

Advances in tailoring the porosity of tannin-based carbon xerogels

Natalia Rey-Raap¹, Andrzej Szczurek², Vanessa Fierro², Alain Celzard², J. Angel Menéndez¹, Ana Arenillas^{1*}

¹ Instituto Nacional del Carbón, CSIC, Apdo 73, 33080 Oviedo, España

² Institut Jean Lamour -UMR CNRS-Université de Lorraine n°7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France

ABSTRACT

Usually, carbon xerogels are obtained from resorcinol-formaldehyde organic gels. However, more cost-effective and eco-friendly carbon xerogels can be synthesized by using tannins instead of resorcinol, provided that a suitable surfactant is added to prevent the collapse of the structure. **The use of tannin, a natural phenolic compound derived from wood, allows obtaining carbon xerogels with controlled porosity, as** the porous properties of these materials can be tailored by an appropriate choice of the synthesis conditions. In this work, tannin-formaldehyde xerogels containing different amounts of surfactant and formaldehyde were synthesized in order to evaluate their effect on the porous structure and chemical composition. It was found that porosity and density depend greatly on the amount of surfactant. The lowest density and highest porosity values -0.34 g/cm³ and 78%, respectively- were obtained by adding 10 wt. % of surfactant. It was also found that S-doped carbon xerogels can be easily synthesized due to the strong affinity between the carbon in the structure and the sulphur from the surfactant. Furthermore, statistical analysis showed that there is interdependence between the effect of formaldehyde and the surfactant, especially in the case of volume and pore size. Hence, the choice of the appropriate surfactant-formaldehyde

*Corresponding author. E-mail: aapunte@incar.csic.es (A. Arenillas)

Tel. +34 985119090

Fax +34 985297662

25 concentration is essential for controlling the formation of the porous polymeric
26 structure.

27

28 **Keywords:** carbon gel, tannin, surfactant, controlled porosity

29

30 **1 Introduction**

31 Carbon gels are porous materials that are obtained by drying and carbonizing organic
32 polymer-based gels (Elkhatat and Al-Muhtaseb, 2011). The great advantage of these
33 materials is that, depending on the preparation method and the nature, concentration and
34 chemical composition of the precursors, the porous structure can be controlled (Matos et
35 al., 2006; Rey-Raap et al., 2014). Hence, their final properties can be tailored to fit the
36 requirement of a specific application. The versatility of carbon xerogels is the reason
37 why these materials are perfect candidates for various applications such as adsorption
38 (Job et al., 2005), hydrogen storage (Zubizarreta et al., 2009), electrode material for
39 supercapacitors or batteries (Braghiroli et al., 2015b; Roberts et al., 2014), catalyst
40 support (Yang et al., 2014), thermal insulators (Tannert et al., 2015), etc.

41

42 The most common method of synthesizing organic gels is by means of the
43 polymerization of resorcinol with formaldehyde in the presence of a solvent (Elkhatat
44 and Al-Muhtaseb, 2011). The organic gel obtained can be dried under supercritical
45 conditions, by freeze-drying process or by evaporation, which give rise to aerogels,
46 cryogels and xerogels, respectively (Rey-Raap et al., 2014). The preparation of aerogels
47 and cryogels involves cumbersome solvent exchange processes and complex drying
48 stages (Al-Muhtaseb and Ritter, 2003). Thus, evaporative drying is the quickest and
49 simplest method and therefore, yields the most cost-competitive materials.

50

51 Although resorcinol and formaldehyde are the most commonly employed reagents, they
52 are costly and harmful to the environment. Consequently, studies with less expensive
53 and greener precursors have been undertaken over the last few decades (Rey-Raap et al.,
54 2015; Szczurek et al., 2014). All the hydroxylated benzenes tested to date contain
55 reactive hydroxyl groups which make them similar to resorcinol in the way they react
56 with aldehydes (Arbenz and Averous, 2014; Lochab et al., 2014). Of all the possible
57 reagents, the use of tannin, a natural counterpart to resorcinol, for the synthesis of
58 carbon gels has attracted a great deal of interest in recent years due to the characteristics
59 of this reagent, which is “eco-friendly”, cheap and non-toxic (Braghiroli et al., 2015a;
60 García et al., 2014).

