Production of activated carbon from Atili seed shells

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Abstract

Activated carbon was produced from atili (black date) seed shells by chemical activation with phosphoric acid as an activating agent. Carbonization was done at temperatures of 350°C, 450°C, 550°C, 650°C and at corresponding resident times of 20, 30, 40, 50 and 60 minutes respectively in a muffle furnace. The study involved the determination of yield, carbon content, burn-off, moisture content, and ash content as well as the temperature and suitable resident time for carbonization. The result showed that, increasing the carbonization temperature from 350°C to 650°C as well as increasing the corresponding resident time from 20 to 60 minutes led to a decrease in carbonization yield as well as an increase in burn off. An increase in carbonization time led to a decrease in ash content while an increase in carbonization temperature led to a decrease in the moisture content. The yield, burn-off and ash content obtained at a carbonization temperature of 650°C and at a corresponding time of 60 minutes were found to be 68.29%, 31.71% and 0.75% respectively while the highest carbon content (99.16) and lowest moisture content (0.09) was obtained at this same temperature and corresponding time. The activated carbon produced gave a yield of 99.37%, ash content (2.01%), moisture content (4.20%), carbon content (93.79%), burn off (0.63%) and pH of 6.752. These properties therefore indicate the suitability of the activated carbon produced.

Keywords

Activated; Carbon; Seed; Shells; Atili; Carbonization; Yield

Introduction

Researches are often aimed at discovering new and better methods of obtaining finished products from available raw materials. Many agricultural by-products that are available at little or no cost for example chicken feathers, rice husks have been reported to be capable of removing substantial amounts of metal ion and organic pollutants from aqueous solutions [1]. In line with this, the production of activated carbon from atili (black date) seed shell was undertaken, which is a natural raw material as well as an agricultural by-product.

Activated carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structure that makes the carbon more absorbent. These properties are obtained when a char is subjected to controlled gasification by oxidizing gases, or when a raw material impregnated with dehydrating agents is subjected to carbonization [2]. Activated carbons are predominantly amorphous solids with large internal surface areas and pore volumes. These unique pore structures play an important role in many different liquid and gas phase applications because of their adsorptive capacity [1].

Lots of agricultural waste and by products have successfully converted to activated carbon, for example, macadamia nutshell, paper mill sludge and peach stones [2].

Atili (*Canarium schweinfurthii bursaraceae*) is the fruit of the perennial tree plant also called "Atili" tree [3]. The Atili tree is a large forest tree with its crown reaching to the upper canopy of the forest, with a long clean, straight and cylindrical bole exceeding 50m. Its diameter above the heavy root swellings can be up to 4.5m. The leaves are pinnate, clustered at the end of the branches, and may be 15-65cm long, with 8-12 pairs of leaflets, mostly opposite, oblong, cordate at base, 5-20cm long and 3-6cm broad with 12-24 main lateral nerves on each sides of the midrib [4]. *Canarium schweinfurthii bursaraceae* is distributed throughout tropical Africa in rain forest, gallery forest and transitional forest from Senegal to west Cameroon and extending to Ethiopia, Tanzania and Angola [4]. In Nigeria, the fruit is called "Ube Okpoko" in Ibo and "Atili" in Hausa. The fruit is commonly found in large quantity in Pankshin, Plateau state of Nigeria and is also produced in similar quantities in other states of the northern and south eastern Nigeria. The fruits contain single triangular shaped seed shell with small projections at the three edges. The seeds are embedded in a purplish green pulp with a desirable sweet but not too sugary taste similar to that of avocado pear. The pulp is of oily consistency and edible. The weight of the fruit ranges from 3.5 to 9g with a predominant average weight of about 5.3g. The fruit is very hard; the seed is normally cooked and yields oil. It is sometimes used as a substitute for Shea butter [3].

The production of activated carbon from agricultural by-products such as, Atili seed shell has potential economic and environmental impacts. First, it converts unwanted low-value agricultural waste to useful, high-value adsorbents. Secondly, activated carbons are increasingly used in water treatment to remove organic chemicals and metals of environmental and /or economic concern. Thirdly, it will reduce the importation of activated carbon, thereby increasing our economic base in the country [1].

