A Comparative Analysis and Characterization of Animal Bones as Adsorbent

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ABSTRACT

Animal bone has been utilized to produce adsorbents for the decolourization of palm oil. The bones used are chicken, dog, goat and cow bones. The bones were carbonized at a temperature of 400^0C in a muffle furnace for one hour in the absence of air. The residue was then ground to a fine particle size of 212 µm for each sample. Chemical activation with 250 ml of 2 M Hydrochloric acid (HCl) was then carried out with further processing to obtain activated carbon from each sample. From the characterization, the following parameters were determined: ash content, moisture content, yield charcoal, fixed carbon, pore volume and bulk (apparent) density. The adsorption capacity of the activated carbons was tested on the bleaching of palm oil. The following analyses were carried out on the bleached oil: iodine value, saponification value and acid or free fatty acid value. The rate of colouration was determine using a colorimeter in which chicken bone was found to be 275, goat bones was 268, dog bone was 261 and cow bones was 220 compared to the colour of the oil before bleaching which was found to be 279. Cow bones had the lowest value for colouration which shows from the result obtained that activated carbon from cow bones is more effective in reducing acidity content of palm oil than those of chicken bones, goat bones and dog bones.

Keywords:adsorbent, activated carbon, decolourization, palm oil, carbonization.

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INTRODUCTION

An adsorbent is a substance usually porous in nature and with a high surface area that can adsorb substance onto its surface by intermolecular forces [1]. Due to the fact that solutes can be distributed between the adsorbent surface and a mobile phase, adsorbents are used as stationary phases in gas-solid and liquid-solid chromatography. Adsorption is the collection of substance unto the face of the adsorbent solids. It is a removal process in which certain particles are bound to an adsorbent particle surface by either chemical or physical attraction and is often confused with absorption where the substance being absorbed penetrates into the other solid[2]. The solid surface in contact with a solution has the tendency of accumulating a surface larger to solid molecules because of the difference of surface forces. Therefore, this causes an adsorption to take place, the adsorption result in the formation of a molecular layer of the adsorbate on the surface of the adsorbent. Often an equilibrium concentration is soon formed at the surface and is normally followed by slow diffusion onto particles of the adsorbent [3]. This phenomenon involves accumulation of substance at interface which can either be liquid-liquid, liquid-gas, gas-solid or liquid-solid. The substance performing the adsorption (solid, liquid, gas, amorphous) is the adsorbent; the adsorbate is a mixture of substance or solution on which the adsorbent is used. Many solid substances are known to possess this power of attracting and retaining molecule or ion upon surface on exposure e.g. activated clay, fuller's earth, silica gel, activated carbon, bauxite and activated alumina etc. The best one among these substances is the activated carbon, produced from organic base material such as coconut shells, palm kernel shells, wood chips, animal bones, corn cobs, rice husk, etc. The raw materials are carbonized to obtain the char or carbonaceous material, which is activated to the highly porous final product. The knowledge that carbon produced by decomposition or wood can remove colouring matters from solution dated back to the 15th century. The commercial application of this property was made first in 1794 when charcoal filters were made first in the British Refinery and

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today it gains prominence in decolourization of palm oil to better quality, flavour and removal of odour for production of edibles.

Animal charcoal also known as bone black, bone char or abaiser, is a granular material produced by charring animal bones. Animal bones are part of the composite that form the body of animals; it basically gives shape and support to animals (Skeletal systems). It contains about 10 % carbon, the remainder being calcium and magnesium (80 %) and other inorganic materials present in the bones [4]. Animal charcoal possesses a higher degree of removing coloring matters from solutions; charcoal is used in art of drawing in form of fine, compressed and powdered charcoal [5].

Carbonization is the term for the conversion of an organic substance into carbon or a carbon containing residue through pyrolysis or destructive distillation. It is often used in organic chemistry with reference to the generation of coal gas and tar from raw coal. Fossil fuels in general are the products of the carbonization of vegetable matter. Carbonization is often exothermic, which means that it could in principle be made self-sustaining and be used as source of energy which does not produce carbon dioxide.

