

## PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM WATER HYACINTH (*Eichornia Crassipes*) AND WATER SPINACH (*Ipomoea Aquatica*).

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### ABSTRACT

*Water hyacinth and water spinach were used as novel precursor materials for the production of powdered activated carbons. They were activated chemically with H<sub>3</sub>PO<sub>4</sub>, KOH, H<sub>2</sub>O<sub>2</sub> pyrolyzed at 450°C and characterized in terms of pH, density, surface area, iodine number, porosity, ash content and moisture content. The surface area (m<sup>2</sup>/g) for the activated carbon samples; WSAP (1069), WHAP (1061), WSAA (1074), WHAA (1060) and WSBA (1009) were high and lied within the range of commercial grades (800-1500). The statistical t-Test analysis was used to determine if there was any significant difference between the surface characteristics of the activated carbons from the water weeds and commercial activated carbon (CAC) using a formulated null hypothesis at 95% confidence level. The study shows that there is no significant difference between the mean values of pH, porosity and density with those of CAC.*

*Keywords: Preparation, Characterization, Activated carbon, Water hyacinth, Water spinach.*

### INTRODUCTION

Many industrial processes result in the release of dyes and heavy metals into the environment. Dyes constitute a large and important group of industrial chemicals among the different pollutants in aquatic ecosystem for which world production was estimated at  $7 \times 10^5$  tones (Rachakornkij et al, 2004). Dyes and metals have been found to be toxic and carcinogenic. This has led to increasing concerns over their effect as environmental contaminants. Most dyes and metals are non-biodegradable and can accumulate in living tissues, thus becoming concentrated through the food chain (Okieimen et al, 2007). Conventional methods used for treating dyes and metals containing wastewaters include coagulation, flocculation, ozonation, reverse osmosis (Nyholm et al, 1992) and lime

precipitation, ion-exchange, membrane separation and electrolytic methods (Okieimen et al, 2007). However, many of these methods have several disadvantages which include cost, incomplete removal of contaminants and generation of other waste products that require disposal and further treatment. There is therefore a growing interest in cost effective, abundant local materials and methods that will be useful in the removal of pollutants from industrial effluents. Many agricultural by-products that are available at little or no cost have been reported to be capable of removing substantial amounts of industrial wastes from aqueous solutions (Okieimen et al, 2007). It has also been reported that agricultural by-products have low resistance to mechanical abrasion (with attrition levels reaching 30%) making

them suitable only for a “once-and for-all” application (Okieimen et al, 2004). Hence, much research interest has been generated in the treatment of industrial effluents through adsorption using activated carbons.

Activated carbons are highly porous, high surface area materials used in industry for purification and chemical recovery operations as well as environmental remediation (Toles et al, 1997). Activated carbons can be made from a variety of precursor materials such as coal, wood, coconut shells, etc by some form of activation process. More recently interests have been generated in the preparation of activated carbon using agricultural by-products as precursor materials. The production of activated carbons from agricultural by-products has potential economic and environmental impacts. First, it converts unwanted, low-value agricultural waste to useful, high value sorbents. Second, activated carbons are increasingly used in water to remove organic chemicals and metals of environmental and/or economic concern. The general method of producing activated carbon is based on carbonizing and activating the carbonaceous precursor material. Activation may be achieved physically by a two stage process involving carbonization of the precursor material followed by controlled gasification (steam flow, temperature, heating rate, etc) of the char; or chemically, by which the precursor material is impregnated with chemical agent, and then heated to a temperature of 450-700°C (Okieimen et al, 2007).

Water hyacinth is an aquatic plant which can live and reproduce floating freely on the surface of fresh waters or can be anchored in mud (Herfjord et al, 1994). It grows in mats up to two meters thick which can reduce light and oxygen, change water chemistry, affect flora and fauna and cause significant increase in water loss due to evapo-transpiration. It also causes problems for marine transportation, fishing and irrigation schemes. It is now considered a serious threat to biodiversity (Hill

et al, 1997). Water Spinach (*Ipomoea aquatica*) is a creeping, herbaceous vine that dwells in muddy stream banks, fresh water ponds and marshes. Water spinach populations have caused environmental damage by creating impenetrable masses of tangled vegetation obstructing water flow in drainage and flood control canals. The veins of the plant create dense impenetrable canopies over small ponds and retention basins creating stagnant water conditions that are ideal breeding environments for mosquitoes (Space and Imada, 2004). The use of carbonized water hyacinth and water spinach have been reported in the adsorption of methylene blue [Tarawou and Horsefall, 2007] and methyl red [Tarawou et al, 2007]. The objective of this study is to prepare and characterize activated carbon from two fresh water weeds; water hyacinth and water spinach and to compare their properties with those of commercial activated carbon.