In this research work, atili (black date) seed shells were used to produce activated carbon in view of their availability, cheapness of material with high carbon and low inorganic content.

Material and method

The Atili (Blackdate) seed shell used in this research work was procured from Jos, Plateau state, Nigeria. The seed shell was washed and dried under the sun for three days, after which it was dried in an oven at a temperature of 105°C for 45mins. The dried seed shell was crushed in a crusher and sieved to obtain particle sizes within the range of 2.0-2.8mm diameter.

About 1.0g of the crushed Atili (Black date) seed shell was weighed and transferred into a beaker. 100ml of distilled water was added and then stirred for one hour. The samples were allowed to stabilize before the pH was measured using a pH meter.

Proximate analysis of the seed shell was carried out and the properties of the seed shell such as the dry matter content, ash content, moisture content, crude fibre content, crude protein content, oil (Ether extract) content, volatile matter and the nitrogen free extract were determined. Proximate Analysis is a partitioning of compounds in a feed into six categories based on the chemical properties of the compounds. The six categories are: moisture, ash, crude protein (or Kjeldahl protein), crude lipid, crude fibre and nitrogen-free extracts (digestible carbohydrates).

2.0g of the sample was weighed into the porcelain crucible and placed in a muffle furnace at 600°C overnight. The crucible and its contents was then transferred into a dessicator and cooled to room temperature, after which it was cooled and weighed as quickly as possible to prevent moisture absorption. The percentage ash content was determined according to Ekpete et al. [1].

A porcelain crucible was dried in an oven for 30min at 105°C. It was placed in a dessicator to cool and then weighed. About 2.0g of the sample was placed in the crucible. The crucible and its contents was weighed and then placed in an oven at 105°C. Thereafter it was removed and allowed to cool in a dessicator. The crucible and its contents were then weighed and the moisture content was determined.

Carbonization was achieved using a muffle furnace. About 5g of the sample was weighed into a clean and previously weighed crucible. The crucible and its contents was weighed and then placed in a furnace and heated at 350°C for 20 minutes after which the crucible and its contents was placed in a dessicator and then weighed. The procedure was repeated for 30, 40, 50 and 60 minutes. The whole procedure was then repeated at 450, 550 and 650°C for 20, 30, 40, 50 and 60 minutes at each temperature. The carbonized materials were then characterized as described above. The weight of the carbonized material was taken before carbonization and the corresponding weight of the material was taken after carbonization. The yield was obtained according to Ringim [5]. The burn off was calculated according to McDougall [6]. The carbon content was obtained according to Ringim [5]. The ash content (%), moisture content (%), of the carbonized sample were also determined.

5g of the sample was weighed and mixed with 15 ml of 60% Ortho-phosphoric acid. The mixture was left to soak for 24 hours and later heated to form paste. The paste formed was then placed in the muffle furnace and calcined at 600°C for 30 minutes in the presence of limited oxygen, after which the sample was cooled in a dessicator, washed with distilled water and dried in an oven at a temperature of 105°C.

Results

Table 1 show the proximate analysis carried out for the atili seedshell in which the ash content (%), moisture content (%), carbon content (%) etc. were determined.

Table 1. Proximate analysis of atili seed shell

Characteristic	Value (%)
Ash content	1.04
Moisture content	3.72
Dry matter	96.28
Carbon content	95.24
Crude protein	2.87
Crude fibre	16.38
Ether extract (oil)	0.67
Nitrogen free extract	79.04

pH of Atili seed shell = 6.582

Table 2 shows the proximate analysis of the carbonized atili seedshell at 650°C.

Table 2. Proximate analysis of atili seed shell carbonized at a temperature of 650°C

Characteristic	Value (%)
Ash content	0.75
Moisture content	0.09
Dry matter	99.91
Carbon content	99.16
Crude protein	0.88
Crude fibre	0.63
Ether extract (oil)	0.00
Nitrogen free extract	96.51

Table 3 show the proximate analysis for the activated carbon produced.

