

# Determination of the Micropore Structures of Activated Carbons by Adsorption of Various Dyestuffs from Aqueous Solution

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In this study, some activated carbons prepared from sour cherry pits under various conditions were investigated. For comparison purposes, the commercial activated carbons Merck-2514 and Merck-2184 were used. The nitrogen adsorption isotherms at 77 K were used as reference for comparison, while p-nitrophenol, methylene blue, orange-II and victoria blue adsorptions were determined from aqueous solution at 298 K. It was clear from the specific surface area values obtained that the best activated carbon was obtained by activation for 4 hours following the chemical activation. Its adsorption properties are closer to the levels of the Merck commercial carbons. It was concluded that the characterization of microporous structure, and the testing of the removal of organic impurities from aqueous solution for active carbons having high adsorption ability from the gas phase, can generally be carried out by adsorption of organic solutes whose molecular sizes are smaller than the micropore size (1.5 nm) of the adsorbent.

**Key Words:** Activated carbon, analysis of pore structure, dyestuff adsorption, N<sub>2</sub>adsorption.

## Introduction

Activated carbons have long been used as adsorbents in industry due to their superior adsorption capacities. Their properties depend on the pore structure, which in turn depends on the preparation conditions as well as the chemical nature of the carbon surface.

Studies on the production of activated carbons, which are both high in quality and economical for industrial studies, are being carried out. The production of high quality activated carbons and the characterization of their pore structures are very important. In order to characterize the pore structures of activated carbons, N<sub>2</sub> gas adsorptions at 77 K and the adsorptions from the liquid phase at 298 K of p-nitrophenol (PNP), methylene blue (MB), orange-II (O-II) and victoria blue (VB) having minimum molecular sizes (not exceeding 1.5 nm) were used as comparison criteria<sup>1,2</sup>.

## Experimental

In this study, the sour cherry pits used to produce the activated carbon were collected from the Diyarbakır region in Turkey. These pits were smashed and particles 2mm in size were obtained. From the graph of weight loss versus temperature, the minimum carbonization temperature, was determined to be 1073 K. Activated carbons were prepared under the following conditions at 1073 K with a heating rate of 5 K/min.

**a-** The particles were carbonized for 1 hour in an ash furnace (C1)

**b-** The particles were carbonized and/or physically activated for 1 hour with CO<sub>2</sub> gas (C2).

**c-** The particles were activated chemically for 6 hours at ratio of 1:1 with a solution of 10% H<sub>2</sub>SO<sub>4</sub>. They were washed several times with distilled water until no acidity was left. Later, they were carbonized and/or physically activated for 1 hour (C3) and for 4 hours (C4) with CO<sub>2</sub> gas.

The activated carbons obtained were ground to 80 mesh. N<sub>2</sub> gas adsorptions were determined at 77 K (Micromeritics, Autosorp -6). The maximum wavelengths of the organic solutes from the aqueous solution were determined to be 318 nm for PNP, 662 nm for MB, 488 nm for O-II and 617 nm for VB by visible spectrophotometer (Shimadzu UV-160). The absorbance values of the solutions were measured at the maximum wavelengths corresponding to the various solute concentrations, and thus working curves were obtained. Then, the contact time with the solution was fixed so that the solid could reach the adsorption equilibrium. In order to accomplish this, 100mL and 10<sup>-2</sup>M solutions were shaken with 0.1g of activated carbon in an aqueous shaker adjusted to a constant temperature of 298 K. In this operation, the contact times were determined to be 31 hours for PNP, 49 hours for MB, 67 hours for O-II and 68 hours for VB.

After the determination of the optimum working conditions, the starting solutions at different concentrations prepared from the 10<sup>-2</sup>M stock solutions were contacted with 0.1g of activated carbon samples dried at 383 K for 16 hours in an aqueous shaker adjusted to 298K for the contact times given above. At the end of the equilibrium contact times, their absorbances were determined at maximum working wavelengths by taking a sufficient amount from the supernatant of solution. Equilibrium concentrations (C) were determined from the working curves by using these absorbances and the adsorbed concentrations (C<sub>a</sub>) were calculated from these values.