Activated carbon is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for absorption or chemical reaction. Almost any carbonaceous material of animal, vegetable or mineral origin can be made into activated carbon when properly treated e.g. from animal bones, wood, corn cobs, coffee, beans, rice husks, fruit peels and nuts shells and minerals such as peat, soft and hard coal tar, asphalt, phloem residues and carbon black [6]. Though there are many commercially available activated carbons, these are still quite expensive [7, 8]. Various researchers [8-14]have carried out studies for simplified and cost effective methods of activation carbon. The most widely used activation carbon process are the treatment of the carbonaceous materials with oxidizing gases such as air, steam or carbon dioxide and the carbonization of the raw materials in the presence of chemical reagents such as zinc chloride, magnesium chloride, calcium chloride or phosphoric acid. The surface area per gram of an adsorbent is called the 'specified surface area'. Active adsorbents have a very high surface area, the surface phenomena adsorption was discovered in 18th century by Scheele in Sweden. Zelmsky used this principle to design a gas mask for protection in war. Substances that reduce the surface tension or solvent are called surface active substance or surfactant. The limiting value of reduction is called 'surface activity' [15].The primary use of activated carbon is in removing pollutants from air or water stream both in the field and in industrial process such as spill cleanup, ground water remediation, portable water filtration, waste water treatment etc. Among the literarily hundreds of other uses are agents in gas masks, pollution control devices such as car catalytic converters and flue gas desulfurization [16]. Activated carbon is also used to remove pesticide residues [17].Modified activated carbon derived from the seeds of widely available plant source of *Martynia annua L and Xanthiyam strumarium* to study the physic-chemical properties of the agricultural waste [18].The removal of copper (II) from aqueous solution using palmyra palm nut (PPN) as potential raw material for the preparation of activated carbon was also investigated. It was discovered that the percentage of Cu^{2+} adsorbed was found to be dependent on adsorbent dosage, pH and particle size [19].

The oil palm produces two main types of oil; the red oil from the mesocarp and kernel oil from the seed [20]. The pulp contain about 50 % oil which is light yellow to red in colour, the colour being due to the presence of carotenes in palm oil contains high concentration of B-carotene equivalent to about 10 mg of vitamin A per 100 g. The presence of B-carotene in palm oil is important to diet but undesirable in other uses of palm oil.Palm oil is composed mainly of palmitic acid and oleic acid hence, saturated and unsaturated fatty acids roughly in equal proportion. Fat and oil obtained in both plant and animal are sources of esters. Esters are very important compound in nature responsible for favourer of many fruit and smells in flowers and they are formed from alcohol propane 1, 2, 3- erol (glycerol) and carboxylic acid with long carbon chain.Esters formed in palmatic acid and glycerol occurs in palm oil. Fat is solid at room temperature while oil is liquid. The unripe fruit have low oil content and a higher proportion of free fatty acids. Palm oil should not contain more than 3 % - 8 % free fatty acid [21]. Decolourization is a bleaching action that involves a process called 'adsorption' in Chemical Engineering. Crude palm oil and fat are decolourized to remove free fatty acids and phosphate and other gummy or mucilaginous materials and to improve the colour, the method of decolourization of oil is originally known which include heating, chemical treatment and bleaching.

2. THEORY
2.1 Ash Content Determination
The ash content is determined using the equation below:

$$(W_2 - W_3)/W_0 \times 100 \hspace{3cm} (1)$$

2.2 Moisture Content Determination
Below is the formula used in the calculation of the moisture content.

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$$\frac{(W_2 - W_3)}{(W_2 - W_1)} \times 100 \qquad\qquad (2)$$

2.3 Yield of charcoal
The yield of charcoal was obtained by using the formula below:

$$\frac{W_0 - AC + MC}{W_0} \times 100 \qquad\qquad (3)$$

2.4 Fixed Carbon Determination
The fixed carbon was obtained using the formula below; assuming sulphur content was negligible in all cases.