61

62 As in the synthesis of resorcinol-formaldehyde carbon xerogels, the concentrations of
63 all the reagents employed to polymerize tannin with formaldehyde (i.e., tannin,
64 formaldehyde, solvent and catalyst), play an important role in tailoring the final
65 properties of these porous materials (Amaral-Labat et al., 2013b; Rey-Raap et al.,
66 2014). These concentrations have been reported in the literature to be related to the pH,
67 the percentage of solids and the weight ratio of tannin to formaldehyde (Amaral-Labat
68 et al., 2013b; Szczurek et al., 2014). The pH has been one of the most studied variables
69 as it has a great influence on the final properties of tannin-formaldehyde carbon gels
70 over the entire range of porosity (Amaral-Labat et al., 2013a; Amaral-Labat et al., 2015;
71 Amaral-Labat et al., 2013b; Szczurek et al., 2011a; Szczurek et al., 2011b). Other
72 studies focused on the influence of the pH and percentage of solids, have reported that a
73 decrease in pH and percentage of solids leads to an increase in macroporosity, while
74 mesoporosity reaches its maximum value with an increase in the percentage of solids

75 (Amaral-Labat et al., 2013b). It should be pointed out that most of the studies reported
76 to date were performed on aerogels and cryogels (Amaral-Labat et al., 2013b; Szczurek
77 et al., 2011a; Szczurek et al., 2011b), since the synthesis of carbon xerogels with tannin
78 as precursor can only be achieved if surfactants are added (Amaral-Labat et al., 2013a;
79 Amaral-Labat et al., 2015). In a study on the synthesis of tannin-based xerogels,
80 Amaral-Labat et al. reported the effect that modifying the concentration of Pluronic F-
81 127 from 5 to 20 wt. % has on the final porous properties (Amaral-Labat et al., 2015).
82 These authors found that xerogels turned from macroporous to mesoporous materials as
83 the amount of surfactant was increased. However, triblock copolymer surfactants such
84 as Pluronic require both an increase in temperature and the addition of an organic
85 solvent to dissolve and, hence, an extra step is required in the synthesis process
86 (Amaral-Labat et al., 2013a; Amaral-Labat et al., 2015). **However, a recently published**
87 **work has demonstrated that tannin-based xerogels can be synthesized by using sodium**
88 **dodecyl sulphate (Rey-Raap et al., 2015). The use of this latter surfactant is expected to**
89 **give rise to S-doped materials. The introduction of heteroatoms during the synthesis**
90 **process is of great importance. For instance, the production of S-doped carbon materials**
91 **can enhance the properties of the started carbons and improve its suitability in some**
92 **applications concerning sorption and energy storage/conversion devices (Kiciński et al.,**
93 **2014).**

94

95 Despite the importance of the concentration of formaldehyde for tailoring the porous
96 properties, the effect of modifying the tannin to formaldehyde weight ratio from 0.5 to
97 0.6 has been evaluated, to the best of our knowledge, in only one study (Szczurek et al.,
98 2011a), that focuses on carbon cryogels. Yet it is essential to appreciate the importance

99 of the concentration of formaldehyde for the polymerization reaction in order to control
100 porous properties of carbon xerogels.

101

102 The aim of the present work is to move a step closer towards the synthesis of tailored
103 porous carbon xerogels by a more cost-effective and environment-friendly route. To
104 achieve this goal, tannin-formaldehyde carbon xerogels were synthesized using different
105 amounts of formaldehyde and surfactant. The surfactant employed in the present study
106 does not require the addition of any organic solvent as it can be easily dissolved in
107 water. All the carbon xerogels synthesized were characterized from the point of view of
108 their chemical and porous structure in order to determine the effect of formaldehyde and
109 surfactant on the final porous properties of the xerogels.

110

111 **2. Experimental**

112 *2.1 Raw materials*

113 Commercial wattle tannin extracted from *Acacia Mearnsii* (De Wild) bark was used for
114 the present study. This raw material was kindly supplied by SilvaChimica (San Michele
115 Mondovi, Italy) under the name of Fintan OP. The industrial extraction process of
116 tannins has been explained in detail elsewhere (Braghiroli et al., 2014). Briefly, fresh
117 bark was subjected to leaching in a sodium bisulphite aqueous solution at 70°C. The
118 resulting solutions were concentrated and then spray-dried to yield a light-brown
119 powder containing 80-82 wt. % of phenolic flavonoid materials, 4-6 wt. % of water, 1
120 wt. % of amino acids and other components such as monomeric and oligomeric
121 carbohydrates consisting of broken pieces of hemicellulose. The light-brown powder
122 thus obtained is referred to as tannin (T).

