Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Güzel, F. and Tez, Z.(1993) 'The Characterization of the Micropore Structures of Some Activated Carbons of Plant Origin by N_2 and CO_2 Adsorptions', Separation Science and Technology, 28: 8, 1609 — 1627
To link to this Article: DOI: 10.1080/01496399308018061
URL: http://dx.doi.org/10.1080/01496399308018061

SEPARATION SCIENCE AND TECHNOLOGY, **28(8)**, pp. 1609–1627, 1993

The Characterization of the Micropore Structures of Some Activated Carbons of Plant Origin by N_2 and CO_2 Adsorptions

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ABSTRACT

In this study, active carbons prepared from almond and hazelnut shells under various experimental conditions were investigated. Merck-2514 and Merck-2184 active carbons were used for comparison. N_2 (77 K) gas and CO_2 (273 and 195 K) gas adsorptions were determined as comparison criteria. Regarding the specific surface area and micropore volume results obtained from these adsorption data, it is concluded that N_2 (77 K) adsorption by itself is inadequate in the characterization of active carbons which are low-sized microporous dominated. In addition, it is concluded that it would be useful to investigate CO_2 (195 and 273 K) adsorption. The iodine and methylene blue tests at 298 K were also applied for the characterization of the carbon adsorbents mentioned. From these data it was seen that the iodine test can be applied as a total porosity indicator and that the methylene blue test can be used as a developed microporosity indicator. These results indicate that the best adsorbents were those prepared from hazelnut shells. Depending on the preparation conditions, the physically activated carbon has an activation time up to 4 hours and has adsorption properties on the level of Merck commercial carbons.

Key Words. Activated carbon; Characterization of carbons; Iodine and methylene blue adsorption; N_2 and CO_2 adsorption

INTRODUCTION

Active carbons are frequently used as adsorbents in industry because of their efficient adsorption capability. This capability is related to the pore structure and the chemical nature of the carbon surface as related to preparation conditions. In other words, by changing the preparation conditions, superior active carbons can be prepared from the same raw materials used for gas-phase or liquid-phase adsorption.

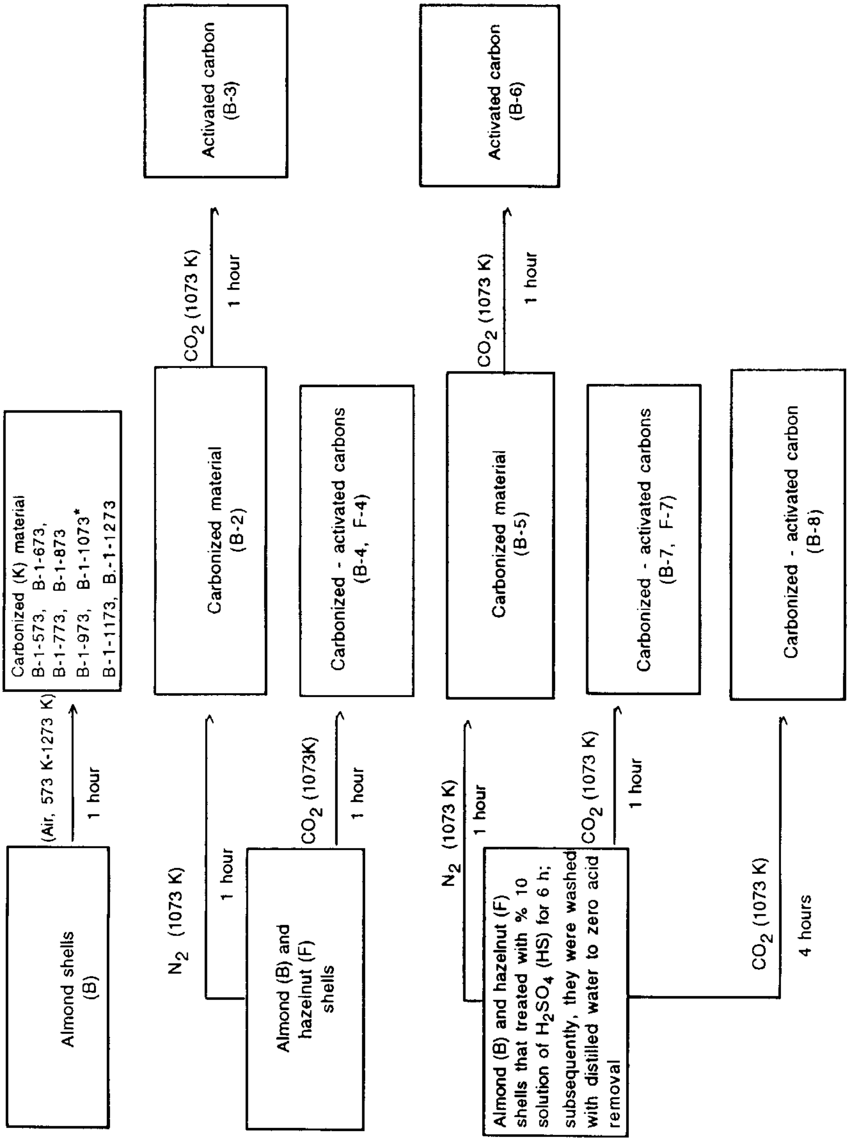
Numerous investigations are conducted in order to obtain active carbon of good quality in an economic way. In this study, almond and hazelnut shells were used under various experimental conditions in order to observe the effects of preparation conditions. Merck-2514 (M-2514) and Merck-2184 (M-2184) carbons were used for comparison. CO_2 adsorption (273 and 195 K), whose minimum molecular dimension is close to that of N_2, was used in addition to N_2 (77 K) adsorption. Furthermore, the iodine numbers (IN) (1) and the methylene blue numbers (MN) (2) were determined at 298 K on all samples.

