Effect of Nutshell Hardness, Chemical and Polymeric Compositions on Porosity and Adsorption Capacity of Nutshell-Based Active Carbons

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Abstract: This study investigated the dependence of iodine numbers, pore volumes and CO_2 based active carbon yields on hardness, crude fibre and major polymeric contents of precursor nutshells of *Thevetia nerrifolia, Cocos nucifera, Hyphaene thebaica, Hura crepitans* and *Calophylum inophylum*. Physico-chemical studies were performed on the precursor raw nutshell followed by separate carbonization of each of the nutshell in the presence of nitrogen at 480°C for 1 h. Subsequently physical activation of chars was conducted at 840°C with CO_2 in a quartz glass tube placed in horizontal furnace. The cellulose content, lignin content, iodine number and BET surface area of prepared active carbons ranged 324.6-412.7, 42.6-293.6, 822.2-1804.0 mg g^{-1} and 551-2738 m^2 g^{-1}, respectively. Micropore volume ranged 0.100-0.702 cm^3 g^{-1} while mesopore volume ranged 0.017-0.053 cm^3 g^{-1}. Four equations that separately relate crude fibre content and hardness-vickers-diameter ratio of precursors to iodine numbers, porosity, micropore volume and yield of active carbon is therefore suggested.

Key words: Active carbons, shell hardness, adsorption capacity, crude fibre, nutshell, porosity, cellulose, lignin

INTRODUCTION

Agricultural wastes like fruit nutshells that constitute public menace contain potential carbon origin. Nutshells are lignocellulosic matter that is available on a renewable basis and could be converted to active carbons with high quality adsorption properties (McDougall, 1991; Maniatis and Nurmala, 1979). Some common applications of active carbon are evident in food, agro-based industries, pharmaceuticals, water purification, air treatment, chemical treatment, oil refinery processing and in nuclear power stations (Ashford, 1994; Ramos *et al.*, 1997). Consequently, most industrialized countries of the world like United States of America and Japan have found the use of active carbon in their industries inevitable (Dai *et al.*, 1995). In 1990, Roskill reported that yearly active carbon consumption of these two industrialized nations was 300,000 metric ton. By 2025, over a million metric ton of active carbon will be required based on 4% increase on 750,000 metric ton in 2002 estimation.

The conversion of feedstock nutshell into active carbons usually comprises of carbonization and activation processes. Carbonization involves decomposition of biomass in an inert atmosphere at temperature <500°C while endothermal reactions of chars in the presence of oxidizing gas like carbon-dioxide or steam is physical activation.

One major area of research is properties of biomass (Antal, 1983). Active Carbon (AC) could be prepared from large variety of carbon containing feed stock but all may not be in commercial quantity and high grade (Ahmedna *et al.*, 2000). Therefore, the choice of precursor material for commercial production of AC becomes necessary. The effects of nutshells properties as initial indicators for selection of good precursor material and process conditions to achieve desired characteristics of AC can not be overlooked. The hardness of nutshells, their physicochemical compositions and major polymeric contents (cellulose, hemicellulose and lignin) of different nutshells do not exist in same proportion. The presence of various amount of ash in raw material is also a pointer of different quantities of inorganic salts in the biomass types. Afrane and Achaw (2007) examined the effect of inherent levels of mineral concentration (ash) on iodine number adsorption and found that AC derived from coconut shell with lesser mineral content exhibited higher iodine numbers. Raveendran *et al.* (1995) also observed

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that mineral matter of biomass and organic composition might play a major role in determining pyrolysis, product distribution and product properties. Furthermore, Rhen *et al.* (2007) found that combustion time for a single woody biomass pellet depended mostly on the raw material composition and to a minor extent on the density. The variation in the extent of decomposition of wood determined the amount of volatiles which fell within the range of 76-86% (Van Loo and Koopejan, 2002). They concluded that the char yield and char combustion rate of a bio-fuel are potentially highly correlated to the chemical composition of the biomass. Raveendran and Ganesh (1998) observed that raw material containing large amount of lignin gave a higher char yield than those with large cellulose and hemicellulose. Humpherys and Ironside (1980) had also earlier pointed out that burning characteristics of various biomass types may differ depending on the composition of the raw material used. Bilba *et al.* (2007) in their study, observed that chemical composition of four natural fibres from banana and coconut trees depended on type of the tree and that the decomposition of the banana fibres was rapid with increasing temperature of pyrolysis.

The commercial production of active carbon utilized common precursor materials like bituminous coal, lignite, peat and some lignocellulosic materials such as wood and coconut shell (Pollard *et al.*, 1992). Majority of commercial active carbon produced has been from natural coal. Some workers have reported possibility of production of active carbon from nutshells (Winifred *et al.*, 1999; Ahmedna *et al.*, 2000; Wan-Daud *et al.*, 2001; Wartelle and Marshall, 2001). However, effect of hardness of precursor nutshells on quality of active carbons has not been reported. Apart from contribution to quality of active carbon from method of production, its quality has also recently been attributed to major polymeric components of the precursor nutshells (Raveendran *et al.*, 1995). Furthermore, there is the fear of depletion of natural coal as well as deforestation of the environment due to continuous use of wood for active carbon preparation. Nutshells are renewable biomass with likely potential for active carbon production. Therefore, the main objective is to relate the effect of physicochemical properties, hardness of nutshells and major polymeric composition of nutshells to each of their corresponding active carbon product characteristics like porosity and adsorption capacity. This enables the selection of good nutshell types for commercial production of active carbon with the aid of carbon dioxide as oxidizing gas.

MATERIALS AND METHODS

Five commonly available types of nutshells were harvested from Northern and Western regions of Nigeria.

The mature nuts of *Thevetia nerrifolia* (yellow oleander), *Hura crepitans* (sand box plant) and *Cocos nucifera* (coconut) nuts were harvested under each plant where they serve as ornamental plant within the University of Ibadan, Ibadan, Nigeria while ripe *Calophylum inophylum* (laurel wood) was harvested from botanical garden of the same University in the Western region of Nigeria between 7°23'47"N and 3°55'E of southern Nigeria. The mature unbroken *Hyphaene thebaica* (dum palm) nuts were harvested from its palm tree from North Eastern part of Nigeria. It thrives well in Sahel and hot dry Savannah between 12-18 N from Senegal to Northern Nigeria, Chad, Zaire and North East Africa and is called goriba in Hausa. The reference carbons are commercial BDH decolourizing carbon powder and BDH granular active carbon. Each of these nutshells were removed mechanically, dried in sun for 4 h and in oven at 110°C for 2 h. They were stored in plastic containers.

