

Preparation of active carbons from a commercial holm-oak charcoal: study of micro- and meso-porosity

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Abstract We studied the influence of the degree of gasification and the choice of activating agent (carbon dioxide, water vapour, or both carbon dioxide and water vapour acting successively) on the activation of samples of a commercial holm-oak wood (*Quercus rotundifolia*) charcoal. To this end, we prepared the active carbon samples using the activating agents at 800, 850, 900, and 950°C for the time required to gasify 20, 40, or 60% of the mass of the charcoal at the moment when the set gasification temperature had been reached. The active carbons were characterised by physical gas adsorption and densimetry. Those prepared with carbon dioxide or water vapour alone had textural characteristics that were better than those of the precursor charcoal. The micropore volume was greater in the samples activated with carbon dioxide than with water vapour. The activation with both carbon dioxide and water vapour successively led to a major increase in porosity, taking into account that these samples presented a 40% burn-off percentage which endowed them with good textural characteristics. In general, as the burn-off percentage increased, so did the micropore and mesopore volumes.

To sum up, holm-oak wood is a good raw material, not only to get barbecue coal, which has been used as a precursor to obtain activated coal, but it also allows the activated coal to develop its microporosity and mesoporosity in a good way, which is suitable for new applications as it is absorbent in liquid phase, gas absorbent, is a constituent part of combustible batteries, etc.

The main interest of this research is the preparation of activated coal and the determination of the size pore distribution obtained, given its great influence in the quality of the activated coal obtained starting from holm-oak wood, what gives a great economic and industrial value in the Southwest of Spain for this raw material.

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Introduction

Active carbons are very porous materials with a highly varied texture. The pores range from micrometer size to those that are so small as to be inaccessible even to the smallest of all molecules, the helium atom, whose diameter is approximately 0.23 nm. The IUPAC classification of pores by size (IUPAC 1972), an adaptation of an earlier classification due to Dubinin (1960a,b), defines the following three classes of pores: macropores with breadths greater than 50 nm; mesopores with breadths between 2 and 50 nm; and micropores with breadths less than 2 nm.

The composition and structure of an active carbon depends on the raw material, the activating agent, and the preparation procedure. These parameters condition the properties of the active carbon, and hence its applications (adsorption processes, electrode material, ion exchange, and so forth) (Smisek and Cerny 1970; Rodríguez Reinoso 1986). Forestry and farming waste form a particularly important group of raw materials for the manufacture of active carbons; literature contains data relating to a great number of active carbons prepared from olive pits (López González and Rodríguez Reinoso 1972; Rodríguez Reinoso et al. 1983; Linares Solano et al. 1984), almond shells (Rodríguez Reinoso et al. 1982), nut shells (Kutics et al. 1984; Kutics et al. 1986), olive tree wood (López González et al. 1986), labdanum (Gómez Serrano et al. 1996), holm-oak wood (Bernalte García 1999), etc.

Commercial holm-oak wood charcoal is made from firewood obtained mainly from pruning, which is usually performed during periods of relative vegetative dormancy of the tree. This charcoal is characterised by its long and slow combustion and high calorific content. It is thus in strong demand for industrial uses, home barbecues, etc.

In the present work, we obtained active carbons from a commercial holm-oak wood charcoal, using carbon dioxide and/or water vapour as activating agents, and varying the burn-off percentage with each activating agent.

Methods

The starting material was a commercial industrially-prepared holm-oak wood charcoal. We fine ground this charcoal in a Retsch, K.G. mod. S.K.1 mill, followed by sieving in an Orto sifter, choosing the $0.32 < \phi < 1$ mm to perform the trials.

The sieved samples were heated from an initial temperature of 30°C to a final temperature of 600, 700, 800, 900, or 1,000°C at a heating rate of 10°C/min in a nitrogen atmosphere (200 ml/min flow rate). The best behaviour was shown by the char that was formed at 600°C (M-600). This is the same thermal behaviour found with other high lignocellulose content raw materials such as labdanum (Pastor Villegas et al. 1993; 1994).

