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Hazel Nut Shells as Raw Material for Active Carbon

by

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Hazel Nut Shells as Raw Material for Active Carbon

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SUMMARY

The hazel nut shells obtained in Turkey is around 120,000 tons per year and they are used only as fuel for domestic purposes. However it can also be used as raw material for the production of some other valuable products such as active carbon. This work concerns with the carbonisation of the hazel nut shells and the subsequent activation of the carbon obtained. It was observed that it was possible to obtain micro and macroporosities on the same body by carbonising and activating of the hazel nut shells. It was also observed that a surface area as high as 1200 $m^2.g^{-1}$ can be obtained after activation with carbon dioxide to 10–15 % burn-off.

INTRODUCTION

The continuous increase in demand for active carbon makes important to seek new and economical raw materials for the production of it. Not only economical factors, but also the adsorption properties that fulfil the special requirements and sufficient hardness to resist adsorption-desorption cycle in industrial usage are of the qualities which are looked for. At present, coal and petroleum cokes are predominantly used for the active carbon production[1,2]. However, the increasing need for the activated carbon which is purer than that produced from cokes and the more and more tightening measures taken for the environmental protection, always hold in the first place, the production of active carbon for the specific requirements. For example, in some instances low and /or no sulphur containing activated carbon can be needed for some special applications. Under these circumstances to use coal or petroleum coke for the production of active carbon is not suitable.

In this work, the carbonisation and the activation of the hazel nut shells which at present are used only as fuel for domestic purposes, are investigated. The yearly growth of the hazel nut in Turkey reaches approximately to 300,000 tons. If it is considered that 40 % of this sum consists of the shell, the yearly amount of carbonisable cellulosic material is 120,000 tons. So it is apparent that hazel nut shells can be an important source of raw material for the production of active carbon. It was thought that it is appropriate to do some investigative works on this material in the context of carbonisation and activation.

EXPERIMENTAL

The hazel nut shells (HN) were obtained from the Fiskobirlik and were ground to pass 1 mm sieve. 100 g of ground HN was soaked in 2% sodium hydroxide solution for twelve hours to eliminate the components which are soluble in sodium hydroxide. Then it was extracted with water in a soxhlet apparatus for four hours to remove the excess of sodium hydroxide that was followed by a second extractive operation, i.e. soaking twelve and extracting four hours, was performed with 5 % hydrochloric acid. When the extraction was completed, the material in the thimble was removed from the soxhlet apparatus and washed with hot water several times until no chloride reaction was observed with silver nitrate solution in the filtrate. Thus extracted material was dried in a vacuum oven at 80 °C and under 500 mm Hg pressure.

25 g of extracted and dried HN aliquots were carbonised separately in nitrogen and carbon dioxide. The pertinent details of the carbonisation apparatus was described elsewhere[3]. They were then situated in the homogeneous heating zone of the tube furnace. Before the carbonisation, the system was purged for one hour either with nitrogen (500 $ml.min^{-1}$) or with carbon dioxide (200 $ml.min^{-1}$) according to the selected carbonisation atmosphere. The furnace was heated up to 850 °C with a heating rate of 5 $°C.min^{-1}$ while nitrogen or carbon dioxide were flowing at a stated speed. The samples were detained under these conditions for three hours. When the heating period was over, the furnace was let to cool down to the room temperature, keeping on the same flow rate of the gas used for carbonisation. No fusion was observed during carbonisation i.e. the product is shrunken pseudomorph of its parent material[4]. The

yield was approximately 20 % and the particle size was reduced to 0.5–0.7 mm range.

The carbonised samples were activated in a modified Stanton TR-1 recording thermobalance, using carbon dioxide as activator. The activation temperature was 850 °C and the flow rate of carbon dioxide was 200 ml.min^{-1}. The time used for activation was ranged from four to twelve hours. The rate of gasification during activation was 1 % per hour. The active carbons thus obtained were kept in a dessicator over silicagel, under nitrogen atmosphere for further experiments.

All details concerning the sample preparation are given in Table-I.

TABLE–I

Experimental Details of Sample Preparation.

Sample No.	Carbonisation atmosphere	Activation	
		Atmosphere	Time, hrs.
HN1	N_2	–	–
HN2	CO_2	–	–
HN3	CO_2	CO_2	8
HN4	N_2	CO_2	4
HN5	N_2	CO_2	8
HN6	N_2	CO_2	12

A conventional volumetric adsorption apparatus was used for the nitrogen adsorption studies at –196 °C., carbon dioxide adsorptions were measured at –78 °C and 0 °C by C.I.Electronics Mark 2 Model C microbalance. The masses of adsorbed carbon dioxide were converted and reduced to STP volumes[6]. Adsorption equilibrium was reached in one hour at $P \leqslant 0.1$ atm and in twenty minutes when $P > 0.1$ atm where P is the total pressure. The volumes of the macro- and microporosities were measured with a mercury porosimeter. Micro combustion method was used to analyse both HN and HN1 carbons.