$$\frac{Y_{ch} - AC - MC}{Y_{ch}} \times 100 \qquad\qquad (4)$$

2.5 Pore Volume Determination
The pore volume of the adsorbent was determined using the formula below.

$$\frac{(W_F - W_I)}{W_I} \times density\ of\ water \qquad\qquad (5)$$

2.6 Bulk Density Determination
The bulk density was determined using the formula below.

$$\frac{Weight\ of\ sample}{Weight\ of\ equal\ volume\ of\ water} \qquad\qquad (6)$$

2.7 Acid Value Determination
The acid value of the bleached oil was determined using the formula below.

$$\frac{Litre\ value\ \times 0.1\ MKOH\ \times 56.1}{Weight\ of\ sample} \qquad\qquad (7)$$

2.8 Iodine Value Determination
The iodine value of the bleached oil was determined using the formula below.

$$\frac{(B - S) \times N \times 0.126}{Weight\ of\ sample} \times 100 \qquad\qquad (8)$$

2.9 Saponification Value
The saponification value of the bleached oil was determined using the formula below.

$$\frac{(B - S) \times 0.5 \times 56.10}{Weight\ of\ sample} \times 100 \qquad\qquad (9)$$

Where, W_0 is the original weight of dry sample; W_1 is the weight of the beaker; W_2 is the weight of crucible + dry sample and W_3 is the weight of crucible + heated sample, W_F is the Final weight of sample + beaker, W_I is the Initial weight of samples + beaker. AC is the Ash content; MC is the Moisture content, Y_{ch} is the yield of charcoal, B is the value for the blank sample, S is the sample investigated, N is the concentration of sample. The Density of water is taken to be equal to 1 g/cm^3.

MATERIALS AND METHODS

3.1 Materials
The apparatus used for producing activated carbon from animal bones and its characterization, activation and decolourization performance are: Sieve, furnace, beakers, colorimeter, desiccator, crucibles, filter paper, water bath and burette. The reagents used are: chloroform, petroleum ether, hydrochloric acid, sodium hydroxide and palm oil.

3.2 Methods
3.2.1 Carbonization and activation
The bone samples collected were washed in water to remove sand, dirt and flesh and sun dried. The sample were placed in different large crucibles and the set up was kept in a muffle furnace at temperature of 400^{0}C for one hour in the absence of air, after which they were removed and kept in a desiccators to allow them cool and dried. The carbonized bones were then crushed in a mortal and placed into flat mug cubs for each samples. The carbonized bones were then activated by measuring 200g of the crushed sample into a beaker which was then made into slung with 250ml of 2 M Hydrochloric acid (HCl). The resulting mixture was heated for one hour, the sample was then filtered off and washed with distilled water to remove the acid on the surface of the sample and then dried in an oven at 80^{0}C for 24 hrs. The dried sample was sieved for a required size i.e. 212 micros and was kept in a small tray. This procedure was done on all carbonized bone sample.

3.2.2 Characterization of the activated Carbon
This involves the justification and specification of some parameters in activated charcoal which are ash content, moisture content, fixed carbon, yield charcoal, bulk density and pure volume.

Ash Content Determination
2 g of dry activated sample was placed in a crucible, weight of crucible plus dry sample was noted and recorded as W_2. The sample was then placed in a furnace at the temperature of 450 ^{0}C for 6 hrs. After which it was removed, placed in a crucible and its content reweighed and recorded as W_3 and the process and the process was repeated twice for all activated carbon simple to get average ash content value.

Moisture Content Determination
5g of sample was weighed into a crucible and the weight of sample plus crucible was noted as W_2 the sample was kept into an oven at 100^{0}C for 24hrs. After which it was removed, was then placed in a desiccators and allow cooling. The sample plus crucible was weighed again and it was noted as W_3. It was repeated twice for all samples to obtain average moisture content value.

Pore Volume Determination
2g of activated carbon was weighed into a beaker and the weight of sample plus beaker was noted as W_0. 50ml of distilled water was into the beaker containing the dry sample and the mixture was boiled for 15minutes. After the air in the pores has been displaced, the sample was drained and the dried superficially and weighed. The weight was recorded as W_F and procedure was repeated twice.

