

Production and Characterization of Activated Carbon from Agricultural Waste (Rice-husk and Corn-cob)

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Abstract: In Nigeria, a lot of material is wasted during the processing of Rice and Corn in terms of the by-products. This study was therefore undertaken to explore the possibility of utilizing rice-husk and corncob in production of activated carbon by steam oxidation and chemical activation processes. The activated carbon produced were characterized by determining their surface area, pore volume, ash content, bulk density, fixed carbon content, carbon yield and porosity. Result showed that steam oxidation process as compared with chemical activation process produced the best activated carbon with corncob carbon being the best in terms of surface area, pore volume and better adsorption capacity. Also, corncob carbon produced from steam oxidation proved to be effective adsorbent in a test conducted with phosphate containing water.

Key words: Activation, carbon, oxidation, adsorption and phosphate

INTRODUCTION

Activated carbon is an amorphous form of carbon, which is specially treated to produce a very large surface area ranging from 300 to 2000 m² g⁻¹. This large surface area implies that the internal pore structure has been very highly developed; it is this structure, which provides activated carbon with the ability to adsorb gases and vapour from gases and dissolved or dispersed substances from liquids. Two distinct types are recognized commercially namely, liquid phase (decolourizing carbon) is generally light fluffy powders and gas phase or vapour adsorbent carbons are hard, dense granular or pellets (Dietz *et al.*, 1944).

Almost any carbonaceous material of animal, vegetable, or mineral origin can be converted into activated carbon if properly treated. Activation is a physical change through which the surface of the carbon is tremendously increased by the removal of hydrocarbon. The properties of the finished materials are governed not only by the raw materials but the method of activation used. The most important physical property is the surface area (Austin, 1984). There is no activated carbon that is effective for all purposes. The applications of activated carbon include-solvent recovery processes, adsorption from by-products stream, vacuum technology, adsorption gas chromatography, catalyst supports and electrode material in electrochemistry, the increasing awareness of

the necessity for environmental safety and pollution control has opened new prospects for activated carbon (Harikrishnan *et al.*, 1998).

Adsorption is a popular method for treating aqueous effluents, which are important for by-product water re-use and conservation. The presence of nutrients in by-products water aggravates eutrophication of water bodies receiving by-products water. Therefore, removal of nutrients in by-products water before discharge is an effective method for control of eutrophication in stream and receiving water. The most important growth-limiting nutrient in wastewater is phosphate specialized tertiary treatment method such as adsorption and precipitation are utilized for phosphate removal from by-products water. Adsorbents in use include activated alumina, powdered aluminum oxide, activated red mud, fly ash blast furnace slag and other materials (Gangoli *et al.*, 1973; Shiao *et al.*, 1977). These adsorbent are however not easily and/or economically available, hence much research interests have been on the investigation of the adsorption characteristics of locally available and economical materials (Bhargava *et al.*, 1993).

Hence, in this study, agricultural by-product namely, rice-husk and corncob were used in producing the activated carbon. The choice of this raw material is based on the idea of developing low-cost adsorbent for water or waste water treatment as well as reducing the effect of environmental degradation posed by agricultural by-product show in Table 1.

Table 1: Surface area, pore volume and mean pore radii for typical solid catalysts (Hassler, 1951 and Schweitzer, 1979)

Catalyst	Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Mean pore radii A°
Activated carbon	500-1500	0.6-0.8	10-20
Activated clays	150-225	0.4-0.52	100
Silica gel	200-600	0.4	15-100
Activated alumina	175	0.39	45
Celite (Kieselguhr)	4.2	1.1	11,000
Fused Copper	0.23	-	-

MATERIALS AND METHODS

Samples:

- Rice-husk: sourced from Otukpo rice mill, Benue State, Nigeria.
- Corn-cob: sourced from a farmhouse at the outskirts of Kaduna, Nigeria.

Chemical activation: One hundred grams of the raw material was mixed with an aqueous solution of ammonium sulphate (activating chemical) made by dissolving 50 g of ammonium sulphate in 300ml of distilled water. The mixture was heated in a mechanical heating mixer at a temperature of 120°C for 3 h to vapourize the water, after which the content was extracted and dried for 12 h. The dried raw material was carbonized in the absence of air in furnace at a temperature of 550°C for 60 min and cooled for 30 min. It was subsequently dried and sized.

Steam activation: One hundred grams of raw material was cleaned and carbonized in a reducing atmosphere to eliminate the bulk of the volatile matter and then loaded into a steam bed. Passing steam at a pressure of 10 bars for 1 hour to develop the porosity and surface area, after which the sample material was dried for 12 h and sized.

