

Adsorptive Efficiency of Activated Carbon from Corncob Compared with Commercial Activated Carbon in the Adsorption of Light Alkanes Contaminant in Hydrogen Gas Product

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Authors' contributions

This work was carried out in collaboration among all authors. Author EAA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MMA and OAB managed the analyses of the study. Author EAA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The adsorptive efficiency of activated carbon produced from corncob was compared to commercial activated carbon in the adsorption of light alkanes contaminant in hydrogen gas product. The adsorption was measured over a constant temperature of 27°C and at pressures up to 125 kilo pascal (kPa) using a gravimetric gas adsorption technique. The light alkanes were adsorbed on activated carbon produced from corncob using chemical method with phosphoric acid as the activating agent. The mass of adsorbent used for the adsorption was from 20 – 60 g. Pore size distribution and characteristic functional groups present on the surface of activated carbon were determined using N₂ adsorption, Brunauer-Emmett-Teller (BET) method and Fourier Transform Infrared spectroscopy (FTIR spectra) respectively. BET analyses were used to characterise the activated carbons. The BET results of the produced activated carbon compared to the commercial activated carbon has a specific surface area of 1237 m²/g and 2048 m²/g and a pore volume of

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0.1162 cm³/g and 0.1959 cm³/g, respectively. FTIR spectra results of the produced activated carbon compared to the commercial activated carbon showed similar band gap at 2337.80 cm⁻¹ with an alkynyl C≡C stretch functional group and a vibration type of carbonyl group (carboxylic OH) at 1550.82 cm⁻¹. Experimental data verified using Langmuir isotherm and Freundlich isotherm adsorption models showed best fit for Langmuir adsorption isotherm model indicating the formation of a monolayer adsorbate on the outer surface of the adsorbent with an adsorptive and uptake capacity of 0.016 Pa⁻¹. The adsorptive efficiency of the produced activated carbon compared to the commercial activated carbon was 1.05wt% and 3.55wt%, respectively. Therefore, based on the results obtained, the produced activated carbon may not completely substitute the commercial activated carbon rather it can be used as a potential blend thereby reducing quantity and cost.

Keywords: Activated carbon; adsorption isotherm; adsorptive capacity; adsorption efficiency; light alkane.

1. INTRODUCTION

Hydrogen obtained from catalytic cracking of hydrocarbons is used for the production of benzene. However, the hydrogen is usually contaminated with light alkanes which are not desirable in this process. Several approaches have been proposed for hydrogen purification and storage. These include high pressure tanks for gaseous hydrogen storage, cryogenic vessels for liquid hydrogen storage, formation of metal hydrides, chemical storage (such as ammonia borane), by using pressure swing adsorption (PSA) and physisorption adsorption on a large number of proposed adsorbents [1].

Among the approaches listed above, physisorption adsorption has gained much attention due to its advantages over other techniques. The advantages of adsorption process in the adsorption of light alkanes contaminant in hydrogen gas product is due to its reversible nature, and relatively high adsorptive and storage capacity [2]. Currently available adsorption measurement techniques are classified into; volumetric, gravimetric and gas flow. The gravimetric technique is used over other techniques in this work because of its ease of operation and correlation of data fitted into the adsorption isotherm model equation on the basis of the mass of adsorbate adsorbed on the adsorbent during adsorption process [3].

Some of the commonly used adsorbents for adsorption process are classified into natural and engineered systems. The natural system includes soil and sediments while the engineered systems include activated carbon, metal oxides, iron exchange resins and biosolids. Activated carbon has gained more advantage over other adsorbents because of its well-developed porosity, low density, good chemical stability, one

of the best available control technologies, ready availability and low cost. Commonly used carbonaceous materials for activated carbon production include wood, coconut shell, corncob, rice husk, oil palm, sugar cane bagasse etc. However, the commercially available products are fairly expensive. Since, a large amount of carbon sorbent is needed for the purification of hydrogen, the expenses involved hamper their application in the gas adsorption process. The use of carbon based on relatively expensive starting materials is also unjustified for most adsorption applications [4]. Most of the industries involved in the purification of hydrogen in Nigeria source the activated carbon from foreign countries. This project seeks to investigate the possibilities of producing activated carbon from cheap, easily sourced and readily available agricultural waste (cheap locally available corncob). The choice of corncob over other waste materials was due to its availability, low cost and its good properties such as high carbon content and low ash content. It is envisaged that activated carbon produced from corncob may eventually compete and be a substitute for the expensive activated carbon imported. This effort is aimed at reducing import bills of Nigeria [5].

The aim of this research is therefore to compare the adsorptive efficiency of the produced activated carbon to that of the commercial activated carbon in the adsorption of light alkanes contaminant in hydrogen gas product.

2. MATERIALS AND METHODOLOGY

2.1 Preparation of Activated Carbon from Corncob

2.1.1 Raw material preparation

Corncob was obtained from a farm settlement located at Maraban Rido in Kaduna State,

Nigeria. The white hard piece was washed with distilled water to remove soil and fiber. The corncob was dried under the sun for 24 h and then in the oven (Gallenkamp/PA2345) at 110°C for 3 h in batches. The dried corncob was then crushed in a grinding machine and sieved to a particle size of 600 micrometer (μm) [6]. Fig. 1.0 presents a picture of the raw corncob sample used in this work.



