PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBONS FORM SOME TANZANIAN CARBONACEOUS AGROWASTES

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ABSTRACT. A study on the properties of activated carbons prepared from agrowastes has been made. Two activation methods have been used to prepare activated carbons from cashewnut shells, coconut shells, rice husks and black wattle wood. The activating agents used were carbons dioxide (at 1200 K) and potassium hydroxide (at 1000 K) for the physical and chemical activation methods, respectively.

The carbons were characterized by the physisorption of nitrogen at 77.4 K using a static volumetric technique. The adsorption data was used to determine BET surface areas and micropore properties. The t-plot methods was used for micropore analysis. The average pore diameters were shown to range from 0.84 to 1.02 nm. The values of surface areas obtained ranged form 362 to 1573 m^2g^{-1}.

The adsorption capacity of the carbons was determined by using dye tests involving iodine number and methylene blue number. Values of up to 1386 and 300 were obtained for iodine and methylene blue numbers, respectively. Both surface area values and, iodine and methylene blue numbers are comparable to commercially used activated carbons.

INTRODUCTION

Activated carbon is a microcrystalline non-graphitic form of carbon that has been processed to develop an internal porosity [1]. Activated carbons are the residues from carbonization and activation of carbonaceous materials such as coal or wood. The carbons are found to have a large pore volume, and as this is derived from very small diameter pores the internal surface area is high, ranging from 500 to 1500 m^2g^{-1} [2]. This highly developed internal pore structure provides activated carbons with the ability to adsorb impurities from gases and liquids. The efficiency of the carbon will, therefore, depend on its accessible surface area, and upon the presence of active sites on the surface at which adsorption may occur [3]. The uses of activated carbon include purification of liquids and gases in processing industry such as vegetable ghee, edible oil, sugar, pharmaceutical and starch making; treatment of industrial effluent, potable water supplies and waste water, and making gas masks [2].

A large number of materials can be used to prepare activated carbons. Almost any carbonaceous material of either animal, vegetable or mineral origin can be converted into

activated carbon if properly treated. For commercial practice, however, the material must be of relatively low cost, abundant and have a high carbon content. The most commonly used in commercial practice are bone char, wood, coconut shell, peat, coal and lignite [2].

In the present study, the preparation of activated carbon from different agrowastes i.e. cashewnut shells, coconut shells, rice husks and wattle wood (*Acacia mearnsii*) has been described. The pore structure of the activated carbons and their decolourizing ability have been determined.

EXPERIMENTAL

Carbonization: A horizontal tube furnace was used for carbonization and activation. Each sample was heated to a temperature of 1200 K and carbonized at this temperature for 30 min. in the inert atmosphere of nitrogen. The yield was found to be 28.3% by weight for cashewnut shells, 25.0% for coconut shells, 20.2% for black wattle wood and 41.5% for rice husks.

Physical activation: Physical activation was done using CO_2 gas as the activating agent. Samples of the carbonized intermediate (char) weighing between 2.0-3.0 g were activated in the silica reactor at 1200 K. The activation time was between 10 min. and 11/2 hr depending on the required percentage carbon burn-off (%CBO).

Chemical activation: Finely ground raw material (5.0 g) was mixed with an aqueous solution of an activating chemical (KOH) at impregnation ratios of 1:2, 1:1. and 2:1, respectively, for each raw material. The mixture was boiled in a 100 ml beaker for 2-3 hr and the resulting paste dried in an oven at 383 K for 3-6 hr. The dried sample was carbonized at 1000 K for 45 min. in a tubular furnace under nitrogen. After cooling to RT the sample was washed with dil. HCl followed by distilled water to remove the activating chemical. The activated carbon was left to dry in the oven at 383 K for overnight.

Measurement of adsorption isotherms: A standard BET volumetric adsorption apparatus was used for the measurement of adsorption isotherms. A Bell and Howell pressure transducer (type 4-366-002-0036 and pressure range: 15 psia) was used to measure absolute pressure in millivolts, which was later converted to pressure in mm Hg using a calibration plot. All corrections to pressure and volume readings and calibration of the adsorption apparatus were made.