Bulk (apparent) Density Determination
The sample was poured into a cylinder of 10ml and weight of sample plus cylinder was recorded as W_2.

3.2.3 Refining and decolourization of palm oil
Degumming of Crude Palm Oil
180g of palm oil was put into separating funnel and 80g of boiling distilled water added to the oil and it was shaken vigorously for about 7 minutes. Two layers were obtained, since the water and gum are denser than oil, the oil settles above the water. The water and gum were decanted off and the de-gummed palm oil was obtained.

Neutralization of Crude Oil
4ml of 0.5 of sodium hydroxide (NaOH) was added to the de-gummed palm oil. The mixture was well stirred and vigorously shaken; it was then filtered off to obtain neutralized oil.

Absorptive Bleaching
The bleaching was effected in a test-tube, provided with a stirrer placed in a water bath. The water bath was kept at a temperature of 100^{0}C throughout the process. 11g of palm oil was weighed into four different test-tubes and 1.1g of activated carbon samples was poured into the oil in the test-tube and the contact time was kept at 30minutes. The mixture was stirred, decanted and analysed.

3.2.4 Characterization of Refined Oil
Acid Value Determination
1ml of decanted oil from the activated carbon was measured into a 250ml conical flask. Ethanol and petroleum were mixed in the same ratio i.e. 1:1 (50ml of ethanol and 50ml of petroleum ether). 100ml of mixture of ethanol and petroleum ether, they are neutralized solvent. 25ml of above mixture was added to each samples and a phenolphthalein indicator solution was added. The content was titrated with 0.1M of potassium hydroxide until pink colour is observed.

Iodine Value Determination
0.5ml of oil sample was measured into a conical flask; 15ml of chloroform was added and shaken vigorously. Wiji's solution was also added and stirred; it was kept in dark place for 30 minutes. After which the iodine was being added. 3 drops of starch solution was added to the mixture which serves as an indicator and was then titrated with sodium thiosulphate until a colourless solution was observed. The above procedure was done on each sample.

Saponification Value
1ml of oil sample was measured into a conical flask; 25ml of alcoholic potassium hydroxide was added to the sample. It was heated for 30minutes and 1ml of phenolphthalein solution was added as an indicator and the solution was titrated with 0.5M of hydrochloric acid. The above procedure was done on each sample.
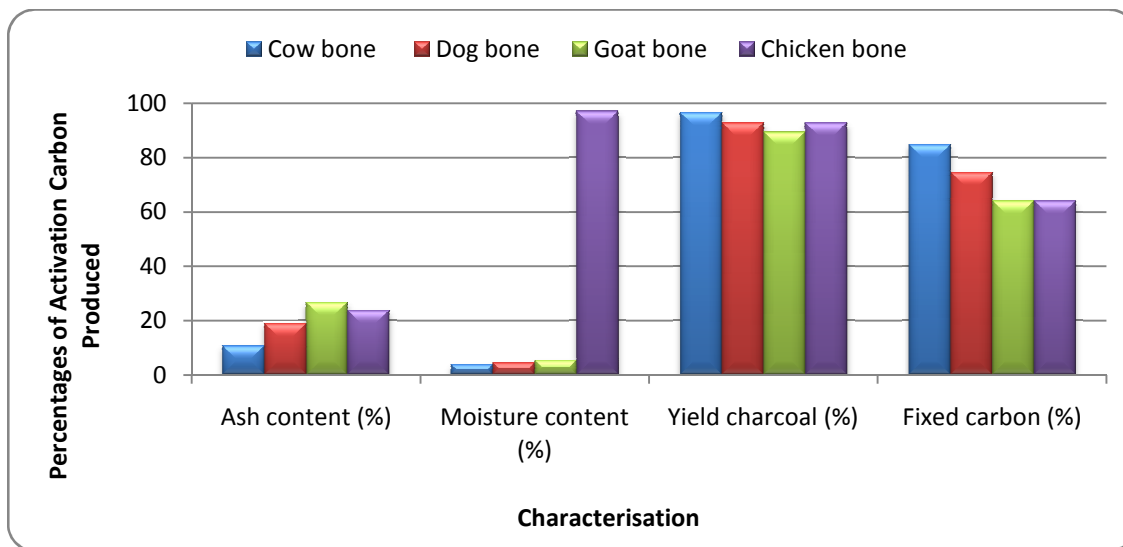
RESULTS