Fig. 1. Picture of raw corncob sample

2.1.2 Carbonisation

The carbonisation of the prepared corncob sample was carried out at the Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria. The procedure was a modification of that reported by Abejirin et al. [7]. In this process, fifteen kilograms (15 kg) of the prepared samples in five batches was placed in a stainless-steel tubular reactor and then into an air tight horizontal tubular furnace (Nabertherm/LH35017) for carbonisation. The carbonisation process was carried out at a temperature of 600°C for 1 h. The process was carried out in an inert atmosphere using nitrogen gas of 99.9% purity, supplied at a rate of 2 mL/min under standard Temperature and Pressure (STP) condition. After adjusting the nitrogen flow, the tubular furnace (Nabertherm/LH35017) was switched on to allow the temperature rise to about 600°C. Once the desired carbonisation temperature of 600°C was attained, the heated samples were held isothermally at the set point for 1 h before cooling down to room temperature under nitrogen flow. The same process was repeated for four other runs following similar procedure.

2.1.3 Chemical activation

The chemical activation of the activated carbon produced from corncob was carried out at Alpha Chemicals Laboratory, Kaduna, Nigeria.

Chemical activation was done using an impregnation ratio of 1:1 on a mass basis (w/v) as against 1:2 as reported by Foo and Lee [8]. To obtain an impregnation mass ratio of 1:1, 10 g of carbonised corncob particles was poured into a beaker containing 10 ml phosphoric acid of 85 wt% purity. The mixture was stirred thoroughly and soaked for 24 h at room temperature before being dried in the oven at 110°C for 8 h. For the washing process, the resulting residue mixture was rinse with 2 M KOH of which 100 ml of KOH was poured into a beaker containing the impregnated activated carbon sample to wash it. The mixture was stirred thoroughly to remove the excess chemicals and then solids were separated using vacuum pump (TEDPELLA/VRP-4) filtration with filter paper. Subsequently, the sample was rinsed sequentially with distilled water until the pH of the wash solution is at 7. The solution pH was measured using a hand held pH meter. The resultant sample was dried at 105°C in the oven for 8 h. This was then followed by characterization of the produced activated carbon.

2.2 Experimental Procedure for The Adsorption Studies

The adsorption experiment for the adsorption of light alkanes contaminant in hydrogen gas product was carried out using the gas adsorption gravimetric technique at constant temperature of 27°C (300 K), masses of adsorbent (AC) between 20 g to 60 g and a pressure between 25 and 125 kPa. Fig. 2 presents the experimental scheme for the adsorption process. Measured for light alkane adsorption. During this experiment, the masses of adsorbent in the column and inlet gas pressure were at a respective interval of 10 g and 25 kPa. Twenty gram (20 g) of the adsorbent was weighed using a digital weighing (AEAdam/PW184) balance and charged into the column. For 20 g of the adsorbent, the inlet pressure of the gas was set at 25 kPa using a pressure gauge (WIKA/Model 910.10). The residence time for the gases inside the column was fixed for 5 minute all through the experiment. After the set time, the outlet stream of the gas was opened and passed through a fume cupboard (FC). After the adsorption process, the adsorbent in the column was then placed in a sealed container and weighed to determine the amount of adsorbate adsorbed by the adsorbent during the adsorption process. The experiment was done in replicate for five runs using the same mass of adsorbent. The procedure was

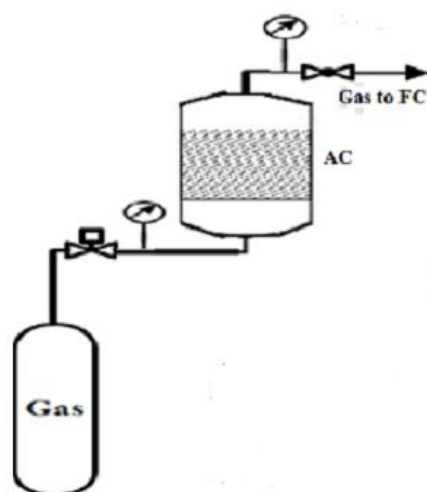


Fig. 2. Experimental scheme for adsorption process

repeated for four values of different masses of adsorbent and inlet pressures respectively as; 30 g and 50 kPa, 40 g and 75 KPa, 50 g and 100 kPa, and 60 g and 125 kPa. For comparison, the procedure was repeated for 20 g of the commercial activated carbon at an inlet pressure of 25 kPa [9].

2.3 Adsorption Isotherms

The conformity of the experimental data obtained from the adsorption process was evaluated with theoretical Langmuir isotherm adsorption model and Freundlich isotherm adsorption model [10].

2.3.1 Langmuir isotherm

The most commonly used model is the Langmuir model. The initial assumptions are that the solid adsorbent has a limited adsorption capacity, all active sites are identical, they can adsorb only one solute molecule (monolayer adsorption), and that there is no interaction between the adsorbed molecules. It means that once a gas molecule occupies a site, no further adsorption can take place on this site. The mathematical equation of Langmuir isotherm is expressed as follows;

$$\frac{P}{n} = \frac{P}{n_s} + \frac{1}{kns} \quad (1)$$

A plot of P/n against P would be a straight line with a slope of $1/n_s$ and intercept at $1/kn_s$. Where n is the number of adsorbed molecules (mol); n_s is the number of surface sites (or, in other words, the number of molecules required to create a monolayer) (mol); k is the adsorption rate (Pa^{-1})

and the pressure, P , of the overlying gas. By measuring P and n the number of surface site and the adsorption rate are calculated.