Dye tests

Determination of iodine number. The method and procedure for the determination of iodine number was followed as given by Sutcliffe Speakman Carbons Ltd [4]. Some minor alterations however were made: the carbon samples were sieved in a 270-mesh sieve (BS) instead of a 325 mesh sieve, and standardization of sodium thiosulfate solution was made

using potassium iodate instead of metallic copper. Sample weights were between 0.5 - 1.0 g.

Determination of methylene blue number. A dry carbon sample (100 mg) was added to 25 ml of methylene blue solution (1.2 g.l^{-1}) in 5% by volume acetic acid. The mixture was stirred at a fast speed for 5 min. After that the sample was filtered by suction through a Whatman No. 40 filter paper. The concentrations of methylene blue were determined photometrically by comparing the light absorbance of the sample with that of reference solution, using a CIBA-CORNING M-252 colorimeter.

RESULTS AND DISCUSSION

The physically activated carbons obtained had percentage carbon burn-off ranging from 20 to 80%. These carbons were named 29% CNS, 50% CNS, 80% CNS, 21% CONS, 36% CONS, 50%CONS, 28% RH, 41% RH, 28% BWW, 57% BWW, 62% BWW, 62% BWW, 31% BWC, 56% BWC and 73% BWC. The figure before the % sign shows the % CBO of the carbon sample while the abbreviations stand for carbons based on: cashewnut shells (CNS), coconut shells (CONS), rice husks (RH), black wattle wood (BWW), black wattle char (BWC).

The data obtained from volumetric adsorption measurements were used to plot adsorption isotherms on a graph plotter. All volumes were converted to adsorption values at STP.

With the help of an IBM computer BET surface areas, S_{BET}, were calculated and compared with t-plot surface areas, S_T. The S_{BET} values are based on the linear portion of the BET plots that ranged from $P/P_0 = 0.05$ to 0.20. This BET range was used for all samples. Later, S_{BET} and S_T were compared with Langmuir plot surface areas, S_{LANG}.

The nitrogen adsorption isotherms were type I, in the Kiselev's classification [5], for both chemically and physically activated carbons. Examples are shown in Fig. 1. This indicates that the carbons are mainly microporous.

The t-plot method was used for micropore analysis. The DR equation [6] may be used to determine the micropore volume but there are several types of deviation from the linear DR plots [6,7] which can make the estimation of the micropore volume difficult. The choice of a standard isotherm for the t-values was made according to IUPAC recommendations [8] that the standard isotherm should be obtained for the particular adsorption system. In this case t-values given by Rodriguez-Reinoso *et al.* [9] were used.

The t-plots were found to divide into two straight lines. The lower points fell on a straight line through the origin. The slope of this line multiplied by 1.547 gave total surface area S_T. The upper straight line represents a fit for multilayer adsorption in the mesopores and macropores. Its slope gave the surface area of wide pores S_{WP}. The difference between S_T and S_{WP} was taken to be the micropore area S_{MP}.
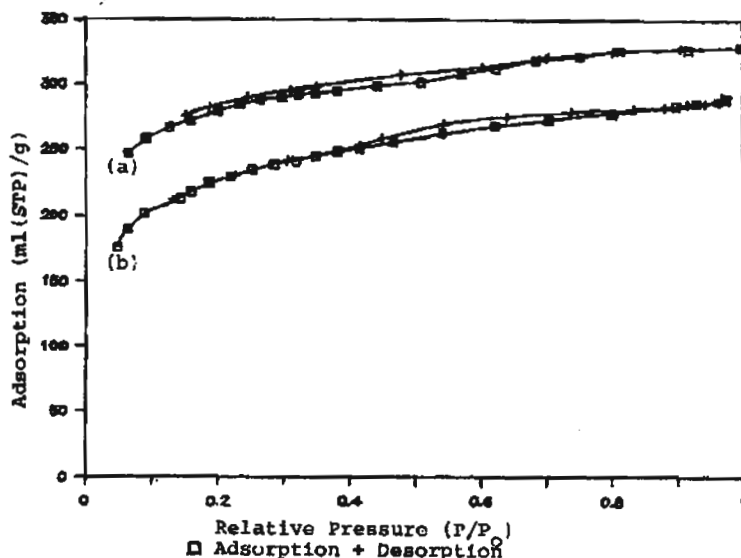
Fig. 1.   Adsorption isotherms for cashewnut shell based carbons: a) 50%
CNS, and b) 80% CNS.

