PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 41, NO. 1, PP. 25-39 (1997)

ACTIVATED CARBON FROM WASTE MATERIALS

Attila BÓTA*, Krisztina LÁSZLÓ*, József VALYON**,
Lajos György NAGY**, Günter SUBKLEW*** and Milan J. SCHWUGER***

* Institute for Physical Chemistry
Technical University of Budapest
H-1521 Budapest, Hungary
**Central Research Institute for Chemistry of the Hungarian Academy of Sciences
(CRIC of the HAS) P.O.Box 17
H-1525 Budapest, Hungary
*** Institute of Applied Physical Chemistry
Research Center Jülich
D-52425 Jülich, Germany

Received: March 1, 1997

Abstract

Waste materials of various origin, such as domestic waste, agricultural by-product (grain husk), tyre rubber, and the light fraction of shredded interiors of cars ('autoshredder light') were converted into final products of active carbon properties by pyrolysis and subsequent steam activation of the waste. Products were tested using the standard measurements for adsorption of iodine and methylene blue. The porous structure was characterized by small angle X-ray scattering, low-temperature nitrogen adsorption measurements and mercury porosimetry. The extent of gasification (burn-off) on activation, the adsorption characteristics, and the pore-size distribution were found to reflect the composition and the fine structure of the waste used as raw material. High surface area microporous active carbon was obtained from agricultural wastes. The burn-off of the pyrolyzed rubber consisting mainly of chemically resistant carbon black was relatively small and activation resulted in essentially meso- and macroporous carbon. Organics in the domestic waste and in the 'autoshredder light' were converted into high surface area active carbon, however, the mass related adsorption capacity of the products was small due to the high fraction of inert inorganic components in the preparations.

Keywords: activated carbon, activated carbon from waste materials.

1. Introduction

Active carbons are produced from fossil coal or various organic raw materials [1]. Generally, good quality adsorbents can be obtained from agricultural refuse [2,3]. The preparation process consists of two subsequent steps. In the first step, usually referred to as pyrolysis or carbonization, the starting material is subjected to dry distillation with exclusion of air. The intermediate obtained is activated through partially gasifying (or burning off) the carbon in reaction with steam. The properties of the carbon products can be controlled by setting the key variables of the activation procedure, such as the temperature, the composition of the activating gas, and the contact time [2,4]. First the amorphous carbon and then, if the activation procedure is continued, whole layers of the carbon crystallites can burn off. As a result, pores are generated; first small pores only and then larger and larger ones [5]. The relations between the processing parameters and the development of porous structure have been extensively studied using various raw materials [6-11].

The neutralization and/or the permanent disposal of industrial and household wastes are quite expensive ways for treating the waste problem and the methods applied for waste processing often involve environmental hazards. The problem can be at least reduced by converting part of the waste into useful products, for instance into products with active-carbon-like properties applicable for abating environmental pollution, e.g., for wastewater purification. Carbon-containing wastes appearing in ever increasing quantity in the industrialized societies, e.g., domestic waste, packing materials, and tyres, are not considered favorable raw materials for the preparation of activated carbon because their composition can be variable and inhomogeneous, furthermore, their carbon content is often low. In spite of these drawbacks investigation on the use of different waste materials for producing activated carbon is strongly motivated by the environmental concerns mentioned. Part of the difficulties can be overcome by selective collection, and processing of the waste. The neutralization of industrial or domestic wastes is often carried out by direct incineration in an oxygen-containing atmosphere or by pyrolysis at 500 – 700 °C with exclusion of oxygen. During pyrolysis, as in the first step of the active carbon preparation, the organic fraction of the waste gets partly carbonized.

In the present work different selectively collected and pyrolyzed wastes and, for comparison, an agricultural by-product were studied. The carbonaceous residue was used as precursor for the preparation of carbon adsorbents by steam activation. The carbon content and the structure of the carbon in the precursors were different. These factors, and the amount and composition of the inorganic components present in the waste were found to determine the pore structure and the adsorption properties of the products obtained.

2. Experimental

2.1. Materials

The wastes investigated as raw materials are as follows: grain husk (HSK), domestic waste (DOW), tyre rubber (GUM), and the light fraction of the shredded interior parts of cars which is consisting mainly of plastics and textile and referred to here as 'autoshredder light' (ASL). The symbols given in parentheses are used for identifying the product made from the corresponding raw material by pyrolysis and activation. The tyre rubber and the 'autoshredder light' were obtained from a car demolition plant, the domestic waste was collected from households. The wastes, including the grain husk which is an agricultural by-product often used for the preparation of commercial activated carbon, were pyrolyzed in incineration plants in Germany.

2.2. Preparation of the Activated Samples

The carbonaceous samples obtained from the incineration plants with unknown thermal history were briquetted first, then a second pyrolysis was carried out at 700 °C in an inert atmosphere for half an hour to form the pyrolyzed precursor of the activated material.

