Original Research Article

PREPARATION AND CHARACTERISATION OF MODIFIED BIOCHAR FROM VITEX DONIANA (BLACK PLUM) SEEDS USING CHEMICAL AND THERMAL TREATMENTS

ABSTRACT

The goal of this research was to produce and characterize modified biochar of Vitex doniana (Black plum) seeds using chemical and thermal treatments. To achieve this, the vitex seed was carbonized for 2 hours at 400°C in a pyrolysis reactor. The resulting char was then impregnated for 24 hours with Phosphoric Acid (H_3PO_4) and potassium hydroxide (KOH) as chemical activating agents before being thermally activated at 400°C, 500°C, 600°C, and 700°C respectively. The purpose of the characterization was to see how the activators and activation temperature affected the adsorbents generated. The quality of absorbents produced was affected by the treatment of char with chemical agents and the activation temperature, according to the results. The samples had distinct functional groups on the surface, according to FTIR analysis, and SEM analysis via microscopy revealed the presence of pores on the surface. Iodine absorption testing reveals that materials activated with KOH had a higher absorption value, peaking at 950mg/g for KOH treated and 600°C activation temperature. The pore diameters and pore volume of KOH samples were determined using BET analysis. The results demonstrate that KOH activated at 600°C has larger pores and a higher pore volume, implying that KOH at 600°C has a higher adsorption capacity. The char sample was also subjected to TGA analysis in order to better understand its behavior in temperature settings.

Keywords: Absorbent, Activated carbon, Biochar, Characterisation, Vitex Doniana

1. INTRODUCTION

Due to the utilization of non-renewable precursors and generally expensive starting materials, such as coal, which are unsuitable for pollution control measures, commercial activated carbons are typically expensive [1]. When there are abundant industrial and agricultural wastes and byproducts that can be modified to produce activated carbon to meet local demand and even export it, most developing countries import it at exorbitant prices [2]. A variety of organic compounds that are carbon-rich can be used to produce absorbents. Researchers have produced activated carbon from cheap and renewable precursors, the majority of which comes from agricultural waste and industrial by-products such as groundnut shell [2], rice husk [3, 4], baggase [4], sawdust [5,6], coconut shell [7], acorn shell [8], empty palm fruit bunch [9], bamboo stem [10], physic nut waste [11], chickpea [12], pruning mulberry shoot

[13], plant seeds [14,15], and tamarind wood [16]. The interesting pore structure of activated carbon results in a very large surface area with which materials can be stored or captured. A special absorbent coveted for its very porous structure that makes it possible for it to efficiently capture and store materials is activated carbon, also known as activated charcoal. In applications that call for the removal of pollutants or undesired materials, such as purification of water and air, environmental remediation, and precious metal recovery, activated carbons are frequently utilized as absorbents in a variety of sectors.

The procedure for making activated carbon is basically by physical or chemical activation depending on the source materials. Usually, the process of carbonizing and activating the initial carbonaceous material provides the basis for the utilization of carbon-rich material [17]. A carbonaceous material is carbonized to remove the majority of the volatile content, and then the resulting char is activated in the presence of activating chemicals, such as CO_2 [18, 19], steam [20, 21], air [22, 23], one or more of these agents combined [24], as a result, the carbon surface releases carbon oxides [25]. The transportation of gas agents to the sample's surface, diffusion through the pores, adsorption on the pore surface, reactivity with the carbon component of these agents, desorption of the resulting products, and their diffusion further into atmosphere are the heterogeneous processes that make this process complex [26]. The advantage of making activated carbon by chemical means is that carbonization and activation can both be accomplished in a single process. The precursor or char material is activated at a high temperature after being combined with the chemical agent. In this process, the substance acts as both oxidizing and dehydrating chemical [27]. Some common chemicals used are KOH [28, 29, 30], K_2CO_3 [31], $ZnCl_2$ [32, 16], H_3PO_4 [33, 31].

