

# Textural properties of Activated Carbons from Wild Cherry Stones as Determined by Nitrogen and Carbon Dioxide Adsorption

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## Abstract

Activated carbons were obtained by activating wild cherry stones with different concentrations of phosphoric acid or zinc chloride at different temperatures. The adsorption of N<sub>2</sub> at 77 K and of CO<sub>2</sub> at 273 K was followed and the data were analyzed by considering different adsorption models. The activated carbons obtained measured high surface area with the most of the surface in all samples located in micropores. Fair agreement was found between the nitrogen surface areas calculated from the BET-, t-,  $\alpha$ - and DR- methods, although the first three are based on surface coverage whereas the latter is based on micropore filling. The carbon dioxide surface areas calculated by the DA equation were smaller than the comparable nitrogen areas. This was ascribed to domination of surface coverage mechanism, the absence of activated diffusion process. Based on this explanation the CO<sub>2</sub>-surface areas as calculated by DA equation should be taken with great reservation.

**Keywords:** Activated carbons, Cherry stones, Textural properties

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## 1. Introduction

Activated carbons occupy a prominent position among current adsorbents as versatile and universal materials. They are used in many economic sectors and concern many industries as diverse as food processing, pharmaceuticals, petroleum, mining, nuclear, automobile and vacuum manufacturing [1, 2]. Activated carbons are also popular adsorbents for use in gas and water purification [3, 4]. They derive their adsorptive properties from the extensive internal pore structure which presents a high surface area available for the adsorption of molecular species [5, 6]. The surface of activated carbons is considered heterogeneous from the point of view of both porosity and surface chemistry. The pore structure heterogeneity is the result of the presence of a wide range of pores that extends in the size from a few to a few hundred angstroms [1, 2]. On the other hand, the surface chemistry of the activated carbon is a result of existence of hetero-atoms such as, oxygen, nitrogen, hydrogen, sulfur and phosphorus [7]. A current trend in the preparation of activated carbons is the use of various kinds of natural coals and waste materials. In recent years, extensive research on activated carbons from agricultural residues has been reported, e.g., apricot stones [8-10], peach stones [11-13], olive stones [14-16], peanut shells [17], date pits [18, 19], wheat straw [20], cotton stalks [21, 22], pecan shells [23, 24], hulls of soybean and rice and many others. Very little has been mentioned about cherry stones [25] although this is a cheap

and abundant agricultural waste of no economical value.

It is well known that activated carbons may be prepared both by physical activation and chemical activation [26]. The former involves primary carbonization of the raw material (below 700°C) followed by controlled gasification at high temperatures ( $\geq 850^\circ\text{C}$ ) in a stream of an oxidizing gas (steam, CO<sub>2</sub>, air or a mixture). The chemical activation involves the impregnation of the precursor with an activating agent (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub>, alkali metal hydroxides) then heat treatment at moderate temperatures (400-700°C) in a one step process [27].

The adsorption capacity of an adsorbent is determined by its texture (surface area and porosity). The textural properties are usually determined from the adsorption of nitrogen at 77 K and the conventional BET equation (28) is used for the quantification of the surface area and porosity. Because the adsorption in micro-porous solids (zeolites and activated carbons) does not take place by successive built-up of molecular layers as admitted by the BET theory. Rather, the enhanced interaction potential in micropores induces an adsorption process described as micropore filling. A different approach for the analysis of the nitrogen adsorption isotherm on microporous sorbents is based on the volume filling of micropores has been described by Dubinin and his co-workers. The Dubinin-Radushkevich (DR) equation [29] was admitted for the quantification of the porosity of activated carbons. Because volume filling of micropores occurs at very low relative pressures, the adsorption of CO<sub>2</sub> at 273 or

298°C was recommended for the quantification of the porosity of activated carbons and molecular-sieve zeolites [30].

In the present study, wild cherry stones were used as a precursor for the preparation of carbons activated with  $ZnCl_2$  or  $H_3PO_4$ . The nitrogen adsorption data obtained at 77 K on the carbons studied were analyzed using methods based on surface coverage (BET method, t-method and  $\alpha$ -method) and also the DR-method based on volume filling of micropores. The  $CO_2$ -adsorption data at 273 K were analyzed using the DA equation [31] which is based on micropore filling. The t-,  $\alpha$ -, DR- and DA-methods allowed also the determination of useful adsorption parameters. One of the objective of this investigation was also to define the limits within which equation based on micropore filling are used in analyzing adsorption data.

## 2. Experimental

### 2.1. Materials

Large stock of dry ground stones "W" was derived from wild black cherry (*Prunus Cerasus* L). Four zinc chloride-impregnated samples WZ20, WZ35, WZ50 and WZ65 were obtained by impregnating portions from the stock W for 48 h, into saturated zinc chloride solutions containing 20, 35, 50 or 65% of their weight, respectively. Four zinc chloride-activated carbon samples were obtained from each impregnated sample by carbonization at 400, 500, 600 or 700°C, in absence of air. Thus, for example, the activated carbons corresponding to WZ20 being designated as WZ20-400, WZ20-500, WZ20-600 and WZ20-700, respectively. Other zinc chloride-activated carbons were prepared by carbonization at 500 and 600°C, of the impregnated sample, in

nitrogen atmosphere to yield samples designated as WZN20-500 and WZN20-600. All carbons produced were washed thoroughly with distilled water until the washings were free from chloride ions then the washed material was dried. More details have been published elsewhere [32].

Phosphoric acid-activated carbons were obtained by impregnating dry crushed stones "W" in 20, 35, 50, 65 or 85 wt% phosphoric acid solution. The resulting mass was heated gradually in absence of air up to 350, 400, 450, 500 or 600°C, respectively over a period of 2h and then maintained at its maximum exposure temperature for a further 3h. After cooling the carbonized mass, it was washed thoroughly with distilled water until the washings attained a pH value of 6.0 where the washed material was dried. These activated carbons were designated so as to refer to the % phosphoric acid and to the activation temperature. Thus, for example, the designation WP35-500 refers to the activated carbon prepared by impregnating apportion from the stock W into 35% phosphoric acid followed by carbonization at 500°C, in limited air. Further details have been given elsewhere [33, 34].