Briquetting was carried out by adding to the dried sample 20 wt % bitumen dissolved in xylene, evaporating the solvent and pressing the solid with about 40 kN/m^2 pressure into platelets of about 3 mm thickness. Platelets were crushed and sieved to get particles of 3 – 5 mm size. The addition of bitumen increased the carbon content of the pyrolyzed materials by 3 – 4 wt %.

Samples were activated in a rotating quartz reactor at 900 °C in an equimolar steam–nitrogen mixture flowing at a rate of 18 g/hour for 30 min [12]. The weight loss due to activation (the extent of burn-off) was determined.

2.3. Characterization of the Materials

Thermoanalytical curves were determined by heating the homogenized and dried materials pre-pyrolyzed in an incineration plant up to 1000 °C in nitrogen at a rate of 10 °C/min, by using a Netzsch STA 409 type simultaneous thermoanalyzer (Netzsch, Germany). The weight loss was assigned to the amount of volatile organic components also removed in the carbonization process. The ash content was determined similarly by measuring the weight of the residue after heating up the sample in air.

Activated products were characterized by the adsorption capacity for iodine and methylene blue, the specific surface area, the volume of pores, and their size distribution. The apparent (bulk) and the 'true' densities were also determined. The 'true' density of the solid matrix was determined by the helium pycnometer method. The bulk density was calculated from the volume of the pycnometer closely packed with the powdered sample and from the sample weight.

Iodine and methylene blue adsorption was determined as described in the booklet of Norit Testing Methods [13]. In the industrial practice these kinds of measurement are generally applied as fast test methods for controlling the quality of carbon adsorbents. According to experience 1 mg iodine adsorbed under the test conditions corresponds to about 1 m^2 surface area determined by the BET method. The quantity of the methylene blue adsorbed is useful to characterize the sorption properties of a carbon towards large organic molecules.

The determination of the low-temperature (77 K) adsorption isotherms for nitrogen and the calculation of the specific surface area and the pore size distribution on the basis of the recorded sorption data was carried out using a type Autosorb1 (Quantachrome, Syosset, New York, USA) computer controlled automatic surface analyzer and data processing system. The pore size distribution of the mesopores and the specific surface areas of the samples were calculated using the Barett–Joyner–Halenda- and the multipoint BET method [14], respectively. Brunauer's t-method [15] was applied to analyze the size distribution of micropores.

Macropores were characterized by mercury porosimetry using a Carlo Erba MI. NE. 100 type poresizer (Carlo Erba, Milano, Italy).

The solid matrix of the samples was studied by small angle X-ray scattering (SAXS) technique. The sample was placed into a 1 mm thick sample holder and covered with Mylar foil. The scattering of Ni-filtered Cu $K\alpha$ - radiation ($\lambda = 0.1542$ nm) was recorded in the $1.5 \times 10^{-2} - 1$ nm^{-1} range of scattering variable, defined as $s = 2(\sin\theta)/\lambda$, where 2θ and λ are the scattering angle and the wavelength, respectively, using a classical Kratky camera and a proportional counter (Anton Paar, Graz, Austria). Data were evaluated by the method based on the moments of the scattering intensity function [16].

3. Results and Discussion

The homogenized and dried wastes pyrolyzed in an incineration plant were characterized by thermoanalytical measurements (*Table 1*). The volatile fraction was found relatively high for each sample indicating that only partial carbonization occurred in the incinerator. Therefore, a second pyrolysis was applied after briquetting to obtain adequately carbonized precursors for the activation treatment. The ash content of the carbonized samples obtained from domestic waste and autoshredder light fraction was much higher than that of the samples obtained from grain husk and tyre rubber and higher than that of most commercial activated carbons. Ash was found

Table 1

Composition of the pyrolyzed materials[a]

Raw material	Ash[b] wt%	Volatile matter[c] wt%	Carbon[d] wt%
Grain husk	11	13	76
Domestic waste	57	31	12
Auto tyre rubber	19	10	71
'Autoshredder light'	65	25	10

[a] All data were determined by thermogravimetric measurements. Large amounts of samples were powdered and homogenized. About 0.1 g of each sample (W) was heated up to 1000 °C at a rate of 10 °C/min. The final weight was determined in air (A) and nitrogen(N).

[b] $(A/W) \cdot 100$

[c] $((W - N)/W) \cdot 100$

[d] $((N - A)/W) \cdot 100$

Table 2

Degree of burn-off during the steam activation of the pyrolyzed wastes and properties of the activated samples

Activated materials	Burn-off[a] [%]	Density[b] [g/cm^3]	a_s,B.E.T. [m^2/g]	Iodine number [mg/g]	Methylene blue ads. [g/100g]
HSK	39	2.03 ± 0.01	1047	810	17.5
DOW	35	2.65 ± 0.02	89	105	2.3
GUM	18	2.04 ± 0.01	136	170	2.0
ASL	30	2.47 ± 0.01	205	280	6.0

[a] Calculated from the weights before and after the activation treatment.

