RESEARCH NOTE

New raw material for activated carbon. I. Methylene blue adsorption on activated carbon prepared from *Khaya senegalensis* fruits

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Abstract

C. E. Gimba, O. Ocholi, P. A. Egwaikhide, T. Muyiwa, and E.E. Akporhonor. 2009. New raw material for activated carbon. I. Methylene blue adsorption on activated carbon prepared from *Khaya senegalensis* fruits. Cien. Inv. Agr. 36(1):107-114. Activated carbons were prepared from *Khaya senegalensis* fruits. Carbonization and activation temperatures were 500ºC and 800ºC, respectively, at residence time of 5 min for each process. Activating agents were 1M each of NaCl, KCl, $CaCl_2$, $MgCl_2.6H_2O$, Na_2CO_3, K_2CO_3, H_2SO_4, and $ZnCl_2$. Particle size was 125 μm and adsorption studies were carried out using methylene blue in aqueous solution as adsorbate through fixed beds in micro columns. Equilibrium data were analyzed using adsorption intensity and capacity parameters from the Freundlich isotherms as well as breakthrough curves. Results were compared with performances of commercial animal charcoal and granular activated carbon. The results suggest that *K. senegalensis* fruits are suitable raw materials for producing activated carbons. The NaCI activated carbon has the best adsorption characteristics which are better than the commercial products.

Key words: Activation, adsorption, carbonization, isotherm *Khaya senegalensis*.

Introduction

It has been reported that the global consumption of activated carbon (AC) was above 500,300 t as at 2003, and it is expected to rise annually by 7% (Maroto-Valer *et al*., 2001). Due to increasing market demand, cheap and readily available alternative precursors are sought while methods of production are developed.

Khaya plants, *Khaya senegalensis (=Swietenia Senegalensis Desr*), is a indigenous hardwood tree of Africa belonging to the family Meliaceae that thrives well in northern Nigeria. It is relatively abundant in Ahmadu Bello University Zaria, Nigeria, the locality where this study was conducted. The roots, wood, stem, bark, leaves, and seeds are used for varios medicinal and domestic purposes (von Maydell, 1990). The fatty acid composition of the seed oil has been investigated previously, and it is composed of stearic acid, palmitic acid, oleic acids and an unidentifiable acid (Okieimen and Eromosele, 1999). However, the fruits, which are globose capsules, have not been reputedly studied like

other parts of the tree. They are considered as garbage or waste which constitutes an environmental problem as much time, money and effort is spent on their disposal. A fully mature tree produces between 200 to 500 or even more fruits per year. The average diameter of a fruit is 4.5 ± 0.17 cm and dry weighs 31.88 ± 3.34 g.

Considering that other parts of the khaya plants have been employed in medicine and many other areas, it was postulated that fruit were possible to use as an adsorbent, particularly when most of the uses of activated carbons are basically expected to be dependent on their adsorption activities. Consequently, the main objectives of this work were to investigate the adsorption characteristics of *K. senegalensis* fruits using methylene blue (MB) by fixed-beds in columns, and to compare the results obtained from AC's prepared with commercial products.

Materials and methods

Preparation of the raw material

Fruit samples were collected around the residential quarters of Ahmadu Bello University Zaria, Nigeria, between December 2004 and March 2005. Fruits were picked, washed and sun-dried before to broken them into small piece sizes with a wooden mortar and pestle and further pulverized into powdered form using a Siebtechnik Milling Machine and sieved into particle size of 125 μm with an Endecotts sieve.

Controls

Commercial powdered animal charcoal (Fischer Ltd. England) was purchased in Nigeria (Cardinal Chemical Supplies Company Zaria, Nigeria), and served as the first commercial control (Control 1). The Control 2 was commercial granular AC (Steve Moore Chemical Company Zaria, Nigeria). The particle size of Control 1 is less than 125 μm while particle size of Control 2 was 425 μm.

Carbonization

Raw sample was weighed (3 g) into six separate copper crucibles and introduced into a Muffle furnace at 500°C for 5 min after which they were then removed and quenched in cold water and sun dried (Gimba *et al.*, 2001). The procedure was repeated until substantial amount of carbonized sample was obtained. This was stored in sealed plastic containers.