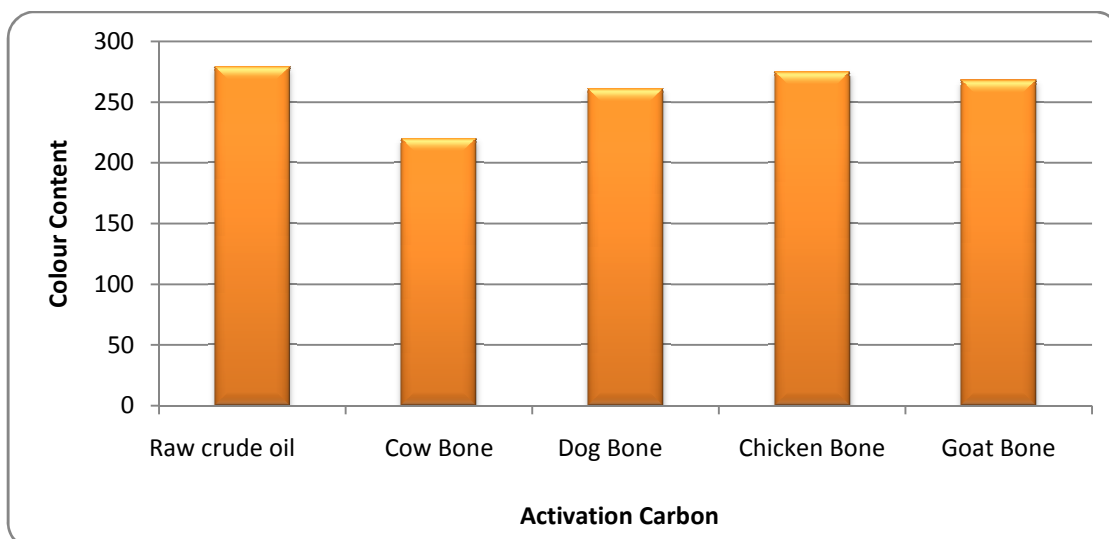**Figure 1: The characterization of activated carbons produced**

Figure 2: Bleaching performance for different absorbents on the palm oil Conversion factor (pt-co) 700.
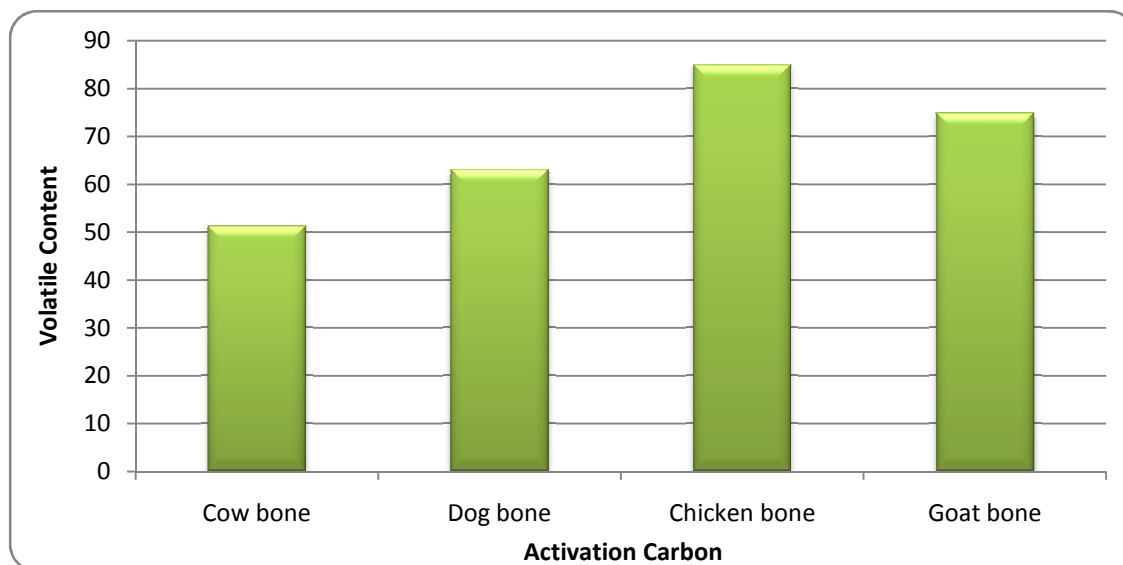