The chars were activated using carbon dioxide or water vapour as activating agent. The operating conditions were as follows: For activation with carbon dioxide or water vapour alone, the sample was heated from the initial temperature of 30°C in a controlled nitrogen atmosphere (200 ml/min flow rate) up to the working temperature set for each trial (800, 850, 900, 950°C). The nitrogen atmosphere was then replaced by the respective activating agent, carbon dioxide or water vapour, at a 200 ml/min flow rate, with these conditions being maintained as long as was necessary to gasify 20, 40, or 60% of the mass of the char sample to reach the temperature of gasification previously established in the nitrogen atmosphere. On completion of the gasification, the atmosphere was changed back to a nitrogen flow to cool the carbon to room temperature. The active carbons prepared with both agents acting in succession

were pre-heated to 900°C in a nitrogen atmosphere (200 ml/min flow rate). The nitrogen flow was then replaced by carbon dioxide (200 ml/min) for as long as was necessary to gasify 10, 20, or 30% of the mass of the initial 900°C char. The carbon dioxide atmosphere was then replaced by a water vapour atmosphere (200 ml/min), until 40% total gasification was reached. This same successive procedure was repeated with the order of the two agents reversed. We thus obtained different active carbon samples, corresponding to the different burn-off percentages at the four working temperatures. These samples will be denoted as:

C – T – %; H – T – %; C% – H%; and H% – C%

where C and H indicate that the activating agent is carbon dioxide or water vapour, respectively, T represents the working temperature, and % the percentage of carbon that has been burnt-off.

To characterise the samples texturally, we used a Quantachrome Autosorb-1 device for physical gas adsorption, with nitrogen as adsorbate (N-48) at 77 K and carbon dioxide (N-48) at 298 K.

Sample densities were determined using a Quantachrome (helium density) stereopyknometer (Shields and Lowell 1985) or by the usual method (mercury density).

Results and conclusions

Adsorption isotherms

The isotherms of nitrogen adsorption at 77 K have been and are still being used as a general method to study the properties of porous solids such as charcoals in general, and active carbons in particular (Baker 1987). This adsorbate has two drawbacks, however. It condenses in the micropores even at relatively low pressures, and it has a low diffusivity at 77 K in the smallest micropores. Indeed, there is data (Gómez Serrano et al. 1998) which shows a greater adsorption at 180 K than at 77 K.

It has been argued (Macías García et al. 1993; Walker 1996) that carbon dioxide adsorption data at 298 K should be used to complete the information on the micropore texture of carbons, since the carbon dioxide molecule has no permanent dipole moment, and the restrictions on the diffusion of adsorbate molecules found in nitrogen adsorption at 77 K should be either non-existent or negligible at the relatively high temperature of carbon dioxide adsorption at 298 K. Also, the saturation pressure of carbon dioxide at 298 K is very high, 48 250 Torr (Rodríguez Reinoso 1986), so that the range of relative pressures in which adsorption takes place is narrow, thereby avoiding any possible condensation and facilitating the formation of an adsorbate monolayer on the surface of the carbon (Marsh and Siemieniowska 1965).

Figures 1 and 2 show, by way of example, the isotherms of nitrogen adsorption at 77 K for the samples activated by carbon dioxide or water vapour at 800°C. A line has been fitted to experimental data points.

The isotherms of nitrogen adsorption at 77 K in the active carbons prepared by means of partial gasification in a carbon dioxide or water vapour atmosphere at temperatures of 800, 850, 900, and 950°C may be considered to be type I in the BDDT classification. Rodríguez Reinoso (1986) recommends subdividing the isotherms of this type into three sub-types, a, b, and c, depending on the shape of the elbow and the slope of the straight line section of the isotherm. The present isotherms of the