Characterization: Characterizing parameters determined were: Surface area, pore or void volume, ash content, volatile content, moisture content, fixed carbon, bulk density, carbon yield and porosity.

Surface area determination: The external surface area per unit volume of a spherical particle of diameter (dp) was calculated from the relation.

$$S_g = \frac{6(m^2 \text{ kg}^{-1})}{\rho_p d_p}$$

Pore (void) volume determination: A known weight of 1.96 g of each of the activated Carbon was immersed in water and boiled for 15 min. After the air in the pores has

been displaced the samples were superficially dried and reweighed. The increase in weight divided by the density of water gives the pore volume.

Ash content determination (Dara, 1991): Two grams of dry sample was placed into a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 900°C. The furnace was left on for one hour after which the crucible and its content was transferred to a desiccator and allowed to cool. The crucible and content was re-weighed and the weight noted. If w_o is the dry weight of the sample and W_{ash} is the constant weight after final drying, then the % ash content (dry basis) is given by:

$$\text{Ash} = \frac{100W_{\text{ash}} (\%)}{W_o}$$

Moisture content determination: Two grams of each sample was weighed and dried in a drier continuously. The drying sample was constantly reweighed at a 10 min interval until a constant weight was obtained. The ratio of the change in weight to the original weight expressed in percentage gives the moisture content given by:

$$\frac{W_o - W_{\text{sh}} (\%)}{W_o}$$

Volatile content determination (Fapetu, 2000): Two grams of the carbon sample each was heated at about 900°C for 10min in a partially closed porcelain crucible placed in a muffle furnace. The crucible and its content was retrieved and cooled in a desiccator.

The difference in weight (W_p) was recorded and the volatile content (VC) determined from:

$$\text{VC} = \frac{(2 - W_p) (\%)}{W_o}$$

Where W_o¹ = oven dry weight of 2 g of Carbon.

Carbon yield determination (Fapetu, 2000): The dried weight, W_o, of each carbon sample was determined. The carbon yield, y_{ch} was determined by:

$$Y_{\text{ch}} = 100W_{\text{ch}}/W_o$$

Where

W_{ch} = weight of Carbon retrieved from the furnace.

W_o = Dried weight of the Carbon sample.

Fixed carbon determination (Fapetu, 2000; Hsisheng, 1998): By assuming that the sulphur content was negligible in all cases. The fixed Carbon Content (FC) is given as:

$$FC = (Y_{ch} - U - VC - Ash) / Y_{ch} (\%)$$

Where

VC = Volatile Content (%)

Ash = ash content (%)

U = moisture content (%)

Y_{ch} = Carbon yield (%)

Bulk density (Apparent density) determinations (Alexeyev, 1998): This provides a method for determining the packed density of a bed of granular activated carbon. It is calculate from the relation.

$$\text{Bulk density (B.d)} = \frac{\text{weight of activated carbon (g mL}^{-1}\text{)}}{100}$$

Adsorption Experiment: This was carried out to study the adsorption isotherm, which was expressed in terms of the Freundlich isotherm. In this experiment, standard phosphate solutions were prepared by dissolving 1 g of anhydrous potassium phosphate in distilled water (Meites, 1963). Seventy five milliliter of 0.5 g L⁻¹ of the potassium phosphate solution were placed in 100 mL bottle with adsorbent doses of 2 g L⁻¹. The contents were shaken in a vertical shaker for 3 h to attain equilibrium concentration. After equilibrium the contents of the bottle were filtered through Whatman No. 1 filter paper and analyzed for residual phosphate concentrations (APHA *et al.*, 1992). The above set of experiments was repeated at other phosphate concentrations of 0.25 g L⁻¹, 0.125 g L⁻¹ and 0.031 25 g L⁻¹. (Ochonogor *et al.*, 2000).

Contact time experiment: This was carried out to determine the rate of phosphate removal as the adsorbent dose and time were varied. In the experiment, 200 mL of 5 g L⁻¹ of anhydrous potassium phosphate were transferred to a 400ml beaker. Thereafter, doses of 1.2 and 3 g of the various activated carbon samples from both the chemical activation and steam oxidation processes were introduced into a beaker and stirred magnetically at moderate speed (Hisashi, 1982).

At time intervals of 5, 20, 25 and 30 min, 5 mL portions was collected and the initial and residual phosphate concentrations were determined by the vanadomolybdophosphoric acid colorimetric method (APHA *et al.*, 1992).

RESULTS AND DISCUSSION

The result of the chemical activation and steam oxidation processes of rice-husk and corncob are in Table 2 and 3, while the rate of phosphate adsorption were presented in Table 4 and 5. as well as in Fig. 1 to 4.

