

## Mesoporous Activated Carbon from Agricultural Byproducts

Polymnia Galiatsatou<sup>1,\*</sup>, Michail Metaxas<sup>1</sup>, and Vasilia Kasselouri-Rigopoulou<sup>2</sup>

<sup>1</sup> Institute of Technology of Agricultural Products, National Agricultural Research Foundation (NAGREF), 1 S. Venizelou, 141 23 Likovrissi, Greece

<sup>2</sup> Department of Chemical Engineering, National Technical University of Athens (NTUA), 9 Iroon Polytechniou, 157 73 Athens, Greece

**Abstract.** Several different activated carbons have been prepared, from olive stones, solvent-extracted olive pulp and peach stones. Both a two-step procedure, carbonization followed by steam activation, and a single-step procedure, carbonization and activation in a single stage, have been applied at temperatures from 770 to 850 °C. The effect of such variables as heating rate during carbonization and activation, final temperature, soaking time and starting material, on the development of pore structure, have been investigated. Porosity and surface area have been evaluated by adsorption of nitrogen at 77 K. Mesoporosity and macroporosity were determined by mercury porosimetry. Scanning electron microscopy and X-ray diffraction analysis revealed useful information on the surface texture and structure respectively. Two-step physical activation of olive stones, with steam, yielded mesoporous structures. Extended time of activation favoured mesopore development. The parent olive stones showed the most homogeneous surfaces. All the activated carbons prepared were amorphous. Their well-developed porosity and large surface area combined with their chemical composition render the activated carbons from agricultural by-products an attractive product.

**Key words:** Activated carbon; mesoporous; agricultural by-products; characterization.

Activated carbons are sorbents with a large surface area and a highly developed porosity, applicable in the removal of contaminants from groundwater and industrial water, and for gas separation and storage etc. [1, 2]. They can be prepared by the carbonization

of carbonaceous materials in the absence of air (pyrolysis) followed by an activation step, which allows the activation agent to react with the carbon (physical activation). The product of simple carbonization is practically inactive and the use of a gas such as steam or carbon dioxide at temperatures between 700 and 1100 °C is required to develop porosity and a relatively large surface area [3, 4]. Activated carbons can also be obtained in a single step operation (chemical activation) by treatment of the carbonaceous material with chemical substances, in order to restrict tar formation, and then carbonization at temperatures lower than those used in physical activation [3, 5]. According to Dubinin, the pores of activated carbons are classified into three groups: micropores ( $d_p < 20 \text{ \AA}$ ), transitional pores (mesopores) ( $20 \text{ \AA} < d_p < 500 \text{ \AA}$ ), and macropores ( $d_p > 500 \text{ \AA}$ ), where  $d_p$  is the pore width [6].

Reports have appeared on the preparation of activated carbons with adequate adsorptive properties, from agricultural by-products [7, 8]. However, the demand for improved products with specific properties continues to increase and it is economically attractive to prepare them from cheap precursors.

Greece, the third largest producer of olive oil in Europe, produces 0.5 million tonnes of olive pulp every year, which are mostly disposed of. Approximately 90% of the olive pulp consists of woody material, which is a rich lignocellulosic precursor. Kiritsakis has reported that the high cost of olive-oil production is mainly due to the low merit of solvent-extracted olive pulp [9].

Our investigation is focused on the influence of olive stone/olive pulp as a raw material and of the preparation methods, on the porosity and structure of

\* To whom correspondence should be addressed

activated carbons. Knowledge of the effects of different variables during the carbonization and activation process is important in controlling the porosity of the final product. Steam activation of the carbonized precursors has been selected for examination since at a given temperature the reactivity with steam is greater than that with other gas reagents (e.g. carbon dioxide). Furthermore, from early on in the activation steam widens the micropores, resulting in more developed mesoporosity [10]. During adsorption, macro- and mesopores allow rapid transport of the adsorbate into the interior of the carbon, for subsequent diffusion into the micropore volume. Consequently, a well-developed porous network in all pore size ranges results in improved adsorption properties of the product. Since the porosity is also dependent on the starting material, we have also prepared activated carbons from peach stone, for comparative studies.

