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Effect of activation methods on the surface properties of carbonized biomass derived from fluted pumpkin stem (*Telfairia occidentalis Hook F*) waste

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ABSTRACT

The effect of chemical activation methods on some surface properties of carbonized biomass produced from fluted pumpkin waste was investigated using three activating reagents: H_3PO_4, $ZnCl_2$ and H_2O_2. The surface properties studied were moisture content, sodium sorption capacity and iodine number. The surface properties of activated carbon were compared with that of the pure carbonized sample. The results obtained shows that the sample activated with H_3PO_4 (AM) with a sodium sorption capacity of 1.52 mmol/g was the most effective for the adsorption of sodium and other cations from solution, while the sample activated with $ZnCl_2$ (BM) with sodium sorption capacity of 1.07 mmol/g has the least affinity for sodium. The iodine number determination also shows that the sample activated with H_2O_2 (NM) has the highest porosity with an iodine number of 60.3 mg/g I_2. This implies that chemically activated carbon produced from fluted pumpkin waste could be utilized as low-cost, economic and environment friendly biosorbents for the removal and recovery of metals and other cations in solution.

Keywords: Activated carbon, activation methods, surface property, fluted pumpkin.

INTRODUCTION

Activated carbon has been widely used as adsorbents, catalyst/catalyst supports, electronic material and energy storage materials due to its high surface area and large pore volume. The specific surface area, pore structure and functional groups of activated carbon determine its applications (Figueiredo et al., 1999). The large pore structure and the high surface area of activated carbon could be controlled by various routes, such as, activation condition (activation agent, temperature and time), precursor etc, while the functional groups are mainly derived from

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activation process, precursor, heat treatment and chemical post treatment.

The functional groups found on the surface of activated carbon mainly contain oxygen, nitrogen, hydrogen, halogen etc. These heteroatoms bond (chemical activation) to the edges of the carbon layer and governs the surface chemistry of activated carbon (EL–Sayed and Bandosz, 2004). Among these heteroatoms, the oxygen containing functional groups (also known as surface oxides) are the widely recognized and the most common species formed on the surface of carbons, which significantly influence their performance in sensor (Lukaszewicz, 1999), energy storage and conversion system (Frackowiak and Beguin, 2001; Chen et al., 2004) and adsorption (Feron and Jansen, 1997; Li et al., 2002). The surface oxygen containing functional groups could be introduced by mechanical, chemical and electrochemical routes (Pittman et al., 1997; Hu and Wang, 2004). These modified surface oxides have been reported to enhance acidic property and improved the hydrophilic nature of activated carbon, which have been favourable for the adsorption of polar molecules.

While nitrogen containing groups could be introduced by ammine treatment, nitric acid treatment or some nitrogen containing molecule reacting with the precursor material especially nitrogen polymers (Carret et al., 2001). The nitrogen containing functional groups generally provide basic property, which enhances the attraction between activated carbon and acid molecule, such as dipole-dipole, H-bonding, covalent bonding and so on. In addition, halogen containing groups could be introduced through activated carbon reacting with halogen at moderate temperature; this modified activated carbon shows potential application in electrochemistry (Perez-Cadenas et al., 2003).

A modified activated carbon containing different functional groups has been used for technological applications such as extracting metallic cations from aqueous and non-aqueous solutions, in catalysis, for treatment of waste and toxic effluents produced by varieties of chemical processes. Based on the many applications of activated carbon, the need to modify as well as to characterize the surface functional groups of carbon materials is on the increase especially using agricultural by- products (wastes) as precursor material (Kadirvelu et al., 2000). Some of the agro-wastes that have been successfully converted to activated carbons include coconut shell (Toles et al., 1999), cassava waste (Horsfall and Abia, 2003), pecan shell (Bansode et al., 2003), wild Cocoyam (Horsfall and Spiff, 2005a, 2005b), just to mention a few. As reported, simple chemical modifications have been shown to markedly enhance the metal ion binding capacity of agricultural by – products (Bansode et al., 2003,). Moreso, the preparation of activated carbon from agricultural wastes has potential economic and environmental impacts. First, it converts unwanted low-value agricultural waste to useful, high-value adsorbents. Second, activated carbons are increasingly used in water to remove organic chemicals and metals of environmental and/or economic concern (Johns et al., 1998).

