PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBONS FROM RICE HUSKS AND SHELLS OF PALM FRUITS

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ABSTRACT

Activated carbons from palm fruit shells (PFS) and rice husks (RH) were prepared using physical and chemical activation processes, respectively. The influence of activation time and temperature (in the case of PFS) and impregnation ratio and carbonization temperature (in the case of RH) on the properties of the resultant carbons were studied. In the case of PFS carbons, there were an increase in adsorption capacity and surface areas with increase in activation time and temperature. The surface area ranged between 292 and 642 $m^2\ g^{-1}$ *at temperature range of between 1000 and 1200 K. In the case of RH carbons, surface areas and adsorption capacity also increased with increase in impregnation ratio and carbonization temperature. However, at temperatures above 1100 K there was a decrease in both surface area and adsorption capacity. The surface areas ranged between 146* $m^2\ g^{-1}$ *and 526* $m^2\ g^{-1}$ *at a temperature range of 1000 to1100 K for the later carbons.*

INTRODUCTION

Activated carbons are highly porous carbonaceous materials. They are obtained as residues after volatile components within source materials are removed. Various carbonaceous materials of animal, vegetable or mineral origin can be used to produce activated carbons (Smisek & Cerny 1970). However, for economical reasons, source materials are required to have high carbon content and should be obtainable cheaply and abundantly.

The development of activated carbons involves carbonization and/or activation of the raw material. Basically, activation is the development of pores in a non-porous raw material by means of chemical reactions. There are two main varieties of the activation process referred to as "physical activation" and "chemical activation" (Smisek & Cerny 1970). Usually physical activation is preceded by carbonization of the raw material. In chemical activation however, carbonisation and activation occur at the same time, and at lower temperatures. During activation, new pores are developed but at the same time the pore sizes of the existing ones are increased giving rise to a more porous product large porosity provides a large surface area, up to about 1500 m^2 g^{-1} (Anon 1985a).

Activated carbons are known to have a heterogeneous pore structure, which according to IUPAC is classified as micropores (radius < 1 nm), mesopores (radius 1 —25 nm) and macropores (radius > 50 nm) (Burwell Jr. 1976). Micro- and mesopores give the carbon its adsorptive capacity whereas macropores allow a rapid access to the meso- and micropores, where the actual adsorption takes place. However, the adsorptive capacity of a given carbon is a function of the type of source material as well as the conditions of activation (Mkayula & Heal 1988). A careful choice of source materials as well as activation parameters is thus very important in the art of developing activated carbons.

Tanzania has an agro-based economy and most of its agricultural waste and by-products, such as rice husks and fruit shells (coconut shells, cashew nut shells, palm fruit shells), are presently being discarded. The disposal procedures are haphazard and sometimes pose a threat to the environment. From an environ-economics point of view, the disposal of the agrowastes is not only hazardous to the environment but also it is a waste of resources. In addition, most of the activated carbons used in industries for various adsorptive purposes are imported.

The suitability of a number of indigenous carbonaceous materials as source materials for production of activated carbons has been explored in our laboratory (Mkayula & Matumbo 1994, Mdoe & Mkayula 1996, Mkayula & Mdoe 1999). These studies have shown that both rice husks and fruit shells can produce quality activated carbons. However, whereas the physical activation process is suitable for fruit shells-based carbons, quality rice husks-based carbons can only be prepared by the chemical activation method. One major setback of the chemical activation method, however, is that the commonly used activating agent (namely potassium hydroxide) causes serious corrosion of silica glassware during the carbonization stage. Thus a search for a mild but inexpensive activating agent is very important.

As part of a continuing program of preparing activated carbons from local source materials using benign and simple methods, the present study has developed and characterized activated carbons from rice husks (from *Oryza sativa* Linn) and shells of palm fruit (from *Elaeis guineensis*). The former carbons were prepared using sodium chloride as an activating agent whereas the latter carbons were prepared using the physical activation method. As far as we are aware, palm fruit shells have not been used before as source materials for activated carbons. The influences of impregnation ratio (*i.e.* the ratio of the activating agent to dry starting material), activation temperature and time, on different physicochemical properties of the prepared activated carbons are described.

METHODS

Rice husks were obtained from milling machines in Morogoro region while shells of palm fruit were obtained in Dar es Salaam. Reagents used were of analytical grade and were supplied by BDH and M & B chemical companies.

The preparation procedures of the activated carbons were as described by Mkayula and Matumbo (1994), except for a few modifications. In the case of PFS carbons the method involved carbonization under inert nitrogen atmosphere followed by activation using CO_2 gas at various temperatures and time intervals. The degree of activation was determined as percentage carbon burn-off (%CBO), which is the percentage loss in weight during the activation process. Activated carbons from rice husks were prepared by chemical activation using sodium chloride as an activating agent instead of potassium hydroxide. The use of potassium hydroxide as an activating agent is disadvantageous in that it corrodes the silica glassware during carbonization. The activating agent (NaCl) was removed by washing thoroughly with distilled water. To check for complete removal of the NaCl, silver nitrate solution was used. The time of activation and carbonization were variable.