EXPERIMENTAL

In this study, almond (B) shells collected from Diyarbakir, Turkey, and hazelnut (F) shells collected from Trabzon, Turkey, were used as the starting raw materials. These shells were first broken, then exposed to heating processes at a heating rate of 5 $K \cdot min^{-1}$ as shown in Scheme 1. The active carbons obtained were crushed at 80 mesh. Later, the carbons prepared from almond shells at various temperatures (573 to 1273 K) were outgassed at 523 K for 2 hours, and the N_2(77 K) and CO_2(273 K) adsorptions were determined. The CO_2(273 K) adsorptions were determined by the single point method with an apparatus similar to that developed by Haul and Dümbgen (3, 4) in 1960. N_2(77 K) and CO_2(195 K) adsorptions of the active carbons prepared from almond shells and hazelnut shells under various conditions were determined. In the determination of IN, dried active carbon (0.4 g) was added to an aqueous solution of 50 mL of 0.1 N I_2/I^-. This was then shaken at 298 K for 45 minutes. After the shaking, the residual iodine concentration was titrated with 0.1 N sodium thiosulfate, and the gram iodine amount adsorbed per 100 g carbon was taken as the iodine number. In the determination of methylene blue adsorption (MBA), a dried sample (0.1 g) was shaken with 100 mL of 2×10^{-5} M methylene blue (MB) solution at 298 K for 45 minutes. Then the residual methylene blue concentration was determined spectrophotometrically at 662 nm. The amount of methylene blue adsorbed in milligrams per gram of active carbons was taken as the MBA value.

RESULTS

Figure 1 shows the percent weight loss versus carbonization temperature. Figure 2 shows N_2(77 K) adsorption isotherms as they relate to the carbons obtained at various preparation temperatures from almond shells.



SCHEME 1 The preparation of active carbons from almond and hazelnut shells. The asterisk indicates the sample used.

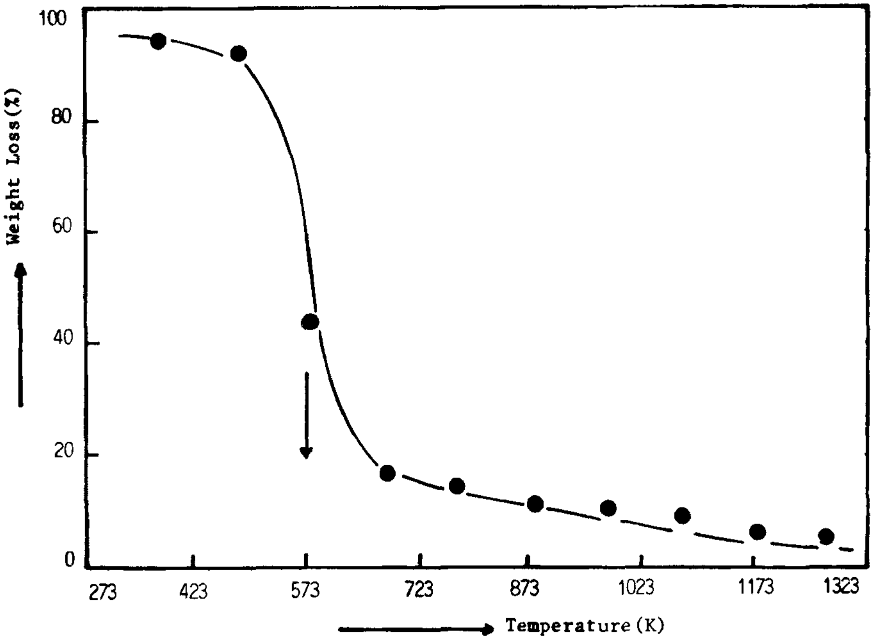


FIG. 1 The change of percent weight loss with the carbonization temperature as related to carbons prepared from almond shells.

Figure 3 shows N_2(77 K) adsorption isotherms as they relate to commercial active carbons and to the carbons obtained at various preparation conditions from almond shells and hazelnut shells.

Figure 4 shows CO_2(195 K) adsorption isotherms. By evaluating the single point adsorption results of CO_2(273 K) in the simplified BET equation suggested by Haul and Dümbgen (3, 4) and by taking the cross-sectional area of CO_2 at 273 K as 0.187 nm^2 (5), the specific surface areas (S_{CO_2}) related to the carbons (B-1-573–B-1-1273) prepared from almond shells at various temperatures were determined (Table 1). These values and the N_2 adsorption isotherms in Fig. 2 were evaluated by the linearized Langmuir adsorption equation. The N_2 surface areas (S_{N_2}) obtained by taking the cross-sectional area of N_2(77 K) as 0.162 nm^2 (6) are given in Table 1.

The isotherms in Figs. 3 and 4 were also evaluated by the Langmuir linear isotherms equation, and the CO_2 surface area (S_{CO_2}) and the N_2 surface area (S_{N_2}) values related to the active carbons prepared under various conditions were calculated by taking the cross-sectional areas as 0.162 nm^2 (6) for N_2(77 K) and as 0.170 nm^2 (5) for CO_2(195 K) (Table 2).