Preparation of active carbon: About 200 g each of the five mature sun dried nutshell types were individually charred in a cylindrical quartz glass tube container (35×7 cm) placed in hollow stainless steel horizontal tubular reactor (Adebowale and Adebowale, 2008).

Low temperature conversion was carried out batch wise on each of the various samples in the laboratory reactor in the presence of nitrogen with flow rate of 1000 mL min⁻¹ at 480°C and heating rate maintained at 10°C min⁻¹ for 1 h. The air in the furnace was first evacuated by allowing N_2 gas to flow in at 1000 mL min⁻¹ for 15 min. The charred samples were allowed to cool in the furnace in a Nitrogen atmosphere till temperature of 200°C when they were removed and covered till they cooled to room temperature. The procedure was duplicated to ascertain the reproducibility of yield.

A 12.0 g of each various nutshell chars were differently loaded in hollow quartz glass tube and placed in char activation horizontal tubular reactor furnace (Carbolite tube furnace, CTF 12/65/550 Model, Italy). The char samples were heated in turn in the presence of CO_2 with flow rate of 500 mL min⁻¹ and at 20°C min⁻¹ heating rate to final temperature of 840°C for a period of 3 h. Prior to activation, the air in the quartz tube was also first evacuated by flow of N_2 gas at 500 mL min⁻¹ for 30 min.

Tropical nutshell types and active carbon analysis: The physical properties (bulk density, moisture content) were determined according to Ahmedna *et al.* (1997) for bulk density while methods recommended by Pearson (1976) and AOAC was used for moisture content. The chemical properties (ash, pH, conductivity) were determined for nutshell types according to AOAC method for ash content while American Water Works Association (AWWA, 1974) standard-13604 (1990) method for active

carbon ash content. Petrov *et al.* (2000) method was used for determination of pH and conductivity of the precursor nutshell while for their corresponding active carbons, American Standard Testing Methods, ASTM (1996) was used.

Measurement of hardness-diameter ratios of nutshells: The measurement of hardness Vickers number for the nutshells was carried out using LECO, Micro hardness Tester LM 700 AT, US and vernier callipers that was used to measure the diameter of the shells. The micro hardness tester, set at a load of 10 g and magnification of ×500 was allowed to impact a pressure that created an indentation on each polished nutshell for 10 sec. The instrument records the value of hardness Vickers number depending on the extent of indentation. The vernier callipers recorded the value of diameter of each of the nutshells.

Measurement of chemical composition of tropical nutshell: Each nutshells were separately ground in a hammer mill and sieved with a standard sieve (DIN4188 prusien, England) to obtain <1 mm particle size. Crude fibre content was determined gravimetrically according to AOAC method while extractives by American National Standard-D1105 (1972) method. Lignin contents of the nutshells were determined spectrophotometrically by acetyl bromide method (Morrison *et al.*, 1995) while hemicellulose and holocellulose were determined gravimetrically (Raveendran *et al.*, 1995; ANSI, 1968). Their cellulose contents were determined by modified method of Kurschner and Hoffer (1931) method. The modification was carried out by pre-treatment of ground air-dried samples with alcohol-benzene mixture using sohxlet extractor for 4 h for each of the samples. The determination of tannin content of each nutshell was determined by spectrophotometric method (Burns, 1971; Nahm, 1992). The CHNS elemental analyses of the five nutshells were carried out with CHNS auto analyser.

Characterization of active carbon
Iodine and methylene blue numbers analysis: The active carbons were characterized by iodine and methylene blue adsorption. Iodine number and methylene blue number are measure of adsorption capacity of any active carbon type. Iodine number indicates the extent of micropore distribution in the carbon (Kirubakaran *et al.*, 1991). It is a measure of iodine molecules adsorbed in the pores and indicates micropore volume capacity. The iodine number which gives an idea of the microporosity was determined by the modified AWWA procedure (AWWA, 1974). The modification involves the centrifugation of the various active carbon-iodine solution mixtures for 5 min prior to

titration with standardised sodium thiosulphate solution in the presence of starch indicator. Methylene Blue (MB) adsorption capacities of the active carbons were measured in accordance with ASTM (1996) standards for active carbons. Thus, 25 mL of MB solution of 1.2 g L^{-1} were poured into plastic containers and 0.2-0.4 g prepared active carbon were added differently to MB solution in each plastic container. The plastic containers and its contents were shaken for 12 h with an Elmer Perkin thermostat shaker to allow equilibration. The concentration of residual MB in solution was then determined at 625 nm using a λ3D-double beam UV visible spectrophotometer, Perkin Elmer after separation of the carbons with a centrifuge. A standard calibration curve of MB at 625 nm was plotted against known concentration of MB solution and used to determine the actual methylene blue adsorption capacity of the active carbons. The results of amount of iodine and methylene blue adsorbed per gram were calculated.

Pore volume analysis and scanning electron microscopy: The micropore volumes of the prepared active carbons were also carried out by n-hexane adsorption method (Bayer *et al.*, 1995). The physical surface morphology was examined using a DSM 9872 Gemni Scanning Electron Microscope (SEM). A thin layer was mounted on the aluminium specimen holder by a double sided tape. It was coated with gold/palladium with a thickness of about 30 nm. The SEM of CO_2-Active Carbons (CO_2-AC's) was recorded at 500x magnifications.

Brunauer Emmett Teller (BET) surface area analysis: The surface areas of CO_2-AC's derived from the various nutshells were measured by Nitrogen isotherms of samples and subsequently Bruanuer Emmett Teller (BET) surface area were recorded on Gemni 2375 Sorptometer (Micrometricss, Neuss, Germany).

Statistical analysis: Analysis of Variance (ANOVA) and separation of means were conducted by the General Linear Model procedures. Comparisons of means of values of physicochemical parameters as well as those of chemical composition of nutshells were analysed using Duncan multiple range data test at 5% probability level.

