Pore Structure and Surface Functional Groups on Six Tropical Fruit Nutshell Active Carbons

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ABSTRACT

Six fruit nutshells, namely: *Thevetia nerrifolia*, *Hura crepitans*, *Hyphaene thebaica*, *Pentachlethra macrophyla*, *Tetracapidium conophorum* and *Cocos nucifera* were carbonised, oxidized with atmospheric air and activated in CO_2 at 840°C for 3 h. The iodine number range of active carbon (AC) was 822-1804 mg/g while BET surface area was within the 551-2738 m^2/g range. The ranges of micropore and mesopore volumes were 0.100-0.210 and 0.017-0.053 cm^3/g, respectively. The dependence of burn off, porosity and BET surface area of ACs on NaOH titratable surface functional groups indicated linearity. The phenol/lactone and carbonyl surface functional groups ranged from 6.002 to 8.294 and from 3.970 to 5.908 mmol H^+ equiv/g carbon, respectively. FT-IR spectra revealed the presence of OH, C=O, and C-O functional groups on surface of the prepared ACs. Their SEM micrographs show pores and crevices all over their surface. These carbons might have potential ability to remove metals and organic compounds from waste water.

INTRODUCTION

The quality of active carbon (AC) is dependent upon the extent of its surface area, number of pores as well as its surface functional groups. Structurally, carbon (C) is made up of tiny graphite-like platelets with a wall of open cavities that form the pore system (Macdougall 1991). The presence of tiny pores on their internal and external surfaces has been attributed to be responsible for adsorption of organic materials, non-polar compounds and metals from gaseous and liquid media (Cox *et al.* 1999; Aktas *et al.* 2001; Rivera-Utrilla *et al.* 2001). AC exhibits a unique adsorption capacity due to an extraordinary large surface area and pore volume (Baker *et al.* 1992). Generally, ACs are prepared following either a single or a two-stage process. Firstly, carbonization, which is the break-down of chemical components and removal of mixtures and volatile matters from precursor materials, leaves a black solid called char, while the physical activation process involves gasification of the char that results in development and increase of porosity and specific surface area (Lutz *et al.* 1998). In physical activation, the reaction between CO_2 and the char matrix is endothermic as shown from the enthalpy value in the equation below (Ganan *et al.* 2006):

$$C + CO_2 \rightarrow 2CO \ \Delta H = 170.7 \ KJmol^{-1}$$

This means that an increase in temperature favours the reaction between CO_2 and C.

It is known that the surface of AC contains both positive and negative charges that make it possible for the carbons to attract free ions in solution or suspensions (Jankowska *et al.* 1991). The treatment of the AC surface with a base makes it an anion exchanger while a powerful cation exchanger is obtained if the AC surface is treated with an acid. However, Mattson and Marks (1971) reported that an ideal AC surface exhibits an electrical double layer. Moreover, oxidation of the C structure involves chemisorption of

atmospheric oxygen (O_2)-forming surface oxides, which further oxidizes other substances on the surface of the C. Some researchers observed that oxidation of the AC surface with air at an elevated temperature resulted in oxidized ACs that have the ability to adsorb both metal ions and organic compounds (Ferro-Garcia *et al.* 1988; Seco *et al.* 1997; Toles *et al.* 1998). Generally, metal uptake is assumed to be a function of polar or acidic surface groups on the C surface. Thus, the presence of O_2 functional groups in a given prepared C depicts that it is possible to oxidize more looselybound hydrogen making the C a better cation exchanger. Bansal *et al.* (1988) asserted that the presence of hetero atoms such as O_2 and sulphur provide charged groups in the C structure. These hetero atoms are located either on sheet edges or within heterocyclic rings containing functional groups in each of the prepared ACs. Major O_2-containing functional groups within the C surface include carbonyls, phenols, lactones and carboxyls while others are quinones, quinone like-structures, carboxylic anhydrides, lactols, etc. (Boehm 1966; Toles *et al.* 1993; Boehm 1994).

The advantages of fruit nutshell as a precursor for the preparation of ACs over other sources of AC can not be ignored. The advantages include: low cost of material, availability as renewable sources, low ash contents, hardness and high density properties that cancels the need of binder as well as the granular form that is maintained during carbonization and activation of the precursor materials (Ferro-Garcia *et al.* 1988). The adsorption capacity of ACs has mainly been attributed to the porous constitution on the surface of the C and exhibition of a large surface area (Lozano-Castelló *et al.* 2001; Cuerda-Correa *et al.* 2006). There are however, recent suggestions by Cuerda-Correa *et al.* (2006) and Toles *et al.* (1998) that O_2-containing functional groups also play a key role in the effective adsorption capacity of ACs. Therefore, this study aimed to produce CO_2-AC from selected fruit nutshells and examine the proportion of various O_2-containing functional groups present in the ACs prepared from the investigated fruit nutshell types. The rela-

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tionships between the proportion of these various O_2-containing functional groups of the ACs and their corresponding porosity or BET surface area are also presented. Another objective was to investigate the effect of quantified O_2-containing functional groups of prepared ACs on the adsorption of organic compounds like iodine and methylene blue molecules. The dependence of percentage burn off, porosity (micropore plus mesopore volumes), iodine number and BET surface area on a NaOH-titratable surface charge; C_2H_5ONa-titratable surface charge and $NaHCO_3$-titratable surface charge were examined.

