

A Comparative Study of the Physico-Chemical Properties of Activated Carbon from Oil Palm Waste (Kernel Shell and Fibre)

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Abstract- A comparative study of the physico-chemical properties of activated carbon of oil palm waste (palm kernel shell (PKS) and oil palm fibre (OPF)) were carried out. The properties evaluated were surface area, moisture content, pH, bulk density, pore volume, porosity, tortuosity, ash content and metal ions present in the oil palm waste. From the analysis the physico-chemical properties of activated carbon of PKS and OPF were, moisture content; 2.15% and 3.34%, ash content; 6.10% and 6.7%, surface area; 1080m²/g and 1030m²/g, pH; 6.7 and 6.6, bulk density; 0.64 and 0.56, porosity; 63.6% and 57.9%, pore volume; 0.69cm³/g and 0.58cm³/g, and tortuosity; 1.57 and 1.72. From the analysis, the activated carbon prepared from palm kernel shell has better Physico-chemical Properties for adsorption than that prepared from oil palm fibre. Also the metal ion analysis revealed that the PKS is composed of 47.60% of potassium and OPF is composed of 73.64% of potassium. Therefore the OPF can be used in the production of organic fertilizer.

Keywords- Oil palm waste, activated carbon, properties

I. INTRODUCTION

Oil Palm (*Elaeis guineensis*) is the most important species in *Elaeis* genus which belongs to the family Palamae [1]. It is cultivated in West Africa and in all tropical areas especially in Malaysia, Indonesia and Thailand [2]. The oil palm fruit is reddish in colour and has a size of large plum, and grows in large bunches. A bunch usually has the weight of 10 to 40 kg. Each fruit consists of a single seed (the palm kernel) and surrounded by a soft oily pulp mesocarp. Oil is extracted from both the fruit pulp and the kernel [2]. The oil extracted from fruit pulp is used for edible purposes, whilst the extracted oil from kernel is used for the manufacturing of soap [3]. Palm oil has now become world's largest source of edible oil with 38.5 million tonnes or 25% of the world's total oil and fat production [4].

While the oil palm industry has been recognized for its contribution towards economic growth and rapid development, it has also contributed to environmental pollution due to the production of huge quantities of by-products from the oil extraction process [5]. The waste products from oil palm processing consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), and palm pressed fibres (PPF) and palm kernel shells, less fibrous

material such as palm kernel cake and liquid discharge palm oil mill effluent (POME) [6].

According to Prasertsan and Prasertsan [7], during processing in the palm oil mill more than 70% (by weight) of the processed fresh fruit bunch (FFB) was left over as oil palm waste. According to Herawan et al [8], two major solid wastes are generated During palm oil processing, which include, the extracted flesh fibre (or called mesocarp) and seed shell (or called endocarp).

Activated carbons are amorphous solid adsorbents that can be produced from almost all carbon-rich materials, including wood, fruit stones, peat, lignite, anthracite, shells and other raw materials [9]. Activated carbon has several important uses [10]. including solution purification such as in the clean-up of cane, beet and corn-sugar solutions, removal of tastes and odours from domestic and industrial water supplies, vegetable and animal fats and oils, alcoholic beverages, chemicals and pharmaceuticals and in waste water treatment. It also finds use in purification of gases, liquid phase recovery and separation processes as well as its use as catalyst and catalyst supports. For liquid purification or decolorising purposes, it is normally used in the powder form whilst for vapour or gas adsorption, it is used in the form of hard granules. Activated carbons are the most widely used industrial adsorbent for removing pollutants from gaseous, aqueous and non-aqueous streams, due to their uniquely powerful adsorption properties and the ability to readily modify their surface chemistry [9]. Its unique adsorption properties result from its high-surface area, adequate pore size distribution, broad range of surface functional groups, and relatively high mechanical strength.

There are two main methods for the preparation of activated carbons. These are physical and chemical activation methods. Physical activation occurs in two stages – thermal decomposition or carbonization of the precursor and controlled gasification or activation of the crude char. The carbonization process causes some increase in porosity, although this is generally insufficient for practical use, and serves to modify the pore structure inherent to the precursor, as opposed to creating it [11]. During carbonization, most of the non-carbon elements such as oxygen, hydrogen, nitrogen and sulphur are eliminated as volatile gaseous products by the pyrolytic decomposition of the source raw material to produce a carbon skeleton possessing a latent pore structure [12]. The activation process helps to develop further this structure by selective gasification of carbon, usually in temperature range

of 600-1200⁰C in steam, CO₂ or O₂ or mixtures of these. Chemical activation involves the treatment of the initial material with a dehydrating agent, such as sulphuric acid, phosphoric acid, zinc chloride, potassium hydroxide, or other substances, at temperatures varying from 400 to 10000C, followed by the elimination of the dehydrating agent by meticulous washing [9]. However, chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating material [13]. In general, the principal properties of manufactured active carbons depend on the type and properties of the raw material used.