Table 3. Proximate analysis of activated carbon

Characteristic	Value (%)
Ash content	2.01
Moisture content	4.20
Dry matter	95.80
Carbon content	93.79

pH of Activated carbon = 6.752

Table 4 presents the yield and some properties of the activated carbon produced.

Table 4. Yield and properties of activated carbon

Sample no	Yield (%)	Ash content (%)	Moisture content (%)	Carbon content (%)	Burn off (%)	Volatile matter (%)
1.	99.37	2.01	4.20	93.79	0.63	97.99

Figure 1 show the carbonization yield with time at different temperatures.

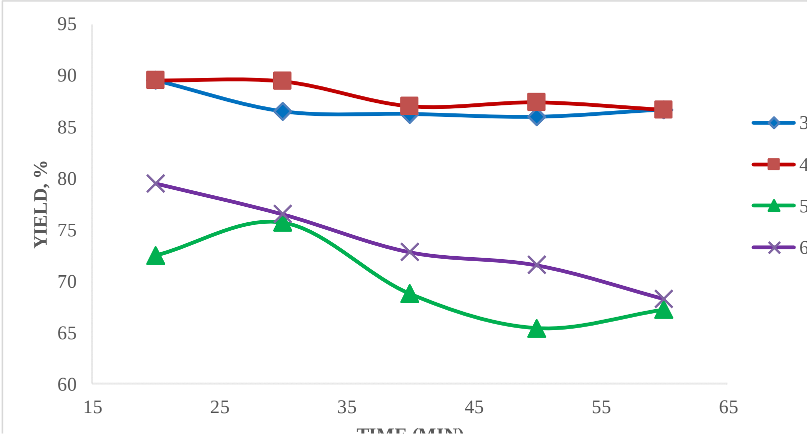

Figure 1. *Variation of carbonization yield with time at different temperatures*

Figure 2 shows the ash content determined after carbonization with time at different temperatures.

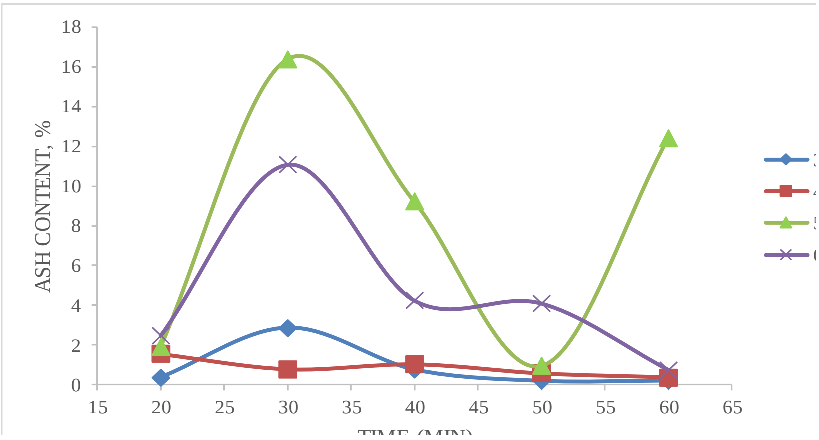

Figure 2. *Variation of ash content (after carbonization) with time at different temperatures*

Figure 3 shows the moisture content determined after carbonization with time at different temperatures.

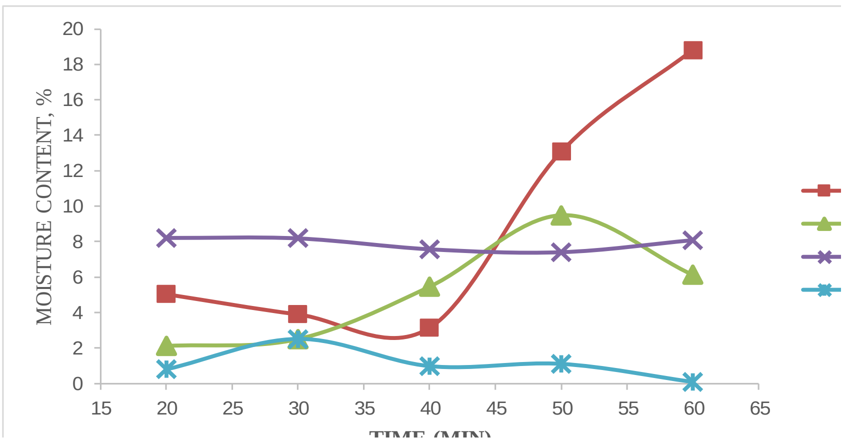

Figure 3. *Variation of moisture content (after carbonization) with time at different temperatures*

Figure 4 shows the carbon content determined after carbonization with time at different temperatures.