2.3.2 Freundlich isotherm

The simple empirical Freundlich model is most commonly used. It is considered to be applicable to many cases, particularly in the case of multilayer adsorption interaction between the adsorbate molecules. The Freundlich model equation is given as;

$$\text{Log} \left(\frac{x}{m} \right) = \text{Log}K + \frac{1}{n} \text{Log} P \quad (2)$$

A plot of $\log (x/m)$ against $\log P$ would be a straight line with a slope of $1/n$ and intercept at $\log k$. Where x is the weight of the gas adsorbed by m in gram of the adsorbent at a pressure p , thus x/m represents the amount of gas adsorbed by the adsorbents per gm (unit mass), k and n are constant at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating that the amount of the gas adsorbed does not increase as rapidly as the pressure.

2.4 Characterization

2.4.1 Proximate analysis

The proximate analysis was carried out at the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. The proximate analysis serves as a simple means for determining the behavior of a solid biomass fuel when it is heated. It determines the moisture

content, volatile matter, ash content and fixed carbon of the fuel. The proximate analysis was determined in accordance with the Official Method of Association of Analytical Chemist. The procedures are as follows [11]:

2.4.1.1 Determination of moisture content

The moisture content of the samples was determined by the test protocol given in American standard testing for materials (ASTM) standard D 2867 – 04. In this protocol, a porcelain crucible and its lid were dried in an oven and allowed to cool in a desiccator. About 5 g of the prepared activated carbon was put in the crucible and covered with the lid and the mass recorded. The crucible and its content together with the lid were placed in the oven for 3 h at a temperature of 105°C then the mass of the dried sample was taken again. The moisture content was evaluated using the relation;

$$\text{Moisture Content} = \frac{P-Q}{P-N} \times 100 \quad (3)$$

Where

N= mass of crucible with lid, g

P= mass of crucible with lid plus original sample, g

Q= mass of crucible with lid plus dried sample, g.

2.4.1.2 Determination of ash content

The ash content of the samples was determined by the American standard testing for materials (ASTM) test protocol D 2866 – 94 procedures for activated carbon. In this protocol, 5 g of the sample was put in a crucible, then placed in a muffle furnace and heated at 550°C for 8 h. Then the crucible was taken out from the furnace and put into the desiccator to cool. After cooling the weight was taken to determine the ash content. The ash content of the prepared AC was evaluated using the relation in equation (4);

$$\text{Ash Content} = \frac{T-R}{S-R} \times 100 \quad (4)$$

Where

R = mass of crucible, g

S = mass of crucible plus original sample, g

T = mass of crucible plus ashed sample, g

2.4.1.3 Determination of volatile matter content

The volatile matter of the samples was determined by ASTM D-3175-07 procedure for activated carbon. In this protocol, 5 g of the

activated carbon was weighed in a crucible, then covered with a lid and placed in a muffle furnace at a temperature of 550°C for 10 minute. Then the crucible was taken out from the furnace and put into the desiccator to cool. After cooling the weight was taken to determine the volatile matter content. The volatile matter content of the prepared was evaluated using the relation in equation (5)

$$\text{Volatile Content} = \frac{F-G}{B-G} \times 100 \quad (5)$$

Where;

B = Mass of crucible, lid and sample before heating.

F= Mass of crucible, lid and content after heating

G= Mass of empty crucible and lid

2.4.1.4 Determination of fixed carbon

The percentage fixed carbon content was obtained by subtracting the sum of percentage volatile matter (PVM), percentage ash content (PAC) and percentage moisture content (PMC) from 100.

2.4.2 Ultimate analysis for produced activated carbon

The ultimate analysis was carried out at the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. The main purpose of an elemental analysis is to determine the elemental composition of the solid fuel substance. The main elements of solid biomass fuels include carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O). The procedure is as follows.

2.4.2.1 Determination of nitrogen content

The amount of nitrogen present in the samples was determined by the Kjeldahl's method [12]. In this method [13], 0.5 g of the sample was weighed into a Kjeldahl digestion tube. 20 cm³ of H₂SO₄ and 3 g of a mixed catalyst consisting of CuSO₄, Na₂SO₄ and selenium powder in the ratio of 1:1:1 respectively, was added into the tube. The tube was heated gently until boiling for about 3 h, and then allowed to cool. The cooled mixture was then diluted with 100 cm³ of distilled water in a volumetric flask. To an aliquot (10 cm³) of the digest, 10 cm³ of 40% NaOH solution was added to the connected Kjeldahl distillation apparatus which converts the ammonium salt to ammonia

and heated to boiling. The amount of ammonia present in the sample was determined by backward titration. The distillate was condensed into the conical flask containing 10 cm³ of 2% boric acid. The ammonia reacts with the acid and the remainder of the acid is then titrated with 25 cm³ of Na₂CO₃ by way of a methyl orange pH indicator.

2.4.2.2 Determination of sulphur content

The percentage of sulphur content present in the samples was determined by the Carius method. In this method, 5 g of the sample was placed in a porcelain crucible and heated in a Carius tube with 0.5 g of Na₂O₂ (Sodium peroxide) at 400°C. The sulphur present in the compound was oxidized to H₂SO₄. By adding 5 cm³ of BaCl₂, BaSO₄ was precipitated. The precipitate was filtered, washed, dried and weighed.

2.4.2.3 Determination of carbon and hydrogen content

The amount of carbon and hydrogen present in the samples was determined by the Liebig method [12]. In this method, 3 g of the sample was weighed into a porcelain boat. The porcelain was then placed in the combustion tube and was heated at 400°C. Pure dry oxygen was slowly passed through the tube. Combustion was completed in 3 h. This results in the formation of CO₂ and H₂O from the carbon and hydrogen present in the compound. They were absorbed in the adsorption tube at the end. The adsorption tube was removed and weighed to determine the amount of CO₂ and H₂O formed in the reaction.

