INVESTIGATION OF THE EFFECT OF CHEMICAL ACTIVATION AND CHARACTERIZATION OF BONE CHAR: COW BONE

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ABSTRACT

In this study, cow bone was carbonized at 800 ^{o}C in 4 hrs cooled to room temperature. The carbonized samples were impregnated with 0.1 M HNO_3 and HCl, before activation at 300 ^{o}C, 400^{o}C and 600 ^{o}C with varying time of 60 min, 90min and 120 min. Characterization on the activated bone char at 400 ^{o}C in 120 min showed highest iodine number (surface area) and adsorptive capacity of 739.43 mg/g , 707 mg/g and 0.5 g/g HCl and HNO_3 respectively. FT-IR analysis showed functional groups such as amine, methylene, carboxylic, aldehyde etc on the non activated bone char. With the activating agents, new functional groups were indicated such as carbon-aromatic and alkyi halides without eliminating the former functional groups. The effect of activating temperature and time was more pronounced on iodine number (surface area), moisture content and ash content.

Keyword: *Chemical activation, surface area, Cow bone, HNO_3, HCL*

INTRODUCTION

Activated charcoal as an amorphous form of carbon can be produced from any form of carbonaceous material or organic precursor; raw materials such as mangrove wood, animal bone, coconut shell and palm kernel shell, bamboo (Tangiuank *et al.,*2009; Ademiliyi *et al*., 2009, nut (*Jatropha curcas* L.), (Viboon *et al* 2008) and groundnut shell (Eboili *et al.,* 2009;). Activated charcoal is used for adsorption, absorption and chemisorptions purposes; the removal of fluoride from water and to filter aquarium water (Ademiliyi *et al*., 2009; Alwan *et al.,* 2012). It also finds application in the sugar refining industry, production of petroleum jelly, the removal of organic dyes from textile waste water, removal of undesirable odour and taste from drinking water, removal of heavy metals and pharmaceutical purposes (Jabit, 2007; Olafadehan *et al* ., 2000; Wikipedia, 2011) etc. Bone char, also known as bone black, ivory black, animal charcoal, or abaiser, is a granular material produced by charring animal bones (Saad *et al*., 2008; Wikipedia, 2011) at 400^{o}C to 500 °C. This is carried out in an oxygen-depleted atmosphere to control the quality of the product as related to its adsorption capacity, defluorization of water, decolourization of sugar and removal of heavy metals. The quality of the bone char can be easily determined by its colour. Black charcoals are usually under charred bones that still contain organic impurities which may impart undesired odor and color to treated waters. White bone chars are over charred bones that present low fluoride removal capacity and Grey-brownish bone char are the best quality chars for absorption applications. The quality of the bone char is usually controlled by the amount of oxygen present in the charring atmosphere (George, 1984), which contains only about 10% carbon, the remainder being calcium and magnesium phosphates (80%) and inorganic material originally present in the bones (Saad *et al* ., 2008; Wikipedia, 2011). Activated charcoal can be divided into two main classes namely granular and powder material,

employed in adsorption of gases and liquid purification[14]. Activated charcoal can be divided into two main classes namely granular and powder material, employed in adsorption of gases and liquid purification[14]. The study of activated charcoal has attracted many research groups in recent times. Different raw materials and activating agents have been used at different temperatures. With activating agent ($ZnCl_2$) on coconut shell, Mozamel *et al*., (2002), observed iodine number of (673%, 53%) at 400°C and (946%, 43%) at 600°C. Ademiluyi *et al*., (2009), reported the effect of processing conditions on the characterization of activated carbon from waste Nigerian based bamboo. Carbonization at 400°C - 500°C and activation at 700°C - 800°C, using various concentrations of HCl acid (0.01M, 0.1M , 0.5M, 1.0M). Highest value of bulk density, pore volume and average particle size[7] was observed with 0.1M at 800°C. Rahman *et al*., (2006), reported the Langmuir type of adsorption isotherm indicating monolayer formation (oxalic acid)) and a sigmoid shaped isotherm, BET (Brunauer Emmett and Teller) type ii isotherm (maleic acid solutions)[10] at low temperatures (300° C-400° C) on coconut shell. Saad *et al.,* (2008), activated camel bone at 800°C for 5 hrs for the removal of Hg(11) from waste water with a BET surface area of 72.24 m^2/g and pore volume of 0.225 cm^3/g. IR spectrum on camel bone charcoal showed structural vibrational bands due to hydroxyl group (3420 cm^{-1}), halogen group (560 cm^{-1}, 605 cm^{-1}) and nitrogen compounds (2360 cm^{-1}) as well as phosphate group (1031 cm^{-1}) on the charcoal surface[11]. Eboibi *et al*., (2009), produced activated charcoal from wal nut shell at a temperature of 110°C for one hour with absorptive capacity of 0.78mg /ml and a bulk density of 0.57 g/ml. Although, a lot of activated charcoal had been studied on bone, coconut shell, walnut shell and bamboo, there is little or no report on activation of cow bone in literature. In this work, cow bone which is in abundant, a waste material (Amassoma abaittor) Bayelsa State, Nigeria, has been used as raw material. FT-IR and iodine adsorption method was used to characterize the activated charcoal.