Agricultural by-products as precursors for the preparation of activated carbons, have minimal cost since they are agricultural wastes. Other precursors such as minerals (e.g. bituminous coal, lignite) have a high degree of inorganic material, of the order of 20% [11], which necessitates demineralization followed by washing steps so that the material obtains certain properties [12] required for the preparation of activated

carbons. In addition, the high content of inorganic material lowers the resulting yield of the final product. Consequently the total cost and time of the preparation process increase. In contrast, the low ash content and the absence of sulphur and heavy metals [7] in the agricultural raw material eliminates some time-consuming and expensive procedural steps. Furthermore it allows the activated carbon to be used in specific applications (in the food and pharmaceutical industries) where high-purity carbons are required.

Thus, the benefits would include removal of a polluting waste product, cheaper materials for environmental protection devices, as well as economic gains for products manufactured from abundant yet untapped sources in Greece.

The objective of this work was to investigate the conditions for preparation of activated carbons with well-developed porosity in the mesopore range, using Greek olive stones and olive pulp as inexpensive carbonaceous precursors.

## Experimental

In this study, olive stones (O), solvent-extracted olive pulp (OP) and peach stones (P) were used as the precursors. The first two materials were supplied by a Greek kernel-oil factory, and peach stones were supplied by Greek canned-fruit factories. The conditions of preparation and the resulting yields are listed in Table 1. The raw

**Table 1.** Preparation conditions and resulting yields of activated carbons

Sample	Time of carbonization (min)	Temperature of activation (°C)	Time of activation (min)	Yield of activated carbon (%)
AC <sub>5</sub> O1 <sup>a</sup>	120	800	40	21.5
ACO2 <sup>b</sup>	120	800	40	17.5
ACO3	90	800	20	25.6
AC <sup>800</sup> O4 <sup>c</sup>	90	770	60	20.1
ACO5	90	800	40	18.9
ACO6	90	800	90	11.8
ACO7	60	800	40	19.9
ACO8	60	800	60	14.3
CAO <sup>d</sup>		800	120	14.8
ACOP1 <sup>e</sup>	120	800	40	20.4
ACPI <sup>f</sup>	90	800	40	25.2

<sup>a</sup> Activated carbon after activation (A) under the conditions indicated, carbonized (C) at 850 °C with a heating rate of 5 °C/min, from olive stone (O).

<sup>b</sup> Activated carbon after activation (A) under the conditions indicated, carbonized (C) at 850 °C with a heating rate of 10 °C/min, from olive stone (O).

<sup>c</sup> Activated carbon after activation (A) under the conditions indicated, carbonized (C) at 800 °C with a heating rate of 10 °C/min, from olive stone (O).

<sup>d</sup> One-step carbonized (C) – activated (A), under the conditions indicated, carbon, from olive stone.

<sup>e</sup> Activated carbon after activation (A) under the conditions indicated, carbonized (C) at 850 °C with a heating rate of 10 °C/min, from solvent extracted olive pulp (OP).

<sup>f</sup> Activated carbon after activation (A) under the conditions indicated, carbonized (C) at 850 °C with a heating rate of 10 °C/min, from peach stone (P).

material was crushed and sieved to have a particle size of 2.5–3.5 mm. Samples were carbonized in a horizontal furnace, at 850 °C (except AC<sup>800</sup>O4, carbonized at 800 °C) with a heating rate of 10 °C/min (except for AC<sub>5</sub>O1, where a 5 °C/min heating rate was applied), for different periods of time. Batches of carbonized material were activated with a heating rate of 10 °C/min under a steam/N<sub>2</sub> flow of 100 ml/min. The CAO sample was activated in a single stage. After each step, samples were cooled to room temperature in a nitrogen flow.

N<sub>2</sub> adsorption at 77 K was examined with an Autosorb 1 N<sub>2</sub>-porosimeter, and mercury intrusion with a Carlo Erba Milestone 200 Hg-porosimeter. X-ray diffraction patterns were obtained with a Siemens D5000 X-Ray Diffractometer. SEM photographs were taken with a Jeol 6100 instrument.