2.4.2.4 Determination of oxygen content

The percentage oxygen content was obtained by subtracting the sum of percentage carbon content (PCC), percentage sulphur content (PSC), percentage hydrogen content (PHC) and percentage nitrogen content (PNC) from 100.

2.4.3 Physical characteristics

The physical characteristics were determined from the BET analysis of the produced activated carbon and the commercial activated carbon at the Centre for Genetic Engineering and Biotechnology, Federal University of Technology, Minna, Niger State. In this analysis, Quantachrome Nova 4200e BET machine was used to determine the specific surface area and pore volume of the particles using the N₂ adsorption-desorption technique.

2.4.4 Chemical characteristics

The chemical characteristics were determined from the FTIR spectroscopic analysis of the produced activated carbon and the commercial activated carbon. This was used to identify the main functional groups on the activated carbon surface that may be involved in the adsorption of light alkane contaminant from hydrogen gas. For this purpose, the samples were thoroughly mixed with dried spectroscopic KBr in a 1:3 ratios, and immediately analyzed using a Shimadzu FTIR-8400S FTIR spectrophotometer equipped with an EasiDiff diffuse reflectance hemisphere accessory (Pike Technologies). FTIR spectra were obtained using 10 scans over the range of 4000–400 cm⁻¹ with a resolution of 2.0 cm⁻¹. The Kubelka-Munk function was calculated from the diffuse reflectance data using the OMNIC software (Thermo Fischer Scientific).

3. RESULTS AND DISCUSSION

3.1 Comparison of Proximate and Ultimate Analysis

The comparison of the proximate analysis of the raw corncob, the produced activated carbon and the commercial activated carbon is presented in Table 1.

Table 1 shows that the raw corncob and the produced activated carbon has relatively close values of percentage moisture content of 7.464% and 7.8% respectively while the commercial activated carbon has the lowest with 2.3%. The moisture content value obtained in this research is also lower than that observed by Ekpete et al. [14] as 19.5% and Ekpete and Horsfall [15] as 10.33% for raw corncob and activated carbon produced from corncob, respectively. The comparatively low moisture contents of these biomasses indicates that they have a higher adsorption tendency when used as adsorbent for adsorption application.

The ash contents of the biomasses varied from 1.134% for raw corncob to 3.68% for the produced corncob activated carbon while the commercial activated carbon was 2.25%. This falls below values obtained for rice husk briquette (16.10%) and melon shell (19.57%) and higher than those of well-known biomass fuel like grape pomace (2.7%) [13]. It was opined that ash values that make a carbon suitable for adsorption should be within a range of 1 – 20%, thus making both activated carbon a better choice for

adsorption application if the ash value is to be considered.

The raw corncob, the produced activated carbon and the commercial activated carbon recorded a volatile content of 76.515%, 25.34% and 27.26% respectively. The fall in values for the produced activated carbon and the commercial activated carbon as expected is as a result of the high volatile content expelled in the raw corncob sample. This will allow for the creation and availability of pore spaces available for efficient adsorption of adsorbate during the adsorption process.

Fixed carbon is the percentage of carbon available for char combustion is a measure of the solid combustible material in solid fuel after the expulsion of volatile matter; its content is used as an estimate of the amount of carbon that will be obtained on carbonization. For the biomasses, it was found to be 14.887, 63.18 and 68.19% for raw corncob, produced activated carbon and commercial activated carbon respectively. The increased fixed carbon values indicate a high yield of carbon that is available for the adsorption of adsorbate during the adsorption process.

The comparative results for the ultimate analysis of the raw corncob, the produced corncob activated carbon and the commercial activated carbon is presented in Table 2.

Table 2 showed that the percentage of carbon in the raw corncob, the produced activated carbon and the commercial activated carbon are 56.29%, 69.62% and 81.24% respectively. The values obtained are lower than the values for coal (82.8%) as reported by Jimoh et al. [16]. However, the values obtained in this study are higher than some other biomasses in other literatures: rice husk briquette (45.2%), groundnut shell (14.99%), corncob (19.73%) and melon shell (21.61%). A good biomass should have high amount of carbon. The high carbon content of the produced activated carbon may be

responsible for its ability to overcome sintering and attrition during the adsorption process thereby preventing wash off.

The sulphur contents of the biomass varied between 1.74% for the raw corncob, 0.18% for produced activated carbon and 0.05% for commercial activated carbon as shown in Table 4. The Sulphur content was observed to fall below 2% in all the samples, which would mitigate the emission of sulphur dioxide (SO₂) into the atmosphere causing acid rain.

From the analysis, nitrogen content is less than 2% for the raw corncob, produced activated carbon and commercial activated carbon with 1.77%, 1.34% and 1.12% respectively. These results are comparable to results obtained for conventional fuels like coal (2.2%) and non-conventional fuels like agricultural wastes such as yam peels (2.67%) [13] and mango peels (2.40%) [17]. The low sulphur content is an indication that Sulphur's interaction with the adsorbate during adsorption process is limited. The amount of nitrogen for the raw corncob is a higher due to the likely effect of fertilizer usage on the farmlands where the samples were collected. The low elemental content values of hydrogen (6.44%, 6.11% and 2.12%) and oxygen (33.76%, 22.75% and 15.47%) for the raw corncob, the produced corncob activated carbon and the commercial activated carbon respectively, may be attributed to the high volatile matter (76.515%, 25.34% and 27.26%) obtained.

