1. Introduction

Activated carbons are the most powerful adsorbents known (Zauro et al., 2018). It is basically a solid material consisting mainly of pure carbon. A characteristic feature is its porous structure and the resulting immense surface area (Meena et al., 2005). Due to its exceptional adsorption qualities, activated carbon is widely used in solution purification, decolorization, and removal of odor at low cost and superior efficiency (Onawumi et al., 2021). Activated carbons work on the principle of adsorption which is an interfacial process involving the collection of gaseous or solute components on the surface of adsorbent solids. This phenomenon is associated with physical attractive forces that bind gaseous and solute molecules commonly known as Van-der-Waals forces. Adsorption is thus a physical process and the substances adsorbed on the solid do not undergo any chemical reaction with the latter. The adsorbing solid is referred to as adsorbent and the substance to be adsorbed from the liquid or gas phase as the solute (Chawdhury et al., 2020). The adsorption power and rate is determined by the kind of activated carbon, the particle size, the pore size and its distribution (Vikash et al., 2017). The importance of porous materials has been recognized since antiquity when porous charcoal was used for its medicinal properties. The worldwide interest in environmental protection and energy conservation has revived the research on porous materials, which have numerous applications such as in catalysis, separation, insulation, sensors and chromatography among others (Borislav et al., 2007).

Activated carbon is being generated from different agricultural precursors, but there is less emphasis on the modification of the existing surface morphology. The study will emphasize on the preparation, modification and characterization of activated carbon to ascertain the disparities on the surface morphology among the adsorbents generated.
2. Materials and Methods

2.1 Equipment and Reagents
Functional groups were determined using FT-IR (Carry630), surface morphology was investigated using scanning electron microscope SEM (JSM-7900F), pH (ST-926), furnace (Sx-2.5-10) was used for carbonization and activation and oven (DHG-9101.ISA) was used for drying. The materials used in this study are zinc chloride from BDH, England, sodium bicarbonate Sigma Aldrich, Germany, sulphuric acid (98 %) from M&B and Hydrochloric acid (36 %) from Sigma Aldrich Germany.

2.2 Plant Sample
Annogeissus leiocarpus plant known as chewing stick tree is available and possessed remarkable hardness, which makes it suitable precursor for the production of activated carbon. The Annogeissus leiocarpus stem was obtained from Kardi Area, Birnin Kebbi Local Government using cutlass and placed in polythene bag and then brought to herbarium for identification in UDUS, botany laboratory unit by Malam Abdulazeez Salihu. The Boucher Number UDUS/ANS/0180 was given.

2.3 Sample Treatment
The method of sample treatment adopted by Itodo (2010) were used. The materials were washed with tap water at least three times and then with distilled water to remove any adhering dirt or impurity. The sample was further sun dried for one week, squashed with hand slightly to remove the unwanted sticks and then placed in an oven at 105 °C for 24 h (Kra et al., 2019). The dried sample was ground and sieved to obtain particles in the size range from 0.106 to 0.250 mm. Approximately 100 g of the powdered materials were placed and stored in an air tight container.

2.4 Carbonization
Powdered material obtained from Annogeissus leiocarpus stem (5 g) of was placed in six different clean crucibles before introduction in the furnace at 500 °C for five minutes after which they were placed in a bath of ice block. The water from the bath was drained and the samples were sun dried. This process was repeated until substantial amount of carbonized sample was obtained (Itodo, 2010).The carbonized sample was washed with 10 % HCl to remove the surface ash, followed by hot water and finally with distilled water to remove the residual acid. The solid particles were sun dried and later placed in an oven at 100 °C for one hour (Rahman et al., 2002; Itodo, 2010).

The yield on the carbonization was calculated from weight before carbonization (Wbc) and after carbonization (Wac). The percentage yield was calculated using Equation 1 (Yoshiyuki and Yutaka, 2001).

\[
\% \text{Yield} = \frac{W_{ac}}{W_{bc}} \times 100 \quad \text{Equation 1}
\]

Wac = is the weight after carbonization and Wbc = is the weight before carbonization.

