Characteristics of activated carbon from peanut hulls in relation to conditions of preparation

Badie S. Girgis [a,*], Samya S. Yunis [b], Ashraf M. Soliman [c]

[a]*Laboratory of Physical Chemistry, National Research Center, Dokki, Cairo, Egypt*
[b]*Chemical Engineering Department, Faculty of Engineering, Cairo University, Cairo, Egypt*
[c]*Chemical Warfare Department, Cairo, Egypt*

Abstract

Powdered dried peanut hulls were treated by one-step procedures to get activated carbon using chemical activation by H_3PO_4, $ZnCl_2$, KOH and thermal activation by steam pyrolysis. Products were characterized by adsorption of N_2 at 77 K and methylene blue (MB) from aqueous solution. Simple carbonization at 700–900 °C yields low adsorbing microporous carbons. Steam pyrolysis at 600 °C generates porosity in the mesopore range. KOH activation results in carbons of low surface area similar to steam pyrolysis, but with much developed mesoporosity, whereas $ZnCl_2$ activation yields a moderate adsorbing carbon, essentially microporous. Treatment with H_3PO_4 at increasing impregnation ratios creates abundant microporosity with extended surface area attaining a maximum at a ratio of 1.0. Considerable loss in porosity accompanies additional activating acid indicating the governing action of the amount of activant. A 50% diluted H_3PO_4 acid results in a carbon with considerable reduction in the internal porosity. Highest removal capacity of MB appears with H_3PO_4-activated carbons, whereas KOH-activated carbons show the weakest uptake for the dye.
© 2002 Published by Elsevier Science B.V.

Keywords: Activated carbon; Peanut hulls; Porosity; Phosphoric acid

1. Introduction

Activated carbons are extremely versatile adsorbents of major industrial significance. They are used in a wide range of applications which are concerned principally with the removal of species by adsorption from the liquid or gas phase, to effect purification or the recovery of chemicals. They also find use as catalyst support. The strong market position held by activated carbon adsorbents relates to their unique properties and low cost compared with that of possible competitive adsorbents.

Activated carbons can be produced from virtually any carbonaceous solid precursor: both naturally occurring and synthetic. Process economics normally dictate the selection of readily available, low-cost feedstocks. Common examples of commercial raw materials are materials of botanical origin (e.g. wood, coconut shell, fruit stones and nut kernels) and degraded or coalified plant matter (e.g. peat, lignite

---

* Corresponding author.

and all ranks of coal). The price of the end product is dependent on the degree of processing required to attain the desired adsorptive properties. The more commonly used activated carbons are produced in neo-commodity volumes by relatively straightforward processing methods, and in powered, granular or formed shapes (pellets, extrudates) [1].

The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon products. Important considerations to be made in selecting a source material includes cost, availability, consistency of quality, and particularly for coals, peat and lignite, the mineral matter and sulfur contents [1]. The principal commercial carbon feedstocks and the proportions in which they are used were summarized by Bansal et al. [2] as: wood, 35; coal, 28; lignite 14; coconut shell, 10; peat, 10 and others, 3%. Due to environmental considerations, agricultural by-products are gaining great importance as precursors to active carbon production. Their importance arises from various aspects: first, they lost their role as major fuel and source of energy; second, they are ever accumulating renewable sources; and third, they are low-ash materials [3]. Recent investigations reported the utilization of various raw lignocellulosic materials: for example, almond shells [4,5], peach stones [6], apricot stones [7], sugarcane bagasse [8], olive stones [9], and corncobs [10].

Basically there are two different schemes for the preparation of activated carbons: physical and chemical activation. Physical, or ''thermal'', activation involves the carbonization of a carbonaceous precursor followed by activation of the resulting char in the presence of some mild oxidizing gases such as carbon dioxide or steam [1,2]. The other method, chemical activation, consists of carbonization at a relatively low temperature (400–700 °C) in the presence of a dehydrating agent (e.g. H_2SO_4, $ZnCl_2$, KOH, and H_3PO_4). These chemical reagents may promote the formation of a rigid matrix, less prone to volatile loss and volume contraction upon heating to high temperatures. Among the numerous dehydrating agents for chemical activation, zinc chloride and phosphoric acid are the most widely used chemical agents. However, the use of phosphoric acid is preferred since the use of zinc chloride has declined due to problems of environmental

contamination with zinc chloride [11]. Its use was reported in the last decade with various agricultural by-products, for example, coconut shells [12], peach stones [6], apricot stones [7], sugar cane bagasse [8], corn cobs [10], and date pit [13]. Activation with KOH has also been reported recently by many authors [14–16], and applied to different raw materials.

