PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBONS FROM CASHEW NUT SHELL LIQUID AND SHELLS

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Activated carbons based on polymerized technical nut shell liquid (CNSL), polymerized cardanol, and cashew nut shells have been produced and characterized by nitrogen and benzene adsorption. High temperature activation to various percentage carbon burn-off gave products whose surface areas ranged between 200 and 1900 m^2g^{-1} and pore volumes between 0.12 and 0.68 ml g^{-1}. Both surface areas and pore volumes increase with increase in burn-off. Activation with potassium hydroxide produces the highest values of both surface areas and pore volumes. Cashew nut shell activated carbons are almost exclusively microporous with an average pore radius of 1 nm. Several analytical techniques give similar trends in the values of surface areas, pore volumes and pore radii.

Key words : Characterization, Activated carbon, Cashew plant

Introduction

The techniques employed for preparing a given carbon fall into two main categories [1]. On the one hand, a natural polymeric material with a high carbon content such as coconut shells, coal, wood or peat is pyrolyzed in the absence of air to temperatures generally greater than 900 K. This is followed by an activation process in which the non-porous carbonized materials is made porous by heating in the presence of an oxidizing atmosphere (oxygen, water and carbon dioxide) [1-4].

So called chemically activated carbons, on the other hand, are produced by mixing a chemical (zinc chloride, phosphoric acid and potassium hydroxide) with a carbonaceous material usually wood and carbonizing the resultant mixture at a temperature of about 700 K [1]. The chemical may be recovered for use after carbonization.

During carbonization the organic precursors are thermally degraded to form products which undergo either condensations or volatilizations reaction. The carbon yield depends on competition between these reactions. The condensation of polynuclear aromatic compounds may produce a carbon whose adsorptive capacity is less developed. The carbonized material is thus activated to develop its porosity [1]. The pore radius of an activated carbon usually ranges from less than 2 nm for micropores through 2.50 nm for mesopores to greater than 50 nm for macropores [5]. The volume of the pores of activated carbons is generally greater than 0.2 ml g^1 and the isothermal surface area is generally greater than 400 m^2g^{-1}.

The behaviour of an activated carbon and hence it's usefulness for a particular application is determined mainly by its structural chemical properties. The structural chemical properties are in turn determined by the nature of the parent material and the method of preparation. If synthetic polymers are used, they may depolymerize leaving no residue, but if carbon is produced, it tends to have a reproducible structure and predictable properties [6]. These carbons would be expensive to produce industrially, so the bulk of carbons are produced from natural polymeric materials with the attendant unpredictability in the final product's properties.

In this work we chose the cashew plant *(Anacardium occidentale)* which is a locally and widely grown cash crop in Tanzania and in some neighbouring countries. The cashew plant bears nuts which contain an ivory coloured edible kernel. The industrial process of recovering the kernel yields as by-products cashew shells and the technically useful reddish brown phenolic cashew nut shell liquid (CNSL) [7]. The 2-3 cm long kidney-shaped nut contains about 22% wt CNSL, about 52% wt shell, and about 23% wt Kernel. The balance of the total nut weight is the thin membrane enclosing the kernel (2% wt) [8].

This work therefore was initiated to deal with one possible way of utilizing carbonaceous by-products, cashew shells and CNSL, as valuable sources of useful activated carbon.

Experimental

Materials. Cashew nut shell liquid (CNSL) and cashew nut shells were collected from a cashew nut processing industry (TANITA) based in Dar es Salaam. The shells contained some small amounts of CNSL which was left behind during the process of recovering the kernel. Very high purity carbon dioxide and oxygen free nitrogen gases were obtained from the British Oxygen Company (BOC). Liquid nitrogen was also supplied by BOC. Potassium hydroxide pellets (assay 98%) and genklene were supplied by BDH Chemicals Ltd. and hydrochloric acid (A.R.grade) was obtained from May and

Baker Ltd. Formaldehyde solution (assay 38%) was supplied by Koch-Light Ltd.

Polymerization of CNSL and cardanol. Almost pure cardanol was obtained by a conventional high vacuum distillation of CNSL followed by further purification of the distillate through a silica gel H60 column.

Each of the starting material, namely, CNSL and cardanol was mixed thoroughly with excess of 38% formalin in a two necked round bottomed flask attached with a reflux condenser and a thermometer. A small amount of 7% sodium hydroxide solution was then added as a catalyst. The mixture was then heated and refluxed to about 343° K for 15 to 20 mins while stirring with a magnetic stirrer. The resinous products obtained were then separated from water and excess formalin by evacuation and later cured overnight in a Heraeus oven at 393°K.