2.5 Activation Process
The carbonized sample (5 g) was mixed with 5cm³ of 1M ZnCl₂ solution. The sample was introduced in to the furnace at 800 °C for five minutes, after which the activated sample was cooled with cold water. Excess water was drained and the activated carbon allowed to dry at room temperature (Gimba et al., 2002; Itodo, 2010). It was then washed with 10% HCl acid to remove surface ash, followed by hot water and then with distilled water to remove the residual acid until the pH of 6-8 is attained (Rahman et al., 2002; Itodo 2010). The generated activated carbon was placed in an oven at 110 °C overnight and stored in an air tight container.

2.6 Chemical Modification of Activated Carbon

2.6.1 Modification with Sulfuric Acid.
Annogeissus leiocarpus stem activated carbon was washed with deionized water until any leachable impurities due to free acid and adherent powder is removed. Wet activated carbon (5 g) was treated with 40% H₂SO₄ (v/v) in the ratio 1:3 in an incubator at 110 °C for 24 h and later soaked with deionized water until the solution pH is 7. Finally, the sample was dried overnight in an oven at 110 °C, cooled at room temperature, and stored in a desiccator (Kadirvelu et al., 2001).

2.6.2 Modification with Sodium Bicarbonate
The prepared activated carbon was washed with deionized water until any leachable impurities due to free acid and adherent powder was removed. Wet activated carbon (5 g) was treated with 40% NaHCO₃ (w/v) in the ratio 1:3 in an incubator at 110 °C for 24h and later soaked with deionized water until the solution pH was 7. Finally, the sample was dried overnight in an oven at 110 °C, cooled at room temperature, and stored in a desiccator (Kadirvelu et al., 2001)
2.7 Characterization of the Activated Carbon

2.7.1 Determination of Moisture Content

Dried sieved AC sample (3 g) was placed on a dry-cleaned and pre-weighed Petri dish dried in oven at 105 °C overnight and then in desiccator for 30 minutes and weighed. This process was repeated three times and the average is taken from which percentage moisture content was calculated as in equation 2 (AOAC, 1990).

\[
\text{Moisture content} = \left( \frac{W_1 - W_2}{W_2} \right) \times 100 \quad \ldots \ldots \ldots (2)
\]

Where \( W_2 \) = weight of sample after drying and \( W_1 \) = Weight of sample before drying

2.7.2 Determination of Ash Content

Copper crucible was heated in a furnace at 500 °C for 2 minutes and cooled in a desiccator and weighed. AC (3 g) was placed in the crucible and then introduced in muffle furnace at a temperature of 500 °C for three hours. It was removed and cooled to room temperature and then placed in the desiccators before weighing. The process was repeated three times and the percentage ash content was determined using equation 3.

\[
\text{Ash content} = \left( \frac{W_2 - W_1}{W_2} \right) \times 100 \quad \ldots \ldots \ldots (3)
\]

Where \( W_1 \) = weight of empty crucible, \( W_2 \) = weight of empty crucible + Fresh sample and \( W_3 \) = weight of crucible + Ash

2.7.3 Determination of Bulk Density

Density was measured on activated sample of < 2mm. It is estimated by placing the product into a graduated cylinder and compacted by tapping on the bench top until an expected volume, \( v \) (cm\(^3\)) was occupied by mass, \( m \) (g). The cylinder was tapped on the bench top until the volume of the sample stop decreasing. The mass and volume were recorded and density was calculated using equation 4 (Yoshiyuki and Yukata, 2005)

\[
\rho = \frac{\text{Mass/Volume occupied}}{\ldots \ldots \ldots (4)}
\]

2.7.4 Determination of Burn Off

Burn off refers to the weight difference between the original char and the AC divided by the weight of the original char with both weights on dry basis (Onawumi et al., 2021).

\[
\% \text{burn off} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100 \quad \ldots \ldots \ldots (5)
\]

\( W_0 \) = weight of char after pyrolysis, washing and drying, \( W_i \) = weight of carbon after activation, washing and drying, \( \% \text{burns off} \) = mass after activation/original mass of char x 100

2.7.5 Determination of Porosity Base on Swellings

Activated carbon (0.5 g) of was dispersed in 20cm\(^3\) water in a graduated tube with the aid of a shaker. This was centrifuged for 10 minutes at 4000 rpm. The resulting volume will be read at final volume \( V_T \) and recorded. Equation 6 is used to calculate the porosity (Ekpete et al., 2017).