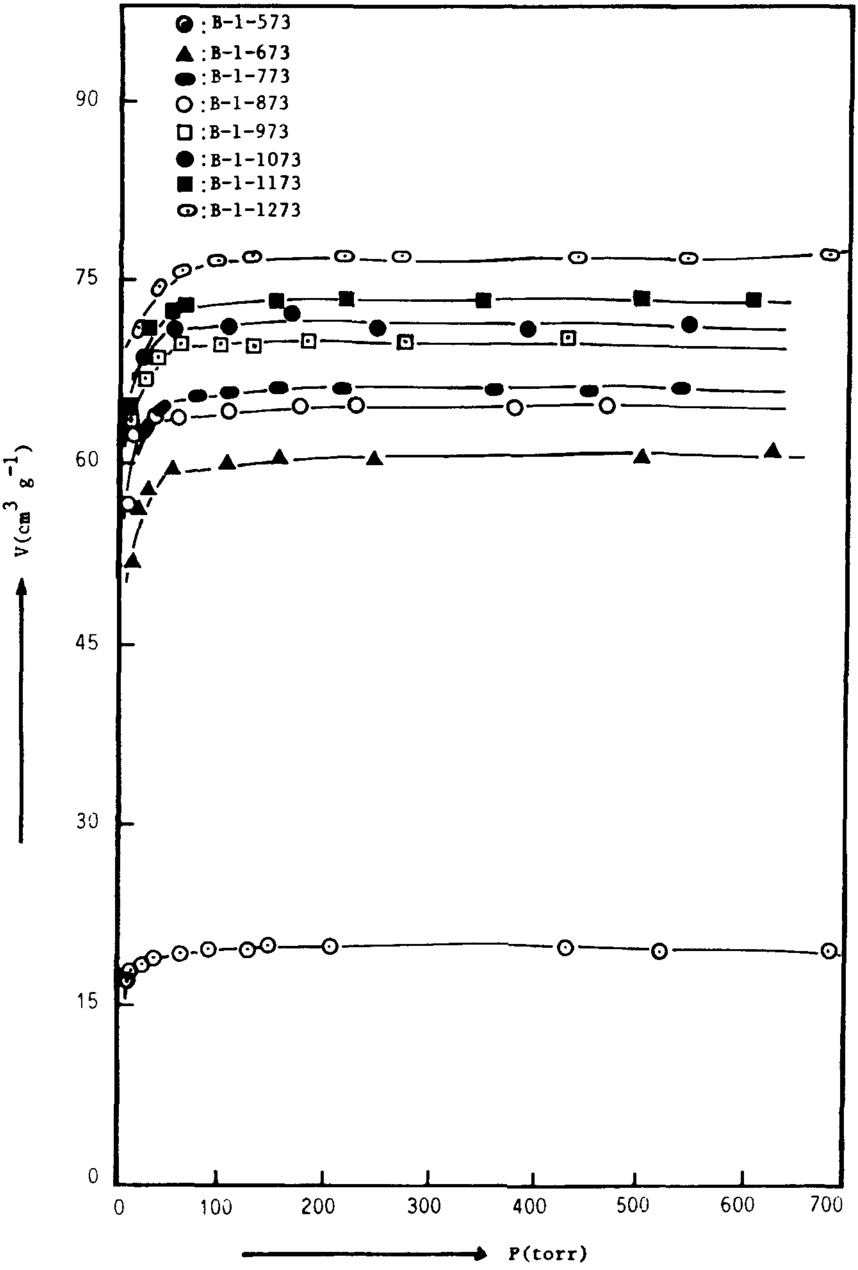


FIG. 2 The N_2(77 K) gas adsorption isotherms related to the carbons prepared at various temperatures from almond shells.

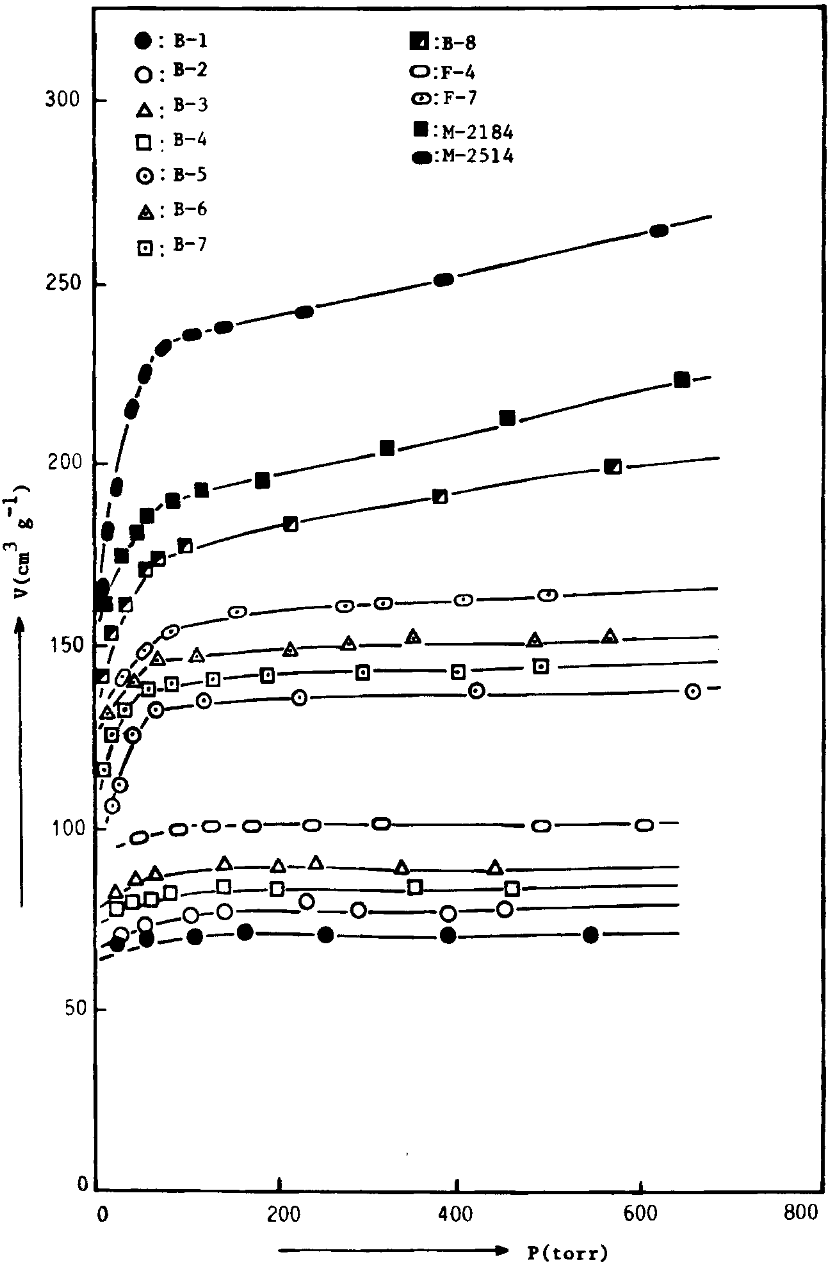


FIG. 3 The N_2(77 K) gas adsorption isotherms related to the active carbons prepared under various conditions.