The intercept, V_{NT}, of the upper line was converted to micropore volume V_{MP} by the following relation;

$$V_{MP} = \frac{V_{NT}M_N}{22414\rho_N}$$

Where M_N is the molecular weight of nitrogen (28.01) and ρ_N is the density of nitrogen at 77 K which is 0.808 gcm^{-3}. The t-value at the point where the two straight lines meet, t_{LP}, represents half pore width if micropores are assumed to be slit-shaped.

A typical t-plot is shown in Fig. 2. Table 1 gives a summary of the computed results from nitrogen adsorption on the activated carbons. Also included are dye test results.

Interpretation of N_2 adsorption isotherms and adsorption data on carbons activated with CO_2: The adsorption isotherms typified by plots in Fig. 1 reveal the porosity characteristics of the carbons. The isotherms are all of type I with a steep rise at low relative pressure and plateau at high relative pressure. It is now widely accepted that the initial part of the type I isotherm for activated carbons represents micropore filling and the slope of the plateau at high relative pressure is due to multilayer adsorption on the non-microporous surface, i.e. in mesopores, in macropores and on the external surface. This initial portion

of the isotherm becomes steeper and rises higher as percentage burn-off increases. This leads to a conclusion that burn-off has produced many more micropores. Narrow hysteresis loops are observed in isotherms of some samples but this could possibly be due to experimental errors caused by insufficient time to reach equilibrium.
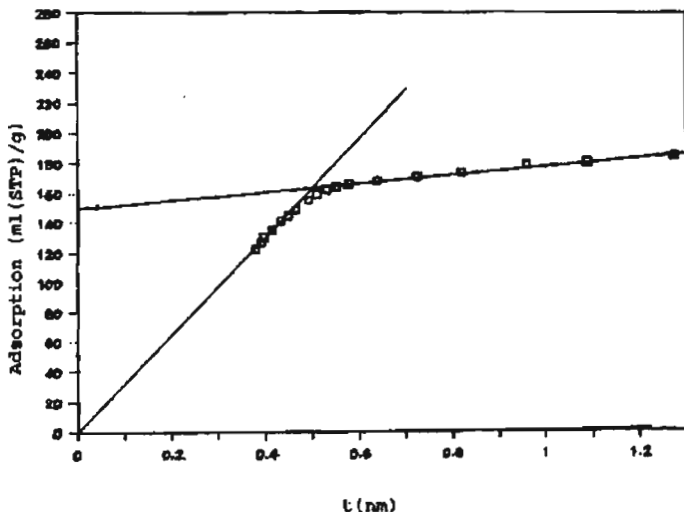

Fig. 2.   V-t plot for carbon sample 57% BWW.

Adsorption data in Table 1 illustrate that the total surface areas S_{BET}, S_{LANG} and S_T increase with burn-off. Notable differences exist among the values of S_{BET}, S_{LANG} and S_T within a given trend. This is due mainly to the assumptions inherent to the theoretical and empirical approaches used in analyzing adsorption data [6]. For instance, since micropores are present in these carbons, the BET multilayer theory does not strictly apply. The areas resulting are therefore to be considered as approximate and for comparison purposes only.

The total volume of micropores also increase with burn-off. The micropore radius derived from the t-plot method was found to be around 0.42 nm and 0.51 nm, that is widths of 0.84 nm to 1.02 nm, for slit-shaped pore model. Since micropore width remains more or less constant, the increase in surface area indicates that new micropores are being produced during activation and that the pores burn-out lengthwise without increasing in width. The areas of mesopores and macropores (S_w) do not increase significantly with increased burn-off. This shows that activation of the type of carbons under consideration tends to favour production of new micropores than joining the present pores to meso- or macropores.

