Microporous and Mesoporous Materials 243 (2017) 28–38

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Preparation of binderless activated carbon monoliths from cocoa bean husk

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ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form
5 January 2017
Accepted 3 February 2017
Available online 5 February 2017

Keywords:
Activated carbon monoliths
Carbon dioxide activation
Microporosity

ABSTRACT

Binderless activated carbon monoliths were prepared from a new lignocellulosic precursor: cocoa bean husk. This study focussed on analysing the role of a lignocellusic-type precursor in the development of binderless carbon monoliths, and the characterisation of the porous texture and mechanical performance of the activated carbon monoliths. The results prove that an adequate combination of the macromolecular components of the cocoa bean husk (lignocellulosic molecules, gums, pectin and fats) together with a laminate macromolecular microstructure made it more suitable for obtaining binderless carbon monoliths, than other lignocellulosic precursors. In addition, the activation of these carbon monoliths gives activated carbon with a higher micropore volume and good mechanical performance.

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1. Introduction

The synthesis of new porous carbon materials (activated carbons), as well as the study of their applications in heterogeneous catalysis, environmental decontamination and gas storage and treatment, is an area of great interest both for chemistry and chemical technology [1]. For example, they are used in huge quantities in industry as desiccants to adsorb the humidity present in gas streams or the environment. Equally important is their application in gas separation [2] and/or purification, as well as their role in pollution control [3]. Similarly, large quantities of adsorbent materials are used in the purification of liquids and to remove various pollutants such as surfactants [4], phenolic compounds [5], anilinic compounds [6], aromatic benzene and naphthalene derivatives [7] and pharmaceutical compounds [8] from wastewater. Another application for adsorbent materials, by reason of their high specific surface area, is to act as a catalyst support [9,10]. Also, high surface ACs can be used in energy storage, providing one of the best examples of a double layer capacitor material [11], and natural gas storage [12].

Also from an economic and environmental point of view, it is advisable to obtain these materials from either green raw materials or by applying processes which involve a lower cost. In this sense, the use of lignocellulosic residues to produce activated carbons has been widely studied as is reflected in recent reviews [13–15] as well as the numerous patents registered, for example [16–19]: U.S. Pat. Nº 5064805 (coconut husk); U.S. Pat. Nº 41616001 A (macadamia nut husk); U.S. Pat. Nº 1543763 (using rice hulls), U.S. Pat. Nº 5883040 (cereal hulls). Furthermore, in order to prepare AC, two main groups of methods have been developed: i) physical activation ("thermal activation") using CO_2 or steam as gasifying agents, and ii) chemical activation, using $ZnCl_2$, H_3PO_4, KOH or NaOH as activating agents. The chemical activation of lignocellulosic precursors using $ZnCl_2$ and H_3PO_4 is frequently used for the production of granular activated carbons [20].

In addition to synthesizing activated carbons with high development of porosity, their physical form should also be taken into account [1,21]. In the above-mentioned preparation methods, the resulting activated carbons are obtained in powder/granular form. In this case, the use of powdered activated carbons is not suitable for treating gas or liquid streams, due to problems of pressure drop in the system, or the problem caused by the appearance of channels when they are present in the adsorption columns. Therefore, different procedures have been developed to form these materials

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http://dx.doi.org/10.1016/j.micromeso.2017.02.015
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into more appropriate geometric shapes for their application in streams: making them into pellets or forming them into cylindrical discs (monoliths) by compaction. In general, in all these procedures, after the preparation of the activated carbon, it is mixed with a binder, given the required shape and then subjected to different thermal treatments like drying, stabilization-curing in air of the binding agent and final carbonisation of the product. Examples include: U.S. Pat. Nº 3864277 that uses polyvinyl alcohol as a binder [22]; U.S. Pat. Nº 5306675 that uses methyl cellulose as a binder with a curing stage for the binder in a microwave [23]; U.S. Pat. Nº 6207264, using an aqueous emulsion of different binders, followed by drying stages at 120 °C and curing at 200 °C [24]; U.S. Pat. Nº 5691270, that has the advantage of not using stages of thermal treatment because it uses a mineral binder, but has the disadvantage of incorporating a mineral load which is not suitable for some applications [25].

In the light of the previous comments, the study performed for this work presents the innovation of employing a lignocellulosic precursor, cocoa bean husk (Spain Pat. Nº PCT/ES2014/070600) [26], that has not been used for developing activated carbons. Another additional aspect of the present study is that it provides a simple procedure for manufacturing activated carbon monoliths without using binders, or additional stages for their consolidation, together an easy activation process: CO_2 activation.

2. Experimental

2.1. Materials and methods

During the extraction of the cocoa beans, cocoa bean husk, which represents 12% of the total weight of the cocoa beans, is generated as waste. Taking into account that world production of dry cocoa beans is 4.5 million tons, this generated approximately 0.54 million tons of cocoa bean husk waste. Due to the increasing consumption of cocoa, the burden of cacao husk waste will continue to rise, becoming more difficult to deal with. For this reason, there is intense research into creating valuable products from this waste, e.g. animal feed [27], food antioxidants [28], dietary fibers [29], pectin production [30]. Cocoa bean husk, as lignocellulosic waste, could also be used as a precursor in activated carbon production, as will be analyzed in this work.

