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## THE PRODUCTION OF ACTIVATED CARBON FOR WATER TREATMENT IN MALAWI FROM THE WASTE SEED HUSKS OF *MORINGA OLEIFERA*

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### ABSTRACT

*Moringa oleifera* is a multi-purpose tree whose seeds can be used as a coagulant in water treatment. The seed husks are currently discarded as a waste, but research has shown that they can be converted into activated carbon by carbonisation at 485°C under N<sub>2</sub> for 30 minutes, followed by activation in steam at 850°C for 5 minutes. Here we report an improved method of carbon production, using a single-stage steam pyrolysis activation that is more appropriate for the intended use. Steam pyrolysis at 750°C for between 30 and 120 minutes produced a high quality microporous activated carbon at a yield of between 11 % and 17 %, with increases in soak time giving improved pore development and more mesoporosity. The apparent N<sub>2</sub> BET surface area of the *M. oleifera* carbon produced by soaking at 750°C for 120 minutes was 730.0 m<sup>2</sup> g<sup>-1</sup>, similar to that of the carbon produced previously by the two-stage process, 734.3 m<sup>2</sup> g<sup>-1</sup>. The phenol adsorptive capacities of the carbons pyrolysed at 750°C were similar to a commercial carbon. These results show that it is possible to produce high quality activated carbon from the waste seed husks of *M. oleifera* using a simple one-stage 750°C steam pyrolysis. This provides a low-cost method of producing activated carbon locally in developing countries for use in water treatment. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

### KEYWORDS

Activated carbon; appropriate technology; developing countries; low-cost adsorbents; *Moringa oleifera*; multi-purpose tree; steam pyrolysis; water purification.

### INTRODUCTION

*Moringa oleifera* is a multi-purpose tree that is found in many tropical areas, where it grows rapidly and is able to survive periods of low rainfall (Morton, 1991). The tree produces large seed pods, which can either be harvested while young and green for food ('Drumstick' in India), or left to dry on the tree. The dried seeds can be crushed to produce a high quality vegetable oil, and the pressed cake can then be used as a coagulant (see below). Parts of the tree are also used in medicine; the leaves contain hypotensive agents (Faizi *et al.*, 1994) and the roots are abortifacient (Nath *et al.*, 1992). The coagulant properties of the crushed *M. oleifera* seed appear to have been discovered first by experimentation by villagers in Sudan (Jahn, 1988),

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and further research has found the coagulant to be as effective as aluminium sulphate in many situations, and its use is being developed on both a village and waterworks scale (Jahn, 1986; McConnachie *et al.*, 1994).

The seed husks are currently discarded as waste when seed is prepared for oil and/or coagulant production. However, it has been found that these husks can be converted into a high quality microporous activated carbon (Pollard *et al.*, 1995). Activated carbon has many uses in drinking water and wastewater treatment, including the removal of taste and odour-producing chemicals (Lalezary-Craig *et al.*, 1988), algal toxins (Donati *et al.*, 1994), pesticides (Miltner *et al.*, 1989) and metals (Budanova *et al.*, 1994). Since commercial activated carbon is expensive, it is seldom possible to use it in water treatment in developing countries. However, substantial research effort has been directed towards the preparation and utilisation of low-cost alternatives to commercial carbon using locally available agricultural by-products (Pollard *et al.*, 1992). A low-cost method of producing activated carbon from *M. oleifera* waste could allow economic use of activated carbon even in poorer countries, and contribute to an appropriate technological solution to improving potable water quality in the developing world.

Previous research by Pollard *et al.* (1995) found that carbonisation of husks under N<sub>2</sub> at 485°C for 30 minutes, followed by steam activation for 5 minutes at 850°C, produced a highly microporous carbon with adsorptive properties similar to commercial activated carbons. This is a complex production process, involving two heating stages, and the use of N<sub>2</sub> gas. In a developing country both chemical and energy costs are high, so any reduction in, or elimination of, the use of chemicals, and any reduction of the energy required for the process will improve the economic case for carbon production. Several simplified activated carbon production processes have been investigated by other workers, with a one-stage 600 - 700°C steam pyrolysis carbonisation being particularly effective (Gergova *et al.*, 1994). The research presented here demonstrates that a simple steam pyrolysis procedure can be used to make a good quality activated carbon from the waste husks of *M. oleifera*, and reproduce the activity and microporosity previously demonstrated at the laboratory scale under more conventional activation conditions.

