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Proximate and Ultimate Analysis of Walnut Shell as a Potential Low Cost Adsorbent using Different Activating Agents (KOH and H_2SO_4)

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Abstract The need to eradicate toxic or unwanted elements present in the environment has given rise to the use of low cost adsorbents. The feasibility of walnut shell as a low cost adsorbent was analyzed via Proximate and Ultimate analysis using two chemically activated agents (KOH and H_2SO_4). The walnut sample was carbonized at a temperature of 564 ºC for one hour and allowed to cool at room temperature for two hours after which the shells were crushed and sieved to various particle sizes. The proximate and ultimate compositions of the samples were determined in accordance with ASTM methods while the physical properties were determined by qualitative and quantitative methods. The results of the physical properties investigated were; pH (7.7 and 6.9), bulk density (573.9 kg/m^3 and 542.7 kg/m^3), pore density (700.5 kg/m^3 and 673.8 kg/m^3 porosity (81.93% and 80.54%), density (635 kg/m^3 and 612.1 kg/m^3), specific surface area (871 m^2/g and 819 m^2/g) for KOH and H_2SO_4 activated walnut shells respectively. The proximate and ultimate analysis gave the following results; % fixed carbon (68.39 and 62.23), % moisture content (13.72 and 16.59), % volatile matter (11.40 and 13.51), % ash content (6.49 and 7.69), % Hydrogen (2.91 and 2.69), % Nitrogen (1.87 and 1.83) KOH and H_2SO_4 activated walnut shells. The percentage Methylene blue removal was found out to be 91.96% and 74.85% for KOH and H_2SO_4 activated walnut shells. The results obtained showed that activated carbon produced from walnut has an excellent adsorptive capacity while KOH performs better than H_2SO_4 in processing activated carbon materials.

Keywords Adsorption, Low-cost adsorbent, Activating agents, Analysis

1. Introduction

As a result of increased domestic, agricultural and industrial activities perpetrated by humans, there is the presence of various toxic elements in the ecosystem which pose a threat to man, his health and the environment at large. To protect humans from this pollutants and toxins, various materials have been investigated to see how they can be used to remove these pollutants from the ecosystem. A large number of suitable adsorbents such as activated carbon, polymeric resins or various low cost adsorbents (non-modified or modified cellulose biomass, chitin, bacterial biomass, etc.) have been studied. Adsorbents are solid substances, usually porous in nature, with a high surface area, that can adsorb chemical substances onto its surface by intermolecular forces, and the process of attracting chemical substances onto the surfaces of adsorbents is called adsorption [1]. Adsorption is present in many natural, physical, biological and chemical systems, and is used extensively in industrial process for the purpose of separation and purifications. Though, there are many commercially available adsorbents for the removal of contaminants, most of these adsorbents are synthetic, with high cost implications. The high cost of commercial adsorbents, especially activated carbons restricts their uses and applications [2], and hence the need to substitute them with the unconventional, relatively cheaper, readily affordable, easily assessable, environmentally friendly and locally

sourced adsorbent cannot be over emphasized. One of such material is walnut shell. Walnut shell is an agricultural waste product and as such has no significant use. Results of some studies showed that walnut shell as an agricultural waste has cellulose structure with low-cost of raw materials and suitable physical properties for the production of activated carbon [3]. There are basically two methods used in the activation of activated carbon. They are the physical activation and the chemical activation. Chemical activation has gained more grounds than physical activation since it gives rise to better adsorbents. The most commonly used activating agents include $ZnCl_2$, KOH, H_3PO_4,H_2SO_4 etc [4]. The main aim of this paper is to evaluate and study the feasibility of walnut shell as a potential low cost adsorbent using different activating agents via its physicochemical properties.

2. Methodology

The raw material, walnut shells were collected from Mile 1 market, Port Harcourt, Rivers State, Nigeria while the activating agents and other chemicals used in the course of the experiment were purchased from a chemical store in Port Harcourt.

In this paper, walnut shell was used as the carbonaceous source material for preparation of the activated carbon. Potassium hydroxide (KOH) and Tetraoxo sulphate VI acid (H_2SO_4) were used as the chemical activating agents as they are the most effective compounds for the production of activated carbons.