Characterization of the carbonized carbon

Elemental analysis. Elemental analysis of the raw and carbonized samples was done by neutron activation analysis at the reactor facility section of Centre for Energy Research and Training (CERT) (Ahmadu Bello University Zaria, Nigeria). The long regime irradiation through a thermal neutron flux was used.

Moisture and dry matter content. An amount of 1.0 g each of the carbonized *K. senegalensis* fruits samples was placed in a clean silica crucible that was previously dried in a desiccator and weighed. They were then dried in an air-circulated oven at 105°C for 3 h after which they were cooled in a desiccator and then weighed. Results were expressed as percentage of the initial weight carbonized samples.

Ash content. Copper crucibles were heated in a furnace at 500°C, then cooled in a desiccator and weighed. The oven dried samples from the previous section were placed in the crucible and transferred into the Muffle furnace at 900°C for 3 h. The crucibles/content were allowed to cool in a desiccator and then weighed to obtain the weight of the ash. The ash content was expresses as percentage of the oven dry weight.

Bulk density. The volume of distilled water displaced by a known mass of the carbonized sample was measured using a measuring cylinder.

Activation of carbonized carbon sample

The activation of the carbonized carbon was executed as described earlier (Gimba *et al*., 2001) using decimolar amounts of each of the following activating agents: NaCl (5.85 g), KCl (7.45 g), CaCI$_2$ (11.1 g), ZnCI$_2$ (13.6 g), K$_2$CO$_3$ (13.8 g), Na$_2$CO$_3$ (10.6 g), H$_2$SO$_4$, and MgCI$_2$.6H$_2$O (20.3 g) (Table 2). Flaky pastes were made by mixing 2 g of carbonized samples with 2 mL of 1M of each of the activating agent solutions that were prepared by dissolving the indicated amount in 60 mL distilled water, transferred to a 100 mL volumetric flask, shaken and made up to the mark with the water.

The mixture was introduced into a Carbolite furnace at 800°C for 5 min after which they were quenched with cold water, washed with distilled water and allowed to dry at room temperature. These AC samples were stored in sealable air tight polythene bags.

Preparation of methylene blue stock solution

The use of methylene blue (MB) to evaluate the adsorption characteristics of carbon has been employed. A mass of 0.12 g of MB (molar mass = 319.8 g) was dissolved in about 10 mL of distilled water, transferred into a 100 mL volumetric flask, shaken and made up as above.

Preparation of columns using the test activated carbons and the controls

Clean columns were bedded with ground glass loaded with 60 mg of each activated carbon sample and then equilibrated with 2.0 mL of distilled water.

Test performed

For each performed, 2.0, 4.0, 6.0 or 8.0 mL of appropriately diluted MB stock solution were passed through the equilibrated column and the absorbance of the effluent taken using a Sherwood 254 digital colorimeter at wave length (λ) = 600 nm. The latter was the λ_{max} previously determined in an absorbance-concentration experiment of the MB (adsorbate) solutions. The effluent concentration of the MB was obtained from a calibration curve previously constructed. Three separate determinations were made for each sample and average value obtained.

Performance evaluation

The performance (%) of each matrix was calculated using the formula below:

Amount of MB adsorbed x 100 / Total amount of MB.

Isotherms and breakthrough curves

For adsorption isotherm, *x/m* was plotted against *C*, where *x* was the amount of MB adsorbed in μmol, *m* was the mass of adsorbent and *C* was the amount of MB that was unadsorbed. The $\log_{10} x/m$ was plotted against $\log_{10} C$ to obtain the Freundlich's isotherm from where the slope (*n*) and intercept (*k*) were obtained from the computer plots. The *n* and *k* values were the parameters used in this aspect of the study. Break through curves were the plots of C*x*/C_s against volume of adsorbate, where C*x* was the effluent concentration and *Cs* was the influent concentration.

Results and discussion

The average values of moisture and ash content of the raw *K. senegalensis* fruits were 6.17 and 3.09%, respectively (Table 1). The carbon yield was 17.32%. While the moisture and ash content are were 6.17 and 3.09%, respectively. The yield of carbon was 17.32%, greater than those reported earlier using coconut shell as raw material (Gimba *et al*., 2001).

Table 1. Physico-chemical properties of sample fruits of *Khaya senegalensis*.