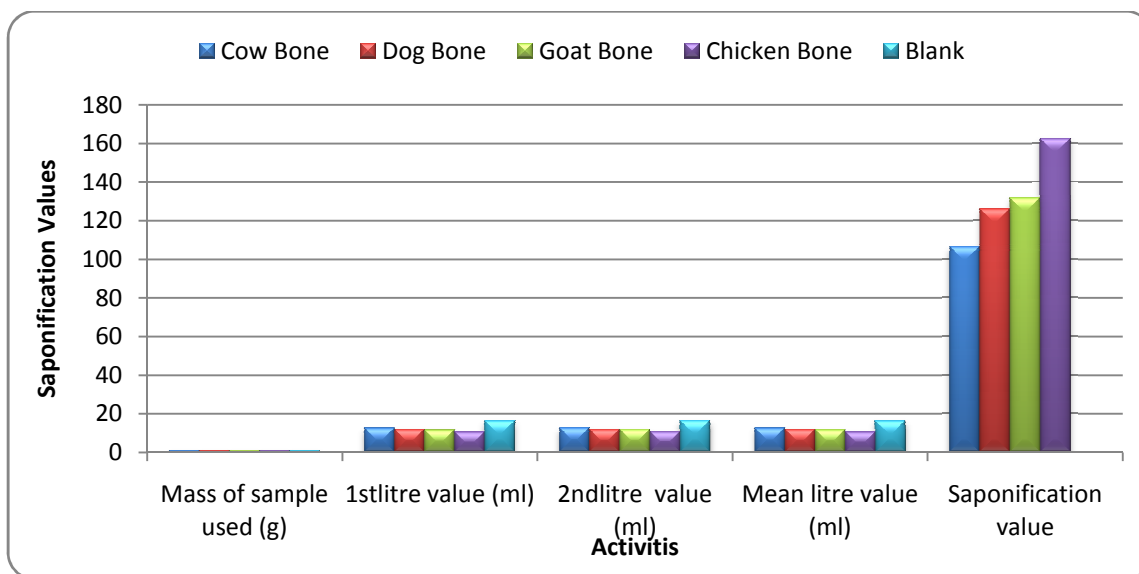**Figure 3: Volatile content of various bones**