### 2.2. Techniques

The adsorption of nitrogen at 77 K and of  $CO_2$  at 273 K was measured using a Micromeritics Gemini III 2375 surface analyzer (Micromeritics, Norcross, CA, USA). Prior to all measurements, the carbon samples were heated at 275°C under a reduced pressure of  $10^{-4}$  Torr.

## 3. Results and Discussion

The adsorption of nitrogen at 77 K proved to be relatively rapid with the equilibrium attained within less than 30 min.

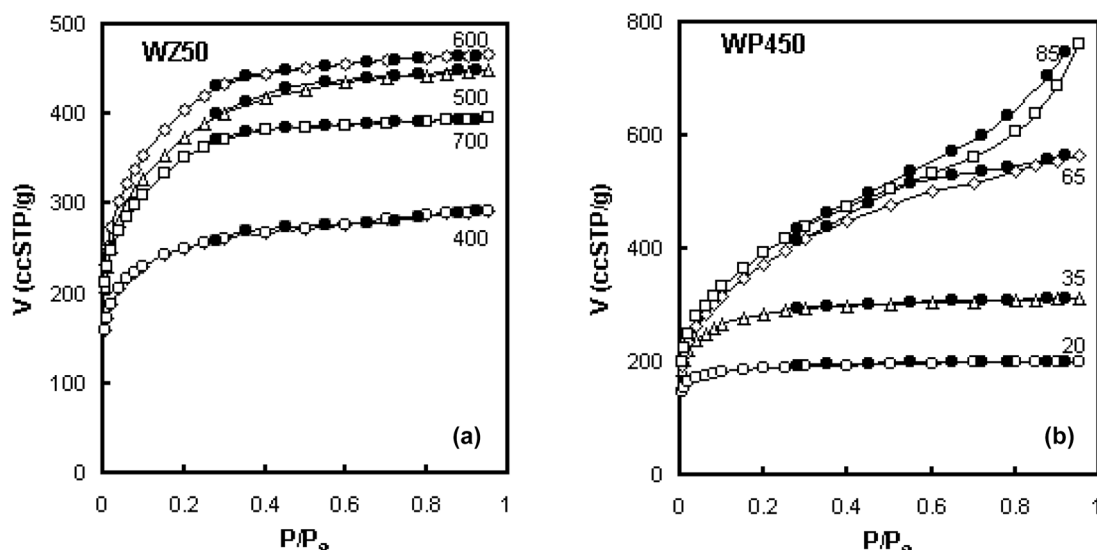


Fig. 1. Representative nitrogen adsorption isotherms at 77 K on some of the carbon Studied.

**Table 1.** Surface areas of the activated carbons studied as determined from nitrogen adsorption at 77 K

Sample	$S_L$ (m <sup>2</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)	$V_T$ (ml/g)	$r_m$ (nm)	$S_t$ (m <sup>2</sup> /g)	$S_\alpha$ (m <sup>2</sup> /g)	$S_{n-\alpha}$ (m <sup>2</sup> /g)	$S_{n-t}$ (m <sup>2</sup> /g)
WZ20-400	653	510	0.209	0.82	599	611	28	25
WZ20-500	852	789	0.340	0.86	823	844	37	35
WZ20-600	694	576	0.244	0.85	684	698	28	27
WZ20-700	503	407	0.178	0.87	480	487	21	26
WZ35-400	768	592	0.268	0.90	678	700	47	45
WZ35-500	1097	870	0.384	0.88	986	1007	42	42
WZ35-600	1220	971	0.428	0.88	1062	1069	45	46
WZ35-700	1091	888	0.382	0.86	959	968	31	30
WZ50-400	1303	920	0.458	0.98	956	968	81	83
WZ50-500	2038	1361	0.671	0.99	1309	1356	144	146
WZ50-600	2092	1457	0.721	0.99	1442	1463	79	80
WZ50-700	1776	1253	0.612	0.98	1269	1283	59	60
WZ65-400	1575	1088	0.545	1.00	1102	1126	115	112
WZ65-500	1966	1791	1.041	1.16	1721	1756	388	382
WZ65-600	1882	1746	1.041	1.19	1709	1733	422	416
WZ65-700	1703	1570	0.913	1.16	1525	1565	332	335
WZN20-500	769	638	0.271	0.85	746	768	20	18
WZN35-500	1352	1085	0.474	0.87	1102	1102	38	40
WZN50-500	2118	1506	0.729	0.97	1470	1508	90	92
WZN65-500	1948	1775	1.035	1.17	1740	1762	355	325
WZN20-600	727	610	0.256	0.84	735	732	25	22
WZN35-600	1228	1094	0.484	0.88	1127	1130	34	35
WZN50-600	2053	1473	0.708	0.96	1449	1469	70	72
WP50-350	1833	1279	0.640	1.00	1287	1311	135	125
WP50-400	2867	1760	0.967	1.10	1733	1722	312	298
WP50-450	3242	1843	1.073	1.16	1810	1790	395	338
WP50-500	3193	1790	1.048	1.17	1779	1780	385	335
WP35-450	1380	1051	0.483	0.92	1122	1137	63	60
WP50-450	3342	1843	1.073	1.16	1810	1790	395	362
WP65-450	1504	1337	0.876	1.31	1315	1314	342	318
WP20-500	863	706	0.304	0.86	818	842	28	32
WP35-500	1480	1110	0.575	0.93	1133	1157	57	64
WP50-500	3193	1790	1.048	1.17	1779	1760	386	388
WP65-500	1503	1360	0.937	1.38	1318	1327	370	392

However, for few samples (those activated with small amount of zinc chloride or phosphoric acid) an equilibrium time of 45 min was required to reach equilibrium at relative pressures  $P/P_0 < 0.1$ . This indicates that almost all the pores were accessible to nitrogen at 77 K. The desorption points were found to lie on the same isotherm as the adsorption data, indicating the absence of hysteresis characteristic of multilayer adsorption and/or the existence of a large fraction of meso-porosity or specific interaction between nitrogen molecules and the carbon surface [35].