EXPERIMENTAL

MATERIALS AND EQUIPMENTS

Cow bone was obtained from Abattoir (Amassoma) Bayelsa State, Nigeria. Concentrated hydrochloric acid, concentrated nitric acid, iodine solution, sodium thiosulphate, starch solution, sugar solution, Distilled water, muffle furnace, 1.18mm mesh sieve, measuring cylinder, cutting machine, pH meter, beaker, conical flask, oven, crucible, crusher, desiccator, centrifuge, bunsen burner, burette and pipette.

CARBONIZATION

The cow bone obtained from Abattoir was cut into small sizes of 2cm with a band cutting machine. The bone pieces were washed in distilled water at 80°C and dried in an oven at 105°C for 4 hours, to remove oily matter and moisture. 2500 g of well dried material (cow bone pieces) was weighed out and introduced into the Muffle furnace and was pyrolysed at 800°C for 3 hours. The carbonized material was allowed to cool to room temperature.

$$Cow\ Bones \frac{800\,℃\ /3hour}{Inert\ Atmosphere} > Bone\ Char + steam + oil + ammonia\ liquor$$

CHEMICAL ACTIVATION

The carbonized material was carefully crushed into powder with the aid of a crusher and sieved using 1.18mm mesh sieve to get particles of uniform size. 20 g of well screened carbonized material was transferred into a beaker and mixed with 5ml of 0.1M acid, until the mixture formed a paste. The paste was then transferred into a dry crucible and finally introduced into the muffle furnace and heated at varying temperatures. It was then cooled to room temperature, washed with distilled water and dried for 3 hours in an oven at 150^0C. The same procedure was repeated for other samples and the final product was kept in an air tight sac. The locally developed activated charcoal was labeled A1, A2, A3, B1, B2, B3,C1, D1, D2, D3, E1 and E2 for characterization.

Table 1 Sample Codes

ACID TYPE	Concentration (mol/L)	Temperature (^{o}C)	Time (Min)	Sample code
HNO_3 ($ACBHNO_3$)	0.1	300	60	A1
	0.1	300	90	A2
	0.1	300	120	A3
	0.1	400	60	B1
	0.1	400	90	B2
	0.1	400	120	B3
	0.1	600	40	C1
HCL (ACBHCL)	0.1	300	60	D1
	0.1	300	90	D2
	0.1	300	120	D3
	0.1	400	60	E1
	0.1	400	90	E2
	0.1	400	120	E3
	0.1	600	40	F1

CHARACTERIZATION OF ACTIVATED CHARCOAL

MOISTURE CONTENT

2.0 g of sample was weighed and placed in an oven at 110^o C for 10 hours, until weight of sample becomes constant and the moisture content was determined using the equation below.

$X_0 = \frac{WI-W2}{W1} \times 100$

Where X_O = moisture content on wet basis, w_1 = initial weight of sample, w_2 = final weight of sample

Bulk Density

10g of sample was weighed out with a balance. It was then completely transferred into 50ml of distilled water using measuring cylinder. The volume of the water displaced was recorded and the bulk density was calculated by dividing the mass of the sample by the volume of water displaced[8].