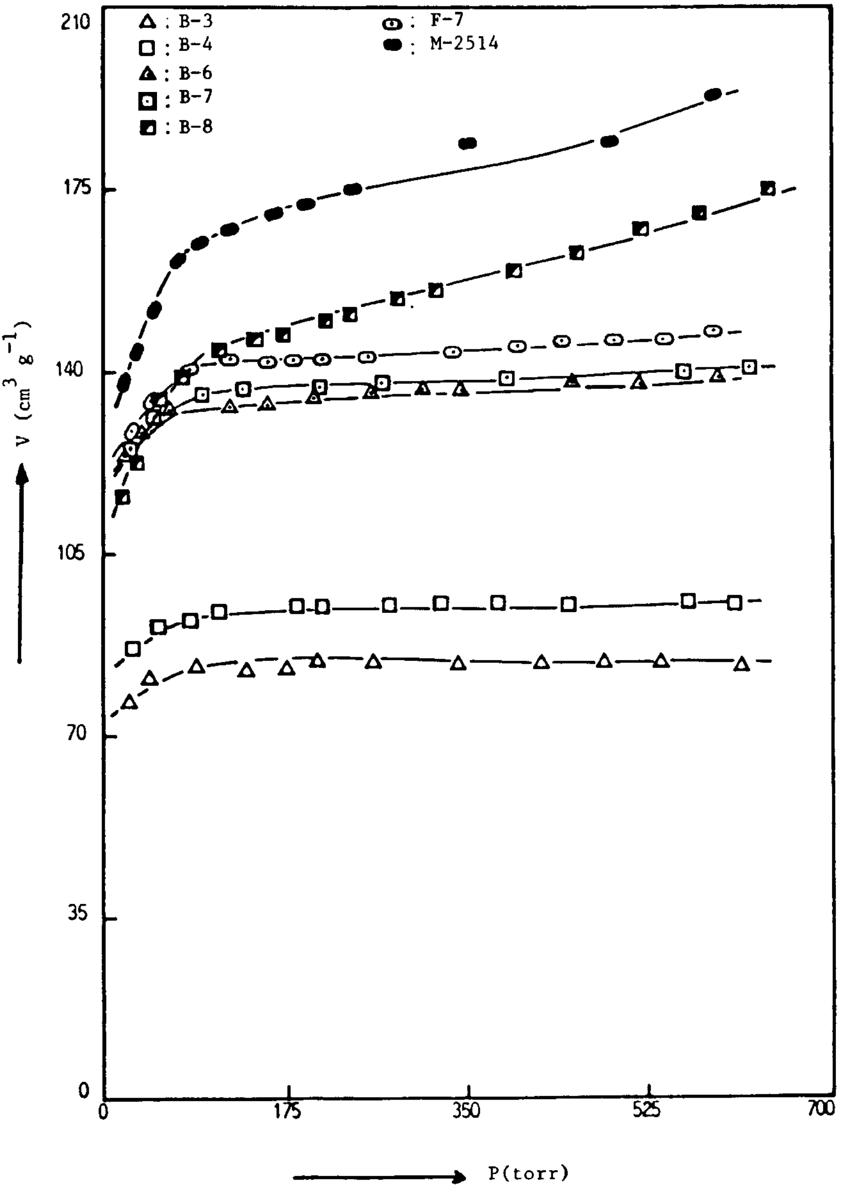


FIG. 4 The CO_2(195 K) gas adsorption isotherms related to the active carbons prepared under various conditions.

TABLE 1
N_2 and CO_2 Specific Surface Area ($m^2 \cdot g^{-1}$) Values Related to Carbons Prepared from Almond Shells at Various Temperatures

Sample	S_{N_2}(77 K)	S_{CO_2}(273 K)
B-1-573	85.9	101.9
B-1-673	263.3	253.3
B-1-773	288.2	301.9
B-1-873	281.8	309.1
B-1-973	304.9	332.4
B-1-1073	309.9	331.1
B-1-1173	319.7	335.0
B-1-1273	334.7	342.4

Furthermore, in the evaluation of the results of N_2(77 K) and CO_2(195 K) adsorptions in the Dubinin–Radushkevich (DR) (7) equation, the DR plots were obtained (Figs. 5 and 6), and the micropore volumes (V_0) related to samples were determined by using these plots (Table 3).

Table 4 contains the micropore volume ($V_{0.30}$) obtained by converting the quantity adsorbed at 0.30 relative pressure into the liquid adsorbate volume and by converting the differences between the quantities adsorbed at 0.95 and 0.30 relative pressures into the liquid adsorbate volumes, the mesopore volume ($V_{0.95} - V_{0.30}$) (8), the microporosity contribution

TABLE 2
N_2 and CO_2 Specific Surface Area ($m^2 \cdot g^{-1}$) Values Related to Various Active Carbons

Sample	S_{N_2}(77 K)	S_{CO_2}(195 K)
B-1	309.9	—
B-2	344.4	—
B-3	374.7	385.7
B-4	369.7	442.3
B-5	607.0	—
B-6	666.1	657.8
B-7	630.0	645.9
B-8	869.0	803.2
F-4	443.7	—
F-7	722.3	676.5
M-2184	974.4	—
M-2514	1160.3	887.5

