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Determination of Sodium Sorption Capacity Using the Boehm Method

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Abstract

Pure carbonized and activated carbons were prepared from fluted pumpkin stem waste. The activating reagents used for this study were: H_3PO_4, $ZnCl_2$ and H_2O_2. Some of the surface properties investigated was surface acidity/basicity and point of zero charge, $_PHpzc$. The surface acidity/basicity was estimated by the multibasic titration method of Boehm and the results obtained show that, the pure carbonized sample (PC) treated with 0.1M of $NaHCO_3$, 0.05M Na_2CO_3 and 0.1M NaOH has the sorption capacities of 0.75mmol/g, 0.56 mmol/g and 0.447 mmol/g respectively. While the acid modified sample (AM) treated with 0.1M $NaHCO_3$, 0.05M Na_2CO_3 and 0.1M NaOH has sorption capacities of 0.413 mmol/g, 0.243 mmol/g and 0.123 mmol/g respectively. These results show that the pure carbonized sample (PC) has higher affinity for acidic species in solution than the acid modified sample (AM). Furthermore, the result obtained from surface basicity shows that, the acid modified sample (AM) with a sorption capacity of 0.233 mmol/g has a higher affinity for basic species in solution than the base modified sample (BM) which has a sorption capacity of 0.0433 mmol/g. The pure carbonized sample (PC) has the strongest basic character with a point of zero charge ($_PHpzc$) of 8.45, while the acid modified sample (AM) has the strongest acidic character with a $_PHpzc$ of 5.82. This study has demonstrated that both the pure carbonized (PC) and the acid and base modified samples of fluted pumpkin stem waste could be utilized as low-cost, economical and environmental friendly biosorbents for the removal and recovery of metals, treatment of odour gases, acidic molecules and some problematic organic molecules from aqueous solution.

Keywords: Activated carbon, surface properties, fluted pumpkin and agricultural waste.

Introduction

Activated carbons are predominantly amorphous solids with large internal surface areas and pore volumes[1]. These unique pore structures play an important role in many different liquid and gas phase applications[2,3]. Furthermore, activated carbons are widely used as adsorbents, catalyst/catalyst supports, electronic materials and energy storage material due to its high surface area and large pore volume[4-5]. Activated carbon can be made from a variety of precursor materials including coal, wood, coconut shell etc. by some form of activation process[6].

Recently, attention has been shifted to agro-waste (agricultural waste) as a source of the preparation of activated carbon. This is due to its low cost, wide availability and good adsorbent properties[7]. All these put together makes the process economically feasible for small scale and large scale industries, researchers and the society at large.

However, a range of agro-wastes have been examined for the production of activated carbon including caladium bicolor[8], cassava bark waste[9], rice husks[10], coconut shell[11] to mention but a few. Also, literature research revealed that fluted Pumpkin (*Telfairia Occidentalis Hook f*) waste has been successfully converted to activated carbon and used in equilibrium sorption of Al^{3+}, Co^{2+} and Ag^{+} in aqueous solution[8].

Inspite of the large market for activated carbon, the choice of raw materials, the development of appropriate methods to make them as good adsorbents and the specific mechanism by which the adsorption of many components especially organics take place on the adsorbents are still ambiguous and challenging[12]. The complete, heterogeneous nature of the activated carbon surface has led to contradicting mechanisms being proposed. As a result, the prediction of adsorption capacity is limited to idealized cases[13]. The heterogeneous surface of activated carbon mainly contains oxygen, nitrogen, hydrogen and halogen. These surface functional groups bonds (chemical activation) to the edges of the carbon layers and govern the surface chemistry of activated carbon[14]. However, the purpose of this study is to investigate some surface properties of pure carbonized and activated carbon from fluted pumpkin stem waste and to determine the ability of the carbons to remove acidic and basic species from aqueous solutions.

Material and Methods

Adsorbent: The adsorbent used for this work is the stem waste of fluted pumpkin (Telefairia occidentalis hook f) obtained from a local market at Agudama – Epie in Yenagoa Local Government Area of Bayelsa State, Nigeria. The wastes were washed with distilled water, sun-dried, cut into pieces, dried in an oven for 2 days at a temperature of 80°C – 100°C to a constant weight and carbonized at optimum temperature of 550^{o}C 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: i. Orthophosphoric acid, H_3PO_4, ii. Zinc chloride, $ZnCl_2$, iii. Hydrogen peroxide, H_2O_2.

