from 1 to unmodified (4.2). Unlike H0S100T
174 (100% tannin submitted to HTC - see Fig. 2), submitting 50S50T to HTC at different pH did
175 not produce any change in the HTC yield. Being at the level of 61.5 ± 1.5 wt. %, the HTC
176 yield of 50S50T was also always much lower than that of H0S100T. The A_{BET} values (around
177 $1 \text{ m}^2 \text{ g}^{-1}$) were almost the same for 0S100T, H0S100T and H50S50T, considering the intrinsic
178 uncertainties of adsorption techniques as soon as very low surface areas are concerned.
179 Therefore, it can be concluded that, after HTC, the materials were not porous.

180 After a second thermal treatment at 900°C , A_{BET} increased from $471 \text{ m}^2 \text{ g}^{-1}$ for tannin
181 directly pyrolysed (C0S100T) to $639 \text{ m}^2 \text{ g}^{-1}$ for CH50S50T 180_u (i.e., at unmodified pH),
182 and even up to $809 \text{ m}^2 \text{ g}^{-1}$ for CH50S50T 180_1 (i.e., at pH 1). The increase of A_{BET} was also
183 observed for the 100% tannin material (CH0S100T) having been submitted to HTC at low
184 pH. Fig. 2 summarises the results of HTC yield and A_{BET} of all these hydrochars H0S100T
185 and CH0S100T (already demonstrated in (Braghiroli et al., 2015b)) and H50S50T and
186 CH50S50T at pH values ranging from 4 to 1. The results on pure tannin are presented here for
187 the sake of comparison to study the effect of sucrose addition.

188 

189 It has already been mentioned that heating tannin in the presence of strong mineral acids
190 favours its condensation/polymerisation reactions by different possible ways to form
191 “phlobaphenes” or “tanner’s reds”, which are high-molecular weight, insoluble molecules
192 (Pizzi, 1983; Braghiroli et al., 2015a). Tannin treated after HTC at 180°C was shown to have

193 a structure similar to that of flavonoid tannin (see [Fig. 1](#)), but presents a much higher level of
194 polymerisation, mainly through the opening of the heterocyclic C2–ring and subsequent
195 partial condensation between C2 (open) to C6 or C8, and partly through some auto-
196 condensation C4 to C6 and C8 (Braghiroli et al., 2015a).

197 On the other hand, sucrose submitted to HTC undergoes hydrolysis that produces glucose
198 and fructose, which decompose into hydroxymethylfurfural (HMF) as the main dehydration
199 product, plus aldehydes (formaldehyde, pyruvaldehyde, etc.) and organic acids (acetic,
200 formic, levulinic acids, etc.), hence producing a rapid pH change from 8 to 3 as shown in the
201 literature (Antal et al., 1990; Ulbricht, 1984; Asghari and Yoshida, 2006). Glucose and
202 fructose can also undergo polymerisation and condensation reactions as reported elsewhere
203 (Antal et al., 1990; Kabyemela et al., 1997; Luijkx et al., 1995; Sevilla and Fuertes, 2009).
204 Titirici et al. (2008) observed that the morphologies and chemical structures of carbons
205 obtained from sucrose are directly related to those of carbons obtained from pure furan. It was
206 also found that such intermediate molecules derived from saccharide dehydration as
207 mentioned above coexist with furans and account for the observed changes of particle size,
208 textural properties and particles aggregation.

209 When both materials (tannin and sucrose) coexist, we can assume that several reactive
210 germs are obtained through hydrolysis of sucrose submitted to HTC. SEM photos show that
211 the average microsphere diameter was reduced from 10 μm for H0S100T (see [Fig. 3a](#)) to 2-5
212 μm by simple addition of sucrose (see [Fig. 3c](#)) for H50S50T, whereas 100% sucrose produced
213 spheres of average size 1-2 μm (see [Fig. 3b](#)). This finding suggests that sucrose reacts faster
214 than tannin, producing more germs and, consequently, smaller spheres are obtained (see [Fig.](#)
215 [3c](#)).

216

217 **Table 1:** Textural properties and elemental analysis obtained for materials 50S50T after HTC and subsequent pyrolysis made at different pH.

	Sample	Yield (wt. %)			Textural Properties						Elemental Analysis (wt. %)					
		HTC	Carbon	Total	S_{NLDFT} ($m^2 g^{-1}$)	A_{BET} ($m^2 g^{-1}$)	$V_{0.97}$ ($cm^3 g^{-1}$)	V_{DR,N_2} ($cm^3 g^{-1}$)	V_{DR,CO_2} ($cm^3 g^{-1}$)	$V_{\mu,NLDFT}$ ($cm^3 g^{-1}$)	C	H	N	S	O	C/O
No HTC	0S100T	-	-	-	-	0.27	-	-	-	-	53.8	5.4	0.6	0.1	40.1	1.3
After HTC	H0S100T180_u	64.6	-	-	-	0.78	-	-	-	-	60.9	4.4	0.8	0.0	33.8	1.8
	H50S50T180_1	63.0	-	-	-	1.22	-	-	-	-	62.6	5.0	0.6	0.2	31.6	2.0
	H50S50T180_2	60.0	-	-	-	1.05	-	-	-	-	62.6	4.3	0.2	0.2	32.7	1.9
	H50S50T180_3	61.2	-	-	-	0.87	-	-	-	-	62.3	4.8	0.8	0.0	32.1	1.9
	H50S50T180_u	61.5	-	-	-	0.84	-	-	-	-	60.9	4.4	0.3	0.0	34.4	1.8
	H100S0T180_u	41.1	-	-	-	1.8	-	-	-	-	65.6	4.4	0.0	0.0	30.0	2.2
After pyrolysis at 900°C	C0S100T	-	44.5	44.5	1416	471	0.20	0.19	0.38	0.32	90.4	0.8	0.6	0.0	8.2	11.0
	CH0S100T180_u	64.6	51.6	33.4	904	608	0.24	0.23	0.28	0.25	88.3	0.9	0.6	0.0	10.2	8.7
	CH50S50T180_1	63.0	50.4	31.8	1132	809	0.35	0.31	0.36	0.32	89.9	1.5	0.8	0.0	7.8	11.5
	CH50S50T180_2	60.0	53.2	31.9	1061	767	0.34	0.29	0.32	0.30	91.5	1.1	1.2	0.0	6.2	14.8
	CH50S50T180_3	61.2	48.4	29.6	984	643	0.27	0.25	0.29	0.27	90.8	2.1	0.8	0.0	6.3	14.4
	CH50S50T180_u	61.5	49.6	30.5	913	639	0.25	0.24	0.28	0.25	91.0	0.5	0.3	0.0	8.2	11.1
	CH100S0T180-u	41.1	51.2	21.1	836	562	0.22	0.22	0.26	0.23	93.0	0.5	0.1	0.0	6.4	14.5

219 A similar effect was found by decreasing the pH down to 2. Small spherical particles of
220 around 2 μm arranged in a necklace structure were indeed obtained in carbons based on either
221 pure tannin (see Fig. 3d) or tannin-sucrose mixture (compare Fig. 3c, 3f, 3g and 3h) submitted
222 to HTC at pH 2. No changes in particle diameter were observed, as their size was nearly
223 constant around 2 μm , irrespective to the HTC temperature: 160, 180 or 200°C. This finding
224 at lower pH is different from what was formerly observed for HOS100T at unchanged pH and
225 160°C, for which irregular spheres were found, indicating that HTC reaction was not finished.
226 By increasing the HTC temperature from 180 to 200°C, bigger and rounded spheres were
227 observed (Braghiroli et al., 2014).

228 Figs. 3b and 3e show SEM pictures of carbon materials derived from 100S0T submitted to
229 HTC at unchanged pH (pH around 4) or at pH 2. HTC of 100S0T at unchanged pH produced
230 mostly monodisperse spherical particles having a size of approximately 1 μm , in agreement
231 with other authors (Titirici et al., 2008; Sevilla and Fuertes, 2009). However, sucrose
232 hydrolysis at pH 2 produced bigger spheres of around 5-10 μm . Zhao et al. (2013) observed
233 the effect of the acidic pH on the formation mechanism of carbon spheres when submitting
234 cellulose to HTC. The compounds obtained from cellulose hydrolysis rapidly react with H^+
235 present in the system through dehydration and polymerisation reactions and lead to hydrochar
236 nucleation. Besides that, they concluded that the acid concentration in the HTC system could
237 also control the shape and the diameter of the carbon spheres.

238 Figure 3

239 Table S1 shows the main characteristics of hydrochars and carbon materials prepared with
240 50% of sucrose (50S50T) at different HTC temperatures (160, 180 and 200°C) and different
241 pH. Some of these results are summarised in Fig. 4 including the total carbon yield and the
242 A_{BET} as a function of HTC temperature at unchanged pH or at pH 2. The HTC yield was
243 around 60% irrespective to the temperature or the pH. After pyrolysis, the total carbon yield

244 appears to be constant, around 30%, whatever the HTC temperature or the pH used
245 beforehand. In the same way, A_{BET} did not change with HTC temperature but was higher for
246 samples prepared at pH 2. Indeed, carbons prepared from hydrochars obtained at pH 2
247 presented an A_{BET} of $735 \pm 32 \text{ m}^2 \text{ g}^{-1}$, while those prepared at unchanged pH had an A_{BET} of
248 $629 \pm 10 \text{ m}^2 \text{ g}^{-1}$.