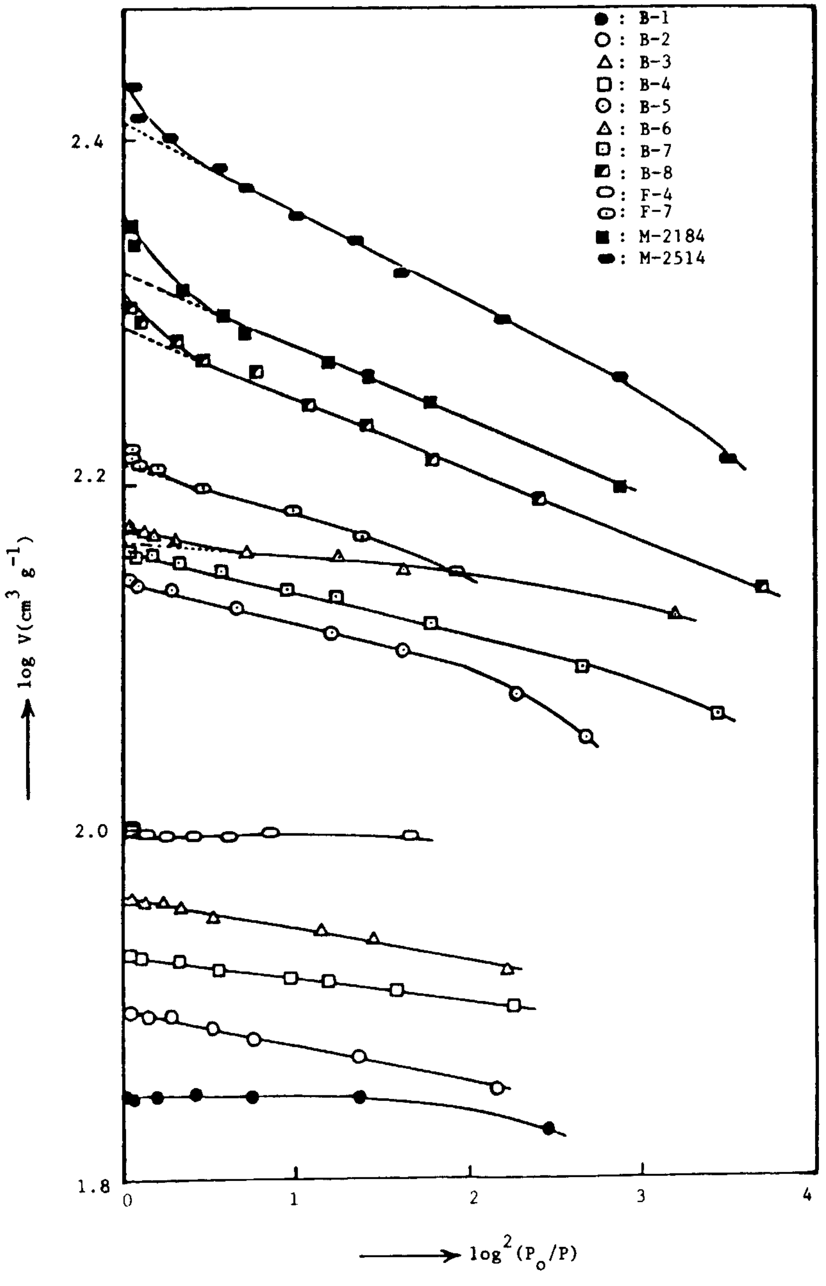


FIG. 5 DR plots of the N_2(77 K) gas adsorption results related to the various active carbons.

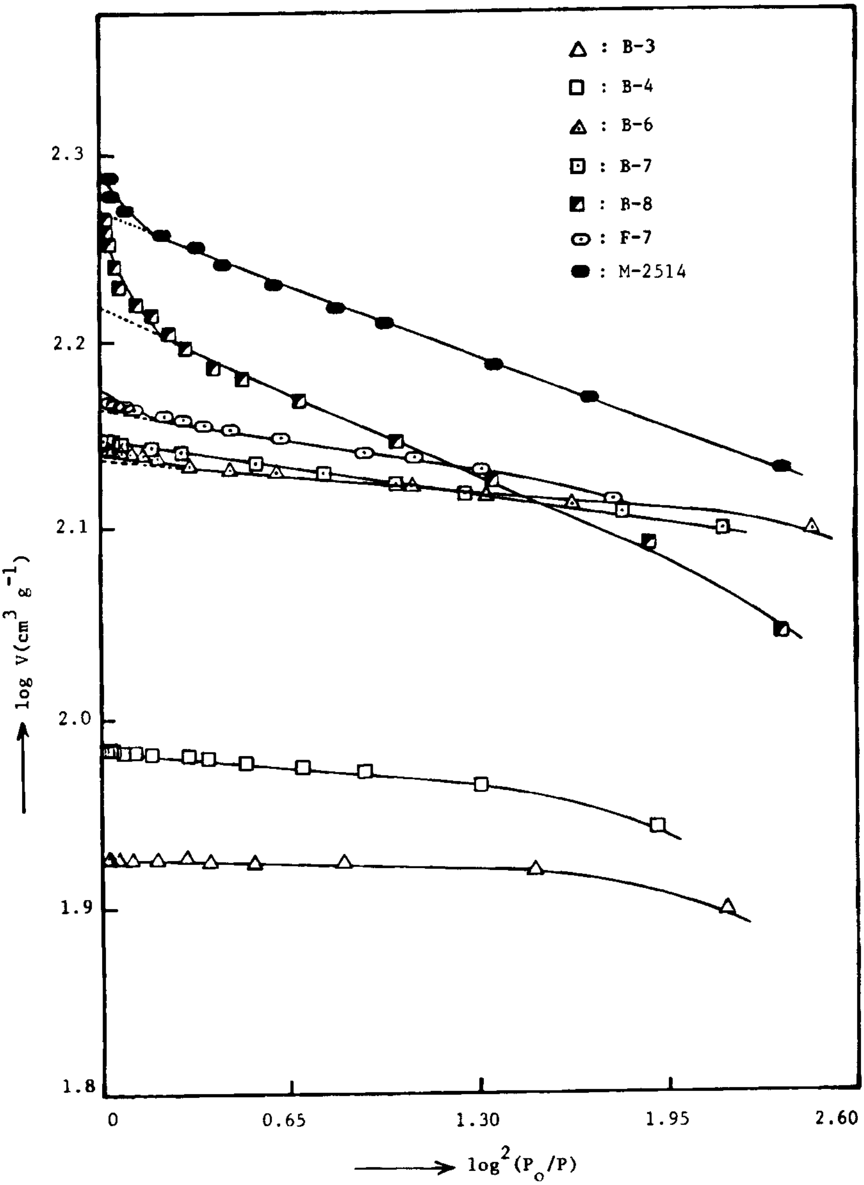


FIG. 6 DR plots of the CO_2(195 K) gas adsorption results related to the various active carbons.