## MATERIALS AND METHODS

The fresh water weeds, water hyacinth (*Eichornia crassipes*) and water spinach (*Ipomoea aquatica*) were collected from the Epie River in Yenagoa of Bayelsa State, Nigeria. The samples collected were washed thoroughly with water and then rinsed with deionized water and air-dried. The air-dried weeds were then cut into smaller pieces and carbonized.

*Carbonization of weed:* The dried plant based biomaterial was placed in a sealed ceramic oven (Carbolite Sheffield, England, LMF4) and was heated at a rate of 5°C min<sup>-1</sup> to 500°C. During the process, the steam generated from de-ionized water in a heated tube was poured into the oven at a rate of 5 cm<sup>3</sup> min<sup>-1</sup> for 4 hours.

Also, the vaporized steam was quickly removed from the oven through the exhaust pipes. Under such oxygen-deficient conditions the biomass was thermally decomposed into porous carbonaceous materials and hydrocarbon compounds. This is the carbonization step of the physical activation process. The carbonized

samples were activated chemically with the reagents  $H_3PO_4$ , KOH and  $H_2O_2$  using the method described by Toles et al (1997). Six different activated carbon samples were produced, namely; WSAP: Water spinach activated with peroxide, WHAP: Water hyacinth activated with peroxide, WSAA: Water spinach acid activated, WHAA: Water hyacinth acid activated, WSBA: Water spinach base activated, WHBA: Water hyacinth base activated.

*Determination of surface area:* In this study the specific surface area of activated carbon was determined using the ethylene glycol method (Cerator and Lutenegeger, 2002). One gram of

oven-dried activated carbon was weighed and transferred into a beaker. 3.0ml of ethylene glycol was measured and gently added to the sample of activated carbon in the beaker. The mixture was carefully swirled until uniform slurry was observed. The slurry was placed in a vacuum desiccator (having anhydrous calcium chloride and ethylene glycol as desiccant) with lid.

Weighing of the ethylene glycol mixture was done at intervals of 10 hours until the difference between two successive weights was less than 0.001g, the weight obtained at this stage was the final slurry weight.

**Table 1:** Slurry weights of ethylene glycol mixtures at different time intervals (in grams).

Weight of Sample (in grams)	WSAP	WHAP	WSAA	WHAA	WSBA	WHBA
Sample+Ethylene glycol	1.3347	1.4167	1.3827	1.3741	1.2984	1.2563
Sample + Slurry (10 hrs)	1.1562	1.3311	1.3315	1.3218	1.2231	1.1903
After 20 hrs	1.1498	1.3159	1.3211	1.3157	1.2163	1.1741
After 30 hrs	1.1429	1.3073	1.3086	1.3085	1.2117	1.1597
After 40 hrs	1.3068	1.3054	1.3083	1.3042	1.2886	1.2028
After 50 hrs	1.3058	1.3035	1.3078	1.3032	1.2886	1.2028

The final slurry weight of samples was obtained after 50 hours, which was used for the calculations. The specific surface area was calculated using equation (1)

$$SSA = \frac{W_{fs} - W_s}{0.000286} = \frac{W_a}{0.000286} \quad (1)$$

Where; SSA is the specific surface area,  $W_{fs}$  is weight of final slurry,  $W_s$  is the weight of sample used,  $W_a$  is the weight of ethylene glycol retained by the sample in grams as in equation (2)

$$W_a = W_{fs} - W_s \quad (2)$$

0.000286 is a constant representing the weight of ethylene glycol required to form a mono molecular layer on a square meter of surface ( $g/m^2$ ) [Cerator and Lutenegeger, 2002].

*Determination of iodine number:* This number was tested using the ASTM D4607-94 method. A standard iodine solution (0.1M) was first titrated against a standard 1.0M solution of  $Na_2S_2O_3 \cdot 5H_2O$  (titrant) and the value was recorded. 50ml of the standard solution of iodine (0.1M) was measured and transferred into a 100ml conical flask and 1g of activated carbon was weighed and introduced into the conical flask. The flask was sealed using cellophane paper and agitated using a mechanical shaker for about 1 hour. After shaking, the sample was filtered into a 25ml conical flask and titrated against 1.0M  $Na_2S_2O_3 \cdot 5H_2O$  until a clear colourless solution was obtained, which is the endpoint using starch indicator.