MATERIALS AND METHODS

Plant materials

Six tropical fruit nutshells, namely *Thevetia nerrifolia* (yellow oleander), *Hura crepitans* (sand box plant), *Hyphaene thebaica* (dum palm), *Pentachletra macrophyla* (oil bean fruit), *Tetracapidium conophorum* (conophor nut) and *Cocos nucifera* (coconut) fruit nuts were harvested from their plants within the University of Ibadan, Ibadan, in the Western region of Nigeria with the exception of *H. thebaica*, which was obtained from the North Eastern part of Nigeria. It thrives well in the Sahel and hot dry Savannah between 12-18 N from Senegal to Northern Nigeria, Chad, Zaire and North East Africa and is termed "goriba" in Hausa. The other five nutshells do well in the rainy region between 7° 23′ 47″ N and 3° 55′ E of southern Nigeria. Each of these fruit nutshells were mechanically removed, dried in the sun for 4 h and in oven at 110°C for 2 h and stored in plastic containers with tight covers at room temperature in the laboratory (the longest period being 14 days) during which various studies on the precursor materials were carried out.

Proximate and ultimate analyses of precursor fruit nutshells

The bulk density and moisture content were determined according to Amendna *et al.* (1997b) and AOAC (1980), respectively. The AOAC method (1980) was also adopted for determination of ash content of fruit nutshell types. The Petrov *et al.* (2000) method was used to determine pH and conductivity of the nutshells' active carbon (NAC).

The ultimate analysis of the six precursor fruit nutshell types were carried out with a Perkin-Elmer 2400 CHN micro auto analyser. Sulphur determination was also carried out in duplicate by elemental microanalysis using a Carlo Erba Elemental Analyser.

Pyrolysis of fruit nutshells

About 200 g of the six mature sun dried fruit nutshells were individually pyrolysed in a cylindrical quartz glass tube container (35 × 7 cm) and placed in hollow 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 a flow rate of 1000 mL/min at 480°C and heating rate maintained at 10°C/min for 1 h. The air in the furnace was first evacuated by allowing N_2 gas to flow in at 1000 mL/min for 15 min. The charred samples were allowed to cool in the furnace in an N_2 atmosphere until the temperature reached 200°C and were then removed. They were covered until they cooled to room temperature in the presence of some atmospheric air which might allow oxidation of the char to a certain extent prior to CO_2 activation. The procedure was duplicated to ascertain the reproducibility of yield.

CO_2 activation of chars

Twelve grams of each of the various fruit nuts shell chars were differently loaded in a hollow quartz glass tube (100 × 2.5 cm) and placed in a 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 a flow rate of 500 mL/min and at 20°C/min heating rate to a final temperature of 840°C for 3 h. The ACs were allowed to cool down in the quartz tube in the presence of CO_2. Prior to activation the air in the quartz tube was also first evacuated by flow of N_2 gas at 500 mL/min for 30 min.

AC analysis

1. Proximate analysis of AC

The bulk density and moisture content of ACs were also determined using the methods of Amendna *et al.* (1997b) and AOAC (1980), respectively while the American Water Works Association (AWWA) standard – 13604 (1991) method was used for AC ash content. The American Standard Testing Methods, ASTM (1996) was used to determine pH and conductivity of the ACs.

2. Porous structure analyses

The surface areas of CO_2-ACs derived from the various fruit nutshells were measured by N_2 adsorption at 77 K using a Coulter SA 3100 Surface Analyser, UK. The *n*-hexane adsorption method (Bayer *et al.* 1995b) was adopted for the determination of the micropore and mesopore volumes of the prepared ACs from the various fruit nutshell types.

3. Adsorption of iodine and methylene blue

The iodine number, which gives an idea of the microporosity, was determined by the modified AWWA procedure (AWWA, 1974). The modification involves centrifugation of the various AC-iodine mixtures for 5 min prior to titration with sodium thiosulphate solution in the presence of a starch indicator. Methylene blue (MB) adsorption capacities of the ACs that depict the extent of mesoporosity of the adsorbent were measured in accordance with ASTM standards for ACs (ASTM 1989a). Thus, 25 mL of MB solution at 1.2 g/L was poured into plastic containers and 0.2-0.4 g of AC prepared from the various fruit nutshells were added differently to MB solution in each plastic container. The plastic containers and their contents were shaken at 200 rpm for 12 h with an Elmer Perkin thermostat shaker to allow for equilibration. The concentrations of residual MB in solution were then determined at 625 nm using a λ3D-double beam UV visible spectrophotometer, Perkin Elmer after separation of the Cs following centrifugation at 500 rpm and 30°C temperature for 5 min. A standard calibration curve of MB at 625 nm was plotted against known concentrations of MB solution and used to determine the actual MB adsorption capacity of the ACs. The results of the amount of iodine and MB adsorbed per gram were recorded.