Vitex doniana also known as black plum is a native tree of Afrotropics and the plant is commonly available in this region of the world. According to *Martin, et. al.* [34] the black plum fruit can be eaten raw, cooked or candied; the jam from it is of good quality and spread more effectively. Also, you can use the pulp's syrup as sweetener; an alternative to artificial and other sugar sweetener. Plant Resources of Tropical Africa (PROTA) plants data resources suggested that Vitex doniana seeds can be roasted and utilized to make a beverage similar to coffee, the dried seeds yield oil that can be used to produce skin cream, resin, and paint because it has high iodine as well as low saponification properties. However, much attention has not been paid to the beneficiation of the seeds; hence seeds are left as nuisance to farmland or environment of plant presence. Also, despite extensive scientific research on activated carbon production from agricultural resources, there is little or no information on its production from the 'Vitex doniana seeds'.

Therefore, this research was aimed at the production and characterisation of activated carbon from biochar of Vitex doniana (Black Plum) seeds using chemical and thermal treatments. Phosphoric Acid (H_3PO_4) and Potassium hydroxide (KOH) were used as chemical activating agents. The successful production of Activated carbon from Vitex doniana seeds will create a means of ultilisation of the seeds and cheaper source of raw material for production of activated carbon; subsequently, contributes to the agricultural waste management for environment sustainability.

2. MATERIAL AND METHODS

Fresh fruits of vitex doniana were collected from Auchi Federal Polytechnic, Auchi in Etsako West local government area of Edo state. The fruits were then soaked for two weeks before it was decorticated. Seeds collected were then washed using deionized water to remove contaminants and allowed to dry for about three weeks to reduce the moisture content in the seeds. Potassium hydroxide (KOH) and Phosphoric acid (H_3PO_4) were procured for activating of the carbonized material.

2.1 Production of Biochar

400g of dry vitex doniana seeds was weighed using a weighing balance; it was then crushed using a pestle. The crushed sample was then transferred into crucibles; then charged into an electric furnace and made to undergo pyrolysis at a temperature of 400°C for 2hours. After cooling, the biochar was weighed and size reduction was carried out on it. Then screened through a >1mm mesh sieve to obtain uniform sample sizes. The final product was then weighed and kept in an air tight container.

2.2 Preparation of Activated Carbon Samples

80g of charred product was carefully weighed and placed in two separate beakers. The samples were then impregnated in a 1:1 weight ratio with 1M of solution of Phosphoric acid (H_3PO_4) and Potassium Hydroxide (KOH) respectively. The impregnated sample was then oven dried at 105°C for 8hr. Final activation of samples was done at a temperature range of 400, 500, 600 and 700°C. 20g of each impregnated sample was placed into the electric furnace at varying temperature of 400, 500, 600 and 700°C and heated for 2hours in an air inert atmosphere. Then samples was allowed to cool and then washed with distilled water until it was neutrality was achieved. The washed samples was then oven dried for 8hr and kept in an air tight container

2.3 Characterization of samples

To ascertain the nature and quality of the produced biochar and its modification the following analysis were carried out on them.

2.3.1 Determination of Percentage Carbon Yield, Bulk Density, Ash content, Percentage Volatility and Moisture Content

To determine the percentage carbon yield, 20g of the crushed Vitex seeds was carbonised in an electric furnace at 400°C in an air-inert condition for 2hr. The furnace was left to cool and the crucible was brought out and further allowed to cool. The carbon residue remaining was weighed and recorded. The procedure was further repeated 2 more times. Percentage fixed carbon was calculated as; $\%Carbon\ yeild = \frac{Average\ charr\ mass}{Mass\ of\ dried\ seeds} \times 100$.

The bulk density of the sample was done using tapped density method for powdered substance. 0.2g of samples was weighed accurately using a weighing balance and placed inside a 10ml measuring cylinder. The cylinder was tapped for 250 times to break up all possible agglomeration and ensure particles are well compacted. The final volume occupied by the samples was recorded from the graduated measuring cylinder. The final bulk density was then calculated as; $Bulk\ density = \frac{Mass\ of\ sample}{Volume\ occupied}$.

The ash content was determined according to approach described by *Ekpete et. al.* [35] just slightly modified. Ashes were measured in crucibles that had been preheated to around 100°C, cooled using a desiccator, and then filled with 2.0 g of each sample and weighed again. After heating the crucibles with the samples to 500°C for 1 hour 30 minutes, they were taken out of the furnace, allowed to cool to ambient temperature in a desiccator, and then weighed again. The equation was used to determine the ash content;

$Ash\% = \frac{Ash\ weight}{Oven\ dry\ weight} \times 100$.