## Results

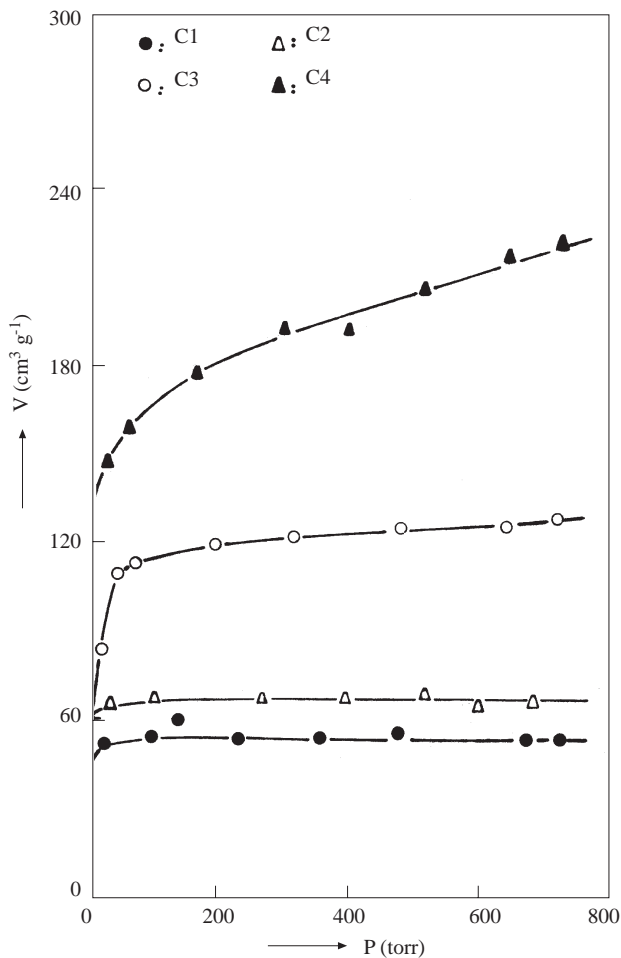
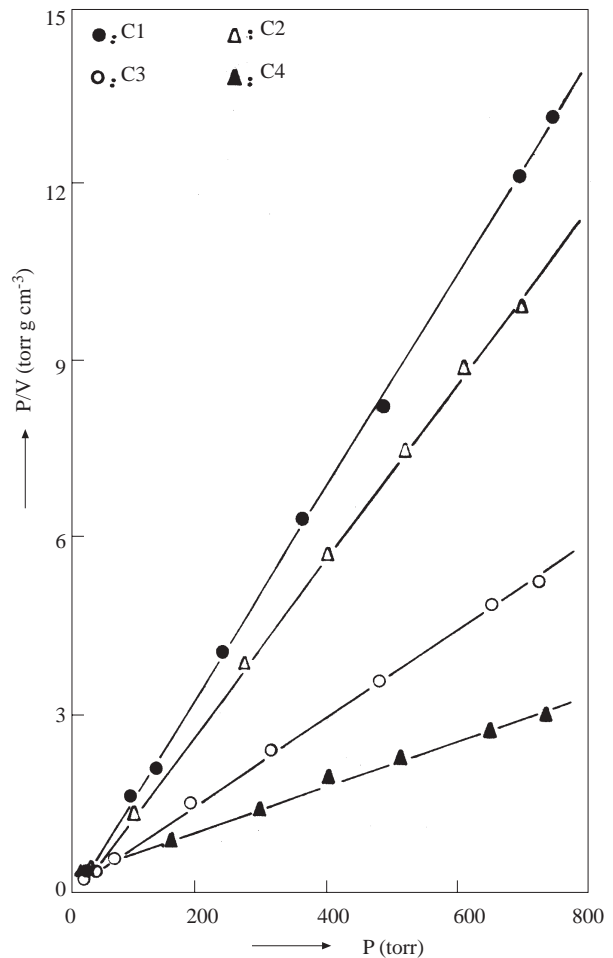
Figure 1 and Figure 2 show the N<sub>2</sub> (77 K) gas adsorption isotherms and Langmuir linear isotherms of the activated carbons prepared from sour cherry pits under various conditions. The monolayer capacities (V<sub>m</sub>) were determined from the inverses of the slopes of the Langmuir linear adsorption isotherms. The specific surface areas S<sub>N<sub>2</sub></sub> (Table 1) were calculated from the following equation:

$$S_{N_2}(m^2 g^{-1}) = \frac{V_m(STPcm^3 g^{-1}) \cdot \sigma \cdot 10^{-20}(m^2) \cdot N_A(mol^{-1})}{22415(STPcm^3 mol^{-1})} \quad (1)$$

where  $\sigma$  is the cross-sectional area occupied by a molecule of adsorbate (this is 0.162 nm<sup>2</sup> for nitrogen at 77 K<sup>3</sup>) and N<sub>A</sub> is the Avogadro's constant.