Table 4 and 5 comparison of the rate of phosphate adsorbed at varying times and adsorbent dose.

Table 2: Characterization of rice-husk activated carbon

Parameters	Steam oxidation Process	Chemical activation Process
Surface area (m ² kg ⁻¹)	1.77×10 ⁵	1.62×10 ⁵
Pore volume (m ³)	4.47×10 ⁻⁶	3.95×10 ⁻⁶
Bulk density (kg m ⁻³)	339.1	369.6
Ash content (%)	33.90	48.20
Moisture content (%)	5.0	4.5
Volatile content (%)	0.03	0.06
Carbon yield (%)	33.91	48.20
Fixed carbon content (%)	84.2	89.5
Void fraction/porosity (×10 ⁻⁶)	1.52	1.46

Table 3: Characterization of corn-cob activated carbon

Parameters	Steam oxidation Process	Chemical activation Process
Surface area (m ² kg ⁻¹)	4.06×10 ⁵	2.05×10 ⁵
Pore volume (m ³)	4.37×10 ⁻⁶	3.72×10 ⁻⁶
Bulk density (kg m ⁻³)	147.6	292.4
Ash content (%)	14.75	29.30
Moisture content (%)	10.5	6.0
Volatile content (%)	0.04	0.06
Carbon yield (%)	14.80	29.24
Fixed carbon content (%)	27.8	78.3
Void fraction/porosity (×10 ⁻⁶)	0.645	1.09

Table 4a: For 1 g of rice-husk and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	50	3
10	52	5
15	56	6
20	56	8
25	60	14
30	64	26

Table 4b: For 2 g of rice-husk and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	52	24
10	52	28
15	60	28
20	60	28
25	64	28
30	68	32

Table 4c: For 3 g of rice-husk and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	64	12
10	66	18
15	70	26
20	72	40
25	76	42
30	78	58

Table 5a: For 1 g of corn-cob and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	68	74
10	76	78
15	76	80
20	96	92
25	100	94
30	100	100

Table 5b: For 2 g of corn-cob and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	88	88
10	96	100
15	100	100
20	100	100
25	100	100
30	100	100

Table 5c: For 3 g of corn-cob and 5 g L⁻¹ of phosphate concentration

Contact time (min)	Percentage of phosphate adsorbed	
	Steam oxidation	Chemical activation
5	100	86
10	100	100
15	100	100
20	100	100
25	100	100
30	100	100

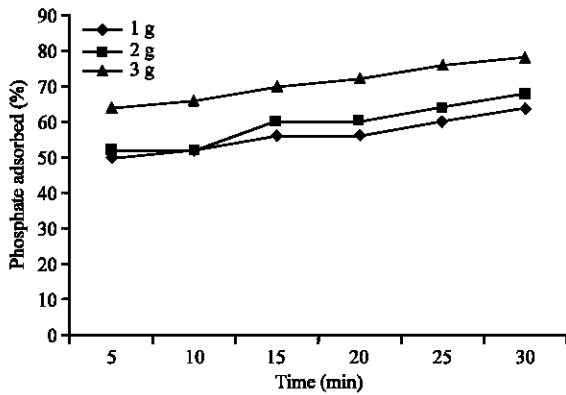


Fig. 1: Rate of Phosphate Adsorbed at varying Time for Steam Oxidation (Rice-husk)

The result of analysis of Table 2 and 3 show that activated carbon produced by corn-cob has the highest surface area of 406 m² g⁻¹, which is quite close to those of a commercial activated carbon of 500 m² g⁻¹ as seen in Table 1.

The bulk density for the two processes complete favourably with standard values of 0.24-0.78 for liquid and gas phase carbon, except corncob carbon from steam oxidation process (Dietz *et al.*, 1944).

The pore volume for both rice-husk and corncob for steam oxidation compete favourably with standard values of commercial carbon of 0.4-1.1.