Properties	Values
Moisture content, %	6.17
Dry matter, %	93.84
Ash content, %	3.09
Bulk density, g·mL⁻¹	0.81
Carbon yield, %	17.32
Raw sample, pH	5.18
Carbonized sample, pH	9.10
KSF-NaCl-AC[1], pH	9.90
Control1 1, pH	8.32
Control1 2, pH	7.25

[1]Control 1 = Commercial powdered animal charcoal (Fischer Ltd. England). Control 2 = commercial granular AC (Steve Moore Chemical Company Zaria, Nigeria).

The previous (Gimba *et al*., 2001).and present results show that the lower the moisture and ash content the greater the % yield of carbonized carbon. It is therefore most probable that fruits of *K. senegalensis* are a better raw material source for producing greater yield of carbon than coconut shell under similar experimental conditions. However the present results are comparable with those reported by Tsai *et al.* (2001) in which corn cobs were used as the precursor.

There was a change from the acidic raw material (pH = 5.18) to the basic carbonized product (pH= 9.10) and to a more basic activated product. For instance, in the KSF-NaCl-AC the pH = 9.90 (Table 1). This is in agreement with earlier work (Cheremisinoff and Ellerbusch, 1978) which showed that alkaline surfaces are characteristic of carbons having vegetable origins. The amount of MB adsorbed is expected to be more favorable as the carbon surfaces become more alkaline (Abram, 1973). The relatively high bulk density of 0.81 g·mL⁻¹ indicates longer period of filtration cycle (Abram, 1973).

With the exception of Br, La and Sm, the element contents were smaller in the raw materials than in the carbonized product (Table 2). The latter generally had about three times the amount of all the other elements detected in the

raw fruit samples of *K. senegalensis*. For Na, its amount was about five times in the carbonized than in the raw. It could be that the carbonization process made the affected elements more vulnerable to detection by reducing the amount of interfering or masking agents such as the protein/volatile components of the raw fruit samples of *K. senegalensis* (Mozammel and Masahirom, 2002). Out of the ten elements detected by the method of analysis, K was the most abundant while Sm was the least abundant in both the raw and carbonized fruit samples. These results were preliminary studies for the characterization of the carbonized carbon from this new source of carbon that can be used for preparing activated carbon.

Table 2. Elemental analysis of raw and carbonized fruit samples of *Khaya senegalensis*.

| Elements	Fruit samples[1]	
	Raw mg	Carbonized mg
Al	212.6±5.9	598.8±8.4
Ca	4493.0±315.0	13920.0±557.0
Mg	339.8±108.7	904.0±136.0
K	10580.0±360.0	29250.0±55.0
Fe	nd	nd
Na	37.9±21.1	190±5.0
Cl	1954.0±53.0	3163.0±73.0
As	nd	nd
La	3.44±0.0	2.74±0.11
Cr	nd	nd
Sm	0.43±0.02	0.22±0.001
Br	7.75±0.27	6.94±0.21

[1]Means ± standard deviation. nd = below detection level.

For the purpose of clarity of presentation of results, most of the latter are conveniently presented in two groups (Figures 1,2). One group for *K. senegalensis* fruits carbon activated with NaCl, KCl, CaCl$_2$, and MgCl$_2$·6H$_2$O and the second group with Na$_2$CO$_3$, K$_2$CO$_3$, H$_2$SO$_4$ and ZnCl$_2$ as the activating agents.

The MB adsorption isotherms showed that the order of adsorption was the same as that of the performance in the previous section and indicate the validity of the performance evaluation (Figure 1,2). The adsorption isotherms of most of the KSF-AC show that the adsorption of the
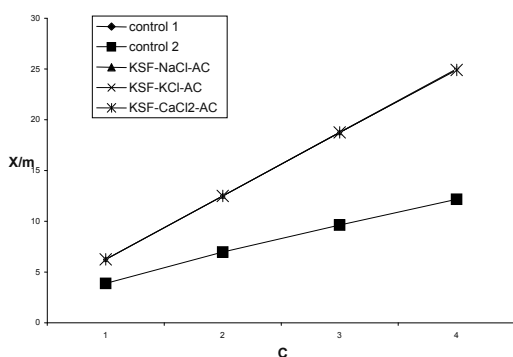
Figure 1. Adsorption isotherms of methylene blue adsorption on controls (1 and 2), KSF-NaCl-AC, KSF-KCl-AC, and KSF-CaCl2-AC at 298K.
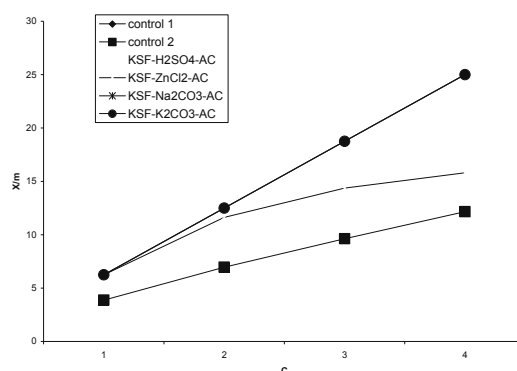
Figure 2. Adsorption isotherms of MB adsorption on controls (1 and 2), KSF-NaCl-AC, KSF-KCl-AC, and KSF-K2CO·-AC