249 Figure 4

250 In order to study the effect of the percentage of sucrose on the hydrochar characteristics,
251 hydrochars based on various proportions of tannin and sucrose were prepared at unchanged
252 pH and at pH 2, summarised in [Table S2](#). We can observe by SEM photos in [Fig. 5a to 5c](#)
253 that, by increasing the weight fraction of sucrose from 25 to 100% at unchanged pH, the
254 sphere diameter decreased from around 10 to 2 μm and they became more individualised and
255 more monodispersed. Polydispersity and higher particle size thus appear to be a consequence
256 of tannin presence in the system at unchanged pH. In the literature, changes of particles
257 morphology produced by mixing two carbon precursors submitted to HTC were also
258 evidenced for microalgae in the presence of glucose added in a mass ratio of 1:1. In that case,
259 the final particles morphology was that of pure glucose but with a double higher average
260 diameter, passing from 1 to 2 μm (Falco et al., 2012). Coming back to the present situation,
261 the effect of adding sucrose at pH 2 was opposite to that observed at unchanged pH. With the
262 addition of sucrose at lower pH, the average sphere diameter increased from 1-2 μm to 2-3
263 μm and finally to around 5-10 μm when the proportion of sucrose increased from 25% ([Fig.](#)
264 [5d](#)), to 75% ([Fig. 5d](#)) until 100% ([Fig. 5f](#)), respectively.

265 Figure 5

266 [Fig. 6a](#) shows the HTC yield of all materials at different proportions of sucrose / tannin and
267 at two pH, unchanged and 2. The dotted lines represent the theoretical yield calculated from

268 the experimental yields of 0S100T and 100S0T (e.g. for 75S25T we have $Y_{HTC, 75S25T} = (75 \times$
269 $Y_{HTC,100S0T} / 100 + 25 \times Y_{HTC,0S100T} / 100)$, in order to observe any synergetic effect between
270 tannin and sucrose during HTC. At pH 2, the experimental HTC yield was very similar to the
271 expected value, so we can conclude that there is no apparent interaction between sucrose and
272 tannin regarding the yield. Acidic pH accelerates HTC reactions, both for sucrose and tannin
273 precursors (Lee et al., 1999; Kim et al., 2001; Trajano and Wyman, 2013) and no differences
274 were observed. At unmodified pH, experimental HTC yield of tannin-sucrose mixtures were
275 higher than those theoretically calculated, suggesting that HTC products of sucrose and tannin
276 interact with each other. At pH around 4, sucrose yielded more solid materials. Its higher
277 HTC kinetics compared to tannin led to more germs with a resulting lower particle size and an
278 enhanced HTC yield. Since at pH 2 the experimental HTC yield was the same as calculated, it
279 can be assumed that a low pH promotes fast reactions to liquid products (Lee et al., 1999;
280 Kim et al., 2001; Trajano and Wyman, 2013) that do not interact with tannin.

281 Figure 6

282 3.2 Porous texture and composition

283 Fig 6b shows the BET area of the same hydrochars as in Fig. 6a but after pyrolysis at
284 900°C. As a general remark, the addition of sucrose to tannin slightly increased A_{BET} . The
285 highest A_{BET} was found for the mixture 50S50T at both pH, but the main effect on the increase
286 of surface area was due to the pH reduction. Fig. 7 shows that the product $A_{BET} \times$ total carbon
287 yield increased with the total carbon yield. This effect is opposite to what is obviously found
288 for carbon activation, whether physical or chemical, which produces higher surface area when
289 the carbon yield decreases, i.e., when the burn-off increases. Besides, by increasing the
290 proportion of tannin mixed with sucrose in HTC conditions, an increase of the total carbon
291 yield can be seen. However, the highest A_{BET} was obtained at equal proportion (50:50) of T
292 and S at pH 2. Such increase of surface area, from 476 to 791 $\text{m}^2 \text{g}^{-1}$, cannot be explained by

293 the decrease of particle diameter from 10 μm (CH0S100T180_u) to approximately 2 μm
294 (CH50S50T180_2), which accounts for less than 1% of the measured A_{BET} . As previously
295 discussed in Braghiroli et al. (2015b), the decrease of particle size might facilitate the
296 evolution of volatile matter and then the development of textural properties.

297 Figure 7

298 All materials were found to be microporous, given their Type I nitrogen isotherms at -
299 196°C, having a vertical part at low relative pressure P/P_0 and an almost horizontal part from
300 $P/P_0 = 0.02$ to 1 as shown in Fig. 8a for CH50S50T180_2 and CH50S50T180_u. The pore
301 size distribution calculated by NLDFT is presented in Fig. 8b for the same samples;
302 CH50S50T180_2 had some porosity in the mesopore range (between 2 and 10 nm), whereas
303 CH50S50T180_u presented an entirely microporous structure. The isotherm of sample
304 prepared at pH 2 presented a slight slope showing the presence of pores broader than 2 nm.
305 Most of the carbohydrates submitted to HTC needed a second thermal treatment, at higher
306 temperature, to increase the porosity of the resultant carbon materials. However, glucose after
307 HTC and subsequent pyrolysis at 900°C was poorly porous and had low surface areas, around
308 30-50 $\text{m}^2 \text{g}^{-1}$ (Zhao et al., 2010). Thanks to the reactivity of tannins in hydrothermal
309 conditions and posterior pyrolysis at 900°C, highly porous material were obtained ($A_{BET} > 600$
310 $\text{m}^2 \text{g}^{-1}$) confirming its potential as precursor for the production of porous carbons.

311 Figure 8

312 As for the chemical composition, Fig. 9a shows the van Krevelen diagram for all
313 hydrochars and carbon materials prepared from tannin and sucrose at different pH and HTC
314 temperatures (160, 180 and 200°C). The main arrow (from 100S0T to HTC_900°C, i.e., from
315 pure sucrose to all carbons obtained by HTC followed by pyrolysis at 900°C) indicates the
316 loss of oxygen and hydrogen, and therefore the increase of carbon content after both thermal
317 treatments (HTC at 160-200°C and pyrolysis at 900°C) (van Krevelen, 1950). The percentage

318 of carbon increased after HTC and obviously even more after pyrolysis. After HTC, samples
319 prepared at unmodified pH retained more oxygen, 30-36 wt. %, than those prepared at pH 2,
320 28-33 wt. %. After pyrolysis at 900°C, carbon derived from hydrochars prepared at
321 unmodified pH retained more oxygen, 6-10 wt. %, than those prepared at pH 2, 3-6 wt. %.

322 [Fig. 9b](#) shows the total amounts of CO and CO₂ gases in mmol g⁻¹ that have been lost
323 during a thermal treatment (TPD analysis) up to 1100°C for materials at different T/S
324 proportions. CO₂ derives from precursors comprising carboxylic acids, lactones and
325 anhydride groups, and CO derives from quinonic and phenolic groups (Figueiredo et al.,
326 1999). Boudouard equilibrium also takes place, modifying the CO/CO₂ ratio. The total
327 amount of released gases (CO + CO₂) was higher for materials HsStT_u prepared without pH
328 modification (0.065-0.075 mmol g⁻¹) than for HsStT_2 prepared at pH 2 (0.036-0.052 mmol
329 g⁻¹). This is in good agreement with their higher amount of oxygen, 32.4-36.3 wt. %,
330 compared to 30.6-32.7 wt. % in HsStT_2 materials, measured by EA ([Table 1](#) and [Table S1](#)).
331 Indeed, tannin in the presence of strong acids undergoes dehydration and condensation
332 reactions (Pizzi, 1983; Braghiroli et al., 2015a), which might have reduced the amount of
333 oxygen in hydrochars.

334 Figure 9

335 Surface atomic concentrations obtained by XPS and contributions to the C1s, O1s and N1s
336 high-resolution spectra of the hydrochars and carbon materials are collected in [Table 2](#) and in
337 [Fig. S1](#) to [S6](#) of the Supporting Information section. Tannin-derived hydrochars presented
338 high oxygen surface concentrations, between 12.6 and 19.6 at. %, but low nitrogen surface
339 concentrations, between 0.3 and 1.3 at. %. No influence of the pH of the medium on the
340 oxygen surface concentration of the hydrochars was evidenced. Sucrose-derived hydrochars
341 contained 17.9 at. % surface oxygen, and a small concentration of nitrogen, 0.3 at. %, in
342 agreement with the chemical composition of sucrose and with the presence of amino-acids

343 coming from the raw sugar beet. As expected, the oxygen concentration of the hydrochars
344 significantly decreased after pyrolysis, and the resultant carbons exhibited oxygen surface
345 concentrations between 2.3 and 11.7 at. %. The concentration of nitrogen varied in the range
346 0.40 – 1.7 at. %, being only present at the surface of carbons prepared at pH higher than 3.