The present study reports the preparation and characterization of activated carbon derived from peanut hulls using single-step activation schemes. These are: chemical activation with H_3PO_4 or KOH, and single-step steam pyrolysis developed by Gergova et al. [17]. This raw material is characterized by a low ash content (2.2%), very low apparent density (0.73 g cm^{-3}) and high degree of porosity [3].

2. Experimental

2.1. Materials

Twelve samples were obtained from dried powdered peanut hulls, as described in Table 1. Samples 1 and 2 were obtained by carbonization at 500 °C for 2 h; the cooled products was soaked in distilled water,

Table 1
Description of tested chars and activated carbons

Sample no.	Conditions of preparation
1	Carbonization 2 h at 500 °C, soaked in H_2O then heated to 700 °C.
2	Same as sample no. 1 but heated for 4 h at 900 °C.
3	Steam pyrolysis for 2 h at 600 °C.
4	Impregnation with 50% $ZnCl_2$, pyrolysis for 6 h at 300 °C, washed then heated for 6 h at 750 °C.
5	Impregnation with 1:1 KOH, pyrolysis for 3 h at 500 °C.
6	Same as sample no. 5 but pyrolysis for 3 h at 700 °C.
7–10	Impregnation with 85 wt.% H_3PO_4 in acid/precursor ratios of 0.5, 0.75, 1.0, 1.6 and heat treated for 3 h at 500 °C.
11, 12	Impregnation with 41 wt.% H_3PO_4 in a 1:1 impregnation ratio, heat treated for 3 or 6 h at 500 °C.

then finally heat treated at either 700 or 900 °C. Sample 3 was prepared by direct treatment with pure steam for 2 h at 600 °C. Carbon 4 was obtained by impregnating the precursor with 50% $ZnCl_2$ then gradually heated to 300 °C where the mass was soaked for 6 h. After cooling, the product was thoroughly washed with distilled water, then subjected to secondary activation by heating at 750 °C for 6 h. Two carbons 5,6 were chemically activated by impregnation with 1:1 (w/w) KOH and heat treated at either 500 or 700 °C. Carbons 7–10 were activated by impregnation with concentrated (85 wt.%) H_3PO_4 in increasing impregnation ratios of 0.5 up to 1.6 (acid/precursor, w/w) followed by heat treatment for 3 h at 500 °C. This temperature had been found as most suitable to perform the process properly. Two more carbons 11,12 were activated by impregnation with 41 wt.% diluted H_3PO_4 in a constant impregnation ratio of 1.0, followed by thermal treatment at 500 °C for either 3 or 6 h. In all chemical activation schemes, the thermal products were thoroughly washed with hot distilled water until washings were nearly of neutral effect.

Preparation of the carbon adsorbents was carried out in a cylindrical steel container (100×110 mm) with a non-tight movable lid. This SS container was admitted into the chamber of a programmable Muffle Furnace Type VULCAN™ 3-55 NAY, for thermal treatment. About 120 g was used for samples 1–4, whereas only 20 g was weighed in case of samples 5–12. Heating was conducted through three stages (to realize controlled evolution of volatiles) with different hold times: usually for 3 min at 200 and 400 °C, and 2–6 h at the final soaking temperature as described in Table 1.

2.2. Characterization of the carbons

The porosity properties were deduced from the adsorption isotherms of N_2 at 77 K, measured by the help of a volumetric apparatus of the conventional type. Some data were obtained by a Sorptometer of the type ASAP 2010 (Micromeritics) which showed insignificant differences from the volumetric apparatus data.

In case of microporous solids, such as activated carbons, the BET concept assuming layer-by-layer building loses its meaning. The t-method and its extensions provide a simple means of comparing the shape of a given isotherm with that of a standard on a non-porous solid [18]. In the original t-method, the amount absorbed (V_a) is plotted against t, the corresponding multilayer thickness calculated from the standard isotherm with a non-porous reference solid [18]. From slopes of the obtained straight lines and intercepts with V_a-axis, the total and non-microporous surface areas (S_t^t, S_n^t) as well as the micropore volume (V_o^t) are estimated [19].