TABLE 3
Micropore Volume ($cm^3 \cdot g^{-1}$) Values Obtained as a Result of the Evaluation in the DR Equation of the N_2(77 K) and CO_2(195 K) Adsorption Results on Various Active Carbons

Sample	$V_0(N_2)$	$V_0(CO_2)$
B-1	0.109	—
B-2	0.122	—
B-3	0.133	0.141
B-4	0.132	0.150
B-5	0.205	—
B-6	0.229	0.226
B-7	0.225	0.221
B-8	0.303	0.253
F-4	0.155	—
F-7	0.252	0.238
M-2184	0.321	—
M-2514	0.395	0.288

TABLE 4
Various Characteristic Pore Volumes ($cm^3 \cdot g^{-1}$) and Percent Micro- and Mesopore Volumes Obtained from Different Relative Pressures on N_2(77 K) Adsorption Isotherms Related to Various Active Carbons

Sample	$V_{0.30}$	$V_{0.95}$	$V_{0.95} - V_{0.30}$	V_μ (%)	V_m (%)
B-1-573	0.031	0.031	0.000	100.0	0.0
B-1-673	0.093	0.093	0.000	100.0	0.0
B-1	0.107	0.110	0.003	97.3	2.7
B-2	0.122	0.123	0.001	99.2	0.8
B-3	0.138	0.140	0.002	98.6	1.4
B-4	0.129	0.131	0.002	98.5	1.5
B-5	0.210	0.216	0.006	97.2	2.8
B-6	0.229	0.236	0.007	97.0	3.0
B-7	0.214	0.221	0.007	96.8	3.2
B-8	0.284	0.322	0.038	88.2	11.8
F-4	0.156	0.158	0.002	98.2	1.3
F-7	0.249	0.260	0.011	95.8	4.2
M-2184	0.294	0.352	0.058	83.5	16.5
M-2514	0.384	0.421	0.037	91.2	8.8

TABLE 5
Values of IN ($mg \cdot g^{-1}$) and MBA ($mg \cdot g^{-1}$) Related to Various Active Carbons at 298 K

Sample	IN	MBA
B-1-573	103.1	0.235
B-1-673	317.3	0.475
B-1-773	325.3	1.098
B-1-873	349.1	1.552
B-1-973	357.0	2.036
B-1-1073	372.9	2.112
B-1-1173	380.8	2.326
B-1-1273	396.7	3.252
B-2	349.1	3.485
B-3	412.3	4.732
B-4	404.8	5.368
B-5	555.3	2.194
B-6	674.3	3.000
B-7	602.3	4.423
B-8	801.2	5.311
F-4	476.0	4.751
F-7	658.5	5.217
M-2184	879.0	Not determined
M-2514	825.0	1.224

$[V_\mu\ \% = (V_{0.30}/V_{0.95}) \times 100]$ and the mesoporosity contribution $[V_m\ \% = (V_{0.95} - V_{0.30})/V_{0.95} \times 100]$ values.

Finally, Table 5 shows IN and MBA values of the samples.

DISCUSSION

Interpretations of the Effect of Working Temperature on the Quality of Active Carbon

In the preparation of high quality active carbons from starting materials of plant origin, one of the important experimental parameters is the working temperature. In this study, the lowest working temperature was 673 K, which can be seen in Fig. 1. It can also be seen in various plots of IN related to carbons (B-1-573–B-1-1273) prepared from almond shells at various temperatures. With the IN used in porosity test in industrial applications, a significant increase was observed in the porosity of carbons prepared up to a preparation temperature of 673 K. An unusual increase is also observed above this temperature in Fig. 7. The organic matter content of the starting samples which could be removed by heating was

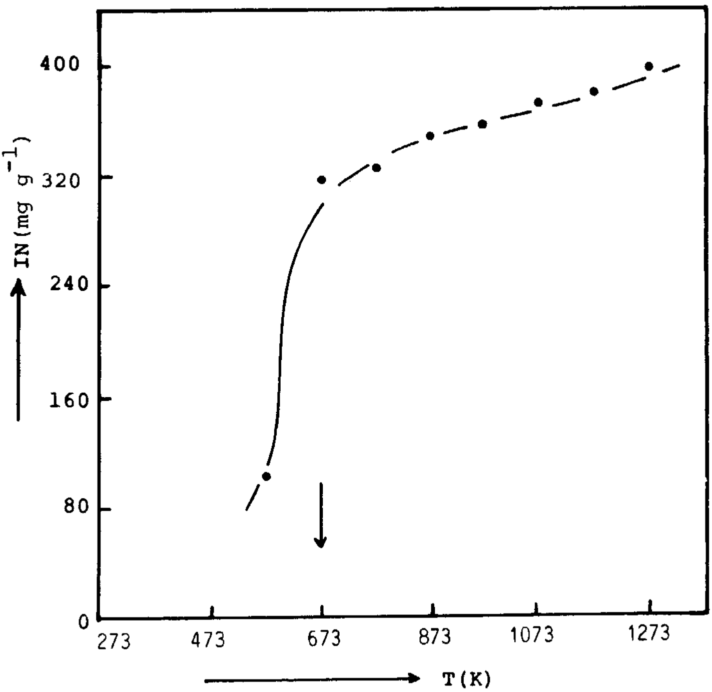


FIG. 7 The change of iodine numbers with carbonization temperature related to the carbons prepared at various temperatures.

not totally removed in the pores, and the quantity of removable organic compounds was increased and there was an unusual porosity increase at 673 K.

The same result was also observed qualitatively in the height of the plateaus of N_2 adsorption isotherms relating with Samples B-1-573–B-1-1273 in Fig. 2. The plateaus of the N_2 adsorption isotherm belonging to Sample B-1-573 went to a lower value whereas the N_2 adsorption isotherms related to the B-1-673–B-1-1273 carbons went at higher values which were close to each other.