347 Deconvolution of the high-resolution XPS spectra allowed identifying chemical bonds that
348 are characteristic of specific functional groups. C1s high-resolution spectra for all samples
349 exhibited an asymmetric peak centred on binding energies (BE) of 284.4 – 284.5 eV (Table 2,
350 and Fig. S1 and S4 in the Supporting Information section). Except for H50S50T180_3, the
351 deconvolution of the C1s high-resolution profiles gave rise to five peaks, CI to CV, with
352 binding energies (BE) between 284.4 and 290.6 eV: CI is assigned to Csp² in hydrocarbons,
353 aromatics and aliphatics; CII is associated with Csp³ and C-O single bonds associated with
354 ethers, phenols and anhydrides; CIII is assigned to C=O double bonds in carbonyls and
355 quinones; CIV corresponds to C-O single bonds in carboxylic groups; and CV is related to
356 plasmon losses or shake-up π - π satellites. In the case of H50S50T180_3, an additional peak
357 C* appeared at an unusually low BE, 283.6 eV. This peak may be associated to pre-graphite-
358 like C in highly aromatic materials (Cagniant et al., 1998; Weckhuysen et al., 1998).

359 The O1s high-resolution spectra of the hydrochars presented, in general, two oxygen
360 contributions (Table 2): O1, assigned to C=O double bonds in quinone-type groups, carbonyls
361 and carboxylic acids; and O2, related to –OH bonds in phenols, C–O–C in ether groups and
362 C=O bonds in ester and anhydride groups. The O1s high-resolution spectra exhibited
363 generally O1, O2 and O3 contributions, O3 being assigned to chemisorbed oxygen, single C-
364 O bonds in esters and anhydrides, and C-O bonds in carboxylic groups and/or water.

365 Finally, the deconvolution of the N1s high-resolution spectra was only possible for
366 samples with surface nitrogen concentrations higher than 1 at. %. Curve fitting was not
367 possible for the N1s high-resolution spectrum of H50S50T180_3 hydrochar, due to the low

368 area of the peak. N1s high-resolution spectra of both hydrochars and carbons exhibited three
369 contributions assigned to three types of functional groups: N6, related to pyridinic nitrogen;
370 N5, related to pyrrolic nitrogen; and NQ, assigned to quaternary nitrogen (Briggs, 2005;
371 Dongil et al., 2011; Weidenthaler et al., 2006).

372 In general, pyrolysis decreased the relative concentrations of the groups related to CII and
373 OII, while increasing the relative amounts of the groups related to the peaks CIII, CIV and OI.
374 This finding means that the concentration of ethers, phenols, esters and anhydrides decreased
375 whereas the concentration of quinone-type groups, carbonyls and carboxylic acids increased
376 as a consequence of pyrolysis.

377 Concerning the structure of the carbons obtained by pyrolysis at 900°C of the
378 aforementioned hydrochars, it can be added that none of these materials are graphitic, as
379 evidenced by their XRD patterns showing very broad and poorly defined (002) and (10l)
380 bands (see for instance (Tondi et al., 2009) and the supplementary information of (Celzard et
381 al., 2019) for typical patterns of carbons based on tannin and tannin-sugar produced at
382 900°C). The corresponding Raman spectra demonstrated the same, but also that these
383 materials are not graphitisable either, unless transition metals are added as graphitisation
384 catalyst, which was not the case here. Typical Raman spectra of carbons based on tannin and
385 tannin-sugar produced at 900°C can be found elsewhere (Celzard et al., 2019; Braghiroli et
386 al., 2017), and prove that the present materials are definitely highly disordered, i.e. very
387 poorly crystallised, carbons.

388 Concerning the morphology, carbon spheres have a wide range of applications, depending
389 on their diameter, pore texture and surface chemistry. For example, they can be used in
390 batteries (Park et al., 2018) or supercapacitors (Zhou et al., 2015), as catalysts (Frusteri et al.,
391 2016, Maciá- Agulló et al., 2010) or even as boosters to produce pure water as we reported
392 recently (Celzard et al., 2019).

393 **Table 2.** Atomic surface concentrations of C, N and O, and contributions to the C1s, O1s and N1s high-resolution XPS spectra of the materials in
 394 terms of peak area fraction (%) at given binding energies (BE, eV).

Sample name	Concentration (at. %)			C1s peak BE (eV) Area (%)						O1s peak BE (eV) Area (%)			N1s peak BE (eV) Area (%)			
	C	O	N	C*	CI	CII	CIII	CIV	CV	O1	O2	O3	N6	N5	NQ	NX
OS100T	80.4	19.6	-	-	284.4 66.1	285.8 29.6	288.2 2.5	289.2 0.9	291.0 0.9	531.7 24.8	532.8 75.2	-	-	-	-	-
H50S50T180_1	81.9	16.8	1.3	-	284.4 65.9	285.7 27.3	287.6 5.6	289.0 0.7	290.3 0.4	531.4 36.1	532.7 63.9	-	398.5 12.2	399.7 59.9	401.1 27.9	-
H50S50T180_2	83.0	15.7	1.3	-	284.4 73.7	285.8 19.4	287.6 4.6	288.9 1.9	290.6 0.4	531.4 41.7	532.7 58.3	-	398.5 28.1	399.7 58.5	401.1 13.4	-
H50S50T180_3	87.1	12.6	0.3	283.6 9.0	284.5 31.4	286.0 44.3	287.6 12.2	289.0 1.0	290.1 2.1	531.8 7.2	533.3 60.8	534.5 32.0	-	-	-	-
H50S50T180_u	84.2	15.8	-	-	284.4 73.7	285.7 20.7	287.6 3.7	289.0 1.6	290.3 0.3	531.7 39.5	532.8 60.5	-	-	-	-	-
H100S0T180_u	81.9	17.9	0.3	-	284.4 65.4	285.6 25.8	287.6 8.1	289.2 0.3	290.4 0.4	531.5 40.1	532.8 59.9	-	-	-	-	-
C0S100T	97.1	2.9	-	-	284.4 66.4	285.5 25.5	287.6 5.7	289.2 1.8	290.5 1.5	531.8 40.4	533.0 54.0	534.5 5.6	-	-	-	-
CH50S50T180_1	97.5	2.5	-	-	284.5 68.7	285.5 23.8	287.6 5.2	289.2 1.4	290.4 1.5	531.6 48.1	532.9 49.4	534.5 2.5	-	-	-	-
CH50S50T180_2	97.2	2.8	-	-	284.5 65.8	285.5 25.8	287.6 5.6	289.0 0.6	290.2 2.2	531.6 41.4	532.9 47.0	534.5 11.9	-	-	-	-
CH50S50T180_3	94.8	3.4	1.7	-	284.4 66.2	285.5 25.3	287.6 5.9	289.2 1.1	290.4 1.5	531.3 46.5	532.8 51.0	534.5 2.5	398.2 28.8	400.3 32.7	401.1 38.5	-
CH50S50T180_u	87.9	11.7	0.40	-	284.4 75.9	286.0 19.5	287.6 3.2	289.2 0.7	290.1 0.4	531.9 53.3	533.2 46.7	-	-	-	-	-
CH100S0T180_u	97.7	2.3	-	-	284.5 67.1	285.6 25.4	287.7 4.8	289.2 0.6	290.4 2.1	532.0 49.2	533.0 47.8	534.5 3.0	-	-	-	-

395

396 3.3 Electrochemical properties

397 Among the carbon materials, C0S100T, CH50S50T180_1 and CH50S50T180_u were
398 selected for studying their electrochemical behaviour. With respect to porous texture,
399 C0S100T and CH50S50T180_1 are among the materials having the highest micropore
400 volumes, although their PSDs are clearly not the same, as suggested by the data of Table 1.
401 With respect to surface chemistry, the most remarkable difference in their surface chemistry is
402 that CH50S50T180_u exhibited higher surface oxygen content than the other two carbons,
403 and that CH50S50T180_1 exhibited higher relative concentrations of quinone and carbonyl
404 groups (OI peak). The latter are the most electroactive oxygen functionalities in acidic
405 electrolytes (Inagaki et al., 2010). Choosing such materials for electrochemical tests was
406 therefore supposed to clarify the understanding of these new carbon materials.

407 At the lowest scan rate of 0.5 mV s^{-1} , cyclic voltammetry (CV) curves of C0S100T and
408 CH50S50T180_1 exhibited more defined peaks of both anodic and cathodic currents than
409 CH50S50T180_u despite possessing a lower concentration of oxygen on their surfaces (Fig.
410 10a). The presence of redox peaks is due to a contribution of the surface oxygen groups to the
411 total capacitance of the electrodes by a pseudocapitance mechanism. Even at this low scan
412 rate of 0.5 mV s^{-1} , CV curves of CH50S50T180_u exhibited a highly distorted profile with
413 respect to the rectangular shape of an ideal electric-double layer capacitor (ELDC). This fact
414 may indicate the existence of kinetic limitations for ion transport, and agrees with the highly
415 microporous texture of the carbon, whose percentage of narrow porosity (width $< 0.7 \text{ nm}$) was
416 the highest of the three materials, 84.0%, and whose percentage of mesoporosity was the
417 lowest one, 0.0%. At the relatively low scan rate of 10 mV s^{-1} , the shape of the CV curves of
418 all the materials clearly deviated from the rectangular one, and no clear peak could be seen
419 (Fig. 10b). This suggests that the behaviour of the supercapacitor electrodes becomes less

420 capacitive and more resistive, due to kinetic limitations, and that pseudocapacitance
421 contribution is negligible, respectively (McDonough et al., 2012).

