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Production of Activated Carbon from Pilli Nut (Canarium Ovatum) using Steam Activation Method

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ABSTRACT
Commercial activated carbon is a wide range of carbonized materials of high degree porosity and high surface area. Activated carbon has many applications in the environment and industry for the removal, retrieval, separation and modification of various compounds and dyes in liquid and gas phases. It is a highly effective absorbent that can be used to remove micropollutants from water. As a result, the demand for activated carbon is increasing. Pilli nut shell has been considered as a hazardous solid waste in the environment. The wasted Pilli nut shell should be used as a low cost source of activated carbon adsorbent. In this study, we investigated the optimum manufacturing conditions for producing activated carbon from ligneous wastes generated from pill nut. Activated carbon was produced from Pilli nut shell by using steam activation in a high temperature muffle furnace. Fast pyrolysis process was carried out prior in fixed bed furnace to produce char before activation process. Experiments were conducted to investigate the influence of various process parameters such as particle size, pyrolysis temperature (300^{o}C, 350^{o}C and 400^{o}C) and activation time on the quality of the activated carbon. In addition, the batch adsorption studies were done by using methylene blue. Pilli nut shells were selected as raw materials. Carbonization and steam activation were performed in a fixed-bed laboratory electric furnace. The optimum conditions for producing activated carbon from pilli nut shells were 1hr, 2 hr and 3hr (carbonization at 300^{o}C, 350^{o}C and 400^{o}C) followed by 1hr, 2hr and 3hr (activation at 300^{o}C, 350^{o}C and 400^{o}C) respectively. The experimental data fitted well with the Langmuir model of adsorption, indicates monolayer coverage of dye molecules at the outer surface of pilli nut carbon. Pilli nuts shell was found to be a viable raw material for the preparation of activated carbon. However, the quality of the activated carbon synthesized was highly dependent on the preparation condition. From the result of the present work, it can be said that smaller size of the sawdust, higher pyrolysis temperature and longer activation time will exhibit a better result in the removal of methylene blue.

Keywords: Activated carbon, Char, Pilli nut shell, methylene blue, raw material

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1. INTRODUCTION

Adsorption in solids is one of the most effective methods for water purification and pollution management in the atmosphere and water, with activated carbon being the most extensively used adsorbent in industry. Global consumption of activated carbon has increased at a compound annual rate of 5.5 percent over the last decade, and this trend is expected to continue in the coming years (8.1 percent in 2018). Due to rapid industrial development and high population growth, the implementation and improvement of drinking water treatment systems, the increase in vehicle ownership rates, the intensification of agriculture, and the expansion of environmental regulations to manufacturing industries, has increased the demand for activated carbon and has surged as a result of new uses, one of which is the growing interest in using these adsorbents to reduce heavy metals emissions from coal-fired power stations.

Another application of activated carbon that is now drawing attention is its use as an adsorbent in post-combustion systems for CO_2 emission reduction and capture (Plaza *et al.,* 2014). Furthermore, the use of activated carbon electrodes in supercapacitors, which take advantage of the electrode's microporous structure to reduce electrical resistance and improve energy storage performance, is on the rise, fueled by a strong desire to develop a new generation of batteries that will significantly boost the electric car (Farma *et al*., 2013). Finally, multiple studies have shown that activated carbon improves agricultural soil fertility, resulting in increased crop yields. Its application as an amendment can result in significant reductions in N_2O, NH_3, and nitrogen leachates (Knowles *et al.,* 2011).

Activated carbon is a type of adsorbent made from carbonaceous materials that have a disordered crystallographic structure with randomly scattered microcrystals. This microcrystalline structure is made up of basic elements like graphene sheets, fullerene, and quasi-graphitic fragments. However, on a macroscopic scale, this microcrystalline arrangement does not extend, resulting in a disorganized and extremely nanoporous structure. As a result, these materials have a large specific surface area (500-1500 m^2/g), a wide range of functional groups (carboxylates, carbonyls, hydroxyls, amines), and a pore size distribution (one to one hundred nanometers). All of these features contribute to their exceptional ability to adsorb a wide range of compounds (Zhang *et al.,* 2014).