For the purpose of determining the amount of volatile matter, 1.0g of sample was heated for 10 minutes at 500°C. The weight of volatile components is the difference between the samples' initial and final weights after heating. The equation was used to compute the volatile substance; $Volatile\ Matter\ \% = \frac{weight\ of\ volatile\ components}{Oven\ dry\ weight} \times 100$.

The materials' moisture content was determined using the thermal drying method. A sample of one gram was weighed and put into evaporating dishes that were clean, dried, and weighed. The dishes were put in an oven set at 105°C to achieve a steady weight. The moisture content is represented by the difference between the carbon's initial and final masses. The formula used to calculate the percentage moisture content (%) is; $Moisture\ content\ \% = \frac{loss\ in\ weight\ upon\ drying}{Initial\ weight} \times 100$.

2.3.2 Iodine Value (IV) Determination

0.2g of each sample's activated carbon was weighed into a beaker, to which 25ml of a standard (0.1M) iodine solution was then added. 20 ml of the clear filtrate was titrated with a standard (0.5M) sodium thiosulphate solution till a persistent pale yellow hue after the combination had been vigorously stirred for 10 minutes. Titration was continued after the addition of 5 ml of the freshly made starch indicator solution, and the process was repeated twice more until a clear solution was obtained. To serve as a blank titration, the titration was also performed with a 25ml quantity of the standard iodine (without activated carbon from the precursor). The following relationship was used to compute the iodine absorption number (IN); $IV = \frac{Wt\ x\ Ms(Vb - Vs)}{2Ma} \times 100$. Where Wt is the iodine's molecular weight, Ms is the thiosulphate solution's molarity (mol/dm^3), Vs is the amount of thiosulphate (in cubic centimeters) used to titrate an aliquot of activated carbon, Vb is the amount of thiosulphate (in cubic centimeters) used to titrate a blank sample, and Ma is the amount of sample (g).

2.3.3 SEM, BET, FTIR and TGA/DTA Analysis

Surface morphology analysis was done for the biochar, and the chemically activated samples with KOH that was thermally activated at temperatures of 500, 600 and 700°C. Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy was used for the study (EDX analysis). Additionally, the internal surface area of activated carbon samples was analyzed using Micromeritics Tristar 3000 V4.02 for BET (Brunauer-Emmett-Teller) surface area method.

The Fourier Transform Infrared Spectrophotometer (FTIR) analysis was conducted to detect the changes in the functional groups of the samples. Using an infrared spectrometer Varian 660 Mid IR Dual MCT/DTGS Bundle (FTIR spectrometer having ATR) with a detector at 4 cm-1 resolution and 200 scans per sample, the spectra were captured in the frequency range of 4000 cm-1 to 500 cm-1. The relationship between wave number and absorption in the refractogram produced by FTIR spectroscopy was noted. Software called IR solution was used to obtain the spectrum.

The thermodynamic parameters related to the thermal processes were assessed after thermogravimetric measurements of prepared biochar were completed. To investigate the sample's thermal stability and offer a general plan for thermal decomposition, TGA and DTA were used. The thermogravimetric analysis used in this laboratory is a Q50 TGA from Shimadzu instruments (Shimadzu TGA - Q50 thermobalance) thermal analyzer.

3. RESULTS AND DISCUSSION

The amount of biochar obtained from the first run was 5.0g, 5.2g and 5.2g respectively for the second and three runs. Average biochar yield is 5.13g. The percentage fixed carbon was 25.65% for vitex doniana seeds. This can be attributed to the fact that the vitex seeds contain a lot of volatile components and mineral matters.

From Fig.1, the bulk density for the samples activated with H_3PO_4 is uniform despite change in activating temperatures up to 700°C. While for those of the samples activated with KOH was the same for the samples activated at 400°C and 500°C with a decrease to 500kg/m^3 at 600 and 700°C.