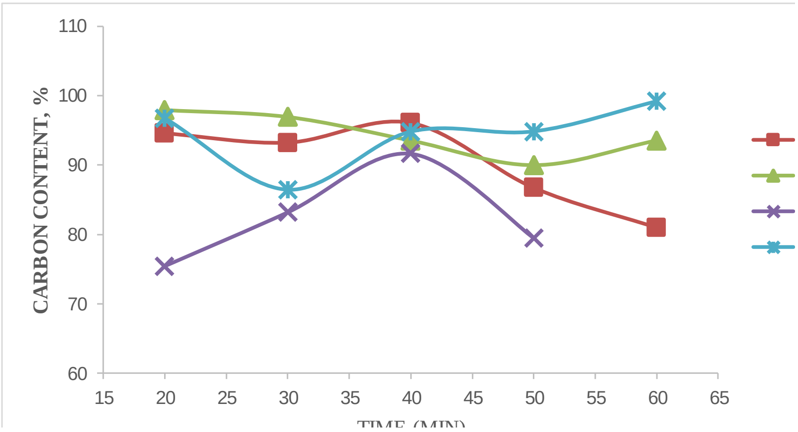

Figure 4. *Variation of carbon content (after carbonization) with time at different temperatures*

Figure 5 shows the amount of burn off determined after carbonization with time at different temperatures.

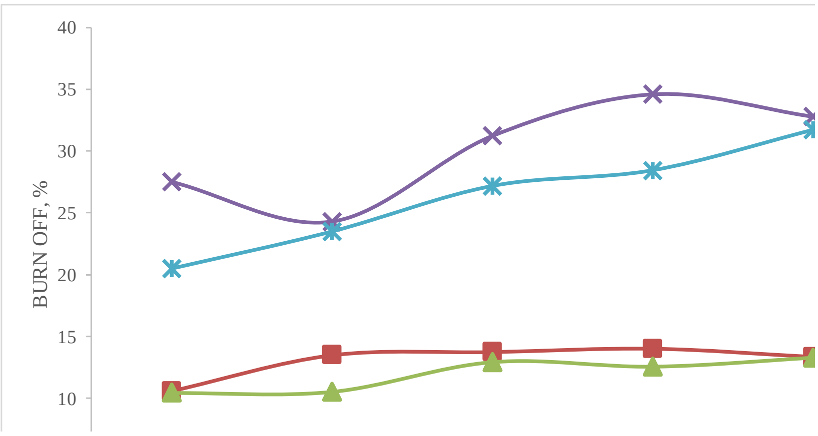

Figure 5. *Variation of burn off (after carbonization) with time at different temperatures*

Figure 6 shows the yield determined after carbonization with time at different temperatures.

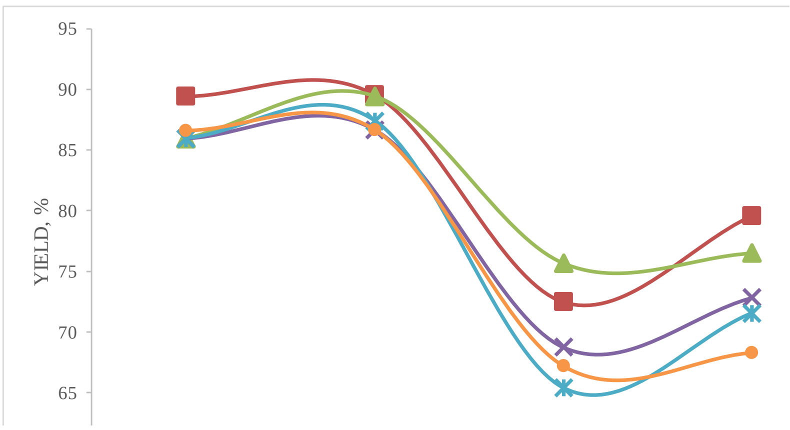

Figure 6. *Variation of carbonization yield with temperature at different times*

Figure 7 shows the ash content determined after carbonization with time at different temperatures.