Bulk density = $\frac{Mass\ of\ sample}{volume\ of\ water\ displaced\ by\ sample}$

Ash Content

2.0g of sample was ignited in a Bunsen flame and cooled in a desiccator. It was transferred into a crucible of constant weight and heated at 750^{o}C for 3 hours in a muffle furnace. The weight of the sample was recorded after cooling it to room temperature. The ash content for sample was determined by dividing the weight difference by the initial mass of sample

Adsorptive Capacity

Adsorptive capacity was determined using decolourizing method. Sugar solution was prepared by adding 100 g of dark brown sugar into 1000 ml of distilled water. 2.5 g of sample was poured into 50 ml of the brown sugar solution and mixed vigorously. It was then observed for colour change after 30 mins. Addition of sample continued until the solution becomes colourless. Therefore, total mass or quantity of the sample divided by the quantity of the brown sugar used , gave adsorptive capacity or decolourizing capacity.

SURFACE AREA

0.5 g of sample was weighed and centrifuged in 0.095M iodine solution. 0.1M sodium thiosulphate solution was titrated against 20 ml of sample. Free aliquot solution (solution obtained after centrifuge) using 5 ml of freshly prepared starch solution as indicator. The volume of the thiosulphate required to titrate 20 ml of blank solution (purely iodine solution) was also determined. All the titrations were done in triplicate and the average value recorded. The concentration of iodine adsorbed by the activated charcoal at room temperature was calculated as the amount of iodine adsorbed in milligrams.

$$\frac{img}{g} = \frac{(\mathrm{B}-\mathrm{S})}{B}.\frac{\mathrm{VM}}{W} \times 253.81$$

Where B and S are the volumes of thiosulphate solutions required for blank and sample titrations respectively. W is the mass of activated charcoal sample, M is the concentration of the iodine solute, 253.81 is the atomic mass of iodine and V is 20 ml aliquot.

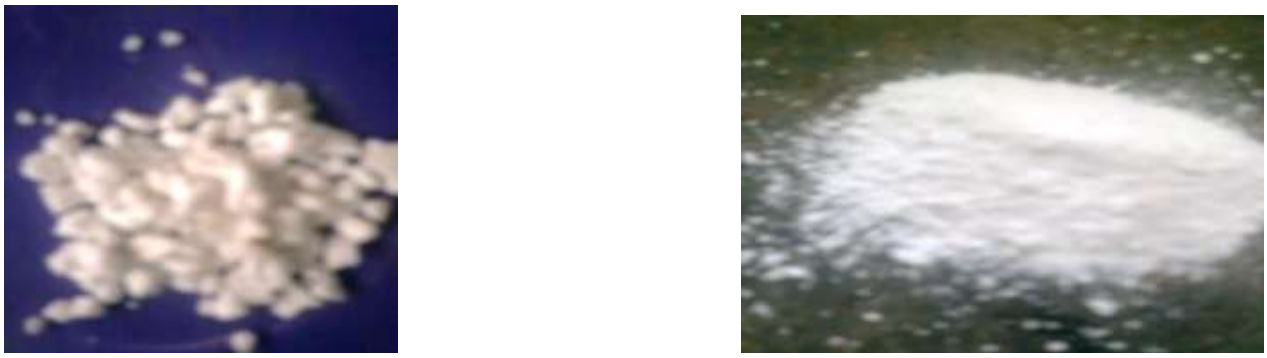
RESULT AND DISCUSSION

Activation increased with an increase in temperature. At low temperatures the activation is low exhibited by low porosity of char. During activation, there is creation of supplemental pores which increases the internal surface. As temperatures increases there is the possibility of pores closing up due to collapse of pores, and this may reduce the surface area of the material. At temperature 400°C, in 120 min, the iodine number and adsorptive capacity were 739 mg/g, 0.5g/g for (0.1 M HCL), while 707mg/g,, 0.5g/g were observed for (0.1 M HNO_3) respectively. As the temperature was increased to 600°C, the values of iodine number