Evaluation of Gas Adsorption Results

Discussions about the Classification of the Isotherms of N_2 Adsorption

Since the active carbons are essentially microporous, their adsorption isotherms are similar to Type I in the BDDT classification which is peculiar

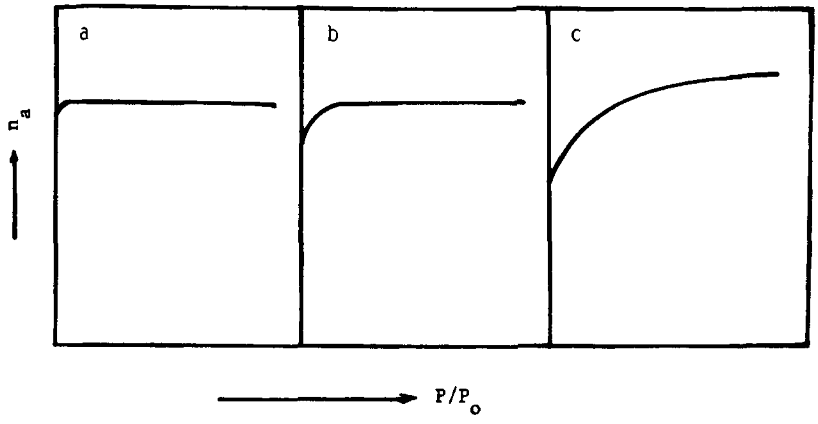


FIG. 8 Different types of isotherms of microporous carbons (8).

to microporous adsorbents. In other words, they had adsorption isotherms of the Langmuir type (5, 6). The adsorption isotherms in Figs. 2, 3, and 4 follow Type I isotherms. The shapes of the isotherms were a function of pore size distribution. On the other hand, it has been suggested that N_2(77 K) adsorption isotherms for microprous carbons are either Type a, Type b, or Type c, which depend on the pore size distribution of the active carbon (8) (Fig. 8). According to this classification, Type a corresponds to active carbons with quite narrow micropores. This type of isotherm gives a plateau parallel to the abscissa within a wide pressure range and has a high adsorption value with a sharp bend. Type b corresponds to active carbons with relatively wider micropores than Type a. This type of isotherm also gives a plateau parallel to the abscissa with a wide bend within the low pressure range. Type c includes mesopores in addition to micropores. Isotherms of this type increase slowly under higher pressure by having a wide bend within a small pressure range.

If we evaluate the isotherms in Figs. 3 and 4 according to the Type a, Type b, and Type c isotherms, we see that the isotherms related to B-1-573–B-1-1273, B-2, B-3, B-4, and F-4 are of Type a, that the isotherms related to B-5, B-6, B-7, and F-7 are of Type b, and that isotherms related to B-8, M-2184, and M-2514 are of Type c.

Discussions about the Results of the Specific Surface Area and the Micropore Volume Obtained from N_2 and CO_2 Gas Adsorption Results

The effect of activation conditions on S_{N_2} is presented in Table 2. A significant increase related to the experimental condition in the specific surface between Samples B-1 and B-2 and between Samples B-3 and B-4 was not observed. However, a specific area increase of about twofold was observed because of a developed micropore size distribution and mesoporosity when these samples were compared with B-5, B-6, B-7, and F-7. When the activation period was increased to 4 hours, the increase with B-8 became two and one-half fold. A similar relationship was also seen in the values of S_{CO_2} (Table 2).

Therefore, the differences coming from the pore structure depend on the preparation conditions as observed when the S_{N_2} (or V_0) values were determined at 77 K and the S_{CO_2} (or V_0) values were determined at 195 K in Tables 1, 2, and 3 were compared. It has been suggested that there is an S_{N_2} (or V_0) $<$ S_{CO_2} (or V_0) relation in carbons and active carbons having quite narrow micropores, that there is an S_{N_2} (or V_0) $\approx$ S_{CO_2} (or V_0) relation in molecular sieve carbons and in active carbons having relatively narrow and homogeneous microporosity, and that there is an S_{N_2} (or V_0) $>$ S_{CO_2} (or V_0) relation in active carbons having wider and quite heterogeneous microporosity (9). On this basis, it is possible to relate S_{N_2} (or V_0) and S_{CO_2} (or V_0) for the samples in this study (Tables 1, 2, and 3):

B-1-573–B-1-1273: $S_{N_2} < S_{CO_2}$
B-3: S_{N_2} (or V_0) $<$ S_{CO_2} (or V_0)
B-4: S_{N_2} (or V_0) $<$ S_{CO_2} (or V_0)
B-6: S_{N_2} (or V_0) $\approx$ S_{CO_2} (or V_0)
B-7: S_{N_2} (or V_0) $\approx$ S_{CO_2} (or V_0)
F-7: S_{N_2} (or V_0) $\approx$ S_{CO_2} (or V_0)
B-8: S_{N_2} (or V_0) $>$ S_{CO_2} (or V_0)
M-2514: S_{N_2} (or V_0) $>$ S_{CO_2} (or V_0)

Although the critical molecular dimensions of N_2 and CO_2 (0.30 and 0.28 nm, respectively) (9) are close, the differences between the values of S_{N_2} (or V_0) and S_{CO_2} (or V_0) come from the intrapore diffusion barrier. That is, the penetration of the N_2 molecules into the quite narrow micropores are inhibited kinetically at the time of measurement since the adsorption measurements obtained with nitrogen gas are completed at a lower temperature of 77 K. Since CO_2 adsorption measurements are carried out at a relatively higher temperature (195 K), the CO_2 molecules can diffuse into the narrower micropores where the nitrogen molecules cannot diffuse because of the increase in the diffusion rate of the gas molecules and the absence of a diffusion barrier. In other words, an increase in the adsorption temperature leads to an increase in the adsorbed amount and causes an increase in the diffusion rate of the molecules which diffuse into the narrow micropores.

