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Production of activated carbons from almond shell

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ABSTRACT

The production of activated carbons from almond shell, using physical activation by CO_2 is reported in this work. The used method has produced activated carbons with apparent BET surface areas and micropore volume as high as 1138 $m^2 g^{-1}$ and 0.49 $cm^3 g^{-1}$, respectively. The activated carbons produced have essentially primary micropores and only a small volume of wider micropores. By FTIR analysis it was possible to identify, in the surface of the activated carbons, several functional groups, namely hydroxyls (free and phenol), ethers, esters, lactones, pyrones and Si–H bonds. By the analysis of the XRD patterns it was possible to calculate the microcrystallites dimensions with height between 1.178 and 1.881 nm and width between 3.106 and 5.917 nm. From the XRD it was also possible to identify the presence of traces of inorganic heteroatoms such as Si, Pb, K, Fe and P. All activated carbons showed basic characteristics with point of zero charge between 9.42 and 10.43.

1. Introduction

Activated carbons are artificial materials characterized by the high surface area and the extensive surface chemistry which are responsible for the significant adsorptive properties of the materials. The selective choice of the precursor and the activation conditions gives us the possibility to design activated carbons for different applications. The industry of activated carbon has been using in the last decades some agricultural and industrial residues with the aim of the valorisation of such residues or sub products. Nowadays, activated carbons are widely used in a large range of applications, such as medical uses, removal of pollutants and odours, gas separation and purification, catalysis and gas storage. One of the main objectives in this research field is the search for new precursors, which are cheap, accessible and with valorisation potential, like industrial and agricultural residues.

Lignocellulosic materials are one of the most important raw materials for the production of ACs. The use of such materials corresponds to the production of more than 300,000 tons/year of activated carbons [1], being wood and coconut the most relevant used materials. Besides the already mentioned precursors, other by-products like eucalyptus wood, vine shoots, vetiver grass, peanut shell, coir pith and chestnut have also been investigated for the production of ACs [2–12].

Almond shell is a by-product of almond production with some interesting features, like high volume and low value. Almond has a mean annual production of about 1.7 million tons [13] mainly in USA, Spain, Syria, Italy, Iran and Morocco. In these countries the valorisation of such by-product could be an important way to add value to a low value product. Despite the existence of some published papers that have reported the production of activated carbons from such by-product using different methodologies [14–16] there is still a need for further research work in this field in order to better understand the production mechanisms and to optimize the available production methods. Therefore, the main aim of this work is to optimize the production conditions by using carbon dioxide and a horizontal furnace in order to obtained tailored materials for liquid phase adsorption of pollutants.

The work now reported has its major innovative aspect on the use of a never reported procedure for the carbonisation stage, done in a single step at 400 °C. The literature review made by us have shown that either the published papers uses chemical activation [15,17–19], either uses carbonisation with two steps [20,21] or in the case of the carbonisation in a single step uses temperatures above 600 °C.

2. Experimental

2.1. Materials

The precursor, almond shell, was crushed and sieved in order to get a standardized particle dimension. For the production of the activated carbons (AC) we have used the 2–4 mm fraction. About 45 g of precursor was weighted and putted in a horizontal tubular furnace, using a suitable container, made of stainless steel with 15 cm length, 3 cm wide and 2 cm high.

The precursor was first carbonized at 400 °C during 1 h, in a N_2 constant flow of 85 cm^3/mL, and then activated at 700 °C and 800 °C, in a CO_2 constant flow of 85 cm^3/mL, during 1, 2, 3, 5 and 7 h, in order to get burn-off within the range of 12 to 70 wt.%. The heating rate for

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Table 1
Precursor characteristics.

Diameter (mm)	2–4
Hemicellulose (wt.%)	25.5
Cellulose (wt.%)	32.5
Lignin (wt.%)	24.8
Ash (wt.%)	1.1
Solid density (g/cm^3)	0.45

carbonization and activation was set at 10 °C/min. After activation the samples were allowed to cool down to 50 °C under N_2 flow before their remove from the furnace. The activated samples were washed in 1000 mL of distilled water during 24 h and then dried at 110 °C for the same period. Each sample was stored in sealed flasks and identified. The samples obtained were designated by indicating the activation (x) temperature using the first number, 7 for 700 °C and 8 for 800 °C, and the activation degree indicated by the burn-off value (y) (general designation: Axy, for instance A822 corresponds to a sample obtained by activation at 800 °C with burn-off value of 22 wt.%).