reduced to 578 mg/g and 321 mg/g but adsorptive capacity increased to 0.75g/g, for (HNO_3) and HCL (See Table 2). Iodine number is a fundamental parameter used to characterize activated charcoal performance. It is a measure of the micro pore content of activated carbon and is obtained by the adsorption of iodine from solution by the activated charcoal sample. The micropores are responsible for the large surface area of activated carbon particles, and are created during activation. Table 3 shows that the values of iodine number obtained using HCL, as the activating agent is 739 mg/g and HNO_3 (707mg/g) which compared favourably to the report by (Ademiluyi *et al*., 2009). Activation was greatly affected with time. The iodine number at 300 ^oC that was run in 120 min was higher A3(128.60 mg/g) compared to 90 min, and 60 min A2(96.45 mg/g) and A1(64.30 mg/g) respectively (See Table 2). A similar trend was observed at 400 ^oC, where B3 (707.28 mg/g), B2(385.79 mg/g) and B1(192.90 mg/g) in 120 min, 90 min and 60 min respectively. The surface functional groups can be easily introduced to the carbon by different activation methods like the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid, nitric acid, hydrochloric acid, zinc chloride ,potassium hydroxide etc. In Figure 1 it can be seen that the charred bone belongs to the grey brownish group, an indication of excellent product In carbonization, the temperature and oxygen must be well controlled. The temperature must be sufficiently high to dry and volatilize all non carbon substances during carbonization. Generally, bone chars are under-charred or over-charred which results in colour difference. For under charred bones, it is normally black in colour and retains odour due to residual volatile materials still contained in the bone. The over-charred bones are white in colour which has less adsorptive capacity towards fluoride in water. The charred bone which is the best is grey brownish in colour.

The FI-IR spectral patterns shown in Figures 3, 4 and 5 were analyzed and compared with known signature of identified materials in FT-IR library (Silverstein *et al* 1981). Figures 3, 4 and 5 display spectra for unactivated bone char, $ACBHNO_3$ and ACBHCL respectively. The spectral pattern obtained for Figure 3, 4 and 5 showed 8, 12 and 13 discernable pecks respectively. Functional groups on each activated carbon are quite similar even with different activation processes. The displayed patterns in the non activated char in Figure 3 shows that the bone material has pronounced functional groups after pyrolysis. The methylene group is detected by –CH stretching at a wave number of 2923 cm-1, which agreed with report in literature (Viboon *et al*., 2008). Aromatics groups are shown by a peak around 1376 and 1457 cm-1. The band 1045cm-1 belongs to the calcium phosphate group while 1089cm-1 is linked to C-O stretching (Menkiti *et al*.,2012). The 1377 cm-1 and 1455 cm-1(Menkiti *et al*.,2012), The aldehyde group of –O–CH3 is found around 2853 cm-1 (Viboon *et al*., 2008). However, the activation methods has introduced new functional groups as displayed in Figures 4. and 5. The spectrum at 3569 cm-1 indicated the presence of –NH2 group of amine. The band at 2012 cm-1 is suspected to be aromatics overtones caused by aromatic rings belonging to the CH_3 group. The band between 700 cm-1 to 900 cm-1 correspond to the adjacent H and aromatics. The alkyl halides are detected from 600 cm-1 to 560 cm-1. The ash content can also affect activated charcoal. It reduces the overall activity of the activated charcoal. The lower the ash value the better the activated carbon for use as

absorbent. Ash content also influences the ignition point of the carbon, which is a major consideration where adsorptions of certain solvents are applied. For activated char with cow bone, the ash content is very low (0.8%) compared to the report in literature (1% baboom) (Ademiluyi *et al*., 2009). This categorized the activated charcoal from cow bone as liquid phase active due to the nature of the values of the ash content (Eboibi ,2009). The moisture content was properly taken care of during the production stages as the percentage moisture content can be negligible. Table 3 shows that the moisture content is low (0.2%) compared to 19.5 %, work done by (Ekpete *et al*.,2011). Activated charcoal is usually purchased based on moisture free basis, a standard properties of a good adsorbent. The density of the charcoal is of course of great importance to many users in estimating the weight required to fill a vessel. Higher density provides greater volume and normally indicates better quality activated charcoal. It finds more importantly, especially when an activated charcoal product is to be investigated for its filterability. This is because it determines the mass of carbon that can be contained in a filter of given solids capacity and amount of treated liquid that can be retained by the filter cake. The bulk density (1.214g/cm^3) compared in literature is higher (0.4g/cm^3) (Eboibi, 2009) .This may be due to the source of material (bone) (See Table 3).