123

124 Formaldehyde (37 wt. % in water, stabilized by 10-15 wt. % of methanol), was supplied
125 by Roth. The sodium dodecyl sulfate and sodium hydroxide were purchased from
126 Sigma Aldrich and from Carlo Erba, respectively.

127

128 *2.2 Preparation of the carbon xerogels*

129 Organic gels were synthesized by the polycondensation of tannin (T) and formaldehyde
130 (F) using deionized water as solvent, sodium hydroxide as catalyst, and sodium dodecyl
131 sulfate (SDS) as surfactant (all the relevant data related to the reagents employed in this
132 study can be found in the Supporting Information). Tannin was first dissolved in
133 deionized water in open glass beakers under magnetic stirring at room temperature.
134 Once the tannin had dissolved, formaldehyde was introduced into the solution. Finally,
135 sodium dodecyl sulfate was added and the resulting mixture was stirred until a
136 homogeneous brown solution was obtained. All the gels were synthesized from 20 mL
137 of precursor solution with a pH value fixed at 5.5 by adding sodium hydroxide. The
138 tannin/formaldehyde weight ratio varied between 0.6 and 2.6 whereas the percentage of
139 solids remained fixed at 25 wt. % for all the samples. The concentration of sodium
140 dodecyl sulfate varied between 0 and 20 wt. %.

141

142 Each precursor solution was poured into a sealed glass tube, **with an inner diameter**
143 **value of 1.4 cm**, which was then placed in a ventilated oven at 85°C for 72 h to undergo
144 gelation and curing. Afterwards, the tube was opened and introduced again into the
145 oven at 85°C for 48 h for the organic gel to completely dry by evaporation of the
146 solvent. Once dry, each xerogel was carbonized at 900°C under nitrogen in a horizontal
147 tubular furnace. The residence time was 2 h and the heating rate was set at 5°C/min. The

148 resultant carbon xerogels were labelled ‘TF’ followed by the tannin-formaldehyde
149 weight ratio and the percentage of surfactant added, e.g., TF-1.2-10%.

150

151 *2.3 Sample characterization*

152 The porous properties of the carbon xerogels were characterized by means of mercury
153 porosimetry (Autopore IV, Micromeritics). Measurements were performed between
154 0.0035 and 414 MPa, and Washburn’s equation was applied to the corresponding data
155 to obtain the specific pore volume and average pore size (see supporting information for
156 more details). Skeletal and bulk densities were determined by helium (Accupyc II 1340,
157 Micromeritics) and envelope (Geopyc 1360 Envelope Density Analyzer, Micromeritics)
158 pycnometry, respectively. The overall porosity was determined from the bulk and
159 skeletal densities. The morphology of the carbon structure was observed using a Quanta
160 FEG 600 scanning electron microscope and the chemical structure was investigated
161 using an Infrared Affinity-1 spectrometer (Shimadzu, Japan) by applying an average of
162 20 scans at a maximum resolution of 4 cm^{-1} over a range of $4000\text{--}400\text{ cm}^{-1}$. For this
163 purpose, pellets were prepared by pressing 1 mg of sample ground together with 100 mg
164 of dry potassium bromide. The chemical composition of the samples was determined by
165 elemental analysis (C, H, O, N, S), using a Vario EL Cube microanalyzer (Elementar).

166

167 *2.4 Statistical analysis*

168 Response surface methodology was applied to the porous characterization data in order
169 to assess the significance of each of the variables studied (amount of anionic surfactant
170 (SDS) and tannin/formaldehyde (T/F) weight ratio) and of any possible synergy
171 between them. Significance was determined by applying an analysis of variance
172 (ANOVA) to each of the four porous properties selected as responses: porosity, bulk

173 density, pore volume and average pore size. The implementation of ANOVA allows the
174 interaction between variables and their effect on the main porous properties to be
175 evaluated with a minimum number of experiments. If the p-values obtained from the
176 ANOVA were smaller than 0.05, the corresponding variable would be assumed to have
177 a significant effect on the response. An optimal design covering all the possible SDS-
178 T/F combinations together with repeated experimental runs were employed to obtain a
179 statistical model that adequately fitted the experimental results. The design matrix was
180 generated by using a Design-Expert 9.0 Trial version from Stat-Ease Inc.

