



HEMP-derived activated carbon fibers by chemical activation with phosphoric acid

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ABSTRACT

Activated carbon fibers were prepared by chemical activation of hemp fibers with phosphoric acid at different carbonization temperatures and impregnation ratios. Surface properties of the activated carbon fibers were significantly influenced by the activation temperature and the impregnation ratio. An increase of either of these parameters produced a high development of the porous structure of the fibers. Activated carbon fibers with apparent surface area of 1350 m²/g and mesopore volume of 1.25 cm³/g were obtained at 550 °C with an impregnation ratio of 3. The activated carbon fibers presented a high oxidation resistance, due to the presence of phosphorus compounds on the carbon surface. The oxidation resistance results suggest that C–O–PO₃ and mainly C–PO₃ and C–P groups act as a physical barrier, blocking the active carbon sites for the oxidation reaction.

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1. Introduction

Hemp is one of the most productive and useful plants known. It grows quickly without any great need of pesticides in most locations and climates with only moderate water and fertilizer requirements, becoming a valuable and environmentally friendly crop.

Hemp has many industrial applications such as the production of paper, textiles, building materials, food, medicine, paint, detergent, varnish, oil, ink, and fuel [1]. However, hemp transformation generates a high proportion of waste. Specifically, the textile industry employs less than 50%_w of the hemp, producing significant amounts of waste [2,3]. Spain produced about 40,000 ton of hemp residue only from the textile industry (2004). Development of recycling processes of such biomass waste is generating great interest, and the production of activated carbons could be an appropriate solution.

The world demand of activated carbon is steadily increasing due to its well-known extensive use as adsorbent for purification and separation in many processes. Activated carbons can be manufactured from many carbonaceous precursors, but the most commonly used raw materials are wood, coal, coconut shells and some polymers [4–8]. The use of several lignocellulosic by-products, such as nutshells, fruit stones, lignin, sugarcane and sawdust from a few rapid growing wood species, as renewable precursors for low cost activated carbon production, is being widely studied [9–23]. The use of hemp residues to produce activated carbon is very feasible and presents the advantage of the potential revalorization of a residual material.

In this respect, preparation of activated carbon fibers by physical activation with steam and chemical activation with ZnCl₂ of hemp fibers have already been reported in the literature [2,3].

The aim of this work is the preparation of activated carbon fibers by chemical activation of hemp fibers with phosphoric acid, analyzing the influence of the activation temperature and the impregnation ratio on the activated carbon porous structure and surface chemistry. The oxidation resistance of the activated carbon fibers was also studied, analyzing the effect of surface phosphorus compounds, retained in the matrix structure upon activation, on the oxidation reaction.

2. Experimental

2.1. Preparation of carbon and activated carbon fibers

The starting materials were hemp fibers supplied by Alsativa (Sociedad Cooperativa Agraria Andaluza del Cádiz, Pórtugos, Granada). Hemp was previously cleaned from leaves and tops and kept at room temperature. The fibers were cut in fractions of around 3 cm long.

The precursor was impregnated by incipient wetness with 85% (w/w) H₃PO₄ aqueous solution at room temperature and dried for 24 h at 60 °C in a vacuum dryer. The impregnation ratio, *R*, (H₃PO₄/precursor mass ratio) varied from 1 to 3.

The impregnated hemp fibers were activated under continuous N₂ flow (150 cm³ STP/min), in a conventional tubular furnace. The activation temperature was reached at a heating rate of 10 °C/min and maintained for 2 h. Different activation temperatures within

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400–550 °C range were studied. The activated samples were cooled inside the furnace maintaining the N₂ flow, and then were washed with distilled water at 60 °C until neutral pH and negative phosphate analysis in the eluate [24]. The resulting activated carbon fibers were dried at 100 °C and weighted to determine the yield of the activation process (weight of activated carbon related to weight of raw material, in dry basis). The activated carbon fibers were denoted by the letter F (fibers) followed by a number corresponding to the impregnation ratio and by a second number representing the activation temperature in degrees Celsius. Some carbon fibers were obtained by carbonization of hemp fibers under N₂ flow at different temperatures without impregnation of the activation agent. The carbon fibers thus obtained were denoted by F followed by the carbonization temperature in degrees Celsius.

2.2. Characterization

The ultimate analysis of the samples was performed in a Leco CHNS-932 system, being the oxygen content calculated by difference. The ash content of the sample was calculated following the ASTM procedure [25].