RESULTS AND DISCUSSION

Physical properties of fruit nutshell biomass: Among the nutshell types, the highest bulk density value (0.65 g mL^{-1}) was observed for *C. nucifera* shell while (0.16 g mL^{-1}) is lowest for *H. thebaica* (Table 1). It has

Table 1: Physicochemical properties of nutshells

Nutshell types	[a]Bulk density (g mL^{-1})	Moisture (%)	Ash (g kg^{-1})	pH	Conductivity (msec cm^{-1})
C. inophylum	0.30±0.07	10.30±0.28	10.7±0.6	5.21±0.01	0.63±0.00
C. nucifera	0.65±0.01	8.90±0.95	5.7±0.3	5.76±0.01	0.35±0.01
H. crepitans	0.42±0.01	9.35±0.41	15.8±0.3	4.89±0.01	0.81±0.01
H. thebaica	0.16±0.01	8.66±0.33	15.0±1.2	4.62±0.01	1.63±0.01
T. nerriofolia	0.55±0.01	10.21±0.73	3.8±0.2	4.65±0.00	0.35±0.01

[a]Based on a particle size of 1.18-2.36 mm values given are means of triplicate results and their standard deviations

been reported that in the course of production of active carbon, the rate of volatization, hardness strength and porosity of carbon are dependent on their starting material bulk densities. A denser biomass will produce a more compact and harder active carbon (Pendyal *et al.*, 1999). The bulk density values obtained for the precursor lignocelluloses nutshells investigated are in agreement with the values of other lignocelluloses materials that varied from 0.37-0.75 g mL^{-1} (Wartelle and Marshall, 2001). The value of 0.65 g mL^{-1} obtained for *C. nucifera* is similar to 0.66 g mL^{-1} obtained for same nutshell by Raveendran *et al.* (1995). Among the nutshells density values shown in Table 1, both *C. nucifera* and *T. nerrifolia* shells are significantly different from other investigated nutshells as well as from each other. These nutshells density values indicate that some of the nutshell types might be a potential for active carbon production.

The moisture contents of the air-dried nutshells were found to be in the range of 8.66-10.30% (Table 1). Some of these values are in agreement with 5.6-9.3% moisture content for peanut shells (Winifred *et al.*, 1999). The variations in the moisture content of the various nutshells might contribute to the rate of volatization during carbonization and activation processes. Among the investigated nutshells, the moisture content (Table 1) of *C. inophylum* (10.30%) is observed to correspond to active carbon with relatively large micropore volume of 0.702 cm^3 g^{-1}. The next highest moisture content values of 9.35 and 8.66% for *H. crepitans* and *H. thebaica*, respectively correspond to the next largest micropore volumes of 0.182 and 0.166 cm^3 g^{-1}. Though, there may not be an existence of distinct trend between the moisture content and micropore volume, there is more or less evidence of positive relationship between the moisture content as well as bulk density of nutshell and the eventual porosity or micropore volume of their corresponding active carbons prepared with carbon dioxide acting as oxidizing gas during activation process. Furthermore, the chemical properties of these nutshells are depicted by ash content, pH and conductivity values as shown in Table 1. The ash content values that ranged from 3.8-15.8 g kg^{-1} of the nutshells studied are lower than values (7.0-29.0 g kg^{-1}) obtained for lignocellulose biomass types reported (Raveendran *et al.*, 1995;

Lutz *et al.*, 2000; Wan Daud *et al.*, 2000; Wan-Daud *et al.*, 2001). Low ash contents are desirable in precursors for active carbon manufacture. It ensures that the blocking of existing micropores in active carbons obtained is prevented and increased surface area is achieved. Table 1 also shows that pH values for the nutshells fell within 4.62-5.76. This implies that the entire nutshells studied are acidic. The higher the ash content, the higher the pH value. However, the low values of ash and pH of precursor nutshells are desirable for active carbon production.

Since, pH is negative logarithm of H$^+$ ion concentration, it may be explained that the variations in pH is dependent upon the H$^+$ or OH$^-$ ion concentrations in the soluble ash contents of the various nutshells. These findings agree with those of Hassler (1963) that explained pH of commercial carbons to be due to inorganic constituents in the precursor. The electrical conductivity of the nutshells which is a measure of potentially water soluble minerals, gave various values. The range of conductance value of nutshell types ranged from 0.35-1.63 msec cm^{-1} with *H. thebaica* having 1.63 msec cm^{-1} as highest value whereas *C. nucifera* and *T. onerrifolia* exhibited least values of 0.35 msec cm^{-1}. Their corresponding active carbon exhibited lower values that fell within the range of 0.07-0.58 msec cm^{-1}. The ash contents of the prepared active carbons are also low (11.4-82.1 g kg^{-1}) with exception of *H. crepitans* having 138.1 g kg^{-1} ash content. The pH values for the entire nutshells studied are significantly different. Similarly, their conductivity values are observed to be significantly different with exception of *C. nucifera* and *T. nerrifolia* which exhibited no significant difference among them but are significantly different from other nutshells investigated.

Hardness-diameter ratio of nutshells: The hardness-diameter ratio of nutshells are also found to relate to active carbon quality parameters (iodine number, porosity and active carbon yield) of CO$_2$ based Active Carbons (CO$_2$-AC's) prepared from these nutshells. From among the CO$_2$-AC's that only allowed passage of small iodine molecules (with no methylene blue adsorption), it is observed that iodine numbers of CO$_2$-based active carbon are inversely proportional to hardness Vickers-diameter ratio of their corresponding nutshells with correlation

coefficient, $R^2 = 0.743$ which is fairly good (Fig. 1). It could also be shown in Fig. 2 that porosity (micropore plus meso pore volumes) are inversely proportional to hardness-diameter ratio of nutshells while its $R^2 = 0.743$ which is also fairly good. However, when micropore volume alone was plotted against the hardness-diameter ratio, the $R^2 = 0.468$ is low and indicates poor fitting. Figure 3 in the other hand indicates a direct positive relationship between CO_2 based active carbon yield and hardness-diameter ratio of nutshells exhibiting a high correlation coefficient, $R^2 = 0.977$.