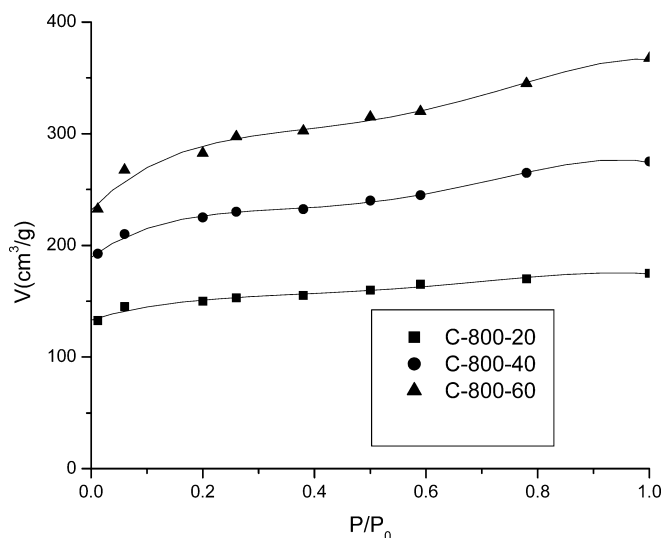


Fig. 1. The nitrogen (g) adsorption isotherm at 77 K of the samples C-800-%

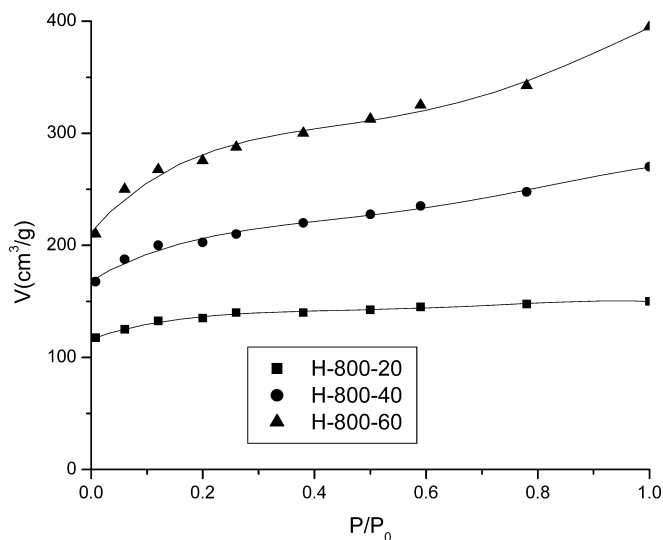


Fig. 2. The nitrogen (g) adsorption isotherm at 77 K of the samples H-800-%

carbons activated with carbon dioxide or water vapour alone may be regarded as type c, characteristic of the active carbons in which there must exist a broad spectrum of micropore sizes together with a well developed mesoporosity.

One also observes that the adsorbed volume increases with greater burn-off percentages, independently of the temperature of the gasification process.

The carbon dioxide adsorption isotherms at 298 K for the different active carbon samples generally appear well-defined until relatively low relative pressures. They might be classified as type I if it were possible to reach a relative pressure equal to unity.

With regard to the isotherms of the samples prepared by successive activation with first, carbon dioxide, and then water vapour, or vice versa, they all presented a gradual increase in the adsorbed volume with greater degree of activation with carbon dioxide, independently of whether this part of the process was carried out before or after the activation with water vapour.

The qualitative information derived from the nitrogen adsorption isotherms was confirmed by the calculations made using these isotherms to determine the micropore and mesopore volumes. It is usually considered that the volume read in each nitrogen adsorption isotherm at $p/p^0 = 0.10$, expressed as a liquid, represents the volume of micropores (V_{mi}), and the difference between this and the value read at $p/p^0 = 0.95$ is an approximate measure of the volume of mesopores (V_{me}) (Gregg and Sing 1982).

Specific surface area

From the nitrogen adsorption at 77 K data, we estimated the specific surface area (S_{BET}) of the active carbons. For comparison, Table 1 lists the values of the specific area, pore volume, and density of the precursor char.

With regard to the values of the surface area (S_{BET}) of the active carbons prepared by partial carbon dioxide or water vapour gasification, and obtained from the isotherms of nitrogen adsorption at 77 K (Table 2), it can be seen that the area increases with increasing activation percentage, independently of the process temperature.

The values of (S_{BET}) for the samples treated successively with carbon dioxide and water vapour, independently of the order, increase with the carbon dioxide activation percentage. This seems to indicate that the carbon dioxide contributes more effectively than the water vapour to the development of porosity.

Porosity

The total pore volume (V_p) of the samples was calculated from the following expression:

$$V_p = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad (1)$$

where ρ_{Hg} and ρ_{He} are, respectively, the densities determined by mercury and helium displacement (Rodríguez Reinoso and Linares Solano 1989).