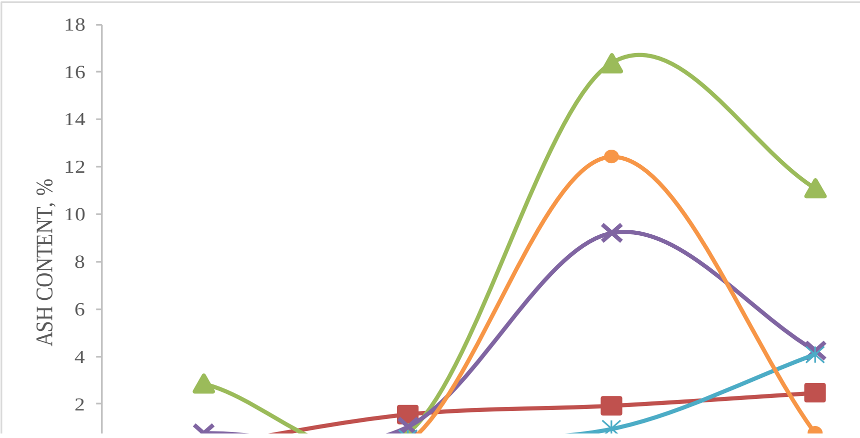

Figure 7. *Variation of ash content (after carbonization) with temperature at different times*

Figure 8 shows the moisture content determined after carbonization with time at different temperatures.

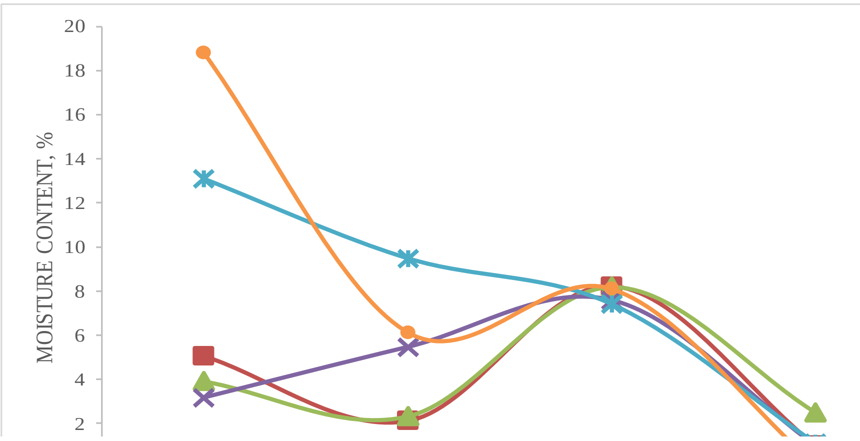

Figure 8. *Variation of moisture content (after carbonization) with temperature at different times*

Figure 9 shows the carbon content determined after carbonization with time at different temperatures.

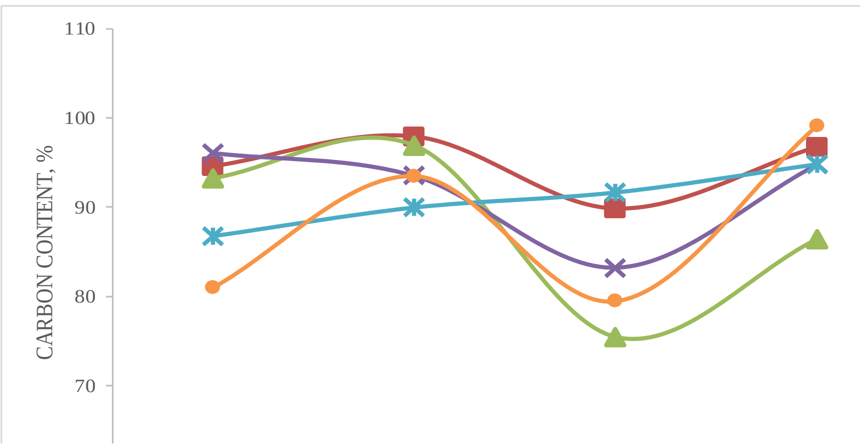

Figure 9. *Variation of carbon content (after carbonization) with temperature at different times*

Figure 10 show the amount of burn off determined after carbonization with time at different temperatures.