Both physical and chemical activation processes were employed to prepare activated carbons which were later characterized by the volumertic adsorption technique. The carbonisation and activation processes were carried out in a Stanton Redcroft thermobalance type TR1. The weight of the samples and the tempearature were recorded by a Servoscribe recorder. The temperature was recorded via a Pt / Pt ; Rd 13% thermocouple. This arrangement also allowed for the measurement of thermogravimetric parameters.

Carbonization. During carbonization, about 400 mg of the starting materials (polymers or cashew nut shells) were placed in a nickel crucible and carbonized in a nitrogen (dried over silica gel and deoxygenated by a BASF catalyst type 311) atmosphere at 1173° K until a constant weight of product was observed, usually after about 15 mins. The heating operation was set to give a linear rise in temperature of 4° K min^{-1} and the nitrogen flow was normally set at 120 ml min^{-1}. The products were cooled in a stream of nitrogen followed by further cooling in a desiccator in which they were stored.

Activation. To activate with CO_2 sample masses of carbon of about 300 mg were initially flushed for 30 mins with nitrogen in the same apparatus used for carbonization. After heating to 1173°K nitrogen was replaced by a CO_2 stream which was maintained for different times depending on the percentage burn-off (% CBO) required. The activated carbons were then cooled in a stream of nitrogen and later stored in a desiccator.

In chemical activation, powdered potassium hydroxide was mixed with carbon in the ratio of 1:4. The mixture was then heated in a dry stream of nitrogen at 4 K min^{-1} to 1073°K and left until a constant weight product was attained. After cooling to room temperature, the sample was washed with dilute HCl followed by distilled water to remove the activating chemical. The activated carbon left to dry in the oven at 383° K for overnight.

Volumetric adsorption apparatus. The volumetric unit used was similar to the one used elsewhere [9]. Samples previously out gassed at 473°K, were between 0.02-0.05g and measurements of volume adsorbed were taken at selected equilibrium pressures which were attained after 30 mins at 77.4°K. The value of the saturation vapour pressure, P°, for nitrogen was measured on a vapour pressure thermometer to 0.01 mmHg.

Gravimetric adsorption apparatus. A conventional gravimetric adsorption unit made by CI Instruments Ltd. was used. The unit essentially had (i) recording vacuum microbalance interfaced with a microcomputer; (ii) high vacuum unit which combined a Speedivac Edwards High Vacuum rotary and mercury diffusion pumps; (iii) mercury manometer and a Pirani gauge for pressure and vacuum measurements, respectively and (iv) thermostat bath equiped with a stirrer and a pump for pumping up water around the sample.

The 60 and 80% CBO sample masses used were between 0.05 and 0.08g. Benzene, the adsorbate used, was relieved of its gas impurities of freezing in liquid nitrogen and evacuating under high vacuum several times. Adsorption measurements on previously degassed samples were taken after equilibration which was detected by a constant weight reading on the computer. A correction was made for the buoyancy effect to the adsorption measurements on the samples. A constant temperature of 298°K around the sample was considered to have been reached after about half an hour.

Results and Discussion

Preliminary results thermogravimetric (TG) runs in nitrogen indicated that the polymer and cashew nut shells yielded about 18% carbon with negligible amounts of ash as observed when the runs were repeated in air. A total of ten samples of so called physically and chemically activated carbons were prepared.

The following acronyms refer to the samples used in this study:

37% CBO-CPAC — Stands for a cardanol polymer activated carbon (CPAC) obtained by activating the carbonized cardanol polymer to 37% CBO in CO_2 at 1173° K the other sample was 50% CBO-CPAC.

28% CBO-LPAC — Stands for liquid polymer activated carbon (LPAC) obtained by activating the carbonized CNSL polymer to 28% CBO in CO_2 at 1173 °K - the other samples

were 55% CBO-LPAC; and 85% CBO-LPAC.

25% CBO-CNSAC   Stands for cashew nut shell activated carbon (CNSAC) obtained by activating the carbonized shells to 25% CBO in CO_2 at 1173° K - the other samples were 45% CBO-CNSAC and 80% CBO-CNSAC.

KOH-CNSAC   Stands for cashew nut shell activated carbon (CNSAC) obtained by chemical activation of shells with potassium hydroxide (KOH) at 1073°K.