The porous structure of the carbon fibers was characterized by N₂ adsorption–desorption at –196 °C, performed in an Omnisorp 100cx equipment (Coulter) and by CO₂ adsorption at 0 °C, carried out in an Autosorb-1 apparatus (Quantachrome). Samples were previously outgassed for at least 8 h at 150 °C. From the N₂ isotherm, the apparent surface area (A_{BET}) was determined applying the BET equation [26]. The α_s method allows to obtain the values of the so-called external surface area (A_s), namely, the surface area associated to the non-microporous structure, the micropore volume (V_s), and the specific surface area (a_s), obtained by the high resolution method proposed by Kaneko et al. [27–29], using a non-porous carbon black (Elftex-120) as standard [30]. The mesopore volume (V_{mes}) was determined as the difference between the adsorbed volume of N₂ at a relative pressure of 0.95 and the micropore volume V_s [27]. From the CO₂ adsorption data, the narrow micropore volume (V_{DR}) and the apparent surface area (A_{DR}) were calculated using the Dubinin–Radushkevich equation [31]. The Horvath–Kawazoe [32] and the Barrett–Joyner and Halenda (BJH) [33] methods applied to the N₂ adsorption data were used to obtain the micropore and mesopore size distributions, respectively.

The surface chemistry of the samples was analyzed by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). TPD profiles were obtained in a custom quartz fixed bed reactor placed inside an electrical furnace. The samples were heated from room temperature up to 900 °C at a heating rate of 10 °C/min in helium flow (200 cm³ STP/min). The amounts of CO and CO₂ desorbed from the samples were monitored with nondispersive infrared (NDIR) gas analyzers (Siemens ULTRAMAT 22). X-ray photoelectron spectroscopy (XPS) analyses of the samples were obtained using a 5700C model Physical Electronics apparatus with MgK α radiation (1253.6 eV). For the analysis of the XPS peaks, the C_{1s} peak position was set at 284.5 eV and used as reference to locate the other peaks [34–36]. The fitting of the XPS peaks was done by least squares using Gaussian–Lorentzian peak shapes. The surface texture of the samples was characterized by scanning electron microscopy (SEM). Scanning electron micrographs were obtained using a JEOL JSM-840 instrument, working at a high voltage of 20–25 kV.

Non-isothermal thermogravimetric analyses were carried out in a gravimetric thermobalance system, CI electronics. The thermobalance automatically measures the weight of the sample and the temperature as a function of time. Experiments were carried out in inert atmosphere (N₂), and in air atmosphere, for a total flow rate of 150 cm³ (STP)/min, employing sample mass of approxi-

mately 10 mg. The sample temperature was increased from room temperature up to 900 °C at a heating rate of 10 °C/min.

3. Results and discussions

Table 1 shows the analytical and structural properties of the hemp fibers used for the preparation of activated carbon fibers. The ash content of the raw material is relatively low. Hemp fibers present a non-porous structure as indicated a negligible adsorption of N₂ at –196 °C and CO₂ at 0 °C.

The evolution of the surface chemistry and the porous structure with the impregnation ratio of phosphoric acid and the activation temperature was studied for hemp fibers. Table 2 shows the yield values and the ultimate analysis of the carbon and activated carbon fibers obtained. Oxygen content was determined by difference. However, the oxygen content values shown in this table are probably overestimated as they may include the amounts of P and Si in the carbons (detected by XPS). The yield values obtained for the hemp-derived carbon fibers prepared at different temperatures are similar to those reported in the literature for other lignocellulosic materials pyrolyzed at comparable temperatures [37,38] (from about 25% for a pyrolysis temperature of 450 °C to about 12% for 800 °C).

The yields for the activated carbon fibers were almost twice than those for the carbon fibers at the same treatment temperature. The phosphoric acid limits the formation of tars during the carbonization treatment, increasing the yield of the remaining solid product [6]. Yield values from 41% to 50% were obtained for the activated carbon fibers at different impregnation ratios and activation temperatures, similar to those obtained from other biomass natural waste [8,18] and slightly higher than those reported for hemp fibers with different activation agents [2,3]. The yield values decrease slightly with the activation temperature and the impregnation ratio studied, as a consequence of a deeper dehydration of the carbonaceous structure of the precursor. The amount of oxygen

Table 1

Analytical and structural characteristics of the hemp fibers used for the activated carbon preparation

	Fiber
Ash content (% db)	3.0
Ultimate analysis (% daf)	
C	43.17
H	5.21
N	0.63
O	50.99
Major components	
Cellulose ^a	67.0
Hemicellulose ^a	16.1
Lignin ^a	3.3

^a Data from Ref. [1].

Table 2

Yield values and ultimate analysis of the hemp-derived carbon and activated carbon fibers

	Yield (% db)	C (% daf)	H (% daf)	N (% daf)	O (% daf)
F450	24.5	81.0	2.6	1.7	14.7
F550	22.0	84.0	3.6	1.8	10.6
F800	12.9	96.9	1.5	0.9	0.7
F1-450	49.8	64.6	2.9	0.4	32.1
F2-450	44.5	78.3	2.6	0.2	18.9
F3-400	42.7	83.8	3.4	0.3	12.5
F3-450	42.2	80.2	3.0	0.2	16.6
F3-500	41.9	77.9	2.2	0.4	19.5
F3-550	41.1	76.6	2.4	0.8	20.2

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