Analysis of the adsorption isotherms was carried out by applying the BET equation to get (S_{BET}), and from constructing the t-plots, to get the surface are (S^t), non-microporous surface area (S_n^t) and the micropore volume (V_o^t). The standard t-curve for non-porous carbon was based on the adsorption data reported by Selles-Perez and Martin-Martinez [20]. The total pore volume (V_p) was estimated from volume of nitrogen (as liquid) held at the relative pressure $P/P^o = 0.95$. A value for mesopore volume (V_{meso}) was evaluated from the volume adsorbed between relative pressures of 0.1 and 0.95 [21].

Since activated carbons are mostly employed in purification purposes from the liquid phase, it becomes essential to test them in this medium. Adsorption of methylene blue (MB), a cationic large size dyestuff, has been one of the most important means of assessing removal capacity from the aqueous phase [17]. For this purpose, a one-bottle test for uptake of MB was tried for the prepared carbons. Thus, 100 ml solution of the dye, of initial concentration 1000 mg l^{-1} was mixed with 250 mg of the finely powdered dried carbon, and shaken for 24 h. The residual concentration was determined by help of a Spectrophotometer, by measuring absorbance at $\lambda = 670$ nm.

3. Results and discussion

The N_2/77 K adsorption isotherms are shown in Fig. 1, the t-plots in Fig. 2 and the evaluated texture parameters are given in Tables 2–4.

3.1. Porosity of thermally treated carbons

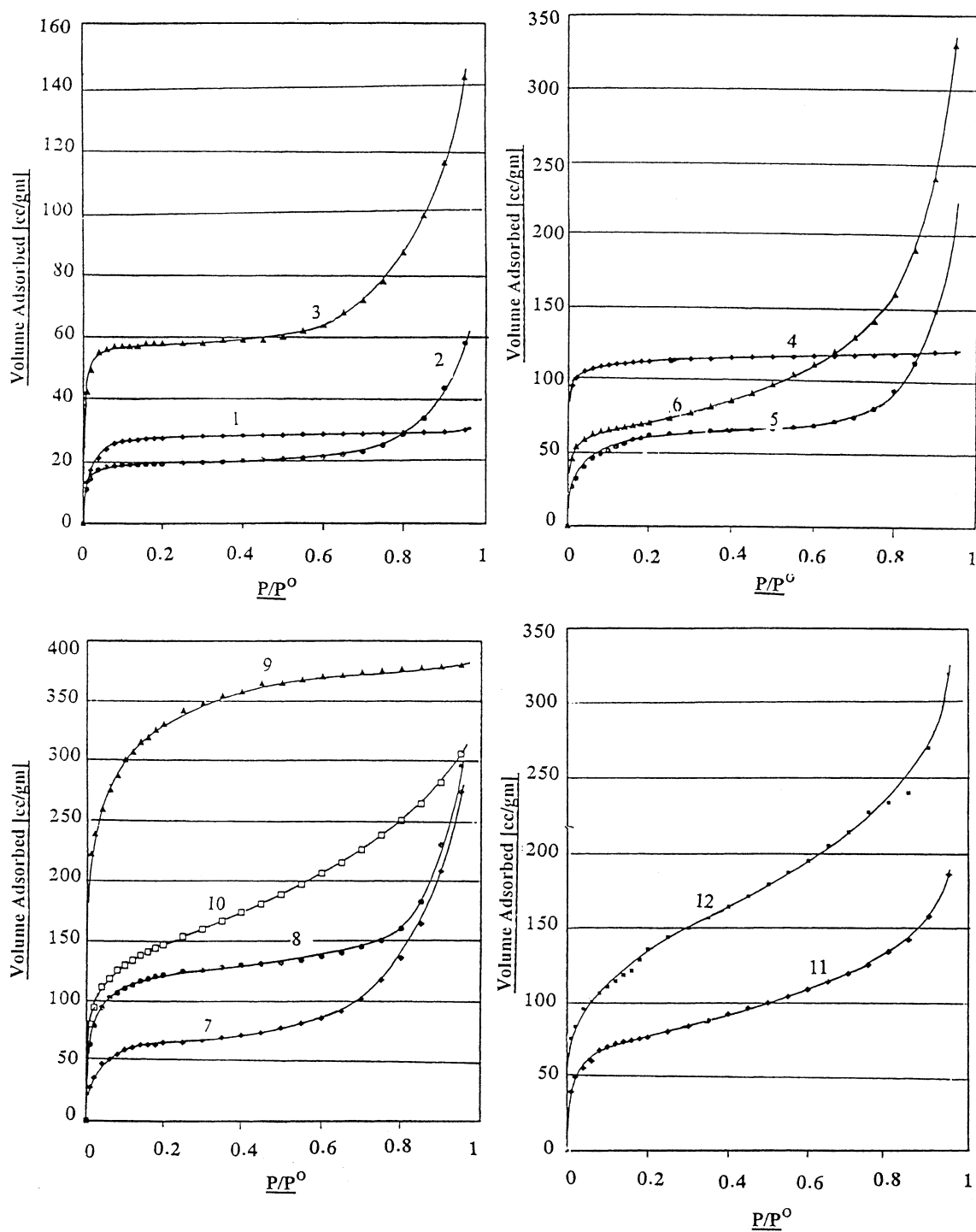It appears from Fig. 1 and Table 2 that simple carbonization at 500 °C, followed by thermal