3.2 Physical Characteristics of the Produced Activated Carbon and Commercial Activated Carbon

The comparative physical characteristics (such as surface area, apparent density, pore volume, pore size) of the produced corncob activated carbon and the commercial activated carbon are presented in Table 3.

Table 1. Comparison of the proximate analysis of the raw corncob, the produced activated carbon and the commercial activated carbon

Parameters	Raw corncob (%)	Produced activated carbon (%)	Commercial activated carbon (%)
Volatile matter	76.515	25.34	27.26
Fixed carbon	14.887	63.18	68.19
Ash content	1.134	3.68	2.25
Moisture content	7.464	7.8	2.3

Table 2. Comparative results for ultimate analysis of the raw corncob, the produced activated carbon and the commercial activated carbon

Parameters	Raw corncob (%)	Produced activated carbon (%)	Commercial activated carbon (%)
Carbon	56.29	69.62	81.24
Hydrogen	6.44	6.11	2.12
Nitrogen	1.77	1.34	1.12
Sulphur	1.74	0.18	0.05
Oxygen	33.76	22.75	15.47

As presented in Table 3, the pore size of the produced activated carbon and the commercial activated carbon was 2.976 nm and 6.250 nm, respectively. According to the IUPAC classification, pores are classified as macropores for pore widths greater than 50 nm, mesopores for the pore range 2 to 50 nm and micropores for the pores in the range less than 2 nm. This implies that the produced activated carbon and commercial activated carbon in this study has more mesopores which falls within the mesopores size range of 2 nm – 50 nm [18].

The BET specific surface area and pore volume of the produced activated carbon obtained as compared to the commercial activated carbon are 1237 m²/g and 0.1162 cm³/g; and 2048 m²/g and 0.1959 cm³/g; respectively. The specific surface area obtained in this study is higher than that presented from other related work using corncob as carbon source material as reported by Sun and Webler [19] with specific surface area of 1069 m²/g and pore volume of 0.11 cm³/g and by with specific surface area of 700 m²/g and pore volume of 0.011 cm³/g. The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. the larger the surface area of the adsorbent, the greater is the extent of adsorption. This indicates that the higher Surface area of the activated carbon obtained in this work would enhance a greater adsorption. The Multi-Point BET plot of the N₂ adsorption-desorption isotherm for the commercial activated carbon and the produced activated carbon is presented in the Fig. 3(a) and Fig. 3(b) respectively.

The apparent densities of the produced activated carbon and the commercial activated carbon are 0.28 g/cm³ and 0.36 g/cm³ respectively. This shows its ability to withstand attrition during adsorption processes. The activated carbon yield obtained was 23.5% is within the literature values reported [13].

3.3 Chemical Characteristics of the Produced Activated Carbon and Commercial Activated Carbon

The chemical characteristics of the produced activated carbon and the commercial activated carbon was determined from the FTIR spectra analysis. Fig. 4 presents the FTIR spectra for the commercial activated carbon and the produced activated carbon. Table 4 presents the peak positions of the major absorption bands. The results from Table 4 indicate that only minor differences between the produced corncob activated carbon and commercial activated carbon samples could be established. However, similarities in band gaps and wavelength between the produced corncob activated carbon and commercial activated carbon samples indicate that chemical transformation has taken place for the former during carbonisation and chemical treatment. The adsorption bands at 3333.10 cm⁻¹ and 3271.38 cm⁻¹, 3510.56 cm⁻¹ and 3471.98 cm⁻¹ are associated with the SP² and SP hybrid orbitals, and SP³ hybrid orbitals respectively. The band at 2785.30 cm⁻¹ and 2793.02 cm⁻¹ which is assigned to the asymmetric C–H band representing the alkyl groups such as methyl and methylene groups, is observed in all the carbons with different intensity. While bands of 2337.80 cm⁻¹, 2214.35 cm⁻¹ and 2121.77 cm⁻¹ are associated with the stretched vibration of the C≡C and C≡N in alkynes and nitriles, respectively. The band around 1550.82 cm⁻¹ and 1527.67 cm⁻¹ are attributed to CO stretching vibrations of carbonyl groups (carboxylic OH), is observed in all the carbons with different intensity. The presence of these functional groups and their enhancement in adsorption abilities of activated carbons agree with the findings of Auta and Hameed [20], and Alkali [21]. The FTIR spectroscopy result indicates that the produced activated carbons are rich in surface functional groups.