Fig. 1 depicts representative nitrogen adsorption isotherms. All the isotherms are Langmuirian in shape being typically type I in the BDDT classification [36], which is characteristic of adsorption on micro-porous adsorbents, with the

absence of hysteresis loop or show very narrow hysteresis, except of WP65 and WP85 samples which exhibit isotherms between VI and I types with a clear hysteresis loop, Figure 1b. Application of the Langmuir equation [37, 38] was satisfactory and covered a wide range of relative pressures. Such plots (not illustrated) enabled the monolayer capacity for each carbon sample to be determined as well as the specific surface area,  $S_L$  (m<sup>2</sup>/g). The corresponding values of  $S_L$  obtained are listed in column 2 of Table 1. The conventional BET equation [28] was also applied over the relative pressure range (0.01-0.15), to determine the monolayer capacity and hence the specific surface area ( $S_{BET}$ ) of each carbon sample adopting the value of 0.16 nm<sup>2</sup> for the cross sectional area of nitrogen molecule at 77 K. Representative linear

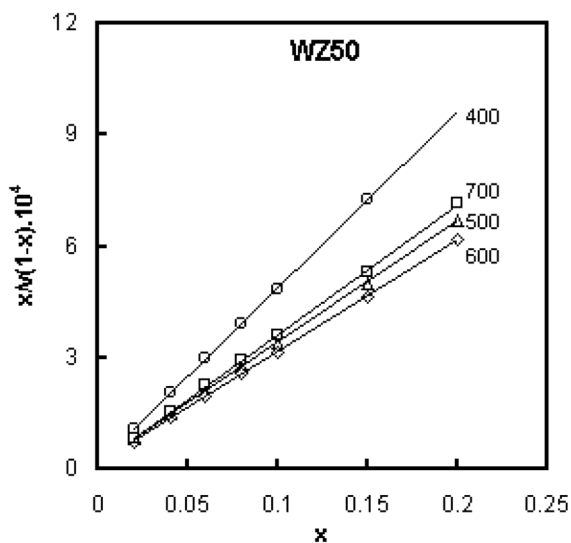


Fig. 2. Representative linear BET plots of some nitrogen adsorption isotherms at 77 K.

BET plots are shown in Fig. 2. The total pore volumes  $V_T$  (ml/g), expressed as the volume of liquid nitrogen adsorbed per one gram carbon at relative pressure of ca 0.95, are listed in column 4 of Table 1. Based on the assumption that the space in the micropores is similar to the space between two parallel plates, the mean pore radius  $r_m$  (nm) could be calculated from the relationship:

$$r_m = 2V_T \times 10^3 / S_{BET}$$

Values of  $r_m$  as calculated for each carbon are listed in column 5 of Table 1.

Two other independent methods were also applied to analyze the nitrogen adsorption isotherms, i.e. the  $t$ -method [39] and the  $\alpha$ -method [40]. In the first method the amount of gas adsorbed (ml/g) is plotted versus multilayer thickness  $t$  (in Å) as measured on a non-porous solid of comparable BET-C constant (Fig. 3). The second method plots the volume of gas adsorbed versus the reduced isotherm ( $\alpha_s$ ) determined on standard non-porous carbon. The adsorption data reported for an olive stone-based non-porous carbon [41] were used for such plots which are depicted in Fig. 4.

The  $t$ -method allows the determination of the specific surface area  $S^l$ , the micropore volume ( $V_{o-t}$ ) and the non-microporous area ( $S_{n-t}$ ). Similarly, the  $\alpha_s$  method allows the determination of the same three parameters but with the notations,  $S_\alpha$ ,  $V_{o-\alpha}$  and  $S_{n-\alpha}$ , respectively.

Inspection of the data recorded in Table 1 reveals the following:

- 1) Activation with zinc chloride should be undertaken at 600°C. Thus, activation at 500°C produced carbons with surface areas lower than those of carbons prepared by activation with zinc chloride at 600°C, whilst activation with zinc chloride at 400°C seems to be incomplete as

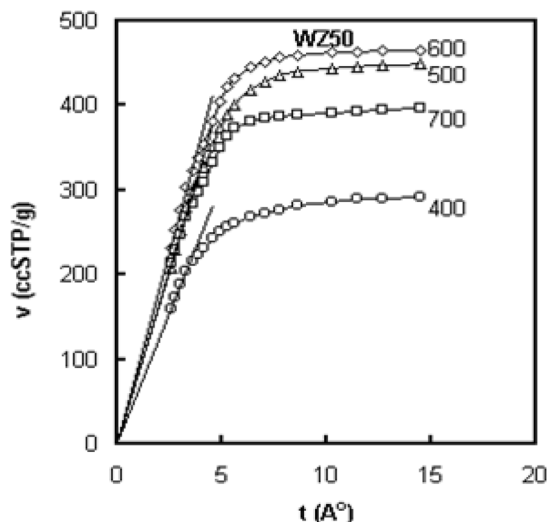


Fig. 3. Representative  $t$ -plots of some nitrogen adsorption isotherms at 77 K.