## MATERIALS AND METHODS

### Materials

*M. oleifera* husks were obtained from Malawi, where they had been produced as a waste product from the production of *M. oleifera* seed. Because of the nature of the seed-husk separation process, this husk material also contained powdered seed, and was not of an even particle size, varying between powder and particles several mm in dimensions. Two commercial reference carbons were used in the phenol adsorption tests, one powdered, Acticarbone TE (CECA S. A., France), and one granular, YAO 14x40 ref. 779 (Eurocarb, Bristol, UK).

### Carbonisation/activation of husks

Carbonisation of *M. oleifera* husks was performed in a Carbolite 12/65 tube furnace, with a purpose-made quartz tube inserted into it (Multi-Lab, Newcastle, UK). This tube connected to Quickfit connections at one end, and a ball and cup joint at the other, allowing flow-through of a controlled gaseous atmosphere. Charges of 30 g of *M. oleifera* husks were placed in a customised quartz combustion boat (Multi-Lab), loaded into the quartz tube and positioned in the centre of the furnace. The temperature of the sample was monitored by a thermocouple probe (type K probe, connected to a P. I. 8013 thermometer from Portec, Milton Keynes, UK) which entered the silica tube through one of the Quickfit connectors and whose tip was positioned just above the sample. Steam, generated by a flask of water on a heating mantle, entered the quartz tube through one of the Quickfit joints at a rate of approximately 2 ml (liquid water) per min. A condenser was connected to the ball and cup joint at the other end of the tube, and the condensed material was collected in a beaker.

The sample was heated at a fixed rate of approximately  $20^{\circ}\text{C min}^{-1}$  to the appropriate temperature, and held at this temperature ( $\pm 10^{\circ}\text{C}$ ) for the time specified. After the furnace had cooled to between  $200$  and  $300^{\circ}\text{C}$ , the carbonised husks (char) were removed, allowed to cool for a few minutes and then weighed to determine the yield. The char was then moved to a desiccator for storage. Chars, duplicated for each set of temperature and time, were later mixed, homogenised and sieved to  $<250\ \mu\text{m}$ , then dried in an oven at  $110^{\circ}\text{C}$  overnight, prior to testing for adsorptive capacity.

#### Aqueous adsorption testing of chars with phenol

A preliminary screening test of the adsorptive capacity of the chars was conducted using a simple single point, aqueous phase phenol adsorption test (Pollard *et al.*, 1995). Char samples ( $0.5\text{g}$ ) were added to  $100\ \text{ml}$  of  $0.01\ \text{M}$  phenol (BDH, UK) solution in  $250\ \text{cm}^3$  Erlenmeyer flasks, which were sealed with Suba-seals, then shaken at  $90\ \text{strokes min}^{-1}$  in a temperature controlled shaker bath for  $24\ \text{h}$  at  $25^{\circ}\text{C}$ . Following uptake, suspensions were vacuum-filtered through a Whatman cellulose nitrate  $0.45\ \mu\text{m}$  membrane filter and residual phenol concentrations were analysed at  $270\ \text{nm}$  using a u.v. spectrophotometer (Shimadzu UV-160A). All determinations were at least duplicated.

#### $\text{N}_2$ BET adsorption testing of chars

Activated chars were analysed by continuous volumetric  $\text{N}_2$  adsorption analysis for surface area characterisation and pore size distribution analysis using a Coulter Omnisorp Model 100 instrument (Centre for Environmental Control and Waste Management, Imperial College, London, UK). A representative carbon sub-sample of approximately  $0.3\text{g}$  was taken from each char under test and outgassed at  $250^{\circ}\text{C}$  for  $8\ \text{h}$  under a vacuum of  $10^{-5}$  torr. A full  $\text{N}_2$  adsorption/desorption isotherm was obtained at liquid  $\text{N}_2$  temperatures using a constant, calibrated  $\text{N}_2$  flow rate of  $0.27\ \text{cm}^3\ \text{min}^{-1}$  and an adsorption cut off  $p/p^{\circ}$  of  $-0.98$ . Analysis of the data was done using the associated instrument software, which employs the  $\text{N}_2$  BET method of calculating apparent surface area, the t-plot analysis for comparing micropore, mesopore and macropore volumes, the BJH method of mesopore and macropore size distribution (Barrett *et al.*, 1951) and the Horváth-Kawazoe model (1983) for analysis of the micropore size distribution (pore widths  $<2\ \text{nm}$ ). The BJH method employs the Kelvin equation for determination of the pore size distribution and assumes a cylindrical pore shape, as does the Horváth-Kawazoe model. The appropriate use and limitations of these models have been discussed previously (Pollard, 1990).