The iodine number was calculated using equation (3)

$$\text{Iodine number (mg/g)} = \frac{M_{wt} \text{ iodine} \times S_{tv} \times M \times 1000}{1000} \quad (3)$$

Where  $S_{tv}$  is the difference between the titre value of the iodine solution and the titre value of carbon sample in iodine solution against  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $M_{wt}$  is the molecular weight of iodine (253.81),  $T_{vi}$  is titre value for iodine (0.1M) solution,  $T_{vc}$  is titre value of carbon sample after shaking with iodine solution, and  $M$  is molarity of iodine solution.  $S_{tv}$  is obtained from equation (4)  $S_{tv} = T_{vi} - T_{vc}$  (4)

The moisture content was calculated using equation (5)

$$\text{Moisture (\%)} = \frac{\text{loss in weight on drying (g)} \times 100}{\text{initial sample weight (g)}} \quad (5)$$

*Determination of Ash content/Volatile matter:*

The standard test method for ash content – ASTM D2866-94 was used. A crucible was pre-heated in a muffle furnace to about  $500^\circ\text{C}$ , cooled in a desiccator and weighed. 1g of activated carbon sample was transferred into the crucible and reweighed. The crucible containing the sample was then placed in a cold muffle furnace and the temperature was allowed to rise to  $500^\circ\text{C}$ . It was removed and allowed to cool in a desiccator. After cooling, it was weighed again.

The ash content was calculated using equation (6)

$$\text{Ash content (\%)} = \frac{\text{Ash weight (g)}}{\text{Oven dry weight (g)}} \times \frac{100}{1} \quad (6)$$

*Determination of pH:* The standard test method for pH of activated carbon ASTM D 3838-80 was used. 1g of activated carbon was weighed and transferred into a beaker. 100ml of distilled water was measured and added to the sample of activated carbon in the beaker and stirred for

*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 a desiccator and weighed. The activated carbon sample was thinly spread in the crucible and weighed. The crucible was then dried in an air-circulation oven at  $105^\circ\text{C}$  to constant weight.

one hour. The sample was allowed to stabilize before the pH was measured using a pH meter.

*Determination of porosity/density:* A cylinder and an aluminum plate were each weighed. A sample of activated carbon was put into the cylinder and reweighed. The sample was then transferred into the aluminum plate and was then put into an oven so as to dry it to a constant weight at a temperature of  $100^\circ\text{C}$  for 60mins. The weight of the dried sample was taken again after drying. A clean, dry, well-corked density bottle was weighed. The bottle was filled with water, corked and reweighed. A small quantity of the sample of the activated carbon was taken and ground to powder, sieved using  $110 \mu\text{m}$  and gradually put into the bottle with a little amount of water added and weighed again.

The density and porosity were calculated using equations (7) and (8) respectively;

$$\text{Density} = \frac{\text{mass of dry sample}}{\text{volume of cylinder}} \quad (7)$$

$$\text{Porosity } (\eta) = V_v/V_t \quad (8)$$

Where  $V_v$  = volume of void,  $V_t$  = total volume.

The volume of void  $V_v$  was obtained by first determining the total volume of the cylinder ( $V_t = \pi r^2 h$ ) used for the experiment and also

determining the volume of solid that is, the activated carbon used ( $V_s = M_s/G_s P_w$ ), where  $r$  = radius of cylinder,  $h$  = height of cylinder,  $M_s$ = mass of solid,  $G_s$ = specific gravity,  $P_w$ = density of water.

Then, volume of void ( $V_v$ ) was obtained as in equation (9)

$$V_v = V_t - V_s \quad (9)$$

## RESULTS AND DISCUSSION

*Surface characteristics:* Table 2 shows the surface characteristics of activated carbon produced from water hyacinth and water spinach.