The shells were washed and rinsed thoroughly with distilled water, air-dried, and later oven dried at 105℃ for 15 minutes. The oven dried sample was carbonized to obtain the carbonized biomass [5].

The carbonization of the air dried walnut shell was carried out using a muffle furnace (Carbolite Sheffield England LMF 4) which allows limited supply of air. Carbonization of the walnut shell samples was performed at 564 ℃ for one hour and allowed to cool at room temperature for two hours after which the shells were ground to particle sizes of 0.5mm before activation with Potassium Hydroxide (KOH) and Tetraoxosulphate VI acid (H_2SO_4) respectively.

About 200cm^3 of 0.5mol/dm^3 of Potassium Hydroxide and Tetraoxosulphate VI acid were poured into two distinct beakers containing 100 ± 0.1g each of two samples of carbonized walnut respectively. The content of the beakers was thoroughly agitated for one hour. The mixture was then transferred to an evaporating dish which was placed in a furnace and heated at 300℃ for thirty minutes. This was allowed to cool and washed 4 times with distilled water to a pH of 6.7 ± 1.0, oven dried at 105℃ for 20 minutes to constant weight. It was then sieved with a 106 µm mesh to obtain a fine powdered activated carbon which was kept in an air tight sample bottle and used for various tests.

The proximate and ultimate compositions of the samples were determined in accordance with ASTM analytical methods while the physical properties were determined by qualitative and quantitative methods.

Characterization of Raw Activated Carbon

The following characteristic properties of activated walnut were studied

2.1. Determination of pH

The standard test method for determination of activated carbon pH was used. 1.0g of walnut activated carbon activated by KOH and walnut activated carbon activated by H_2SO_4 respectively were weighed and transferred into a beaker. 100ml of distilled water was measured and added and stirred for 20 minutes. The samples were allowed to stabilize before the pH was measured using a pH meter and samples were run in triplicates [6].

2.2. Determination of Bulk Density

A 100ml beaker was weighed and labelled w_1 and then filled with 100mL of KOH activated walnut sample, weighed and recorded as W_3. The volume of the cylinder was recorded as w_2. The same procedure was carried out for the H_2SO_4 activated sample.

The bulk density was calculated using the formula:

$$\text{Bulk density} = \frac{w_3 - w_1}{w_2} \quad (1)$$

2.3. Determination of Pore Density

A 100mL beaker was weighed and labelled W_1. 100mL of activated carbon is then turned into a 100ml beaker and bumped for about 20-30 minutes until all the pores were filled thereby leaving space above the sample contained in the beaker. The sample was then filled and bumped continuously until it reached the 100mL mark of the beaker. The weight of the sample after bumping plus that of the beaker was weighed and recorded as W_3 while the volume of the beaker was recorded as W_2. This procedure was run in duplicate for each sample of KOH and H_2SO_4 impregnated walnut shells**.** The pore density was calculated using the formula

$$\text{Pore density} = \frac{w_3 - w_1}{w_2} \quad (2)$$

2.4. Determination of Porosity and Tortuosity

The porosity of samples of KOH and H_2SO_4 impregnated walnut shells were calculated using the formula

$$\text{Porosity} = \frac{\text{Bulk density}}{\text{Pore density}} \quad (3)$$

While the tortuosity was calculated using the formula below for both samples

$$\text{Tortuosity} = \frac{1}{\text{Porosity}} \quad (4)$$

2.5. Determination of Specific Gravity

The weight of a cleaned, dried and empty pyconometer was weighed and recorded as w_1. Pure distilled water was filled into the pyconometer and the weight of the water plus pyconometer was weighed and recorded as w_2. The water was then poured out and filled with activated carbon sample, the weight of the pyconometer and biomass was weighed and recorded as w_3. The specific gravity procedure run in duplicate for both samples of KOH and H_2SO_4 impregnated walnut shells and was calculated with the formula:

$$\text{Specific gravity} = \frac{w_1 - w_3}{w_1 - w_2} \quad (5)$$

2.6. Determination of Density

The density of activated carbon was calculated by dividing the known weight of the sample that filled the pyconometer by the measured volume of that same sample. This was carried out for both samples of KOH and H_2SO_4 impregnated walnut shells.