The method and procedure recommended by Sutcliffe Speakman Carbons Ltd (Anon 1985b) was followed in the determination of percentage ash.

For the determination of metal content, 0.46 g of oven dry rice husks were mixed with 10 cm^3 of 66% HNO_3 in a beaker and boiled gently. When no more brown fumes of NO_2 were evolved, 5 cm^3 of perchloric acid were added and gentle boiling continued until almost all the material had dissolved. The mixture was then filtered through a glass crucible (porosity 4) and washed three times with distilled water. The filtrate and washings were put into a 100 cm^3 volumetric flask and diluted to the mark with distilled water. The solution obtained was analyzed for metal content using a Perkin-Elmer model 2380 atomic absorption spectrophotometer.

The method and procedure for the determination of iodine number was followed as given by Sutcliffe Speakman Carbons Ltd (Anon 1985b). Some minor alterations, however, were made: the carbon samples were sieved in a 270-mesh sieve (BS) instead of a 325 mesh sieve, and standardisation of sodium thiosulphate solution was made using potassium iodate instead of metallic copper. Sample weights were between 0.5 and 1.0 g.

The method and procedure for the determination of methylene blue number was followed as given by Mkayula and Matumbo (1994).

For the determination of molasses number, a dry carbon sample (0.6 g) was added to 20 cm^3 of 0.614 g dm^{-3} of molasses. The mixture was stirred at a fast rate for a couple of minutes. The sample was then filtered by suction through a Whatman No. 40 filter paper. The concentrations of molasses was determined photometrically by comparing light absorbance of the sample with that of a reference solution using CIBA-CORNING M-252 colorimeter at 540 nm wavelength.

RESULTS AND DISCUSSION

Physicochemical properties of the Rice Husks-Based Carbons

The percentage char obtained at a fixed time during carbonisation decreased with increase in temperature (Table 1). This is due to the fact that as the temperature increases the degree of pyrolysis increases and more of the non-carbonaceous volatile materials are removed from the rest of the char. The ash content of the resultant activated carbons, however, seems to be less affected by both the impregnation ratio and activation temperature. The percentage ash ranged between 36 and 41%. This range is comparable to that observed earlier in activated carbons prepared from rice husks but using potassium hydroxide as an activating agent (Mdoe & Mkayula 1996). The metals present in the carbon samples (on w/w basis) include calcium, magnesium, sodium, lead, zinc and iron (Table 2). The amount of ash in the rice husks based carbons is generally higher than in other commercially available carbons, such as coal and coconut shells (Anon 1992). The ash content thus depends mainly on the type of source material.

Table 1: Effect of temperature and impregnation ratio on various physicochemical properties of activated carbons prepared from rice husks

Impregnation ratio	Temperature (K)	% char yield*	%Ash content	Mo(No)	Mb(No)	I(No)	SA ($m^2 g^{-1}$)
1:2	973	79	34	68	10	44	146
1:2	1073	74	37	89	12	67	175
1:1	973	83	41	101	14	39	204
1:1	1073	66	36	112	24	61	350
2:1	973	77	35	156	19	48	277
2:1	1073	72	36	268	36	176	526
2:1	1200	61	36	62	22	104	321
Average error		± 2	± 2	± 5	± 2	± 6	± 10

The dye test results are presented as averages of three runs

*% Char yield = (weight of the obtained char / weight of original dry RH) x 100%.

Mo(No) = molasses number, Mb(No) = methylene blue number, I(No) = iodine number, and SA = surface area.

Table 2: Metal content of rice husks from Morogoro, Tanzania

Type of metal	Al	Ca	Cd	Cu	Fe	K	Mg	Na	Pb	Zn
Conc. (mg/g) ± 0.003	nil	0.22	nil	nil	0.24	0.34	0.28	0.26	0.07	0.05

Iodine, methylene blue and molasses dyes have been used as standard laboratory methods for testing the adsorption capacity of activated carbons (Anon 1985b). In fact internal surface area in activated carbons can be extrapolated from the value of methylene blue number. The area covered by 1 mg of methylene blue is 1.46 m^2 for graphatized carbon black (Mikhail & Robens 1983). From this relationship the surface areas calculated for the rice husks-based carbons were found to range from 146 to 526 $m^2 g^{-1}$, values that fall within the range of commercial grades activated carbons (Anon 1992). The surface areas are also comparable to those of RH-based carbons prepared using KOH as an activating agent (Mkayula & Matumbo 1994). However, the surface areas determined by this method are only for pores that are more than 1.5 nm wide. This is because iodine number, methylene blue number and molasses number correspond to pores of sizes greater than 1.0 nm, 1.5 nm and 2.8 nm in diameter, respectively (Ahmad *et al.* 1990). Generally surface areas determined by methylene blue number are lower than those obtained by nitrogen physisorption as nitrogen can be adsorbed even in areas not accessible by methylene blue (Mkayula & Matumbo 1994).