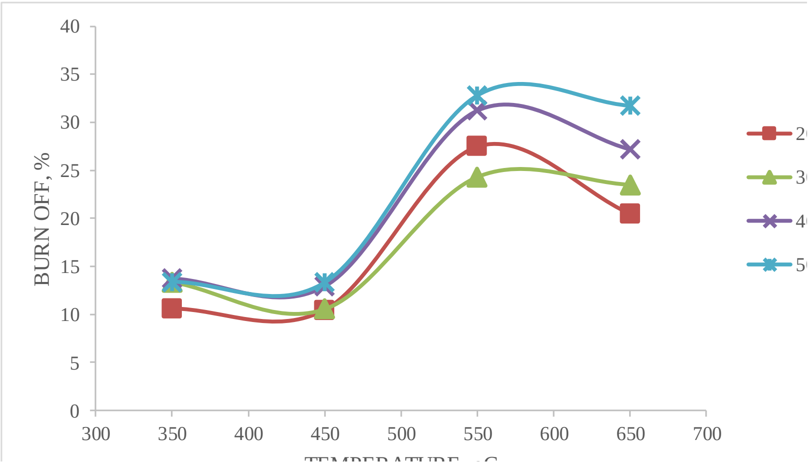

Figure 10. *Variation of burn off (after carbonization) with temperature at different times*

Discussion

Characterization of atili seed shells

Since activated carbon is manufactured from naturally occurring raw materials, its properties will obviously be variable. In order to minimize variability, it is necessary to be very selective in raw material source and quality and practice a high level of manufacturing quality control [7]. The cellulosic structure of the atili seed shell determines the end product characteristics. The activated carbon obtained depends on the type of raw material used and its initial processing prior to carbonization and activation [7]. Since the manufacturing process involves the removal of volatile matter from the raw material, the economic relationship between the price, availability, and quality of the raw material on the one hand, and its volatile content on the other is important [6]. The result of the proximate analysis in Table 1 showed a low amount of moisture (3.72%), and ash content (1.04%) whereas the carbon content (95.24%) was high. Also, the ether extract (oil) (0.67%), crude fibre content (16.38%) and crude protein content (2.87%) were low. This characteristic of the atili seed shell therefore makes it a good precursor for the manufacture of activated carbon since low content in organic materials is important to produce activated carbon with low ash content. The low amount of moisture and ash content therefore indicates that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used in column or fixed-bed reactors [1]. Low ash content is an important property of the precursor as ash content can lead to increase hydrophilicity. It can have catalytic effects, causing restructuring process during regeneration of used activated carbon.

This is believed to adversely affect the strength of the final product [2]. Ash content reduces the overall activated carbon. It also reduces the efficiency of reactivation, therefore, the lower the ash content, the better the activated carbon for use as adsorbent [1]. From Table 1, the crude fibre content of the atili seed shell was found to be 16.38%. Crude fibre refers to the fine hairlike structure of animal, vegetable, mineral, or synthetic origin. Fibres are classified according to their origin, chemical structure or both. Crude fibers could be animal fibers, vegetable fibers, mineral fibers and synthetic fibers [8]. The crude fibre found in the atili seed shell is the vegetable fibre and they are predominantly cellulose. This makes the atili seed shell a good precursor for the manufacture of activated carbon.

The dry matter content was found to be 96.28% and the moisture content of the atili seed shell was found to be 3.72%. Activated carbon is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, example, 3, 8, 10%. For many purposes, this moisture content does not affect the adsorptive capacity, but obviously it dilutes the carbon [2]. This therefore implies that the starting raw material for the manufacture of the activated carbon must have a low moisture content and a high dry matter content in order to produce activated carbon with low moisture content. Similarly, from Table 1, the crude protein content and ether extract of the atili seed shell were found to be 2.87% and 0.67% respectively. Crude protein and ether are organic compounds and since low content in organic materials is necessary to produce activated carbon with low ash content [2], atili (black date) seed shell is suitable for use in the manufacture of activated carbon.