RESULTS AND DISCUSSION

The results of the micro combustion analyses of HN and of carbonisation product are presented in Table-II. The low ash and no sulp-

TABLE II
Results of analyses of HN and HN1

Sample	Volatile Matter, %	Ash, %	C, %	H, %	N, %	S, %
HN	38.7	0.7	46.0	5.8	–	–
HN1	–	0.3	92.4	1.1	–	–

hur content of the carbon are noticeable characters of the carbonisation products.

The Langmuir isotherms of nitrogen (at –196 °C) and carbon dioxide (at –78 °C and 0 °C) on carbonised and activated samples are shown in Figures- 1,2 and 3 respectively. The surface areas calculated from the Langmuir Equiaton[7] are tabulated in Table III. In Figure 4, the variation of surface areas (calculated from –78 °C carbon dioxide adsorption data) with time is presented. Employing the volumes of carbon dioxide taken from the adsorption isotherms at 0 °C and Dubinin Equation[8] (D) values are calculated. The developed form of the equation is as follows[9]:

$$\log_{10} V = \log_{10} V_0 - \frac{B\times T^2}{\beta} \log^2_{10}(P_0/P), \quad (B\times T^2)/\beta = D$$

where;

V: amount adsorbed at equilibrium pressure P, V_0: micropore capacity, P_1: saturation vapour pressure of adsorbate at T °K, B: constant, β: affinity coefficient of adsorbate relative to nitrogen.

In this form, a plot of $\log_{10}$ V against $\log^2_{10}$ (P_0/P) is linear, the intercept at $\log^2_{10}$ $(P_0/P) = 0$ equalling to $\log_{10} V_0$, the gradient being equal to (D). According to Dubinin (D) is a measure of the diameter of the microporosity which is not uniform in size and shape in carbons. The range of size and shape is considerably large. But as it is reported (D), is a function of the mean diameter and has a semi-quantitative importance.[10,11]. The variation of (D) values with activation time is presented in Figure 5. V_0 value, determined from Dubinin plot, signifies in experimental terms, the volume of adsorbate in the micropores, but it does not necessarily designates the total volume or space of the micropores within the carbon. This is due to the packing mode of the adsorbate molecules. The packing mode of the adsorbate molecules in the micropore differing in size and shape can not be the same as the arrangement in the bulk liquid phase. Under these circumstances; it can be assumed that converting the volume of adsorbate to the surface area is identical to the transforming the volume of the adsorbate into the real micropore volume.

In the trade of active carbon, it customary to express adsorption capacities as "effective surface areas". To estimate effective surfaces, the molecular cross-sectional areas taken were 16.2 (Å)^2 at –196 °C for nitrogen, 17.0 (Å)^2 and 18.7 (Å)^2 for carbon dioxide at –78 °C respectively[12]. Saturation vapour pressures used for nitrogen was 1.00 atm at –196 °C and for carbon dioxide they were 1.86 and 34.4 atm at –78 °C and 0 °C respectively. The surface areas thus calculated from Langmuir equation and molecular cross-sectional areas are tabulated in Table III.

TABLE III

Surface Areas of the Carbonised and Activated HN

Sample No.	Surface Area, $m^2 .g^{-1}$		
	N_2 -196 °C	Carbon Dioxide	
		-78 °C	0 °C
HNI	99	558	508
HN2*	663	612	462
HN3	897	673	623
HN4	982	809	809
HN5**	1209	1010	1012
HN6**	1573	1527	1277

* : 1 % gasification
** : 10 – 15 % gasification

The variation of micropore volume with pore diameter, calculated using the data obtained from mercury porosimeter measurements is presented in Figure 6.

As it can be seen from Table III, hazel nut shells can be carbonised and activated with carbon dioxide to obtain an end product that can have a surface area as high as 1000 $m^2 .g^{-1}$ or more. The surface area in microporosity of the non activated material (HN1) is only in the range of 500 $m^2. g^{-1}$ calculated from the carbon dioxide adsorption isotherms.