Residues of cocoa bean husk were provided by Chocolates Valor S.A. (Villajoyosa, Alicante). They were ground in a helix grinder to obtain a very fine powder, which was then washed with H_2SO_4 (10% vol.) for 24 h with agitation. The washed solution was filtered and the solid paste was washed with distilled water. It was then dried in an oven at 60 °C. Furthermore, for comparison, other lignocellulosic precursors commonly used in this type of studies were also treated, like for example almond shell (Alm), walnut shell (Wal), coconut shell (Coco), and one that had not been used before, loquat stones (Loaq), following the same washing and drying process at 60 °C. The biochemical and mineral composition of the lignocellulosic precursors used in this study can be found in the supplementary information.

Cylindrical discs (monoliths) were prepared from each washed and dried precursor using uniaxial compression of a certain quantity of the sample in a 1.45 cm diameter mould, applying a force of from 0 to 68 kN. Also for comparison monoliths were prepared of unwashed cocoa bean husk. The quantity needed for the dimensions of this mould was about 0.4 g and the pressure exerted was 180 MPa, except for the loquat stones where 420 MPa were required to form consolidated monoliths.

The monoliths were carbonised in a tube furnace (⌀ 6 cm, L 150 cm) in an inert atmosphere (N_2 100 cm^3/min) up to 1000 °C, at a heating rate of 10 °C/min, and maintained for 30 min at the maximum carbonisation temperature. Experimental thermal treatments (with the same atmospheric conditions and heating rate) were also applied to cocoa monoliths at different temperatures, 215, 330, 415, 510, 750 and 900 °C. After the thermal treatment the monoliths were weighed to determine carbonisation performance through the weight difference.

The carbonised monoliths (C) were activated in a tube furnace according to the following thermal treatment program: heating in N_2 100 cm^3/min to 880 °C, changing to a stream of CO_2 100 cm^3/min, maintaining for different time periods (1–10 h), and once the period was over, turning off the oven and using a stream of N_2 during cooling. Activation percentage (BO) was determined by mass balance. The nomenclature of the monoliths of activated cocoa bean husk (AC) includes two figures indicating BO (i.e. CA44, indicates cocoa monoliths with an activation percentage of 44%).

2.2. Characterisation

All the monoliths obtained at different temperatures were measured (diameter and thickness) with a calliper (Mituyoto ± 0.01 mm), before and after treatment. In order to determine contraction/expansion of the monoliths during the thermal treatment we also performed experimental thermo-mechanical analyses (TMA- TA Instruments Q400). The conditions were: expansion probe, load 0.02 N, N_2 purging (60 cm^3/min), heating ramp 10 °C/min, maximum temperature 500 °C, maintenance for 15 min at maximum temperature. The changes in dimensions are visible to the human eye, so photographs were taken as examples of the monoliths. The internal morphology of the monoliths was analyzed with a scanning electron microscope (SEM: Hitachi S-3000N).

The behaviour of the cocoa husk during carbonisation was analyzed in a thermogravimetric experiment (TG) with equipment from TA Instruments, SDT 2960. Ten milligrams of washed husk were put onto the sample holder of the thermal balance and subjected to a thermal treatment in an atmosphere of N_2 (60 cm^3/min). The temperature program consisted of a heating ramp of 20 °C/min up to 950 °C. Once this temperature was reached the N_2 was replaced with synthetic air and the temperature was maintained for some 15 min.

The G and D bands of the carbon monolith were also analyzed using Raman spectrometry (dispersive Horiba Jobin-Yvon: LabRAM with a 600 grooves/mm grating, Laser DPSS 532 nm laser and 2 mW of power on the sample, and a confocal Microscope with a 10× objective and 0.25 numerical aperture).

The crystalline structure of the monoliths obtained was determined by powder x-ray diffraction (XRD) (Seifiert diffractometer JSO Debye-Flex 2002, with Cu K_α radiation). Experiments were made on the un-ground and ground discs.

Skeletal density (ρ_{He}) was determined by a helium pycnometer (AccuPyc 1330 Pycnometer; Micrometrics). 0.5 g of previously degassed sample were used at 150 °C, in vacuum (1 Pa) over night. The density of the discs (ρ_{piece}) was determined by measuring their dimensions. The measurements were taken in triplicate and the values obtained had an error of less than 5%.

The porous texture of the carbonised monoliths and the activated monoliths was characterized by physical gas adsorption (N_2 at -196 °C and CO_2 at 0 °C) in two different volumetric instruments (Autosorb 6-B and Autosorb-6, respectively). It should be noted that the characterisation was performed with both the whole and ground monoliths. No differences were observed between the obtained isotherms. Before performing the adsorption tests the samples were degassed in vacuum at 250 °C for 4 h. The apparent surface area was determined with the B.E.T. (Brunauer-Emmett-Teller) equation [31]. The Dubinin-Radushkevich equation (DR

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