(a) unactivated Bone char (b) Activated charcoal

Figure 1. Cow bone (a) before and (b) after chemical activation

Table 2. Iodine No, Adsorptive capacity and pH of activated cow bone char

SAMPLE CODE	IODINE NO (mg/g)	ADSORPTIVE CAPACITY (g)	pH
A1	64.30	1.25	7.01
A2	96.45	1.25	7.01
A3	128.60	1.0	6.88
B1	192.90	1.0	7.02
B2	385.79	1.0	7.05
B3	707.28	0.5	6.9
C1	321.49	0.75	7.04
D1	64.30	1.0	7.02
D2	109.3	1.0	7.01
D3	160.75	1.0	7.0

E1	257.19	0.75	6.89
E2	385.79	0.625	6.9
E3	739.43	0.5	6.97
F1	578.69	0.75	6.8

Table 3 Ash content, Moisture content and Bulk density of activated cow bone char

SAMPLE CODES	ASH CONTENT %	MOISTURE CONTENT %	DENSITY (g/cm^3)
A1	1.5	3.2	1.302
A2	1.4	0	1.317
A3	1.8	3.8	1.305
B1	3.2	3.0	1.230
B2	1.8	2.2	1.278
B3	2.4	0.2	1.469
C1	2.6	1.2	1.560
D1	1.6	1.6	1.307
D2	0.8	0.6	1.342
D3	1.2	0.6	1.214
E1	1.4	0	1.354
E2	1.4	6.8	1.337
E3	2.4	5.2	1.350
F1	1.8	0	1.28

Table 4. Properties of the activated cow bone char of 0.1M HCl, 400°C in 120 min

	Present Work (400° C)		Reference
ACTIVATING AGENT	**HCL**	**HNO_3**	
IODINE NUMBER (mg/g)	739	707	600-1200 (George 1984)
ADSORPTIVE CAPACITY (g/g)	0.5	0.5	0.3-0.5 (Ekpete, 2011)
pH	6.9	6.97	6-7 (Ekpete 2011)
MOISTURE CONTENT%	5.2	0.2	2-8 (Ademiliyi, 2009)
ASH CONTENT %	2.4	2.4	≤ 8 (Ademiliyi, 2009)
BULK DENSITY (g/cm^3)	1.350	1.469	0.77 (Ekpete, 2011)