The nitrogen adsorption isotherms on 25, 45, 60 and 80% CBO-CNSAC samples are summarized in Fig. 1. All the isotherms have very steep initial branches followed by almost horizontal plateaus which become less well defind at higher relative pressure (P/P°). The data points on their desorption branches (not shown on the figure) lie almost on the same path as those on the adsorption branches. In contrast the adsorption isotherms(Fig.2 for 28% CBO-LPAC) on the polymer based activated carbons showed a hysteresis at P/P° greater than 0.4. The data points on the desorption branch at all relative pressures greater than 0.4 lie slightly above those of the adsorption branch. This feature was more pronounced for nitrogen adsorption isotherms on polymer based carbons with higher percentage carbon burn-off.

Nitrogen adsorption on most of the samples approximately fits the type 1 isotherm, in the Kiselev's classification [10]. This is indicative of the presence of an extensive microporous structure [11]. These carbons are suited in application such as molecular sieving and gas storage. It is widely accepted that the initial part of type 1 isotherm for activated carbons represents a physisorption process called micropore filling as opposed to monolayer-multilayer physisorption in wider (meso- or macro) pores represented by the slope of the plateau at higher relative pressures. The steep rise at low pressure as seen in these isotherms, that also becomes even more steep with an increase percentage burn off, suggests that burn off is producing many more micropores. Benzene adsorption measurements were carried out on two separate samples namely 60% CBO-CNSAC and 80% CBO-CNSAC. The amount of benzene adsorbed in mg g^{-1}, and the corresponding pressure and temperature were recorded and subsequently processed by a microcomputer interfaced with the microbalance. The data obtained was used to plot the benzene adsorption isotherms depicted in Fig.3.

The two isotherms have very steep initial branches followed by less well defined plateaus whose slopes increase slightly with increasing P/P°. Also it is noticeable that the
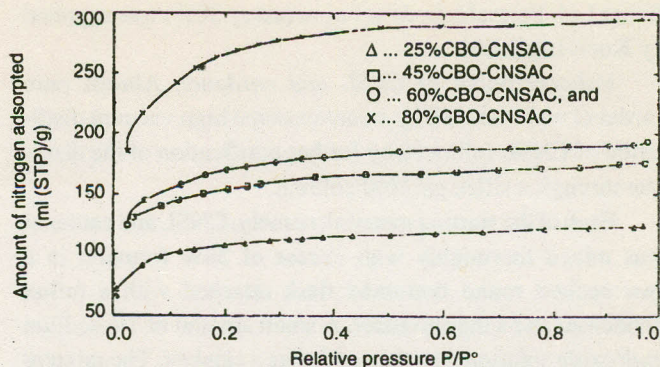

Fig. 1. Nitrogen adsorption isotherms for samples of cashew nut shell activated carbon (CNSAC) with different percentage carbon burn-offs (CBO) in CO_2 at 1173° k.
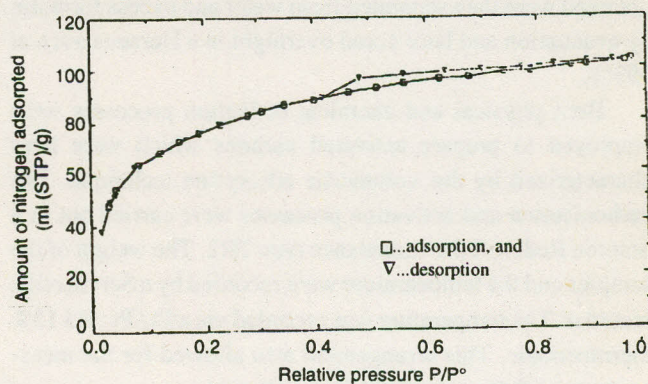

Fig.2 Nitrogen adsorption/desorption isotherm for the CNSL polymer based activated carbon (25% CBO-LPAC in CO_2 at 1173° K).
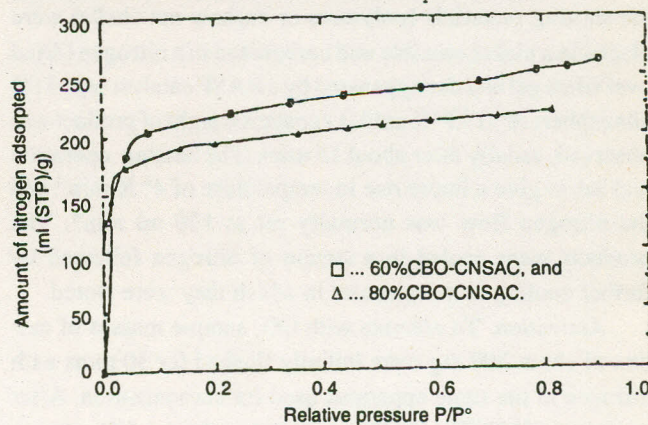