Fig. 1. Adsorption isotherms of N_2 at 77 K for chars, steam-pyrolyzed carbons and activated carbons. (Sample numbers refer to Table 1.)
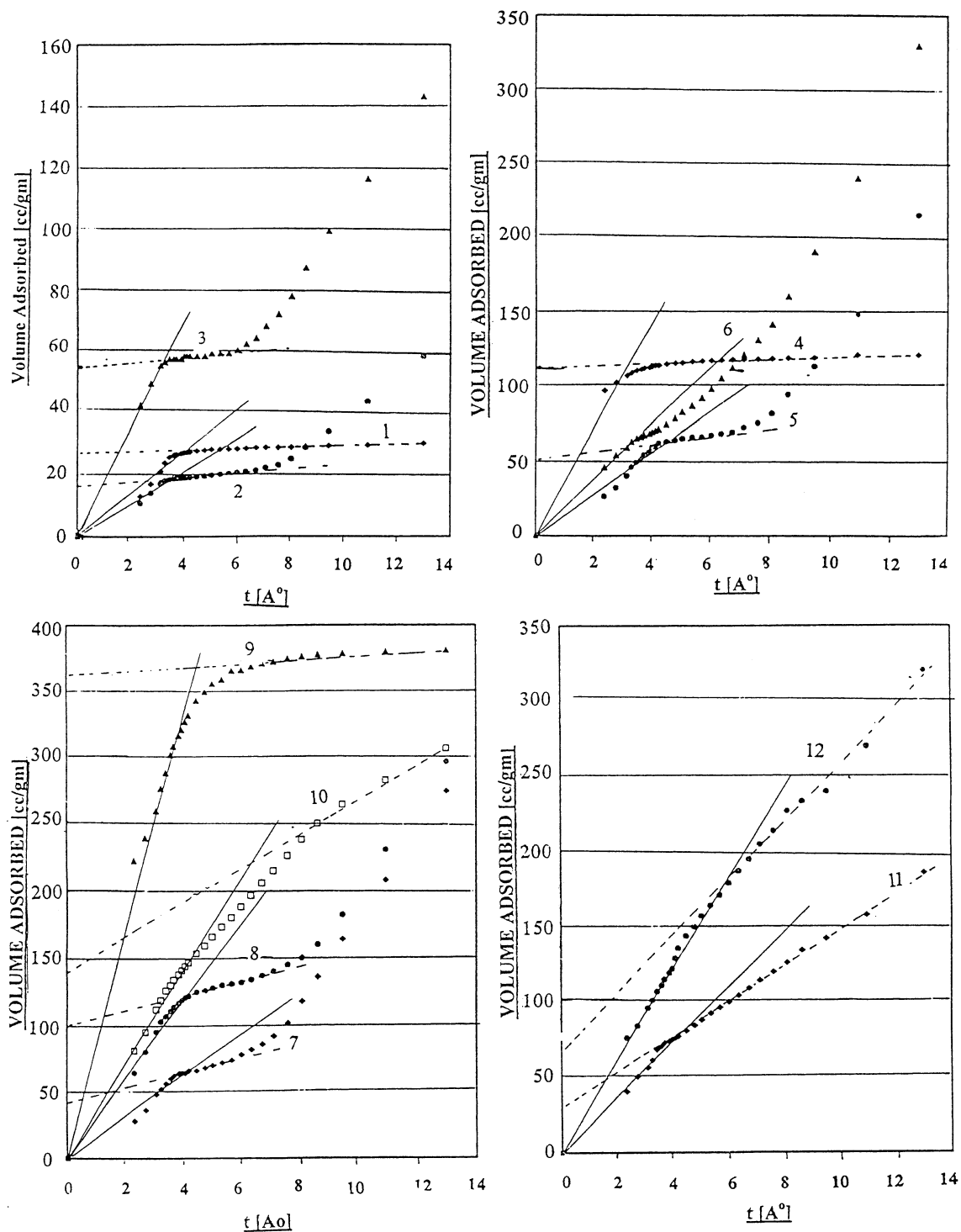
Fig. 2. *t*-Plots of N$_2$ at 77 K isotherms for chars, steam-pyrolyzed carbons and activated carbons. (Sample numbers refer to Table 1.)