The carbons present significantly higher values of (V_p) (Table 2) than the chars. In the light of the (V_p) values, one deduces that when a single activating agent is involved, the porosity is more developed in the carbon dioxide gasified samples than in the water vapour samples. Also, when the two agents were used together, and taking into account that the burn-off percentage attained with these samples was only 40%, better results were obtained than with carbon dioxide or water vapour alone and an identical burn-off percentage. This suggests that the first activating agent acts to cleanse the surface and/or to produce an incipient porosity that the second activating agent can develop, with this

Table 1. Textural characteristics of the char

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_{mi} ($cm^3 \cdot g^{-1}$)	$V_{DR}(N_2)$ ($cm^3 \cdot g^{-1}$)	V_{me} ($cm^3 \cdot g^{-1}$)	V_{ma} ($cm^3 \cdot g^{-1}$)	ρ_{Hg} ($g \cdot cm^{-3}$)	ρ_{He} ($g \cdot cm^{-3}$)	V_p ($cm^3 \cdot g^{-1}$)
M-600	120	0.06	0.07	0.04	0.25	0.96	1.45	0.35

Table 2. Surface area and total porosity of the active carbons

Samples	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	ρ_{Hg} ($\text{g} \cdot \text{cm}^{-3}$)	ρ_{He} ($\text{g} \cdot \text{cm}^{-3}$)	V_{ρ} ($\text{cm}^3 \cdot \text{g}^{-1}$)
C-800-20	523	0.85	1.93	0.66
C-850-20	580	0.85	1.98	0.67
C-900-20	590	0.86	1.98	0.66
C-950-20	550	0.85	2.03	0.68
C-800-40	780	0.83	2.03	0.71
C-850-40	840	0.84	2.01	0.69
C-900-40	806	0.85	2.07	0.70
C-950-40	793	0.85	2.06	0.69
C-800-60	1030	0.80	2.09	0.77
C-850-60	904	0.81	2.06	0.74
C-900-60	1110	0.82	2.12	0.75
C-950-60	950	0.81	2.11	0.76
H-800-20	456	0.90	1.91	0.59
H-850-20	550	0.91	1.96	0.59
H-900-20	420	0.82	2.01	0.59
H-950-20	454	0.91	1.98	0.59
H-800-40	708	0.87	2.00	0.65
H-850-40	690	0.88	2.01	0.64
H-900-40	640	0.89	2.08	0.64
H-950-40	625	0.87	2.01	0.65
H-800-60	960	0.86	2.03	0.67
H-850-60	987	0.85	2.04	0.68
H-900-60	789	0.85	2.10	0.70
H-950-60	692	0.84	2.08	0.71
C30-H10	784	0.79	2.01	0.77
C20-H20	705	0.81	2.02	0.73
C10-H30	692	0.80	2.03	0.75
H30-C10	812	0.73	2.03	0.88
H20-C20	848	0.74	2.06	0.86
H10-C30	885	0.73	2.05	0.88

conjoint action being more marked when the carbon dioxide is the second agent.

Microporosity

In order to extract more information about the micropore volume from the nitrogen and carbon dioxide isotherms, we applied the Dubinin-Radushkevich equation (Dubinin and Radushkevich 1947):

$$\log W = \log W_0 - D \log^2 (p^0/p) \tag{2}$$

where W is the adsorbed amount, expressed as liquid volume, at each value of p/p^0 , and W_0 is the total volume of the micropore system per gram of adsorbent. The notation used for W_0 is $V_{\text{DR}}(\text{N}_2)$ or $V_{\text{DR}}(\text{CO}_2)$ to indicate whether the value was obtained from the data of nitrogen adsorption at 77 K or from carbon dioxide at 298 K, respectively.

The micropore volumes calculated by this procedure are listed in Table 3. One sees that the values obtained from the carbon dioxide adsorption isotherms,

$V_{\text{DR}}(\text{CO}_2)$, are, for all the active carbons prepared, greater than those corresponding to the nitrogen adsorption isotherms, $V_{\text{DR}}(\text{N}_2)$. The likely reason is that the carbon dioxide adsorption process may include effects of activated diffusion as a consequence of the isotherms of this adsorbate having been obtained at much higher temperatures than in the nitrogen case. It should also be observed that the values of $V_{\text{DR}}(\text{N}_2)$ are of the same order of magnitude as those read in the adsorption isotherm for the value of $p/p^0 = 0.1$.