Chemical composition of nutshells: The chemical composition of the nutshell precursors is shown in Table 2. Among the nutshells studied, *T. nerrifolia*
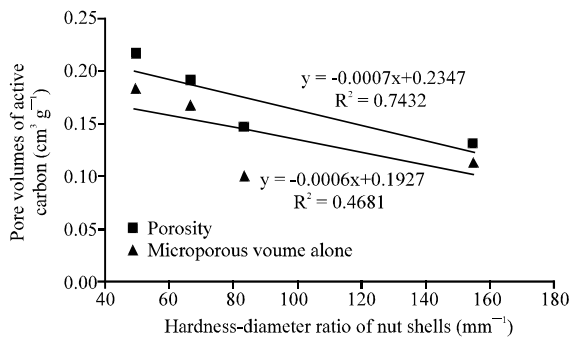
contained the largest crude fibre value (650.8 g kg^{-1}) while the lowest value of 336.7 g kg^{-1} was obtained for *C. inophylum*. Thus, the different nutshells could be ranked in the order of increasing crude fibre content as follows: *C. inophylum<H. crepitans<H. thebaica<C. nucifera<T. nerrifolia.*

The crude fibre content of *T. nerrifolia* is higher than that of *C. nucifera* which had been utilized successfully for production of quality active carbons. In addition, Fig. 4 shows a definite pattern between the crude fibre content of the nutshells and the quantity of iodine adsorbed per gram of their corresponding CO_2 based AC. Among the prepared active carbons, their iodine number values correlated well with their corresponding crude fibre contents of nutshells with high correlation coefficient, $R^2 = 0.928$ (Fig. 4) whereas Fig. 5 shows that their porosity (micropore volume plus mesopore volume) and micropore volume of CO_2-AC's alone are inversely proportional to the crude fibre content of their corresponding nutshell with $R^2 = 0.992$ and 0.941, respectively. An exception was observed with *C. inophylum* CO_2-AC. This might be attributed to the fact that only *C. inophylum* active carbon developed pores that could allow passage of both small iodine molecules and large methylene blue molecules. Therefore, carbonization and activation processes might have created enough large pore sizes and allowed passage of both molecules.

In line with observation in this research, some investigators have also pointed out the dependence of char or active carbon yield and porosity on the thermal stability of lignocellulosic components (Lignin, cellulose and hemicellulose) during carbonization or activation processes (Lutz *et al.*, 2000; Mackay and Roberts, 1982).
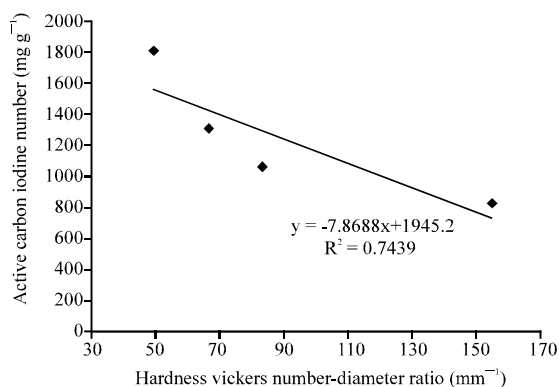

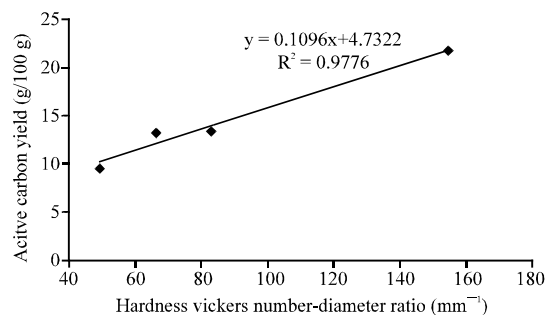Fig. 1: Plot of active carbon iodine number versus hardness vickers number-diameter ratio of nutshells

Fig. 2: Plot of active carbon pore volumes versus hardness vickers number-diameter ratio of nutshells

Fig. 3: Plot of active carbon yield versus hardness vickers number-diameter ratio of nutshells

Table 2: Chemical composition of fruit nutshells

Biomass types	Crude fibre (g kg^{-1})	Cellulose (g kg^{-1})	Hemicellulose (g kg^{-1})	Lignin (g kg^{-1})	Extractives (g kg^{-1})	Tannin (mg g^{-1})
C. inophylum	336.7±0.2[b]	344.8±1.8[b]	604.5±1.1[g]	42.6±0.1[a]	8.2±0.4[a]	2.45±0.0[b]
C. nucifera	628.4±0.7[f]	335.1±1.5[b]	446.5±1.8[f]	63.2±0.4[ab]	154.8±0.7[de]	11.65±0.0[g]
H. crepitans	385.2±1.5[c]	412.7±6.6[f]	398.1±3.5[e]	47.4±1.7[ab]	141.9±0.0[d]	17.40±0.3[i]
H. thebaica	475.9±0.7[d]	324.6±1.6[b]	168.4±0.6[b]	293.6±1.3[d]	212.7±0.6[f]	10.60±0.0[f]
T. nerrifolia	650.8±0.2[g]	371.9±3.1[bc]	242.3±0.3[c]	270.9±1.2[d]	115.0±1.5[c]	1.55±0.0[a]

Means followed by the same letters within the column are not significantly different p<0.05. Results are expressed as the means±SD for three replications
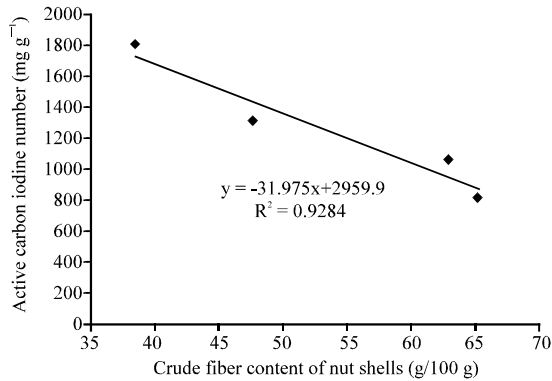
Fig. 4: Plot of active carbon iodine number versus crude fiber content of nutshells
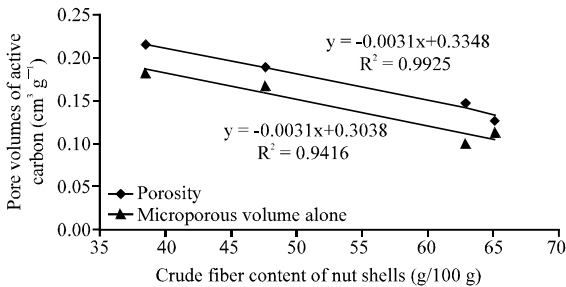