Recently, increasing attention has been focused on using abundant biomass wastes as a feedstock for activated carbons [8]. preparation of activated carbons from agricultural by products has been given serious attention due to the growing interest in low cost activated carbons from renewable biomass, especially for applications concerning treatment of drinking water and wastewater [14]. Oil-palm shell and the fibre is a good candidate of raw materials for the production of activated carbon with a highly developed porosity and surface area because of the following reasons: the considerably high carbon content and relatively low price. It has been shown that the oil-palm shell has 55.7% of carbon content compared to oil-palm fibers (49.6%), coffee shells (50.3%), and sugar cane bagasse (53.1%) [15]. The relatively low price is because the raw materials are available as wastes, where they are free to be obtain in small quantity or low price in huge quantity [8]. They are produced mainly in South East Asia (Malaysia, Indonesia, and Thailand), Africa (Nigeria and Cameroon), and several southern provinces of China [8]. Therefore utilization of these cheap and abundant wastes is proposed to convert them into activated carbons.

Palm kernel shell and fibre are agricultural waste obtained from palm produce is a typical raw material used for activated carbon production and this help to reduces waste and increases management. The choice of the local product for activated carbon production is based on the large quantity of Oil palm grown in Nigeria. These agricultural wastes (waste biomass) impact negatively on the environment because of indiscriminate disposal of such wastes. Hence producing activated carbon from these wastes is an alternative method of waste reduction and reuse. Therefore the aims of this work were to characterize the activated carbon of Palm Kernel Shell (PKS) and Oil Palm Fibre (OPF) and perform a Comparative Study on their Physico-chemical Properties.

II. MATERIAL AND METHODS

A. Sample Collection and preparation

The oil palm wastes (fibre and shell) were collected from a traditional palm oil industry in aluu obio-akpor local government area rivers state Nigeria. The oil palm wastes were washed severally with distilled water in order to remove dirt's and dusts. They sample was further sun-dried for 4 days and later grounded to obtain a powder form of the waste. The powder waste was then sieved with 500µm mesh. This portion

of the powder sample was then kept in air-tight containers for further analysis.

B. Chemical activation and carbonization

Activated carbon was generated from the oil palm waste using chemical activation method, the powdered oil palm waste sample (30g) were treated with 1M solution of k₂CO₃ and NaHCO₃. This was activated for 40mins at a carbonization temperature of 800⁰C. The activated carbon produced was washed with 0.5 M acetic acid solution, rinsed thoroughly with distilled water until the pH is within 6-7, sun-dried and sieved. The portions retained on the mesh were oven dried for 1 h and stored in an airtight container.

C. Determination of the Physiochemical Properties of the activated carbon oil palm waste.

1) pH Measurement

1 g of the sample were weighed and dissolved in 3 ml of de-ionized water. The mixture was heated and stirred for 3 minutes to ensure proper dilution of the sample. The solution was filtered and out and its pH was determined using a digital pH meter [13].

2) Determination of Moisture Content

The hydroscopic moisture content was determined using the ASTM method d280-33. Clean empty nickel porcelain were oven dried at 110⁰C cooled in a desiccator and then weighed. 1g of the samples (palm kernel shell and fiber activated carbon) was measured into the porcelain separately and the weights were recorded. The porcelain and its content were then oven dried at 110⁰C to a constant weight for 3 hours. The percentage moisture content was calculated using the formula [13]:

$$X_o = \frac{W_1 - W_2}{W_1} * 100 \quad (1)$$

Where:

X_o = Moisture content on wet basis

W₁ = Initial weight of sample, g

W₂ = Final weight of sample after drying (g)

3) Ash content Determination

Ash content determination was done according to the ASTM D2866-94 method [16]. Dry AC sample (1.0g) was placed in to a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000⁰C. The furnace was left on for one hour after which the crucible and its content was transferred to desiccator and allowed to cool. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (W_{ash}). Then the % ash content (dry basis) was calculated from the equation

$$\text{Ash}\% = \frac{W_{\text{ash}}}{W_o} * 100 \quad (2)$$

Where; W_{ash} = Weight of ash (grams).

W_o = is the dry weight of carbon sample before ashing.

4) Pore volume Measurement.

The samples (1 g each) were collected and transferred completely into a 10 ml measuring cylinder in order to get the total volume of the sample. The sample was then poured into a

beaker containing 20 ml of deionized water and boiled for 5 min. the content in the beaker was then filtered, superficially dried, and weighed. The pore volume of the sample was determined by dividing the increase in weight of the sample by the density of water [13].