$$\text{Density} = \frac{\text{Mass of biomass}}{\text{Volume of biomass}} \quad (6)$$

2.7. Determination of Surface Area

The surface area of the walnut shell sample is estimated using the Sear's method. 1.5g of the sample was measured and dissolved in 100mL distilled water. The mixture was then properly agitated by stirring, the Pasteur pipette was used to add little quantities of concentrated HCl to the mixture until a pH of 3 was obtained and 2-3 drops of phenolphthalene was added to the mixture. The solution was titrated with 28ml of 0.1M of NaOH to the initial pH of 7. The volume (titre reading) was then recorded. This procedure was carried out in duplicate for both samples of KOH and H_2SO_4 impregnated walnut shells

$$\text{Surface area} = (32 \times \text{Titration Volume}) - 25 \quad (7)$$

2.8. Determination of Methylene blue Number

Methylene blue number is correlated with ability of activated carbons to adsorb colour and high molecular weight substances. It was measured by the extent of adsorption in milligrams of methylene blue adsorbed by 2 grams of activated carbon in equilibrium with a solution of methylene having a concentration of 2.0mg/L. 1200 mg/l methylene blue stock solution was prepared. The sample was diluted to give 2.0M concentrations.

Proximate Analysis

The proximate analysis of walnut activated carbon sample was followed by the procedure given below [6].

2.9. Moisture Content

20g of the sample was put in a crucible, covered with a lid and weighed using a weighing balance. The crucible was placed in the hot air oven at 105℃ with its lid removed and dried for 1.30 hrs. The crucible was taken out, immediately covered with the lid, cooled in a desiccator and weighed. This was carried out for both samples of KOH and H_2SO_4 impregnated walnut shells. The percentage moisture content was calculated as follows:

$$\text{Moisture (\%)} = \frac{\text{Loss in weight on drying}}{\text{Initial sample weight}}(g) \text{ x } 100 \qquad (8)$$

2.10. Ash Content

The standard test method for ash content-ASTM D2866-94 was used. The crucible was pre-heated in the muffle furnace at 750+ 25℃ for 1.5 hours. The crucible was placed in the desiccator, cooled to room temperature and weighed. 20g of the sample which was dried in the hot air oven at 150℃ for 3 hours was put in the crucible and the crucible was placed back in the muffle furnace at 750±25℃for 1.5 hours. The crucible was taken out of the furnace, placed in the desiccator, cooled to room temperature and weighed. This was carried out for both samples of KOH and H_2SO_4 impregnated walnut shells. The percentage ash content was calculated as follows [6]:

$$\text{Ash (\%)} = \frac{\text{Ash weight}}{\text{Oven dry weight}}(g) \text{ x } 100 \quad (9)$$

2.11. Volatile Matter Content

20g of sample was put in the crucible. The crucible was placed in a muffle furnace at 920+10℃, covered with lid, and placed for exactly 7 minutes. The crucible was taken out, allowed to cool and weighed. This was carried out for both samples of KOH and H_2SO_4 impregnated walnut shells. The volatile matter was calculated as follows [7]

$$\text{VM (\%)} = \frac{\text{Weight of volatile matter}}{\text{Oven dry weight}}(g) \text{ x } 100 \quad (10)$$

2.12. Fixed Carbon

After the ash was separated, what was left was carbon; percentage fixed carbon was then calculated by subtracting the sum of volatile matter, moisture content and ash from 100 [6].

Fixed carbon = 100 – (VM+ MC + ash) (11)

Ultimate Analysis

Ultimate analysis which involves the determination of carbon and hydrogen, nitrogen, sulphur and ash were also determined based on the American Society of Testing and Materials (ASTM) D3178, D3179 and D3177 standards. The oxygen was obtained by subtracting the percentage of ash, carbon, hydrogen, nitrogen and sulphur from 100.