The size of the microporosity of the mentioned sample is only 5–6 Å (see Fig. 6). The surface of the same sample (HN1), calculated from the nitrogen adsorption isotherm is 99 m^2. g^{-1} only. This is a good example for the restricted diffusion of nitrogen molecule encountered in ultramicroporous carbons. Sample HN2 on the other hand presents 600 m^2. g^{-1} surface area at about 1 % of burn-off. By comparing the surfaces of HN1 and HN2, it can be concluded that just a slight activation removes the carbon atoms that restrict the entrance of adsorbate molecules into microporosity[13]. Comparison of the surface areas of HN5 and HN6 (see Table III) with the others shows that the possible highest microposity is reached in the 10–15 % gasification range. The reasonable agreement in surface areas implies to the micropore structure which is accessible to different size of adsorbate molecules at various adsorption temperatures.

The mercury porosimeter measurements indicate the occurence of the microporosities in the 2–20 Å diameter range up to 0.2 ml. g^{-1} pore volume and about 11 % burn-off, as observed in the sample HN4. However, if the activation is extended to 15 % of gasification, the micropores become wider as it is observed in the sample HN6. As it can be seen from the Fig. 6, the porosity widens in such a way that 0.6 ml.g^{-1} pore volume is included in the pore size range from 20 Å to 200 μm diameter. According to Dubinins' classification this range of porosity is named as macroporosity. Thus HN6, in addition to macroporosity, contains about 0.6 ml.g^{-1} of pore volume in microporosity, assuming the density of liquid carbon dioxide is 1.0 g. cm^{-3} (12).

The carbon dioxide adsorption is measured on different carbons at various temperatures[9]. For all these materials i.e. charcoals, carbon blacks, polyvinylcyanide carbon and polyfurfuryl alcohol carbon, the slope (D) of the potential energy equation was found to be in the range of 9.0×10^2 – 17.8×10^2. The (D) values found in this work fall in this range (see Fig. 5). (D) values are inversely proportional to β which is a relative measure of heat of adsorption. Therefore, at constant temperature (D) will decrease as the heat of adsorption increases. Thus if the amount of gas adsorbed is high, particularly at low pressures, (D) values should be low. As it can be seen from the Figures. 2 and 3, the amount of carbon dioxide is considerably high for the carbons prepared from hazel nut shells. Thus, (D) values have to be in their lowest levels. On the other hand most of the molecular sieve carbons have the lowest (D) values[14]. That is, for these materials, the adsorbate molecule has a significant attractive interaction with more than one wall of the pore. Therefore, the heat of adsorption will be high. For carbon dioxide adsorption at 0 °C, (D) is equal approximately to 9.0×10^2 for the HN1 and it steadily increases to nearly 16.0×10^2 as the material is progressively activated in carbon dioxide at 850 °C to 15% gasification (see Fig. 5), that is activation enlarges the pores occured during the carbonisation. If the relatively good concordance of the surface areas is combined with the observation made on the variation of the (D) values and if the mercury porosimeter measurements are taken in consideration, it can be assumed that activation of the carbonised hazel nut shells may offer molecular sieve properties up to a certain extent.

During the carbonisation of the hazel nut shells the loss of orginal weight is approximately 80%, mainly as water and in lesser quantities other small molecules i.e. carbon monoxide, carbon dioxide, detected by gas chromatography, similar to that of the carbonisation of other cellulosic materials[14]. The resultant product is shrunken pseudomorph of the parent material, as the fibrilar structure of the cellulose is not changed during thermal degradation[4]. However, during carbonisation a considerable amount of large shrinkage cracks are developed due to the internal stresses created by heat. They are detected in mercury porosimeter on the sample HN1 (see Fig. 6). The comparatively low surface areas can be attributed to these quite large cracks.

As it was stated before, activation to about 15% gasification is resulted in development of micro- and marcoporosities in the same sample (HN6). This observation can be interpreted such as that the surfae oxidation which takes place during activation is not even throughout the surface. Thus the occurence of the selective oxidation up to a certain extent can be assumed. The same sort of event is observed in the carbonisation and activation of polyfurfuryl alcohol[2,15]. This unevenly proceeding selective oxidation is connected to the presence of some inorganic impurities[16]. It is thought that in activation process C-CO_2 interaction is initiated by the catalytic action of the existing inorganic atoms (impurities) at some centers of the surface and once it is started it turns into an autocatalytic process which may extend the gasification up to the production of macropores. On the other hand, in some parts of the surface where no inorganic atoms are present C-CO_2 interaction proceeds to its normal way resulting in microporosity. Thus the pore structure obtained in these cases contains micro- and macroporosities on the same body as it is observed in the HN6 carbon. This effect may however be advantageous in some industrial applications, as this type pore structure gives improved transportation to adsorbate molecules between the centers of the carbon particles[17]. The selective oxidation can also be used to explain the possible molecular sieve properties.