Increase in impregnation ratio and activation temperature leads to an increase in surface area (Fig. 1). This also leads to increase in adsorption capacity (Table 1). However, the surface area and the adsorption capacity of the carbon sample fell slightly at 1200 K, regardless of the impregnation ratio. The increase in surface area with increase in impregnation ratio is attributable to the process that takes place during chemical activation. In the process, a chemical that is normally applied as a strong solution at an elevated temperature penetrates the structure of the source material, swells it and opens up its cellulose structure. On carbonization the chemical acts as a support and does not allow the resulting char to shrink. After the extraction of the chemical from the carbonized char an activated carbon is obtained. The porosity of the resultant carbon depends on the volume of the activating agent that is freed from the pores (Smisek & Cerny 1970). Indeed, it has been observed that the pore sizes of activated carbons increase with increase in impregnation ratio (Smisek & Cerny 1970). Increase in surface area is a result of creation of more micropores and possibly widening of the existing ones. Hence increase in porosity and widening of existing pores means also that there is a possible increase in active sites as well as accessibility to the sites. This may explain the increase in adsorption capacity with increase in impregnation ratio and temperature. However, normally carbons with high activity are obtained at relatively lower temperatures, 873 —973 K (Smisek & Cerny 1970), a reason for the decrease in surface area at temperatures above 1100 K.

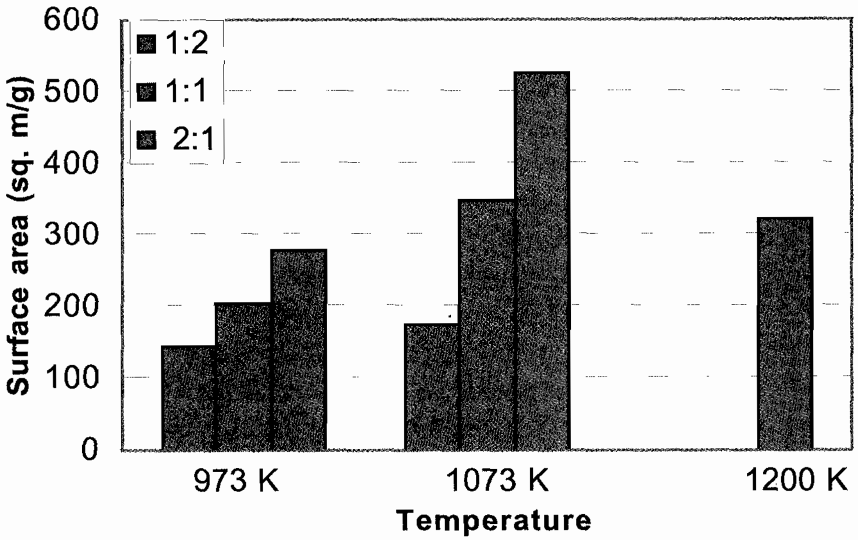

Fig 1: The effect of temperature and impregnation ratio on surface areas of the rice husks-based carbons. Rice husks collected from Morogoro, Tanzania

Physicochemical properties of the palm fruits shells-based carbons

The influence of activation time and temperature on percentage carbon burn-off, surface area and adsorption capacity of the carbons prepared from palm fruit shells was also studied and results given in Table 3 and Figure 2. Generally, %CBO, surface area and adsorption capacity increase with increase in activation time as well as activation temperature. This observation can be explained by considering the mechanism of pore development, which involves carbonization of a source material and activation of the intermediate char.

Table 3: Effect of temperature and activation time on various physicochemical properties of activated carbons prepared from palm fruit shells from Dar es Salaam, Tanzania

Temperature (K)	Time (min)	%CBO	Mo (No)	Mb (No)	I (No)	SA ($m^2 g^{-1}$)
973	20	8.6	145	200	934	292
	40	11.0	142	200	967	292
	60	17.0	147	280	1275	409
1173	20	9.8	152	240	1134	350
	40	10.3	150	240	1400	350
	60	19.3	152	260	1467	380
1200	20	16.4	1662	300	1300	438
	40	23.7	1662	400	1508	584
	60	24.3	1665	440	1567	642
Average error		± 4	± 5	± 2	± 6	± 10

The dye test results are presented as averages of three runs

Mo(No) = molasses number, Mb(No) = methylene blue number, I(No) = iodine number, and SA = surface area.