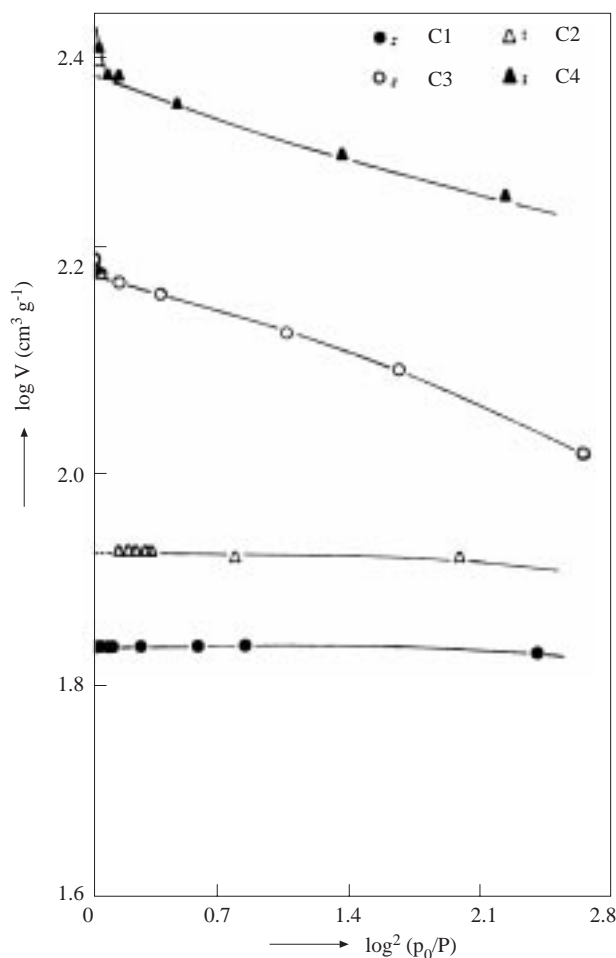
**Table 1.** Surface areas ( $\text{m}^2 \text{g}^{-1}$ ) and accessible surface area ratios (%) according to the different adsorbates related to the various activated carbons.

Sample	$S_{N_2}$	$S_{PNP}$	$S_{MB}$	$S_{O-II}$	$S_{VB}$	$\frac{S_{N_2}-S_{PNP}}{S_{N_2}}$	$\frac{S_{N_2}-S_{MB}}{S_{N_2}}$	$\frac{S_{N_2}-S_{O-II}}{S_{N_2}}$	$\frac{S_{N_2}-S_{VB}}{S_{N_2}}$	$\frac{S_{MB}}{S_{PNP}}$	$\frac{S_{O-II}}{S_{PNP}}$	$\frac{S_{VB}}{S_{PNP}}$
C-1	234.7	121.9	12.4	5.9	2.8	48.1	94.7	97.5	98.8	10.2	4.8	2.3
C-2	289.1	167.3	17.90	8.5	5.8	42.1	93.8	97.1	98.0	10.7	5.1	3.5
C-3	497.3	406.5	101.9	48.3	16.6	18.3	79.5	90.3	96.7	25.1	11.9	4.1
C-4	695.2	639.3	173.6	87.7	39.9	8.0	75.0	87.4	94.3	27.2	13.7	6.2
M-2184 <sup>(a)</sup>	974.4	952.6	382.1	165.1	85.6	2.2	82.0	91.3	94.5	18.9	9.2	5.8
M-2514 <sup>(a)</sup>	1160.3	1103.8	208.9	101.5	63.5	4.9	60.8	83.1	91.5	40.1	17.3	9.0