Fluted pumpkin stem waste has been used for activated carbon production because it is cheap and readily available. Literature research revealed that several tons of stem wastes are produced daily in market places and in homes all over Nigeria, but are scarcely useful. A single stem with leaves weighing 12 kg produces less than 200 g of leaves, leaving over 11 kg stem as waste and therefore create an environmental nuisance (Horsfall and Spiff, 2005b). Therefore, the purpose of this study is to investigate the effect of chemical activation methods on the surface properties of carbonized biomass of fluted pumpkin (*Telfairia occidentalis Hook F*) stem waste.

Abbreviations

AM --Acid Modified, H_3PO_4

- BM---Base Modified, $ZnCl_2$
- NM--Neutral Reagent Modified, H_2O_2
- PC---Pure Carbonized Fluted Pumpkin Waste Biomass

MATERIALS AND METHODS

Adsorbent

The adsorbent used for this work is the stem waste of fluted pumpkin (*Telfairia occidentalis Hook F*) obtained from a local market at Agudama – Epie in Yenagoa Local Government Area of Bayelsa State, Nigeria. The fluted pumpkin wastes were washed with distilled water, sun-dried, cut into pieces, dried in an oven for 2 days at a temperature of 80–100 ^oC to a constant weight and carbonized at an optimum temperature of 550 ^oC for two hours. The carbonized sample was ground into a fine powder using mortar and pestle. This powder was divided into 2 portions. The first portion was left as pure carbonized fluted pumpkin waste (PC) while the second portion of the powder was taken for activation.

Activation of sample

The activating reagents employed for this work were:

- Orthophosphoric Acid, H_3PO_4
- Zinc Chloride, $ZnCl_2$
- Hydrogen Peroxide, H_2O_2

25.00 ± 0.01 g each of carbonized sample was weighed and transferred into three different beakers containing 500 ml of 0.05 M H_3PO_4, $ZnCl_2$ and H_2O_2 respectively. The content of each beaker was thoroughly mixed and heated on a hot plate until it formed a paste and then pyrolysed at 500 ^oC for two hours. After cooling, it was washed with distilled water to a constant pH and dried at 100 ^oC for three hours. Thus, four different adsorbents were produced.

- Fluted pumpkin waste activated with Orthophosphoric acid, H_3PO_4
- Fluted pumpkin waste activated with Zinc chloride, $ZnCl_2$.
- Fluted pumpkin wasted activated with Hydrogen peroxide, H_2O_2.
- The pure carbonized fluted pumpkin waste (PC).

Determination of moisture content

The standard test method for moisture in activated carbon as in ASTM D2867-99 was used. A crucible was dried, cooled in desiccators and weighed. The activated carbon sample was then thinly spread in the crucible and weighed. The crucible was then heated in an air circulation oven at 106 ^oC to constant weight. The moisture content was calculated using the equation 1.

$$\text{MoistureContent}(\%) = \frac{\text{Loss in weight on drying x100}}{\text{Initial sample weight (g)}}$$

Determination of sodium sorption capacity

Sodium sorption capacity was determined in order to compare the total sorption capacity of the activated and pure carbonized carbons for cations. This was achieved by contacting 200 mg (0.2 g) of each sorbent with 25 ml of 0.1 M NaOH and the resultant mixture was allowed to equilibrate on a mechanical shaker for 72 hours. Each mixture was then filtered to remove the adsorbent and the filtrate of each mixture was back titrated with 0.1 M HCl.

Determination of iodine number

One gram (1.0 g) of absorbent was weighed into a sample bottle and 30 ml of 0.1 M I_2 solution was added and the mixture shaken in a mechanical shaker for one hour.

After shaking, the mixture was filtered into a conical flask and titrated against 0.1 M $Na_2S_2O_3.5H_2O$.

RESULTS AND DISCUSSION

Moisture content

The moisture content of the fluted pumpkin stem waste biomass was found to be 68.26%. While the moisture content of the pure carbonized and modified samples are presented in Table 1.

Sodium sorption capacity

The sodium sorption capacities for the various samples of the carbon are presented in Table 2. The sodium sorption capacity for the various samples of carbon was determined to find out the affinity of the various samples of fluted pumpkin waste biomass (activated and pure carbonized) for sodium compounds in aqueous solution.