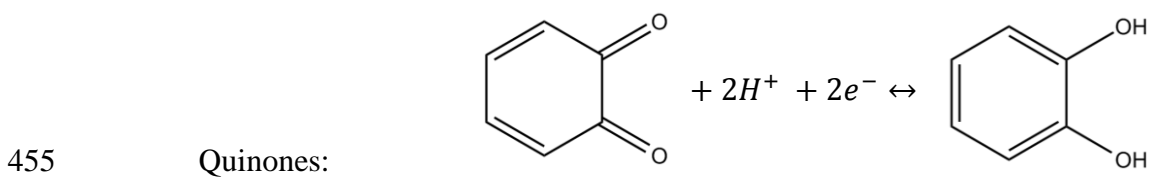
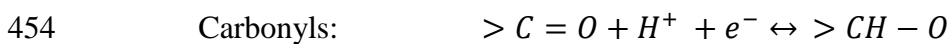
422 The studied electrode materials yielded similar values of specific capacitance in the entire
423 range of investigated scan rates. At the lowest scan rate of 0.5 mV s^{-1} , specific capacitances of
424 51, 57 and 58 F g^{-1} were exhibited by C0S100T, CH50S50T180_1 and CH50S50T180_u,
425 respectively (Fig. 10c). These capacitance values progressively decreased when the scan rate
426 increased, due to the increasing resistance to diffusion of electrolyte ions into the pores. At
427 100 mV s^{-1} scan rate, the specific capacitance was 15 F g^{-1} for all the materials (Fig. 10c),
428 which corresponds to capacitance retentions of 30.4, 26.6 and 26.3% for C0S100T,
429 CH50S50T180_1 and CH50S50T180_u, respectively (Fig. 10d). The lower capacitance
430 retention of CH50S50T180_1 and CH50S50T180_u compared to C0S100T indicates the
431 existence of more important kinetic limitations at increasing scan rates due to their high
432 fractions of narrow porosity, 71.4 and 84.0%, respectively. The CV results agree with a
433 previous study on molasses-derived carbons, in which the materials prepared by HTC
434 exhibited, in the studied potential window, lower capacitances than those that were directly
435 pyrolysed, mainly due to their narrow porosities and low electrical conductivities (Sanchez-
436 Sanchez et al., 2016).

437 Figure 10

438 In order to determine the pseudocapacitance contribution to the overall capacitance of the
439 materials, interfacial capacitances at different scan rates, C / S_{NLDFT} , were plotted versus
440 oxygen surface concentrations (Fig. S7a of the Supporting Information section). The
441 interfacial capacitance was calculated by considering S_{NLDFT} instead of A_{BET} , since it has been
442 previously shown that this approach is more appropriate for materials mainly comprising
443 narrow pores, such as in the present case (Sanchez-Sanchez et al., 2016). In general, higher
444 surface oxygen concentrations were not related to higher interfacial capacitances in the entire

445 range of studied scan rates. This should mean that the pseudocapacitance contribution of the
 446 materials is lower than the capacitive contribution, for which the porous texture is the key
 447 parameter.

448 Oxygen functional groups have a great influence on the electrochemical properties of
 449 carbon materials (Anjos et al., 2013; Tanaka et al., 2015). Hydroxyl, carbonyl and, especially,
 450 quinone groups, have been proved to yield more capacitance than carboxyl, anhydride or
 451 lactone groups in acidic aqueous electrolytes thanks to their Faradaic reactions (Inagaki et al.,
 452 2010). Redox reactions involving these groups are the following (Oh et al., 2014):



457 where the symbol > represents the surface of the carbon material. Protons, H^+ , are not only
 458 simply adsorbed on the oxygen functional groups, but are involved in the electrochemical
 459 reactions.

460 As a consequence of these Faradaic reactions, redox peaks can appear on the anodic and
 461 cathodic branches of the CV curves of the carbon materials. CV curves obtained in a three-
 462 electrode cell in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte, measured at 0.5 mV s^{-1} scan rate and
 463 considering the first cycle of cycling, are displayed in Fig. 11. These curves exhibited two
 464 redox processes associated to peaks 1 and 2 appearing in the anodic and cathodic branches,
 465 which are represented by the “ox” and “red” superscript, and are defined by two parameters:

466 (i) peak current, I_p , which is the current at the maximum of the peak; and (ii) peak potential,
467 E_p , which is the potential at the maximum of the peak (Fig. 11a, 11c and 11e).

468 Figure 11

469 For the samples C0S100T and CH50S50T180_1, no second anodic peak, $I_{p,2}^{ox}$, was seen,
470 indicating the irreversibility of the associated redox process. In contrast, the first peak could
471 be clearly observed both in the anodic and cathodic branches and appeared in the five cycles
472 studied at scan rates from 0.5 to 5 mV s⁻¹ for C0S100T, and from 0.5 to 2 mV s⁻¹ for
473 CH50S50T180_1 and CH50S50T180_u. This suggests that the associated redox system may
474 be quasi-reversible in the aforementioned scan rate intervals. The highly distorted CV curves
475 with respect to the expected rectangular shape of an ideal electric-double layer capacitor at
476 scan rates above 2 or 5 mV s⁻¹ did not allow differentiating clear redox peaks. Therefore, the
477 reversibility of the redox system 1 was studied up to a maximum scan rate of 5 mV s⁻¹. The
478 formal potentials of peak 1 vs SCE reference, calculated as $E^0 = 1/2 (E_{p,1}^{ox} + E_{p,1}^{red})$, were
479 0.425, 0.424 and 0.444 V for C0S100T, CH50S50T180_1 and CH50S50T180_u,
480 respectively. The reversible character of the redox process was evaluated through the
481 following criteria:

482 1) *Peak separation*, $\Delta E = E_{p,1}^{ox} - E_{p,1}^{red} \leq 0.059 / n$, where $E_{p,1}^{ox}$ and $E_{p,1}^{red}$ (V) are the
483 maxima of the anodic and cathodic peaks, respectively, and n is the number of transferred
484 electrons: Considering the transfer of 1 electron, the peak separation was lower than 0.059 V
485 at the lowest scan rate of 0.5 mV s⁻¹ for the three materials, suggesting the reversibility of the
486 redox process. ΔE generally increased above 0.059 V as the cycle number increased, which
487 indicates that the redox process was progressively less reversible due to the gradual
488 transformation of surface groups into non-electroactive species. However, ΔE was
489 progressively lower than 0.059 V at the scan rate of 0.5 mV s⁻¹ for the sample C0S100T,
490 suggesting a higher reversibility of the redox process (Fig. 11b, 11d and 11f). This can be

491 explained by the improvement of the surface wettability during the cycling process, which
492 facilitates the contact between the surface functionalities and the electrolyte ions, so that
493 redox reactions are easier to occur, and also by the higher fraction of pores involved in the
494 materials as the cycling process goes on (Jiang et al., 2013). Varying the scan rate in cyclic
495 voltammetry allows varying the diffusion layer thickness, thus enabling the control of the
496 electrochemical process either by electron transfer or by mass transport. The diffusion layer is
497 thicker at low scan rates, and thinner as the scan rate increases. Electrochemical processes
498 reflect the competition between reactions at the electrodes and diffusion, so that faster scan
499 rates favour electrochemical irreversibility, which is controlled by the electron transfer rate,
500 and the peak potentials are thus shifted. This trend is clearly observed in Fig. S7b of the
501 Supporting Information section, which shows the progressive separation of maxima of the
502 peaks associated to the redox process 1 at increasing scan rates from 0.5 to 2 mV s⁻¹ for a
503 representative sample, COS100T (McDonough et al., 2012). When the peak potentials remain
504 constant with increasing scan rates, the involved redox process is reversible. Fig. 12b, 12d and
505 12f show the progressive increase of the peak potentials of the studied samples, $E_p^{ox,red}$, at
506 increasing scan rates, $\ln s$, indicating the quasi-reversibility of the involved redox system
507 (Gómez et al., 2011).

508 2) *Ratio of anodic to cathodic currents, $I_{p,1}^{ox} / I_{p,1}^{red} \approx 1$, where $I_{p,1}^{ox}$ and $I_{p,1}^{red}$ (A) are the*
509 *currents at the maximum of the anodic and cathodic peaks, respectively:* When the peak
510 currents, I_p , for the oxidation and reduction reactions are the same, i.e., $I_{p,1}^{ox} / I_{p,1}^{red} = 1$, the
511 redox process is reversible (Bard and Faulkner, 2001). The current ratios of the studied
512 samples at scan rates ranging from 0.5 to 2 mV s⁻¹ were 0.98 ± 0.04 , which indicates the
513 quasi-reversibility of the redox process.