When the values of S_{N_2} and S_{CO_2} related to B-1-573–B-1-1273 were compared, it was seen that these carbons belong to the class of the low dimensional microporous carbons since $S_{N_2} < S_{CO_2}$. Consequently, the N_2 adsorption method gives low adsorption data. In such carbons, CO_2 adsorption treatment gives more meaningful results.

Interpretations Relating to Evaluation of the Industrial Testing Methods

Activated carbons are commonly used to clear aqueous solutions. The choice of adsorbent is made based on the proper model materials carrying the given pollution groups. One of the most used indicators is methylene blue (MB) which has a diameter of about 1.5 nm, is middle sized, and is an organic molecule (10).

Paprowicz argued that the most important factors affecting methylene blue adsorption (MBA) are the pore structure of carbons, the concentration, the raw material, the method and level of activation, and the chemical character of the surface. He stated that although the active carbons activated by chemical methods had many micro- and mesopores, their MBAs were smaller. He stated that this came from either the difference of the pore shapes or the chemical interaction of the adsorbed particles with the carbon surface. He also stated that his experimental findings decreased the chemical activation of MBA (10).

From our evaluation of the MBA values of the various activated carbons in Table 5, we can say from the adsorption values of B-2 and B-5, of B-3 and B-6, and of B-4 and B-7 that MBA depends on the chemical nature of the surface and that the chemical activation decreases the MBA, which is a cationic dyestuff in an aqueous medium.

It was observed that this value increased when the physical activation period was lengthened to 4 hours (B-8). M-2184 adsorbs all the MB within the limits of a given test whereas M-2514, having a greater S_{N_2} value, has a quite small MBA value when compared with the other samples. S_{N_2} values of carbon from hazelnut shells in the same medium (air) but at different temperatures and the MBA values (Table 4) of these carbons show a smooth change. However, there were not any smooth changes between the S_{N_2} values (Table 2) and the MBA values (Table 5) of carbons prepared under different conditions. The MBA values are a function of the developed micropore size and the mesoporosity as stated by Paprowicz (10) and Avom et al. (2). That is, B-2, B-3, B-4, F-4, B-5, B-6, B-7, F-7, and M-2514 have V_m at a negligible level, as can be seen in Table 4, besides a large surface area. That is why methylene blue does not flow into narrow micropores ($\geq$1.5 nm) in as short a time as the 45 minutes used for the MB test. In other words, methylene blue shows lower adsorption values because of the diffusion barrier. When B-7 and B-8 are compared, the B-8 obtained increased by raising the activation period to 4 hours since the V_m value increased because of mesoporosity besides the development of micropores, and the diffusion barrier gradually vanished. In the example of M-2184, this barrier vanishes since this sample has a large V_m value (Table 4) due to a developed micropore and mesopore size, and it adsorbs all the MB molecules in a short time.

As a result, we can say from these experimental data that the MB test can be used to characterize activated carbons obtained as a result of long-term physical activation used to increase the microporosity ratio and to increase the negative acidic groups (negatively charged) on the surface.

Iodine adsorption is independent of oxide complexes on the surface, and van der Waals forces determine whether adsorption is carried out from an aqueous solution containing potassium iodide (11).

When we evaluate the IN values (Table 5) in our work, it is seen that they do not depend on the chemical character of the surface if B-2 and B-5, B-3 and B-6, B-4 and B-7, and F-4 and F-7 samples are compared among themselves. If B-4, B-7, and B-8 are compared, the shapes of the different sized pore structures depend on the preparation conditions although the starting raw material is the same. The IN values increase if the activation period is increased to 4 hours.

Since the iodine molecules are quite small and spherical, and enter all the pores in a short time, this could be used as a porosity test. Furthermore, when the S_{N_2} values in Tables 1 and 2 and the IN values in Table 5 are compared, there is a parallelism between these values although there is not any theoretical relation between them.

General Conclusions and Suggestions

The most important factors in the preparation of high quality active carbons are the starting materials and the conditions during preparation. 1) All the experimental results we obtained in this study prove that active carbons prepared from hazelnut shells are better than those prepared from almond shells. Since the amount of the organic components reacting with the reagents (H_2SO_4 and CO_2) either in the liquid phase or in the gas phase was greater than those of almond shells, a more porous structure resulted. 2) If we compare the preparation conditions, two-stage physical activation (the activation with carbon dioxide after carbonization in a nitrogen atmosphere) gave better results for whatever time one uses hazelnut shells or almond shells, and whether these are exposed to chemical activation or not. The active carbon obtained as a result of carbonization and activation in a carbon dioxide atmosphere gave some results close to those in the two-stage method. The active carbons obtained as a result of the carbonization and activation in a nitrogen media have a lower adsorption capacity relative to the active carbons mentioned above. Since nitrogen has a pore-penetrator function, carbon dioxide deepens and widens pores, especially at high temperatures. That is, it increases the ratio of mesopore volume to micropore volume. Because carbon dioxide gas reacts with elementary graphite microcrystals in the carbon structure and it removes carbon atoms burning at the pore sides during activation, it leaves an active carbon having a more defective structure, i.e., contains different types of pores. A narrow dimensional microporous active carbon was obtained since the nitrogen gas did not react with the carbonaceous components during activation.

Carbonization and activation processes with carbon dioxide have some advantages in the single-stage method because they can be applied easily.

In this study, sulfuric acid was used as an activator from the liquid phase. It may play a role in opening the pores besides its dehydration and oxidation effects. It may also prepare a path by which the activator molecules penetrate into the solid through physical activation.

Higher quality active carbons can be prepared by long-term (4 hours) physical activation with carbon dioxide gas after activation with sulfuric acid.

ACKNOWLEDGMENTS

The authors are indebted to Dr. F. Rodriguez-Reinoso and Dr. J. de D. Lopez-Gonzales for their contributions to this article. The financial support by the Dicle University Research Foundation, Grant DUAP 88-FF-92, is gratefully acknowledged.

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Received by editor June 1, 1992