SEM analysis

The physical surface morphology was examined using a DSM 9872 Gemni Scanning Electron Microscope (SEM). A thin layer was mounted on the Al specimen holder by a double-sided tape. It was coated with Au/Pd, with a thickness of about 30 nm. The SEM of CO_2-AC's was recorded at 500× and 3000× magnifications.

O_2-containing surface functional groups

The various major types of O_2-containing functional groups on AC pore surfaces were determined following the method of Boehm (1966) as modified by Toles *et al.* (1998). It involves titration with a basic solution of increasing potential such as C_2H_5ONa, NaOH and $NaHCO_3$. The procedure employed is the addition of 0.24-0.26 g of each NAC into 25 mL each of the basic solutions of 0.05 M of C_2H_5ONa, NaOH and $NaHCO_3$, and then stirred for 20-24 h to form slurry. The slurry was then filtered and a 10 mL aliquot of filtrate was added to 15 mL of 0.05 M HCl. The HCl neutralizes unused basic solution and also prevents further reaction with atmospheric CO_2. The solution was then back titrated with standardized 0.05 M NaOH that neutralized excess HCl. The total surface functional groups were determined from a volume of NaOH required when C_2H_5ONa was used as titrant while total titrable negative surface charge was represented by the volume of NaOH needed when NaOH or $NaHCO_3$ were initially stirred with the AC

(Toles *et al*. 1999). The results were recorded as mmol H^+ equivalent/g C. The experiments were duplicated.

FTIR spectroscopy

The FT-IR spectra of the fruit NAC types were recorded between 4000 and 400 cm^{-1} using a Nicolet Awatar 330 FT-IR spectrometer (Thermo Electron Corp., USA). Pellets were prepared separately by mixing each of the C samples thoroughly with KBr at a 1:500 C/KBR ratio in a small size agate mortar. The resulting mixture was compacted in a Nicolet Awatar ro hydraulic press at 10 torrs for 3 min and the scan was run.

Statistical analyses

Analysis of variance (ANOVA) and separation of means were conducted by general linear model procedures. Comparisons of means of values of O_2-containing surface functional groups of fruit NACs were analysed using Tukey's multiple range data test at the 5% probability level.

RESULTS AND DISCUSSION

The data obtained for physicochemical properties of the prepared six CO_2 nutshells ACs and ultimate analysis of the precursor nutshells are presented in **Tables 1** and **2** while values describing micropore and mesopore volumes as well as Brunaer Emmett Teller surface area (BET), iodine and methylene blue (MB) numbers of the NACs are shown in **Table 3**. The distributions of surface charge as well as estimation of pore size range are also presented in **Tables 4** and **5**, respectively. **Figs. 1-4** depict the NaOH-titratable surface charge in mmol H^+ equiv/g against percentage burn off, porosity (micropore plus mesopore volumes), iodine molecule uptake and BET surface area of the ACs, respectively while the distribution of the surface functional groups in mmol H^+ equiv/g on the prepared AC pore surface are presented in **Fig. 5**.

Fig. 6A-F represents SEM micrographs for the studied CO_2 NACs.

Physicochemical properties of nutshell ACs

The bulk density obtained for all the prepared ACs in this study fell within the range of 0.45–0.63 g/mL (**Table 1**), which are higher than the minimum requirement (0.25 g/mL) for application in removal of pollutants from waste water (AWWA 1991). The *C. nucifera* precursor with the highest bulk density value (0.63 g/mL) exhibited the lowest burn off value of 35.5% while 73.64 and 72.77% burn off values obtained for *T. conophor* and *H. crepitans* had lowest

bulk density values of 0.55 and 0.45 g/mL, respectively. Since the same conditions of carbonization and activation processes were used for the preparation of these ACs, it seemed that each of the individual precursor materials had inherent properties which are differently resistant to heat and carbonization–activation conditions applied and in turn caused variation in the percentage of burn off values. This might contribute to the variability of densities of these ACs. Furthermore, AC yield values of 21.63, 13.38, 13.13, 11.96, 29.29 and 9.58% were obtained for *T. nerrifolia*, *C. nucifera*, *H. thebaica*, *T. conophorum*, *P. macrophyla* and *H. crepitans*, respectively while their corresponding burn off values obtained are 37.54, 33.59, 67.07, 73.64, 70.71 and 72.77%. There seems neither to be any trend between the burn off value and bulk density of the ACs nor between their yield and percentage burn off (**Table 1**). All the pHs of the studied NACs were found to be basic in agreement with reports of Wartelle and Marshall (2001) who studied physicochemical properties of some CO_2-NACs. An exception is *T. nerrifolia*, which had a pH of 4.4. Their ash content values are also relatively low (1.14–11.55%) with the exception of *P. macrophyla* and *H. crepitans*, which exhibited high values (**Table 1**). The conductivity values for all the investigated ACs fell within 0.07–1.30 ms/cm. **Table 2** shows the distribution of C, H, N, S and O_2 elemental contents of the precursor materials. Their C content values are similar and high enough for AC production. Their values ranged between 44.63 and 47.97% while hydrogen content fell within the 5.11–6.05% range. Their nitrogen content fell within the range of 0.13–1.34% and only *T. conophorum* recorded 0.19% for sulphur content of the precursor material. The C content of precursor materials used are indicative that they could be used for AC production while their O_2 and nitrogen contents contribute to the hetero atoms that eventually form O_2-containing functional groups on the surface of C during the carbonization-activation process.