adsorbate (MB) was that of the C-1 curves (linear curves) of the General Adsorption Isotherms (Giles *et al*., 1960).This means that the MB penetrates into the AC more than the solvent (water) in line with (Mozammel and Masahirom, 1978) as the adsorption is dependent on the concentration of the adsorbate. The non-linear adsorption isotherm of $MgCl_2 \cdot 6H_2O$-AC indicates unfavorable adsorption of the adsorbate by this matrix.

The order of *n* values (Table 3) of MB adsorption by the AC, in terms of the AA, were: $NaCl = KCl = CaCl_2 < Na_2CO_3 = K_2CO_3 < H_2SO_4 <$ Control 1 < Control 2 < $ZnCl_2$ < $MgCl_2.6H_2O$. The smaller the value of *n* $(1 < n < 10)$ the higher the adsorption intensity (Rozada *et al*., 2002; Weber Jr., 1973).

Table 3. Calculated *n* and *k* values of methylene blue adsorption from the Freundlich's isotherms.

Sample[1]	n	k
Control 1	2.85	6.83
Control 2	3.47	3.29
KSF-NaCl-AC	1.69	16.50
KSF-KCl-AC	1.69	16.50
KSF-CaCl$_2$-AC	1.69	16.50
KSF-MgCl$_2$-AC	11.99	1.46
KSF-Na$_2$CO$_3$-AC	2.20	10.40
KSF-K$_2$CO$_3$-AC	2.20	10.40
KSF-H$_2$SO$_4$-AC	2.31	9.36
KSF-ZnCl$_2$-AC	4.93	4.68

[1]Control 1 = Commercial powdered animal charcoal (Fischer Ltd. England). Control 2 = commercial granular AC (Steve Moore Chemical Company Zaria, Nigeria). KSF = *Khaya senegalensis* fruits. AC = activating agent.

The *k* values, which indicate the adsorption capacities of the AC, ranks thus (in terms of the AA): $NaCl = KCl = CaCl_2 > Na_2CO_3 = K_2CO_3 > H_2SO_4 >$ Control 1 > $ZnCl_2$ > Control 2 > $MgCl_2 \cdot 6H_2O$. The greater the *k* values the higher the adsorption capacity of an AC for the adsorbate. The previous sections on performance evaluation and adsorption isotherm show parity in the adsorption behavior of the Control 1 and some of the most effective KSF-AC carbons, for instance, NaCl, $CaCl_2$, KCl and Na_2CO_3-AC (Figure 1). However, the Freundlich isotherm parameters clearly showed that the newly produced KSF-AC activated with NaCl or $CaCl_2$ or KCl have greater adsorption intensity and capacity than the commercial carbons. All the results consistently showed that $MgCl_2 \cdot 6H_2O$ is not a good activating agent for *K. senegalensis* fruit. This might be due to the presence of the molecules of water of crystallization which might have blocked the active sites for adsorption of the MB.