[b] The 'true' density was measured by helium pycnometry.

to consist mainly of silicates insoluble in water. The higher ash contents are reflected in the higher densities of the activated products (*Table 2*).

In the present work the same steam activation was used for all the carbonized precursors to transform them into carbon adsorbent..

Because of the high carbon and the low ash content the pyrolyzed grain husk is a favourable raw material for the production of activated carbon. The product obtained here is quite similar to commercially available microporous active carbons suggesting that a suitable raw material can be converted to good-quality activated carbons with the procedures used in the present work. Data given for HSK can be used as reference when a comparison of the other processed wastes to an ordinary active carbon is intended to be made.

The carbon-to-gas conversion on activation, i.e. the extent of 'burn-off' is given in *Table 2.* While the GUM precursor contained about the same amount of carbon as the HSK precursor, the burn-off was relatively low probably because the carbon present in the GUM sample is mainly in the form of chemically more resistant carbon black particles. The too high carbon loss is unfavourable especially for 'ash rich' carbonized samples since it not only results in pores but decreases also the amount of the activated carbon component in the adsorbent product. It was found, however, that the weight losses given for the samples of high ash content as 'burn-off', i.e. for DOW and ASL cannot be directly related to the amount of carbon gasified since colloidal-size inorganic particles are carried away from the samples by the nitrogen–steam mixture passing through the reactor during the activation treatment. This may explain that no simple correlation could be established between the extent of burn-off and the adsorption properties.

The BET areas, the iodine and the methylene blue numbers generally used for characterizing carbon adsorbents indicate that very different products were obtained from the different starting materials (*Table 2*). Comparison of the corresponding numerical values of the BET area and the iodine number of the samples shows that, with the exception of HSK, the numbers differ more than expected for common activated carbons. The adsorbents showing higher adsorption affinity towards iodine than nitrogen must be of a chemical character different from that of plain active carbons. Thus, data suggest that the inorganic components present in the waste have a modifying effect on the surface properties of the carbon product.

Both the porous structure and the chemical character of the adsorbent is reflected in the strength of interaction with the adsorbed nitrogen. The well-known D–R isotherm equation derived on the basis of the volume-filling theory of micropores was applied to fit the low-pressure part of the experimental isotherms shown in *Fig. 1.* The parameters of the D-R equation were determined. The characteristic energies of adsorption (E_a) which provide the differential molar heat of adsorption at an adsorbed amount equal to the 1/e fraction of the saturation capacity were compared for the preparations. The characteristic energies are 6.5 and 7.3 kJ/mol for the ASL and GUM, respectively. A low E_a value of 3 kJ/mol characterizes the adsorption interaction of nitrogen with DOW while a value as high as about 15 kJ/mol was obtained for HSK. The E_a value of HSK which is significantly higher than that of the other samples can be attributed to the pronounced microporous character of the preparation. The data for ASL, GUM and DOW correspond essentially to adsorption on surfaces within larger pores where the strength of interaction may also be affected by the inorganic impurities present.