181

182 **3 Results and discussion**

183 *3.1 Statistical analysis*

184 Response surface methodology was applied to the four variables selected as responses:
185 porosity, bulk density, pore volume and average pore size. Porosity and bulk density
186 were adjusted to a quadratic function, whereas pore volume and average pore size were
187 fitted to a cubic function. The R-squared values for porosity, bulk density, pore volume
188 and average pore size were 0.90, 0.93, 0.89 and 0.96, respectively, indicating that the
189 calculated results are in good agreement with those obtained experimentally. Moreover,
190 the data obtained by employing a least square technique indicate that the model applied
191 to each response is significant (the ANOVA data for each response variable are shown
192 in Tables S1, S2, S3 and S4 in the Supporting Information). The linear and quadratic
193 terms for the amount of surfactant have a significant effect on porosity and density,
194 whereas the volume and the average size of the pores depend on linear, quadratic and
195 cubic terms of the amount of surfactant, and also on the T/F weight ratio and the
196 interaction between the SDS and T/F weight ratio. Figure 1 shows the three-dimensional
197 surface plots constructed on the basis of model equations that represent the response

198 surface curves of the independent variables (T/F weight ratio and percentage of
199 surfactant) versus the dependent variables: porosity (Figure 1a), bulk density (Figure
200 1b), pore volume (Figure 1c) and average pore size (Figure 1d). From the ANOVA
201 analysis it can be inferred that the four variables studied are highly dependent on the
202 percentage of surfactant, while the T/F weight ratio significantly affects only on the
203 volume and average size of the pores.

204

205 Figure 1. Three-dimensional surfaces representing the effect of the T/F weight ratio and
206 percentage of surfactant on the porosity (a), bulk density (b), pore volume (c) and
207 average pore size (d) of tannin-based carbon xerogels.

208

209 *3.2 Effect of the surfactant*

210 In Figures 1a and 1b, clear differences can be observed when the percentage of
211 surfactant is modified. By adding 10 wt. % of surfactant, all the carbon xerogels exhibit
212 the lowest density and highest porosity values, 0.34 g/cm³ and 78%, respectively. An
213 increase in the percentage of surfactant to above 10 wt. % causes a slight decrease in
214 porosity from 78% to 70%. Conversely, a decrease to below 10 wt. % leads to materials
215 with a poorly developed porous structure, with an average porosity of less than 20% if
216 no surfactant is added.

217

218 The effect of the anionic surfactant (SDS) on the final porous structure of TF carbon
219 xerogels can be attributed to the polymerization of the tannin and formaldehyde. Since
220 reactive hydroxyl groups give tannin a reactivity towards formaldehyde similar to
221 resorcinol (Amaral-Labat et al., 2013a; Arbenz and Averous, 2014), it is possible to
222 deduce a mechanism for the reaction based on the well-known polymerization reaction

223 between resorcinol and formaldehyde. Hence, the first step in the polymerization of
224 tannin and formaldehyde can be assume to be the formation of tannin anions via
225 hydrogen abstraction (Rey-Raap et al., 2014). Formaldehyde is then added to them to
226 form hydroxymethyl derivatives which are linked to each other by methylene and ether
227 bonds. As the reaction proceeds, the number of bonds between the rings increases,
228 leading to the formation of the polymer backbone and, in turn, three-dimensional cross-
229 linked polymer clusters (Rey-Raap et al., 2014). However, two points must be borne in
230 mind when using tannin as precursor for the synthesis of carbon gels (Rey-Raap et al.,
231 2015): i) the larger amount of OH groups in tannin molecules compared to those of
232 resorcinol will probably leave a larger number of unreacted OH groups and ii) as the
233 large size and lack of flexibility of tannin molecules cause steric hindrance, the addition
234 of formaldehyde will be less effective than if resorcinol is used. As a result, a poorly
235 branched structure, whose mechanical strength will not be able to counteract the
236 capillary forces created during drying, is formed. Hence, the material shrinks, leading to
237 the collapse of the polymeric structure and to a poorly developed porosity. The addition
238 of sodium dodecyl sulfate (anionic surfactant) prevents shrinkage due to the repulsive
239 forces among the tannin anions generated during the polymerization reaction and, as a
240 result, the structure of the xerogel forms further away from the SDS micelles (Matos et
241 al., 2006). Furthermore, due to these repulsive forces, the formation of methylene and
242 ether bonds is retarded and, consequently, a longer time is required for the completion
243 of the sol-gel reaction. The time required for the accomplishment of the sol-gel reaction
244 is directly related to the growth and formation of clusters: longer times lead to the
245 formation of a small number of large clusters. The differences in cluster size are clearly
246 shown in Figure 2a and 2b, where SEM images of samples with 5 wt. % and 10 wt. %
247 of surfactant are displayed. An increase in the concentration of surfactant from 5 wt. %

248 to 10 wt. % gives rise to structures with larger clusters and, as a result, with a greater
249 porosity (Figure 1a). On the other hand, an excessive amount of surfactant leads to the
250 formation of a poorly cross-linked polymeric structure and to a more heterogeneous
251 material (Figure 2c) with a broader pore size distribution, as shown in Figure S2 in the
252 Supporting Information.