Fig. 5: Plot of active carbon pore volumes versus crude fiber content of nutshells
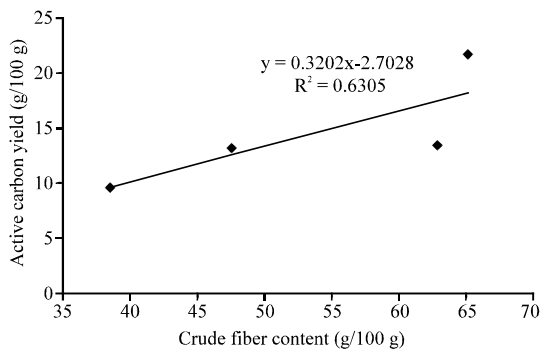

Fig. 6: Plot of active carbon yield versus crude fiber content of nut shells

Further more, a linear graph was obtained for plot of active carbon yield versus crude fibre content with a moderate correlation coefficient $(R^2) = 0.630$ (Fig. 6). Therefore, for CO_2 based active carbons that allow only passage of iodine molecules and disallows that of MB molecules, their active carbon yields is found to be directly proportional to crude fibre contents of their corresponding nutshells. This study has also revealed that the separate plots of cellulose, cellulose-hemicellulose or extractives/tannin contents of nutshells with each of the active carbon quality parameters (iodine

number, porosity, micro pore volume and active carbon yield) are poorly correlated as their correlation coefficients (R^2) values fell within the range of 0.009-0.402 (plots not shown). Consequently, from among all physico-chemical and polymeric chemical composition variables of precursor nutshells, it could be suggested that resultant model equations with high correlation coefficients could be used for prediction of active carbon yield, iodine numbers, porosity and estimation of micropore volumes of CO_2-ACs prepared from unknown nutshells within probability of 5% level. These equations are as follows:

Active carbon yield:

$$Y_1 = 0.1096X_1 + 4.7322; (R^2 = 0.978) \qquad (1)$$

Iodine number:

$$Y_2 = -31.975X_2 + 2959.9; (R^2 = 0.928) \qquad (2)$$

Porosity:

$$Y_3 = -0.0031X_3 + 0.3348; (R^2 = 0.993) \qquad (3)$$

Micropore:

$$Y_4 = -0.00031X_4 + 0.3038; (R^2 = 0.942) \qquad (4)$$

Equation 1 shows Y_1 value as active carbon yield while the X_1 value is the hardness-diameter ratio of unknown precursor nutshell. Equation 2-4 show that take Y_2-Y_4 values as iodine number, porosity and micropore volumes respectively while their corresponding X_2-X_4 values are the crude fibre contents of unknown precursor nutshells. These equations are found to be applicable to active carbons with small pore size that could allow passage of iodine molecules but disallow the passage of large molecular size of methylene blue molecules. Furthermore, all nutshells investigated were found to be predominantly cellulose in composition while *T. nerrifolia* and *H. thebaica* contain relatively larger quantity of lignin (Table 2). For all the nutshells, their cellulose content range were found to be 324.6-417.8 g kg^{-1} while hemicellulose contents ranged from 114.0-618.4 g kg^{-1}. The low lignin content values of 42.6, 47.4 and 63.2 g kg^{-1} were found for *C. inophylum, H. crepitans* and *C. nucifera*, respectively. The high value of lignin 270.9 g kg^{-1} was obtained for *T. nerrifolia*. However, the nutshells of *T. nerrifolia* exhibited adequate cellulose and hemicellulose contents for active carbon preparation. Therefore, the low lignin, high cellulose and hemicellulose contents of most of these nutshells are good indicators that these precursor nutshells could be utilized as cheap renewable precursor for active carbon production.

For the cellulose content values, *C. nucifera*, *C. inophylum* and *H. thebaica* are not significantly different from each other but are significantly different from both *H. crepitans* and *T. nerrifolia*. All the five nutshells are statistically significantly different in their crude fibre content values as well as in their hemicellulose and tannin contents. It is also noted that there is no significant difference among lignin content values obtained for *C. inophylum*, *C. nucifera* and *H. crepitans* nutshells (Table 2). However, they are significantly different from *H. thebaica* and *T. nerrifolia*.

The comparison of Table 2 shows that *C. inophylum* with the highest cellulose-hemicellulose content and very low lignin exhibited the largest micropore volume (0.702 cm³ g⁻¹) in its corresponding active carbon product. More so, the micropore volume of 0.182 cm³ g⁻¹ for *H. crepitans* corresponds to next highest cellulose-hemicellulose content. These nutshells also have low lignin content. However, *H. thebaica* derived active carbon also exhibited next relatively large micropore volume of 0.166 cm³ g⁻¹ whereas its cellulose-hemicellulose content (293.6 g kg⁻¹) exhibited the highest (Table 2). This might be due to large percentage of extractives, 212.7 g kg⁻¹ of *H. thebaica* released during carbonization and activation processes. The extractives are normally burnt off contributing to creation of pores within the carbon matrix which probably determines the extent of micropore volume.

Table 3 shows that the percentage yield of chars obtained from the nutshells investigated fell within the range of 20.14-40.53% while their corresponding active carbon yield fell within the range of 6.66-21.63%. It is found that the variations in percentage yield of both chars and active carbons are not wholly dependent upon their lignocellulose composition of each nutshell type. The variations might be partly attributable to individual precursor material inherent ability to resist thermal effects. As a result of differences in thermal stability of the components (lignin, cellulose and hemicellulose) of the nutshells, various volumes are created within their active carbon which may in turn affect their yield. The findings is therefore not in line with those of Raveendran and Ganesh (1998) who reported that large lignin content

within a raw material contribute more to their char yield than precursor material with larger cellulose and hemicellulose content during carbonization. Comparing Table 2 and 3, it is observed that *C. inophylum* and *H. crepitans* with low lignin values of 42.6, 47.4 and 80.1 g kg⁻¹, respectively gave a higher char yield of 40.53 and 35.20 g kg⁻¹, respectively while nutshells like *T. nerrifolia* with high lignin content value of 270.9 g kg⁻¹ gave lower char yield value of 34.60%. Thus, Lignin content is not the only component that increases char yield but cellulose, hemicellulose as well as textural nature in terms of hardness and crude fibre content of precursor material specifically contribute to char yield and subsequently active carbon yield.