Table 2
Characteristics of carbons obtained by carbonization or steam pyrolysis

Sample no.	Percentage yield	S_{BET} [m^2/g]	S^t [m^2/g]	S_n^t [m^2/g]	V_p [ml/g]	V_o^t [ml/g]	V_{meso} [ml/g]
1	30	97.1	108.7	4.2	0.053	0.043	0.006
2	30	80.8	79.7	17.9	0.171	0.022	0.061
3	27	253	257	17.4	0.223	0.079	0.134

treatment at 700 or 900 °C, produces low-capacity adsorbing carbons. Raising the secondary treatment temperature from 700 to 900 °C leads to a loss in total surface area, and increase in both total pore volume and non-microporous surface area. This means that pore widening takes place as a result of wall burning between micropores, which leads to an increase in internal porosity and reduction in micropores associated with high surface area. It is well recognized that micropores are characterized by high surface area due to their tremendous number and depth in the activated particles, whereas they constitute a lower fraction of internal porosity (pore volume) in comparison to meso and micropores [2]. Such trend is exhibited in both the shape of the adsorption isotherm and t-plots as revealed by upward rise at high pressures (or t-values); this means the generation of abundant meso- and macropores demonstrating such high adsorption values.

Pyrolysis at 600 °C in presence of a flow of steam shows a measurable effect in developing porosity. Thus, the surface is more than doubled and the total pore volume indicates a 4-fold increase. Steam pyrolysis, in one step, at 600 °C, thus enhances carbon porosity; however, within meso-pores as evident from their volume. Here, the external (or non-micropore) surface area is increased but to small extent. This single-step steam pyrolysis appears to be promising in producing an activated carbon, although with a low-adsorbing capacity under the tried condition.

3.2. Porosity of chemically activated carbon (ZnCl$_2$ or KOH)

The adsorption isotherms of this group of carbons display different effects of ZnCl$_2$ and KOH activation. Zinc chloride results in an essentially microporous carbon as evident from its typical type I (Langmuir) isotherm and t-plot. Mesoporosity is demonstrated from both low ratios of (S_n^t/S^t) and (V_{meso}/V_p) which amount to 5–8% (Table 3). A moderate surface area-carbon is obtained with a very low pore volume due to the prevalence of micropores associated with low internal pore volume.

Activation with KOH, a procedure reported recently by many authors for coal and lignocellulosic materials [14–16], seems to be ineffective to activate peanut hulls under test conditions. Low-surface-area products are obtained, $S_{BET} = 230–270$ m^2/g, but with relatively appreciable pore volumes mostly within the meso/macropore range. Enhanced wide porosity accompanies raising the temperature from 500 to 700 °C; the mesoporosity increase as evident from their content ($V_{meso}/V_p = 0.76$ to 0.80 and $S_n^t/S^t = 0.2$ to 0.68). It appears that KOH activation in a 1:1 ratio is not potentially effective in producing activated carbon at either 500 or 700 °C.

3.3. Characteristics of carbons activated with phosphoric acid

In case of series 1, treated with concentrated H$_3$PO$_4$ (85 wt.%), it appears that raising the impreg-

Table 3
Characteristics of carbons activated by ZnCl$_2$ or KOH

| Sample no.	Percentage yield	S_{BET} [m^2/g]	S^t [m^2/g]	S_n^t [m^2/g]	V_p [ml/g]	V_o^t [ml/g]	V_{meso} [ml/g]
4	30	420	510	23.7	0.195	0.173	0.017
5	32	228	215	50.1	0.335	0.076	0.255
6	27	268	291	199	0.514	0.033	0.411