\[
\text{Porosity} (\alpha) = \left( \frac{V_w}{V_T} \right) \quad \ldots \ldots \ldots (6)
\]

Where, \( V_w \) = volume of water, \( V_T \) = final volume of water after centrifugation and \( \alpha \) = Porosity

2.7.6 Determination of Volatile Matter

An empty crucible was weighed and then the sample (1 g) was added in to crucible with lid and weighed. This was kept in muffle furnace at a temperature of 910 °C for seven minutes, after which it was taken to desiccator for 30 minutes to cool down (Kra, 2019). %Volatile matter was calculated using equation 7.

\[
\frac{100x(100-Y-X) - X(100-Z)}{(Y-X)(100-Z)} \quad \ldots \ldots \ldots (7)
\]

Where \( Y \) = Mass of crucible, lid and sample before heating, \( X \) = Mass of crucible, lid and content after heating, \( Z \) = Mass of empty crucible and lid, \( M \) = % moisture content.

2.7.7 Determination of pH

AC (3 g) was mashed and soaked in 10 cm\(^3\) distilled water, boiled for 5 minutes and allowed to cool (Yoshiyuki and Yukata, 2003) 1% solution (w/v) of the samples were made using distilled water. A pH of the supernatant was obtained after 1 hour and pH electrode was dipped into the solution and the value was read from the meter. Samples with undesirable pH were washed continuously until a pH of 6 - 8 was reached (Ahmedna et al., 2000).

2.7.8 Determination of Fixed Carbon (% Carbon Content)

Fixed carbon content of the AC was determined using the procedure employed Kra, (2019). The relation for obtaining the carbon content is given in equation 8

\[
\text{Fixed Carbon} = 100 - (\%\text{Moisture content} + \%\text{Volatile Matter} + \%\text{Ash Content}) \ldots \ldots \ldots (8)
\]

2.7.9 High Resolution Electron Microscope (HRSEM)

Scanning electron microscope (HRSEM) was used to check the surface morphology of the
activated carbon (AC, AMAC and BMAC) produced from *Annogeissus leiocarpus* stem. About 0.5 g of the samples each were sprinkled on to aluminium or carbon tape adhesives upheld on metallic disk coated with gold.

3. Results and Discussion

3.1 Results

Table 1: Proximate analysis of the adsorbents produced from *Annogeissus leiocarpus*.

| Parameters               | AC       | AMAC/H₂SO₄ | BMAC/NaHCO₃ |
|-------------------------|----------|------------|-------------|
| Yield (%)               | 67.3 ± 0.03 | ----------- | ----------- |
| Burn off (%)            | 22.7 ± 0.01 | ----------- | ----------- |
| Bulk density (g/cm³)    | 0.85 ± 0.01 | 0.52 ± 0.01 | 0.65 ± 0.02 |
| Porosity (%)            | 2.31 ± 0.03 | 1.8 ± 0.03  | 1.9 ± 0.01  |
| pH                      | 7.12 ± 0.02 | 6.1 ± 0.02  | 7.9 ± 0.01  |
| Moisture content (%)    | 3.32 ± 0.03 | 2.1 ± 0.25  | 2.2 ± 0.03  |
| Ash content (%)         | 8.72 ± 0.01 | 6.1 ± 0.23  | 7.6 ± 0.01  |
| Volatile matter (%)     | 11.23 ± 0.01 | 12.2 ± 0.04 | 11.9 ± 0.02 |
| Fixed carbon (%)        | 76.73 ± 0.01 | 79.6 ± 0.23 | 78.3 ± 0.24 |

Figure 1: FT-IR spectrum for AC

Figure 2: FT-IR spectrum of AMAC/ H₂SO₄
Figure 3: FT-IR spectrum for BMAC/NaHCO$_3$

Figure 4: Scanning Electron Micrograph of AC at different magnification

Figure 5: Scanning Electron Micrograph of AMAC/ H$_2$SO$_4$ at different magnification
3.2 Discussion

The results of physicochemical analysis obtained in table 1 were subjected to statistical analysis using one-way ANOVA. The p-value (0.001) for the different adsorbents prepared, indicate that there was significant difference among the parameters investigated on the adsorbents, when alpha value was set at 95% confidence level.