As such this study agrees with (Rhen *et al.*, 2007) that reported that combustion time of woody biomass depended mostly on raw material composition and to a minor extent on density. Van Loo and Koopejan (2002) also supported that variation in the extent of decomposition of raw material determined the amount of volatiles produced and eventual char yield. However, active carbon yield is found to be more dependent on the hardness-Vickers number ratio than lignin, cellulose or hemicelluloses contents as its correlation co-efficient, $R^2 = 0.978$ is better than 0.009-0.402 range for cellulose, hemicelluloses and lignin contents.

In another study, Table 4 shows the ultimate analysis of each of the tropical nutshells studied as well as their corresponding Higher Heating Value (HHV). Among the investigated tropical nutshell types, *C. nucifera* contained the highest carbon content (47.81%) while *H. crepitans* contained the least (44.63%). These values are in agreement with carbon content values of 36.9-50.2% for agricultural wastes reported in literature (Raveendran *et al.*, 1995). On the basis of carbon content, these nutshells types are good potential precursor materials for active carbon production. The higher heating values of these tropical nutshell types were found to fall within the range of 21.5-26.6 MJ kg⁻¹. These values are higher than 15.29-19.78 MJ kg⁻¹ reported and the value of 20.50 MJ kg⁻¹ determined for coconut shell is similar to 22.3 MJ kg⁻¹ obtained for coconut shell in this study (Raveendran *et al.*, 1995). However, these values

Table 3: Carbon yields and some physicochemical properties of carbondioxide-based nutshell active carbon

Fruit nutshell types	[b]Char yield (weight%)	[b]Active carbon yield (weight%)	[a]Bulk density (g mL⁻¹)	Ash (g kg⁻¹)	pH	Conductivity msec cm⁻¹
C. inophylum	40.53±0.04	6.66	0.62±0.13	5.92	9.80	0.31±0.02
C. nucifera	20.14±0.61	13.38	0.63±0.14	1.14	8.50	0.07±0.00
H. crepitans	35.20±0.02	9.58	0.45±0.10	13.81	10.00	0.46±0.03
H. thebaica	39.88±3.66	13.13	0.58±0.10	8.21	9.89	0.58±0.03
T. nerrifolia	34.60±0.21	21.63	0.50±0.06	1.33	4.30	0.08±0.00
*Decolourizing carbon (BDH)	NA	NA	0.44±0.03	2.19	3.20	0.11±0.01
**Activated carbon (BDH)	NA	NA	0.47±0.01	16.58	3.70	0.58±0.02

*Commercial activated carbon (powder), **commercial activated carbon (granular), NA means not applicable; [a]based on 0.212-0.500 μm particle size and on free air dry basis; [b]Calculated from initial weight of precursor fruit nut shells

Table 4: *HHV and ultimate analysis of biomass fruit nuts shells

Fruit nut shells types	Ultimate analysis (weightt%)					O/C	HHV (MJ kg^{-1})
	C	H	N	S	O		
C. inophylum	44.89±0.18	5.55±0.08	0.41±0.02	0.00	49.15±0.24	1.09	25.4
C. nucifera	47.81±0.06	5.89±0.26	0.13±0.13	0.00	46.17±0.32	0.97	22.3
H. crepitans	44.63±0.04	5.99±0.06	0.42±0.15	0.00	48.92±0.26	1.10	26.6
H. thebaica	45.36±0.05	6.03±0.01	0.22±0.00	0.00	48.39±0.04	1.07	26.5
T. nerrifolia	45.65±0.15	6.05±0.12	0.16±0.05	0.00	46.15±0.22	0.97	21.5

*HHV: Higher Heating Value while O/C depicts oxygen carbon ratio

Table 5: Adsorption capacities and pore volumes of commercial and CO_2-active carbons

Active carbon source	Iodine number (mg g^{-1})	Methylene blue number (mg g^{-1})	Methylene blue adsorbed (%)	Vme (cm^3 g^{-1})	Vmi (cm^3 g^{-1})	BET (m^2 g^{-1})
C. inophylum	1482.8	233.60	68.4	0.051	0.702	993
C. nucifera	1061.5	<0.10	NA	0.045	0.100	2738
H. crepitans	1804.0	<0.10	NA	0.033	0.182	1209
H. thebaica	1309.2	<0.10	NA	0.023	0.166	877
T. nerrifolia	822.2	<0.10	NA	0.017	0.113	551
*Decolourizing carbon (BDH)	784.9	54.30	36.6	0.193	0.006	526
**Granular activated carbon (BDH)	873.1	70.05	61.6	0.127	0.079	751

+Active carbon prepared from various sources of fruit nut shells using CO_2 as activating agent; Vmi depicts microporous volume while Vme represent mesoporous volume; *represent commercial decolourizing powder (BDH chemicals) and **represent commercial activated carbon (BDH chemicals)

obtained are <30.0, 29.7 and 31.8 MJ kg^{-1} values for British standard, commercial kiawe and commercial resquite values, respectively (Paddon, 1987) as well as lower than kukui (31.13 MJ kg^{-1}) nutshells (Dai *et al.*, 1995). Moreover, the higher heat content values of all the tropical nutshells studied are a little >22.8 MJ kg^{-1} obtained for commercial briquette. Consequently, these values indicate that higher temperature and longer time might be required for production of quality chars and active carbons in line with Dai *et al.* (1995). It should be noted that the type of activating agent used might also be affected by process conditions.