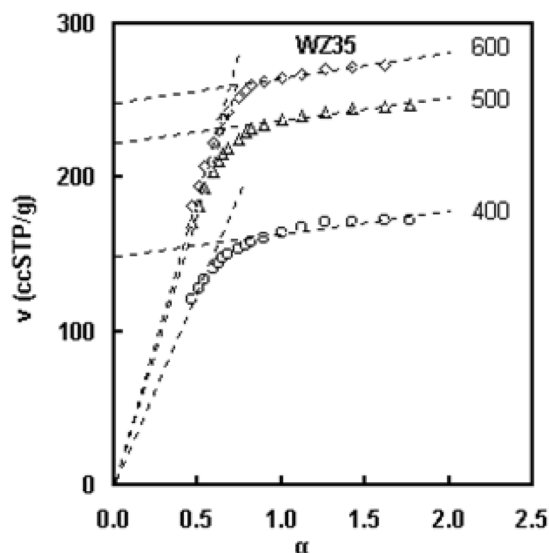


Fig. 4. Representative  $\alpha$ -plots of some nitrogen adsorption isotherms at 77 K.

predicted by the low  $S_{BET}$  values of samples activated with zinc chloride at this low temperature. Activation with zinc chloride and probably with other activating agent may be controlled by mass and heat transfer. The rise of the temperature of activation with zinc chloride to 700°C was also associated with a decrease in the surface area. At 700°C the vapor pressure of zinc chloride considerably increases and this is probably associated with a considerable loss of this activating agent (42). Generally, activation with zinc chloride in nitrogen atmosphere proved to be more effective than in a limited air. Thus, for example  $S_{BET}$  of WZN35-500 is about 24% higher than  $S_{BET}$  of WZ35-500 and  $S_{BET}$  of carbon

WZN65-600 is 26% higher than  $S_{\text{BET}}$  of the sample designated WZ65-600.

- 2) Activation with phosphoric acid should be undertaken at 450°C. Thus, activation at 500°C produced activated carbons with surface areas slightly lower than those of carbons prepared by activation at 450°C. Also activation with phosphoric acid at 400°C was slightly lower than activation at 450°C. The activation with phosphoric acid at 350°C is considerably lower and seems to be incapable of generating such textural variations.
- 3) The surface areas calculated through the application of the t-method and  $\alpha$ -method are comparable. These two methods are based on a standard non-porous material and each method can be used to complement the other. The data listed in Table 1 show that, in most cases, the  $S_{\text{BET}}$  values were lower than the  $S^t$  and  $S_\alpha$  values; however, the difference was not high and may be attributed to the BET model being based on multilayer coverage, which is not precisely the case in the adsorption on activated carbons where most of the pores accommodate only a limited number of layers as indicated by the values of their mean radii (column 5 of Table 1). Some pores may accommodate only two layers, each on one of the opposite pore walls, and some pores may accommodate only one layer shared between the opposite walls. In addition, some pores may even be inaccessible to adsorbate molecules. It should be noted from the data in Table 1 that the calculated  $S_L$  values were very high relative to the  $S_{\text{BET}}$ ,  $S^t$  and  $S_\alpha$  values, an unsurprising fact since the Langmuir model is based on monolayer adsorption and in most cases monolayer capacities as determined by the application of the Langmuir model lie beyond the equilibrium pressures employed. For this reason, the Langmuir model cannot be used for interpreting adsorption data for activated carbons.
- 4) The surface area located in the region of micro-porosity represents a large fraction of the total surface area and consequently the surface located in the non-microporous region would be only a small fraction of the total surface area of the activated carbon studied. This may be predicted from the data recorded in columns 8 and 9 of Table 1 detailing the values of  $S_{n-t}$  and  $S_{n-\alpha}$ , respectively. Indeed, the mean pore radius  $r_m$  for most carbons investigated was less than 1.0 nm, indicating the predominance of micro-porosity. However, for some activated carbons the values of  $r_m$  was slightly higher than 1.0 nm, which may be attributed to the fact that  $r_m$  was calculated from a relationship including  $S^{\text{BET}}$  which is based on multilayer adsorption.
- 5) The surface areas of activated carbons obtained via activation with zinc chloride or with phosphoric acid were generally high. However, the mechanism of activation with phosphoric acid is different from that with zinc chloride. Although both activating agents affect the course

of dehydration and precursor carbonization, activation using zinc chloride proceeds via removal of hydrogen as HCl from the carbonaceous materials rather than methane and/or lower hydrocarbons [43]. Whereas phosphoric acid dehydrates the carbonaceous material during carbonization and this leads to accelerate charring and aromatization of the carbon skeleton, inhibits shrinkage and collapse of the particles and develops an extensive pore structure [44].

The physical adsorption of gases and vapors by microporous solids, in general, and by active carbons, in particular, may also be described by Dubinin's theory as developed in successive stages (45-47). In its present formulation, the theory of micropore filling may be expressed by the Dubinin-Astakhov (31) equation which may be expressed as:

$$V = V_0 [-(A/\beta E_0)^n]$$

Where  $V$  represents the volume filled at temperature  $T$  and relative pressure  $P/P_0$ ,  $V_0$  is the total volume of micropores, the quantity  $A$  is equal to  $RT \ln(P_0/P)$  and  $n$ ,  $E_0$  and  $\beta$  are specific parameters of the system under investigation. The DA equation is applicable over the relative pressure range  $0.005 < P/P_0 < 0.1$ . Where the influence of any non-microporous surface area is negligible. For typical active carbons, the exponent  $n$  is equal to 2 which corresponds to the original empirical equation postulated by Dubinin and Radushkevich in 1947 and known as the DR equation:

$$V = V_0 \exp [-B (T/\beta)^2 \log^2 (P_0/P)]$$

The parameter  $B$  has the dimensions  $\text{K}^{-2}$  and is called the structural constant being related to the characteristic energy  $E_0$  by

$$E_0 (\text{kJ/mol}) = 0.01914/B^{0.5}$$

The DR and DA equations are both based on the observation that a plot of  $V$  versus  $(RT)^2 \ln^2 (P_0/P)$  or  $A^2$  leads to an unique curve for a given adsorbate. The range of appli-

