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Towards a feasible and scalable production of bio-xerogels

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GRAPHICAL ABSTRACT

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ABSTRACT

Hypothesis: The synthesis process of carbon xerogels is limited, mainly due to two drawbacks that prevent their introduction onto the market: (i) the long time required for producing the material and (ii) the reagents used for the synthesis, which are costly and harmful to the environment. Microwave radiation is expected to produce a reduction in time of more than 90%, while the use of tannin instead of resorcinol will probably result in a cost-effective carbonaceous material.
Experiments: Resorcinol–tannin–formaldehyde xerogels containing different amounts of tannin, either with or without a surfactant (sodium dodecyl sulphate), were synthesized by means of two different heating methods: conventional and microwave heating. The effects of the surfactant, the heating method and the addition of tannin upon the porous structure and the chemical composition of the final materials were evaluated.
Findings: It was found that the addition of surfactant is essential for obtaining highly porous xerogels when using tannins. The heating method also plays an important role, as conventionally synthesized samples display a greater volume of large pores. However, tannins are less sensitive to microwave radiation and their use results in tannin–formaldehyde xerogels that have a porous structure and chemical composition similar to those of resorcinol–formaldehyde xerogels.

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1. Introduction

Carbon xerogels are porous materials that are obtained by drying and carbonizing an organic gel [1]. The organic gel is usually synthesized by the polymerization of hydroxylated benzenes and aldehydes in the presence of a solvent [2]. These materials have attracted interest due to the fact that their porous structure and chemical composition can be controlled by the right choice of synthesis conditions [3–5], to produce a wide range of tailor-made and purpose designed materials, whose characteristics meet the needs of specific applications. Hence, it can be said that carbon xerogels are high value-added materials that have a strong commercial potential. However, the synthesis process is handicapped by two major drawbacks that prevent their introduction onto the commercial market: (i) the conventional synthesis process, which involves heating the precursor solution in an electric furnace, requires several days to produce organic xerogels [2]; and (ii) the most common reagents used for the synthesis, resorcinol and formaldehyde, are costly and harmful to the environment [6].

In 2011, Calvo et al. addressed the first drawback by applying microwave radiation to all three stages of the synthesis process: sol–gel reaction, curing and drying. By this heating method, a reduction in time of more than 90% was achieved (from several days to 5–6 h), while the materials obtained displayed similar chemical and porous properties to those conventionally synthesized [7,8]. Organic xerogels synthesized by microwave heating are generally prepared from resorcinol and formaldehyde and, as mentioned above, these reactants are harmful to the environment. However, some authors have reported that by means of conventional synthesis it is possible to obtain carbon gels by using phenol [9], cresol [10,11], tannins [6,12] or cellulose [13] as hydroxylated benzenes and furfural [14] or hexamethylenetetramine [15] as aldehydes.

Of all the possible reagents mentioned above, tannins are considered to be the most viable option at industrial scale as they are “eco-friendly”, cheap and non-toxic [16]. Condensed (flavonoid) tannins are phenolic compounds derived from wood. Because they contain reactive hydroxyl groups, they are similar to resorcinol in the way they react towards aldehydes and are transformed from sols to gels [17]. These advantageous chemical characteristics explain why in recent years the number of studies on the use of tannins for the synthesis of different carbonaceous materials has increased [16–20]. The first study to deal with the use of tannins for the synthesis of carbon gels was focused on the synthesis of aerogels and cryogels [19,20], since xerogels gave rise to highly dense materials with a poorly developed porous structure. Amaral-Labat et al. were the first to synthesize highly porous tannin-based xerogels by adding Pluronic F-127 as surfactant [17]. Nevertheless, a period of ten days was needed to obtain these conventionally synthesized xerogels. Furthermore, in order to dissolve the Pluronic, it was necessary to use an organic solvent, which increased the cost of the final product.

The aim of the present work is to address the two main drawbacks that have so far prevented the fabrication of a cost-competitive carbonaceous material at industrial scale and its commercialization, by means of the microwave-assisted synthesis of tannin–formaldehyde xerogels. An attempt has been made to synthesize organic xerogels by conventional and microwave heating using tannin instead of resorcinol. Moreover, an anionic surfactant, which does not require the addition of an organic solvent, was employed to produce highly porous materials. All of the synthesized xerogels were characterized from the point of view of their chemical and porous structure so as to determine the effect of using tannin instead of resorcinol and to ascertain possible differences in properties due to the synthesis method employed.

2. Materials and methods

2.1. Raw materials

Commercial wattle tannin extracted from Acacia Mearnsii (*De Wild*) barks was used for the present study. This raw material was kindly supplied by SilvaChimica (San Michele Mondovi, Italy) under the name Fintan OP. The industrial extraction process of tannins has been explained in detail elsewhere [16]. Briefly, fresh bark was leached 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, the remaining components being monomeric and oligomeric carbohydrates in the form of broken pieces of hemicellulose. As from now, the light-brown powder thus obtained will be referred to simply as tannin (T).

Other chemicals used included resorcinol (Sigma Aldrich, 99%), formaldehyde (Roth, 37 wt.% in water, stabilized by 10–15 wt.% methanol), sodium dodecyl sulphate (Sigma Aldrich) and sodium hydroxide (Carlo Erba).

2.2. Preparation of organic xerogels

Organic gels were synthesized by the polycondensation of resorcinol (R), tannin (T) and formaldehyde (F) using deionized water as solvent, sodium hydroxide as catalyst and sodium dodecyl sulphate (S) as surfactant. The method employed for preparing the precursor solutions was the same in all cases. Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. Once the resorcinol had dissolved, tannin was added, still under stirring at room temperature, until complete dissolution. Formaldehyde was then introduced into the solution. Finally, sodium dodecyl sulphate 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. The final pH value was adjusted to 5.5 by adding sodium hydroxide. In all cases, the resorcinol–tannin/formaldehyde weight ratio and the percentage of solids were fixed at 1.2 and 25 wt.%, respectively. Ten different precursor solutions using different amounts of tannin, ranging from 0 to 100 wt.% to replace resorcinol either partly or completely, were prepared. Anionic surfactant was added to five of these solutions, in amounts that would ensure that their concentration was 5 wt.%, whereas the other five solutions were kept surfactant-free. Each solution was split into two batches and subjected to two different heating methods: conventional (C) or microwave (MW) heating. The resultant organic xerogels obtained after drying (see details below) were labelled ‘RTF’ followed by the percentage of tannin used to replace the resorcinol, i.e., 0, 25, 50, 75 and 100 wt.%. An ‘S’ was appended to the name of those samples containing surfactant. Finally, ‘C’ or ‘MW’ was added to indicate the type of heating applied. For example, the sample RTF-75-S-MW refers to a microwave-assisted synthesized xerogel prepared with 75 wt.% of tannin (the other 25 wt.% being resorcinol) and 5 wt.% of surfactant.

2.2.1. Conventional synthesis

The precursor solutions were poured into sealed glass tubes which were then placed in a ventilated oven at 85 °C for 72 h to undergo gelation and curing. Afterwards, the tubes were opened and introduced again into the oven at 85 °C for 48 h for the purpose of completely drying the organic gels by evaporation of the solvent. This temperature was selected according to the procedure proposed by Job et al. for the conventional synthesis of RF xerogels [2].