## RESULTS

#### Characteristics of char production

The yields obtained under various temperatures and times are shown in Table 1. The steam pyrolysis process gave reproducible yields, with duplicate runs differing by less than 1%. As the soaking temperature was increased, the yield reduced. There was little effect on yield of different soak times at  $500$  and  $600^{\circ}\text{C}$ , but at higher temperatures the yield was considerably reduced by longer soak times.

The material condensed from the off-gases contained both a black, tarry component and a yellowish-white material. The condensate had a strong, unpleasant smell.

#### Characterisation by phenol adsorption

The single point phenol adsorption test showed that phenol uptake increases as yield reduces (Table 1 and Figure 1). However, all three chars produced at  $750^{\circ}\text{C}$  showed similar adsorptive behaviour, in spite of the increased burn-off in S750/120, with 11.4% remaining, as compared to S750/30, with an approximately 50% higher yield of 16.6%. All the chars produced at  $750^{\circ}\text{C}$  had a phenol adsorptive capacity similar to the commercial powdered activated carbon, Acticarbon TE, though lower than the commercial granular carbon Eurocarb YAO (Table 1).

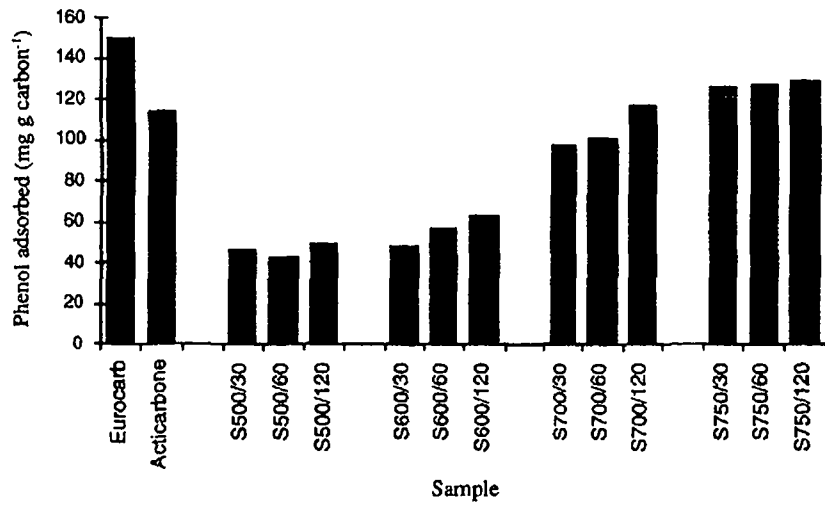


Figure 1. Phenol adsorption results.

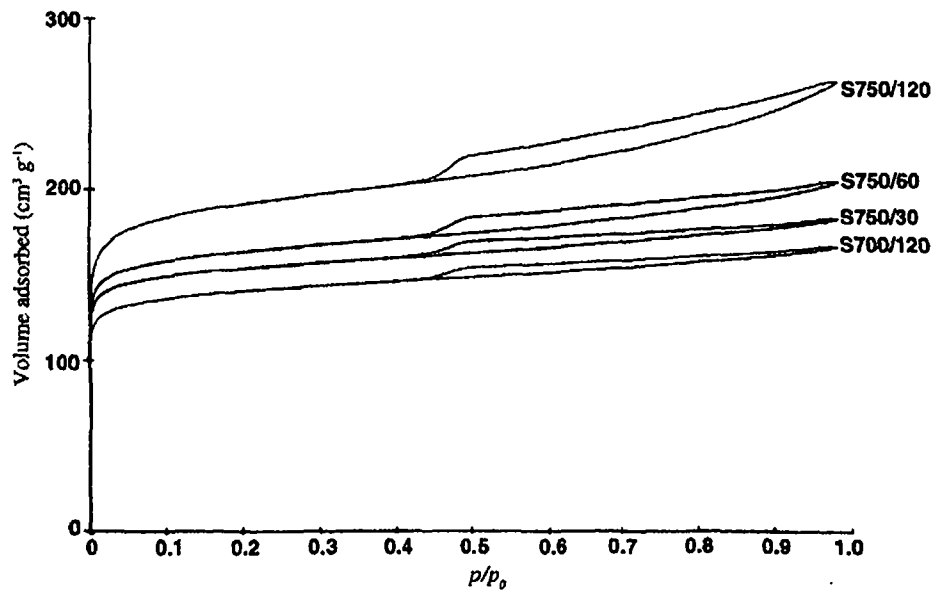


Figure 2. Nitrogen adsorption isotherms.