Physicochemical parameters are very important in activated carbon production for a particular chemical process (Chowdhury et al., 2012). Yield %, Ash content, moisture content and porosity were among the physicochemical parameters investigated. The high yield for AC (67.3 %) could be due to complete degradation of lignin, hemi cellulose and cellulose during pyrolysis process (Ajala and Ali, 2020).

Porosity decreases in the order: AC > BMAC/NaHCO₃ > AMAC/H₂SO₄ the percentage of micropore volume might result to higher adsorptive capacity of small molecule. AMAC/ H₂SO₄ appeared to have a good micropore volume. The results were supported by the findings of Hai (2018).

A pH of all the adsorbents were observed in this study was in line with the 7.5 pH value reported by Boadu et al., (2018). Ekpete et al. (2017) stated that the pH value within the range of 6-8 is usually acceptable for adsorption process. The pH value affects the surface and binding capacity of adsorbent due to exchange of Hydrogen ion (H⁺) with metal ion. Therefore, the pH value of the activated carbon shows that the washing process was completed. Hence it will have an immense impact on the adsorptive capacity of activated carbon.

Ash content refers to non carbon materials that do not combine chemically with the carbon surface. Good activated carbon is expected to have low ash content. The value obtained in Table 1 were 6.1 %, 7.6 % and 8.72 % for AMAC/H₂SO₄, BMAC/NaHCO₃ and AC respectively which are in agreement with findings of Sabino et al., (2016) who reported that less than 15 % ash content is more efficient, hence the lower the ash value the better the activated carbon for adsorption process. Another study conducted by Sanni et al., (2017) obtained an ash content of 7. 2 % and Ajala and Ali, (2020) reported 11.8 % which indicate the presence of high inorganic content in the raw material used in the production of activated carbon. Another study conducted by Ahmaruzzaman et al., (2010) obtained closely related values on different activated carbon samples. Therefore, the lower ash content obtained in this study shows that the activated carbon could be very good for adsorption studies.

Low moisture content is said to be good for activated carbon production. In this study, it was found to be 2.1 %, 2.2 % and 3.32 % which were relatively low and within the range of 1- 5 % reported by Sanni et al., (2017). Higher value of moisture content may dilute the adsorbent and increase its weight in adsorption process, which in turn has immense effect in reducing the efficiency of the activated carbon. Therefore, the low values indicate that the activated carbon has greatly developed an adequate porosity through the activation process (Meena et al., 2005). Studies has shown that the moisture content of less than 5 % allow higher adsorption of pollutant (Hock and Zain, 2015). The FT-IR spectra for three different category of activated carbon AC, AMAC / H₂SO₄ and
BMAC / NaHCO₃ are shown in figure 1, 2 and 3 respectively, indicating the appearance of several functional groups. This indicates that the surface modification increased the functionality on surface of activated carbon by creating more adsorption site. The broad OH absorption on AC disappeared for both, AMAC/ H₂SO₄ and BMAC / NaHCO₃. This could be due to excessive drying during modification process. Modification induced chemical reaction which causes bonds making and bonds breaking, this is the reason why some bonds that are originally present have disappeared, while the new ones are now seen (Shivakumar et al., 2012). It can be noticed that activated carbons shared some common peaks and values which justified the fact that they have the same sources. The new peaks that appeared after oxidation for AMAC/H₂SO₄ and BMAC / NaHCO₃, were between 1700 to 1890 cm⁻¹ for AMAC / H₂SO₄ and around 1690 to 1740 cm⁻¹ for BMAC / NaHCO₃. These absorptions correspond to the C=O stretching vibration for acid halide, carboxylic acid and transition metal carbonyl with AMAC / H₂SO₄ while in BMAC / NaHCO₃ the C=O stretching vibration stands for primary amide conjugated aldehyde, aliphatic ketones and aldehyde are some of the functionalities also obtained by Ekpete et al. (2017). Acid and base modifications of activated carbon increase the adsorptive capacity of activated carbon. This is supported by a study conducted by Lasaona et al., (2019) which investigated the influence of mineral acid modification and observed each acid produce activated carbon surface with unique functional groups and properties. The scanning electron micrograph for AC, AMAC/ H₂SO₄ and BMAC/NaHCO₃ are shown in figures 4, 5 and 6 respectively. The SEM enables the direct observation of the changes in the surface microstructures of the carbons due to the modifications. Studies are available which have reported the utilization of SEM analysis that shows the surface modification changes in the developed adsorbent (Borislav et al., 2007). Looking at the images, there is clear demarcation in the surface morphology of the three different adsorbent modifications. Large numbers of pore spaces are seen in AMAC / H₂SO₄ and least are seen in the AC with BMAC / NaHCO₃ showing an average number of pore spaces. Although both AMAC / H₂SO₄ and BMAC / NaHCO₃ are good adsorbent AMAC / H₂SO₄ appears to be the best with better surface morphology. The finding of this research work is in line with the result obtained by Boadu et al. (2018). Another similar work conducted by Tan et al. (2008) reported that the enhanced pore formation might be due to the diffusion of modification agent in to the rudimentary pores created during pyrolysis and consequent acceleration of its reaction with activated carbon surface. Pore development in a char during pyrolysis plays a crucial role in improving the total pore volume. Therefore, it can be inferred that the surface morphology of activated carbon strongly depends on the preparation method. Sanou et al. (2020) revealed that modification agents such as acid and base have the ability to promote the formation of new pore on the surface there by increasing the adsorptive capacity of the activated carbon.