The oxygen: Carbon ratio values for all the investigated lignocelluloses biomass types are approximately unity (Table 4). This may be indicative that there may be more functional groups apart from pore volumes that might be responsible for available effective surface area or adsorption capacity of the prepared CO_2 active carbons. Table 5 shows adsorption capacity of the prepared carbon dioxide based active carbons. It shows that most of the prepared carbons are microporous as indicated by the ratio of micropore to mesopore volumes for all the CO_2-based active carbons prepared (Table 5). The micropore volume for all the CO_2-based active carbons prepared nutshells ranged within 0.100-0.702 cm^3 g^{-1}. The value of mesopore volume was found to fall within the range of 0.017-0.051 cm^3 g^{-1} for CO_2 active nutshells studied which is in agreement with values (0.05-0.07 cm^3 g^{-1}) reported in literature (Adebowale and Adebowale, 2008). *C. inophylum* exhibited relatively higher MB adsorption compared to other nutshells derived CO_2-based active carbons which showed no MB adsorption. This might be due to the small pore sizes within the prepared CO_2-based active carbon and could not adsorb the large MB

molecules. The MB numbers of 233.6 mg g^{-1} obtained for *C. inophylum* active carbon is >54.3 and 95.0 mg g^{-1} values obtained for commercial granular active carbons (BDH) and commercial powdered active carbon, respectively. From Table 5, it is however observed that all the active carbons were able to adsorb smaller molecular size iodine molecules though with varying capacity. It was also observed that the highest iodine number is exhibited by *H. crepitans* (1804.0 mg g^{-1}) and followed by *C. inophylum* (1482.8 mg g^{-1}). All other iodine number values of CO_2-based active carbon are above 1000 mg g^{-1} indicating high surface area with exception of *T. nerrifolia* that was found to be 822.2 mg g^{-1}. Moreover, the iodine numbers of commercial decolourizing carbon (784.9 mg g^{-1}) and that of granular active carbon (873.1 mg g^{-1}) are lower than the values obtained in this study. The BET surface for the prepared nutshell active carbons are 551, 877, 993, 1209 and 2738 m^2 g^{-1} for *T. nerrfolia, H. thebaica, C. inophylum, H. crepitans* and *C. nucifera*, respectively. These values are within the minimum range of 500-1500 m^2 g^{-1} needed for industrial application and removal of small molecules from aqueous solution (Bansal and Goyal, 2005).

The observation of micrographs of Fig. 7 and 8 show the surface physical morphology of the CO_2-AC derived from different nutshells.

It can be seen that the external surface is full of various shapes and sizes of pores and crevices. Some of the shapes of pore are rectangular while some are oval. It shows that the precursor materials as well as carbonization and activation methods of preparation are adequate. Their applicability in industries and environmental remediation for adsorption of gases as well as small size molecules like metal ions and other small organic molecules can not be over looked.
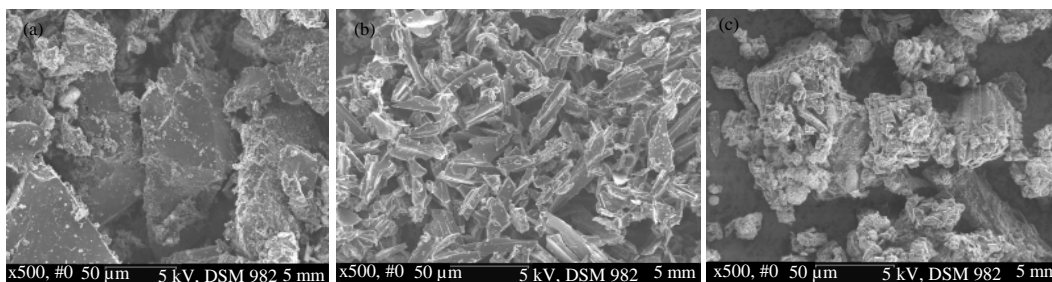
Fig. 7: SEM micrographs of active carbons derived from various fruit nutshells using CO_2 as activating agent at x500 magnification; A = *T. nerrifolia*; B = *C. nucifera*; C = *H. thebaica*
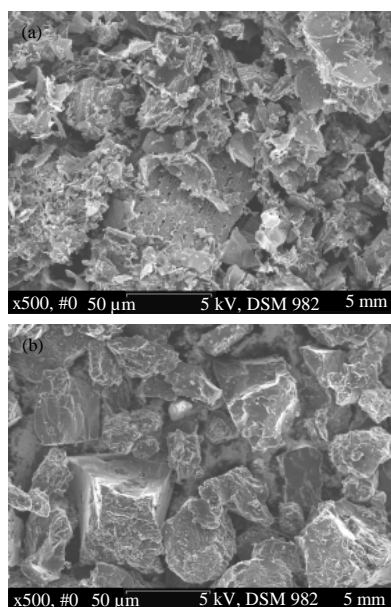

Fig. 8: SEM micrographs of active carbons derived from various fruit nutshells using CO_2 as activating agent at magnification of x500; D = *H. crepitans*; E = *C. inophylum*

CONCLUSION

In this study, it is found that the iodine numbers, porosity and active carbon yield of CO_2-based active carbons are more dependent on hardness-Vickers-diameter ratio of nutshells and upon their crude fibre contents than upon cellulose, hemicellulose and lignin contents when CO_2 is used as activating agent. Therefore, it can be inferred that the proportion in which these factors to a larger extent (hardness-diameter ratio, crude fibre contents) and to a lesser extent factors (cellulose/hemicellulose and lignin contents) combined in a given nutshells might be some of the requirements needed to achieve desirable result of a quality active carbon. It also explains the variations in the surface area of nutshell CO_2-ACs.

REFERENCES

ANSI, 1968. American National Standard-D1103 Standard Method of Test for Alpha-Cellulose in Wood. American National Standards Institute, USA., pp: 336-338.

ASTM, 1996. Standard Testing Method for pH of Activated Carbon, D3838-80, 15.01. Annual Book of ASTM Standards, USA., pp: 531-532.

AWWA, 1974. Standard for Granular Activated Carbon B. 1st Edn., American Water Works Association, USA., pp: 604-680.

Adebowale, K.O. and Y.A. Adebowale, 2008. Active carbon from low temperature conversion chars. Electronic. J. Environ. Agric. Food Chem., 7: 3304-3315.

Afrane, G. and O.W. Achaw, 2007. Effect of the concentration of inherent mineral elements on the adsorption capacity of coconut shell-based activated carbon. Bioresour. Technol., 99: 6678-6682.

Ahmedna, M., M.M. Johns, S.J. Clarke, W.E. Marshall and M.M. Rao, 1997. Potential of agricultural by-product based activated carbon for use in raw sugar decolorization. J. Sci. Food Agric., 75: 117-124.