25.00 ± 0.01g each of carbonized sample was weighed and transferred into three different beakers containing 500ml of 0.05M 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^{o}C for two hours. After cooling, it was washed with distilled water to a constant pH and dried at 100^{o}C for three hours. Thus, four different adsorbents were produced: i. Fluted pumpkin waste activated with Orthophosphoric acid, H_3PO_4, ii. Fluted pumpkin waste activated with zinc chloride, $ZnCl_2$. iii. Fluted pumpkin waste activated with Hydrogen peroxide, H_2O_2. iv. The pure carbonized fluted pumpkin waste (PC).

Determination of Surface Acidity/Basicity using Boehm Titration Method: One gram (1.0g) of adsorbent was contacted with 15ml solutions of 0.1M $NaHCO_3$, 0.05M Na_2CO_3 and NaOH for acidic groups and 0.1M HCl for basic groups /sites at room temperature for two days. At the end of the required time, the aqueous solutions were filtered and the filtrates were back titrated with 0.1MHCl for acidic groups and 0.1M NaOH for basic groups. According to this method $NaHCO_3$ neutralizes only carboxylic groups; lactones are determined by the difference between the groups neutralized by Na_2CO_3 and $NaHCO_3$ and the difference between the groups[15]. However for the neutralization of basic groups / sites the remaining HCl solution was back titrated with 0.1M NaOH.

Determination of Point of Zero Charge $_P$Hpzc: To measure the point of zero charge, $_P$Hpzc, 0.1g of adsorbent was added to 20ml solution of 0.2M NaCl with an initial pH of 5.63, thereafter, the solution was adjusted to a pH of 6.05 with a solution 0.1M NaOH. Then, the containers were sealed and placed on a shaker for 24 hours, after which the solutions were filtered and the pH of each filtrate was measured. Thus, the point of zero charge pHpzc occurs when there was no change in the $_P$H after contact with the adsorbent.

Results and Discussion

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.

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

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[16,17].

Table 2 shows the surface acidity of activated, pure and carbonized samples of fluted pumpkin waste.

Surface Acidity: The results of the surface acidity of activated and pure carbonized samples of fluted pumpkin waste biomass treated with 0.1M $NaHCO_3$, 0.05MNa_2CO_3 and 0.1M NaOH are shown in table 2. For 0.1M $NaHCO_3$, the result follows the order, PC (0.75mmol/g) >NM (0.630mmol/g) > BM (0.610mmol/g) >AM(0.413mmol/g), while 0.05M Na_2CO_3 results follows the order: PC (0.560mmol/g) > BM (0.323mmol/g) >Nm (0.313mmol/g) > AM (0.23mmol/g) and for 0.1M NaOH, the result follows the order: PC (0.447mmol/g) >BM (0.164mmol/g) >NM (0.147mmol/g) >AM (0.123mmol/g) respectively.

Table-2
Surface Acidity of Activated and Pure and Carbonized Samples of Fluted Pumpkin Waste

	0.1M $NaHCO_3$ (mmol/g)	**0.05M Na_2CO_3 mmol/g)**	**0.1M NaOH (mmol/g)**
Sample	**Range Mean Std**	**Range Mean Std**	**Range Mean Std**
AM	0.400 – 0.420 (0.413 ± 0.009)	0.240 – 0.250 (0.243 ± 0.004)	0.120-0.130 (0.123 ± 0.004)
BM	0.600 – 0.640 (0.610 ± 0.008)	0.310 – 0.340 (0.323 ± 0.013)	0.150-0.170 (0.164 ± 0.008)
NM	0.620 – 0.640 (0.630 ± 0.008)	0.300 – 0.320 (0.310 ± 0.008)	0.1420-0.160(0.147± 0.009)
PC	0.680 – 0.880 (0.75 ± 0.092)	0.520 – 0.600 (0.560 ± 0.033)	0.440-0.460 (0.447 ± 0.009)

AM = Acid Modified, H_3PO_4, BM = Base Modified, $ZnCl_2$, NM = Neutral Reagent Modified, H_2O_2, PC = Pure Carbonized Fluted Pumpkin waste.