Physical activation and chemical activation are the two primary methods for producing activated carbons. Physical activation is the most prevalent method of producing activated carbon. There are two stages to this process. The precursor material is pyrolyzed in an inert environment at a medium-high temperature (300-800 °C) during the first stage, known as carbonization. The volatile component of the precursor material, which is generated by permanent gases and tars, is released during this process, and a carbonaceous residue enriched in carbon aromatic rings, known as char, with a porous structure, is obtained. Because some of the chemicals produced during decomposition, primarily tars, re-polymerize and condense on the surface of the particle, filling or clogging the pores, this initial porosity has a low adsorption capacity. As a result, a subsequent activation cycle is necessary, in which these tar deposits are removed, therefore boosting the current porosity and adsorption capacity.

Char is activated at a higher temperature (700-1000 °C) in the presence of an activating agent in the second step. During this process, the carbonaceous matrix of the fuel undergoes numerous heterogeneous reforming processes in a reducing environment, resulting in partial gasification of the char, which develops a huge porous structure and increases its specific surface area. The following processes occur during the initial stage of the activation process: removal of tar deposits, opening of rudimentary pores generated during pyrolysis, and formation of new pores. Pore-widening becomes the major effect over a long activation period, while pore deepening and new pore production are substantially inhibited. As a result, more meso and macropores emerge, and BET surface area and pore volume decrease as activation time increases (Zhang et al., 2014).

Because of the endothermic nature of their reactions, carbondioxide and steam are the most commonly used activation agents. Carbon dioxide is generally used because of its reduced reactivity at high temperatures, making the activation process easier to manage. Furthermore, carbondioxide activation favors microporosity development in the early phases of activation, but steam activation favors microporosity widening, therefore activated carbons made with steam have a lower micropore volume at the expense of greater meso and macropore volumes (Molina-Sabio *et al*., 1996). In any case, the partial pressure of the gasifying agent and the conditions of the activation process are the most important factors in the development of the microporous structure, and thus, depending on the precursor material and process conditions, both CO_2 and steam can be suitable gasifying agents (Aworn *et al*., 2008; Rambabu *et al.,* 2015).

A chemical activation procedure can also be used to create activated carbon. The precursor is impregnated with activating chemical agents such as KOH, H_3PO_4, or $ZnCl_2$ in this case. The precursor is then carbonized at moderate temperatures (550 °C) and the resulting activated carbon is washed to eliminate any remaining activator traces and to recover the chemical agent for subsequent generation cycles of activated carbon. Activated carbon has traditionally been made from wood, nuts, coal, petroleum wastes, lignite, and polymers, all of which are very expensive and non-renewable, with the exception of wood. As a result, scientific interest in the manufacture of activated carbon from byproducts and biomass wastes (so-called activated biochar) has developed in recent years (Ahmad *et al.,* 2016; Rajapaksha *et al.,* 2016; Tan *et al.,* 2016) in the search for renewable and cost-competitive alternatives.

When compared to standard activated carbon, the key advantage of alternative-source activated carbon is its high availability and low cost. Furthermore, tests conducted with these alternative activated carbon materials in a variety of applications (e.g., water purification, elimination of polluting gases, heavy metal removal,) have shown that they perform at least as well as commercial activated carbon or other much more expensive alternatives like carbon nanotubes and graphene (Tan *et al.,* 2017). Since 2000, numerous studies have been carried out in the experimental field using a diverse range of residual biomass precursor materials (corn, rapeseed, barley, almond shells, walnut, pistachio, peanut, acorn, rice, palm, olive pomace, cherry bones, date bones, bamboo, cotton stalks, miscanthus, sicyos etc), with the field of study currently expanding.

The majority of published investigations on the physical activation process focus on preparing activated carbons from residual biomass sources, improving the parameters of the activation process with carbon dioxide or steam, and subsequent physical and chemical characterisation (Bouchelta *et al.,* 2008; Okutucu *et al.,* 2011; Demiral *et al.,* 2011; Sahin, and Saka, 2013). A far lesser number of studies (Lua *et al.,* 2006; Bouchelta *et al.,* 2012) have looked at the impact of the carbonization process conditions on the subsequent activation stage.

Finally, studies have concentrated on the maximizing of certain carboxyl, hydroxyl, and amino functional groups that can be coupled with metals via ion exchange, complexation, or electrostatic attraction for specific purposes such as heavy metal adsorption. The main aim of this work is to determine the physicochemical properties of activated carbon produced and the optimum manufacturing conditions for producing activated carbon from ligneous wastes generated from Pilli nut.

2. MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

The Pilli nuts were purchased at Eke Alulu market in Enugu, eastern part of Nigeria. They crushed into smaller granules and was later ground into fine particles. The powdered form of the samples were sieved using 0.250μm sieve in civil engineering department of the University of Ilorin, Nigeria. The material was pyrolysized in a fluidized bed furnace at different temperature range.

The pyrolysis process was undergone at temperature 300, 350 and 400^{o}C for half an hour. Then, the char produced was discharged from the first cyclone of the fluidized bed furnace. This pyrolysis method produced variety of char at different temperature and time. Activation of the char was done by using steam average flowrate 300cc/min at temperature 300, 350 and 400^{o}C in a muffle furnace for 1 and 2 hours (Sathe *et al.,* 2021) .

2.2 Carbonization and Activation

The crushed Pilli nuts were weighed and packed at 200 g per sample and placed in the furnace.The crushed, weighed, carbonized sample was activated.

2.3 Procedure for Activation

The Pilli nut was crushed and carbonized using the specially designed furnace, nitrogen gas was passed through the furnace instead of oxygen gas not to allow the sample from turning into ash at some fixed temperatures and time. After which the carbonized samples were cooled, weighed and also re-weighed for activation. The re-weighed carbonized samples were placed in the furnace and nitrogen gas was passed through the furnace to avoid the carbonized samples from turning into ashes. This was done at a fixed time and temperatures (Alstrom *et al.,* 2019).

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameters

Physicochemical parameters of powdered raw Pilli nuts shell, Carbonized char and activated carbon were presented Tables 3.2., 3.3a, 3.3b and 3.4 The parameter studied are bulk density, moisture content, ash content, pH, conductivity, lignin, extractive fibre, crude fibre and cellulose content for the raw sample.

3. Physicochemical Properties of Raw samples of fine Pilli nuts

It can be deduced from Table 3.2 that the powdered raw Pilli nut shell is acidic and has higher tendency of conducting heat and electricity. The moisture content obtained is within acceptable limit. This shows that the Pilli nut can be used to produce effective activated carbon which can be applied in the industry.

Table 3.2: Physicochemical properties of raw ground Pilli nuts

S/N	SAMPLE 1	SAMPLE 2	SAMPLE 3
pH	5.994	5.985	5.990
Conductivity	233.4	242.6	230.8
Moisture Content (g)	15.04	14.05	27.44
Cellulose content (g)	22	64	10
Crude Fiber	2.6	2.0	0.9
Extractive Fiber	5.7	6.2	9.0
Lignin (%)	84	11.8	21.4
Bulk density (g)	1.192	1.184	1.188

3.3 Physicochemical Properties of Char and Activated Carbon

Tables 3.3a and 3.3b below shows the experiment carried out on Pilli nut shells which was activated and done three times (300^{o}C, 350^{o}C, and 400^{o}C) 3hrs each respectively. It is slightly acidic and has a high conductivity which means it can conduct electricity and contains some soluble ions in its solution.

Burn off and solid yield

The char and activated carbon produced were weighed to determine the burn off or mass loss due to the pyrolysis and activation processes. The results of the calculated burn off rates and yields for char, produced during pyrolysis step are shown in Tables 3.3a and 3.3b. The expression “burn off” stands for the percentage of the total mass lost during each of the two steps of the activation process. It refers either to the conversion of the pilli nut shell into char (pyrolysis step) or the gasification of char to activated carbon (activation step). This includes the mass lost during both the pyrolysis and gasification (activation) steps relative to the initial mass of the pili nut shell (Leng *et al.,* 2021).

PH of Char And Activated Carbon

pH is a measure of how acidic or basic, water or a solution is. This ranges from 0-14, with 7 being neutral. pHs of less than 7 indicate acidity, whereas a pH of greater than 7 indicates a base it's a real measure of free active amount of free hydrogen and hydroxyl ions in water or solutions. pH is important in solution quality assessment as it influences many biological, physical and chemical processes within a solution and water body. The pH for both char and activated carbon were slightly alkaline, but activated carbon has a stronger alkaline pH than the char. This may be due to further indirect gasification of the char during activation. It is a known fact that variations in pH affect physical, chemical and biological processes in water and solutions. Low pH increases the adsorptive power of activated carbon when being applied.