<sup>(a)</sup> From Ref. 5

**Figure 1.** The nitrogen (77 K) gas adsorption isotherms related to the active carbons.

**Figure 2.** Langmuir linear adsorption isotherms ( $\text{N}_2$  at 77 K) related to the activated carbons.

Furthermore, in the evaluation of the results of  $\text{N}_2$  (77 K) adsorption by the Dubinin-Radushkevich (DR)<sup>3,4</sup> equation, the DR-plots were obtained (Fig. 3), and the micropore volumes ( $V_o$ ) of the samples were determined by using these plots (Table 2). In addition, Table 2 contains the micropore volume ( $V_{0.30}$ ) and the mesopore volume ( $V_{0.95}-V_{0.30}$ )<sup>1,5</sup>. The micropore volume was obtained by converting the quantity adsorbed at a relative pressure of 0.30 into the liquid adsorbate volume. The mesopore volume ( $V_{0.95}-V_{0.30}$ )<sup>1,5</sup> was found by converting the differences between the quantities adsorbed at relative pressures of 0.95 and 0.30 respectively into the liquid adsorbate volumes. The microporosity contribution [ $V_\mu\% = (V_{0.30} \times 100 / V_{0.95})$ ]

and the mesoporosity contribution [ $V_m\% = (V_{0.95}-V_{0.30}) \times 100/V_{0.95}$ ] values were determined and are shown in Table 2.



**Figure 3.** DR plots of the  $N_2$  (77 K) gas adsorption results related to the active carbons.

**Table 2.** Various characteristic pore volumes ( $\text{cm}^3 \text{g}^{-1}$ ) and percent micro- and mesopore volumes obtained from different relative pressures on  $N_2$  (77 K) adsorption isotherms related to various activated carbons.

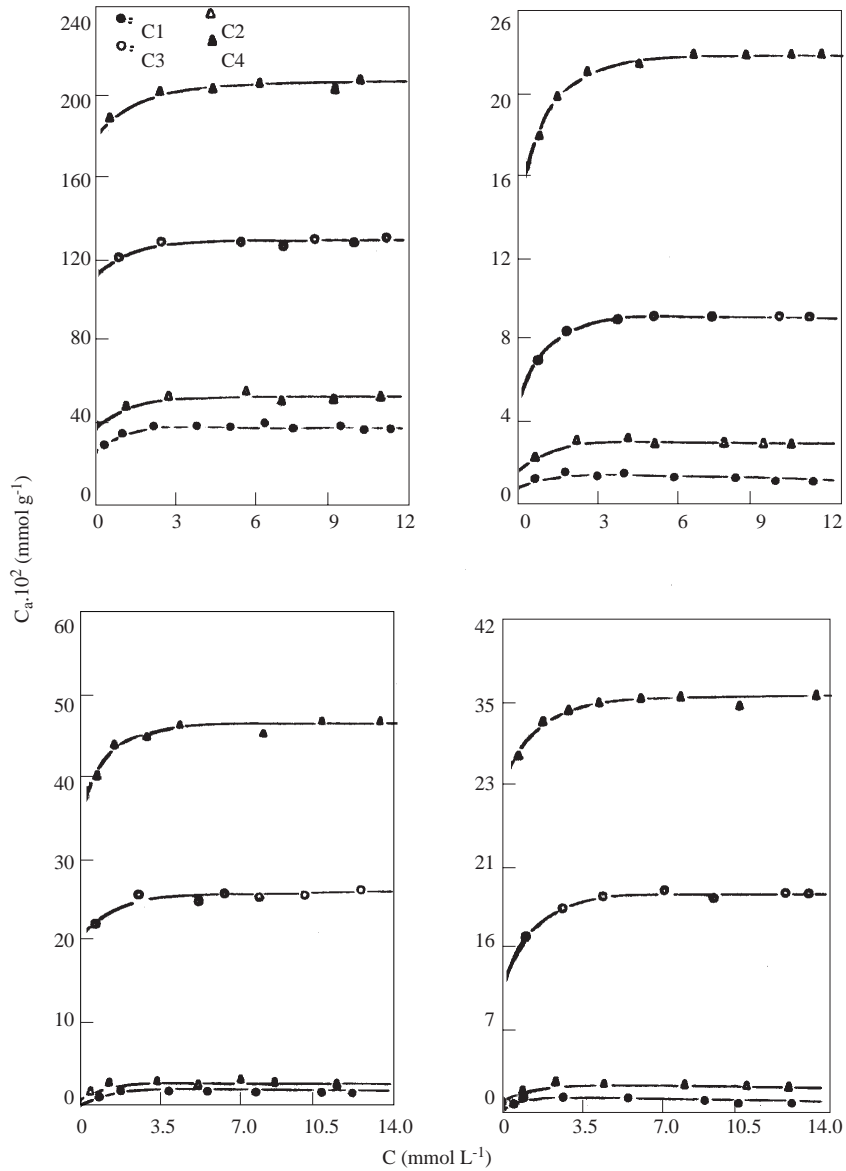
Sample	$V_0$	$V_{0.30}$	$V_{0.95}$	$V_{0.95}-V_{0.30}$	$V_\mu$ (%)	$V_m$
C-1	0.085	0.082	0.082	0.000	100.0	0.0
C-2	0.104	0.102	0.106	0.004	96.2	3.8
C-3	0.193	0.187	0.201	0.014	93.0	7.0
C-4	0.310	0.291	0.345	0.054	84.3	15.7
M-2184 <sup>(a)</sup>	0.321	0.294	0.352	0.058	83.5	16.5
M-2514 <sup>(a)</sup>	0.395	0.384	0.421	0.037	91.2	8.8