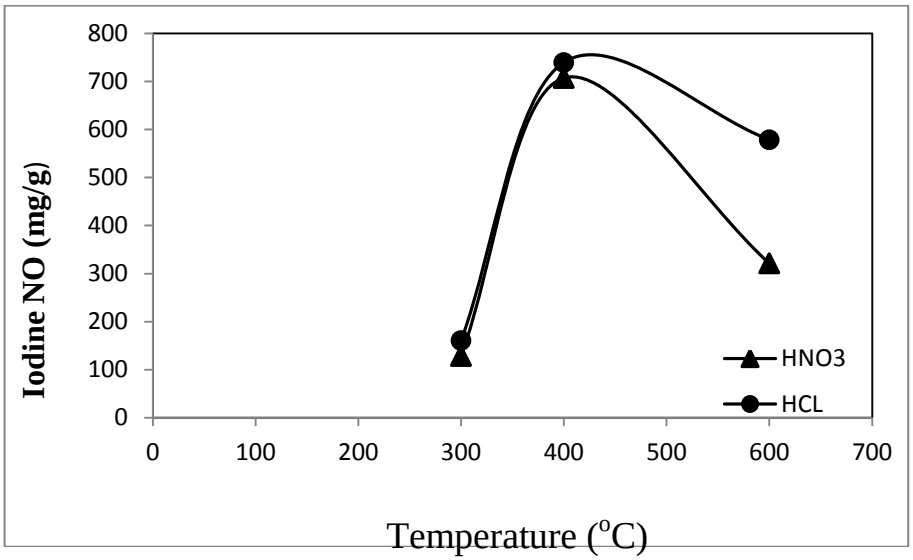


Figure 2. Iodine number of activated charcoal at various temperature

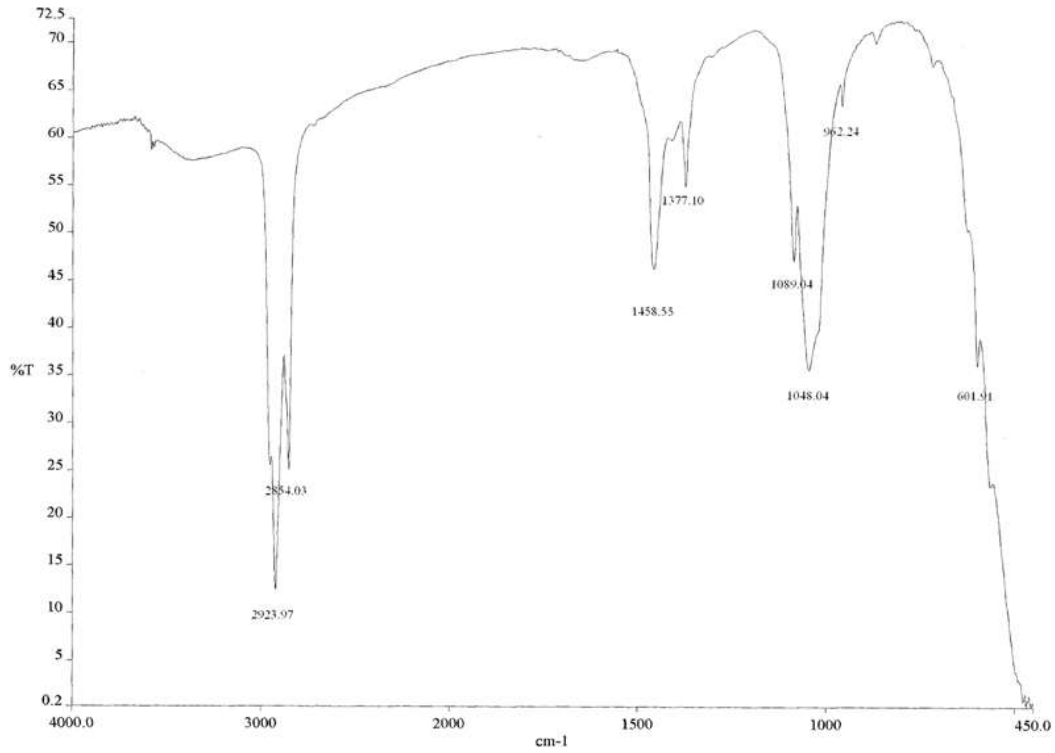


Figure 3. FT-IR Spectrum of unactivated cow bone char

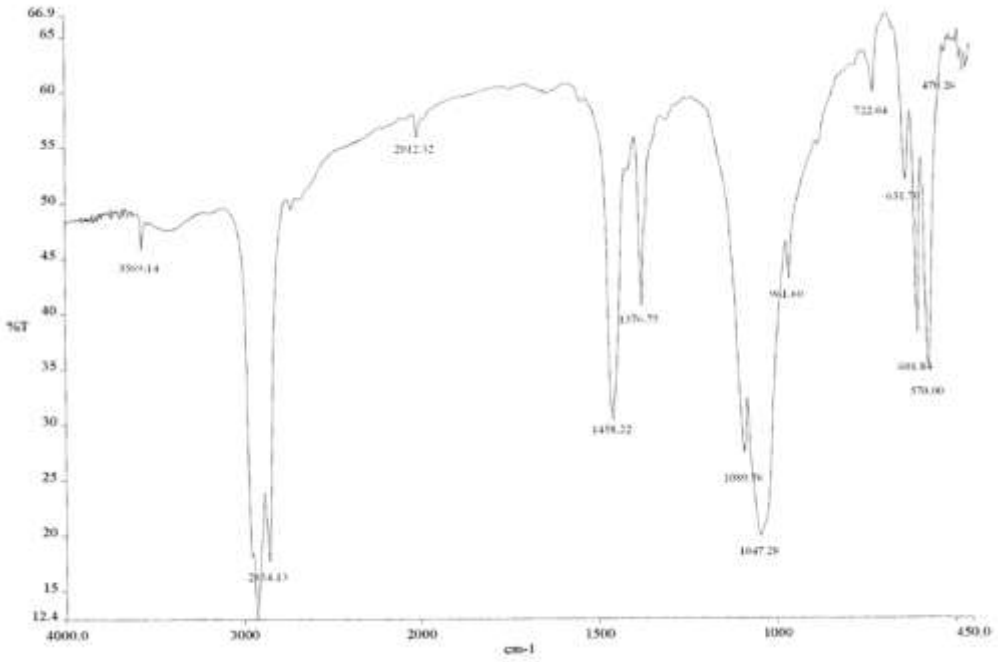


Figure 4. FT-IR Spectrum of Activated charcoal ($HN0_3$)