253

254 Figure 2. SEM images of organic TF xerogels with 5 wt. % (a), 10 wt. % (b) and 20 wt.
255 % (c) of surfactant.

256

257 The elemental analysis data in Table S5 in the supporting information clearly show that
258 the anionic surfactant is prevalent in the organic samples, since the sulphur content
259 increases from 0 to 7-9 wt. % (on dry basis) when the amount of surfactant is increased
260 from 0 to 20 wt. %. The infrared spectroscopy spectra of the organic xerogels in Figure
261 3 indicate that the surfactant interacts with the polymeric structure, as a result of which
262 new functionalities are incorporated into the final material.

263

264 Figure 3. FT-IR spectra of SDS anionic surfactant and organic TF xerogels with 5 wt.
265 %, 10 wt. % and 20 wt. % of surfactant.

266

267 Sample TF-1.2-0% presents a more intense band at around 3300 cm^{-1} , associated to O-H
268 stretching vibrations, than samples TF-1.2-10% and TF-1.2-20%, and a more intense
269 band at *ca.* 1600 cm^{-1} attributed to the characteristic modes of aromatic rings (Lochab et
270 al., 2014). This is probably due to the incorporation of the carbonaceous chains of the
271 surfactant that gives rise to materials with a lower concentration of OH groups and to a
272 lower aromatic ring content. On the other hand, the incorporation of SDS induces a

273 higher concentration of aliphatic C-H, as a result of which samples TF-1.2-10% and TF-
274 1.2-20% display more intense bands at 2900-2800 cm^{-1} and 1400-1500 cm^{-1} than the
275 pristine organic xerogel (Viana et al., 2012). Also, samples with surfactant present a
276 new type of surface group corresponding to the sulphur content and as a consequence,
277 an absorption band at *ca.* 1230 cm^{-1} attributed to the SO_2 asymmetric vibrations appears
278 (Viana et al., 2012). This functional group is probably also responsible for the presence
279 of the peaks at wavenumbers lower than 1100 cm^{-1} . Some authors point out that the
280 values corresponding to these peaks may vary according to the way in which the
281 molecules are packed (Viana et al., 2012).

282

283 The data obtained from the infrared spectroscopy spectra are in good agreement with
284 the results of the elemental analysis of the carbon xerogels in Figure 4. The results
285 obtained are in agreement with the idea that not all the surfactant is released as volatile
286 matter during carbonization, probably due to the strong affinity between sulphur and
287 carbon. These results are of great interest, as not only are cheaper and more
288 environmentally-friendly materials obtained, but also S-doped materials, which are
289 useful for a wide range of applications (Kiciński et al., 2014).

290

291 Figure 4. Sulphur content in organic and carbon xerogels.

292

293 *3.3 Effect of formaldehyde*

294 The T/F weight ratio hardly affects the density and porosity of the carbon xerogels
295 within the range studied (Figure 1a and 1b). However, the volume and average size of
296 the pores differ greatly when the T/F weight ratio is modified. In general, as with RF
297 carbon xerogels, an increase in the concentration of formaldehyde shifts the chemical

298 equilibrium towards the products, favouring the addition reaction. This suggests that
299 clusters form and grow faster, resulting in TF structures with a large number of small
300 clusters, as illustrated in Figure 5. However, in TF carbon xerogels, there is also
301 interdependence between the effect of the formaldehyde and that of the surfactant, as
302 shown by the data from the statistical analysis mentioned above, on the basis of which
303 different porous structures can be tailored depending on the SDS-T/F combination
304 employed to prepare the precursor solution.

305

306 Figure 5. SEM images of carbon xerogels with 10 wt. % of SDS and a T/F weight ratio
307 of 2.6 (a) and 1.2 (b).

308

309 Formaldehyde not only accelerates the formation and growth of clusters but also creates
310 more interconnections between the clusters (Rey-Raap et al., 2014), leading to highly
311 branched structures. Hence, when the concentration of surfactant is low (below 10 wt.
312 %), carbon xerogels synthesized with a large amount of formaldehyde have a lower
313 volume of pores of smaller size, as shown in Figure 6. As can be seen, the pore sizes
314 range from 0.8 to 11 μm .