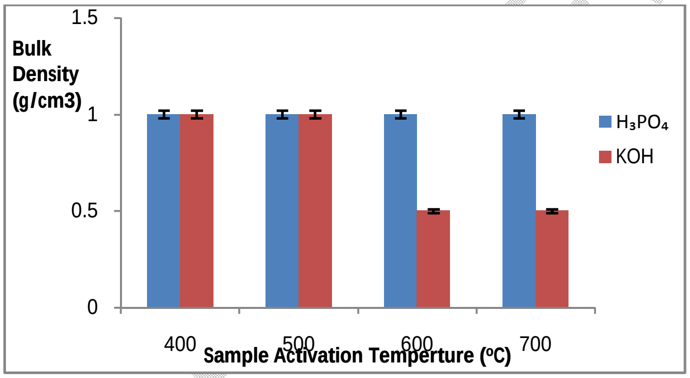

Fig. 1. Chart of Bulk Density of activated samples

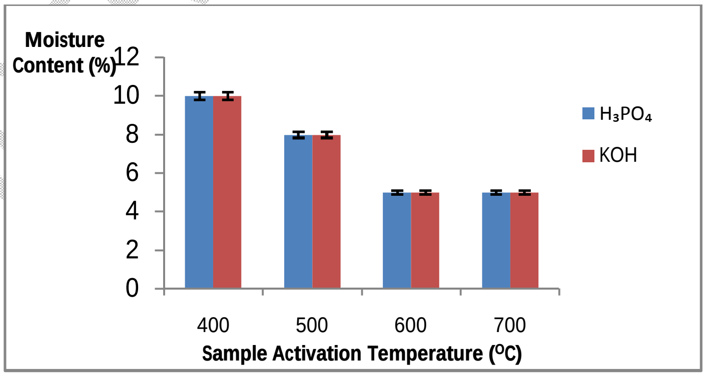

Fig. 2. Chart of Moisture Content of activated samples

The moisture content result as presented in Fig.2, both chemical activated samples was 10% moisture content which was the same at activation temperatures of 400 and 500 °C. However, as the temperature increases to 600 and 700°C, the moisture content reduces 5% for both chemical activated samples. This shows that moisture content reduces with increase in activation temperature despite the activating agents. Ash content and volatile matter play a significant impact in influencing the pores' quality in the manufactured activated carbon. Excessive ash can cause the pores in the activated carbon to get clogged, reducing the activated carbon's surface area [36]. The chart in Fig.3 shows the results obtained for ash content (%) and volatility (%) for the char and the chemically activated samples. The ash content of the sample was lower when compared to that of the char and the activated samples. For the activated samples there was a decrease in ash content with increase in activation temperature; from 12% in Char to as low as 2.5% and 3.5% for sample treated with H_3PO_4 at 700^0C and KOH at 700^0C respectively. Samples activated with KOH have higher ash content compared to those activated with H_3PO_4. The inorganic substance initiates the development of the metal oxide in the furnace during the pyrolysis process as seen in the EDX results in Fig.5. Also, the results as presented in Fig.3 show the percentage of volatility of the samples reduced with increase in activation temperature. The percentage of volatile matter reduce from 24% as seen in the char to 7% and 8% for sample treated with H_3PO_4 at 700^0C and KOH at 700^0C respectively. The level of ash content and volatility of the samples activated with KOH was relatively higher when compared with those activated with H_3PO_4.