The results of surface acidity in table 2 indicates that PC has the highest affinity for the adsorption of acidic components in aqueous solution, while AM exhibited the least affinity for acidic species. Furthermore, the results also show that among the three reagents contacted with the activated and the pure carbonized samples of the fluted pumpkin waste biomass, $NaHCO_3$ is the most favoured reagents for adsorption.

At the edges of the condensed, polyaromatic sheets that constitutes the building blocks of activated carbons, heteroatoms, that is atoms other than carbon are encountered that define the chemical characteristics of activated carbon surfaces. Oxygen is an important heteroatom that commonly occurs in the form of carboxylic acid groups, phenolic hydroxyl groups and quinine carbonyl groups. Activated carbons assume an acidic character when exposed to oxygen between 200 to 700^0C or to oxidants such as nitric acid, or nitric and sulphuric acid mixtures in aqueous solution. The increased acidity is primarily explained by the formation of carboxylic acid, phenolics hydroxyl groups and other acidic functional groups [18]. Thus, the result indicates that an acid treated carbon has the highest sorption capacity for basic species in aqueous solution.

Surface Basicity: The surface basicity experiment was carried out in order to verify the affinity of the various biomasses for basic species in aqueous solution. The results generated are presented in table 3.

Table-3
Surface Basicity of Activated and Pure Carbonized Samples of Fluted Pumpkin Waste biomass

_	Sodium Sorption Capacity (mmol/g)	
Sample	**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

From the above results, the adsorption capacity for basic species in aqueous solution of the fluted pumpkin waste biomass was in the order: AM (0.233mmol/g > PC (0.0203mmol/g) > NM (0.113 mmol/g) >BM (0.043mmol/g) respectively.

As reported in literature, the basic character of activated carbon arises primarily from delocalized л electrons on the condensed polyaromatic sheets. These electrons-rich Lewis based sites develop as oxygen is removed from the activated carbon surface, e.g. by heat treatment in an inert atmosphere or by treatment with nitrogen containing groups, cyclic amides e.t.c. This treatment not only removes inherently bound acidic groups, but also other oxygen –containing functionalities that decrease the basicity of activated carbons by attracting and thus localizing л – electrons of the condensed polyaromatic sheets. Thus the removal of oxygen renders an activated carbon surface basic and less polar, a desirable trait when adsorption of organic contaminants from aqueous solution is the primary objective[15,19]. The highest surface acidity of the AM sample (table 3) arises from carbonization followed by chemical oxidation of the fluted pumpkin waste biomass with H_3PO_4, which gives the treated carbon more oxygen –containing functional groups as stated in literature[18]. While the strongest basic character exhibited by the sample PC, arises from the precursor material (i.e. fluted pumpkin stem waste) followed by carbonization (i.e. heating in an inert atmosphere). Several studies have shown that thermal (heat) treatment has been used to produce activated carbon with basic character and such carbons were effective in the adsorption of some organic hydrocarbons[20].

Point of Zero Charge, pHpzc: The results obtained from the determination of point of zero charge are presented in table 4.

Table-4
$_P$Hpzc of Activated and Pure Carbonized Samples of Fluted Pumpkin Waste Biomass

Sample	Point of zero charge ($_P$Hpzc)
AM	5. 82
BM	6. 82
NM	6. 61
PC	8.45

The point of zero charge, $_P$Hpzc results show that AM exhibited the strongest acidic character, while PC exhibited the strongest basic character.

Conclusion

In this study, pure carbonized and activated carbons were prepared from fluted pumpkin stem waste biomass and the surface properties such as; surface acidity /basicity and point of zero charge pHpzc were investigated. For surface acidity/basicity, the pure carbonized sample, PC has the highest affinity for acidic species, while the sample activated with H_3PO_4 (AM) has the highest affinity for basic species in aqueous solution. The PC also, exhibited the strongest basic character while the sample activated with H_3P_O4 exhibited the strongest acidic character. Thus, the results of this investigation has shown that both the pure carbonized and activated carbon for the treatment of effluent contaminated with odour gases, acidic gases and possibly problematic organics could be effectively prepared from low-cost, economical and environmental friendly agro-wastes such as fluted pumpkin (Telfairia occidentalis Hook f) stem waste biomass.

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