Advances in tailoring the porosity of tannin-based carbon xerogels

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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

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

Keywords: carbon gel, tannin, surfactant, controlled porosity

1 Introduction

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

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

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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).

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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

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

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

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

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

2. Experimental

2.1 Raw materials

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

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

2.2 Preparation of the carbon xerogels

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

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

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

2.3 Sample characterization

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

2.4 Statistical analysis

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

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

3 Results and discussion

3.1 Statistical analysis

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

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

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

3.2 Effect of the surfactant

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

The effect of the anionic surfactant (SDS) on the final porous structure of TF carbon xerogels can be attributed to the polymerization of the tannin and formaldehyde. Since reactive hydroxyl groups give tannin a reactivity towards formaldehyde similar to resorcinol (Amaral-Labat et al., 2013a; Arbenz and Averous, 2014), it is possible to 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. %

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

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

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

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

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

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

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

Figure 4. Sulphur content in organic and carbon xerogels.

3.3 Effect of formaldehyde

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

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

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

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

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

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

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

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

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

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

4 Conclusions

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

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

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