Fig. 3. Benzene adsorption isotherms for samples of cashew nut shell activated carbon (CNSAC) witgh different percentage carbon burn-offs (CBO) in CO_2 and at 1173° K.

amount of benzene absorbed is larger for the 80% CBO-CNSAC than for the 60% CBO-CNSAC sample. The isotherms in Fig. 3 corroborate the pattern observed in Fig. 1 for the nitrogen adsorption isotherms, thus confirming the observed effect of carbon burn-off on the adsorption properties of these samples.

Analysis of nitrogen adsorption isotherms. In spite of the knowledge weakness of its theoretical foundation the Burnauer-Emmel-teller (BET) method still remains the most

widely used procedure for surface area determination. The theory was developed by applying Langmuir's ideas to multilayer adsorption. The BET and Langmuir equations have both been used to interpret the nitrogen isotherms and the results are included in Table 1.

The BET and Langmuir were generally good straight lines. However, most of the cashew nut shells based carbons gave BET plots which had slightly negative intercepts with negative BET constants (C). The BET surface area, S_{BET}, was calculated over the entire BET relative pressure range (0.05 - 0.35). The BET monolayer capacity, V_{MBET}, the Langmuir monolayer capacity, L_{ML}; and the Langmuir surface area, S_L, were evaluated and are presented in Table 1.

Since an isotherm contains a vast amount of information to be scrutinized an attempt was made to calculate the pore size distribution using the Dollimore and Heal (a de Boer variation) method [12]. This enabled, besides obtaining pore size distributions plots, the estimation of cumulative areas, S_{CUM} (Table 1), and cumulative micropore volume, V_{CUM} (Table 2).

From pore size distribution plots the average radius, r_p, at maximum peak height and the corresponding value of the maximum peak height (MPH) are shown in Table 2 under columns 2 and 3, respectively.

The t-plots [11,13], being one of the methods for comparing the shape of a given isotherm with that of standard isotherm of a non-porous solid, was employed to determine the micropore volumes and surface areas. The t-plots were plotted using de Boer's t-values [13] for nitrogen adsorption on aluminium hydroxide and oxide as a standard. The IUPAC recommends a standard isotherm based on the particular adsorption system involved. However, standard values for carbons were not available, so the deBoer's t-values were thought to be adequate for this work. Parameters evaluated

TABLE 1. MONOLAYER CAPACITIES [(V_{MBET} AND V_{ML}) ML (STP) g^{-1}] AND SURFACE AREAS (m^2 g^{-1}) CALCULATED BY DIFFERENT METHODS.

1 SAMPLE (%)	2 V_{MBET}	3 V_{ML}	4 S_{BET}	5 S_L	6 S_{CUM}	7 S_{MP}	8 S_{WP}	9 S_T
37CPAC	50.0	79.7	217.8	346.9	259.9	242.8	3.1	245.9
50CPAC	56.8	92.7	247.4	403.4	274.6	260.4	14.6	275.0
28LPAC	56.9	107.1	247.8	466.3	277.5	273.9	5.3	279.2
55LPAC	105.4	201.6	458.9	877.7	434.0	425.4	14.1	439.5
85LPAC	106.0	220.1	461.3	958.1	467.0	444.9	26.3	471.2
25CNSAC	74.3	123.4	323.4	537.1	471.3	405.5	4.2	409.7
45CNSAC	112.9	175.1	491.3	762.2	650.1	587.0	5.4	593.2
60CNSAC	117.6	194.5	511.7	846.8	731.3	616.2	6.2	621.6
80CNSAC	186.1	298.8	810.1	1300.6	1082.3	975.4	7.0	982.4
KOH-CNSAC	277.7	436.7	1508.7	1900.8	1624.6	1608.4	5.4	1613.8

TABLE 2. SUMMARY OF THE COMPUTED RESULTS FROM N$_2$ ADSORPTION ON SAMPLES OF ACTIVATED CARBONS.