514 3) *Scan rate dependence of peak current, $I_p^{ox,red} \propto s^{1/2}$, where $I_p^{ox,red}$ (A) is the current at*
515 *the maximum of the anodic or the cathodic peaks and $s^{1/2}$ (V^{1/2} s^{-1/2}) is the square root of the*

516 *scan rate*: A linear relationship between $I_p^{ox,red}$ and $s^{1/2}$ indicates that the redox process is
517 quasi-reversible (Gómez et al., 2011) As shown in Fig. 12a, 12b and 12c, $I_p^{ox,red}$ versus $s^{1/2}$
518 leads to linear relationships for the studied samples, with determination coefficients close to 1,
519 thus indicating that the concerned redox processes are quasi-reversible. From these linear
520 relationships and applying the Randles-Sevcik equation (Eq. 2), the diffusion coefficients, D_0 ,
521 of the processes were calculated (McDonough et al., 2012). The Randles-Sevcik equation
522 reads:

$$523 \quad I_p = 0.4463 n F A C [(F D_0 s) / (R T)]^{1/2} \quad (2)$$

524 where I_p (A) is the peak current, n is the number of electrons transferred in the reaction, F (C
525 mol⁻¹) is the Faraday constant, A (cm²) is the electrode area, C (mol L⁻¹) is the concentration
526 of the diffusing species in the bulk of the electrolyte, D_0 (cm² s⁻¹) is the corresponding
527 diffusion coefficient, s (V s⁻¹) is the scan rate, R (J mol⁻¹ K⁻¹) is the universal gas constant and
528 T (K) is the temperature. Considering that $n = 1$ and $C = 1$ mol L⁻¹ (H₂SO₄), the diffusion
529 coefficients were found to be 1.602×10^{-13} , 1.156×10^{-13} and 6.973×10^{-14} cm² s⁻¹ for
530 C0S100T, C50S50T180_1 and C50S50T180_u, respectively. These values are considerably
531 lower than those obtained for well-established redox processes in other doped carbons used as
532 electrode materials, such as graphene-polyaniline (PANI) nanocomposites or PANI systems
533 alone, suggesting a hindered ion transport (Gómez et al., 2011). Therefore, activation for
534 opening the porosity and developing it further appears necessary for improving the
535 electrochemical performance of these materials. For instance, we have recently shown that
536 CO₂ activation allows increasing the surface area of tannin-derived mesoporous carbons up to
537 nearly 2000 m²/g and maintaining high-rate capability when increasing the current density up
538 to 80 A/g (Castro-Gutiérrez et al., 2019). The same kind of behaviour can therefore be
539 expected with the present samples.

540

Figure 12

541 **4. Conclusions**

542 Tannin-sucrose blends mixed in various proportions were submitted to hydrothermal
543 carbonisation (HTC) at different pH and temperatures, and then pyrolysed at 900°C under
544 nitrogen flow. Microporous carbon spheres with BET areas as high as 810 m²/g, without
545 further activation, were produced. Adding more sucrose produced microspheres of lower
546 particle size due to the increased amount of germs produced by the HTC of sucrose.

547 HTC was confirmed to be an interesting low-cost and environment-friendly step to tune the
548 properties of the resultant carbon materials, modifying their porous texture and their chemical
549 composition, and thus broadening the range of their properties and therefore of their
550 applications. The preliminary electrochemical tests reported here were carried out to select the
551 most promising materials for further research. Although the carbon electrodes presented a
552 quasi-reversible redox reaction concerning oxygen groups, their narrow pores hindered
553 transport of electrolyte ions and led to low values of capacitance retention when increasing
554 the current density and the scanning rate. Activation should significantly improve this results,
555 and will be the object of a forthcoming study.

556

557 **Acknowledgements**

558 The present research was partly made possible by the support of the Region Lorraine and
559 University of Lorraine through the programme ‘Jeunes chercheurs’. The French authors also
560 gratefully acknowledge the financial support of the CPER 2007-2013 “Structuration du Pôle
561 de Compétitivité Fibres Grand’Est” (Competitiveness Fibre Cluster), through local (Conseil
562 Général des Vosges), regional (Région Lorraine), national (DRRT and FNADT) and
563 European (FEDER) funds.

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756 Synthesis and properties of porous carbons based on tannin-sucrose mixtures treated in
757 hydrothermal conditions
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760 Captions of the Figures

761 **Fig. 1:** Main flavonoid unit contained in Mimosa tannin extract.

762 **Fig. 2:** Changes of HTC yield of H0S100T180 and H50S50T180 hydrochars obtained at
763 different pH, and BET areas of the corresponding carbons after subsequent pyrolysis at 900°C
764 (dashed lines are just guides for the eye).

765 **Fig.3:** Typical SEM images of carbon materials (i.e., pyrolysed at 900°C) based on: tannin
766 (CH0S100T) and sucrose (CH100S0T) submitted to HTC at 180°C with, a) and b)
767 unmodified pH and d) and e) pH 2, respectively; based on 50S50T samples submitted to HTC
768 at 180°C with c) unmodified pH and f) pH 2; and finally based on 50S50T samples submitted
769 to HTC at pH 2 g) at 160°C and h) 200°C.

770 **Fig. 4:** Total carbon yield and BET area of HTC materials (H50S50T) prepared at different
771 HTC temperatures (160, 180 and 200°C) at unmodified pH and pH 2, and of pyrolysed
772 (900°C) CH50S50T carbons.

773 **Fig. 5:** Typical SEM images of carbon materials (i.e., pyrolysed at 900°C) based on sucrose
774 and tannin mixed in proportions ranging from 25-75 to 100-0 (from left to right) and
775 submitted to HTC at unmodified pH (a, b, c) and pH 2 (d, e, f).

776 **Fig. 6:** a) HTC yield of materials made at 180°C at different T/S proportions and of
777 CH50S50T samples prepared at 160 and 200°C; b) Corresponding BET areas A_{BET} after HTC
778 and subsequent pyrolysis at 900°C. The dashed lines in a) were calculated (see text), and are
779 just guides for the eye in b).

780 Fig. 7: BET areas A_{BET} (open symbols) and product Total carbon yield $\times A_{BET}$ (full symbols)
781 as a function of the total carbon yield for materials at different T/S proportions after HTC at
782 180°C and subsequent pyrolysis at 900°C.

783 Fig. 8: a) Nitrogen adsorption-desorption isotherms (full and open symbols, respectively) at -
784 196°C for CH50S50T180_2 and CH50S50T180_u samples; and b) their pore size
785 distributions determined by the DFT method (slit-like pore geometry).

786 Fig. 9: a) Van Krevelen diagram for all materials before (100S0T and 0S100T) and after HTC
787 (H100S0T and H0S100T) at 160, 180 and 200°C, at unmodified pH (HsStT_u) and at pH 2
788 (HsStT_2) and posterior pyrolysis at 900°C (HTC_900°C); and b) total amounts of CO and
789 CO₂ gases produced during TPD analysis for materials after HTC at 180°C at different weight
790 fractions of tannin.

791 Figure 10. Cyclic voltammetry (CV) results obtained in a three-electrode cell in 1 mol L⁻¹
792 H₂SO₄ electrolyte: (a) CV curves recorded at 0.5 mV s⁻¹ scan rate; (b) CV curves recorded at
793 10 mV s⁻¹ scan rate; (c) Specific capacitance of the samples at scan rates between 0.5 and 100
794 mV s⁻¹; (d) Capacitance retention at scan rates between 0.5 and 100 mV s⁻¹.

795 Figure 11. Cyclic voltammetry (CV) results obtained in a three-electrode cell in 1 mol L⁻¹
796 H₂SO₄ electrolyte: (a, c, e) CV curves recorded at 0.5 mV s⁻¹ scan rate for the first cycle,
797 showing the redox peaks on both anodic and cathodic branches; (b, d, f) Evolution of the
798 potential difference (ΔE) between the maxima of the anodic and cathodic peak 1 as a function
799 of the cycle number; CV curves were recorded at scan rates between 0.5 and 5 mV s⁻¹ for
800 C0S100T, and between 0.5 and 2 mV s⁻¹ for CH50S50T180_1 and CH50S50T180_u.

801 Figure 12. (a, c, e) Dependence of the anodic and cathodic peaks currents, $I_{p,ox}$ and $I_{p,red}$, on
802 the square root of the scan rate, $s^{1/2}$; (b, d, f) Evolution of the peak potentials, $E_{p,ox}$ and $E_{p,red}$,
803 versus the natural logarithm of the scan rate, $\ln s$.