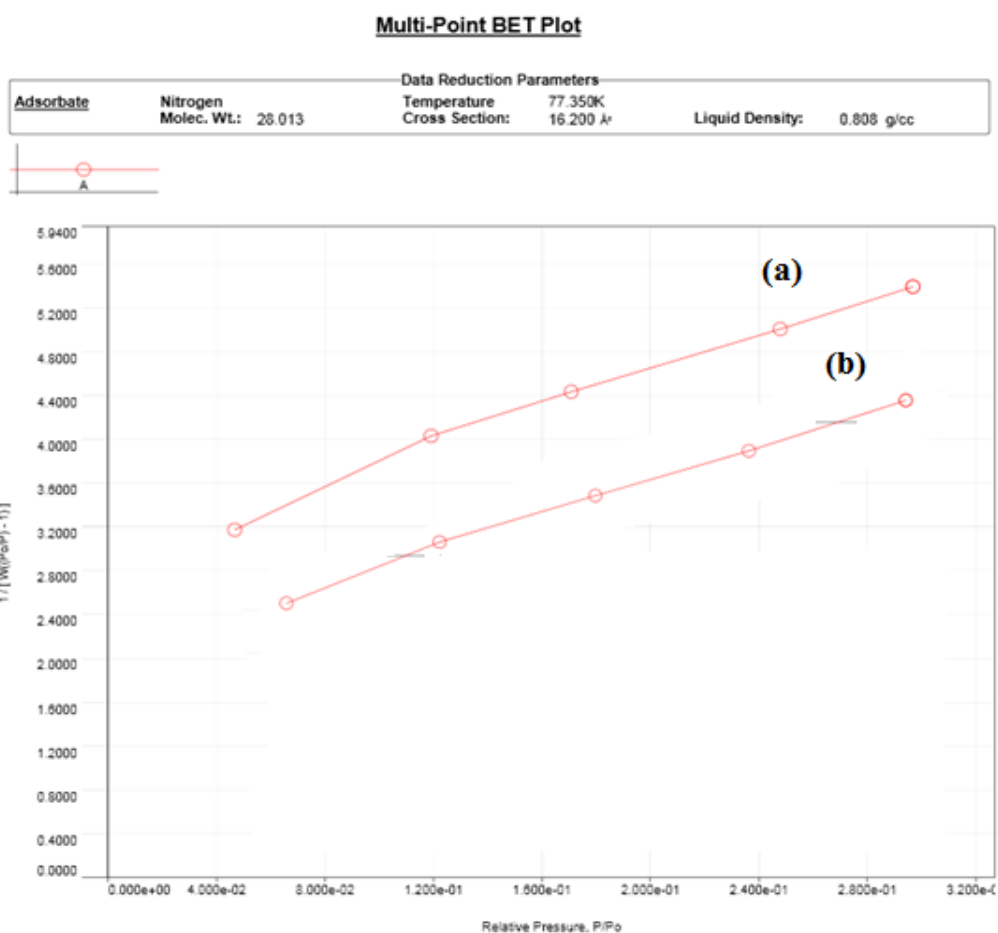


Fig. 3. Multi-point BET plot for N₂ adsorption-desorption isotherm for (a) the commercial activated carbon and (b) the produced activated carbon

Table 3. Comparative physical characteristics of produced activated carbon and the commercial activated carbon

Parameters	Produced activated carbon	Commercial activated carbon
BET specific surface area (m ² /g)	1237	2048
Micropore volume (cm ³ /g)	0.1162	0.1959
Average pore width (nm)	2.976	6.250
Apparent density (g/cm ³)	0.28	0.36
Carbon yield (%)	23.5	-

Table 4. The peak positions of the major absorption bands for the produced activated carbon and the commercial activated carbon

IR band frequency [cm ⁻¹]		Functional group assignment
Produced activated carbon	Commercial activated carbon	
1550.82	1527.67	CO stretching vibrations of carbonyl groups
2214.35	2121.77	Carboxylic OH
2337.8	2337.8	C≡N stretch
2785.3	2793.02	Alkynl C≡C stretch
3333.1	3271.98	Asymmetrical stretching of aliphatic chain C-H
3510.56	3471.98	SP ² and SP hybrid carbon SP ³ hybrid carbon

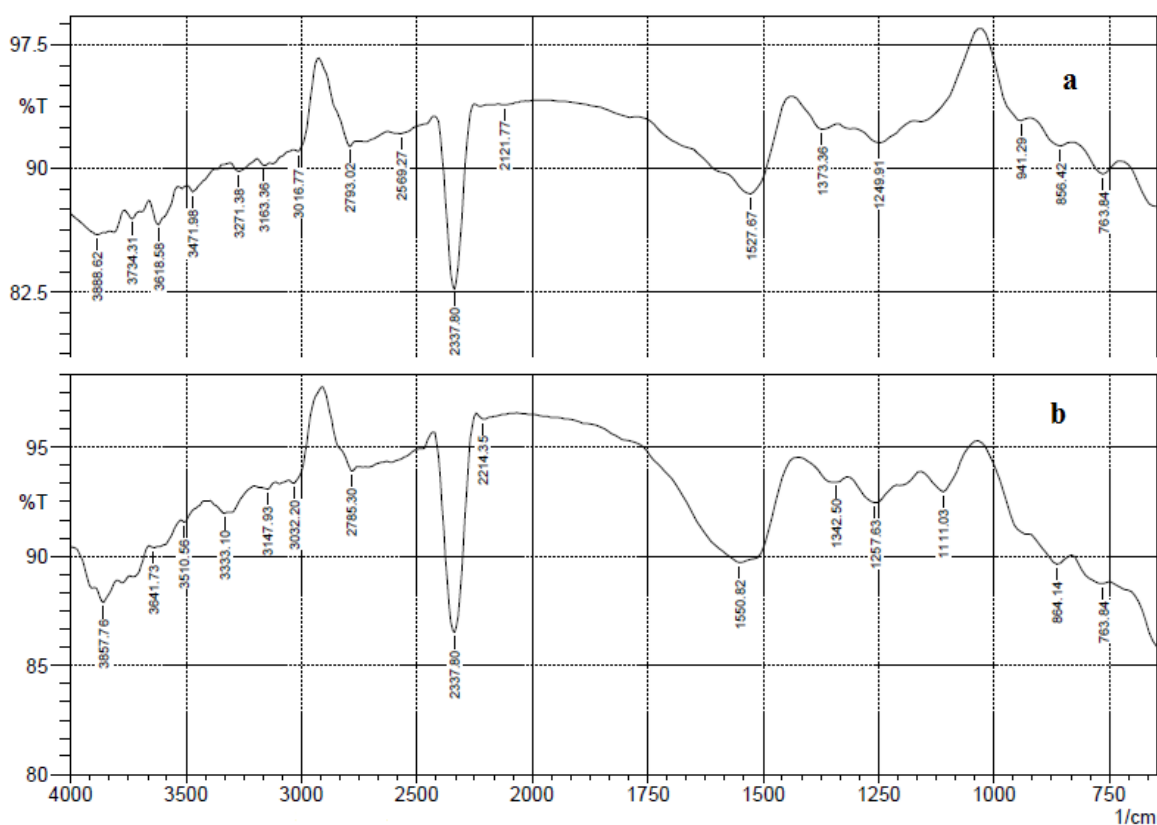


Fig. 4. FTIR spectra of (a) commercial activated carbon and (b) produced activated carbon