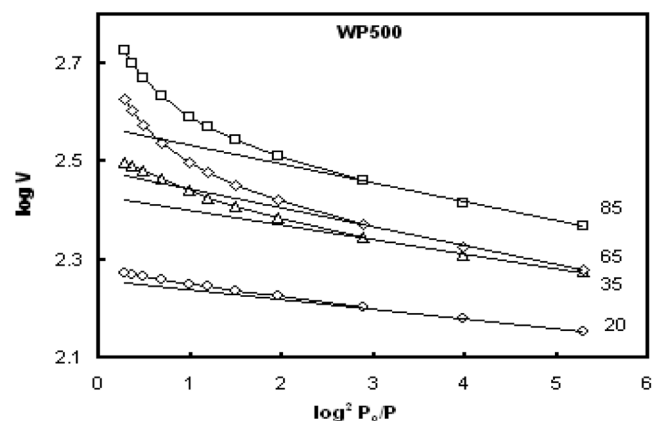
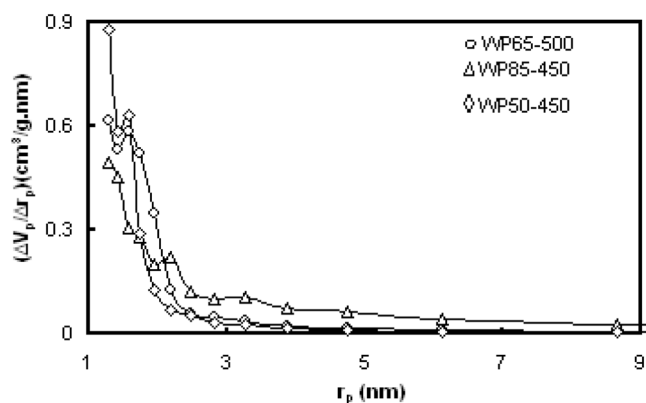


Fig. 5. Representative DR plots of some nitrogen adsorption isotherms at 77 K.



**Fig. 6.** Representative pore size distribution plots of some WP samples.

capability of the classical DR equation has been verified for many reported adsorption measurements [48].

The people on surface chemistry still hold conflicting opinions on the state of the adsorbate in a microporous adsorbent. Strong evidence needs to be provided to give prominence for one postulate or another. For this reason, the nitrogen adsorption data obtained in this study from quite a large number of chemically-activated carbons, have been interpreted here by applying the DR equation and comparing some of the adsorption parameters thus obtained with those determined from the BET,  $\alpha$ - and  $t$ -method. Representative DR plots are depicted in Fig. 5, showing that the linear plots covering a range of relative pressure were obtained. However, upward deviation from linearity at relative high  $P/P_0$  values were observed, corresponding to micropores of sizes close to the meso-porosity region.

Fig. 6 shows representative pore size distribution of some

**Table 2.** Application of DR equation to the nitrogen adsorption data at 77 K

Sample	$V_{o-DR}$ (ml/g)	$V_{o-\alpha}$ (ml/g)	$V_{0.1}$ (ml/g)	$V_n$ (ml/g)	$S_{DR}$ (m <sup>2</sup> /g)	L (nm)	$E_0$ (kJ/mol)	$r_m$ (nm)
WZ20-500	0.278	0.268	0.270	0.022	785	0.75	22.0	0.86
WZ20-600	0.230	0.221	0.223	0.014	650	0.76	21.6	0.85
WZ35-500	0.344	0.345	0.339	0.040	972	0.85	19.4	0.88
WZ35-600	0.375	0.387	0.376	0.053	1060	0.85	19.4	0.88
WZ50-500	0.493	0.529	0.506	0.203	1392	0.98	17.0	0.98
WZ50-600	0.521	0.650	0.547	0.199	1473	0.98	17.0	0.99
WZ50-700	0.454	0.592	0.479	0.158	1283	0.94	17.6	0.98
WZ65-400	0.411	0.436	0.416	0.134	1162	1.00	16.4	1.00
WZ65-500	0.611	0.730	0.633	0.430	1727	1.16	14.2	1.16
WZ65-600	0.579	0.711	0.610	0.462	1635	1.09	15.1	1.19
WZN20-500	0.252	0.251	0.246	0.019	712	0.74	22.3	0.85
WZN35-500	0.424	0.438	0.400	0.050	1198	0.85	19.4	0.87
WZN50-500	0.545	0.650	0.562	0.182	1547	0.96	17.2	0.97
WZN65-500	0.606	0.743	0.627	0.420	1713	1.17	14.1	1.17
WZN20-600	0.244	0.235	0.237	0.012	690	0.73	22.5	0.84
WZN50-600	0.551	0.640	0.553	0.177	1500	0.98	17.2	0.98
WZN65-600	0.655	0.829	0.694	0.454	1850	1.09	15.1	1.12
WP50-350	0.481	0.514	0.489	0.159	1357	1.00	16.4	1.00
WP50-400	0.612	0.700	0.637	0.355	1729	1.09	15.1	1.10
WP50-450	0.617	0.718	0.650	0.457	1743	1.14	14.5	1.16
WP50-500	0.594	0.715	0.628	0.454	1679	1.12	14.7	1.17
WP50-600	0.573	0.700	0.611	0.443	1620	1.07	15.4	1.17
WP20-450	0.289	0.303	0.287	0.023	817	0.81	20.4	0.86
WP35-450	0.412	0.465	0.452	0.071	1162	0.90	18.0	0.92
WP65-450	0.469	0.524	0.450	0.408	1321	1.12	14.7	1.31
WP85-450	0.497	0.430	0.441	0.680	1405	1.14	14.5	1.61
WP20-500	0.281	0.298	0.287	0.023	794	0.82	20.2	0.86
WP35-500	0.416	0.416	0.421	0.099	1175	0.99	16.6	1.17
WP50-500	0.594	0.715	0.628	0.520	1679	1.12	14.7	1.17
WP65-500	0.469	0.560	0.554	0.468	1325	1.13	14.6	1.38
WP85-500	0.578	0.456	0.603	0.927	1632	1.14	14.5	1.76

WP samples. For WP85 activated carbons one peak is clearly observed, which is located in the mesopore region with pore size between 2 and 3 nm. On the other hand, most pores of the other carbons are below 2 nm.