## Results and Discussion

Activated carbons were analysed in terms of pore size/ pore size distribution and apparent surface area by using the isotherm of N<sub>2</sub> at 77 K, and mercury porosimetry was used to define the average pore radius and pore size distribution (above 30 Å) of the samples. There is considerable overlap between these two methods, but they are best regarded as complementary.

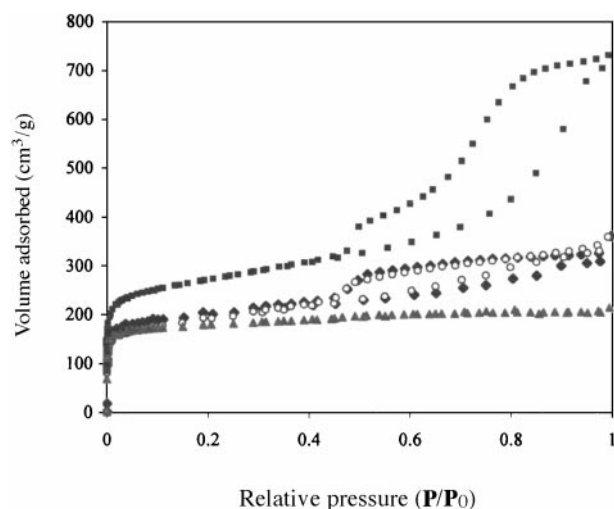
The N<sub>2</sub> adsorption isotherms at 77 K, of the products from olive stones (O), solvent-extracted olive pulp (OP) and peach stones (P) are demonstrated in Fig. 1. The ACP 1 isotherm corresponds to type I of the IUPAC classification [13], exhibiting a knee at  $P/P_0 < 0.01$ , typical for relatively narrow micropores, whereas the ACO5, ACOP1 and CAO isotherms show a hysteresis loop, characteristic of mesopores. The results of the N<sub>2</sub> porosimetry in terms of BET apparent surface area, total pore volume and *t*-method micropore

**Table 2.** Pore volumes and apparent surface areas for activated carbon series

Sample	$V_{\text{total}}$ (cm <sup>3</sup> /g)* at $P/P_0 = 0.995$	$V_{\text{micro}}$ * (cm <sup>3</sup> /g)	Apparent surface area* (m <sup>2</sup> /g)
AC <sub>5</sub> O1	0.52	0.10	544
ACO2	0.94	0.16	940
ACO5	0.56	0.17	751
ACO7	0.49	0.17	694
ACO8	0.77	0.14	802
CAO	0.99	0.16	879
ACOP1	0.56	0.16	691
ACP1	0.33	0.20	686

\* Relative standard deviation 3%.

volume [14] are shown in Table 2. The *t*-method compares the shape of the isotherm under test with that of a solid chemically similar to the sample, and known to be free from pores and especially micropores. For the BET surface area determinations, the molecular area of N<sub>2</sub> at 77 K, i.e. the area occupied by an adsorbate molecule in the completed monolayer, was taken as 16.2 Å<sup>2</sup> [15]. From these measurements, it is obvious that the carbonization rate plays a significant role in both surface area and mesopore volume evolution. Comparison of the AC<sub>5</sub>O1 and ACO2 samples shows clear evidence that a twofold increase of heating rate during carbonization (from 5 °C/min to 10 °C/min) resulted in lower yields, and higher total volume and surface area. Furthermore, for samples ACO7 and ACO8, with the same conditions of carbonization and a slight difference in the retention time at the final temperature during activation, increased retention time tends to increase the total pore volume and surface area, and the micropore volume seems to be reduced. Comparison of the ACO8 to CAO having similar time of thermal treatment, shows that CAO has higher micropore and total pore volume up to  $d_p = 2500$  Å ( $P/P_0 = 0.995$ ). On the other hand, comparison of the ACO2, ACO5 and ACO7 samples where only the residence time at carbonization temperature is varied, indicates that the surface area and total pore volume increase with this time. It worth noting that the period between 90 and 120 min is critical, since reordering of the char structure yields a material with decreased micropore volume. If we compare the data for ACOP1 and ACO2, we note that the nature of the starting material exerts a remarkable influence on the aforementioned structural properties. The same conclusion arises after comparison of ACP1 with ACO5, where use of peach stone favours a