In some industrial applications of the active carbon, on the other hand, the adsorption of the polar substances has to be considered. In these cases, the structure of the active carbon and the extent of surface-oxygen complexes are of importance[18]. If heat treatment is used in the regeneration of the active carbon after adsorption process, the stability of the surface-oxygen complexes becomes an important property to take into consideration in the first place, as these complexes are directly influential on the deterioration of the surface and on the consumption of active carbon[19]. The stability of the surface-oxygen complexes was found to be quite satisfactory (80% at 250 °C) for the carbons prepared from the raw materials containing oxygen in their original forms, such as polyfurfuryl alcohol (2% oxygen) and "Whatman" ashless filter paper (cellulose, 4% oxygen). The carbonisation of these materials at 850 °C followed by 30% of gasification produces active carbons that have appreciably stable surface-oxygen complexes[20]. If it is remembered that the basic component of the hazel nut shells is cellulose and that the carbon produced from it contains approximately 3% of oxygen, they can form a raw material perfectly suitable to produce active carbon that exhibits a high surface-oxygen complex stability.

As it was stated in the introduction section that the production of the hazel nut amounts to 300,000 tons per year[21]. This amount correspons to 120,000 tons of carbonisable cellulosic material per year, assuming 40% of the whole fruit consists of the shell. The hazel nut shell which at present solely used as fuel for domestic purposes, offers a potential for the production of 1900 tons/year vegetable oil, 47,000 tons/ year of destructive distillation residue and 55,000 tons/year different sort of active carbons. As it can be seen from this study, by carbonising hazel nut shell, it is possible to meet the need of the active carbon of the country. Further, it is still possible to obtain a tarry residue which is useful as a raw material to produce veterinary medicines.

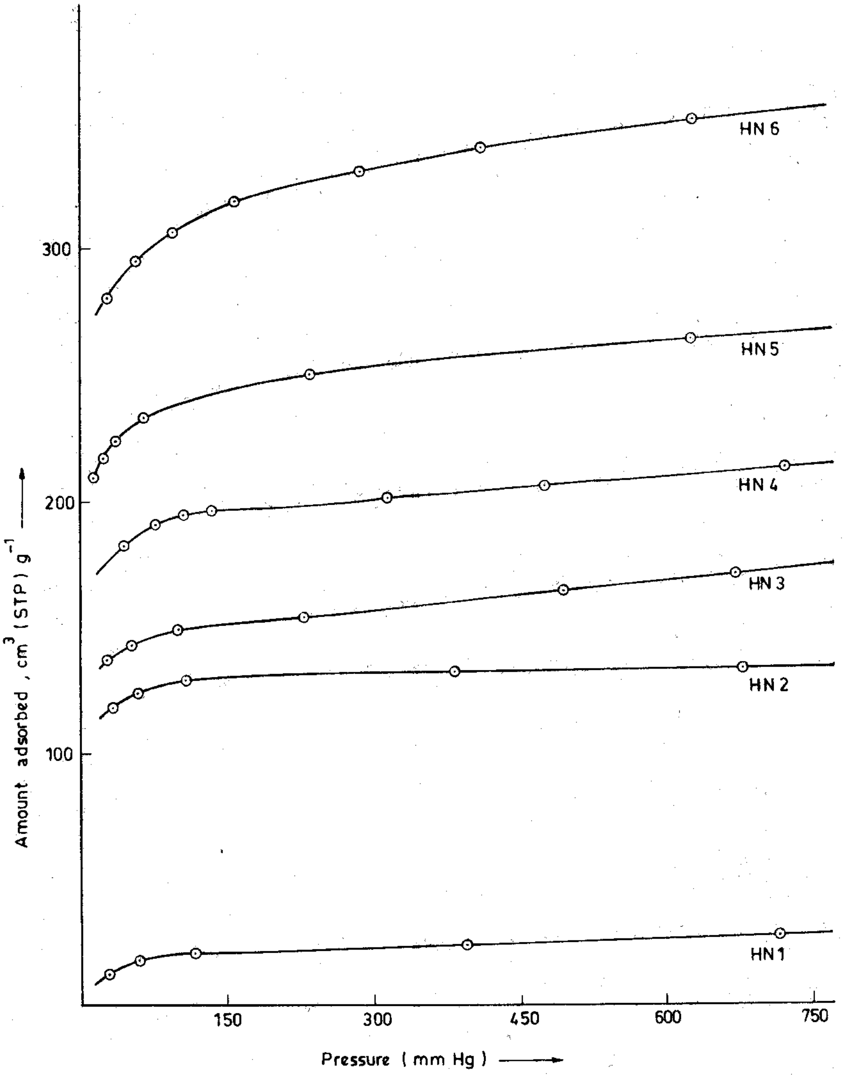

Fig 1. Langmuir istoherms of nitrogen on carbonised and activated hazel nut shells at –196 °C.