The breakthrough curves (Figures 3 and 4) show that, the control 1, NaCl-AC, $CaCl_2$-AC, Na_2CO_3-AC and K_2CO_3-AC gave ideal curve, KCl-AC, H_2SO_4-AC and $ZnCl_2$-AC gave normal curves while the Control 2 and $MgCl_2 \cdot 6H_2O$-AC gave abnormal curves. The Control 1, NaCl-AC, $CaCl_2$-AC, Na_2CO_3-AC and K_2CO_3-AC curves coincided along the concentration axis up to the highest value of 8 mL of MB solution. This means that the matrices have great enduring capacities (Mozammel and Masahirom, 1978). Amongst the KSF-AC, the NaCl-AC, $CaCl_2$AC, Na_2CO_3-AC and K_2CO_3-AC have the greatest adsorbing endurance, followed by KCl-AC, H_2SO_4-AC and $ZnCl_2$-AC and the least, $MgCl_2 \cdot 6H_2O$-AC.
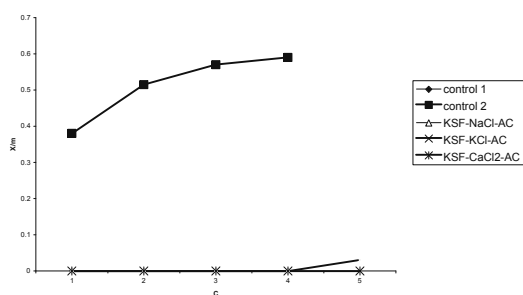
Figure 3. Breakhthrough curves of MB adsorption on controls (1 and 2), KSF-NaCl-AC, KSF-KCl-AC, and Ca C12-AC at 290K
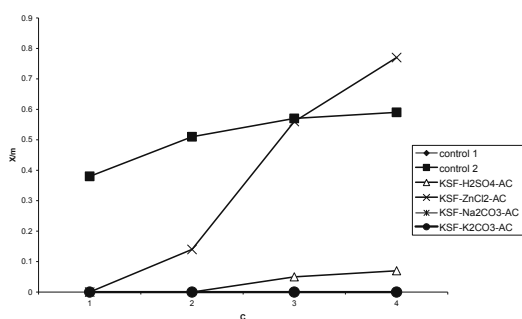
Figure 4. Breakhthrough curves of MB adsorption on controls (1 and 2), KSF-H2SO4-AC, KSF-ZnC12-AC, KSF-Na2CO3-AC and KSF-K2CO3-AC at 290K

The F values calculated were not significant (p < 0.01). Therefore differences between treatments were not statistically significant (Table 4).

The results obtained in this study have unequivocally proved that *K. senegalensis* fruit is a potential raw material for producing activated carbon. The adsorption capacity and intensity for MB outweigh those of the commercial products employed as controls in this study. The ready avalability of the raw material and the relatively cheap activating agents, especially NaCl, suggest that the cost of production of the activated carbon will be relatively low.

Table 4. Results of the statistical analysis performed.

Samples	Mean methylene blue adsorbed Moles, (X)[1]	SD[1]	CL[1]	F[1]	SE[1]
Controls	1.104	0.06	X±0.11	-	0.02
KSF-AC[2]	1.419	0.04	X ±0.04	2.25	0.016

[1]X is the mean of methylene blue (MB) adsorbed in moles by the respective samples. SD is the standard deviation. CL is the 95% confidence limit. F is the F test values calculated. SE is the standard error.
[2]KSF-AC = *Khaya senegalensis* fruits-activated carbon.

Resumen

C. E. Gimba, O. Ocholi, P. A. Egwaikhide, T. Muyiwa y E.E. Akporhonor. 2009. Nueva materia prima para carbón activado. I. Absorción del azul de metileno en carbón activado de frutos de *Khaya senegalensis*. Cien. Inv. Agr. 36(1):107-114. Carbón activado se preparó a partir de frutos de *Khaya senegalensis*. Las temperaturas de carbonización y activación fueron 500 y 800°C, respectivamente, con un tiempo de exposición de 5 min para cada proceso. Los agentes activantes fueron 1M de NaCl, KCl, CaCl$_2$, MgCl$_2$.6H$_2$O, Na$_2$CO$_3$, K$_2$CO$_3$, H$_2$SO$_4$, o ZnCI$_2$. El tamaño de partícula fue 125 µm. Los estudios de adsorción se realizaron empleando azul de metileno en solución acuosa como adsorbente a través de substratos fijos en microcolumnas. La información de equilibrio se analizó empleando parámetros de intensidad y capacidad de adsorción de las isotermas de Freundlich como también las curvas de quiebre. Los resultados se compararon con el comportamiento de carbón comercial de origen animal y carbón activado granulado. Los resultados sugieren que los frutos de *K. senegalensis* son apropiados como materia para producir carbón activado. El carbón activado con NaCI tuvo la mejor adsorción y resultó mejor que el producto comercial.

Key words: Adsorción, carbón, carbón activado, carbonización, isoterma, *Khaya senegalensis*.

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