Table 1. Summary of the computed results for N_2 adsorption on the activated carbons and dye test results

Carbon Sample	Activation time (min.)	S_{BET} m²/g	S_{LANG} m²/g	S_T m²/g	S_{WP} m²/g	S_{MP} m²/g	S_{MEN} m²/g	V_{MP} cm³/g	t_{LP} (nm)	I (No)	MB (No)	Ratio of I (No): MB (No)
29% CNS	10	369	623	362	44	318	185	0.158	0.511	546	127	4
50% CNS	20	521	948	1044	119	925	255	0.390	0.414	641	175	3.5
80% CNS	30	801	1160	815	46	769	330	0.383	0.501	887	226	4
28% BWW	20	667	1072	710	26	684	134	0.332	0.471	520	92	5.5
57% BWW	60	522	973	507	32	475	210	0.245	0.510	756	144	5
62% BWW	75	477	695	473	24	449	219	0.217	0.485	897	150	6
21% CONS	20	648	977	732	21	711	92	0.313	0.450	557	63	9
36% CONS	60	998	1444	1061	34	1027	126	0.465	0.463	675	87	8
50% CONS	90	1422	1961	1573	54	1519	333	0.665	0.434	987	228	4
28% RH	20	118	300	128	21	107	61	0.042	0.510	62	42	1.5
41% RH	60	-	-	-	-	-	67	-	-	42	46	1
31% BWC	20	418	584	506	17	489	130	0.223	0.455	467	89	5
56% BWC	60	-	-	-	-	-	238	-	-	981	163	6
73% BWC	90	-	-	-	-	-	438	-	-	1096	300	3.5
1:2 CNS	45	441	650	410	26	414	260	0.199	0.471	693	178	4
1:1 CNS	45	545	783	-	-	-	433	-	-	852	295	3
2:1 CNS	45	859	1170	863	32	831	433	0.384	0.447	856	300	3
1:2 BWW	45	626	867	702	26	676	51	0.294	0.428	674	35	19
1:1 BWW	45	680	1037	-	-	-	146	-	-	674	86	8
2:1 BWW	45	776	1184	879	23	856	190	0.375	0.450	1386	130	11
1:1 CONS	45	542	747	-	-	-	215	-	-	640	147	4
2:1 CONS	45	1081	1535	-	-	-	390	-	-	707	267	2.5
1:1 RH	45	823	1195	914	33	881	397	0.380	0.421	610	272	2

However, when %CBO is greater than 50, a decrease in the total surface area is observed and particularly due to a decrease in the surface area of micropores. This can be explained as due to pore coalescence, that is, the micropores are broken down and joined together into large pores. In activated carbons having very high specific surface areas, every third or second carbon atom forming the lattice can contact the adsorbate or activating agent [10], hence further gasification can easily coalesce the micropores into large pores. Consequently a decrease in total specific surface area is observed.

The carbons have been prepared from different raw materials and this has an effect on their adsorptive characteristics. For the same %CBO different results are obtained, in terms of specific surface area, micropore volume, iodine number and methylene blue number, for different activated carbons prepared from different raw materials.

The results shown in Table 1 illustrate that different raw materials behave differently during activation. Whereas carbons from cashewnut shells and black wattle wood are burnt-off easily i.e. in few minutes, those from coconut sells and rice husks take longer to achieve the same magnitude of CBO. Char obtained from rice husks has been found to produce a greater resistance towards gasification. This is probably due to having too small amount of previously existing micropores, and also the pores may be blocked by ash during gasification, and thus preventing the diffusion of the gaseous activating agent (CO_2) from reaching the reaction surfaces. For the case of coconut shell carbon, increased activation time seems to have an effect of producing more micropores.