**Fig. 1.** Adsorption isotherms of N<sub>2</sub> at 77 K on activated carbons from (O) olive stones, (OP) solvent extracted olive pulp, (P) peach stones. ● ACO5; ○ ACOP1; ▲ ACP1; ■ CAO

**Table 3.** Measurements of various textural properties for activated carbon series

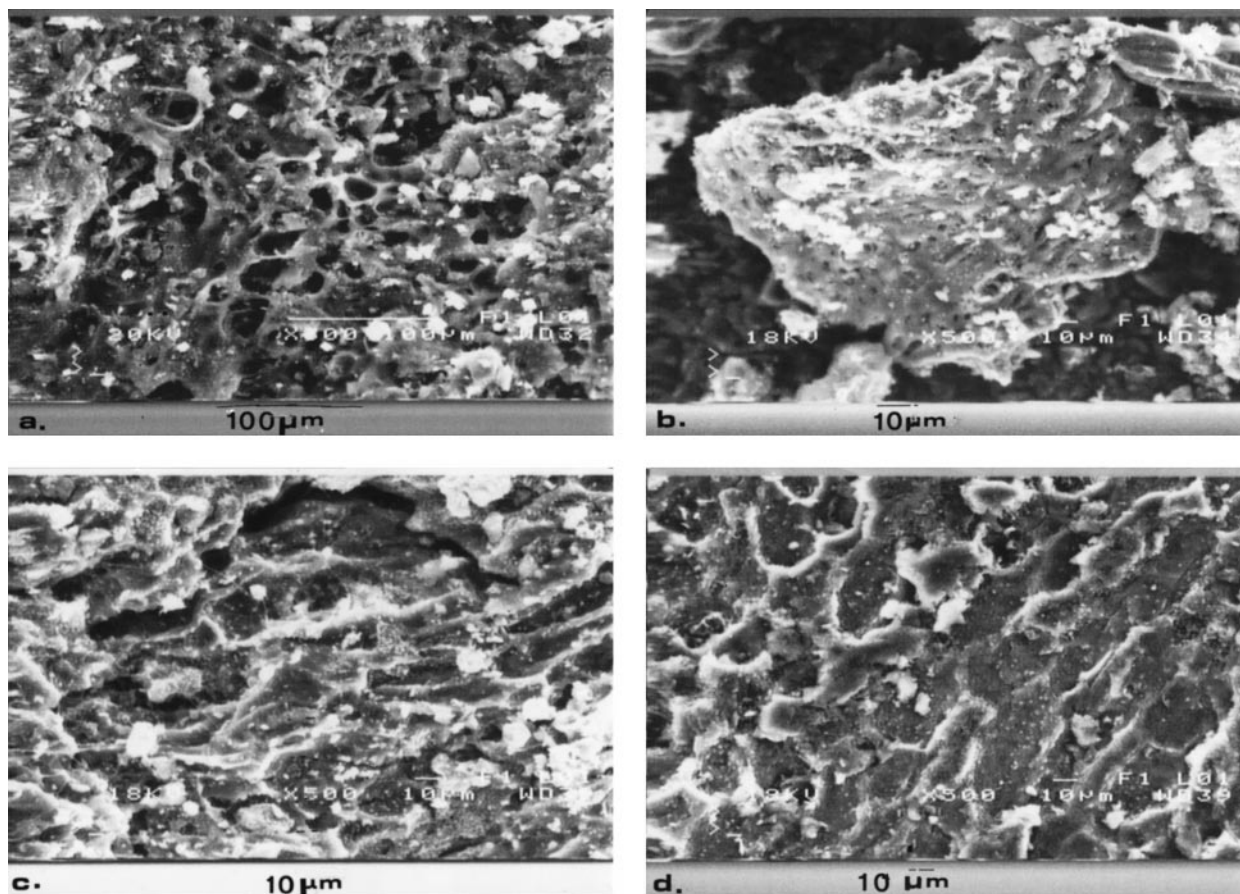
Sample	$V_{\text{meso}}^*$ (cm <sup>3</sup> /g) 40 Å < $d_p$ < 500 Å	$V_{\text{macro}}^*$ (cm <sup>3</sup> /g) $d_p$ > 500 Å	Surface area* (m <sup>2</sup> /g)	Average pore radius (Å)	Corrected bulk density (g/cm <sup>3</sup> )	Porosity (%)
AC <sub>5</sub> O1	0.078	0.16	21.0	50	1.20	22.5
ACO2	0.190	0.52	49.6	300	1.00	38.0
ACO3	0.087	0.16	25.2	50	1.10	21.4
AC <sup>800</sup> O4	0.110	0.28	30.8	50	0.99	27.9
ACO6	0.310	0.57	77.7	160	1.10	49.2
ACO8	0.290	0.67	74.8	150	1.26	54.9
CAO	0.210	0.20	56.4	50	1.00	28.8