<sup>(a)</sup> From Ref. 5

Figure 4 and Figure 5 show respectively the adsorption isotherms and Langmuir linear isotherms of the dyestuffs, from aqueous solutions at 298 K on all of the activated carbons. The monolayer capacities,  $C_m$ , were found from the reciprocal value of the slopes of the Langmuir linear adsorption isotherms (Fig. 5).

The specific surface area related to the dyestuffs ( $S_D$ ) (Table 1) was calculated from the following equation<sup>6</sup>:

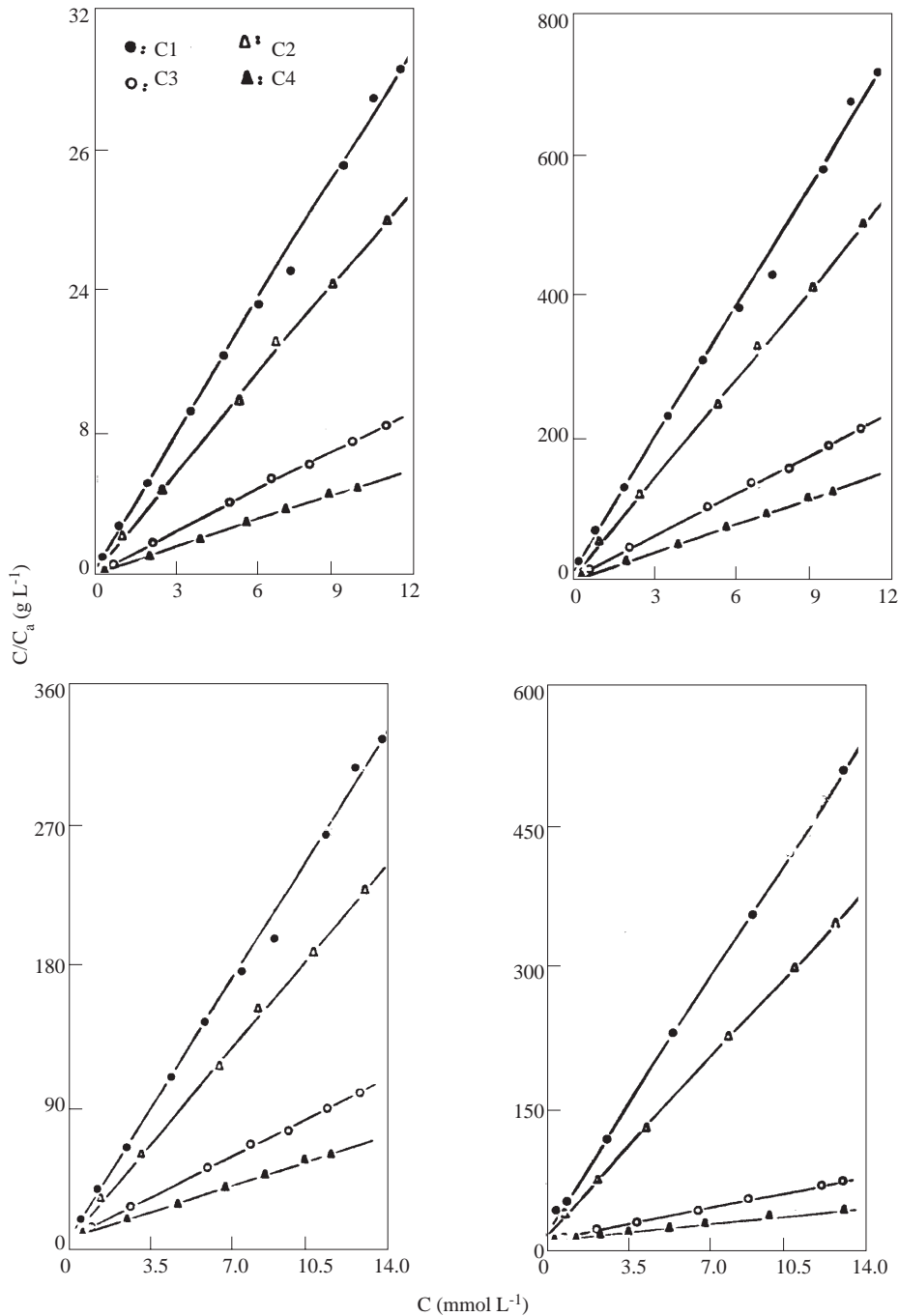
$$S_D(m^2g^{-1}) = \frac{C_m(mol \cdot g^{-1}) \cdot \sigma \cdot 10^{-20}(m^2) \cdot N_A(mol^{-1})}{n} \quad (2)$$