Table 2 shows the ultimate analysis of each of the tropical fruit nutshells investigated. The C content of each of the nutshell types are arranged in decreasing order as follows:

T. conophorum < C. nucifera < P. macrophyla < T. nerrifolia < H. thebaica < H. crepitans.

These values are in agreement with C content values of 36.9–50.2% for agricultural wastes reported by Raveendran *et al*. (1995). On the basis of C content, these nutshells seemed to be good potential precursor materials for AC production. The presence of O_2 provides an initial basis for O_2-containing functional groups within an AC matrix during its preparation. It could be suggested that there may be functional groups apart from pore volumes that might be responsible for available effective surface area or adsorption capacity of the prepared CO_2-ACs.

Table 1 Physico-chemical properties of carbon dioxide active carbons.

Nutshells' active carbon	Bulk density (g/mL)	pH	Ash content (%)	Conductivity (ms/cm)	Yield (%)	Burn-off (%)
T. nerrifolia	0.50 ± 0.06 ab	4.4	1.33	0.08 ± 0.00 a	21.63	37.54
C. nucifera	0.63 ± 0.14 c	8.5	1.14	0.07 ± 0.001 a	13.38	33.59
H. thebaica	0.58 ± 0.10 bc	9.9	8.21	0.58 ± 0.026 c	13.13	67.07
T. conophorum	0.55 ± 0.10 bc	10.0	11.55	0.95 ± 0.017 d	11.96	73.64
P. macrophyla	0.58 ± 0.10 bc	9.9	12.64	1.30 ± 0.001 e	29.29	70.71
H. crepitans	0.45 ± 0.10 a	10.0	13.81	0.46 ± 0.026 e	9.58	72.77

Percentages of burn off and yields are based on the initial quantity of the chars activated and are within ±5 % error probability for all the samples; Values (Means ± SD) followed by the same letter are not significantly different at P < 0.05 as determined by Tukey's HSD means separation test.

Table 2 Ultimate analysis of nutshell precursor materials.

Nutshells' active carbon	Ultimate analysis (wt %)				
	C	H	N	S	O
T. nerrifolia	45.65 ± 0.15 c	6.05 ± 0.12 b	0.16 ± 0.05 a	0.00	45.77 ± 0.22 d
C. nucifera	47.81 ± 0.06 cd	5.89 ± 0.26 b	0.13 ± 0.13 a	0.00	45.60 ± 0.32 c
H. thebaica	45.36 ± 0.05 b	6.03 ± 0.01 b	0.22 ± 0.00 a	0.00	46.89 ± 0.04 e
T. conophorum	47.97 ± 0.21 d	5.90 ± 0.09 b	1.34 ± 0.08 b	0.19 ± 0.01	41.17 ± 0.06 a
P. macrophyla	46.47 ± 1.85 ab	5.11 ± 0.16 a	0.92 ± 0.01 b	0.00	45.00 ± 0.43 b
H. crepitans	44.63 ± 0.04 a	5. 99 ± 0.06 b	0.42 ± 0.15 a	0.00	47.34 ± 0.26 f

Values (Means ± SD) followed by the same letter are not significantly different at P < 0.05 as determined by Tukey's HSD means separation test.

Table 3 Characterization of nutshell active carbons.

Nutshells' active carbon	Vmi (cm³/g)	Vme (cm³/g)	Iodine number (mg/g)	MB number (mg/g)	BET (m²/g)
T. nerrifolia	0.113	0.017	822.2	< 0.1	551
C. nucifera	0.100	0.045	1061.5	< 0.1	2738
H. thebaica	0.166	0.023	1309.2	< 0.1	877
T. conophorum	0.161	0.050	1131.3	29.3	758
P. macrophyla	0.210	0.024	1161.2	35.8	779
H. crepitans	0.182	0.033	1804.0	< 0.1	1209

Vmi, Vme, MB and BET represent micropore volume, mesopore volume, methylene blue and Brunauer Emmett Teller surface area of the nutshell active carbons, respectively.

Properties of porous structure ACs

Table 3 shows that the micropore volume, V_{mi} for all the studied NACs are in the range of 0.100–0.210 cm³/g while their mesopore volume, V_{me} ranged from 0.05 to 0.017 cm³/g.