### Characterisation by N<sub>2</sub> BET adsorption

Nitrogen adsorption isotherms were determined for the four carbons with the highest burn-off, and highest phenol adsorption (Figure 2). All isotherms exhibited Type I/Type IV (microporous/mesoporous) characteristics with closed loop hysteresis but tight initial micropore filling. The hysteresis loop was classified as H4 (Gregg and Sing, 1982), more indicative of slit or plate-like pore configurations, hence the need for caution in interpretation of the surface area and micropore volume data (Pollard, 1990). The carbon with the lowest burn-off, S700/120, exhibited Type 1 isotherm characteristics, according to the BDDT classification (Gregg and Sing, 1982), with limited hysteresis. As burn-off increases, the isotherm increases in Type 4 characteristics, toward a more mesoporous structure. The width of the hysteresis loop also increases at higher burn off, and moves away from a horizontal plateau, which is indicative of increased mesoporosity.

The purpose of the analysis of the N<sub>2</sub> adsorption isotherm data in this work is to enable comparison between the carbons produced, and limited comparison with those carbons produced by other workers. Used in a comparative sense, the data is useful in assessing the effects of different preparative techniques and in optimising carbon production (Pollard *et al.*, 1991).

The apparent surface areas for the carbons were determined using the linearised BET equation and a molecular area of  $0.162 \times 10^{-18} \text{ m}^2$  for N<sub>2</sub>. This apparent surface area increased with increasing burn-off (Table 2), to a maximum of  $730.0 \text{ m}^2 \text{ g}^{-1}$  for S750/120. This compares well with the surface area of  $734.3 \text{ m}^2 \text{ g}^{-1}$  found for the *M. oleifera* carbon produced in previous work (Pollard *et al.*, 1995).

The t-plot analysis of micropore, mesopore and macropore volumes and surface areas demonstrates that these also increased as burn-off increased (Table 2). The maxima were found in the S750/120 carbon, with a micropore volume of  $0.25 \text{ ml g}^{-1}$ , a combined mesopore and macropore volume of  $0.1 \text{ ml g}^{-1}$  and a mesopore and macropore surface area of  $112 \text{ m}^2 \text{ g}^{-1}$ . As expected, the mesopore and macropore volumes are particularly strongly affected by increased burn-off, with S750/120 having almost double the volume of S750/60, whilst the micropore volume only increases by just over 10%. This leads to a fall in percentage of the pore volume that is due to micropores, from 82% in S750/60 to 72% in S750/120. The micropore volume of S750/120 is about half that found in the previous *M. oleifera* work, but the mesopore and macropore volume is 40% higher.

Table 1. Char yields and phenol adsorbance results

Sample	Production conditions		Yield		Phenol adsorbed	
	Temperature °C	Soak time min	% mean	± s. d.	mg/g carbon mean	± s. d.
S500/30	500	30	24.1	± 0.1	46	± 2.9
S500/60	500	60	24.7	± 0.1	43	± 3.9
S500/120	500	120	23.5	± 0.2	49	± 2.6
S600/30	600	30	22.0	± 1.3	48	± 1.8
S600/60	600	60	22.4	± 0.4	57	± 0.4
S600/120	600	120	22.0	± 0.8	63	± 0.6
S700/30	700	30	19.7	± 0.2	97	± 0.2
S700/60	700	60	18.5	± 0.1	101	± 2.6
S700/120	700	120	17.3	± 0.4	117	± 1.1
S750/30	750	30	16.6	± 0.2	126	± 0.2
S750/60	750	60	15.1	± 0.1	127	± 2.7
S750/120	750	120	11.4	± 0.5	129	± 2.0
Acticarbone					114	± 2.0
Eurocarb					150	± 8.9

The Horváth-Kawazoe plots of micropore distribution (not shown) had a single, sharp peak at an effective pore diameter of just less than 0.6 nm, with the height of this peak ( $dW/dR$  representing the micropore distribution) at a maximum in S700/120 ( $dW/dR = 15.5$ ), and a minimum in S750/120 ( $dW/dR = 9.7$ ), providing further evidence of the reducing proportion of micropores in the carbons with higher burn-off.