Iodine number

The iodine number of the carbon samples is presented in Table 3.

Table 1: Moisture content of pure and activated carbon samples.

Sample	Moisture content (%)
AM	16.35 ± 0.22
BM	17.23 ± 0.15
NM	19.03 ± 0.05
PC	21.33 ± 0.32

Table 2: Sodium sorption capacity of activated and pure carbonized samples of fluted pumpkin waste biomass.

Sample	Sodium sorption capacity (mmol/g)	
	Range	Mean ± Std
AM	1.45 – 1.55	(1.52 ± 0.047)
BM	1.05 – 1.10	(1.07 ± 0.024)
NM	1.30 – 1.35	(1.32 ± 0.024)
PC	1.40 – 1.55	(1.47 ± 0.071)

Table 3: Iodine number of activated and pure carbonized samples of fluted pumpkin waste biomass.

Sample	Iodine number (mg/g I_2)
AM	54.3
NM	60.3
BM	59.3
PC	55.3

The moisture content indicates that the volatile materials present in the fluted pumpkin were removed during carbonization. The analyses (Table 1) showed a low amount of moisture, indicating that the particle density is relatively small and that the carbon should be an excellent material for use in column or fixed bed reactors. The moisture contents of the carbon samples are comparable to other materials used for batch analysis (Ekpete et al., 2010; Tarawou et al., 2010).

As indicated in Table 2, the sodium sorption capacity for the various samples were in the range; AM 1.45–1.55 mmol/g (1.52 ± 0.047), BM 1.05–1.10 mmol/g (1.07 ± 0.024), NM 1.30–1.35 mmol/g (1.32 ± 0.024), PC 1.40–1.55 mmol/g (1.47 ± 0.071) respectively. Hence, the Sodium Sorption Capacity of the fluted pumpkin waste biomass follows the order; AM (1.52 mmol/g) > PC (1.47 mmol/g) > NM (1.32 mmol/g) > BM (1.07 mmol/g). The result shows that AM being the most acidic among the samples had the highest sorption capacity for sodium and its compounds, while BM has the least affinity for sodium and its compounds. Thus, this result indicates that acid modified carbon could be a suitable adsorbent for the sorption of sodium and other cations from aqueous solution. Acid treated carbon generally oxidizes the activated carbon surface, it enhances acidic property, removes mineral elements and improves the hydrophilic nature of the carbon surface, thus causing an increase in the total number of surface oxygen - containing functional groups (Figueiredo et al., 1999). The results of this study are similar to those of other researchers (Mostafa, 1997; Moreno et al., 1997).

The iodine number measures the porosity of a material by adsorption of iodine from a solution on it. A sample with a higher iodine number is of higher porosity. Table 3 shows that the iodine number in mg/g follows the order: NM (60.3 mg/g) > BM (59.3 mg/g) > PC (55.3 mg/g) > Am (54.3 mg/g). Thus, the results obtained from this work indicate that, NM with highest Iodine Number (60.3 mg/g) is of the highest porosity among the various samples of the fluted pumpkin waste. This implies that, Neutral Modified (NM) activated carbon will be a good adsorbent where a high micropore content of the adsorbate is needed for adsorption to occur.

Conclusion

Fluted pumpkin (*Telfairia occidentalis Hook F*) stem waste has, all the while, been regarded as waste, thus creating environmental nuisance; but this study has shown that the stem wastes of fluted pumpkin can be processed into activated carbon and utilized as low-cost, economic and environmental friendly adsorbents for the removal of toxic and recovery of valuable metals from solutions and industrial wastewater. Thus, producing activated carbon from fluted pumpkin will help to reduce it as a waste in the environment as well as providing an affordable technology for the manufacture of activated carbon for small and medium-scale industries in Nigeria. Furthermore, the experimental results show that chemical activated samples (e.g. H_3PO_4) of the fluted pumpkin waste biomass would be more effective for the adsorption of sodium and other cations from aqueous solution than the pure carbonized fluted pumpkin waste biomass. NM has the highest iodine number and hence most porous of the carbon samples. BM has the lowest sodium sorption capacity and therefore has the least affinity for sodium and its compounds.

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