Table 2 lists some of the adsorption parameters determined from the DR equation and also includes parameters determined in other ways for the sake of comparison. It will be seen from Table 2 that the characteristic energy of adsorption ranged between 14.4 and 22.5 kJ/mol, i.e. they all lie in the range of physical adsorption. This is not surprising for nitrogen in particular since this molecule seldom undergoes specific interaction with any adsorbate surface at 77 K [35]. The narrow range in which  $E_o$  exist may be taken as an evidence for the location of the major fraction of porosity in the micropore region. The values of  $L$  (nm),  $=16.5/E_o$  [3], which give the pore half-width are listed in column 8 of Table 2 and indicate micropore type for most carbons investigated. The  $L$  values determined for few carbon samples were slightly larger than 1.0 nm. It should be also noted that the  $L$  values determined are either equal to or slightly smaller than the values of  $r_m$  listed in column 10 of Table 1. This may be attributed to the fact that  $r_m$  values represent average pore radii which contain a contribution from the non-micropores existing in a given sample.

If the micropore volumes as determined by the DR equation are converted to equivalent surface areas, it is possible to obtain a set of  $S_{DR}$  ( $m^2/g$ ) values (column 7 of Table 2). It will be noted that all the  $S_{DR}$  values listed are considerably smaller than the comparable  $S_L$  values, with the difference reaching about 40% in the case of sample WZ50-500. It has been mentioned already that the Langmuir model on which  $S^L$  values are based gives monolayer capacities beyond the equilibrium pressure and hence conversion of the monolayer capacities into specific surface areas is of limited significance.

Fair agreement exists between the comparable values of  $S_{DR}$ ,  $S_{BET}$ ,  $S_o$  or  $S_v$ , despite the fact that the three latter values are based on models that consider surface coverage whereas  $S^D$  is based on a model that considers the filling of small micropores. This suggests that the micropores in the samples studied fall into more than one class. Indeed, micropores may be subdivided into ultramicropores (less than 0.5 nm radius) in which adsorption is controlled by activated diffusion, small micropores with  $0.5 \text{ nm} < r < 1.5 \text{ nm}$  and supermicropores with radii within 1.5-2.0 nm range [44]. Different approaches should therefore be considered for the correct characterization of microporous carbons [48].

It remains now to point out that the analysis of the nitrogen adsorption data determined at 77 K for all the carbons studied here could give some evidences in favor of the surface coverage mechanism. These evidences are: (i) the rapid attainment of adsorption equilibrium of nitrogen at 77 K for all the carbons studied. This refers to the absence of activated diffusion process and consequently the absence of

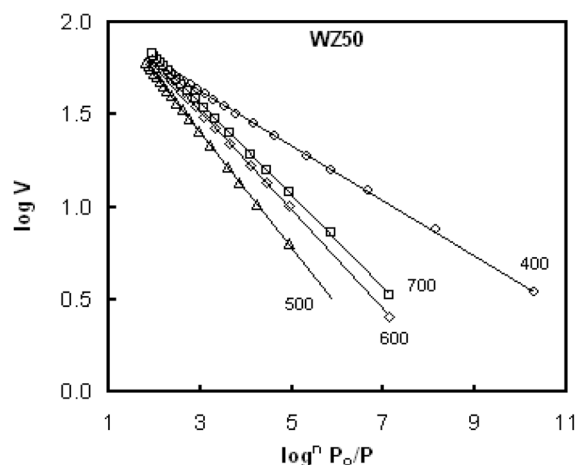


Fig. 7. Representative DA plots of carbon dioxide adsorption isotherms at 237 K.

ultramicroporosity in which pore filling would be expected. (ii) All the nitrogen adsorption isotherms were characterized by very steep initial portions, well developed knee bends and location of monolayer capacities at  $P/P_o \leq 1.0$ . (iii) The DR equation was successfully applied within the relative pressure range 0.005-0.06 whereas the BET equation fits the data within the relative pressure range 0.01-0.15. Thus, although the two equations are based on two different postulates, the ranges of relative pressure within which they fit the adsorption data overlap. (iv) The fair agreement between  $S_{BET}$ ,  $S_o$ ,  $S_v$  and  $S_{DR}$  may be considered as an additional evidence for the predominance of the surface coverage mechanism.

The adsorption of carbon dioxide at 273 K has been recommended as a substitute for nitrogen adsorption at 77 K as a means of determination of surface areas and porosities of microporous sorbents, in general, and microporous carbons in particular [43]. However, this is only true when the adsorption of nitrogen proved to be energy diffusion controlled process. To shed a new light on this argument, the adsorption of carbon dioxide at 273 K was studied. In the pressure range 5-800 Torr. The corresponding adsorption data arising were interpreted on the basis of the DA equation, the linear plots obtained being predicted in Figure 6. The value of  $n$  used in the DA equation was adjusted to obtain the most satisfactory linear plot with the least scatter of points. Application of the DA equation allowed the determination of the micropore volume  $V_{o-DA}$  ( $ml/g$ ), which could be converted into equivalent surface area  $S_{DA}$  ( $m^2/g$ ). Other textural parameters determined for the various samples studied included  $E_o$  (kJ/mol),  $k$  ( $nm \text{ kJ/mol}$ ) =  $13.028-1.53 \times 10^{-5} E_o^{3.5}$  and the pore half-width  $\times$  (nm) =  $k/E_o$  [47]; the corresponding values obtained are listed on columns 8, 7 and 6 of Table 3.