3.4 Isotherm Adsorption Study

Isotherms were measured for light alkane adsorption at constant temperature of 27°C (300 K) and a pressure between 25 and 125 kPa. The experimental data were described using the Langmuir equation and Freundlich equation.

3.4.1 Langmuir isotherm

Parameters for the Langmuir fits are shown in Table 5.

Where,

n = number of mole of the adsorbed molecules (mol)

P = the pressure of the overlying gas (kPa)

m = mass of the adsorbent (gram) before adsorption

M = mean mass of the adsorbent (gram) after adsorption

x = the weight of the gas adsorbed (gram)

$x = M - m$

Std = standard deviation of the weight of gas adsorbed

The Langmuir fits are shown in fig. 5. The constants that characterize the Langmuir model were determined by nonlinear regression analysis. The graph depicts Monolayer adsorption and fit appropriately to Type I Adsorption Isotherm. The characteristic Type1 Isotherms indicates that the activated carbon is mainly microporous materials.

Table 5. Parameters for Langmuir equation

m(g)	M(g)	x(g)	Std	n(mole)	n(mmole)	P(kPa)	P/n
20	20.21	0.21	0.0122	0.013125	13.125	25	1.904761905
30	30.26	0.26	0.0158	0.01625	16.25	50	3.076923077
40	40.32	0.32	0.0136	0.02	20	75	3.75
50	50.38	0.38	0.0141	0.02375	23.75	100	4.210526316
60	60.43	0.43	0.0126	0.026875	26.875	125	4.651162791

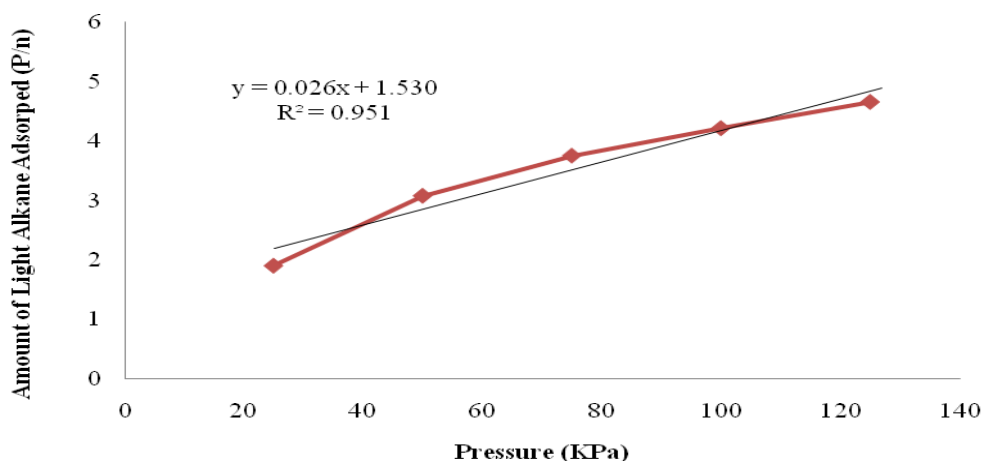


Fig. 5. Langmuir adsorption isotherm

3.4.2 Freundlich isotherm

Parameters for the Freundlich fits are shown in Table 6.

Where,

- P = the pressure of the overlying gas (KPa)
- m = mass of the adsorbent (gram) before adsorption
- M = mean mass of the adsorbent (gram) after adsorption
- x = the weight of the gas adsorbed (gram)
- x = M – m

x/m = amount of gas adsorbed by the adsorbents per gram (unit mass)

k = adsorption rate

n = number of surface sites

Std = standard deviation of the weight of gas adsorbed

A plot of x/m against P is shown in Fig. 6. The constants that characterize the Freundlich model were determined by nonlinear regression analysis. The adsorptive capacity k and n are obtained from the exponential equation on the plot.

Table 6. Parameters for Freundlich equation

m(g)	M(g)	x (g)	Std	m(g)	P(kPa)	x/m
20	20.21	0.21	0.0122	20	25	0.0105
30	30.26	0.26	0.0158	30	50	0.008666667
40	40.32	0.32	0.0136	40	75	0.008
50	50.38	0.38	0.0141	50	100	0.0076
60	60.43	0.43	0.0126	60	125	0.007166667