These values are in agreement with 0.11–0.25 cm³/g for microporous volume and 0.05–0.09 cm³/g mesoporous volume reported by Petrov *et al*. (2000) for AC derived from furfural. Our pore volumes are also in line with 0.21–0.35 cm³/g microporous volume and 0.05–0.15 cm³/g mesoporous volume for CO_2 pecan shell-based Cs (Johns *et al*. 1999). Moreover, a linear relationship ($r^2 = 0.8785$; P < 0.05) was observed between porosity (micropore plus mesopore volumes) and the percentage burn off (graph not shown) that supports the findings of Johns *et al*. (1999). Furthermore, the BET surface area value is found to be highest with *C. nucifera* (2738 m²/g) and least (551 m²/g) for *T. nerrifolia* NAC (**Table 3**). These BET surface area values is within the range (500–1500 m²/g) required for industrial application especially in treatment of waste waters and removal of small molecules from aqueous solution (Cooney 1980; Vohler *et al*. 1986; Baçaoui *et al*. 2001; Bansal and Goyal 2005). These BET surface area values are also higher than 424–791 m²/g obtained for seven nutshell activated C prepared from almond (*Terminalia catapa*), black walnut (*Juglans nigra*), English walnut (*Juglans regia*), macadamia nut (*Macadamia integrifolia*), pecan shells (*Carya illinoinensis*) (Wartelle and Marshall (2001). **Table 3** also indicates that these NACs are microporous as observed from their pore volumes as well as from their iodine and MB blue numbers. Iodine number is adsorption capacity that indicates the extent of micropore volume distribution within the C matrix (Kirubakaran *et al*. 1991). Methylene blue number measures adsorption capacity and estimates mesoporosity of a given AC. All the NACs exhibited high adsorption capacity in that their iodine number fell within the range of 822–1804 mg/g while *T. conophorum* and *P. macrophyla* recorded an MB number of 29.3 and 35.8 mg/g adsorption capacity, respectively. The other NACs showed no adsorption of large MB molecules. The percentage burn off chars of the six nutshells were found to be in the range of 33.59–73.64% and compared favourably with burn off (25–65%) of seven nutshells reported by Wartelle and Marshall (2001). The MB number capacity obtained for *T. conophorum* and *P. macrophyla* might be due to a high percentage burn off (70.71–73.64%) (**Table 1**) of these fruit nutshell chars during its conversion to AC that widened the existing pores to the extent of allowing the passage of large MB molecules through the pores. An exception is *H. crepitans* with high percentage burn off value (72.77%) that exhibited no MB adsorption capacity. This might be attributable to some other inherent physicochemical properties of the *H. crepitans* nutshell that do not allow widening of the old pores but probably allows creation of new pores on the surface of the AC and as such a high iodine number was obtained for it. It is however known that CO_2 activation develops a porous structure at a given temperature slowly and it favours microporosity development (Arriagada *et al*. 1994; Rodriguez-Reinoso *et al*. 1995; Johns *et al*. 1999).

Effect of O₂-containing functional groups

Among other parameters of AC, the distribution of O_2-containing functional groups play a key role in determining the potential applicability of such adsorbent in metal ion or organic adsorption. This distribution of functional groups on the AC surface might be dependent on the method of carbonization/activation processes adopted as well as on the physicochemical nature of the precursor material used (Gergova *et al*. 1993). It has been established that ACs adsorb both organic compounds and metal ions depending on proportion of non-polar or polar acidic surface groups on the C (Seco *et al*. 1997). Furthermore, **Fig. 1** represents the dependence of percentage burn off on NaOH-tritatable surface charge which gave a linear relationship with correlation coefficient, $r^2 = 0.8614$ at P < 0.05 while the evidence of linearity for dependence of porosity (micropore + mesopore volumes) on NaOH-tritatable surface charge with a correlation coefficient of $r^2 = 0.9277$ at P < 0.05 is informative of the possible presence of acidic groups (carboxyls, phenolics and lactones) (**Fig. 2**).

These functional groups might contribute to the extent of pore volume and surface area creation on the C surface.
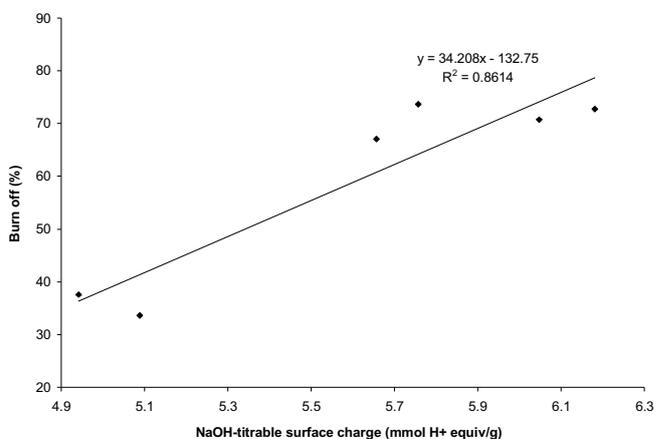