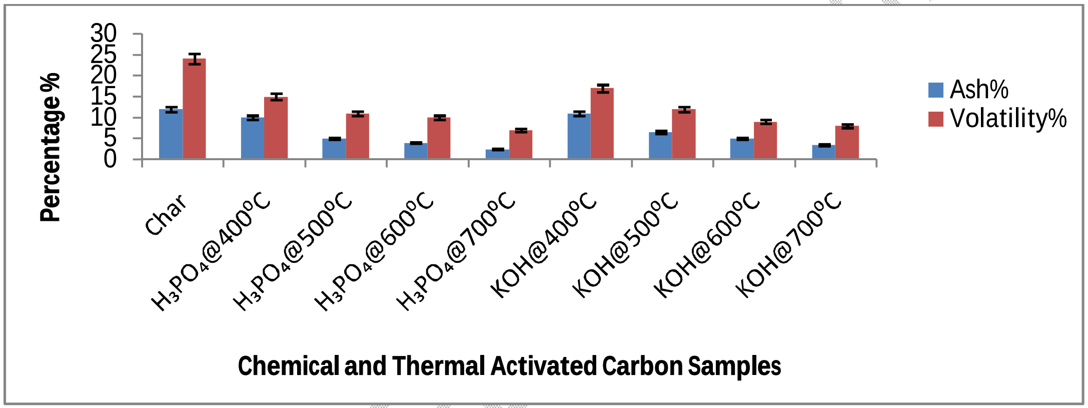

Fig3. Results for Percentage Ash Content and Volatility of Samples

Iodine value of activated carbon gives an estimation of the absorption capacity. Fig.4 shows the iodine absorption value of the different samples produced in mg/g of iodine to activated carbon weight ratio. The precursor showed the lowest iodine value at 127mg of iodine adsorbed per gram of sample of the precursor, which can attributed to the fact that the pores are not quite developed. The Char shows some improvement of 206.3mg/g as carbonization releases volatile substances. The highest IV was seen at 950mg/g for the sample chemically activated with KOH at 600°C. From the results, IV increased with increase in activation temperature for both samples chemically activated from 400°C to 600°C. There was an IV decreased to 624mg/g and 381 mg/g at 700°C for sample treated with KOH and H_3PO_4 respectively. This may be attributed to the functional groups present in the samples or a collapse of the pore structures of the samples at 700°C. A comparison of the chemically activated samples shows samples activated with KOH had higher IV absorption than those activated with H_3PO_4.

Table1. shows BET analysis results which give information on the pore volume and also pore diameter of the absorbents produced with KOH activation at 500°C, 600°C and 700°C respectively and char for control. The pore diameter of the char sample is 2.046nm with a pore volume of $0.041cm^3g^{-1}$ which was greatly improved with chemical and thermal activation as shown. The pore diameter of the samples was largest at 3.384nm with a pore

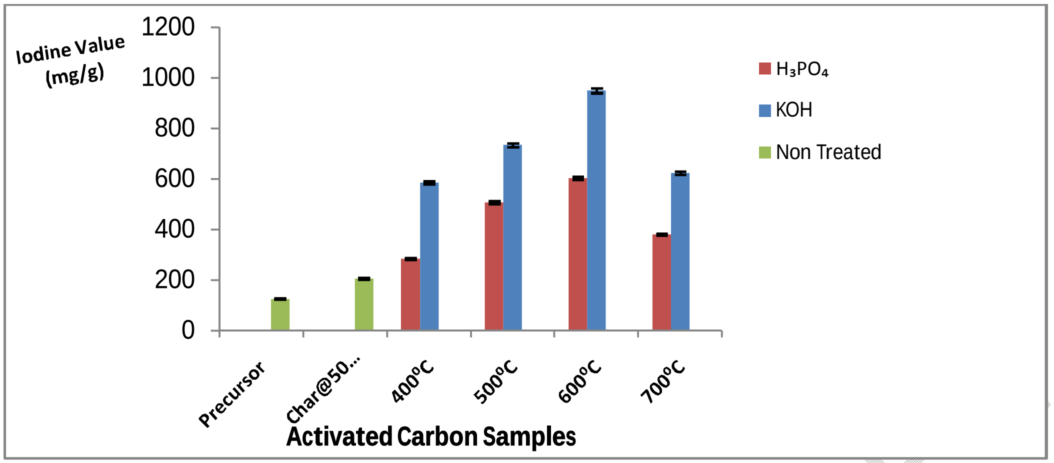

Fig. 4. Iodine Absorption Value of Samples

volume of 0.088cm^{3}g^{-1}for sample treated with KOH and thermally activated at 500°C. The sample activated at 700°C shows a high pore diameter at 3.361nm but with a very small pore volume of 0.0095cm^{3}g^{-1}. Thus, the pore structure of the activated sample collapses with increase in activation temperature further than 600°C.