During carbonization, most of the non-carbonaceous materials are first removed in gaseous form and then freed atoms of elementary carbon are irregularly grouped into elementary micro crystallites (Smisek & Cerny 1970). The irregular arrangement creates free interstices that trap tarry hydrocarbons on their way out. The resulting carbonized material thus tends to have low adsorption capacity due to the blockage of the interstices. Such carbonized material can only be activated by removing the tarry substances through heating them in a steam of activating gas such as CO_2. In the process, disorganized carbon is burnt-off first, then the reaction proceeds on carbon atoms at the edges and corners of elementary micro crystallites, sites that are very reactive. The development of a highly porous activated carbon is thus associated with the degree of burn-off (Smisek & Cerny 1970). This explains why our carbon samples show an increase of surface area and adsorption capacity with increase of %CBO.

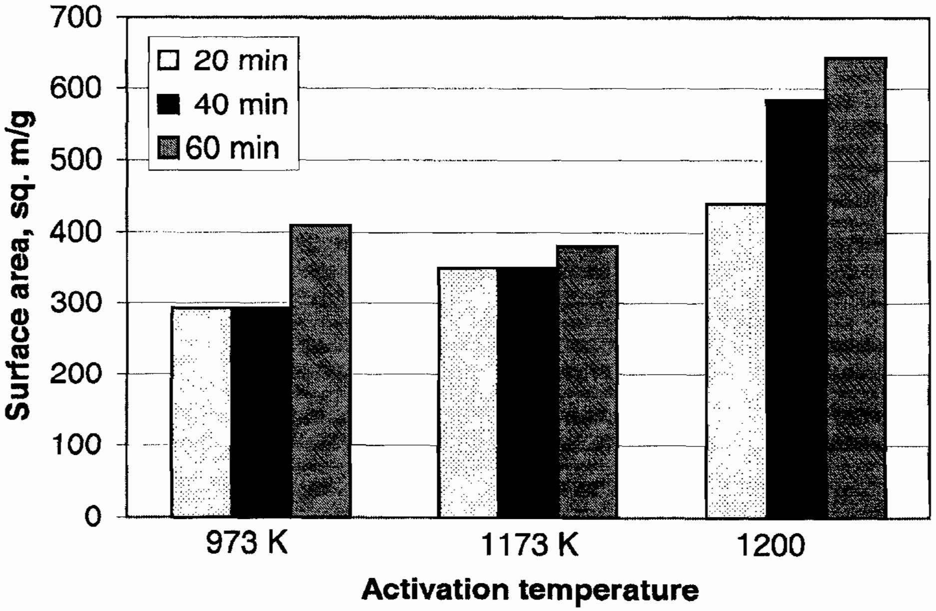

Fig 2: The effect of temperature and activation time on surface areas of the carbons prepared from palm fruit shells from Dar es Salaam, Tanzania

Just like in the case of chemical activation, the physical activation also creates more micropores and widens the existing ones. This leads to an increase in surface area as %CBO increases. However, when the %CBO exceeds 50%, the widening of the existing pores coalesce them resulting in reduction of the total surface area of the carbons (Mkayula & Matumbo 1994). In the present study, the %CBO ranged between 10 and 25% and surface areas of the PFS carbons (as determined by methylene blue number) ranged between 292 and 642 m^2 g^{-1}. Dye test result showed values of molasses number, methyl blue number and iodine number to range between 142 - 1665, 200 - 440 and 934 —1567 for the three dyes, respectively; values that compare well with most commercial activated carbons (Anon 1985b). The values however, are higher than those observed for RH carbons. The high ash content in the RH carbons can be the reason for this observation, an aspect that is currently being studied.

CONCLUSION

Palm fruit shells and rice husks were used to prepare activated carbons using physical and chemical activation methods, respectively. The carbons showed surface areas ranging from 130-530 m^2 g^{-1} and 300 —650 m^2 g^{-1} for the rice husks- and palm fruit shells-based carbons, respectively. The surface areas for both systems are comparable to those of commercially used activated carbons (Anon 1992). Generally, the adsorption capacity of the palm fruit shells-based carbons was higher than that of rice husks-based carbons, as reflected also by the surface areas. In the case of rice husks-based carbons the surface area and hence adsorption capacity increased with increase in impregnation ratio and temperature (up to 1000 K). On the other hand, increase in activation temperature and time increased percentage carbon burn-off, surface area and hence adsorption capacity of the carbons derived from palm fruit shells. It can be concluded that palm fruit shells and rice husks can produce activated carbons of good quality using the preparation methods described in the present study.

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