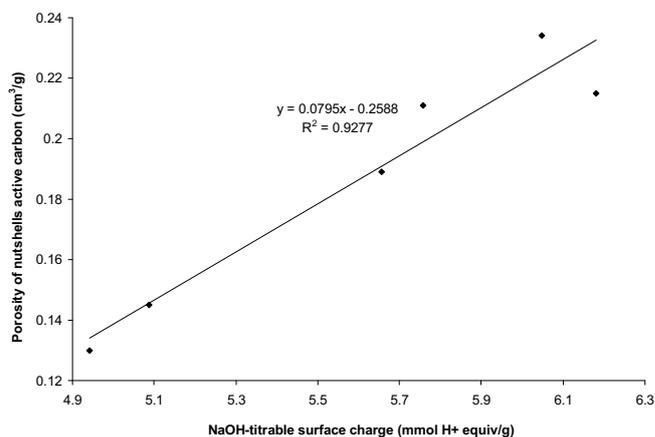**Fig. 1 NaOH-titrable surface charge versus burn off for nutshell active carbons.**

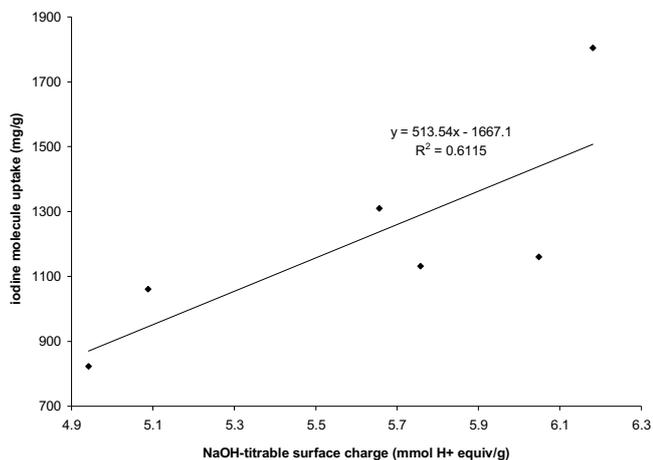**Fig. 2 NaOH-titrable surface charge versus porosity for active carbon nutshell types.**

$$y = 513.54x - 1667.1$$
$$R^2 = 0.6115$$

Fig. 3 NaOH-titrable surface charge versus iodine uptake for nutshell active carbon.

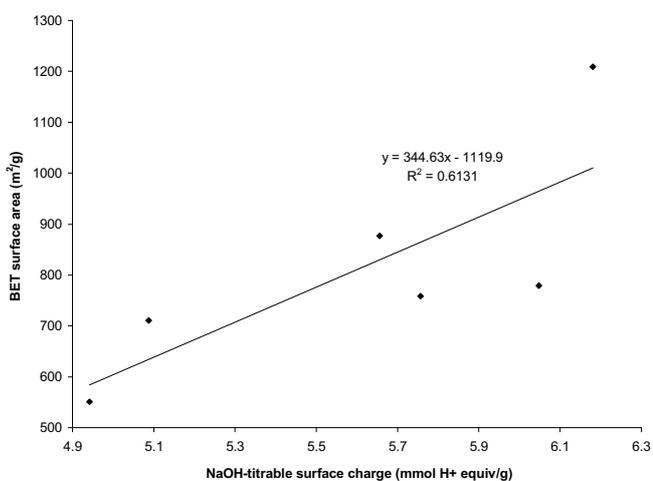$$y = 344.63x - 1119.9$$
$$R^2 = 0.6131$$

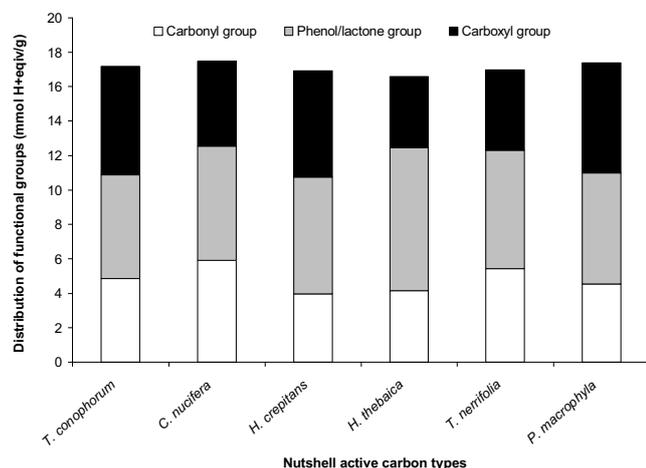**Fig. 4 NaOH-tritrable surface charge versus BET surface area.**

Fig. 5 Surface functional group content for nutshell active carbon.

The extent of percentage burn off is dependent on certain physicochemical parameters that could also predict the pore volume as well as surface area of ACs. Thus, $r^2 = 0.6115$ for linear dependence of iodine number of the NACs on a NaOH-titratable surface charge was found to be moderate (**Fig. 3**). Likewise, the linear dependence of the BET surface area of the investigated nutshells on titratable surface charge was also found to be moderate since its $r^2 = 0.6338$ at P< 0.05 (**Fig. 4**).