Samples activated with a single gasification agent

Figures 3 and 4 show that for the samples activated with a single gasification agent, as the burn-off percentage rises, so too does the volume of micropores, independently of the process temperature. The lines shown in these figures are merely straight lines connecting data points, and no mathematical relationship is implied. This was to be expected after what had been observed for the gas adsorption isotherms. The micropore volume corresponding to the carbon dioxide gasified samples is greater than that obtained with water vapour. This behaviour may be due to a variety of causes. Some workers have indicated that,

Table 3. Pore volumes of the active carbons

Samples	V_{mi} ($\text{cm}^3\cdot\text{g}^{-1}$)	$V_{\text{DR}}(\text{N}_2)$ ($\text{cm}^3\cdot\text{g}^{-1}$)	$V_{\text{DR}}(\text{CO}_2)$ ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{me} ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{ma} ($\text{cm}^3\cdot\text{g}^{-1}$)
C-800-20	0.231	0.232	0.300	0.040	0.389
C-800-40	0.346	0.347	0.385	0.084	0.280
C-800-60	0.415	0.415	0.423	0.123	0.232
C-850-20	0.254	0.255	0.314	0.040	0.376
C-850-40	0.359	0.360	0.390	0.083	0.248
C-850-60	0.379	0.381	0.414	0.123	0.238
C-900-20	0.251	0.252	0.303	0.046	0.363
C-900-40	0.357	0.358	0.380	0.102	0.241
C-900-60	0.383	0.383	0.420	0.129	0.238
C-950-20	0.244	0.244	0.296	0.049	0.387
C-950-40	0.357	0.357	0.363	0.098	0.235
C-950-60	0.385	0.386	0.422	0.125	0.250
H-800-20	0.206	0.206	0.289	0.026	0.358
H-800-40	0.290	0.292	0.306	0.106	0.254
H-800-60	0.403	0.403	0.414	0.182	0.085
H-850-20	0.241	0.240	0.290	0.057	0.292
H-850-40	0.301	0.301	0.309	0.102	0.237
H-850-60	0.320	0.320	0.409	0.181	0.179
H-900-20	0.178	0.179	0.281	0.056	0.175
H-900-40	0.275	0.276	0.290	0.085	0.280
H-900-60	0.305	0.304	0.349	0.108	0.287
H-950-20	0.202	0.202	0.275	0.054	0.334
H-950-40	0.274	0.275	0.288	0.079	0.297
H-950-60	0.289	0.289	0.329	0.070	0.351
C30-H10	0.340	0.341	0.361	0.107	0.323
C20-H20	0.312	0.312	0.341	0.102	0.316
C10-H30	0.289	0.290	0.336	0.084	0.377
H30-C10	0.319	0.319	0.332	0.096	0.465
H20-C20	0.334	0.335	0.338	0.093	0.433
H10-C30	0.340	0.340	0.360	0.081	0.459