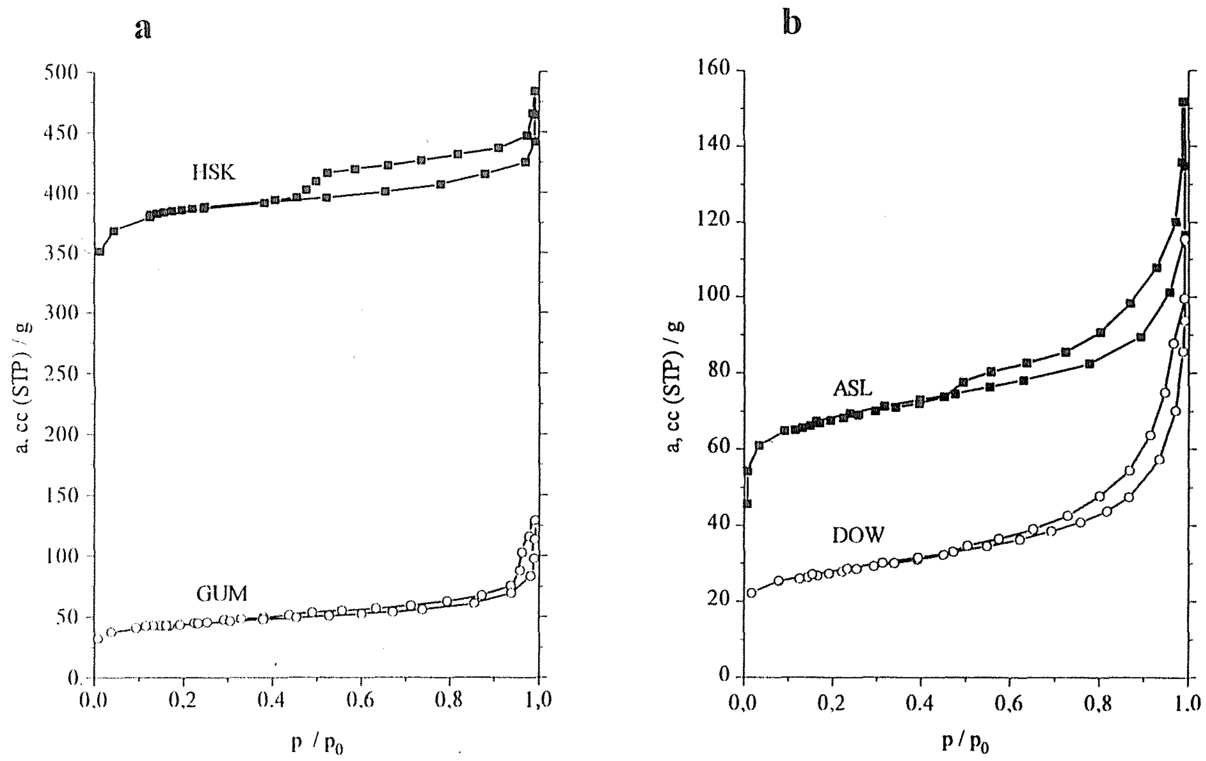

Fig. 1. Adsorption isotherms for nitrogen at 77 K on adsorbents prepared from carbon-containing wastes of different origin by pyrolysis and steam-activation. Grain husk (HSK), tyre rubber (GUM) (a); 'autoshredder light' (ASL), and domestic waste (DOW) (b) were used as raw material. Before the measurements the samples were pretreated by evacuation at 570 K for three days

Table 3
Total volume of the pores in different pore size ranges

Samples	Volume of micropores[a] [cm^3/g]	Volume of the mesopores [cm^3/g] N_2-ads.[b]	Volume of the mesopores [cm^3/g] Hg-porosimetry[c]	Total volume of pores [cm^3/g] Hg-porosimetry[d]
HSK	0.650	0.058	0.083	0.862
DOW	0.056	0.105	0.096	0.564
GUM	0.081	0.210	0.668	1.106
ASL	0.125	0.076	0.087	0.670

[a] Determined by the B-point method [14] from the isotherms in *Fig. 1*.
[b] The volume of the pores in the pore size range of 4 < Radius, nm < 100 obtained from the adsorption isotherms as the volume of liquid state N_2 filling up the pores in the $0.65 < p/p_0 < 0.99$ range of relative pressure.
[c] The volume of the pores in the pore size range of 4 < Radius, nm < 100 obtained by mercury porosimetry as the volume of mercury filling up the pores in the 77.8 to 1947 bar pressure range.
[d] The volume of the pores in the pore size range obtained by mercury of $4 <$ Radius, nm $< 0.6 \cdot 10^3$ porosimetry as the volume of mercury filling up the pores in the 1.3 to 1947 bar pressure range.

The porous structure of the preparations was characterized in the pore-size regions of the micro- and mesopores on the basis of the low-temperature adsorption/desorption isotherms for nitrogen (*Fig. 1*). The meso- and macropores were studied by mercury porosimetry. The pore volume of the micropores in the samples is small when compared to that of HSK, but a significant pore volume can be assigned to the size region of the mesopores (*Table 3*). Data given in *Table 3* allow to compare the mesopore volumes determined by two independent methods, i.e., by adsorption and mercury porosimetry. Considerable difference was found in the differently measured data for the GUM. This is suggesting that in this sample a large fraction of the pores is closed and not available for adsorption of nitrogen, but, these pores can break open for intrusion of mercury under the high pressure applied in mercury porosimetry.

The adsorption isotherms of *Fig. 1* were converted into t-plots (*Fig. 2*). The t-plots provide the adsorbed amount (a) as a function of the average thickness of the adsorbate layer on a flat surface with an identical surface structure as the adsorbent examined (t). It should be understood that for a non-porous material the t-plot is a straight line starting from the origin and its slope is proportional to the surface area. For a porous material the slope decreases if some of the pores are filled up and hereby the surface available for adsorption decreases. Upward deviation from the straight