Interpretation of N_2 adsorption isotherms and adsorption data on carbons activated with KOH: The nitrogen adsorption isotherms are all type I in the Kiselev's classification

indicating that the carbons are microporous. No hysteresis loops are observed. The micropore radius (t_{LP}) obtained from the t-plots is between 0.42 and 0.47. This range is even narrower than that of 0.42-0.51 observed from physically activated carbons. This is an indication that a more or less uniform microporous structure has been produced by this activation method.

Table 1 presents the adsorption data for the carbons activated with KOH. The surface areas S_{BET}, S_{LANG} and S_T all increase with an increase in impregnation ratio. This trend is observed for all samples. The micropore volume also increases with impregnation ratio. Dye test results show that iodine number and methylene blue number increase with the degree of activation (impregnation ratio). Increased impregnation ratio therefore increases activity.

Interpretation of dye test results: Dye tests, i.e., iodine number, methylene blue number have been used in this research to determine generally the adsorptive characteristics of the carbons. The results in Table 1 show that adsorption capacity is increased by increasing the %CBO and impregnation ratio.

The tests can as well be used for pore structure analysis and determination of surface area, iodine number, methylene blue number and molasses number correspond to pores of sizes greater than 1.0, 1.5 and 2.8 nm in diameter, respectively [11]. According to IUPAC classification of porous adsorbents, pores of sizes less than 2.0 nm in diameter are micropores [12]. But, since iodine and methylene blue are adsorbed even in the wider pores, we can not rely upon this method for analysis of pore size distribution.

The surface areas, S_{MBN} in Table 1 are surface areas of pores greater than 1.5 nm in diameter calculated on the basis of methylene blue number. The area covered by 1 mg of methylene blue is reported to be 1.46 m^2 for graphitized carbon black [13]. The areas, S_{MBN}, given in Table 1 are lower than those obtained from BET or t-plot methods. This is because S_{MBN} represents the surface area of pores greater than 1.5 nm diameter only, which include some of the micropores, and the meso-and macropores. This observation leads to a conclusion that the carbon tested possess heterogeneous character in the micropore structure. Heterogeneous micropore structures are common in strongly or overactivated carbons, resulting from the burning out of walls between adjacent micropores [14].

CONCLUSION

The carbons prepared from agrowastes are highly microporous and therefore useful for adsorption in the vapour phase e.g. recovery of volatile solvents and gas purification. A very small increase in the mesopore surface of carbons prepared in this study suggests that these methods of preparation seem not to favour the formation of mesopores in the carbons. A significant increase in micropore surface area is obtained by activation up to a carbon burn-off of 50% and impregnation ratio of 2:1. The ratio of iodine number to methylene blue number, I (No) : MB (No), decreased when %CBO was increased from 36 to 50 and from 56 to 73 for coconut shell and black wattle carbons (BWC), respectively

(Table 1). This implies that mesopores have been produced by increasing the degree of activation (carbon burn-off) as it has been reported for some other carbons [15]. The mesopore surface formed at 50% CBO was too small to produce hysteresis in the adsorption isotherm.

Activation with CO_2 is suitable for the raw materials used except rice husks. The activated carbons from rice husks had low values of S_{BET}, iodine number and methylene blue number. Chemical activation with KOH was suitable for all the raw materials used.

The surface areas attained for the carbons range from 362 to 1573 m^2g^{-1}. These surface areas are comparable to those obtained for the commercially used activated carbons [1,16].

The iodine numbers of the carbons prepared in this work are within the specification given for typical activated carbon grades [1].

Methylene blue number is now used for evaluating carbons in water purification [13] and the activated carbons prepared in this work are therefore suitable for that purpose.

It can be concluded that all the raw materials used in this research can produce commercially useful activated carbons.

A method of carbonizing wood in crude pits dug in the ground has been found useful and is therefore recommended. The charcoal produced in this way from black wattle wood was activated and tested (sample 31% BWC, 56% BWC and 73% BWC). The results show that the method is suitable.

ACKNOWLEDGEMENTS

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