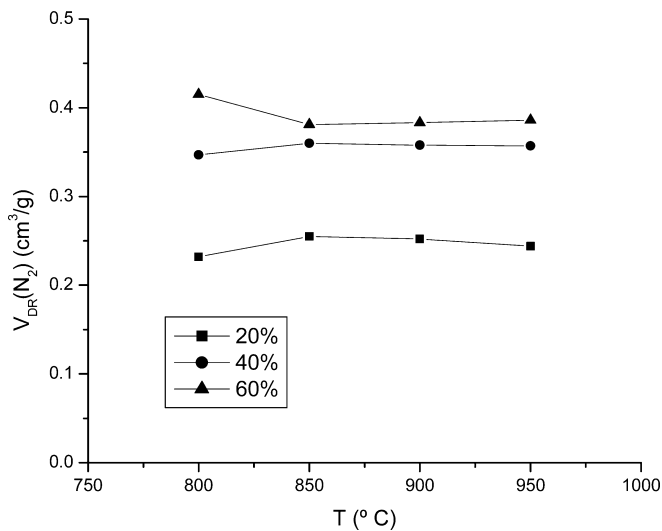


Fig. 3. Pore volume vs. temperature for the carbon dioxide activated samples

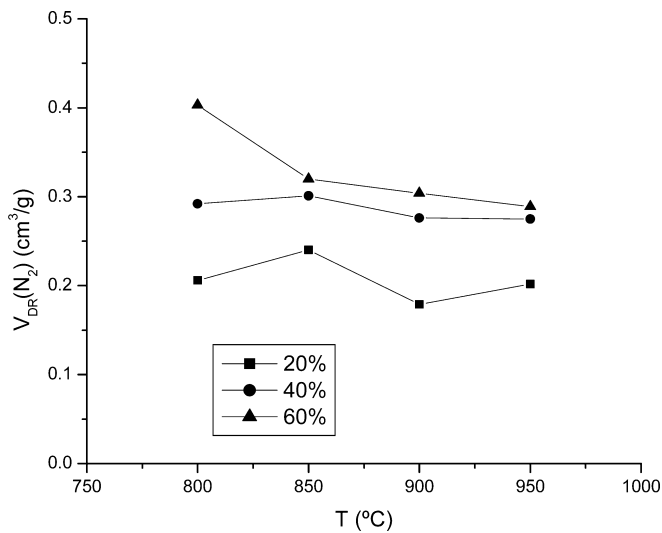


Fig. 4. Pore volume vs. temperature for the water vapour activated samples

amongst other possibilities, the presence of hydrogen would probably inhibit the reaction of water vapour with carbon (Gadsby et al. 1946), or the presence of oxygen would reduce the yield of the process since it burns the surface (Reif 1952), etc. Also, two quite clearly defined types of behaviour are seen. On the one hand, the samples prepared with a burn-off percentage of 20 and 40% present a similar behaviour, with the best results for the micropore volume in both cases being for the samples prepared at 850°C. On the other hand, for the samples prepared with a burn-off percentage of 60%, the trends in the results are similar, but now the best results are obtained for a process temperature of 800°C. This seems to indicate that the higher burn-off percentage favours the development of

microporosity at lower temperatures. This behaviour is related to the creation of micropores during the first phase of the gasification of the carbon, and to an enlargement of a fraction of pores when the temperature is greater than 850°C with a concomitant decrease in microporosity.

Samples obtained with successive applications of the two activating agents

With regard to the micropore volume of the samples obtained with successive applications of the two activating agents, one observes the same general pattern described above for the agents separately, i.e., the micropore volumes obtained from the carbon dioxide isotherms at 298 K are greater than those determined from the nitrogen isotherms at 77 K. Also in perfect agreement with the previous results, the microporosity values are lower when carbon dioxide is used as the first agent rather than when used as the second. This suggests that carbon dioxide favours the development of porosity, which, as was seen before, is created to a lesser degree by the water vapour.

Mesoporosity

Samples activated with a single gasification agent

Table 3 lists the values of the mesopores volumes (V_{me}). The volumes corresponding to the water vapour activated samples are generally greater than those for the carbon dioxide cases. This may be related to the loss of microporosity in the water vapour samples with regard to the carbon dioxide samples. For a fixed gasification percentage and by varying the temperature, the mesopores volume remains practically constant, while for a fixed temperature, the mesopores volume increases with the increasing degree of gasification. This suggests that the progressive gasification of the product affects micropores and mesopores similarly, i.e., as was the case with the micropore volume, when the burn-off percentage increases so does the mesopores volume.

The behaviour of the samples with a burn-off percentage of 20% presents an irregular variation of the mesopores with temperature, independently of whether the activating agent was carbon dioxide or water vapour. At a burn-off percentage of 40 or 60%, however, the carbon dioxide gasified samples show similar patterns of variation, with the greatest mesopores value being reached at 900°C, especially when the burn-off percentage was 60%.

In the water vapour activated samples, there was again a parallelism in the variations of the mesopores volumes, with the best results now being obtained at 800°C, especially for the sample corresponding to a burn-off percentage of 60%. That the values obtained in this case are greater than the previous ones may reflect the enlargement of the micropores in these samples, also seen in the lesser degree of microporosity.

Samples obtained with successive applications of the two activating agents

In the samples obtained with successive applications of carbon dioxide and water vapour, when the water vapour was used as the first of the two agents there was an increase in mesopores volume with an increasing degree of activation, whereas when carbon dioxide was used as the first agent, the reverse phenomenon occurred, with a decrease in mesopores volume.

To sum up, holm-oak wood is a good raw material, not only to get barbecue coal, which has been used as a precursor to obtain activated coal, but it also allows the activated coal to develop its microporosity and mesoporosity in a good way, which is suitable for new applications as absorbent in liquid phase, gas absorbent, constituent part of combustible batteries, etc.

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