4. Conclusion

The prepared and modified activated carbon, AC, AMAC / H₂SO₄ and BMAC / NaHCO₃ used in this study, were observed to have low moisture content (2 - 3.4 %), ash content (6 – 8 %) and volatile matter (11 – 12.2 %), but high fixed carbon (70 – 80 %), yield (67.6 %), pH values (6 – 8 %). The results from FT-IR analysis clearly identified appearance and disappearance of carbonyl and hydroxyl groups. The SEM results also accurately explained the surface morphology of the adsorbents generated. AMAC / H₂SO₄ appeared to have favourable characteristics over BMAC / NaHCO₃ and AC, validated by the statistical analysis which indicated that there was significant difference (P < 0.05) on the physicochemical parameters investigated among the adsorbents. On the basis of good characteristics, the adsorbents generated can be considered as an excellent precursor for the production of activated carbon.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

Ahmedna, M., Marshal, W and Rao, M (2000). Production of Granular activated carbon from selected Agric by products. Journal of Bioresource and Technology,71(2): 113 – 123. http://doi.org/10.1016/s0960-852(99)00070-X

Ahmaruzzaman, M. and Vinod, K. (2011). Rice husk and its ash as lowcost adsorbent in water and waste water treatment. Journal of Industrial and Engineering Chemistry,50(24):108119. http://doi.org/10.1012/ie201477c

Ajala, L.O. and Ali, E.E (2020). Preparation and characterization of groundnut shell – based activated charcoal. Journal of applied Science and Environmental Agriculture.
Atheba, P., Drogui, P. (2020). Journal of Applied Science, Environment and Management. 24(12): 2139-2146. https://doi.org/10.4314/jasem.v24i12.20

AOAC, (1990). Association of official analytical chemist. Official methods analysis. 15th edition. Washington DC: 147-158.

Boadu, K.O., Joel, O.F., Essumang, D.K., and Evbuomwan, B.O (2018). Comparative study on the physic chemical properties and heavy metal adsorption capacity of chemical activated carbon from farm kernel, coconut and groundnut shells. Journal of Applied Science, Environment and Management. 22(11):1833-1839. http://dx.doi.org/10.4314/jasem.v22i11.19

Borislav, D. Z., Jirl, J. I., Martin, S. and Josef, V (2007). Pore classification in the characterization of porous material: A perspective. Central European Journal of Chemistry.5(2):385-396. http://doi.org/10.2478/s11532-007-0017-9

Chowdhury, R. I., Chowdhury, S., Mazumder, M. A and Al Ahmed, A (2020). Removal of lead ions from water and wastewater: A review on the low-cost adsorbent. 7(3): 2895-2915. http://doi.org/10.1007/s13201-022-01703-6

Ekpete, O. A., Marcus, A. C. and Osi, V (2017). Preparation and characterization of Activated carbon from plantain (Musa paradisiacal). Hidawi Journal of Chemistry.12:185. http://doi.org/10.1155/2017/8635615

Hia, N. T (2018). Activated carbon from golden shower upon difference chemical activation methods: synthesis and characterization. Adsorption Science and Technology. 36 (2): 95-133. http://doi.org/10.1177/0263617416684837

Hock, P. E and Zain M. A (2018). Activated carbons by zinc chloride activation for dye removal.11(2):99-106. http://doi.org/10.2478/acs-2018-0015

Itodo, U.A (2010). Comparative studies on the preparation, absorption and evaluation of activated carbon from selected animal and agricultural waste. A Ph D Thesis UDUS.