Characterization of carbonized seed shells

It has been recognized that for an effective activated carbon, the preliminary carbonization process is very essential. Carbonization involves loss of volatile materials which are presumably fewer in smaller particles than in the larger ones and escape of the volatiles increases with increasing temperature [9]. The processing of activated carbon therefore basically involves selection of parameters that effect the activated carbon production, carbonization process and type of activation [2]. Therefore, parameters such as temperature, ash content, yield, and burn off, moisture content, carbon content and resident time for carbonization will affect the overall texture, quality and quantity of the carbonized product with the attendant effects on the ash, moisture and possibly metal contents [9]. It is therefore important to closely monitor the carbonization process to obtain a definite characteristic data. It is hoped that the results obtained in this study would give more specific optimum conditions for carbonization of atili (black date) seedshell.

Burn off

Burn off is used to denote the degree of carbonization, which is the loss of char (in percentage by mass) that is allowed to occur. Low burn off are usually undesirable as they lead to low surface area which in turn may lead to a low adsorption capacity for target molecules [10]. From Figure 5, it can be seen that at constant temperature, the burn off increased with time. In Figure 10, it was observed that at a constant time, the burn off increased with an increase in temperature. It can therefore be inferred that an increase in carbonization temperature leads to an increase in the burn off and similarly an increase in carbonization time leads to an increase in burn off.

Yield

Figure 1 showed that, at constant temperature, the carbonization yield decreased with increase in time though a few fluctuations were observed. Similarly, Figure 6, it can be seen that at constant time, the carbonization yield decreased with increase in temperature. Carbonization temperature therefore significantly affects the production yield of the activated carbon. The decrease in carbonization yield with time is as a result of volatilization of organic materials which results in formation of activated carbon. The yield of the final product which is inversely proportional to the extent of burn-off, decreases as the residence time in the kiln is increased, and is markedly dependent on the temperature of activation, which obviously affects the rate of burn-off or gasification [6].

Carbon content

From Figure 4, fluctuations were observed in the variation of carbon content with time at constant temperature and similarly from Figure 9, fluctuations were observed in the variation of carbon content with temperature at constant time but it was observed that at a carbonization temperature of 650°C and corresponding carbonization time of 60 minutes, the highest carbon content (99.16%) was obtained. Therefore since, high carbon content in a material is needed for the production of activated carbon [2], the carbonized sample at 650°C at 60 minutes was further used to produce the activated carbon due to its high carbon content.

Moisture content

Figure 8 showed that the moisture content of the carbonized sample decreased with increasing temperature and at constant time while Figure 3 showed fluctuations in the variation of moisture content with time at constant temperature, although it was observed that the lowest moisture content (0.09%) was recorded at temperature of 650°C and corresponding time of 60minutes. Though moisture content does not affect the adsorptive power but it dilutes the carbon [2], therefore, the carbonized sample at 600°C at 60 minutes was further used to produce the activated carbon due to its very low moisture content.

Ash content

Figure 2 showed a decrease in ash content with increase in carbonization time at constant temperature while Figure 7 showed fluctuation in the ash content at increasing temperature and constant time. Low ash content is one of the most important requirements for the manufacture of activated carbon. The major reasons for this relate to the fact that the ash content may catalyze certain undesirable effects, and is believed to adversely affect the strength of the final product [6]. Ash content also influences the ignition point of the carbon- this may be a major consideration where adsorption of certain solvents is concerned [7]. The ash content obtained at a carbonization temperature of 650°C and at a corresponding time of 60 minutes was low (0.67%), thereby making the carbonized material at this temperature and time to be suitable for activation.