5) Bulk Density and Porosity Determination

The Bulk density and Porosity determined by the method of Vera [16]. A cylinder and an aluminum plate were each weighed. A sample of activated carbon (PKS and PF) were placed into the cylinder, reweighed and transferred into the aluminum plate and then oven dried to a constant weight at a temperature of 105°C for 60 mins. The weights of dry sample were recorded after drying. A cleaned, dried well-cooked density bottle was weighed. A small quantity of sample of activated carbon was taken and ground to powder; sieved using 110 µm mesh size, and gradually put into the density bottle with a little amount of water added and weighed. The volume of void (V_v) was obtained by first determining the total volume of the cylinder ($V_t = \pi r^2 h$) used for the experiment and also determining the volume of the AC used:

$$V_s = \frac{M_s}{G_s P_w} \quad (3)$$

Where r = radius of cylinder, h = height of cylinder, M_s = mass of cylinder, G_s = specific gravity, P_w = density of water. The volume of void (V_v) was obtained as:

$$V_v = V_t - V_s \quad (4)$$

The bulk density and porosity were calculated as:

$$\text{Bulk density (B.d)} = \frac{\text{mass of carbon sample}}{\text{volume}} \quad (5)$$

$$\text{porosity}(\eta) = \frac{\text{Volume of void}}{\text{Total volume}} \quad (6)$$

6) Surface Area Determination

The specific surface areas of the samples were determined using the European Spot Method used by [17] and [18]. This method is an offshoot of the technique used in determining the cation exchange capacity of drilled formation shale: in this method, (i) the methylene blue solution was prepared by mixing 1.0 g of dry powder PKS and OPF with 200 mL of deionized water, then (ii) 10 g of oven-dry PKS and OPF with 30 mL of deionized water; (iii) the methylene blue solution to the PKS and OPF suspension in 0.5 mL increments; (iv) for each addition of MB, mix the PKS and OPF suspension for 1 min, remove a small drop of the suspension, and place it on Fisher brand filter paper P5; (v) if the unabsorbed methylene blue forms a permanent light blue halo around the adsorbent aggregate spot, then "end point" has been reached (i.e., the MB has replaced cations in the double layer and coated all the mineral surfaces); and the specific surface is determined from the amount of MB required to reach the end point. The relationship between specific surface and MB used is [18].

$$S_s = \frac{1}{319.87200} \frac{1}{0.5N} A_v A_{MB} \frac{1}{10} \quad (7)$$

Where N is the number of MB increments added to the soil suspension solution, A_v is Avogadro's number (6.02

$\times 10^{23}/\text{mol}$), and A_{MB} is the area covered by one MB molecule (Typically assumed to be 130 \AA^2 ($1 \text{ \AA} = 0.1 \text{ nm}$)).

D. Determination of Heavy metal contained in the Sample.

The Heavy metals contained in the activated carbon (PKS and OPF) were determined using a Perkin Elmer Atomic Absorption Spectrophotometer.

III. RESULT AND DISCUSSION

A. Physico-chemical characterization

Physico-chemical characteristics of activated carbons are shown in Table 1. The value of the pH and the moisture content of the palm kernel shell, bulk density and the oil palm fibre are the same with the within the range of those gotten by [19]. Ash reduces the overall activity of activated carbon and it reduces the efficiency of reactivation [20]. The presence of ash has been shown to inhibit surface development [21]. From the analysis, the palm kernel shell has higher surface area than the oil palm fibre and can be as a result of the oil palm fibre having higher ash content than the palm kernel shell; consequently low surface area is observed in carbons with high ash content [22].

TABLE 1: PHYSICO-CHEMICAL CHARACTERISTICS OF ACTIVATED CARBON OF PALM KERNEL SHELL AND OIL PALM FIBRE

Physico-chemical Property	Palm Kernel Shell	Oil Palm Fibre
pH	6.1	6.6
Bulk density(g/cm ³)	0.64	0.56
Ash Content (%)	6.1	6.7
Porosity (%)	63.6	57.9
Surface area (m ² /g)	1080	1030
Pore Volume	0.69	0.58
Moisture Content	2.15	3.43

The most important property of activated carbon is its adsorptive capacity, which is related to its specific surface area. Generally, the higher the surface area, the larger is its adsorptive capacity [23]. Therefore the palm kernel shell having higher surface area and porosity will have higher adsorptive capacity than the oil palm fibre and this corresponds to the result obtained from [19].

The pH also affects the rate of activated carbon adsorption. Activated carbon is more effective at low pH than high pH [13]. The value of pH obtained in this work is ideal for adsorption purposes as maximum adsorption of metals by most activated carbon occur at this pH [19]. Carbons of pH 6-8 are useful for most applications [24].