Kadivelu, K., Kavipriya, M., Karthika, C., Vennilamani, W. and Pattabatpis, S (2003). Utilization of various Agricultural waste for Activated carbon preparation and application for removal of dyes and metal ions from aqueous solution. Bioresources Technology. 87: 129-132. http://doi.org/10.1016/s0960-852(02)00201-8

Kra, D.O., Allou, N.B., Atheba, P., Drogui, p. and Trokourey, A (2019). Preparation and characterization of activated carbon based on wood (accia aurileaformis). Journal of encapsulation and adsorption science. 9:63-82. https://doi.org/10.4236/jeas.2019.92004.

Lesaona, M., Miba, R. P. V., Mtunzi, F. M., Klink, M. J., Ejidike, P and Pakade, V. E (2019). Influence of inorganic acid modification on Cr(vi) adsorption performance and physicochemical properties of Activated Carbon. South African Journal of Chemical Engineering.28: 8-18. https://hdl.handle.net/10520/EJC-15d4f933c

Meena K.J., Mishra G.K., Rai P.K., Chitra R., and Nagar P.N. (2005). Removal of heavy metals from aqueous solution using carbon aerogal as an adsorbent. Journal of Hardours material122:161-170. http://doi.org/10.1016/j.jhamzat.2005.03.024

Onawumi, O.O.E., Sancoremi, A.A. and Bello, O.S (2021). Preparation and characterization of activated carbon from groundnut and egg shells as viable precursors for adsorption. Journal of Applied Science and Environmental Management. 25(9):1707-1713. http://doi.org/10.4314/jasem.v25i9.24

Rahman, A., Saad, B and Rizai, S (2002). Absorption characteristics of malachite green on activated carbon derived from rice husk produced by chemical thermal process. Bioresource and Technology. 90(14):1578-1583. http://doi.org/10.1016/j.biortech.2004.12.015

Sanni, E. S., Emetere, M. E., Odigure, J. O., Eleovbokhan, V. E., Agboola, O. and Sadiku, E.R (2017). Determination of optimum condition for the production of activated carbon from separate varieties of coconut shell. International Journal of Chemical Science. 4.1-6. https://doi.org/10.1155/2017/2801359

Sanou, Y., Kolawale, C. B., Tiendrebeogo, R., Kabore, R. and Tchakala, I (2020). Physicochemical and Spectroscopic properties of two laterite soils for application in arsenic water treatment. international Journal of Multidisciplinary Research and Development. 7(5): 12-17. https://doi.org/10.1080/257665299.2020.1766799

Sivakumar, B., Kannan, C. and Karthikeyan, S (2012). Preparation and Characterization of activated carbon from Balsamodendron caudatum wood waste through various process. Rosayan Journal of Chemistry. 5(3): 321-327. ISSN: 0974-1496

Vikash, R. A., Vikrant, S. V and Amol, P. K (2017). Activated Carbon as Adsorbent in Advance Treatment of wastewater.
Characterization and Modification of Activated Carbon Generated from Annogeissus…

Journal of mechanical Engineering. 14(4):36-40. http://doi.org/10.9790/1684-1404023640

Yoshiyuki, S., Yutaka, K. (2005). Pyrolysis, Animal and Human waste, physical and chemical characteristics of the pyrolytic product. Bioresource Technology. 81(1): 45-52. http://doi.org/10.1080/09593330.808240

Zauro, S. A and Badalamoole, L (2018). Pectin graft copolymer-montmorillonite composite: Synthesis, swelling and divalent metal ion adsorption. Separation Science and Technology. 53 (14): 2170-2185. http://doi.org/10.1080/01496395.2018.1446987