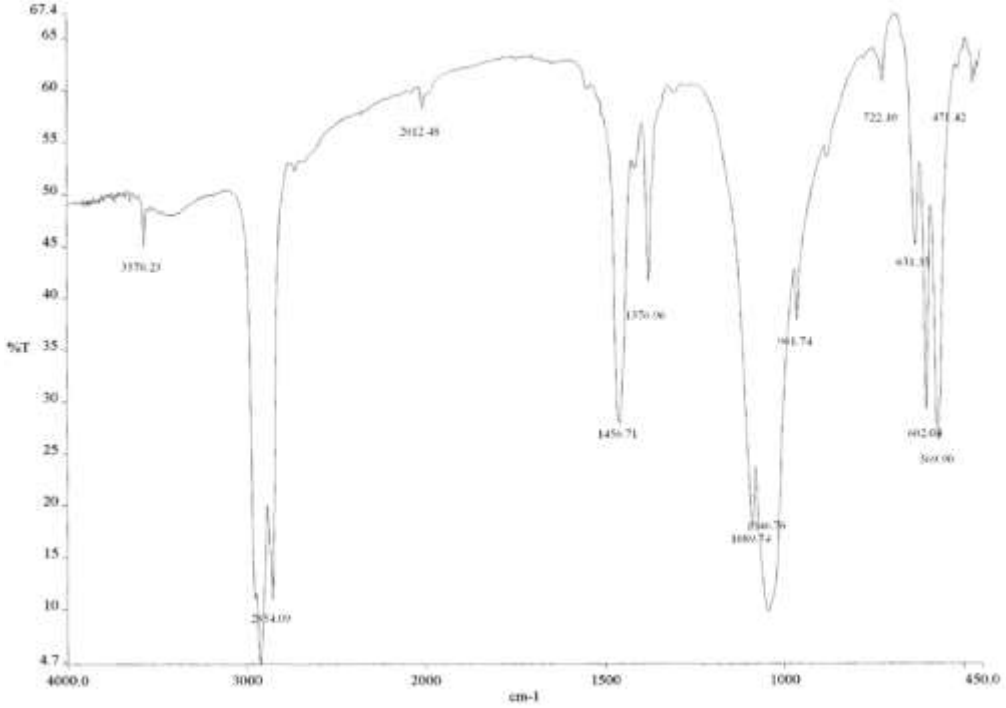


Figure 5 FT-IR Spectrum of Activated charcoal (HCl)

CONCLUSION

In this work chemical activation was carried on cow bone material using 0.1 M of HCL and HNO_3 at varying temperatures (300 – 600 ^oC) and time.(60-120 min). At 400^o C, and 120 min, iodine number of 707 mg/g and 739 mg/g were obtained for HNO_3 and HCL, predicting presence of micro pores. Increasing the temperature to 600 ^oC greatly reduced the iodine number but increased the adsorptive capacity from 0.5 to 0.75 for both methods. The ash content and moisture for HNO_3 increased from 2.4 to 2.6 and 0.2 to 1.2 respectively. For HCL, both ash content and moisture content showed a decrease from 2.4 to 1.8 and 5.2 to 0. Advantages offered by using cow bone charcoal over many other adsorbents include low cost, availability, and good efficiency. From this study, activation with HCL at 400^{0}C and at 120 min showed very high characterization values compared to that of HNO_3. However, values obtained from the methods are comparable to values found in literature (See Table 4).

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Nomenclature

B,S	Volume of thiosulphate Blank and sample	= m^3
I	iodine number	= mg/g
V_m	volume of aliquot	= m^3
M	Concentration of iodine	= mol/L
X_o	Moisture content	= %
W_1	initial weight of sample	= g
W_2	final weight of sample	= g

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