Conductivity of Char and Acivated Carbon

Electric conductivity is the ability of substance or material to conduct electric current and is related to the amount of dissolved minerals in water and solution but does not give an indication of which metal or ions present. It is also the measurement of the electric conductance per unit distance in an electrolytic or aqueous solution and shows the property of a porous materials' (e.g char and activated carbon) ability to transmit soluble ions in water. The ability to conduct heat is measured as microSiemen per centimeter (µS/cm). The conductivity value for the char ranges from 0.22 µS/cm - 0.91µS/cm which is too low as shown in Table 3.3a but increases after activation. The activated carbon has a high conductivity greater than that of char and it ranges from 42.9 µS/cm – 91.4 µS/cm which is a high conductivity compared with the char. Analysis was done at different temperatures (300^{0}C, 350^{0}C and 400^{0}C) and time (1hr, 2hr and 3hr) respectively.

Bulk Density of Char And Activated Carbon: Bulk density being the property of powders, granules and other divided solids is used to determine how compact the char or activated carbon is in the air or is a measure of the mass of the char/activated carbon per volume. It is not an intrinsic property of material because it can change depending on how the material is being handled. The bulk density of char ranges from 0.59g/ml- 0.65g/ml while that of activated carbon ranges from 0.56g/ml – 0.62g/ml, which when compared with the char falls within the same value range.

Table 3.3a: Physicochemical Properties of Char

TEMP (^{o}C)	300			350			400		
Time (sec)	1hr	2hr	3hr	1hr	2hr	3hr	1hr	2hr	3hr
M_i (g)	200	200	200	200	200	200	200	200	200
M_f (g)	82.32	85.57	88.67	83.26	85.08	83.92	83.69	87.44	82.32
Yield (%)	58.84	57.22	55.67	58.37	57.46	58.04	58.16	56.28	58.84
Degree burn off (%)	41.16	42.78	44.33	41.63	42.54	41.84	41.84	43.72	41.16
Moisture content (%)	6.8	7.0	8.4	6.0	5.6	6.2	6.4	6.2	6.0
Bulk density (g/mL)	0.62	0.59	0.62	0.61	0.61	0.65	0.61	0.65	0.60
pH	7.9	7.3	7.0	7.4	7.3	7.2	7.6	7.7	7.3
Conductivity	0.44	0.34	0.44	0.58	0.36	0.91	0.52	0.22	0.48

Table 3.3b: physicochemical properties of Activated Carbon.

EXPERIMENT	300°C	350°C	400°C
Bulk density (g/mL)	0.62	0.61	0.56
Moisture content (%)	6	5.4	5.8
pH	8.4	8.5	8.2
Conductivity (µS/cm)	74.3	91.4	42.9
W_i (g)	40	40	40
W_f (g)	30.22	31.28	31.52
Yield (%)	0.24	0.22	0.21
Degree Burn off (%)	99.76	99.76	99.78

3.4 calibration curve of Methylene Blue

Table 3.4 shows the UV scanning of methylene blue solutions at different concentration. They were scanned under UV Spectrophotometer to get the Absorbance and the wavelength. The maximum wavelength was 688. The methylene blue solutions were prepared and added to them were different masses of activated carbon. This determines how effective the activated carbon can remove the methlene blue or remove colour from the aqueous solution.The higher the absorbance, the more effective is the activated carbon.

Table 3.4: Absorbance and Wavelength of methylene blue

Concentration (mg/L)	Absorbance	Wavelength
0	0	0
3	0.132	664
6	0.215	665
9	0.295	681
12	0.330	688
15	0.452	685
18	0.480	683
20	0.486	674

4. CONCLUSION

Pilli nut shell that is a waste of Pilli processing and consummation could be a recommendable source of activated carbon production to absorb micropollutants from waste water. Pilli nuts shell was found to be a viable raw material for the preparation of activated carbon. From the result of the present work, it can be concluded that smaller size of the sawdust, higher pyrolysis temperature and longer activation time will exhibits a better result in the removal of methylene blue. However, the quality of the activated carbon synthesized was highly dependent on the preparation condition. The main goal is to investigate the optimum manufacturing conditions for producing activated carbon from ligneous wastes generated from Pilli nut.

The optimum condition in this study for the preparation of activated carbon in Pilli nut, pyrolysized at 400^{o}C and activated with steam at 400^{o}C for 2 hours. The effects of parameters, such as temperature, activation time, pH condition and other physicochemical properties have effect on the activated carbon preparation. In addition, the present study showed that Pilli nut was considerably efficient in the removal of methylene blue from aqueous solution. The experimental data were fitted well with the Langmuir model of adsorption, which indicates the monolayer coverage of dye molecules at the outer surface of Pilli nut carbon.

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