Table1. BET analysis result of activated carbon samples

Samples	Surface Area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore Diameter (nm)
Char	31.255	0.041	2.046
KOH/500^{0}C	48.042	0.052	3.004
KOH/600^{0}C	51.713	0.088	3.384
KOH/700^{0}C	50.462	0.0095	3.361

The morphology of the samples as shown in Fig.5 also validates the visible increase in pores with temperature increase. The char morphology (Fig. 5a) has micro pore structures which are just on the surface of the carbon and are under developed. In the micrograph in Fig. 5b,c,d, the samples activated with KOH at 500°C , 600°C, and 700°C show well developed pores which can be attributed to the process of chemical and thermal activation that help to improve the pore structure. From the FTIR spectra of samples in Fig.6, several peaks are exhibited indicating several functional groups which in turn is important for the possible mechanism of absorption [37]. All samples spectrum show peak between 3200cm^{-1} and 3400cm^{-1} which reflects O-H stretching vibration of hydroxyl group in alcohols, phenols or absorbed water. Peak seen in region of 2840cm^{-1} to 3000cm^{-1} reflects C-H asymmetric stretching vibration of CH_2 functional groups which confirms the presence of Alkanes. The peaks in region of 1650cm^{-1} to 1800 reflects C=O stretching vibration in conjugated ketone, aldehyde, carbonyl and amide groups. The sample treated with KOH with thermal treatment at 700°C, Fig.6 (d) shows a sharp peak at 1600cm^{-1} reflecting C=C stretching in alkenes different from other samples. Peaks in the region of 1300cm^{-1} to 1600cm^{-1} reflect stretching vibrations from C-H bending which indicates alkanes and aldehydes groups. Peaks between

1000cm^{-1} to 1260cm^{-1} reflects C-O stretching from aromatic ether, alky aryl ether, vinyl ether, aliphatic ether, ester, and alcohol group.