\* Relative standard deviation 3%.

micropore structure with lower total volume and surface area.

The characteristics of these activated carbons, as determined by mercury porosimetry, are listed in Table 3. These results indicate that using the same rate of carbonization and activation, of the order of 10 °C/min, produces a much more developed porosity in the meso/macropore region as well as an increased specific surface area (AC<sub>5</sub>O1, ACO2). On the other hand, a 20-

min increase of retention time at the final activation temperature has a much more favourable effect than a 60-minute increase at the final carbonization temperature, on the dynamics of mesopore and surface area development (ACO2, ACO8). Comparison of ACO8 with AC<sup>800</sup>O4 clearly shows that an activation temperature of 770 °C does not favour selective burning of the interior of the particle, with subsequent creation of porosity. Furthermore, a carbonization temperature of

**Fig. 2.** SEM micrographs of (a) ACO5 (×500), (b) CAO (×300), (c) ACOP1 (×300), (d) ACP1 (×300) activated carbons

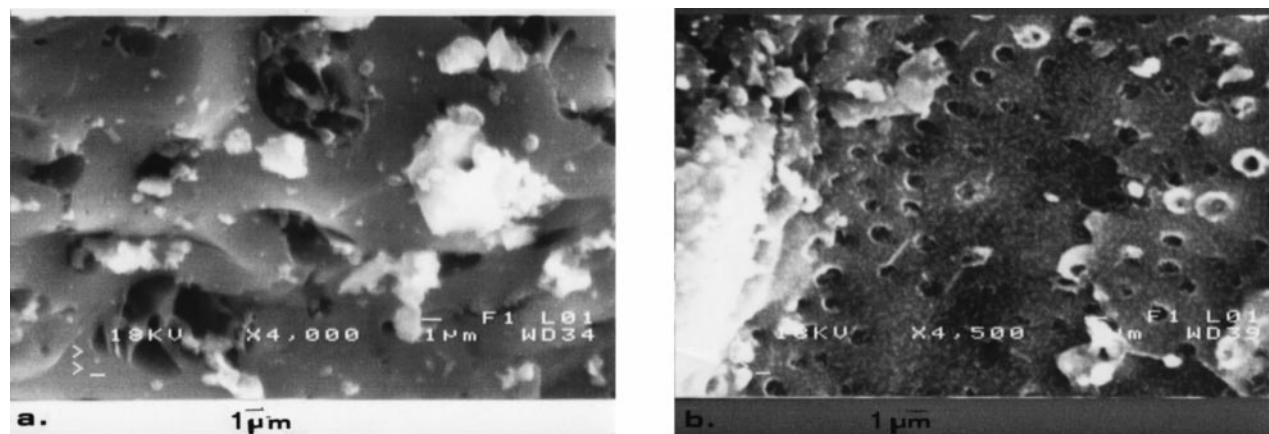


Fig. 3. SEM micrographs of (a) CAO ( $\times 4000$ ), (b) ACP1 ( $\times 4500$ ) activated carbons