The data recorded in Table 3 show that the value of  $n$  decreased and the pore diameter increased - a conclusion

**Table 3.** Application of the DA equation to carbon dioxide adsorption data at 273 K

Sample	D	n	$S_{DA}$ (m <sup>2</sup> /g)	$V_{o-DR}$ (ml/g)	x (nm)	k nm.kJ/mol	$E_t$ kJ/mol
WZ20-400	0.120	2.00	498	0.185	0.76	12.31	21.8
WZ20-500	0.157	1.85	689	0.256	0.84	12.53	19.4
WZ20-600	0.127	2.00	573	0.213	0.79	12.38	21.0
WZN20-500	0.128	2.00	611	0.227	0.79	12.38	21.0
WZN20-600	0.095	2,27	511	0.190	0.74	12.24	22.2
WZ35-500	0.186	1.75	777	0.289	0.90	12.63	18.3
WZ35-600	0.202	1.75	863	0.321	0.97	12.72	17.0
WZN35-500	0.212	1.80	935	0.348	0.99	12.74	16.7
WZN35-600	0.177	1.80	744	0.295	0.91	12.63	18.2
WZ50-500	0.312	1.45	1106	0.411	1.21	12.89	13.6
WZ50-600	0.269	1.60	1057	0.430	1.11	12.84	14.8
WZN50-500	0.291	1.55	1157	0.393	1.16	12.86	14.3
WZN50-600	0.266	1.68	1098	0.408	1.10	12.83	15.0
WZ65-500	0.275	1.60	990	0.368	1.13	12.85	14.6
WZ67-600	0.285	1.60	1030	0.383	1.15	12.86	14.3
WZN65-500	0.310	1.55	1167	0.434	1.21	12.88	13.7
WZN65-600	0.335	1.50	1321	0.491	1.24	12.90	13.3
WP20-450	0.188	1.70	741	0.276	0.91	12.64	18.1
WP20-500	0.172	1.80	685	0.255	0.89	12.61	18.5
WP35-450	0.241	1.65	885	0.329	1.04	12.78	15.9
WP35-500	0.257	1.60	927	0.345	1.07	12.82	15.4
WP50-450	0.332	1.50	1254	0.466	1.25	12.90	13.2
WP50-500	0.323	1.50	1172	0.436	1.23	12.89	13.4
WP65-450	0.424	1.35	1251	0.465	1.43	12.95	11.7
WP65-500	0.385	1.70	1159	0.431	1.35	12.93	12.2
WP85-450	0.351	1.60	1109	0.413	1.29	12.92	12.8
WP85-500	0.286	1.80	937	0.349	1.15	12.86	14.3

which agrees with previously reported data [49]. The values of k were comparable for all the carbons studied, ranging between 12.24 nm kJ/mol for WZ20-600 and 12.95 nm kJ/mol for WP65-450. Generally k increased as the value of L increased. In addition, all the values of the characteristic energy,  $E_o$  (11.7-22.2 kJ/mol) lies in the range for which physical adsorption would be predicted, with  $E_o$  increasing as the value of L decreased in agreement with the postulates of adsorption in micro- porous adsorbents.

Column 4 of Table 3 lists the equivalent surface areas  $S_{DA}$  (m<sup>2</sup>/g) as calculated from the application of the DA equation to the carbon dioxide adsorption data measured at 273 K. Generally, the  $S_{DA}$  values are lower than the comparable nitrogen surface areas as obtained through the application of the BET, t-,  $\alpha$ - or DR-method. One may attribute this to the difference between the large cross sectional area of carbon dioxide molecule 0.187 nm<sup>2</sup> at 273 K while that of nitrogen molecule at 77 K is 0.162 nm<sup>2</sup>. This explanation can only be accepted if we assume that both nitrogen adsorption and carbon dioxide adsorption proceed via surface coverage. Based upon this assumption, the different adsorption temper-

ature may give a good reason for the low CO<sub>2</sub>-areas compared with N<sub>2</sub>-areas. Physical adsorption being an exothermic process decreased with the increase of temperature. To summarize, carbon dioxide adsorption at 273 or 298 K is a suitable probe for the characterization of the texture of microporous carbon, provided that this carbon contains at least a fraction of porosity inaccessible to nitrogen molecule at 77 K. The textural parameters of ultramicropores-free carbons, as determined by carbon dioxide adsorption at 273 or 298 K should be taken with great reservation.

#### 4. Conclusions

Activation with zinc chloride has been undertaken at 400-700°C with the maximum efficiency exhibited at 600°C, whereas activation with phosphoric acid occurred at 350-600°C with the maximum efficiency determined at 450°C.

Carbons obtained by activating wild cherry stones with zinc chloride or phosphoric acid are characterized by high surface areas 500-1800 m<sup>2</sup>/g with the large fraction of the



surface located in micropores.

Micropores are those pores having diameter  $\leq 2.0$  nm. However, due to the sensitivity of this region to the heat and mass transfer, the state of the adsorbed material in the micropore region may change within a very narrow range. This region is better subdivided according to the pore diameter into sub-region in which the state of the adsorbed molecules or their orientation on the surface assume a certain state. Micropores with diameters  $\leq 0.5$  nm (ultra-micropores) may be inaccessible to nitrogen molecules at 77 K because in these pores the adsorption is an activated diffusion controlled process. The adsorption of carbon dioxide at 273 K is recommended as a substitute of nitrogen adsorption at 77 K to characterize the texture of ultra-microporous sorbents.

In case of absence of activated diffusion adsorption, the adsorption data of carbon dioxide at 273 K may give incorrect figures for the textural parameters. In such sorbents, the entire pore structure is accessible to nitrogen molecules at 77 K, the mechanism of surface coverage predominates and comparable values for the textural parameters could be obtained when different methods of analysis are used.