Ahmedna, M., W.E. Marshall and R.M. Rao, 2000. Production of granular activated carbon from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresour. Technol., 71: 113-123.

American National Standard-D1105, 1972. Standard Method for Preparation of Extractive-Free Wood. American National Standards Institute, USA., pp: 340-341.

Antal, Jr. M.J., 1983. Lignocellulose Pyrolysis. In: Advances in Solar Energy Society, Boer, K.W. and J.A. Duffie (Eds.). American Solar Energy Soc., New York, pp: 175-255.

Ashford, R.D., 1994. Ashford's Dictionary of Industrial Chemicals. London Wavelength Publishers, Ltd., London.

Bansal, R.C. and M. Goyal, 2005. Activated Carbon Adsorption. Taylor and Francis Group, UK., ISBN: 9780824753443, Pages: 497.

Bayer, E.S., A. Maurer, C.J. Deyle and M. Kutubuddin, 1995. Recovery of activated carbons from wastes via low temperature conversion II. Anal. Evauation applicability Fresenius. Environ. Bul., 4: 539-544.

Bilba, K., M.A. Arsene and A. Ouensanga, 2007. Study of banana and coconut fibers: Botanical composition, thermal degradation and textural observations. Biores. Technol., 98: 58-68.

Burns, R.E., 1971. Method of estimation of tannin in grain sorghum. Agron. J., 63: 511-512.

Dai, X., N. Norberg and M.J. Antal Jr, 1995. Production of charcoal and activated carbon at Elevated Pressure. Divission Fuel Chem., 40: 285-287.

Hassler, J.W., 1963. Active Carbon. Chemical Publishing Company, New York.

Humpherys, F.R. and G.E. Ironside, 1980. Charcoal from New South Wales Species of Timber. 3rd Edn., Forestry Commission of New South Wales, New South Wales, Australia, ISBN-13: 9780724061600, Pages: 58.

Kirubakaran, C.J., K. Krishnaiah and S.K. Seshadri, 1991. Experimental study of the production of activated carbon from coconut shells in a fluidized bed reactor. Ind. Eng. Chem. Res., 30: 2411-2416.

Kurschner, K. and A. Hoffer, 1931. A new quantitative cellulose determination. Chem. Zeit, 55: 161-181.

Lutz, H., G.A. Romeiro, R.N. Damasceno, M. Kutubuddin and E. Bayer, 2000. Low temperature conversion of some Brazillian Municipal and industrial sludges. Bioresour. Technol., 74: 103-107.

Mackay, D.M. and P.V. Roberts, 1982. The influence of pyrolysis conditions on yield and microporosity of lignocellulosic chars. Carbon, 20: 95-104.

Maniatis, K. and M. Nurmala, 1979. Activated carbon production from tropical biomass for energy. Proceedings of the 6th International Conference on Industry and Environment (IE'79), Elsevier Science Publishers, London, UK.

McDougall, G.J., 1991. The physical nature of activated carbon. J. South Afr. Inst Mining Metall., 91: 109-120.

Morrison, I.M., E.A. Asiedu, T. Stuchbury and A.A. Powell, 1995. Determination of lignin and tannin contents of cow pea seed coats. Annal. Botany, 76: 287-290.

Nahm, K.H., 1992. Practical guide to feed, forage and water analysis: Accurate analysis with minimal equipment. 1st Edn., Yoo Han publishing Inc, Seoul, Korea republic, 132-133.

Paddon, A., 1987. Review of the available data concerning the amount charcoal and fuel wood in Sudan. Field Project Document No. 22, FAO, Khartoum, Sudan, pp: 1-12.

Pearson, D., 1976. The Chemical Analysis of Food. 7th Edn., Longman Group Ltd., London, UK.

Pendyal, B., M.M. Johns, W.E. Marshall, M. Ahmedna and R.M. Rao, 1999. The effect of binders and agricultural by-products on physical and chemical properties of granular activated carbon. Bioresour. Technol., 68: 247-254.

Petrov, N., T. Budinova, M. Rozvigoruva, E. Ekinci, F. Yardim and V. Minkova, 2000. Preparation and characterization of carbon adsorbents from furfural. Carbon, 38: 2069-2075.

Pollard, S.J.I., G.D. Fowler, C.G. Sollars and R. Perry, 1992. Low-cost adsorbents for waste and waste water treatment: A review. Sci. Total Environ., 116: 31-52.

Ramos, R.L., J.R. Rangel-Mendez, J. Mendozabarroi, L. Fuentes-Rubio and R.M Guerrerocoronado, 1997. Adsorption of cadmium (II) from aqueous solution onto activated carbon. Wat. Sci. Technol., 35: 205-211.

Raveendran, K. and A. Ganesh., 1998. Adsorption characteristics and poor development of biomass pyrolysis of char. Fuel, 77: 769-778.

Raveendran, K., A. Ganesh and K.C. Khilart, 1995. Influence of mineral matter on biomass pyrolysis characteristics. Fuel, 74: 1812-1822.

Rhen, C., M. Ohmen, R. Gref and I. Wasterlund, 2007. Effect of raw material composition in woody biomass pellets on combustion characteristics. Biomass Bioenergy, 31: 66-72.

Van Loo, S. and J. Koopejan, 2002. Handbook of Biomass of Combustion and Co-Firing. Earthscan, Enschede, The Netherlands, ISBN-13: 9781844072491, Pages: 442.

Wan Daud, A.W.M., W.S. Wan-Ali and Z.M. Sulaiman, 2000. The effects of carbonization temperature on pore development in palm-shell-based activated carbon. Carbon, 38: 1925-1932.

Wan-Daud, A.W.M., W.S. Wan-Ali and Z.M. Sulaiman, 2001. Effect of carbonization on the yield and porosity of char produced from palm shell. J. Chem. Technol. Biotechnol., 76: 1281-1285.

Wartelle, L.H. and W.E. Marshall, 2001. Nut shells as granular activated carbons: Physical, chemical and adsorptive properties. J. Chem. Technol. Biotechnol., 76: 451-455.

Winifred, W., W.S. Chung and E.M. Wayne, 1999. Utilization of peanut shells as adsorbents for selected metals. J. Chem. Technol. Biotechnol., 74: 1117-1121.