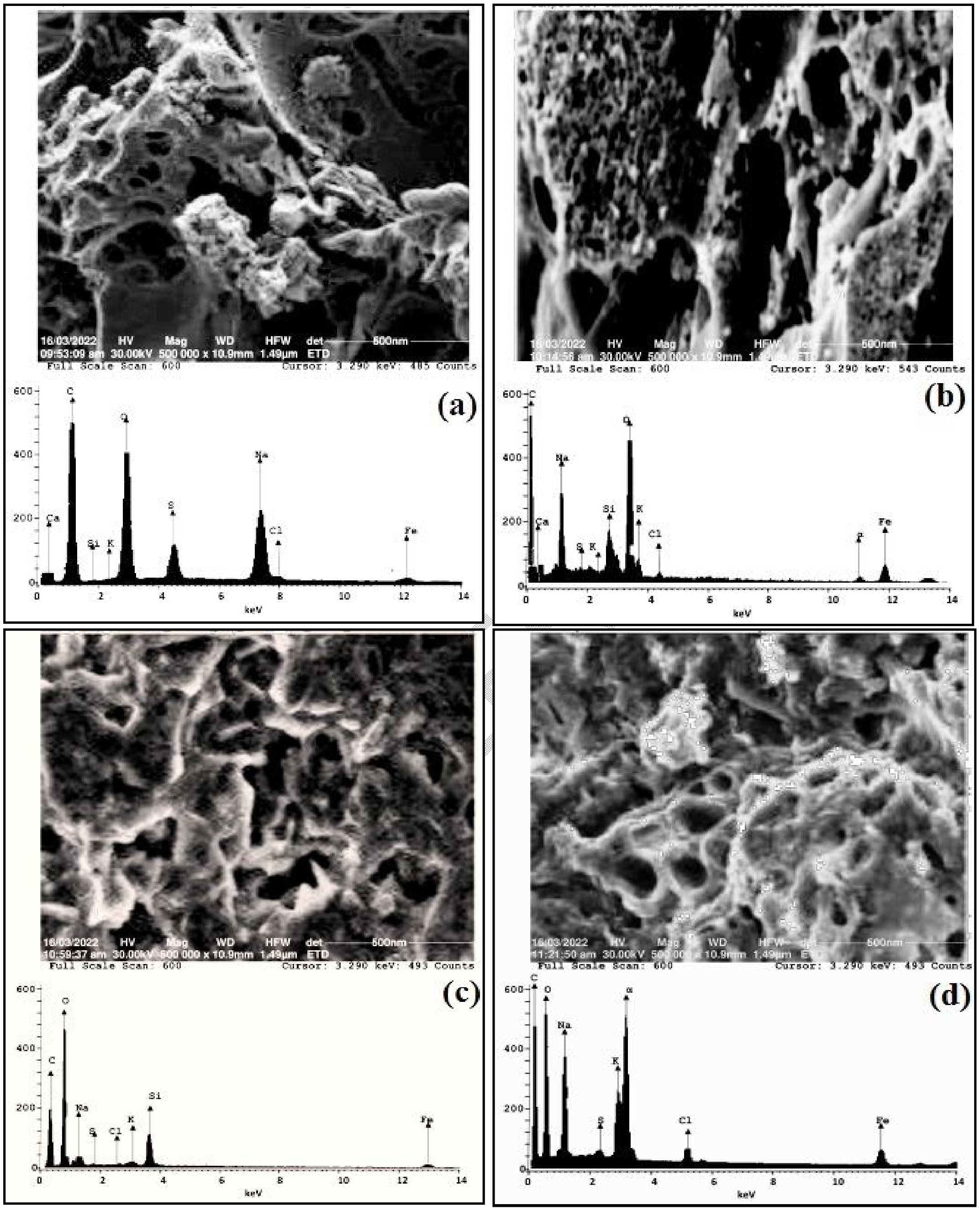

Fig. 5. SEM Micrographs/EDX analysis (a) Char (b) KOH@500°C (c) KOH@600°C & (d) KOH@700°C

Fig.6 Peak at 800.32cm^{-1}(a), 708.03 cm^{-1}(b), 974.21 cm^{-1}(c), and 762.11 cm^{-1}(d) reflect Out-of-plane bending vibrations of C-H group in the aromatic rings, which indicates the presence of Alkanes. Peak at 650.41cm^{-1} (Fig.6a) reflects C=C stretching vibration which indicates

Carbonyl groups. Peak at 654.38cm^{-1} (Fig.6b) exhibited C–O–C stretching vibrations of carboxyl groups.

Thermogravimetric analysis was done to show the behavior of the precursor under different thermal conditions. From figure 7, the TGA curve shows an initial fall; this first fall between the region of 200-300°C could be due to the eradication of moisture content from the precursor. The DTA and TGA curves show that there was a transition after 500°C to 600°C. A further change is shown by the DTA curve slightly before 700°C which may have resulted to the collapsing of the pores structure as observed also from the BET and SEM results.