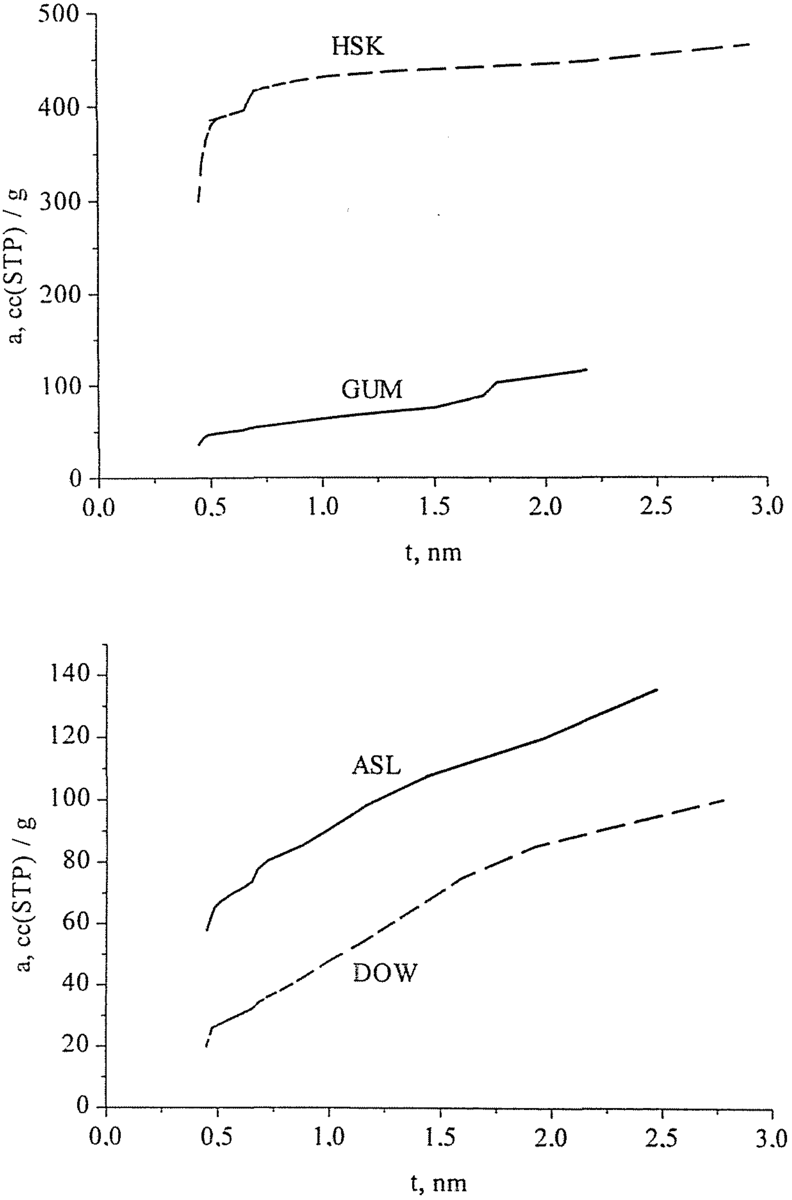

Fig. 2. t-plots calculated from the isotherms in *Fig. 1.* The average thickness of the adsorbed layer (t) on a flat surface as a function of the relative pressure of nitrogen (p/p_0) was obtained using the Halsey equation ($t = 0.34[-5/lnp/p_0]^{1/3}$).

line indicates the presence of capillary condensation in the pores. Thus, not only 'a' but also 't' must be known as a fuction of the relative pressure for constructing a t-plot. In lack of appropriate t-functions for different materials the generally applied treatment to the problem is the use of some kind of a 'universal t-curve' [14]. In the present work the t-function given by the well-known Halsey equation was adopted for calculating the t-plots. Although this approach involves some inaccuracy, the t-plots obtained allow to draw qualitative conclusions of the pore structures of the preparations studied. The micropore character of the HSK is convincingly demonstrated. In the DOW and ASL samples pores with all sizes are about equally represented from the size ranges of micropores to mesopores, however, the total micropore volume is small since micropores can develop mainly from the carbon-containing components present originally in relatively small amounts in the raw materials (*Fig. 2*).

In the curves representing the distribution of the mesopore volume by pore size a sharp peak appears at about the 2 nm pore radius for all the samples (*Fig. 3*). A second peak can be observed on the curve of the GUM sample around 20–30 nm. This peak may reflect the original structural feature of the raw material since the carbon black used in rubber manufacturing consists of crystallites of about the same size.

Mercury porosimetry revealed pronounced differences between the macroporous structure of GUM and the rest of the samples (*Fig. 4*). The macropores of $10^3 - 10^4$ nm radius were not produced during activation from the precursor of GUM probably because the resistance of the carbon black in this sample is higher against gasification during steam activation than that of the carbonaceous components of the other precursors.