Moisture content tended to be unusually low for PKS and OPF showing that these carbons were properly prepared and handled. It should be noted that when exposed to air the AC are capable of adsorbing moisture from atmosphere. This normally could lead to high moisture content [16].

The high micro porosity in palm kernel shell activated carbon suggests potential applications in gas-phase adsorption for air pollution control [25].

B. Heavy Metal Component of the Oil Palm Waste

Heavy metals are natural components of the Earth’s crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. Copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Results of heavy metal analysis of the sample are shown in Table 2 below. The result reveals that the toxic metals such as: Cadmium (Cd), Chromium (Cr), Lead (Pb), and Nickel (Ni) were below the detection limit of the equipment, whereas, Zinc, Calcium, Potassium, Copper, Iron and Magnesium were detected in the sample.

TABLE 2: HEAVY METAL CONTENT OF THE SAMPLE

Heavy metals (mg/kg)	Palm kernel Shell	Oil Palm Fibre
Magnesium	50.96	57.69
Copper	4.54	3.34
Zinc	8.61	16.84
Potassium	118.70	579.10
Iron	34.51	45.89
Calcium	32.06	83.37
Nickel	--	--
Cadmium	--	--
Chromium	--	--
Lead	--	--

Potassium is oxidized easily, thus reducing the available oxidizing agents [26]. The high concentration of Potassium in this sample and the presence of other metals like zinc, Calcium and Magnesium makes it suitable for use in conditions reactions where reduction is paramount [26]. Also since the toxic metals were not detected in the activated carbon of palm kernel shell and oil palm fibre, the oil palm waste can be used in removing these toxic metals from waste water.

From Fig.1 below: It can be observed that the percentage composition of Potassium in the sample is higher than other metals in the sample, with the percentage composition of Potassium in oil palm fibre higher than that in the palm kernel shell.

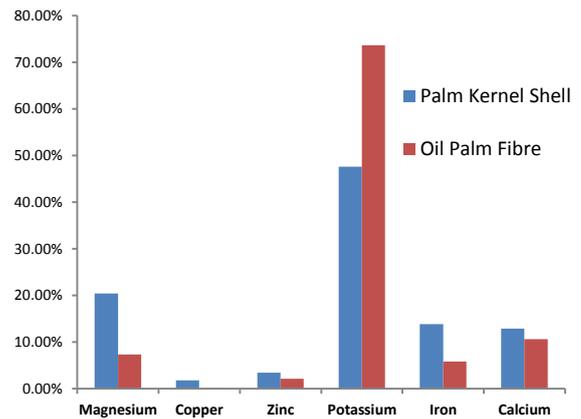


Fig 1. Heavy Metal Component of the Oil Palm Waste

The high concentration of Potassium in the sample especially in the oil palm fibre, justifies its usage as organic fertilizer since Potassium is needed by plants in large quantities [26].

C. Statistical analysis of variance using ANOVA

The result of the statistical analysis of the oil palm waste using ANOVA is shown in Table 3.

TABLE 3: ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	18671E2	6	3111E2	1756.7	1.84E-09	4.28
Columns	204.5	1	204.5	1.15	0.323895	5.98
Error	1062.8	6	177.14			
Total	18684E2	13				

From the table, the value of sum squares (SS) is 18671E2 along the rows which is higher than that along the column (204.5). Also the mean of square (MS) along the rows is greater than that along the column. This implies that the parameters can be compared along rows than along the columns.

The value of $F_{calculated}$ is 1756.7 while that of $F_{critical}$ is 4.28 along the rows. Along the columns the $F_{calculated}$ is 1.15 while that of $F_{critical}$ is 5.98. The result indicates that the value along the rows, $F_{calculated}$ is greater than $F_{critical}$ ($F_{cal} > F_{crit}$) despite the P- value is less than 1. Therefore the null hypothesis is rejected, hence the alternative is accepted. Therefore along the rows a larger difference exists between the physico- chemical properties of palm kernel shell and oil palm fibre. However, along the columns there are no existences of difference because the value of $F_{critical}$ is greater than $F_{calculated}$. Therefore comparison cannot be made within the parameters.

IV. CONCLUSION

The experimental analysis has shown that the activated carbon prepared from palm kernel shell has better Physico-chemical Properties for adsorption than that prepared from oil palm fibre. Also with analysis of variance comparative can only be valid within the oil palm waste and null within the parameters. From the heavy analysis of the PKS and OPF, they are suitable for removal of toxic metals such as Cadmium, Lead and Chromium, since these toxic metals are not detected in them. Also the oil palm fibre is suitable for the production of organic fertilizer as a result of the high amount of Potassium detected in them.

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