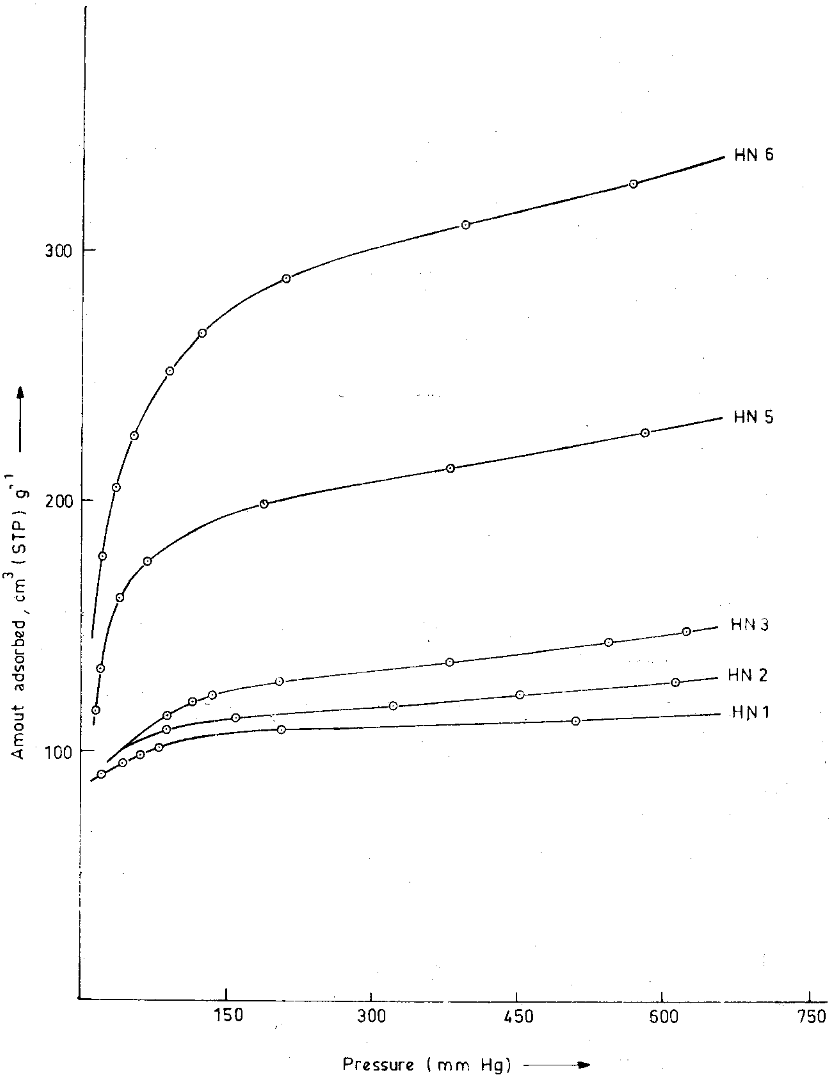

Fig 2. Langmuir isotherms of carbon dioxide on carbonised and activated hazel nut shells at −78 °C.