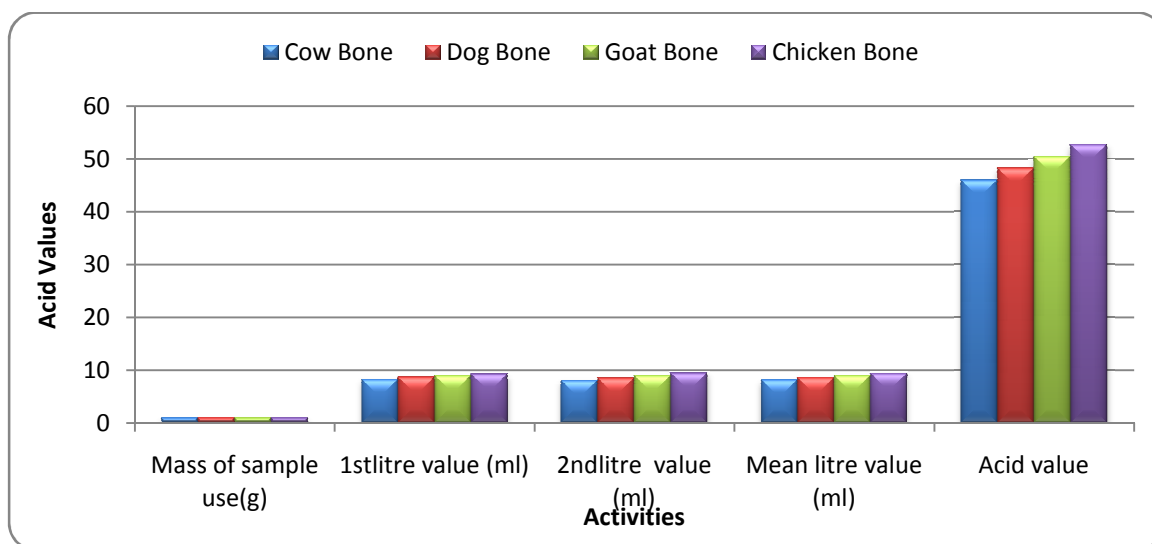**Figure 4: Saponification value of the bleached oil**
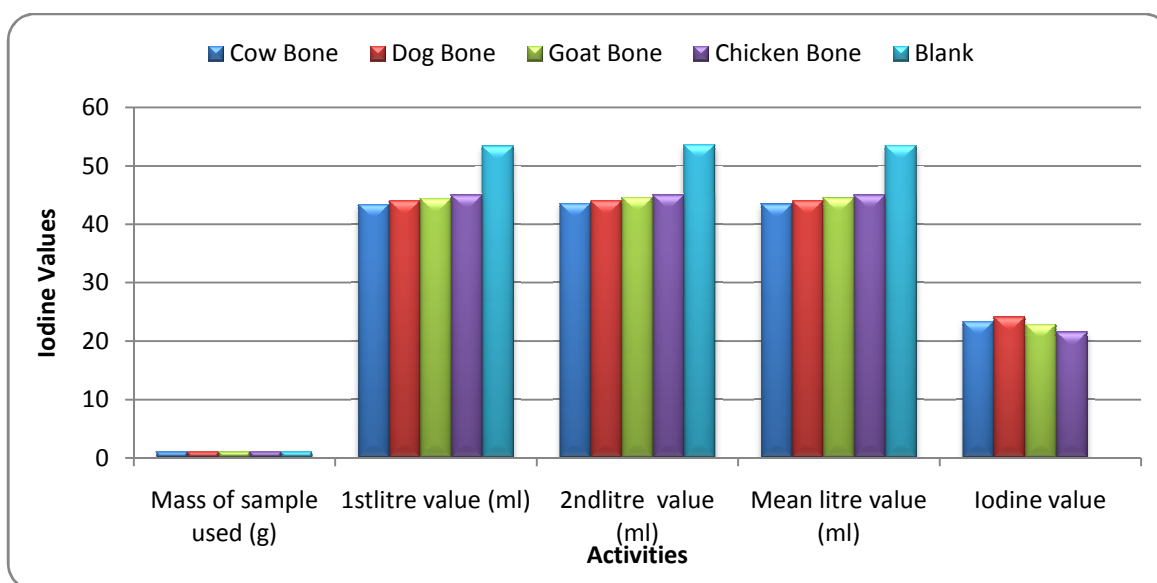

