COMPARED ADSORPTIVE PROPERTIES OF ACTIVE CARBONS FROM OLIVE STONES AND ALMOND SHELLS

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INTRODUCTION

There is no doubt about the growing needs of active carbons with a low producing cost and having adequate adsorptive properties and other specific properties. This paper reports some basic information on the adsorptive properties of active carbons prepared from olive stones, a waste-product from the manufacture of olive oil in mediterranean countries, and from almond shells. Both raw materials are rather abundant and low priced, and have adequate botanical structures (1) to give hard active carbons allowing re-cycling in adsorption processes.

EXPERIMENTAL

Olive stones and almond shells were crushed and washed in diluted sulphuric acid followed by refluxing in water to total acid removal. The raw materials were then carbonized under nitrogen with a heating rate of 5ºC min^{-1} at 850ºC with a soaking time of 1 hour, the yield being about 27% for olive stones and 23 % for almond shells. The carbonized products were activated in carbon dioxide at 825ºC for different periods of time to give a wide range of burn-off.

The adsorption of N_2 at 77 K and CO_2 at 195 and 273 K has been carried out using conventional McBain silica spring balances (2). The volumes of meso- and macroporosities were determined using a mercury porosimeter manufactured by Carlo Erba. Chemical analyses of the raw materials and carbonised products are given in Table 1.

Table 1

	C%	H%	N%	S%	Ash%
olive stones	48.2	5.7	0.0	0.0	0.03
carbonized olive stones	94.6	1.0	0.0	0.0	0.21
almond shells ...	47.8	6.0	0.4	0.4	0.10
carbonized almond shells	94.6	0.7	0.4	0.4	0.29

RESULTS

Examples of adsorption isotherms of nitrogen at 77K on active carbons from olive stones (samples named O-time of activation) and from almond shells (samples named A-time of activation) are contained in Fig. 1. The adsorption isotherms of CO_2 at 273 K on the same samples are included in Fig. 2. The adsorption isotherms of the carbonized and not activated products are included in Fig. 1 and Fig. 2 as O-C and A-C, respectively.

As it can be deduced from Fig. 1 and Fig. 2, activated olive stones adsorb in a greater extent than those from almond shells. The surface areas of all samples are included in Table 2.

Table 2

Surface area of carbons (m^2 g^{-1})

	N_2 (77K)	CO_2(195K)	CO_2(273K)
O-C	74	584	532
O-2	959	864	715
O-8	1342	1241	984
O-16	1889	1692	1340
A-C	115	531	550
A-2	673	523	-
A-8	954	888	710
A-16	1446	1360	869

The as-carbonized materials exhibits some restriction of nitrogen adsorption at 77K and this is characteristic of diffusional resctrictive processes in ultramicroporous carbons (3), restriction which is eliminated with activation.

The variation of surface area with time of activation is shown in Fig. 3 (from carbon dioxide adsorption at 273K) where there is a linear increase in surface area with the time of activation in both kinds of active carbons, but the increase is faster for the activated olive stones.

The mercury porosimetry measurements show the development of porosity on activation; there is a development of mesoporosity in the activated carbon from olive stones in a higher extent than in those from almond shells, but in the later active carbons there is a greater develppment of macroporosity. In both cases the more activated samples have about 0.3 cm^3 g^{-1} of pore volume in pores of 200 nm to 200 μm diameter in the case of carbons from almond shells and about 0.6 cm^3 g^{-1} in the case of carbons from olive stones.

Since according to Dubinin (4) the gradient D of the equation of Dubinin-Radushkevich is a measure of the diameter of the microporosity of the adsorbent, the variation of the gradient D from isotherms of adsorption of carbon dioxide at 273 K with extent of activation is in Fig. 4. As it can be seen, the diameter of microporosity is larger in active carbons from olive stones and increases faster with activation.

Consequently with the above considerations, it can be deduced that olive stones and almond shells, both very abundant in medite rranean countries can yield active carbons with large effective surface areas, relatively high hardness and the specially important characteristics of very low ash content and low sulphur content.

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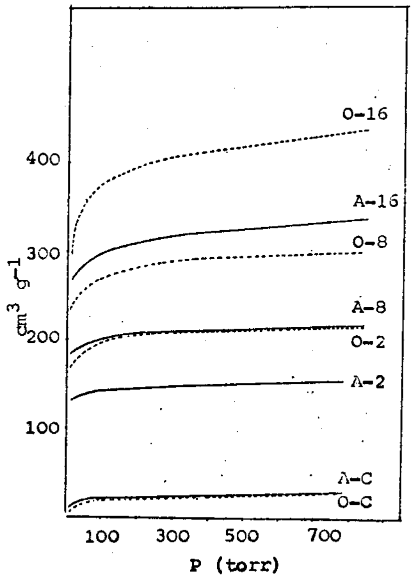

Fig. 1

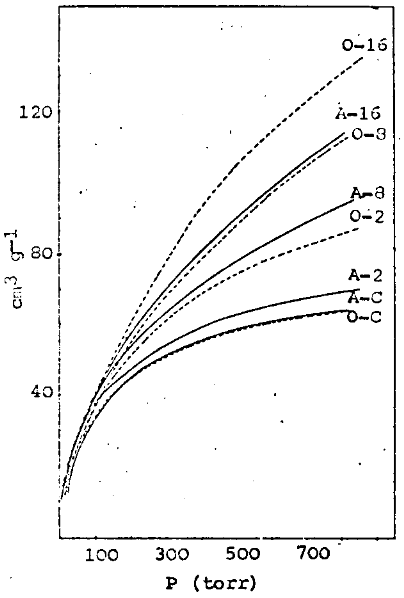

Fig. 2

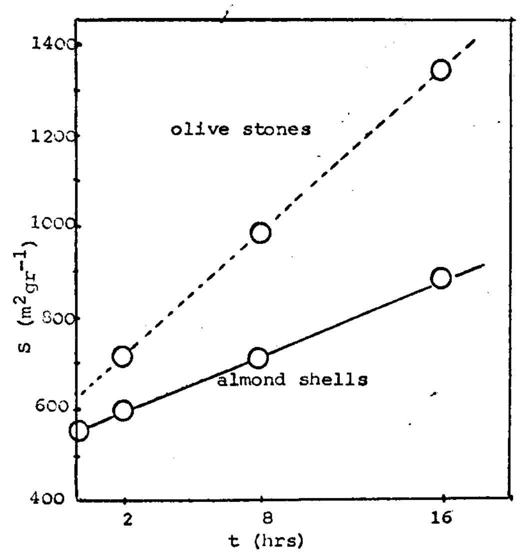

Fig. 3

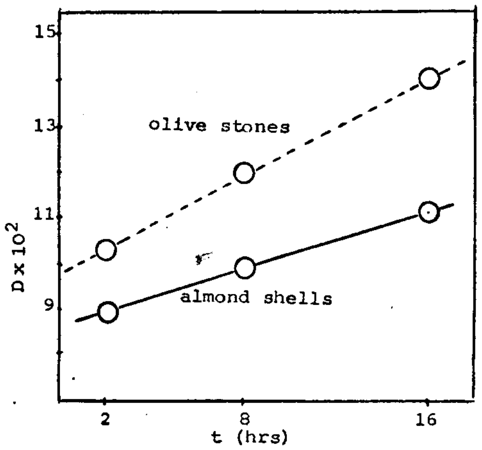

Fig. 4