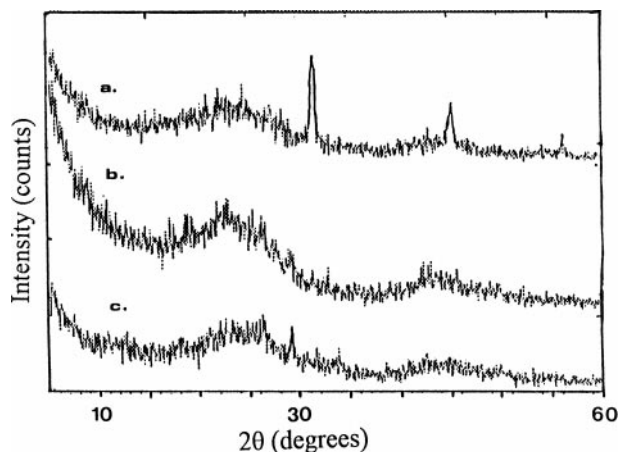
800 °C even for 90 min, instead of 850 °C for 60 min seems not to improve the sorption characteristics of the resulting activated carbons. By comparison of ACO8 with ACO6 we note that similar mesopore volume, surface area, porosity and average pore radius are obtained when either 60 or 90 min is applied as the soaking time, at both carbonization and activation temperature. Comparison of ACO3 with ACO6 reveals that extended activation time widens the porosity and enlarges the volume and surface area. Finally, comparison of ACO8 with CAO, which have similar yield, clearly shows that the two-step procedure results in active carbons with higher average pore radius, higher macropore volume for pores  $d_p > 2500 \text{ \AA}$  and mesopore volume for pores  $d_p > 40 \text{ \AA}$ . Summarizing the results of the  $N_2$  77 K and mercury porosimetry tests, we would say that the two-step steam activation of olive stones produced carbons with mainly mesopore structures, the development of which is favoured by extended activation time. Solvent-extracted olive pulp yielded carbons with intermediate mesopore structures, compared to those from olive stones, and the activation of peach stones resulted in microporous products with significantly lower BET surfaces.

Scanning electron microscopy (SEM) was used to picture the surface texture of the carbons [16]. X-ray diffraction (XRD) was used to determine the composition and the kind of structure (polycrystalline/microcrystalline or amorphous) of the samples [17].

SEM micrographs of ACO5, CAO, ACOP1 and ACP1 samples (Fig. 2) show the development of the porosity of these materials upon activation with steam. The ACO5 sample (Fig. 2a) appears to have well

developed macropores of the order of 5–50  $\mu\text{m}$  whereas the CAO sample (Fig. 2b) has macropores of the order of 1–5  $\mu\text{m}$ . Comparison of these two materials indicates that the two-step physical activation of the same precursor results in more homogeneous surfaces, whereas the pore development during the single-step activation seems to occur as an unrestrained process. The ACOP1 sample (Fig. 2c) shows crackings, prolonged slit pores of the order of 10  $\mu\text{m}$  and an extensive number of distinct deposited inorganic microcrystals. The peach sample (Fig. 2d) is rather inhomogeneous, with rough texture and a large number of shallow cavities and cylindrical pores of 1  $\mu\text{m}$  diameter on the surface. Finally, from Fig. 3a we observe that the CAO sample has a relatively smooth surface and well shaped cylindrical pores, but the surface of the ACP1 sample (Fig. 3b) is rough and harsh. The textures for both materials appear rich in small crystals of inorganic matter inside the pores as well as on the outer edge.