2.13. Determination of Hydrogen and Nitrogen content

The relationship below was used to calculate the Hydrogen and Nitrogen content for both samples of KOH and H_2SO_4 impregnated walnut shells.

Table 1: Relationship between ultimate and proximate parameters

	%C	=	0.97C + 0.7(VM – 0.1A) – M(0.6-0.01M)
	%H	=	0.036C + 0.086 (VM – 0.1 x A) – 0.0035M^2(1-0.02M)
	$\%N_2$	=	2.10 – 0.020VM
Where			
	C	=	% of fixed carbon
	A	=	% of ash
	VM	=	% of volatile matter

3. Results and Discussion

The results of the physicochemical properties, proximate compositions, ultimate composition and percentage methylene blue removal number are presented in Table 2,3,4 and 5 respectively.

Table 2: Physicochemical composition of KOH and H_2SO_4 activated walnut shells

Parameters	KOH activated walnut shells	H_2SO_4 activated walnut shells
pH	7.7	6.9
Bulk Density (kg/m^3)	573.9	542.7
Pore Density (kg/m^3)	700.5	673.8
Porosity(%)	81.93	80.54
Tortuosity	1.2205	1.2416
Specific gravity	0.6667	0.6299
Density (kg/m^3)	635.0	612.1
Specific Surface Area (m^2/g)	871	819

Table 2 lists the values of pH, bulk density, pore density, porosity, tortuosity, specific gravity, density and surface area determined for KOH and H_2SO_4 activated walnut shells respectively.

The pH of a substance is a numeric scale used to know how acidic or basic a solution is with a pH of 7 being neutral. The pH of a solution from which adsorption occurs influences the extent of adsorption. Because, hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. The majority of colored materials encountered with the industry are negatively charged and ordinarily carbons will give greater decolourisation with increase in acidity of the solution, the pH of the adsorbent itself is an important factor, as this may affect the pH of the liquid. The pH of chemically activated (using KOH and H_2SO_4) walnut samples are near neutral which will be helpful for the treatment of all classes of dye, waste water and drinking water purification as well as removal of heavy materials. It can be seen that the pH of H_2SO_4 impregnated walnut has a better pH value than that of KOH impregnated walnut although that of KOH is still well within the limits. The pH values obtained are in the range of acceptable limit.

Bulk density refers to the weight per unit volume of sample. It provides a bird eye view regarding the floatability property of the adsorbent [8]. It suggests that if the activated carbon is added to water it will sink and that with result in better contact with the adsorbate and thereby leading to effective adsorption process. From the table above, the bulk density of KOH activated walnut shell (573.9 kg/m^3) is greater than that of H_2SO_4 activated walnut shell (542.7 kg/m^3), therefore more adsorbate can be adsorbed via the KOH activated walnut sample as a result of better contact time as it sinks in the solution.

Porosity is one of the main factor for increasing the adsorptive power of an activated carbon. Porosity is related to the bulk density and specific gravity of activated carbon. Porosity describes the number of pores present in a sample [9]. Porosity therefore enhances adsorption capacity of the adsorbent. From the table 2 above, porosity is in the order KOH activated walnut shell > H_2SO_4 impregnated walnut shell. H_2SO_4 and KOH decompose the tissue of the carbon precursor; it also creates some new pores and voids. The activating agent permeates these tiny pores or voids, which increase the contact area between the activating agent and the carbon precursor. Consequently, this promotes the release of volatiles from the carbon structure and widens the micro pores in the original carbon structure, converting them into mesopores. The pores produced by KOH activation is greater than that produced by the H_2SO_4.

From previous studies, it has been established that the extent of adsorption increases with the increase in surface area of the adsorbent [10]. Hence finely powdered metals and porous substances having large surface areas perform well as adsorbents. Consequently, KOH activated walnut with a larger specific surface area of $871m^2/g$ than that of H_2SO_4 activated walnut with a surface area of $819m^2/g$ will pose as a better adsorbent.