The lower correlation coefficient, r^2 value for dependence of BET and iodine number on NaOH-titratable functional groups might be due to a scatter of its data compared

to porosity and percentage burn off. The BET surface area value for *C. nucifera* was not included in the plotted values because it exhibited a very high BET surface area of 2738 m^2/g. This value is in line with a BET value of over 2400 m^2/g obtained for *C. nucifera* (coconut shell) via combination of $ZnCl_2$ and CO_2 activation process (Hu and Srinivasan 2001). These observations suggest that the extent of microporosity and/or BET surface area might be a function of the amount of carbonyls, phenols and lactones on the surface of the NAC.

It has been noted that total surface functional groups, total surface negative charge and surface charge values could be excluded from each other to obtain classification of carbonyl, phenols/lactones and carboxyl groups for the NACs and is depicted in **Fig. 5** (Toles *et al.* 1999).

The quantity of phenol/lactone groups on the C surface exceeded those of carbonyls and carboxyl groups. Among all the NACs studied, *H. thebaica* exhibited the largest quantity (8.294 mmol H^+ equiv/g C) of phenol/lactone groups on its C surface while lowest quantity of phenols/lactones (6.002 mmol H^+ equiv/g C) was obtained for *T. conophorum*. It was also observed that *P. macrophylla* had the largest value (6.365 mmol H^+ equiv/g C) of carboxyl group while the lowest value of 4.128 mmol H^+ equiv/g of C was obtained for *H. thebaica* NAC. The carbonyl group on the surface of the C for all the NACs fell within 3.970–5.908 mmol H^+ equiv/g of C. *C. nucifera* recorded the highest carbonyl group while *H. crepitans* had the lowest. The values of each of the various O_2-containing functional surface groups obtained in this study was found to be higher than values reported by other researchers for oxidized nutshell samples (Johns *et al.* 1999; Toles *et al.* 1999). The higher quantities of O_2-containing surface functional groups might be attributable to exposure of nutshell chars to atmospheric air oxidation during the carbonization stage that could have caused oxidation of its surface before the activation process was carried out. Moreover, variations in the inherent physico-chemical properties of different nutshells could also be responsible for this high quantity. Since these nutshell chars were oxidised prior to activation, the values of the total negative charges are higher than those of total functional group charge (**Table 4**). Consequently, it could be inferred that the NACs prepared in this study might have more potential for adsorption of metal ions than organic compounds. The total negative charge of *P. macrophyla* and *H. crepitans* show no significant difference but they are significantly different from *T. nerrifolia*, *C. nucifera*, *H. thebaica* and *T. conophorum* (**Table 4**).

In the case of total functional group charge, there exists no significant difference between *T. conophorum* and *P. macrophyla* but these are however significantly different from the other four NACs. The total functional group charge of the six NACs that ranged from 3.255 to 4.477 mmol H^+ equiv/g are within values (1.0–4.0 mmol H^+ equiv/g) obtained for five nut crop Cs by Toles *et al.* (1999) Since similar carbonization, oxidation and activation conditions were used for preparation of these ACs, it could be inferred that the development of the O_2-containing functional groups on the surface of these nut shells might be dependent on the quantity of C, N, S and O_2 contents of the NACs.

Table 4 Distribution of surface charge on active nutshell carbon.

Nutshells' active carbon	Total negative surface charge (mmol H^+ equiv/g)	Total functional surface charge (mmol H^+ equiv/g)
T. nerrifolia	4.942 ± 0.030 a	3.614 ± 0.037 c
C. nucifera	5.088 ± 0.013 b	4.477 ± 0.035 e
H. thebaica	5.636 ± 0.041 cd	3.255 ± 0.023 a
T. conophorum	5.757 ± 0.004 d	3.959 ± 0.023 d
P. macrophyla	6.048 ± 0.023 e	3.904 ± 0.007 d
H. crepitans	6.181 ± 0.004 e	3.420 ± 0.024 b

Values (Means ± SD) followed by the same letter are not significantly different at P < 0.05 as determined by Tukey's HSD means separation test.

FT-IR of nutshell AC types

All FTIR spectra obtained for the CO_2-NACs showed several similarities and little diverse variations. One major similarity is the broad band that ranged between 3404 cm^{-1} and 3448 cm^{-1} for all the NACs. The bands are associated with stretching vibrations of OH groups, in line with Petrov *et al.*'s (2000) findings. The band was weak and shallow for *T. nerrifolia* and *E. pursaeta.* The adsorptions at 3100 cm^{-1} for *C. nucifera* and *C. inophylum* are weak and the observed band corresponds to C–H vibrations representing sp^2 C atoms (Sanchez *et al.* 1994; Petrov *et al.* 2000). The stretch vibrations of C=O in ketones and aldehydes are found in the range of 1700–1735 cm^{-1} for all the prepared NACs with the exception of *H. thebaica* and *H. crepitans* that exhibited no C=O stretching vibration. The C=O functional group is attributable to aliphatic ketones, aldehydes and carboxyls formed in air atmosphere (Petrov *et al.* 2000). The C=O stretch vibrations, which correspond to vibrations of C=O in carboxylic acids (-COOH), were assigned stretching vibrations between 1637–1685 cm^{-1} for the entire NAC. The prepared ACs also showed strong or weak adsorption at 1685 and 1654 cm^{-1} while *H. thebaica*, *H. crepitans* and *C. nucifera* depicted only adsorption at 1654 cm^{-1}. In the case of the C–O bond in ACs, the 1360–1150 cm^{-1} range has been found to represent C-O bands in simple ethers, acid anhydrides and alcohols for our samples. Furthermore, the stretching vibrations at 1470–1350 cm^{-1} are attributable to vibrations due to deformation and are corresponding to aliphatic structures. The NACs also exhibited stretching vibrations of 1508–1560 cm^{-1} that are associated with variations in aromatic rings and are attributed to quinone structures (Petrov *et al.* 2000). The band at 858 cm^{-1} represents C–H out-of-plane bending in benzene derivatives, while the band at 418 cm^{-1} represents a C-heteroatom vibration. They are suggested to be basic groups of cyclic ketones and other keto-derivatives (Guo and Lua 2000). The range of IR values observed are similar to the ones observed by Duran-Valle *et al.* (2006) for the preparation of charcoal from cherry stones.