2.2. Characterization

All activated carbons were chemical and structural characterized by infrared analysis (FTIR), elemental analysis (EA), X-ray diffraction (XRD) and nitrogen adsorption at 77 K. FTIR spectra were recorded using a Perkin Elmer model Paragon 1000PC spectrophotometer using the KBr disc method, 100 scans between 4000 and 450 cm^{-1} with 4 cm^{-1} resolution. The pellets were prepared using 1 mg of AC and 500 mg of KBr and mixing them in an agate mortar. The mixture was pressed at 10 tons for 3 min using a Specac press. The pellets were oven dried at 110 °C during 3 h and then allowed to cool down in a desiccator. The Elemental Analysis was carried out in a Euro Vector Elemental Analyzer, Euro Vector Instruments. The X-ray diffraction patterns were obtained using a Bruker AXS-D8 Advance Powder Diffractometer equipped with a CuKα radiation (40 kV, 30 mA) with wavelength of 0.150619 nm at a step size of 0.020º between 5.000 and 60.020º. The nitrogen adsorption at 77 K was carried out in a Quadrasorb-Tri, Quantachrome Instruments. The samples were initially degassed, in a Masterprep unit, Quantachrome Instruments, at 400 °C for a period of 4 h, at a stepwise of 1 °C/min. The isotherms were analysed using different methods such as Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich (DR) and αs. The precursor's cellulose and lignin content was determined by Agroleico (Porto Salvo, Portugal) using Portuguese Standards NP2029 and ME-414, respectively, the point of zero charge was determined by mass titrations as described elsewhere [22].

3. Results and discussion

3.1. Precursor characterisation

The precursor has low ash content, as can be seen in the Table 1, which can be considered as an advantage for the production of activated carbons. Also, the content in lignin is similar to the hemicellulose and cellulose. The lignin content, when compared with other lignocellulosic precursors, can be considered quite high.

The FTIR spectrum of the precursor, shown in Fig. 1, point up the presence of some typical bands of lignocellulosic materials belonging to functional groups such as hydroxyl, ethers, esters, aldehydes and Si–H bounds. The wide band at 3406 cm^{-1} is ascribable to ν (O–H) vibrations in hydroxyl groups. It was possible to identify the presence of methylene groups by the detection of ν (C–H) and δ (C–H) absorption bands. These bands, located in the spectrum at 2927 and 1467 cm^{-1} are connected to C–H asymmetric stretch and C–H bend vibrations, respectively [23,24]. The stretching vibrations in aromatic rings produce absorption bands between 1510 and 1450 cm^{-1} [24], which can produce some band overlapping in this region of the spectrum. A very valuable vibrational band of the group $-CH_3$ appears at 1391 cm^{-1} related to δ_s (C–H). The band at 1741 cm^{-1} is caused by carbonyl stretching vibrations namely aldehyde group. Between 1711 and 1427 cm^{-1} the ν (C=C) absorption bands emerges. The bands at 1659 and 1691 cm^{-1}, are caused by alkenyl C=C stretch and the band at 1599 cm^{-1} can be due to conjugated C=C. The aromatic skeletal bands appear at 1513 and 1502 cm^{-1}. The band at 1368 cm^{-1} is ascribable to δ (O–H) vibrations and to ν (C=O) vibrations [25]. The attributed O–H vibrations belonging to primary, secondary, tertiary or phenol can be evaluated by the relative position of the C–O stretching frequency. The bands centred in 1161, 1110 and 1059 cm^{-1} belong to ν (C–O) vibration in tertiary, secondary and primary alcohol, respectively. The band at 1250 cm^{-1} may be related to esters (e.g. CH_3–CO–O-), epoxides, as well as with acyclic C–O–C groups conjugated with carbon–carbon double bounds (C=C–O–C) in olefinic or aromatic structures (e.g. ethers such as –OCH_3) [23]. The bands in the range 900–700 cm^{-1} can be attributed to C–H deformation due to out-of-plane vibrations. These bands are assigned to aromatic structures with isolated aromatic hydrogens (891 cm^{-1}) and two adjacent hydrogens per ring (832 cm^{-1}) [26]. We also can identify the presence of Si–H bonds around 891 cm^{-1} due to ρ_w Si–H and at 2000–2200 cm^{-1} (ν SI–H).

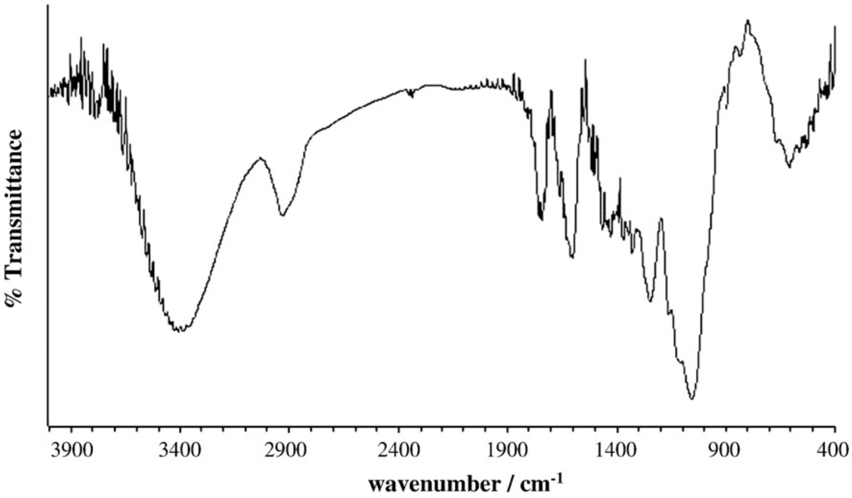

Fig. 1. FTIR spectrum of the precursor.