## References

- [1] Salame, I. I.; Bandosz, T. J. *J. Colloid and Interface Sci.* **1999**, *210*, 367.
- [2] Bansal, R. C.; Donnet, J. B.; Stoeckli, H. F., "Active Carbon", Marcel Dekker, New York, 1988.
- [3] Parrick, J. W. "Porosity in Carbons: Characterization and Application"; Edward Arnold, London 1995.
- [4] Youssef, A. M.; El-Nabarawy, Th.; Samra, S. E. *Colloids and Surfaces* **2004**, *235*, 135.
- [5] Youssef, A. M.; Alaya, M. N.; Nawar, N. *Adsorp. Sci. Technol.* **1994**, *11*, 225.
- [6] Youssef, A. M.; Ghazy, T. M.; El-Nabarawy, Th. *Carbon* **1982**, *20*, 248.
- [7] Marsh, H.; Heintz, E. A.; Rodriguez-reinoso, F., (Eds), "Introduction to Carbon Technologies", Univ. Alicante, Alicante 1997.
- [8] Gergova, K.; Eser, S. *Carbon* **1996**, *34*, 879.
- [9] Philip, C. A.; Girgis, B. S. *J. Chem. Technol. Biotechnol.* **1996**, *67*, 248.
- [10] Bota, A.; Laszlo, K. *Per. Polytech. Ser. Chem. Eng.* **1997**, *41*, 19.
- [11] Sayilkan, H.; Cetinkaya, B. *Chem. Acta. Turc.* **1991**, *19*, 257.
- [12] Molina-Sabio, M.; Rodriguez-Reinoso, F.; Caturla, F.; Selles, M. J. *Carbon* **1995**, *33*, 1105.
- [13] McDonald, J. A. F.; Quinn, D. F. *J. Porous Mat.* **1995**, *1*, 43.
- [14] Gonzalez, M.; Molina-Sabio, M.; Rodriguez-Reinoso, F. *Carbon* **1994**, *32*, 1407.
- [15] Molina-Sabio, M.; Gonzalez, M.; Rodriguez-Reinoso, F.; Speulveda, A. *Carbon* **1996**, *34*, 505.
- [16] Ridriguez-Vaero, R. M.; Escandell, M. M.; Molina-Sabio, M.; Rodriguez-Reinoso, F. *Carbon* **2001**, *39*, 320.
- [17] Romero, L. C.; Bonomo, A.; Gonzo, E. E. *Adsorp. Sci. Technol.* **2003**, *21*, 617.
- [18] El-Dein, H. A., M.Sc Thesis, Aleppo Univ. Aleppo, Syria 2002.
- [19] Girgis, B. S.; El-Hendawy, A. A. M., Proc. 1<sup>st</sup>. Arab. Conf. Appl. Chem. Nov. 1997, 341.
- [20] Banat, F.; Al-Asheh, S.; Makhadmeh, L. *Adsorp. Sci. Technol.* **2003**, *21*, 597.
- [21] Cordero, J. B.; Sanchez, A. A. M.; Tena, A. F.; Sanchez, J. L. M.; Castellanos, R. B., *Afinidad* 1988, XLV (412) 78.
- [22] Abdel-Raheim, A. A. H., Ph. D. thesis, Mansoura University, Egypt 2001.
- [23] Attia, A. A.; El-Hendawy, A.; Khedr, S. A.; El-Nabarawy, Th. *Adsorp. Sci. Technol.* **2004**, *22*, 411.
- [24] Ahmedana, M.; Johns, M. M.; Clarke, S. J.; Marshall, W. E.; Rao, R. M. *J. Sci. Food Agric.* **1997**, *75*, 117.
- [25] Ammar, G. M., Ph. D. Thesis, Mansoura University, Egypt 2005.
- [26] Lussier, M. G.; Shull, J. C.; Mueller, D. J. *Carbon* **1994**, *32*, 1493.
- [27] Youssef, A. M. *Carbon* **1975**, *13*, 1.
- [28] Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *69*, 309.
- [29] Dubinin, M. M.; Zaverina, A. D.; Radushkevich, L. V. *Zh. Fiz. Khim.* **1947**, *21*, 1351.
- [30] El-Wakil, A. M.; Youssef, A. M.; Tollan, K. *Separation. Sci. Technol.* **1990**, *26*, 445.
- [31] Dubinin, M. M.; Astakhov, V. A., *Izv. Akad. Nauk SSSR, Ser.* **1971**, *5*.
- [32] Youssef, A. M.; El-Shobaky, G. A.; El-Nabarawy, Th. *Surf. Technol.* **1978**, *7*, 451
- [33] Khalil, L. B. *Adsorp. Sci. Technol.* **1996**, *13*, 317.
- [34] Hourieh, M. A.; Alaya, M. N.; Youssef, A. M.; El-Sejariah, F. *Adsorp. Sci. Technol.* **1999**, *17*, 675.
- [35] Mikhail, R. Sh.; Youssef, A. M.; El-Nabarawy, Th. *J. Colloid Interface Sci.* **1979**, *70*, 467.
- [36] Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.
- [37] Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2219.
- [38] Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1368.
- [39] Lippens, P. C.; de Boer, J. H. *J. Catal.* **1965**, *4*, 319.
- [40] Sing, K. S. W. *Chem. Ind. (London)* **1968**, 1520.
- [41] Sella-Perez, M. J.; Martin-Martinez, J. M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1237.
- [42] Youssef, A. M. *Carbon* **1974**, *12*, 433.
- [43] El-Nabarawy, Th.; Mostafa, M. R.; Youssef, A. M. *Adsorp. Sci. Technol.* **1997**, *15*, 59.
- [44] Dubinin, M. M., Chemistry and Physics of Carbon, Walker, Jr. P. L., Ed, Marcel Dekker, New York, 1966, 51.
- [45] Alaya, M. N.; Hourieh, M. A.; El-Sajariah, F.; Youssef, A.

- M. Adsorp. Sci. Technol.* **2001**, *19*, 321.
- [46] Dubinin, M. M. *Carbon* **1985**, *21*, 359.
- [47] Dubinin, M. M.; Stoeckli, H. F. *J. Colloid Interface Sci.* **1980**, *75*, 3.
- [48] Alaya, M. N.; Hourieh, M.A.; Youssef, A. M.; El-Sejarieh, F. *Adsorp. Sci. Technol.* **2000**, *18*, 27.
- [49] Finger, G; Bulow, M. *Carbon* **1979**, *17*, 87.