Table 4
Characteristics of carbons obtained by H_3PO_4 activation

Sample no.	Percentage yield	S_{BET} [m²/g]	S^t [m²/g]	S_n^t [m²/g]	V_p [ml/g]	V_o^t [ml/g]	V_{meso} [ml/g]
7	22	240	238	114	0.427	0.062	0.334
8	27	466	481	108	0.467	0.151	0.288
9	22	1177	1247	22	0.597	0.570	0.123
10	36	544	540	349	0.487	0.084	0.274
11	28	278	288	194	0.296	0.036	0.179
12	22	466	483	300	0.501	0.103	0.325

nation ratio (X_p) from 0.5 to 1.0 is accompanied by considerable generation of porosity in the microporous range (Table 4). An increase in apparent surface area, as well as in total and micropore volumes, appears with reduction in the non-micropore surface area and mesopore volume (Fig. 3). Further increase in X_p to 1.6 leads to a loss in internal porosity particularly in the micropores. An outstanding increase in wider pores (meso/macro) is noticed as evident from both values of mesopore area and volume. This high impregnant ratio seems to enhance higher gasification associated with pore widening on the expense of micropores.

Activation with H_3PO_4 has been postulated to affect the precursor, during the impregnation stage, in many respects. Thus, the acid introduced into the material plays a double role: (1) it produces hydrolysis of the lignocellulosic material with subsequent partial extraction of some components, thus weakening the particle which swells, and (2) the acid
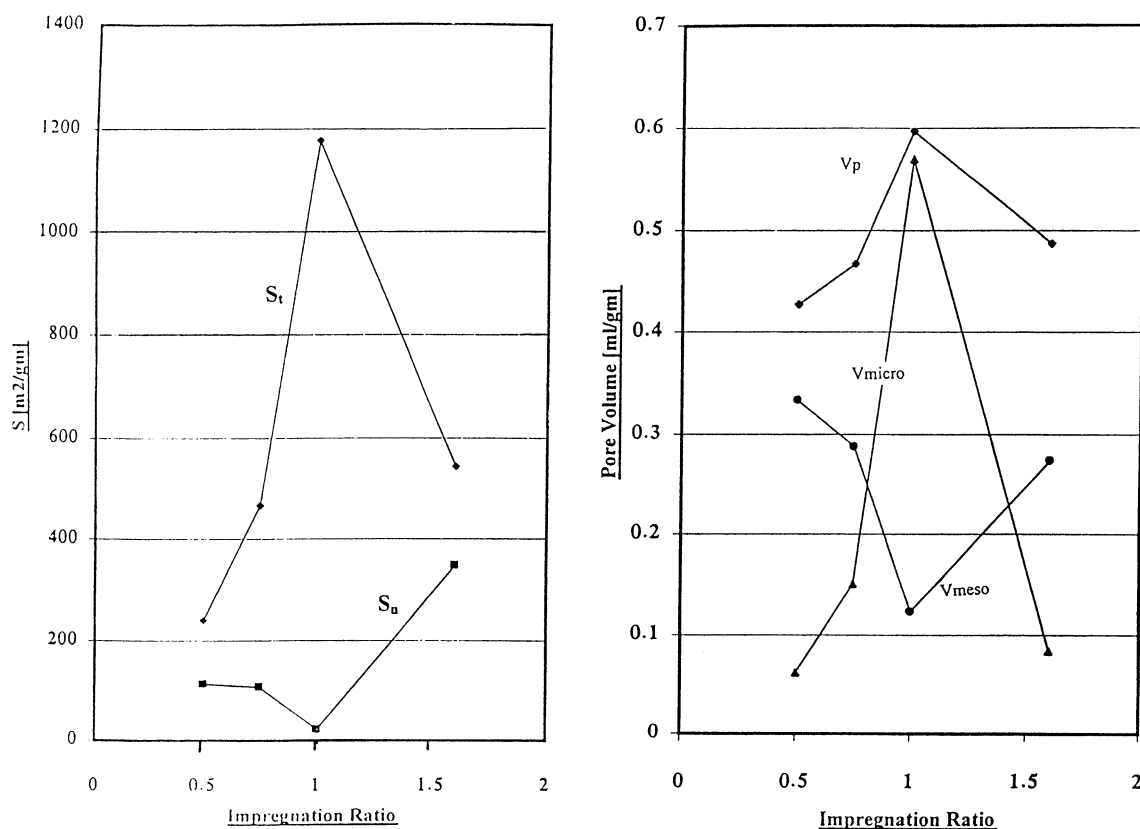
Fig. 3. Influence of impregnation ratio with H_3PO_4 on surface areas and pore volumes within different ranges.

occupies a volume which inhibits the contraction of the particle during the heat treatment, thus leaving a porosity when it is extracted by washing after carbonization [6]. These two factors predict the effect of both impregnant ratio and concentration in determining the degree of porosity evaluation. The former effect (X_p) is confirmed above, where an optimum ratio of 1.0 is most effective, and the extra acid ($X_p = 1.6$) blocks the primary botanical porosity preventing generation of microporosity with widening in pores. The second effect, impregnant concentration, will be demonstrated and illustrated below.