Table 3: Proximate composition of KOH and H_2SO_4 activated walnut shells

Parameters	KOH activated walnut shell	H_2SO_4 activated walnut shell
Fixed Carbon (%)	68.39	62.23
Moisture content (%)	13.72	16.59
Volatile matter (%)	11.40	13.51

The proximate analyses as presented in Table 3 showed a low amount of moisture, ash and volatile matter, indicating that the particle density is relatively small and that the biomaterial should be an excellent raw material for adsorbents to be used in column or fixed-bed reactors for both samples. Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of
reactivation, the lower the ash value therefore the better the activated carbon for use as adsorbent [11]. The both samples (KOH and H_2SO_4 activatedwalnut shells) were found to be rich in moisture and volatile matter. However, the moisture and volatile content were found to decrease from H_2SO_4 activated walnut shell to KOH activated walnut shell. During carbonization and activation processes, organic substances become unstable as a result of the heat causing the molecules to break their bonds and linkages [12]. During activation step, volatile matter is released as gas and liquid products which evaporates off leaving a material with high carbon content.

As can be seen from Table 3, the proximate composition depends not only on the precursor i.e. the walnut shell, it also depends on the activating agent used (as KOH and H_2SO_4 activated walnut samples both bring about different results). Therefore, the kind of activating agent used is also to be noted. The activated carbon prepared by H_2SO_4 activation show higher values of volatile content, ash content and moisture content than the activated carbon prepared by impregnation of KOH. Consequently, the activated carbon prepared by KOH has a higher content of fixed carbon. Ash is non-carbon or mineral additives, that does not combine chemically with the carbon surface. It consists of various undesired mineral substances, which become more concentrate on activation and comprises of 1-20 % and primarily depends on the type of raw material. High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity [13].

Table 4: Ultimate composition of KOH and H_2SO_4 activated walnut shells

Parameters	**KOH activated walnut shell**	**H_2SO_4 activated walnut shell**
Carbon(%)	68.39	62.23
Hydrogen(%)	2.91	2.69
Nitrogen(%)	1.87	1.83

Concerning the ultimate composition, the content values of carbon are consistent with those of fixed carbon. H_2SO_4 impregnated walnut < KOH impregnated walnut based on the carbon content. The same sequence is followed for the Hydrogen content. As expected, the Nitrogen content is low for both samples.

Table 5: Percentage removal of methylene blue

Activated Carbon	**Initial dye conc. (mg/L)**	**Final dye conc. (mg/L)**	**% Removal of methylene blue**
KOH activated walnut shells	3.71	0.298	91.96%
H_2SO_4 activated walnut shells	3.71	0.933	74.85%

The methylene blue value represents the adsorptive capacity of activated carbon for molecules with dimension similar to methylene blue and the surface area which results from the presence of pore sizes greater than 1.5 nm. From the table above, it is quite obvious that the percentage removal of methylene blue is higher for KOH activated walnut sample (91.96%) than H_2SO_4 activated walnut sample (74.85%). This is directly proportional to the surface areas of the both samples. KOH activated walnut sample which has a higher surface area and porosity yields an adsorbent with more ability to adsorb methylene blue.

4. Conclusion

The results obtained showed that chemically activated walnut shell (using KOH and H_2SO_4 activating agents respectively) is an excellent adsorbent due to its high % fixed carbon, high surface area, large porosity, low % ash content with KOH proving to be a better activating agent than H_2SO_4.

Percentage removal of Methylene blue dye was used as a yardstick to determine the adsorption capacity of walnut shell. KOH activated walnut sample removed 91.96% of Methylene blue dye while H_2SO_4 activated walnut sample removed 74.85% of the same concentration of Methylene blue dye. This result also showed that walnut activated

carbon is a good adsorbent with high adsorption capacity when activated with the right activating agent. The prepared activated carbon derived from walnut shell using KOH activating agent compared favorably to walnut shell using H_2SO_4 activating agent. The study to develop adsorbents from agricultural wastes will among several benefits contribute to measures for decreasing the environmental degradation caused by dumping of agricultural wastes.
The physicochemical, proximate and ultimate properties of activated walnut shell based adsorbent indicate its potential use as an adsorbent for applications in treatment system.

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