SEM morphology of NAC types

The micrographs of **Fig. 6A-F** reveal the surface physical morphology of the NACs. It could be observed that the external surface is full of various shapes and sizes of pores and crevices. It indicates that the precursor materials as well as the method of preparation are adequate. **Table 5** also presents estimated values of pore size distribution range, which are derived from the SEM micrographs (Alam *et al.* 2008).

Pore sizes have been classified by the International Union of Pure and Applied Chemistry (IUPAC) into three types: 1) macropores that have an average diameter of >50 nm; 2) mesopores with an average pore diameter that falls within the range of 2–50 nm; 3) micropores with values <2 nm. The pore size distribution could also be classified using the BJH model and t-plot method into micropores with <2 nm, mesopores with values between 2 and 96 nm, which shows that macropores are included in the mesopore group since <5% of the macropores contribute to the total pore size distribution (Gregg *et al.* 1982; Johns *et al.* 1999). Since average pore size distribution range values obtained from the SEM analysis (**Table 5**) are in the range of 0.09-2.56 nm for all the CO_2-ACs derived from the various fruit
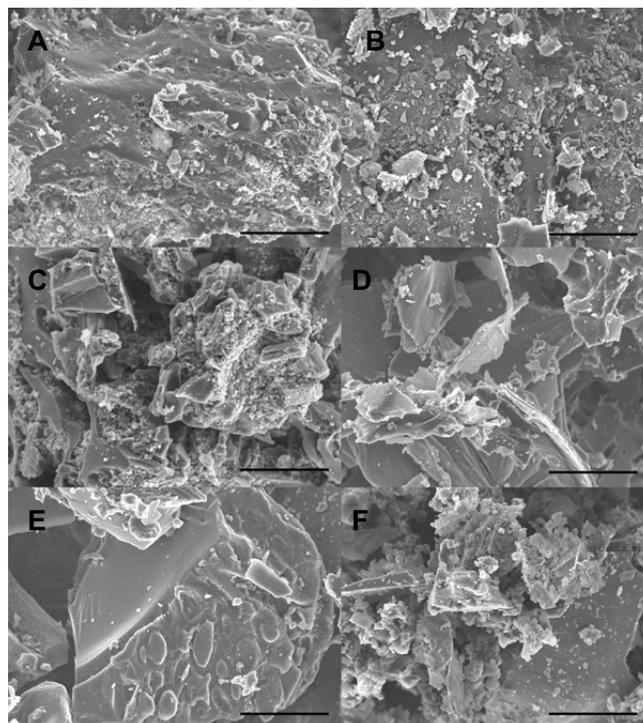

Fig. 6 SEM micrograph of CO_2 active carbon of (**A**) *Thevetia nerrifolia*, (**B**) *Cocos nucifera*, (**C**) *Hyphaene thebaica*, (**D**) *Hura crepitans*, (**E**) *Tetracarpidium conophorum* and (**F**) *Pentachlethra microphyla*. X3000. Bars = 10 um.

nut shells, the Cs prepared are therefore microporous. Their applicability in industry and environmental remediation to adsorb gases as well as small size molecules like metal ions and other small organic molecules cannot be overlooked.

CONCLUSION

On the basis of correlation coefficient, r^2, it has been discovered that among all the parameters examined, total potential BET surface area and porosity are not only dependent upon the extent of creation of pores on the surface of the AC but that surface functional groups contribute to the adsorption capacity of the NACs. The presence of surface functional groups in various proportions of carbonyls, phenols/lactones and carboxyl on the CO_2-NACs are confirmed. Thus, these Cs could be potential adsorbents for removal of both small organic molecules and metal ions from waste water.

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Table 5 Estimation of pore size range from SEM analysis.

Fruit nut active carbon types	Pore size range (nm)
T. nerrifolia	0.09 - 0.54
C. nucifera	0.10 - 0.31
H. thebaica	0.12 - 2.47
T. conophorum	0.22 - 1.33
P. macrophyla	0.09 - 2.56
H. crepitans	0.19 - 1.90

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