315

316 Figure 6. Pore volume (columns) and average pore size (dots) of carbon xerogels
317 synthesized from precursor solutions with different T/F weight ratios and surfactant
318 concentrations.

319

320 Due to the synergy between the formaldehyde and surfactant, the effect of
321 formaldehyde can be reversed by increasing the concentration of surfactant to above 10
322 wt. %. This is probably because the higher number of micelles slows down the reaction

323 rate, causing the formation of a smaller number of clusters but of larger size, and also
324 because of the more heterogeneous material (Figure 2). This effect, combined with the
325 fact that a smaller concentration of formaldehyde gives rise to weaker structures, results
326 in materials with a mechanical strength that is not able to counteract the capillary forces
327 created during drying and hence the materials shrink. As a result, materials with a lower
328 volume of pores of smaller average size are obtained (Figure 6).

329

330 The samples with 10 wt. % of surfactant deserve special mention because in their case,
331 an increase in the T/F weight ratio results in a large increase in average pore size,
332 whereas the pore volume decreases slightly, as shown in Figure 6. This behaviour is
333 opposite to that generally found for carbon xerogels where structures with smaller pores
334 also have lower pore volumes (Rey-Raap et al., 2014). In the present study, an increase
335 in the T/F weight ratio leads to the formation of a small number of large clusters (Figure
336 5) and therefore to pores of a larger size (Figure 6). However, as the concentration of
337 formaldehyde is lower, the structure is less branched and a certain degree of shrinkage
338 takes place during drying, resulting in a slight decrease in pore volume.

339

340 In general, when the amount of surfactant increases, porosity passes through a
341 maximum, while when the T/F weight ratio is modified, the porosity increases or
342 decreases depending on the amount of surfactant added, due to the high interdependence
343 between these two variables. From these results, it can be seen that the right choice of
344 SDS-T/F combination is essential for controlling the formation of the polymeric
345 structure and for tailoring the porous properties of tannin-based carbon xerogels so that
346 they fit the requirements of a specific application.

347

348 As an example to demonstrate the importance of being able to control the porous
349 properties, the thermal conductivity of the organic TF xerogels synthesized by adding
350 10 wt. % of surfactant and different concentrations of formaldehyde (TF-2.6-10%, TF-
351 1.2-10% and TF-0.6-10%) was measured, taking into account that materials are
352 considered insulating if their thermal conductivity value is typically lower than 50
353 mW/m/K. As mentioned above, Figure 6 shows that as the amount of formaldehyde
354 increases, the average pore size decreases, whereas the pore volume increases. These
355 porous properties have a great effect on the thermal conductivity of the materials.
356 Sample TF-2.6-10% exhibits a thermal conductivity of 65 mW/m/K, corresponding to a
357 poor insulating material, whilst sample TF-1.2-10% and TF-0.6-10% present values of
358 51 and 39 mW/mK, respectively. In short, modification of the formaldehyde
359 concentration gives rise to materials with porous properties that lead to different
360 insulation capacities. **Accordingly, in order to use carbon xerogels as insulating**
361 **materials the appropriate process conditions should be chosen.**

362

363 **4 Conclusions**

364 In the present work, highly porous tannin-based carbon xerogels have been successfully
365 synthesized. An appropriate selection of the amount of surfactant and formaldehyde
366 allows controlling the formation of the polymeric structure and thus, the porous
367 properties. Materials synthesized are more cost-effective and environmentally “greener”
368 than the commonly used resorcinol-formaldehyde xerogels, **due to the use of tannin, a**
369 **natural compound industrially obtained from wood. Moreover, tannin-based xerogels**
370 **can be compared to resorcinol-formaldehyde xerogels with respect to porosity and**
371 **density. However, these “greener” materials have higher volume of large pores due to**
372 **the nature of tannin molecules and the need to use surfactants. Hence, tannin-based**

373 carbon xerogels synthesized have certain limitations for those applications requiring
374 narrow mesopores, but are totally useful in those applications in which larger pore sizes
375 are required. Furthermore, an additional advantage is that the surfactant used in the
376 present work allows sulphur to remain trapped inside the structure, which can be used as
377 a basis for obtaining S-doped carbons.

378

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388

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