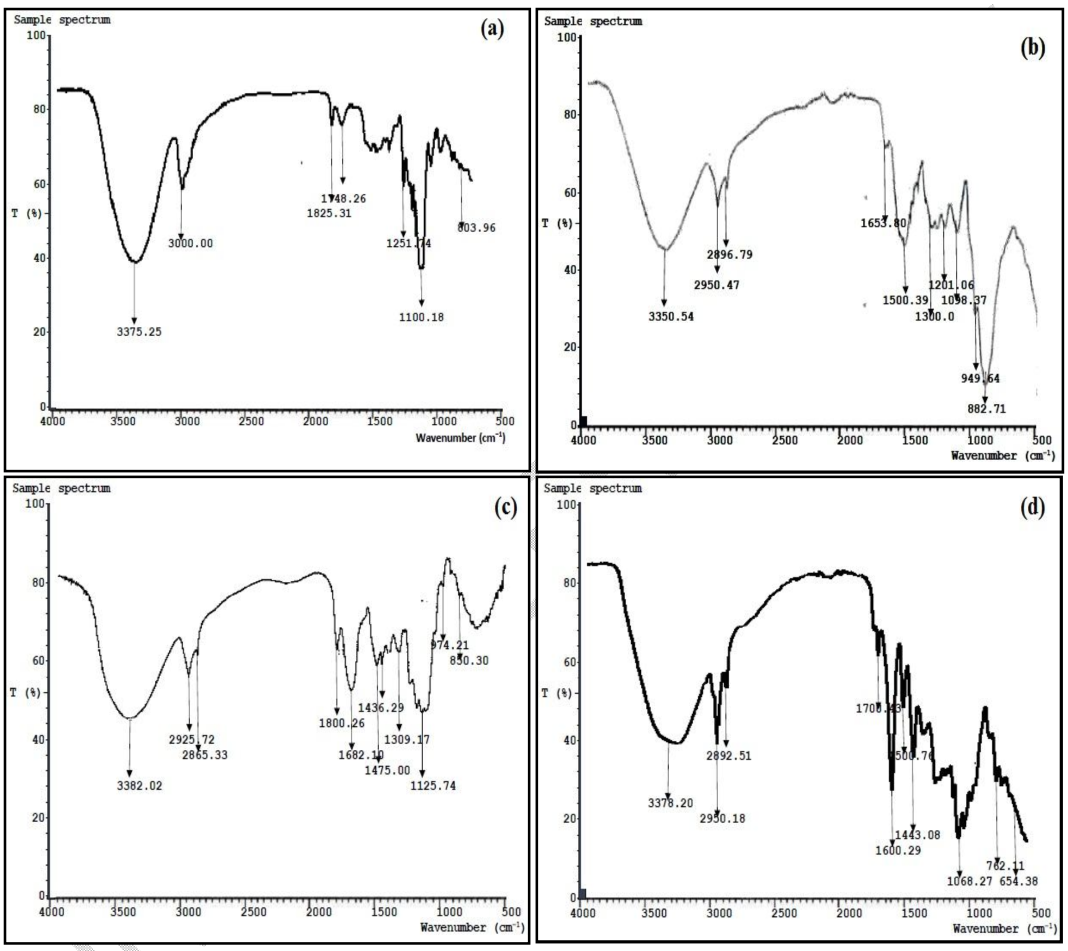

Fig. 6. Samples FTIR Spectrum (a) Char (b)KOH@500°C (c)KOH@600°C (d)KOH@700°C.

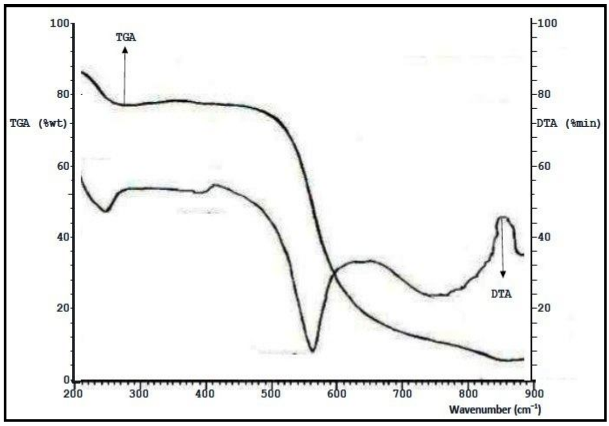

Fig 7. TGA/DTA of the precursor sample

4. CONCLUSION

Activated carbon samples with good adsorbent characteristics and tendencies were produced from Vitex doniana (Black plum) seeds with an average percentage fixed carbon yield of 25.65%. Samples activated with H_3PO_4 and KOH used for the activation of the Vitex doniana char gave appreciation ash content, moisture content, bulk density as well as presence of volatile matter results. However, KOH activated samples gave higher iodine value absorption values of comparatively with a highest value of 950mg/g. Chemical treatment of Vitex doniana seed char with KOH will produce a better activated carbon for absorption purposes. From the BET, morphology and functional groups characterization analysis for these samples, the results show that the samples has well developed pores and pore volume and contains a lot of functional groups on the surfaces. The presence of different functional groups will result to different affinity towards different contaminants thus adsorption capacity of the various samples produced. The effect of thermal activation was also seen as the pores development, pore size, and pore volume were affected with change of temperature. The highest pore size and pore volume of 0.088cm^{3}g^{-1} and 3.384nm results were obtained from the sample thermally treated at 600^{0}C. The pore size and pore volume also give an estimation of the absorption capacity of the absorbents; larger pore size implies large molecules can be adsorbed while more pore volume means more molecules can occupy available spaces. Thermally treated samples at 700^{0}C showed a decline in pore size as well as pore volume; the morphology and Spectra analysis of sample also indicates a deviation and collapsing of developed pores. Clearly, the development of samples by treating Vitex doniana seeds char with KOH and thermal treatment at 600^{0}C gave a good grade of activated carbon with good absorption characteristics.

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