The XRD studies, performed on the same series of activated carbon, show a clear difference for these materials. The CAO sample (Fig. 4a) appears much more crystalline, showing three peaks at  $2\theta$  values of  $31^\circ$ ,  $45^\circ$ , and  $56^\circ$ . These peaks are attributed to the inorganic microcrystals deposited (mixtures of various oxides such as those of calcium, silicon, magnesium, iron, aluminium, etc.) This is confirmed by Fig. 5a where the XRD pattern of ash from CAO reveals the same peaks as the CAO sample itself (Fig. 4a). This is confirmed by Fig. 5b, which shows that the CAO sample, after treatment with 10% v/v sulphuric acid for 6 h to remove the inorganic matter, shows a completely amorphous structure. The XRD pattern on the ACOP1



**Fig. 4.** XRD patterns of (a) CAO, (b) ACP1, (c) ACOP1 activated carbons

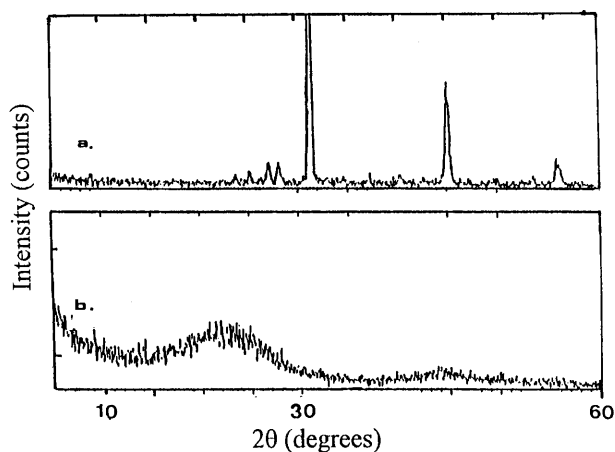
sample (Fig. 4c) compared with that of CAO, shows small peaks with shifted interlayer spacing ( $d$ -values), due to its different ash profile.

On the other hand, the XRD pattern of ACP1 (Fig. 4b), indicates a totally amorphous material lacking any crystallinity due to its lower ash content.

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## References

- [1] C. A. Toles, W. E. Marshall, M. M. Johns, *Carbon* **1997**, *35*, 1407.
- [2] S. Sircar, T. C. Golden, M. B. Rao, *Carbon* **1996**, *34*, 1.
- [3] M. Smicek, S. Cerny, *Active Carbon*. Elsevier, Amsterdam, 1970.
- [4] F. Rodriguez-Reinoso, M. Molina-Sabio, *Carbon* **1992**, *30*, 1111.



**Fig. 5.** XRD patterns of (a) CAO ash, (b) CAO activated carbon washed with 10% v/v  $H_2SO_4$  for 6 h

- [5] A. Ahmadpour, D. D. Do, *Carbon* **1997**, *35*, 1723.
- [6] M. M. Dubinin, *Chem. Rev.* **1960**, *60*, 235.
- [7] P. Galiatsatou, *PhD Thesis*. NTUA, Athens, 1993.
- [8] A. M. Warhurst, G. D. Fowler, G. M. McConnachie, S. J. Pollard, *Carbon* **1997**, *35*, 1039.
- [9] A. Kiritsakis, *Olive Oil*, 2nd Edn. Agricultural Association Publications, Thessaloniki, 1988, pp. 129–138.
- [10] F. Rodriguez-Reinoso, M. Molina-Sabio, M. T. Gonzalez, *Carbon* **1995**, *33*, 15.
- [11] V. Minkova, M. Razvigorova, M. Goranova, L. Ljutzkanov, G. Angelova, *Fuel* **1991**, *70*, 713.
- [12] R. Ch. Bansal, J. P. Donnet, F. Stoeckli, *Active Carbon*. Marcel Dekker, New York, 1988.
- [13] S. Brunauer, L. S. Deming, W. E. Deming, E. J. Teller, *J. Am. Chem. Soc.* **1940**, *62*, 1723.
- [14] B. C. Lippens, J. H. de Boer, *J. Catalysis* **1965**, *4*, 319.
- [15] S. J. Gregg, K. S. W. Sing, *Adsorption Surface Area and Porosity*, 2nd Edn. Academic Press, London, 1982, p. 61.
- [16] K. Gergova, S. Eser, *Carbon* **1996**, *34*, 879.
- [17] V. Suresh Babu, M. S. Seehra, *Carbon* **1996**, *34*, 1259.