Carbonization temperature

For activated carbon to have the desired properties, the temperature of carbonization must be well controlled. The temperature must be sufficiently high to dry and volatilize all non-carbon substances during carbonization. If the temperature of carbonization is too high, it greatly affects the activity of the carbon produced. The same applies to the temperature at which the carbonized product is activated. The temperature of carbonization and activation influences the molecular architecture of the carbonized material, leading to increase in surface area and internal pores. The carbonization temperature of the raw materials during analysis can determine the exact temperature for decomposition of organic materials, during the

Issue 25, July-December, 2014
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activation process for activated carbon production [11]. The results indicate that the most appropriate carbonization temperature for atili (black date) seed was 650^{o}C. Increasing the temperature beyond this range may increase the rate of internal burning which would affect the type and nature of the pores developed during carbonization and the ultimate properties of the carbonized product [9].

Characterization of the produced activated carbon

Characterization of activated carbon (AC) is very important in order to classify activated carbon for specific uses. The characteristics of activated carbon depends on the physical and chemical properties of the raw materials as well as the activation method used [2]. The activated carbon produced gave a yield of 99.37%, ash content (2.01%), moisture content (4.20%), carbon content (93.79%), burn off (0.63%) and pH of 6.752 as shown in Table 3. These properties therefore indicate the suitability of the activated carbon produced, since activated carbon should have the following properties; Low ash content [6], Low moisture content (to avoid diluting the carbon) [2], High carbon content [2], and High yield.

The pH value is one of the factors that influence the adsorptive behaviour of activated carbon from aqueous solution. Carbon generally has a low affinity for ions, particularly those with a high charge-to-surface ratio, and pH can affect ionicity [6]. Activated carbon pH of 6-8 is acceptable for most applications in decolourization, and water treatment [10]. The acid or basic nature of an activated carbon depends on its preparation and inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was subjected to. Activated carbon pH may influence colour by changing the pH of the solution. Such a change affects the pH sensitive fraction of solution colorants causing unreliable colour measurements [10]. The pH of the activated carbon produced was 6.752. Carbon yield is the amount of original precursor remaining after pyrolysis and activation treatment. The carbon yield is change, when different activation conditions are used [2]. The carbon yield of the activated carbon produced was found to be 99.37%.

Proximate analysis of carbonized atili seedshells at 650°C

In Table 2, the crude fibre content of the atili seed shells was found to be 0.63%. It was observed that the crude fibre content reduced from an initial value of 16.38% to 0.63% after carbonization at 650°C and at a residence time of 60minutes. It can therefore be inferred that the carbonization process decreased the crude fibre content of the atili seed shells. Low content in organic materials is important to produce activated carbon with low ash content [2]. Similarly, from Table 2, the Ether content of the atili seedshells carbonized at 650°C and at a residence time of 60 minutes was found to be 0.00%. It was observed that the Ether content reduced from an initial value of 0.67% to 0.00% after carbonization. It can therefore be inferred that the carbonization process completely removed the Ether content of the atili seed shells. The crude protein content of the atili seedshells reduced from an initial value of 2.87% to 0.88% after carbonization at 650°C and at a residence time of 60 minutes. The dry matter content was found to be 99.91% and the moisture content was found to be 0.09%. Activated carbon is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, example, 3, 8, 10%. For many purposes, this moisture content does not affect the adsorptive capacity, but obviously it dilutes the carbon [2].

Conclusions

In the production of activated carbon from atili seed shells, the following conclusions can be drawn:

÷ atili seed shell is a suitable precursor for the production of activated carbon due to its availability, high carbon content, low ash content, low moisture content, sufficient volatile content, low degradation upon storage;

÷ The highest carbon content (99.16) and lowest moisture content (0.09) was obtained at a carbonization temperature of 650^{o}C and at a corresponding time of 60 minutes;

÷ The yield, burn-off, ash content obtained at a carbonization temperature of 650^{o}C and at a corresponding time of 60 minutes were found to be 68.29%, 31.71% and 0.75% respectively;

÷ The yield, ash content, moisture content, carbon content, and burn off of the final activated carbon were found to be 99.37%, 2.01%, 4.20%, 93.79% and 0.63% respectively thereby indicating the suitability of the activated carbon produced;

÷ The pH of the raw atili seed shell was found to be 6.582 while that of the activated sample was found to be 6.752.

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