The small angle X-ray scattering (SAXS) curves of the activated samples are shown in *Fig. 5*. On replotting the data according to the Guinier approximation, no linear log I vs. s^2 plots were obtained even for the smallest values of the s variable. This means that the size of the particles is far from uniform in the materials and a single Guinier radius cannot be assigned to these colloidal systems. In order to determine characteristic particle sizes from the SAXS measurements, the method of moment was applied. The calculated parameter was the reduced chord length (l_r). The reduced chord length represents the average length of all segments drawn across the matrix in all directions, which is defined by the following equation:

$$l_r = \int_0^\infty s l(s) ds / 2\pi \lim_{s \to \infty} s^3 l(s) \; .$$

The correlation length and the corresponding average crystallite size were not determined since they could not be derived from the scattering pattern

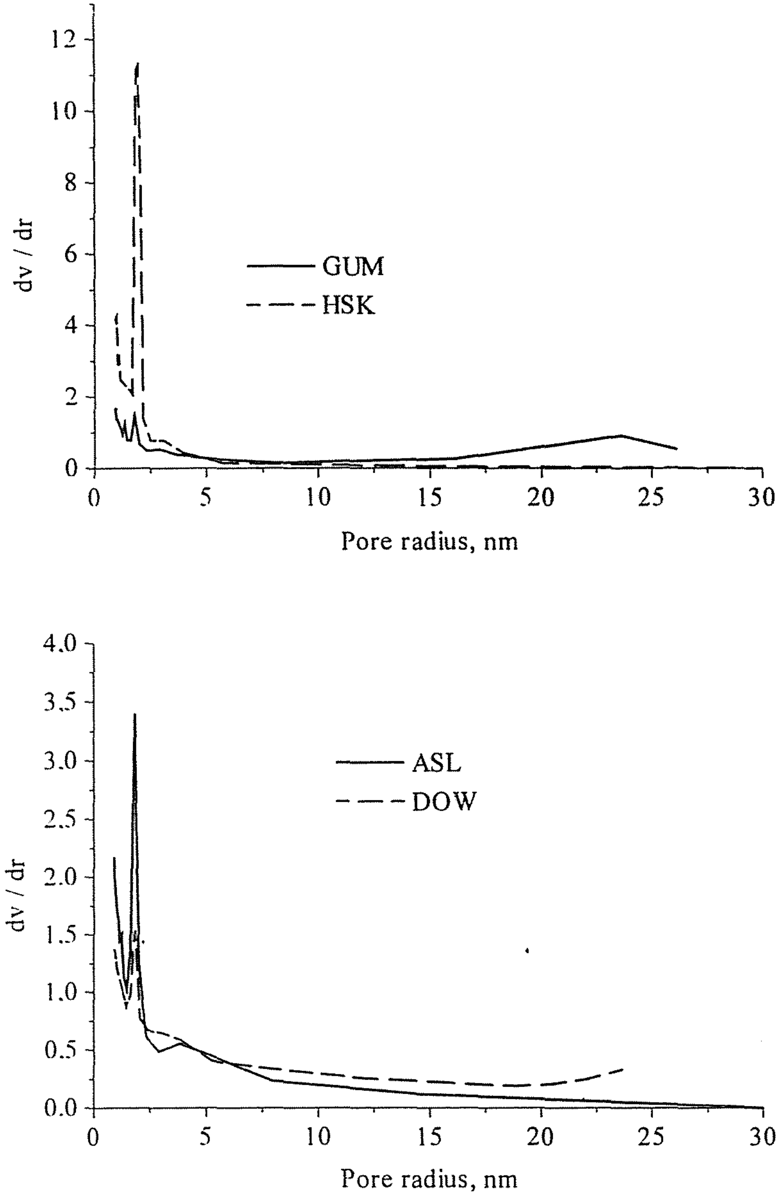

Fig. 3. Size distributions of the mesopores calculated by the BJH method [14] from the isotherms of *Fig. 1*