804 Synthesis and properties of porous carbons based on tannin-sucrose mixtures treated in
805 hydrothermal conditions

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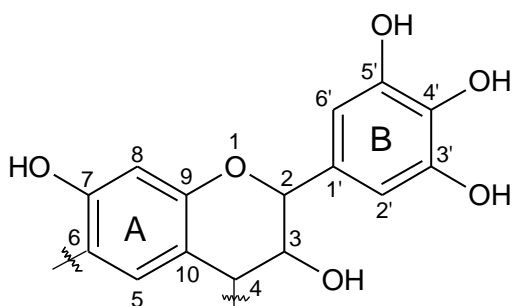
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Figure 1

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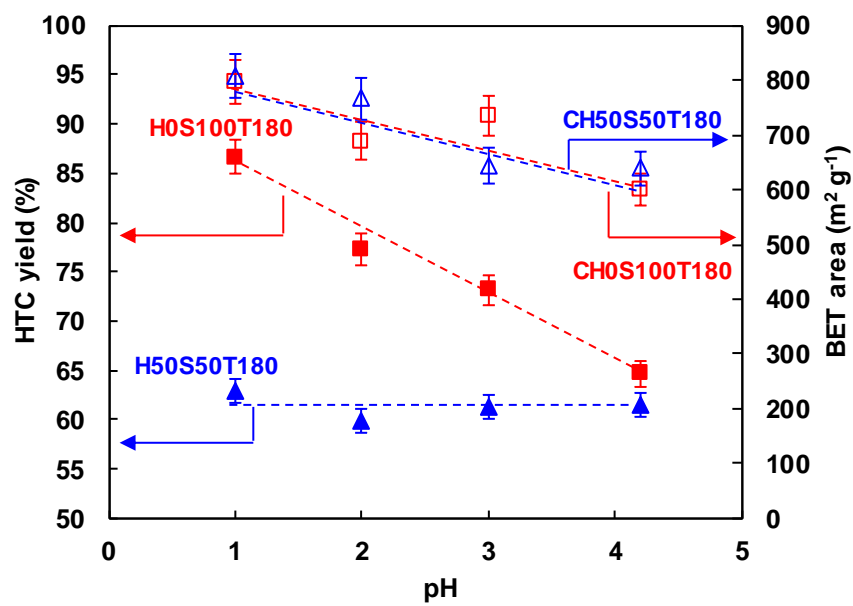
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Figure 2

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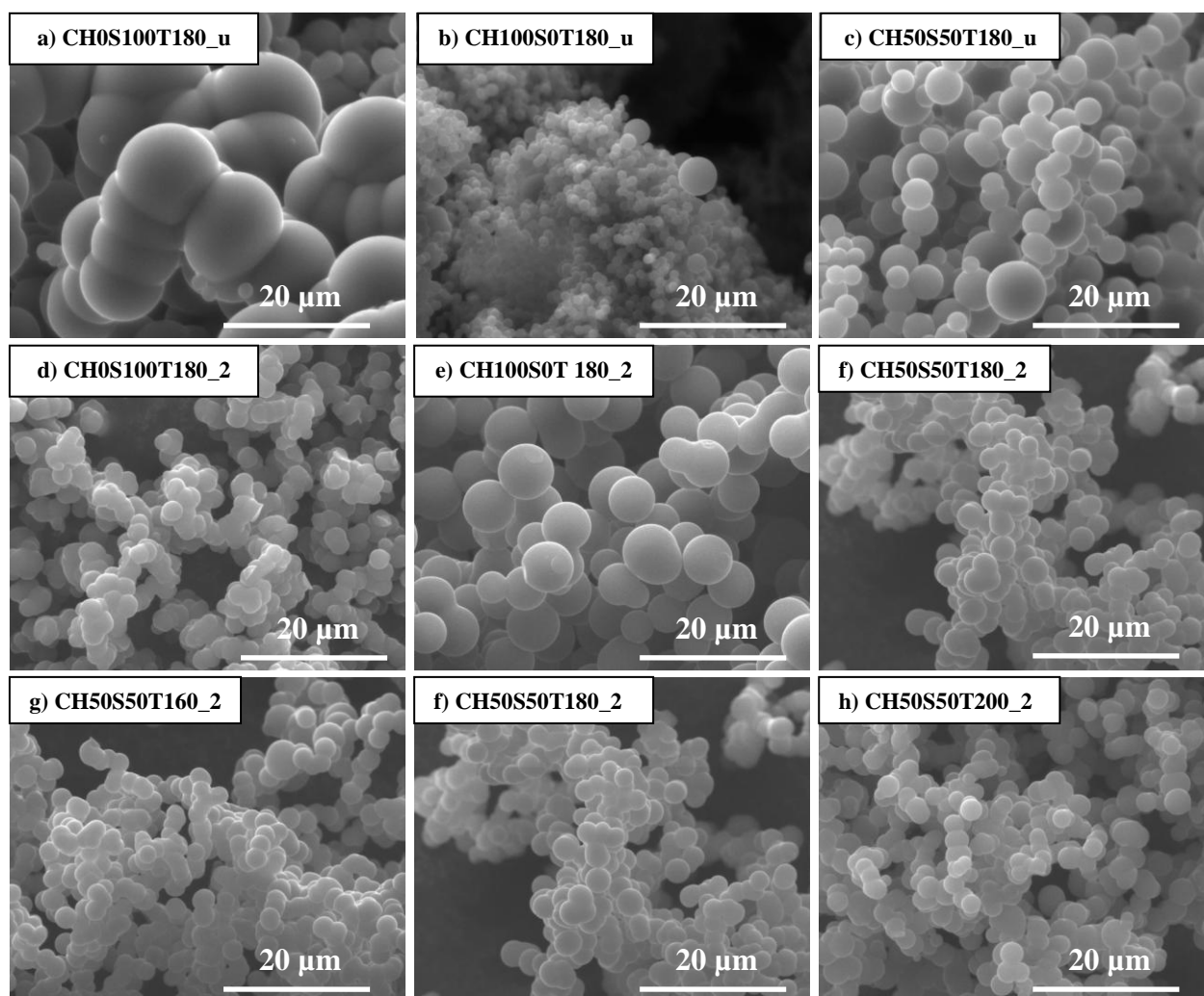
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Figure 3

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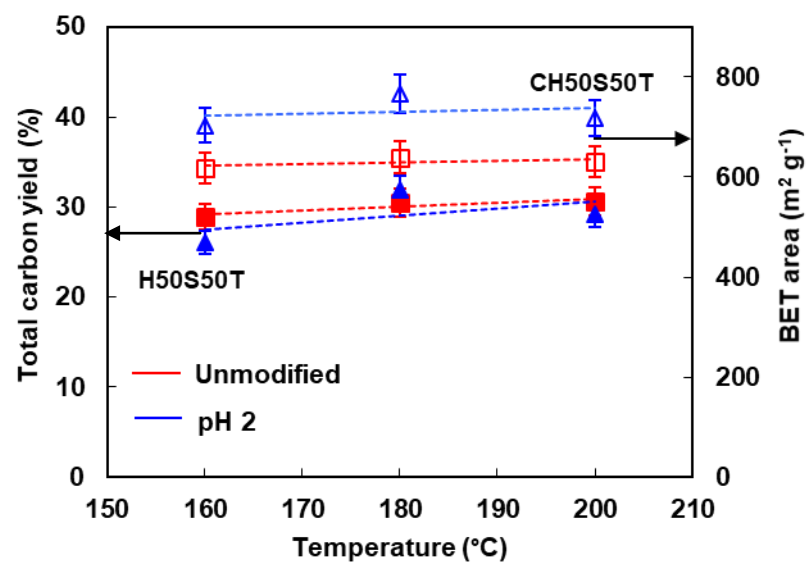
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Figure 4

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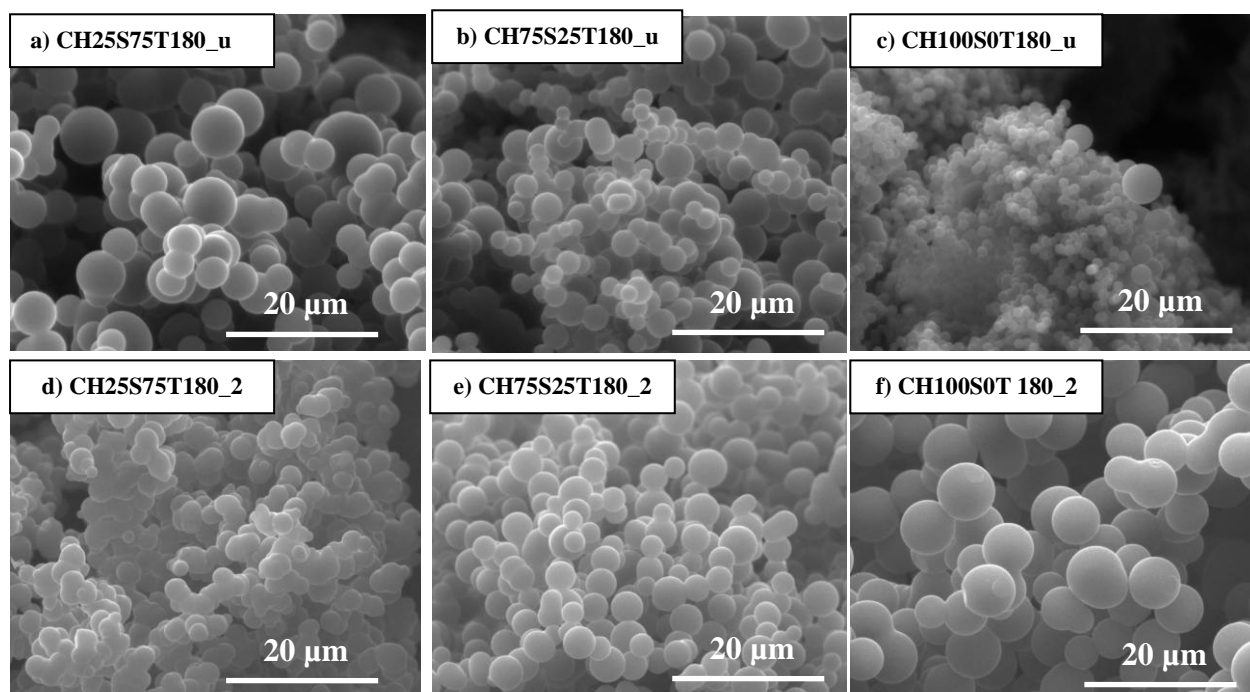
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Figure 5