Figure 5: Acidity value of the bleached oil

Figure 6: Iodine value of bleached oil

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RESULTS AND DISCUSSION

Details of results obtained are shown in the appendix. Figure 1 shows the characterization of activated carbon produced from cow bones, dog bones, goat bones and chicken bones respectively. Bones was carbonized at 400 °C and sieved with particle size of 212 μm, it was observed that activated carbons from cow bones has the best values in its ash content (10.75 %), moisture content (3.9 %), pure volume (0.30), yield charcoal (96.58 %) and fixed carbon (84.83 %). Hence, the most effective adsorbent must posse's low properties of ash content, moisture content and pure volume. Higher are the property yields of charcoal, fixed carbon and bulk density. The higher the surface area and the carbon content,themore effective the activated carbon produced. Figure 2shows the rate of the bleaching performance of the samples. The adsorbent (cow bones) gave a better bleaching of 220 (pt-co), compared with the colour of raw oil before bleaching of about 279 (pt-co), the dog bones of 261 (pt-co), goat bones of 275 (pt-co) and chicken of about 275 (pt-co). The sample with the lowest number of colouration shows a better bleaching capacity in which cow bones produced the lowest in colouration.Figure 3 describes the rate of the volatile content of the bones samples, 85 % for chicken bones, 74.9 % for goat bones, 63.1 % for dog bones and cow bones has the lowest volatility of about 51.3 %. Figure 4 is the saponification value of the bleach sample, with chicken bone giving the highest value of 162.69, followed by goat bones of 131.84, dog bones of about 126.23 and cow has the lowest saponification value of 106.59.Figure 5 shows the acid value of the bones, which shows that cow bone has the least acid value, and thus of better quality. Figure 6shows the iodine value of the bleached oil in which chicken bones has the lowest value of iodine 21.573 and cow bones has the highest value of iodine 25.33. The results obtained depicted that the cow bone is richer in iodine content.

Table 1: Summary of the characterization of activated carbons produced.

Activated carbon	Cow bone	Dog bone	Goat bone	Chicken bone
Weight of samples (g)	2	2	2	2
Particle size (μm)	212	212	212	212
Ash content (%)	10.75	19.00	26.75	23.75
Moisture content (%)	3.9	4.5	5.4	97
Yield charcoal (%)	96.58	92.75	89.33	92.8
Fixed carbon (%)	84.83	74.56	64.01	64.02
Pore volume	0.30	0.38	0.52	0.46
Bulk density	2.56	2.24	2.32	2.32

Table 4: Results for Saponification value of the bleached oil

Activated carbon	Mass of sample used(g)	1stlitre value(ml)	2ndlitre value(ml)	Mean litre(ml)	**Saponification value**
Cow Bone	1.00	12.60	12.80	12.70	**106.59**
Dog Bone	1.00	12.00	12.00	12.00	**126.23**
Goat Bone	1.00	11.70	11.90	11.80	**131.84**
Chicken Bone	1.00	10.60	10.80	10.70	**162.69**
Blank	1.00	16.40	16.60	16.50	

Table 5: Results for acidity value of the bleached oil

Activated carbon	Mass of sample use(g)	1stlitre value(ml)	2ndlitre value(ml)	Mean litre value(ml)	**Acid value**
Cow Bone	1.00	8.30	8.10	8.20	**46.002**
Dog Bone	1.00	8.70	8.50	8.60	**48.246**
Goat Bone	1.00	9.00	9.00	9.00	**50.490**
Chicken Bone	1.00	9.30	9.50	9.40	**52.734**

Table 6: Result for iodine value of bleached oil

Activated carbon	Mass of sample used (g)	1stlitre value(ml)	2ndlitre value (ml)	Mean litre value(ml)	**Iodine value**
Cow Bone	1.00	43.40	43.60	43.50	**23.38**
Dog Bone	1.00	44.00	44.00	44.00	**24.11**
Goat Bone	1.00	44.40	44.60	44.50	**22.84**
Chicken Bone	1.00	45.00	45.00	45.00	**21.57**
Blank	1.00	53.40	53.60	53.50	_

CONCLUSION

The results obtained from the research conducted into the production, characterization and analysis of adsorbents obtained from the animal bone showed that they meet the standards for use as commercial adsorbents with regards to the yield charcoal, moisture content, fixed carbon and pore volume. Cow bone showed the lowest pore volume of 0.30, showing its greater adsorbent quality. Furthermore,the bleaching capacity of activated carbon produced from cow bones gave the lowest value of 220 (pt-co), compared to the values obtained from the chicken bones, goat

bones and dog bones, which shows that is more effective in the decolourization of palm oil. Therefore, the activated carbon from cow bones is more effective than those from dog bones, goat bones and chicken bones.

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