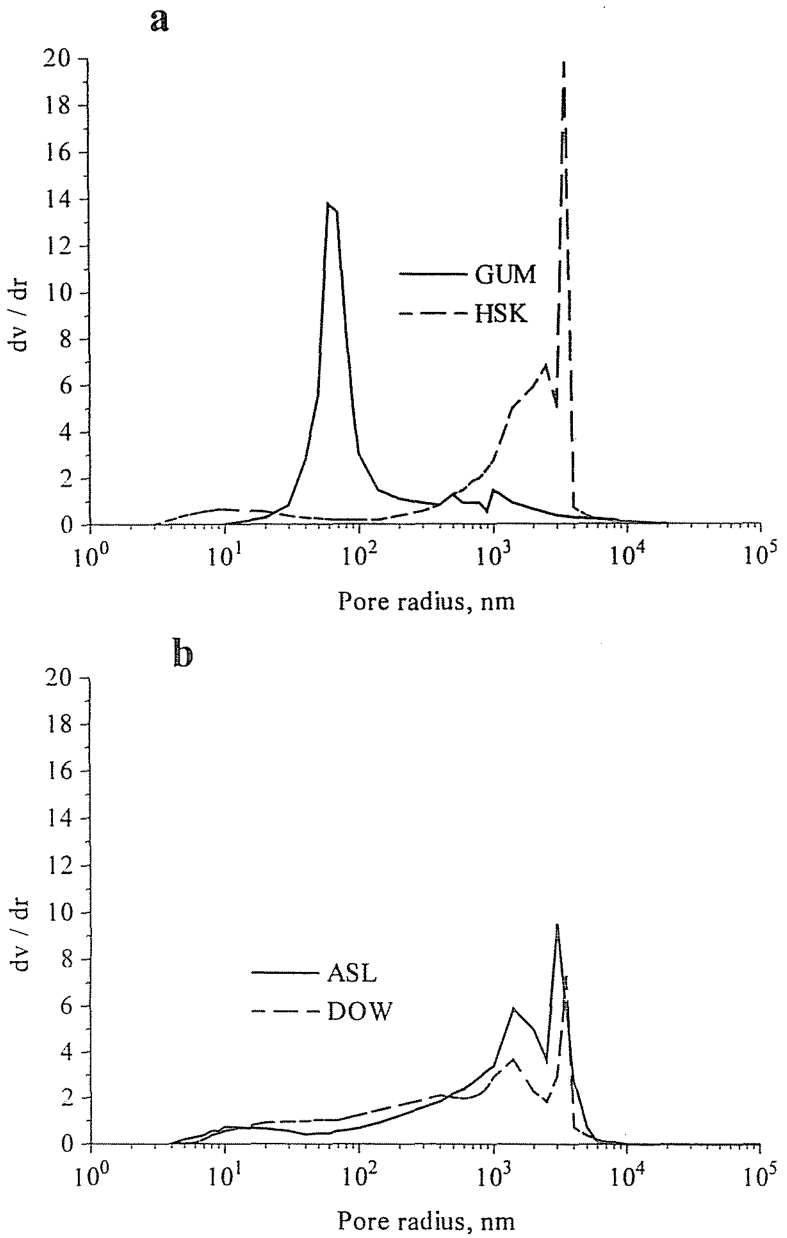

Fig. 4. Size distributions of the meso- and macropores determined by mercury porosimetry for the activated grain husk (HSK), tyre rubber (GUM) (a); 'autoshredder light' (ASL), and domestic waste (DOW) (b)

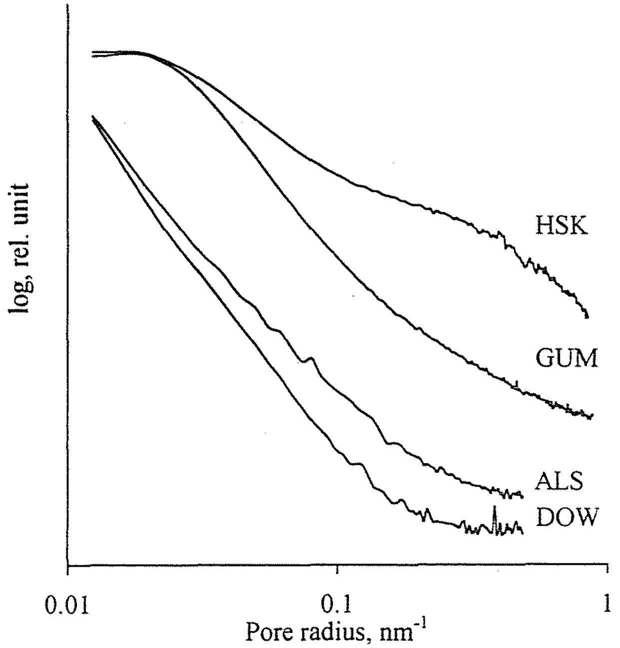

Fig. 5. Small angle X-ray scattering curves of the activated samples. The scattered intensity (I) was plotted against the absolute value of the scattering vector (s)

with the accuracy required to be of any use in characterizing the preparations studied.

The porous material was considered as a two-phase system comprising solid matter and voids (pores). From the reduced chord length the average lengths in the solid and the pores, l_m and l_p, respectively, were derived as $l_m = l_r/P$, and $l_p = l_r/(1-P)$, where P is the volume fraction of the pores in the sample [17]. The calculated parameters are given in *Table 4*. l_p was found not to differ very much from the corresponding pore size determined by the adsorption method. It is conceivable that the average chord length determined carries meaningful information about the texture of the preparation built up of elements non-uniform in size. The chord length in the matter gives the one-dimensional average thickness of the pore walls. The walls in our samples are significantly thicker than 0.5 – 1.0 nm usually obtained for microporous systems. Assuming cylindrical pore geometry and taking l_p as the average pore diameter the specific surface areas of the samples (S_p) were calculated (*Table 4*). Since the contribution of the dimensions of the larger voids is larger to the average pore size than the contribution of the surface of the same pores to the BET surface area, it is expected that the surface area obtained from SAXS data is smaller than the area determined by the adsorption methods. With the exception of the results for HSK, the SAXS surface areas are larger than the corresponding areas calculated from the adsorption isotherm of nitrogen (cf. data in *Table 2* and *4*). This may suggest that the 'ash rich' samples have closed pores which are detected by SAXS but are inaccessible for the nitrogen adsorbate.