**Figure 4.** Adsorption isotherms (298 K) of the dyestuffs from the aqueous solution related to the activated carbons. a: PNP; b: VB; c: BM; d: O-II

The value of  $\sigma$  is  $0.525 \text{ nm}^2$  for PNP,  $1.200 \text{ nm}^2$  for MB,  $1.200 \text{ nm}^2$  for O-II and  $2.700 \text{ nm}^2$  for VB.  $n$  shows the covering factor, which reflects the average number of dye ions in a micelle, or the aggregation number since the dyestuffs were adsorbed from aqueous solution in the form of ionic micelle. This value was 2 for MB, 3 for O-II and 9 for VB<sup>6-9</sup>. In addition, the surface area portions  $S_{N_2} - S_o/S_{N_2}$  that the

solute from solution cannot reach relative to nitrogen and the portions ( $S_D / S_{PNP}$ ) of the other solutes for reaching the surface relative to PNP, which was considered an ideal adsorbate in adsorption from the liquid phase<sup>6</sup>, are shown in Table 1.



**Figure 5.** Langmuir linear adsorption isotherms (298 K) of dyestuffs from the aqueous solution related to the activated carbons. a: PNP; b: VB; c: MB; d: O-II

## Discussion

Since the activated carbons are basically microporous, the adsorption isotherms are similar to Type 1 in the Brunauer-Deming-Deming-Teller (B.D.D.T.) classification, which is specific to microporous adsorbents<sup>1</sup>. In other words, they give adsorption isotherms of the Langmuir type<sup>1,5,8,9</sup>. The nitrogen adsorption isotherms in Figure 1 resemble Type 1. The form of the isotherm is a function of the distribution of the pore size.

On the other hand, it is suggested that the nitrogen adsorption isotherms are similar to Type 1a, Type 1b and Type 1c, which are the subgroups of the Type 1 isotherm, depending on the pore-size distribution of the activated carbon<sup>1</sup>. Type 1a corresponds to activated carbons having quite narrow micropores, Type 1b corresponds to activated carbons having wider micropores than Type 1a, and Type 1c corresponds to activated carbons containing mesopores in addition to the developed microporosity. If we evaluate the isotherm in Fig. 1, it can be seen that the isotherm of C1 is Type 1a, the isotherms of C2 resemble Type 1b and the isotherms of C3, C4, M-2184<sup>5</sup> and M-2514<sup>5</sup> are similar to Type 1c. The micro- and mesopore contributions given in Table 2 confirm this.

The adsorption isotherms from the liquid phase seen in Figure 1 are also similar to L-Type in the Giles classification<sup>10</sup>. (B.D.D.T).

It can be seen in Table 1 that there was a large difference between the  $S_{N_2}$  and  $S_{PNP}$  values. Sample C1 contained quite narrow micropores, and the size of the PNP molecule was greater than that of nitrogen. When the sample was obtained by elongating the physical activation time to 4 hours the  $S_{N_2}$  and  $S_{PNP}$  values were nearly the same. This was not a surprising result. Since the minimum molecular size of nitrogen is 0.30nm<sup>10</sup>, and that of PNP is 0.46nm<sup>9</sup>, and these values are close to each other, solutes penetrate into the pores in the same manner. According to this investigation of the penetration of solutes in the pores of activated carbons, C2 developed more microporosity, while C3 and C4, particularly C4, contained mesopores in addition to the developed microporosity.