1 SAMPLE %	2 r_p nm	3 MPH* m3g^{-1}/m	4 V_{CUM} ml/g	5 Micropore Volume (ml/g)	6	7	8	9
				V_{MPT}	V_{MPD}	V_{MPL}	V_{MPL}	V_{MPS}
37CPAC	1.05	104.8	0.12	0.12	0.12	0.12	0.12	0.12
50CPAC	1.15	134.2	0.14	0.13	0.14	0.15	0.13	0.15
28LPAC	1.15	125.6	0.16	0.15	0.14	0.25	0.14	0.19
55LPAC	1.25	232.1	0.30	0.27	0.26	0.41	0.26	0.37
85LPAC	1.25	281.1	0.34	0.27	0.27	0.45	0.27	0.42
25CNSAC	0.85	159.9	0.19	0.18	0.14	0.22	0.14	0.19
45CNSAC	0.95	218.1	0.28	0.26	0.25	0.31	0.26	0.28
60CNSAC	1.05	340.9	0.38	0.29	0.29	0.33	0.29	0.32
80CNSAC	1.05	436.9	0.46	0.44	0.45	0.54	0.45	0.48
KOH-CNSAC	0.85	583.7	0.58	0.57	0.67	0.69	0.67	0.68

* The maximum peak weight.

and given in Table 1 were total surface area, S_T; surface areas of micropores, S_{MP}; and surface areas of wider pores, S_{WP}. Also evaluated was the micropore volume, V_{MPT}, given in Table 2.

Dubinin-Radushkevich pore filling plots were made. In cases where low pressure data deviated upwards, due to multilayer adsorption, these points were left out to restrict the analysis to the micropore filling region. The deviation of these plots from a straight line is common [14], mainly because the theory is empirical. The Dubinin-Radushkevich plot implies a Raleigh distribution of surface adsorption energies. Other distribution functions, such as Gaussian, log Gaussian and skewed Gaussain have been suggested [15]. These plots were also made as log (adsorption) against adsorption energy E. The average deviations of the points from a theoretical curve were taken as goodness of fit. The values of the micropore volumes calculated on the basis of each method for each sample are given in Table 2. In this table V_{MPD} is by the Dubinin-Radushkevich method; and V_{MPG}, V_{MPL}, and V_{MPS} are by Gaussian, log Gaussian and skewed Gaussian methods, respectively.

The various methods used do not in themselves provide absolute values of the micropore properties. Rather it is the general observed trends due to variation in the starting materials and method of activation that are of interest. Tables 1 and 2 provide just that kind of information. Both surface areas and pore volumes increases with increase in carbon burn-off. The assumptions inherent to the theoretical and emperical approaches used in analysing adsorption data are responsible for the noticeable differences which exist among the various values of surface areas and volumes within a given trend [11].

Activation with potassium hydroxide produces the highest values of both surface areas and pore volumes (Tables 1 and 2). This particular treatment deserves further study since it produces a product which has a very high adsorption capacity suited for applications such as gas storage. High percentage burn-off of polymer based carbons showed a slight wider pore development as seen by an increase in the surface areas of wider pores, S_{WP}, in column 8 of Table 1. This suggests that a few micropores grew to become wider pores.

The chasew nut shell based carbons, however, retained their microporosity and this indicates that micropore development involved creation of new micropores as seen by the almost constant average pore radius, r_p, in column 2 of Table 1 and Table 2.

Conclusion

The results obtained in this investigation have provided an insight into the development potential of the locally obtainable natural materials for their use in the production of good quality activated carbons. Both values of surface areas and pore volumes are comparable to those of commercial varieties manufactured by companies such as NORIT [3] and used for different purposes.

Cashew nut shell's activated carbons are almost exclusively microporous with an average pore radius of 1 nm. This makes them good candidates for applications such as in water treatment, molecular sieving and metal recovery.

Polymerisation of cashew nut shell liquid and cardanol which is a component of CNSL was undertake in an attempt to make a more controlled reproducible product. Destructive distillation of the shell liquid always leaves behind a polymerized material which is often referred to as coal tar. The polymer based carbons prepared in this work behaved like coal based carbons in that adsorption isotherms of the samples subjected to increasing percentage carbon burn-off showed some hysteresis indicative of formation of mesopores. Mesopore development is essential if the carbons are to be used as supports for the noble metal catalysts.

Work is now in progress to try to relate the adsorption capacities and chemical structural properties of these carbons to different areas of applications.

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