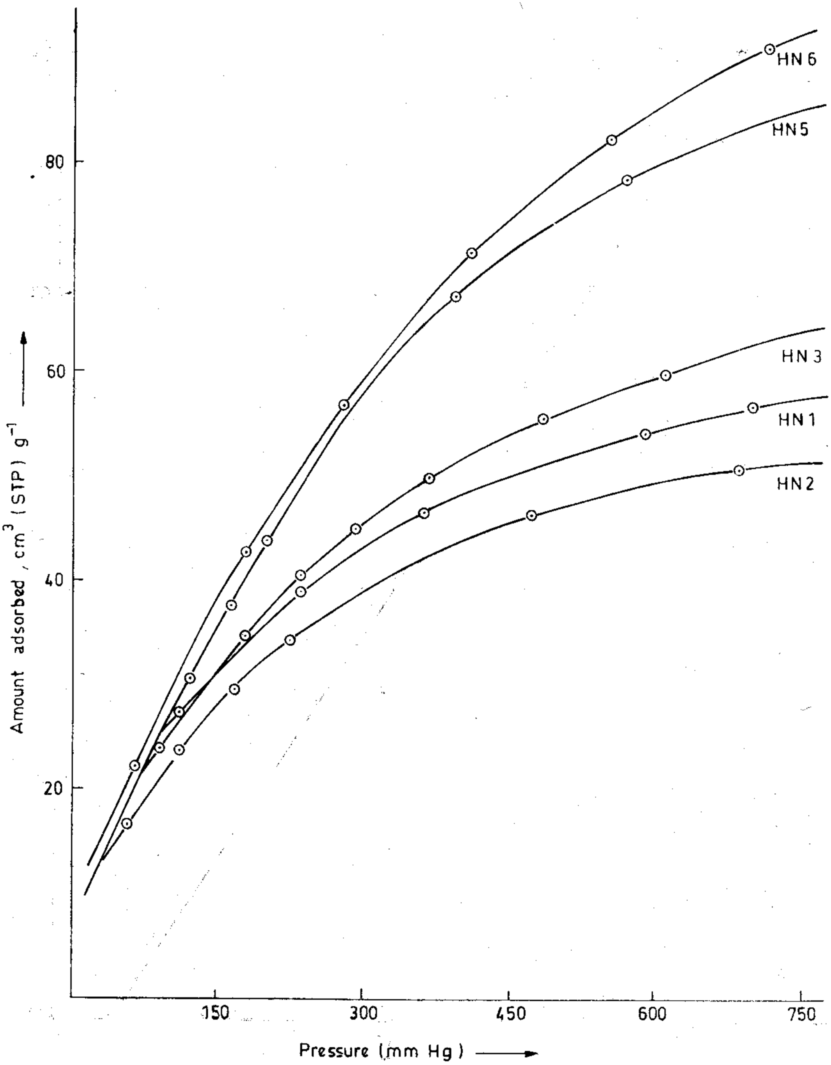

Fig 3. Langmuir isotherms of carbon dioxide on carbonised and activated hazel nut shells at 0 °C.