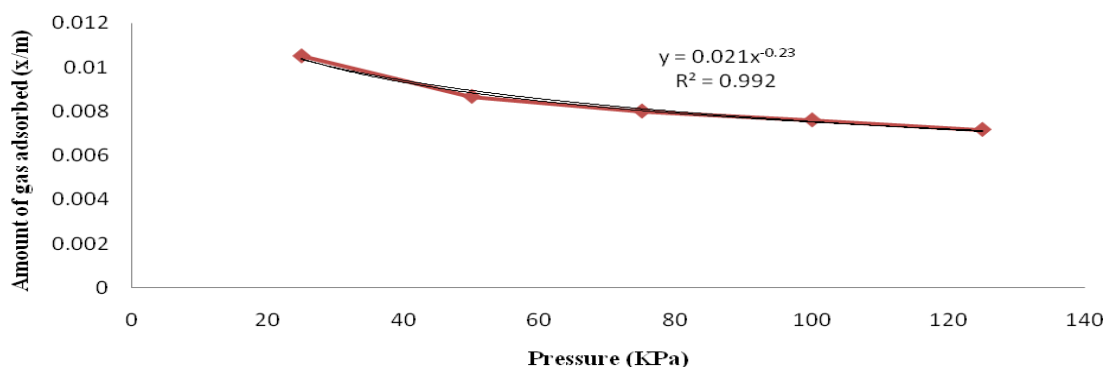


Fig. 6. Freundlich adsorption isotherm

Table 7. Adsorptive capacity of Langmuir and Freundlich isotherm at 27°C

Models	R ² Value	Experimental n values	Adsorptive capacity, k(Pa ⁻¹)
Langmuir Isotherm	0.951	38	0.016
Freundlich Isotherm	0.992	-4	0.021

Table 8. Adsorptive efficiency of produced activated carbon and commercial activated carbon

S/N	wt. of adsorbent (g)	Mass of adsorbate adsorbed (g)	Std	Percentage Adsorption efficiency (wt%)
1	20	0.21	0.0122	1.05
2	30	0.26	0.0158	0.87
3	40	0.32	0.0136	0.8
4	50	0.38	0.0141	0.76
5	60	0.43	0.0126	0.72
6*	20	0.71	0.0018	3.55

* Commercial activated carbon adsorbent used at the Kaduna refinery (Nigeria)

3.5 Adsorptive Capacity from Adsorption Isotherm Model

Table 7 gives the experimental adsorptive capacity of the Langmuir adsorption Isotherm model and the Freundlich adsorption Isotherm model.

It can be seen from Table 7 that the R^2 values exceed 0.9 for all isotherm models, suggesting that all models closely fitted the experimental results. An adsorption isotherm is characterized by certain coefficients, the values of which express the surface properties and affinity of the adsorbent and can also be used to find the exact adsorptive and uptake capacity [12]. Based on the coefficients of the Langmuir isotherm model, ns values, for light alkanes adsorption onto corncob activated carbon at 27°C, is greater than 1 ($ns=38$). The plot shows a resemblance to a typical type I adsorption isotherm type model and an adsorptive and an uptake capacity of 0.016 Pa⁻¹ all indicates a favorable adsorption in figure 1. The results obtained with the Freundlich isotherm model showed that the value of $1/n$ ($n = -4$) decreased with the increasing pressure. From Fig. 2, the n value in the Freundlich adsorption isotherm model is less than 1 with no resemblance to any of the five different types of adsorption isotherm type models indicating that the adsorption of light alkane onto the prepared corncob activated carbon does not fit its model despite having a higher adsorptive and uptake capacity of 0.021 Pa⁻¹. Therefore, the Langmuir adsorption isotherm model showed best fit for the experimental data indicating the formation of a monolayer adsorbate on the outer surface of the adsorbent, [22] with an adsorption and uptake capacity of 0.016 Pa⁻¹.

3.6 Comparison of Adsorptive Efficiency for Produced Activated Carbon and Commercial Activated Carbon

The percentage adsorptive efficiencies in wt% of the various masses of adsorbents are illustrated in Table 8. From Table 8 it can be observed that, the produced activated carbon had the highest adsorptive efficiency at 20 g by adsorbing 1.05%wt of the light alkanes sample. Table 8 also presents the adsorptive efficiency of the commercial activated carbon used by the Kaduna Refinery with an uptake capacity of 3.55%wt at 20 g of adsorbent used. The adsorptive efficiency of the commercial activated carbon is higher than that of produced adsorbent from corncobs activated carbon. This is in agreement with other studies. In that the extent of adsorption depends directly upon the surface area of the adsorbent, i.e. the larger the surface area of the adsorbent, the greater is the extent of adsorption. A higher surface area of 2048 m²/g obtained for the commercial activated carbon compared to a surface area of 1237 m²/g obtained for the produced activated carbon may be attributed to this difference [23].

4. CONCLUSION

The proximate analysis of the produced activated carbon compared to the commercial activated carbon has a fixed carbon content of 63.18% and 69.62%, respectively. The ultimate analysis of the produced activated carbon compared to the commercial activated carbon has an elemental carbon content of 68.19% and 81.24%, respectively. The physical characteristics of the produced activated carbon compared to the

commercial activated carbon has a specific surface area of 1237 m²/g and 2048 m²/g and a pore volume of 0.1162 cm³/g and 0.1959 cm³/g, respectively. The chemical characteristics in the FTIR spectra results of the produced activated carbon compared to the commercial activated carbon showed similar band gap at 2337.80 cm⁻¹ with an alkynyl C≡C stretch functional group and a vibration type of carbonyl group (carboxylic OH) at 1550.82 cm⁻¹. Experimental data verified using Langmuir isotherm and Freundlich isotherm adsorption models showed best fit for Langmuir adsorption isotherm model indicating the formation of a monolayer adsorbate on the outer surface of the adsorbent with an adsorptive and uptake capacity of 0.016 Pa⁻¹. The adsorptive efficiency of the produced activated carbon compared to the commercial activated carbon was 1.05wt% and 3.55wt%, respectively. Therefore, based on the results obtained, the produced activated carbon may not completely substitute the commercial activated carbon rather it can be used as a potential blend thereby reducing quantity and cost.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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