Choosing the maximum effective impregnation ratio of 1.0 but employing a 50% diluted acid shows the results in Table 4. Carbon 11 is much inferior to the corresponding carbon 9 impregnated with the concentrated acid. It displays an activated carbon with a very low surface area, mostly within mesopores. Prolonged treatment to 6 h, at this diluted acid (carbon 12), enhances porosity as obvious from all parameters; however, it still presents a moderate adsorbing quality. It is, more or less, similar to a carbon impregnated with a lower ratio of 0.75 (carbon 8) in case of the concentrated acid. These results mean that the effect of concentration of the introduced acid during early stages extends to prevail in the carbonization stage. In both carbons 9 and 11, the amount of introduced acid is the same in the final stage; however, they differ markedly due to the acid action in the primary impregnation–drying step. Carbon 11 is in fact more comparable to carbon 7 activated with half the impregnation ratio ($x_p = 0.5$), but still shows a lower porosity (V_p, V_{meso}, and V_{micro}).

3.4. Uptake of methylene blue from aqueous solution

Table 5 summarizes the amount of the dye adsorbed (Q_a, mg/g) in the single-bottle tests as shown by the different carbons. It includes also two other characteristics, namely S_{MB} and %R, that is, the area accessible to the dye molecules using the assigned area of 120 A^2 covered by an adsorbed molecule and an aggregate number $n = 2$ [22]. The second parameter (%R) presents the percentage dye removed under test conditions. A ratio of surface area accessible to MB compared to N_2-surface area (S_{MB}/S_N) is also given in the same Table 5.

Table 5
Adsorption capacity of methylene blue, percentage dye removal and area accessible to MB

Sample no.	Q_a [mg/g]	S_{MB} [m^2/g]	S_{MB}/S_N	%R
1	46.9	56	0.58	11.7
2	53.6	64	0.79	13.4
3	45.0	54	0.22	11.1
4	103.2	124	0.34	25.9
5	31.0	38	0.16	7.7
6	42.2	50	0.19	10.5
7	197.6	236	0.98	49.4
8	327.2	391	0.83	81.9
9	384.4	460	0.39	96.1
10	388.5	464	0.85	97.2
11	111.6	134	0.48	27.9
12	193.7	232	0.50	48.5

Chars obtained at either 700 or 900 °C remove low amounts of the dye ($R \sim 12\%$ and $Q_a \sim 50$ mg/g). The porosity accessible to MB increases as temperature increases (0.58–0.79) due to pore widening. Although steam pyrolysis enhances porosity, yet the dyke uptake is small and covers less than 1/4 of the internal surface area. This confirms the abovementioned microporosity character of this carbon.

Chemical activation with $ZnCl_2$ promotes carbon porosity, raises removal capacity, and becomes more accessible to the bulky dye molecules (about 1/3 of internal structure). Potassium hydroxide-activated carbons exhibit diminished uptake of MB as observed in both %R ($\sim 9\%$) and Q_a-value (~ 37 mg/g). Although these carbons were postulated to develop considerable mesoporosity, yet the presence of residual potassium ions seems to inhibit uptake of the cationic dye.

Increased impregnation ratio of H_3PO_4 up to 1.0 is associated with considerable improvement in dye uptake and removal capacity, which becomes almost complete at an X_p of 1.0. A parallel decrease in ratio of area accessible to the dye appears in same direction, indicating the generation of micropores unavailable to the dye molecules. It is well established that adsorption of methylene blue generally measures the porosity within the range of ≥ 15 A° [17]. Carbon-10, activated in the highest impregnation ratio of 1.6, sustains a high uptake and removal capacity of the dye, although it exhibits less than half the surface area of the previous carbon. This should be ascribed to its well-developed mesoporosity as pointed above.

Dilute impregnant inflicts a considerable reduction in efficiency of MB removal, which is due to the less-developed porosity in these carbons. Increased soaking time from 3 to 6 h enhances MB uptake, yet the available ratio of surface area is still the same.