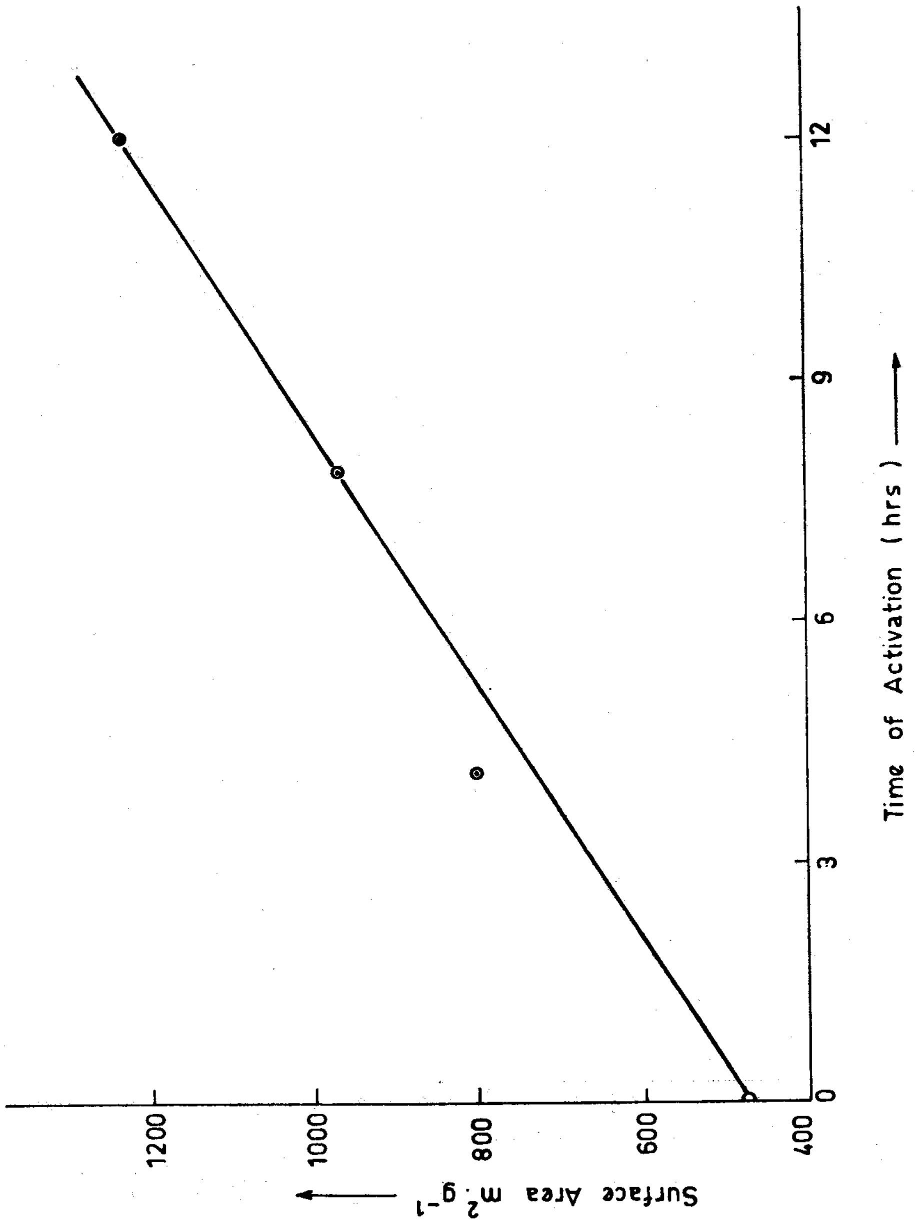

Fig 4. The development of surface area with time of activation, calculated from −78°C carbon-dioxide adsorption.

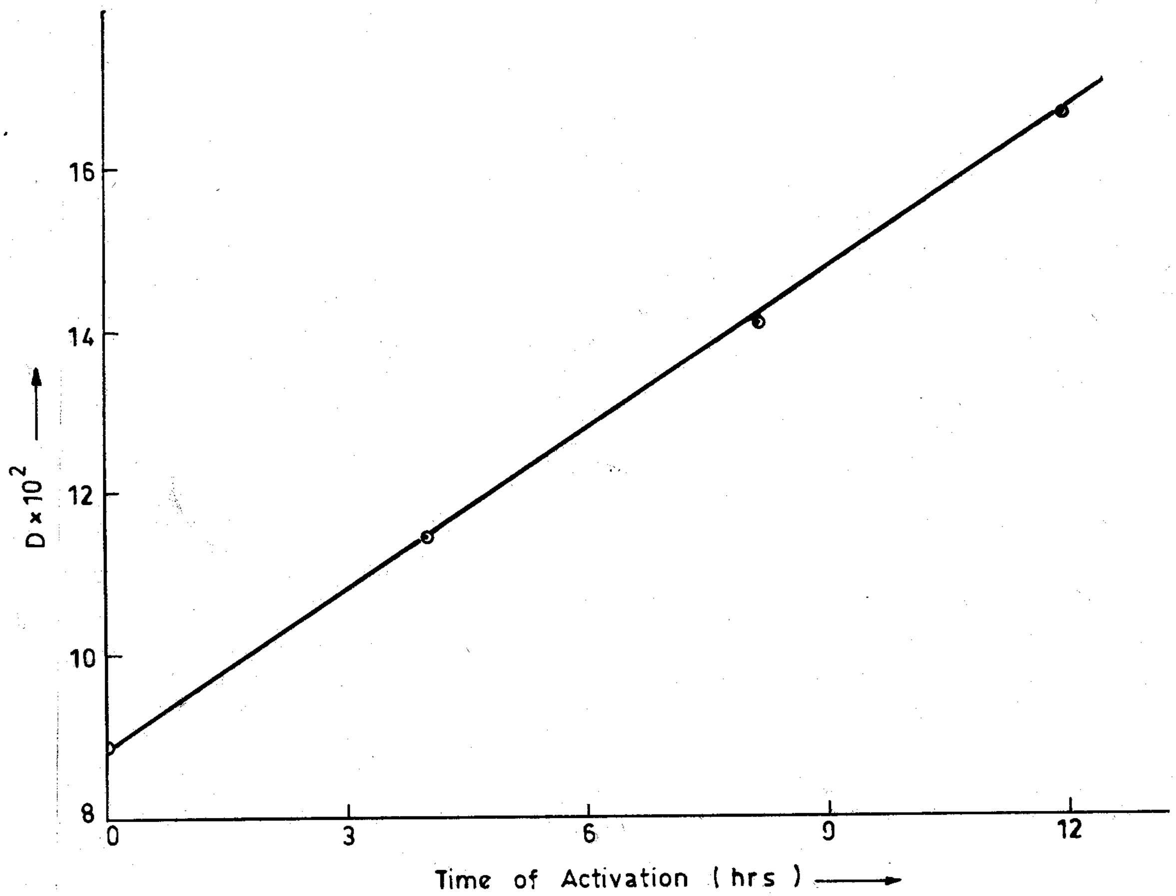

Fig 5. The variation of "D" values with time of activation calculated from 0 °C carbon dioxide istoherms.