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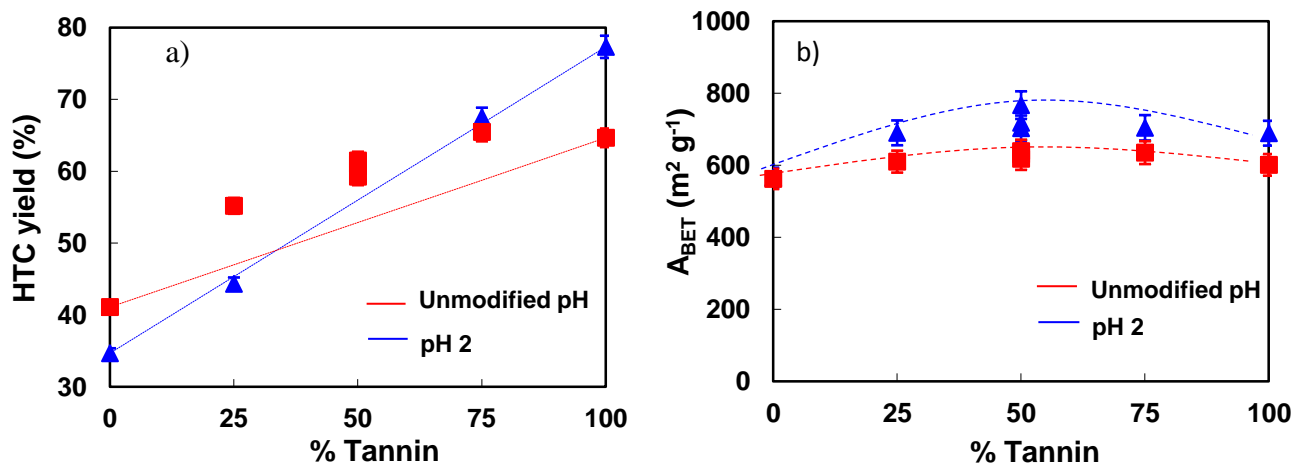
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Figure 6

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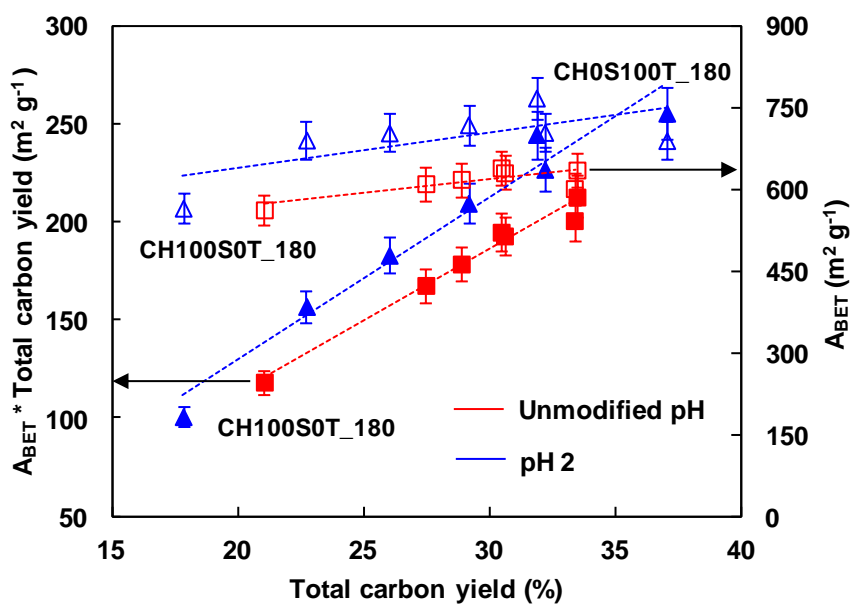
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Figure 7

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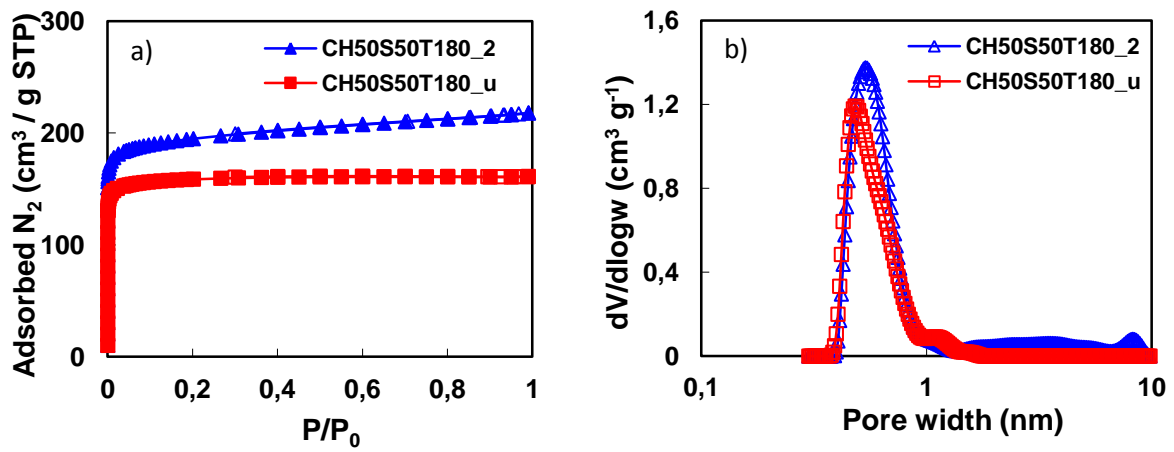
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Figure 8

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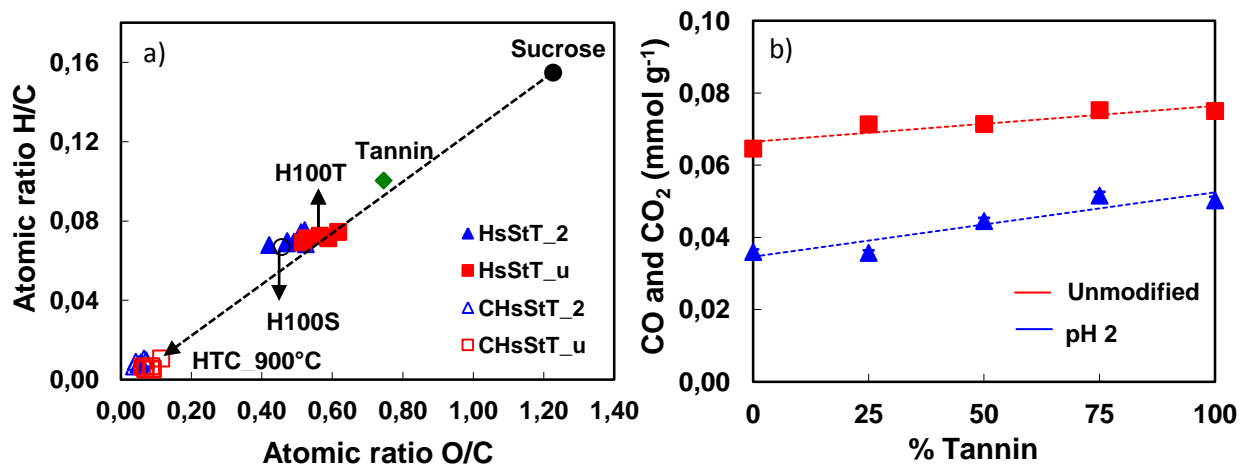
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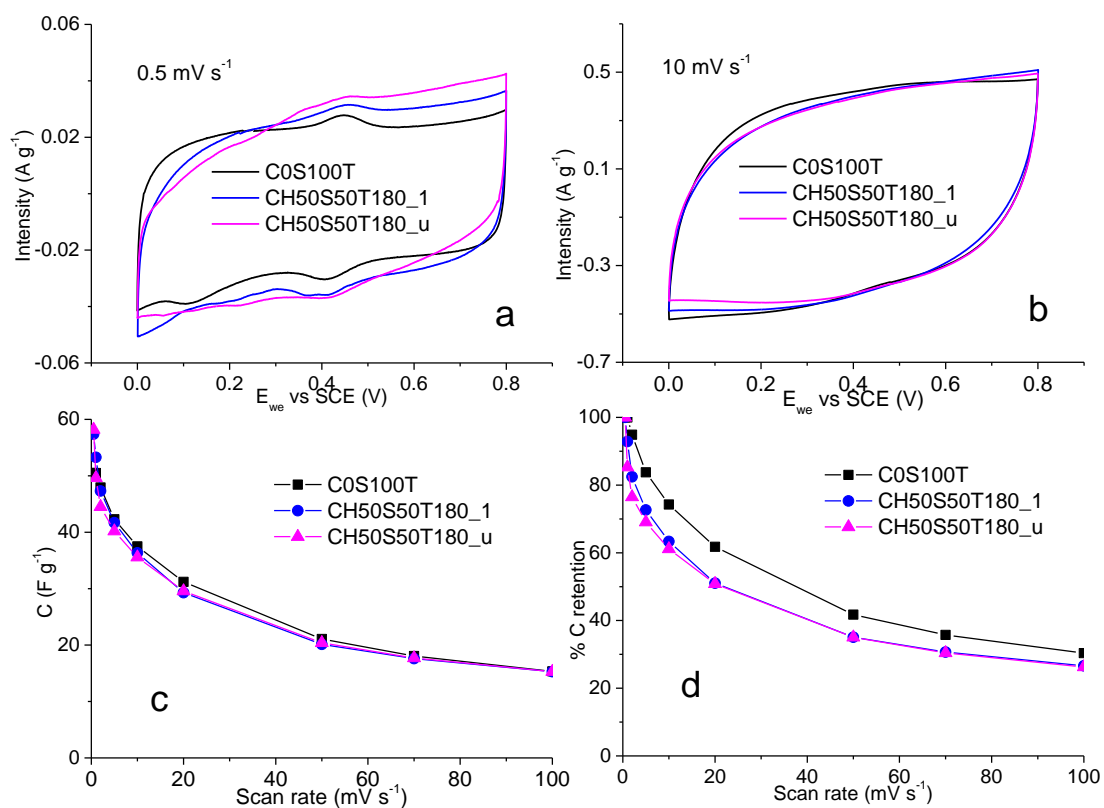
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Figure 10