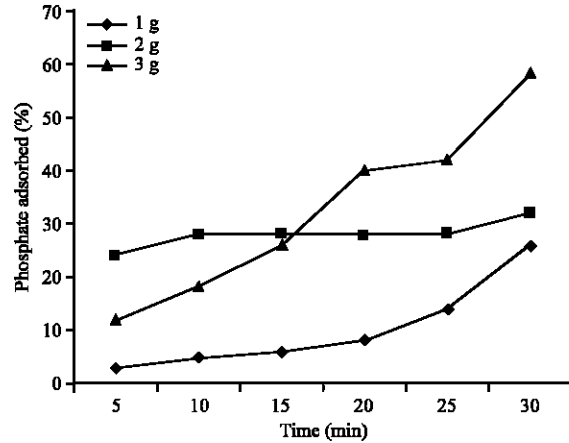


Fig. 2: Rate of Phosphate adsorbed at varying Time for Chemical Activation (Rice-husk)

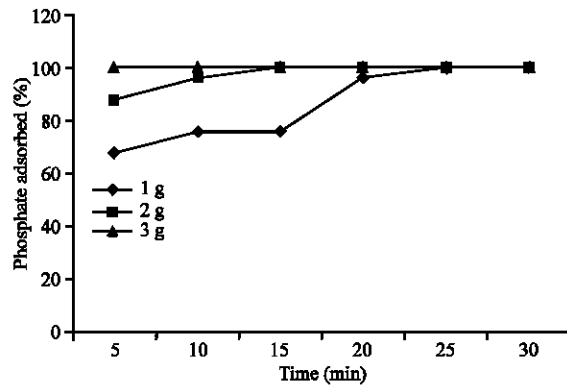


Fig. 3: Rate of Phosphate adsorbed at varying Time for Steam Oxidation (Corn-cob)

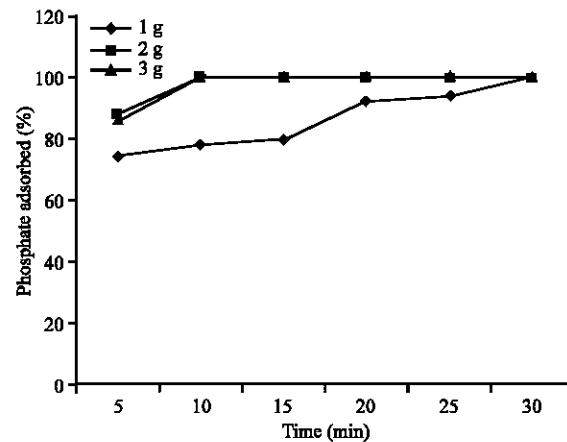


Fig. 4: Rate of Phosphate adsorbed at varying Time For Chemical Activation (Corn-cob)

The ash content with chemical activation process resulting to higher ash content of 48.20% for rice-husk. This is an indication of the level of impurity present in it. (Zadok *et al.*, 1985; Meites, 1963).

The moisture content of carbon from steam oxidation process has the highest moisture content of 10.50% for corncob while chemical activation process has a least moisture content of 4.5% for rice-husk.

The volatile content present in the carbon for the two processes are within the close range, however, both processes meet up with permissible volatile content of 0.6-1.4% for blast furnace coke (Wolfson, 1978).

The fixed carbon content data show that chemical activation process gives the highest carbon yield of 89.50% for rice-husk, while steam oxidation process has the least of 27.8% carbon yield for corncob. This implies that the chars of carbon produced by steam oxidation process are more carbonized than those of the chemical activation process during the pyrolysis operation (Foley, 1986).

The adsorption rate was closely studied in Table 4 and 5 with carbon produced from chemical activation and steam oxidation processes, respectively. It was observed that, the rate of phosphate removal varies with the various adsorbent doses of 1, 2 and 3 g L⁻¹ with initial phosphate concentration of 5 g L⁻¹.

Between 5 and 30 min, the percentages of phosphate removal for chemical activation process were 26, 32 and 58% for rice-husk and 100% for corncob at various adsorbent doses of 1, 2 and 3 g L⁻¹.

Similarly, the rate of adsorption for steam oxidation process between 5 and 30 min were 64, 68 and 78% for rice-husk and 100% for corncob with doses of 1, 2 and 3 g L⁻¹. A close look on the above results show that carbon produced by steam oxidation process gives a better percentage of phosphate removal, with corncob carbon ranking the best adsorbent. This could be due to its larger surface, which gives it a highly developed internal pore structures.

Finally, the natures of the plots are indicative of the nature of formation of the layers on the adsorbent surface. The time variation curves for phosphate removal were smooth and continuous, indicating the formation of monolayer coverage on the surface of the adsorbent (Ochonogor *et al.*, 2000).

CONCLUSIONS

The activated carbons produced from agricultural by-products were characterized and their performance was determined using phosphate adsorption studies. The results showed that activated carbon produced from corn-cob by steam oxidation process had a surface area comparable to those of commercial ones as can be seen from Table 2 and 3.

The carbon produced by steam oxidation process gave higher phosphate removal efficiency than carbon samples produced by chemical activation process, which

shows that method of activation can affect the properties of activated carbon produced.

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