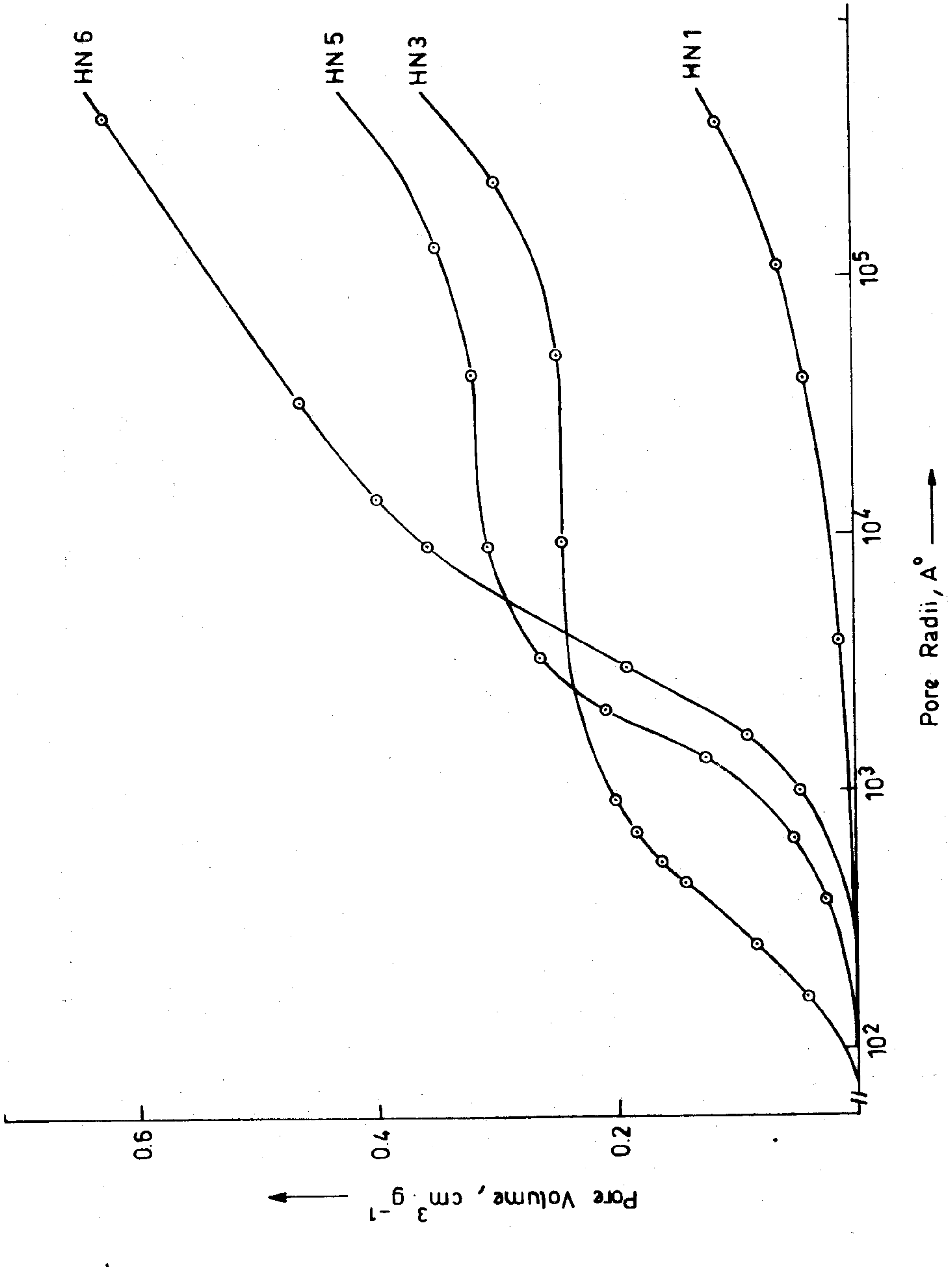

Fig 6. The variation of pore valume with pore diameter.

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ÖZET

Ülkemizde Yılda yaklaşık olarak 120.000 ton kadar fındık kabuğu artık olarak ele geçmekte ve hemen hemen tamamı ısınma için yakıt olarak kullanılmaktadır. Halbuki bu artığın, örneğin aktif karbon üretiminde olduğu gibi, yararlanılabilir diğer ürünlerin elde edilmesinde ham madde olarak kullanılması mümkündür. Bu çalışmada fındık kabuğunun karbonizasyonu ve elde edilen karbonun aktivasyonu konu olarak seçilmiştir. Karbonizasyon ve aktivasyon yolu ile değişik büyüklüklerde gözeneklerin aynı örnek üzerinde elde edilebileceği ve % 10–15 kadar gazlaştırma ile 1200 $m^2.g^{-1}$ değerine ulaşabilen yüzey alanlarının elde edilebileceği gözlenmiştir.