Table 4

Structural parameters determined by small angle X-ray scattering measurement

Samples	Porosity[a]	Range of inhomogeneity l_r [nm]	Range of inhomogeneity in matter l_m [nm]	Range of inhomogeneity in pores l_p [nm]	Specific surface area[b] S_p [m^2/g]
HSK	0.62	1.6 ± 0.1	2.2	5.9	765
DOW	0.55	4.5 ± 0.2	7.8	9.5	183
GUM	0.58	3.0 ± 0.1	4.2	10.4	378
ASL	0.64	1.6 ± 0.2	2.3	5.5	647

[a] Calculated as $P = 1 - \rho/\rho He$ where ρ and ρHe are the bulk and the true densities, respectively.

[b] Calculated as $S = 4 \cdot 10^3(1 - P)P/(l_r\rho)$ where ρ is the bulk density.

4. Conclusions

Using the pyrolysis/steam activation procedure, commonly used for the preparation of active carbon adsorbents, for different selectively collected waste materials, even for those of low carbon content, wastes can be converted into products showing properties which are in some respects similar to those of activated carbons. Voids among irregularly stacking carbon crystallites formed a microporous pore system only when an agricultural by-product was used as starting material. Macroporous adsorbents of relatively small pore volume were obtained from the 'ash rich' wastes due to their low carbon content. The high burn-off was found to result in pores of large sizes. Shorter activation of the precursors obtained from such samples is suggested to generate microporous adsorbents with larger surface areas. The chemical character of the surface influencing the adsorption properties depends on the amount and nature of the non-carbonaceous components of the waste used as raw material. The adsorbents were tested in water purification using different model waste water systems. The promising results obtained will be discussed in a following study.

Acknowledgement

This work was supported by the Scientific and Technological Working Program between Hungary and Germany under Project No. 65 and Hungarian Research Fund (OTKA) No. 1443. We thank Dr M. Hegedüs (CRIC of the HAS, Budapest, Hungary) for the porosimetric measurements.

This paper is dedicated to the memory of Claus Frischkorn PhD., who was the promoter of these studies.

References

1. SMISEK, M. – CERNY, S.: Active Carbon, Manufacture, Properties and Applications. Elsevier, Amsterdam (1970).
2. GERGOVA, K. – GALUSHKO, A. – PETROV, N. – MINKOVA, V.: *Carbon*, Vol. 30, p. 721 (1992).
3. RODRÍGUEZ-REINOSO, F. – MOLINA-SABIO, M.: *Carbon*, Vol. 30, p. 1111 (1992).
4. WIGMANS, T.: *Carbon*, Vol. 27, p. 13 (1989).
5. DUBININ, M. M.: Microporous Structures of Carbonaceous Adsorbents, Characterisation of Porous Solids (Proc. of the Symposium held at the Universite de Neuchatel, Switzerlands), (1978).
6. DUBININ, M. M.: *Carbon*, Vol. 20, p. 195 (1982).
7. SETOYAMA, N. – RUIKE, M. – KASU, T. – SUZUKI, T. – KANEKO, K.: *Langmuir*, Vol. 9, p. 2612 (1993).
8. MCENANEY, B.: *Carbon*, Vol. 26, p. 267 (1988).
9. STOECKLI, H. F.: *Carbon*, Vol. 28, p. 1 (1990).
10. GERGOVA, K. – PETROV, N. – ESER, S.: *Carbon*, Vol. 32, p. 693 (1994).
11. LUSSIER, M. G. – SHULL, J. C. – MILLER, D. J.: *Carbon*, Vol. 32, p. 1493 (1994).
12. NOSZKÓ, H. L. – BÓTA, A. – SIMAY, Á. – NAGY, L. GY.: *Periodica Polytechnica*, Vol. 28, p. 293 (1984).
13. Norit Testing Methods, Norit N. V.-Holland, Special publication.
14. GREGG, S. J. – SING, K. S. W.: Adsorption, Surface Area and Porosity. London, Academic Press, 1967.
15. MIKHAIL, R. SH. – BRUNAUER, S. – BODOR, E. E.: *J. Colloid Interface Sci.*, Vol. 26, p. 45 (1968); ibid. Vol. 26, p. 54 (1968).
16. JÁNOSI, A. – STOECKLI, H. F.: *Carbon*, Vol. 17, p. 465 (1979)
17. GLATTER, O. – KRATKY, O.: Small Angle X-ray Scattering. London, Academic Press, 1982.