4. Conclusions

Activated carbons are obtained at 500 °C from peanut hulls pre-impregnated with concentrated H_3PO_4 at increased acid/precursor ratios. Porosity developed as a function of increased impregnation ratio to attain a maximum at a value of 1.0, where the product is essentially microporous with high surface area and total pore volume. Additional acid adversely affected the extent of internal porosity but is associated with developed mesoporosity. A 50% diluted H_3PO_4 results in carbons with inferior porosity and promoted mesoporosity; this points to the essential role played by the impregnant in the early impregnation–dehydration stage. Simple carbonization at 700–900 °C produces carbons with low porosity, which is enhanced to some extent consequent to the single-step steam pyrolysis. Traditional activation with $ZnCl_2$ results in a microporous carbon with moderately developed porosity. Chemical activation with KOH (at 500–700 °C) proved to be weakly effective in producing good-quality activated carbons, while mesoporosity is enhanced with temperature. Phosphoric acid-activated carbons are the best in the uptake of MB from aqueous solution (200–400 mg/g). Carbons with low dye uptake (30–100 mg/g) are those chemically activated with $ZnCl_2$, KOH, steam pyrolyzed or chars. Thus, high-quality carbon can easily be produced from peanut hulls through chemical activation with H_3PO_4 in a ratio of acid/precursor of 1.0 (w/w) and heat treated at 500 °C.

References

[1] F. Derbyshire, M. Jagtoyen, M. Thwaites, in: J.W. Patrick (Ed.), Porosity in Carbon, Characterization and Applications, Arnold, London, 1995, p. 228, Chap. 9, et seq.
[2] R.C. Bansal, J.B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York, 1988, p. 2.
[3] W. Heschel, E. Klose, Fuel 74 (1995) 1786–1791.
[4] F. Rodriguez-Reinoso, M. Molina-Sabio, Carbon 30 (1992) 1111–1118.
[5] D. Cazorla-Amoros, D. Ribes-Perez, M.C. Ramon-Martinez, A. Linares-Solano, Carbon 34 (1996) 869–878.
[6] M. Molina-Sabio, F. Rodriguez-Reinoso, F. Caturla, M.J. Selles, Carbon 34 (1996) 457–462.
[7] C.A. Philip, B.S. Girgis, J. Chem. Tech. Biotechnol. 67 (1996) 248–254.
[8] B.S. Girgis, L.B. Khalil, T.A.M. Tawfik, J. Chem. Tech. Biotechnol. 61 (1994) 87–92.
[9] F. Rodriguez-Reinoso, M. Molina-Sabio, M.T. Gonzalez, Carbon 33 (1995) 15–23.
[10] B.S. Girgis, Bull. NRC (Egypt) 22 (1997) 89–95.
[11] H. Teng, T.S. Yeh, L.Y. Hsu, Carbon 36 (1998) 1387–1395.
[12] J. Laine, A. Calafat, M. Labady, Carbon 27 (1989) 191–195.
[13] B.S. Girgis, A.N.A.M. EL-Hendawy, Proc. 1st Arab Conference on Applied Chemistry, Cairo, 1997, pp. 341–352.
[14] D. Lebgaa, P. Ehrburger, E. Papirer, J.B. Donnet, H. Stoeckli, Bull. Soc. Chim. Fr. 131 (1997) 1723–1732.
[15] A. Ahmadpour, D.D. Do, Carbon 35 (1997) 1723–1732.
[16] A. Abdul Rahman, K.R. Cliffe, The 1997 jubilee research event, IChemE (1997) 177–181.
[17] K. Gergova, N. Petrov, S. Eser, Carbon 32 (1994) 693–702.
[18] IUPAC' 84, Pure Appl. Chem. 57 (4) (1985) 603–619.
[19] J.C.P. Broekhoff, B.G. Linsen, in: B.G. Linsen (Ed.), Physical and Chemical Aspects of Adsorbents and Catalysts, Academic Press, 1970, p. 1, et seq.
[20] M.J. Selles-Perez, J.M. Martin-Martinez, J. Chem. Soc., Faraday Trans. 87 (1991) 1237–1243.
[21] V. Gomez-Serrano, C. Valenzuela-Calaharro, J. Pastor-Villegas, J. Biomass Bioenergy 4 (1993) 355–364.
[22] C.H. Giles, A.P.D.D. Silva, A.S. Trivedi, Proceedings of the International Symposium on Surface Area Determination, Bristol, 1969, 1970, p. 317.