The values  $S_{N_2} - S_o/S_{N_2}$  and  $S_D/S_{PNP}$  in Table 1 reflect the micropore analyses. This ratio is considerably lower in samples C3 and C4. This shows a relatively narrow microporosity. When the physical activation time is prolonged to 4 hours, this ratio decreased considerably in sample C4, and the commercial activated carbons M-2514 and M-2184 gave equal values. This means that mesoporosity exists in addition to the developed microporosity.

By arranging the surface area values (Table 1) obtained from solutes of various sizes, it can be seen that the surface area values obtained as a result of the adsorption of the solutes on all of the worked activated carbons decreased in the following order:  $S_{PNP} > S_{MB} > S_{O-II} > S_{VB}$ , since the molecular sizes of the solutes increase in the order  $PNP < MB \leq O-II < VB$ <sup>6,7</sup>. Diffusion into the pore becomes more difficult. Furthermore, the penetration of the dyestuff molecules becomes more difficult because of the aggregation since the organic dyestuffs are adsorbed in the form of ionic micelles from the aqueous solution and the number of the dyestuff ions (n) (aggregation number) increases as follows:  $MB (n = 2) < O-II (n = 3) < VM (n = 9)$ <sup>6,7</sup>. Consequently, the surface areas determined by the adsorption from the solution changes as follows:  $MB < O-II < VB$ .

The surface area values that the solutes of various sizes can not reach relative to nitrogen increase for the same activated carbon as follows:  $S_{N_2} - S_{PNP}/S_{N_2} < S_{N_2} - S_{MB}/S_{N_2} < S_{N_2} - S_{O-II}/S_{N_2} < S_{N_2} - S_{VB}/S_{N_2}$ . This increase originates from the pore structure, and varies depending on different preparation conditions.

In this study, the micropore analysis of the present activated carbons, or the molecular sieve effect, was

determined from the  $S_o/S_{N_2}$  values in Table 1 on the basis of PNP, which is considered an ideal adsorbate. When the MB is taken as a solute sample, the ratio into which the MB and PNP molecules can penetrate for C1, C2 and C3 samples is small. This indicates a quite narrow microporosity. In the activated carbon obtained by prolonging the physical activation time to 4 hours, the ratio for (C4) becomes greater. This is an indication of a developed microporosity and mesoporosity. The same relationship is observed in the values  $S_{O-II}/S_{PNP}$  and  $S_{VB}/S_{PNP}$ . This ratio decreases for some of the activated carbons (e.g. C-4) as follows:  $S_{MB}/S_{PNP} > S_{O-II}/S_{PNP} > S_{VB}/S_{PNP}$ . This decrease has been evaluated as a function of the variation of pore structure depending on different preparation conditions, as can be seen in Table 1.

It is clear that, in the characterization of the activated carbons that have high adsorption capacities from the gas phase, organic solutes with molecular sizes not exceeding the maximum micropore size (1.5nm) gave quite useful results for the understanding of the micropore structure.

In the preparation of a good quality activated carbon, the most important factors besides the starting raw material are the preparation conditions. In view of the preparation conditions, two-step physical activation/carbonization after chemical activation with sulfuric acid usually gives a better result. Since the physical activator function of carbon dioxide gas is hole-drilling in a pore, especially at higher temperatures carbon dioxide works as a pore-driller and expander, which means it increases the ratio of mesopore to micropore volumes. Since carbon dioxide reacts with elementary graphite microcrystallites quickly, the carbon atoms at the sides of the pore are removed as a result of the burning during the activation, yielding an activated carbon that has a more defective structure and includes different types of pores. The process of carbonization and/or activation with  $CO_2$  in a single-step has some advantages since it is applied easily and practically. The sulfuric acid used as an activator in this study acts as an opener of the "doors" of pores, in addition to the effects of dehydration and oxidation. Furthermore, it leads the activator molecules towards the solid.

Consequently, it can be said that every activated carbon has a memory originating from its production, since the adsorbent acquires a different pore structure from all kinds of physical and chemical activation, and this structure is reflected in the adsorption properties. Also, the characterization of pore structure of activated carbons will be useful in making dyestuff adsorptions with different molecular sizes from solutions other than nitrogen gas adsorptions (77K).

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