#### DISCUSSION

These results have shown that it is possible to produce a high quality activated carbon from the waste husks of *M. oleifera*, using a simple one-stage, 750°C, steam pyrolysis. Carbon produced by soaking at 750°C for 120 minutes has a similar  $N_2$  BET apparent surface area to that produced by a two-stage process, carbonisation at 485°C followed by steam activation at 850°C, though it is less microporous and more mesoporous and macroporous.

As burn-off increases, it seems that both microporosity and the larger pores develop, presumably by widening of micropores to mesopores (Wigmans, 1989), whilst more micropores are being opened. It is likely that if higher temperatures are used for the steam pyrolysis, at some point the surface area will begin to reduce, as the pores are burnt out. It is possible, though, that a carbon pyrolysed at 800°C might have an apparent surface area higher than that of S750/120, though this would probably be at the expense of reducing yield. Further work is intended on higher temperature carbons. The balance between yield and adsorptive capacity is an important consideration in the application of this process; S700/30 and S700/120 have a single-point phenol adsorption capacity within a few percent of each other, but the yield of S700/30 is 50 % higher, and it requires 90 minutes less heating time, therefore saving energy. Future work will include evaluation of the most effective and economical method of producing carbons suitable for the adsorptive roles required (discussed below).

The characteristics of the carbons produced in this work appear to be similar to those produced by Gergova *et al.* (1994) by steam pyrolysis of plant materials. This work found that steam pyrolysis at 700°C for 120 minutes led to a BET surface area of 820  $m^2 g^{-1}$  in apricot stones, 574  $m^2 g^{-1}$  in almond shells and 541  $m^2 g^{-1}$  in cherry stones, comparable with those found in this work. Rodríguez-Reinoso *et al.* (1995) used a more conventional two-stage carbonisation and activation process to compare the actions of steam and  $CO_2$  as activating agents. Their work found that microporosity widening occurred from the early stages of the activation process when steam was used as an activating agent at either 750 or 800°C, as has been found in these experiments. In contrast, microporosity widening occurs later with  $CO_2$  as an activating agent. Steam was found to produce a wider range of pore size distribution than  $CO_2$ , with a larger development of mesoporosity and macroporosity, both of which are useful for adsorbing larger molecules and providing transport routes to the micropores.

Table 2. Results from  $N_2$  isotherm analysis, compared with the *M. OLEIFERA* carbon produced in earlier work Pollard *et al.*, 1995)

Sample	$N_2$ BET surface area ( $m^2/g$ )	Micropore volume (ml/g)	Mesopore & macropore surface area ( $m^2/g$ )	Mesopore & macropore volume (>2 nm, ml/g)	Volume in micropores (%)
S700/120	539.8	0.20	55.3	0.030	87
S750/30	588.1	0.21	61.8	0.032	87
S750/60	625.1	0.22	75.6	0.048	82
S750/120	730.0	0.25	111.6	0.098	72
$N_2$ 485/30, S850/5 (Pollard <i>et al.</i> , 1995)	734.3	0.57	77.9	0.07	89

The composition of the off-gases and condensate was not determined in this study, but work on steam pyrolysis volatiles from apricot stones and coconut husks found that typical components of lignocellulosic gases include derivatives of phenol, guaiacol, veratrol, syringol, resorcinol, free fatty acids and the esters of fatty acids (Razvigorova *et al.*, 1994). Whether it would be possible to find a use for this material is not clear, otherwise it will have to be disposed of; fortunately it is likely to be readily biodegradable.

This research project will be continuing in association with The Polytechnic, the University of Malawi, in Blantyre, Malawi, where we will be developing the techniques for bulk production of the activated carbon in Malawi. In addition to the seed husks, we intend to investigate the possibility of producing carbon from the seed pods, which make up more than 50 % of the mass of the fruit, and which are currently discarded. We will also be examining applications of the carbon, particularly concentrating on water quality problems produced by algal blooms, including taste, odour and toxins, since algal blooms are a problem in reservoirs in Malawi and other regions of southern Africa (Scott, 1991). Further work is also underway in association with the Environmental Engineering group at the University of Leicester, Leicester, UK, to develop market analyses and business plans for *M. oleifera*-derived oil, coagulant and activated carbon.

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