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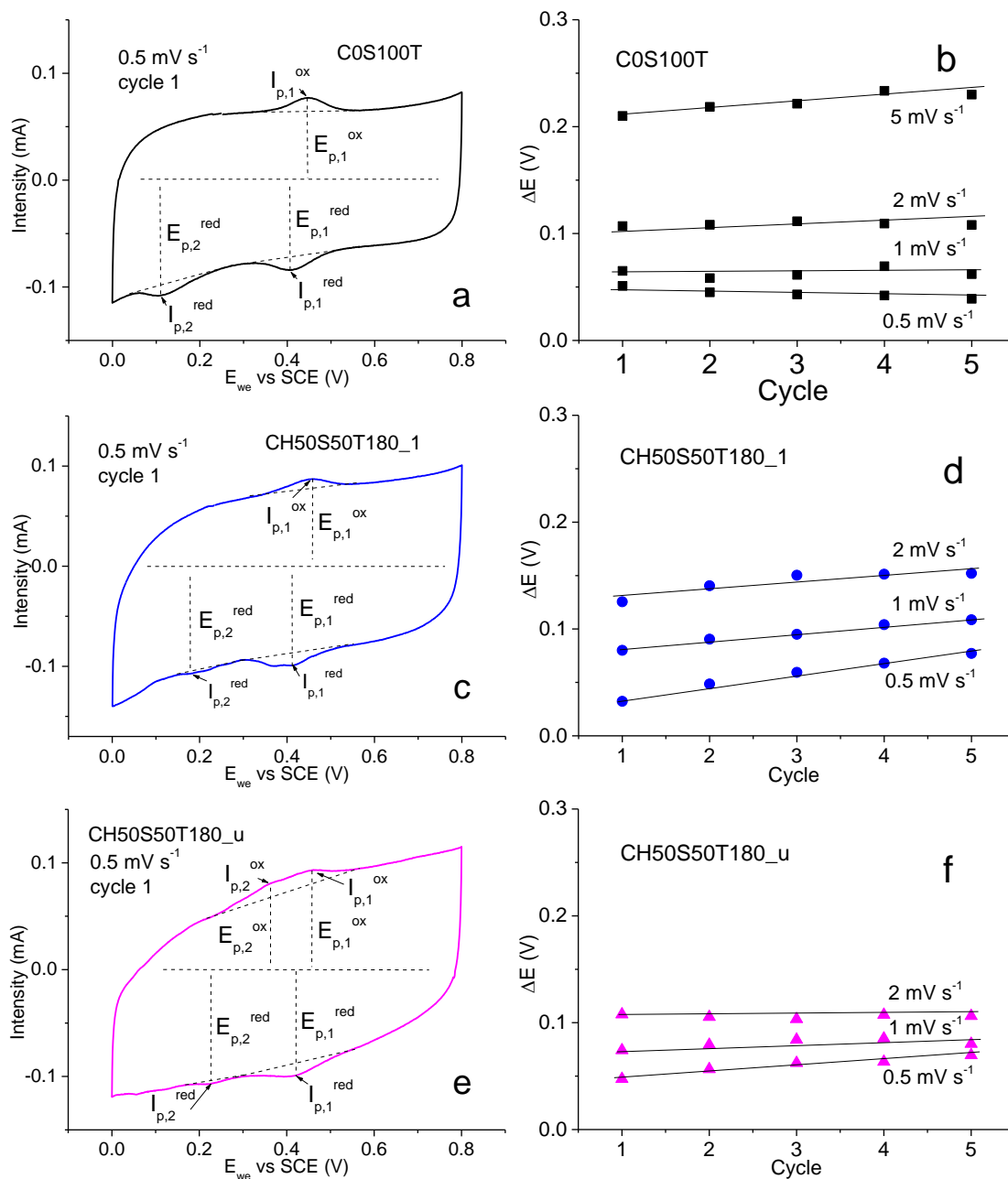
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Figure 11



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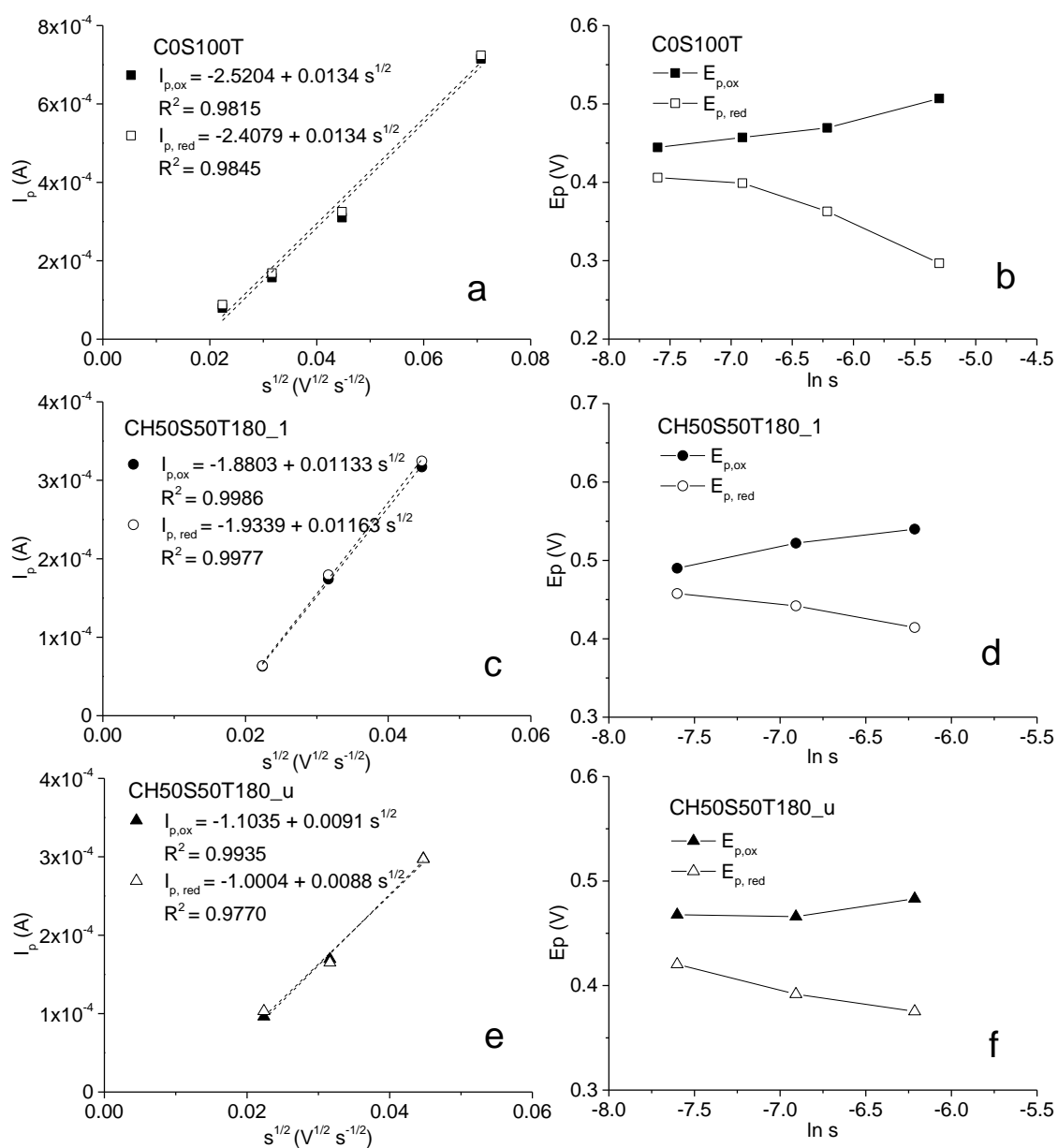
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Figure 12

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