**Table 2:** Surface characteristics of activated carbon derived from water hyacinth and water spinach

Activated Carbon	WSAP	WHAP	WSAA	WHAA	WSBA	WSBA
pH	8.1±0.1	8.0±0.1	6.8±0.1	6.9±0.8	8.9±0.2	8.3±0.2
Density (g/cm <sup>3</sup> )	0.23±0.10	0.20±0.05	0.30±0.09	0.26±0.05	0.25±0.06	0.25±0.06
Porosity	0.88±0.01	0.91±0.01	0.78±0.01	0.89±0.02	0.87±0.06	0.93±0.02
Surface area (m <sup>2</sup> /g)	1069±10	1061±12	1074±11	1060±9	1009±13	709±15
Moisture Content	16.9±0.2	23.7±0.2	24.4±0.1	19.8±0.1	15.7±0.0	20.6±0.3
Ash Content (%)	21.0±0.6	22.4±0.1	26.5±1.0	27.6±0.9	27.0±0.3	20.8±0.2
Iodine number	279.1±0.1	152.2±0.2	203.2±0.1	152.4±0.1	253.6±0.2	177.5±0.2

From the properties shown in table 2 above, there is a low amount of moisture and ash content, thus the activated samples should be good adsorbents for use in column or fixed-bed reactors. Ash content can affect activated carbon performance that is, it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation. Therefore, the lower the ash content the better the activated carbon for use as adsorbent. Table 2 also shows appreciable porosity for the activated carbon samples. Porosity describes the number of pores present in a sample. Porosity therefore enhances adsorption capacity of an adsorbent, and the higher the porosity, the higher the adsorption capacity of the adsorbent. From table 2, porosity is in the order WHBA (0.93) > WHAP (0.91) > WHAA (0.89) > WSAP (0.88) > WSBA (0.87) > WSAA (0.78).

The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micropores that adsorption largely takes place. It is a measure of the micropore content of the activated carbon and is obtained by the adsorption of iodine from solution by the

activated carbon sample. Most widely used commercial activated carbons have specific surface areas of the order of 800-1500 m<sup>2</sup>/g (Bansal et al, 1988). From table 2, the surface area for the activated samples; WSAP (1069), WHAP (1051), WSAA (1074), WHAA (1060) and WSBA (1009) were fairly high and lied within the range of commercial grades, while the surface area for WHBA (709) was slightly lower than the lower value for CAC (800). These values show that the activated carbon samples have relevant solute- solution adsorption properties. Large surface area is generally a requirement for good adsorbent. The pH value of activated carbon is a measure of whether it is acidic or basic. Activated carbon, when coming out of the kiln tends to be a bit basic, with a pH of around 8. Too high a pH indicates too much contaminant. Too low a pH, especially for acid washed activated carbon, means that the acid has not been properly rinsed away. For most applications, activated carbons are specified for a pH of 6-8 (Ahmedna et al, 2000). From table 2, the pH of the activated carbon samples were in the order WHBA (8.3)> WSBA (8.2)> WSAP (8.1)> WHAP (8.0)>

WHAA (6.9) > WSAA (6.8). The pH values of the activated carbon samples are therefore within the specified pH range of activated carbons. Density determines the amount of carbon that can be contained in a filter of a given solids capacity and the quantity of the treated liquid that is retained by the filter cake (Hutchin, 1988). A typical density number of activated carbon for use is 450-550 grams per liter. Density is affected by the raw material used and the degree of activation. From table 2,

the density for the various activated carbon samples are WSAA (0.30) > WHAA (0.26) > WHBA (0.25) = WSBA (0.25) > WSAP (0.23) > WHAP (0.20) in grams per liter.

**Comparison of Surface Properties:** The surface properties of commercial activated carbon (CAC) and activated carbons produced from water hyacinth and water spinach were compared and given in table 3.

**Table 3:** Comparison of surface properties between commercial activated carbon (CAC) and activated carbons derived from water hyacinth and water spinach

Activated Carbon	CAC	WSAP	WHAP	WSAA	WHAA	WSBA	WHBA
pH	9.2	8.1	8.0	6.9	6.9	8.9	8.3
Density (g/cm <sup>3</sup> )	0.68	0.23	0.20	0.30	0.26	0.25	0.25
Porosity	0.96	0.88	0.91	0.78	0.89	0.87	0.93
Surface area (m <sup>2</sup> /g)	1095	1069	1061	1074	1060	1009	709
Moisture Content	12.6	16.9	23.7	24.4	19.8	15.7	20.6
Ash Content (%)	2.9	21.0	22.4	26.5	27.6	27.0	20.8
Iodine number	850	279.1	152.2	203.2	152.4	253.6	177.5

**Student's t-Test Analyses:** The surface properties of the activated carbon derived from water weeds were compared with commercial activated carbon. The statistical t-Test analyses was carried out to determine if there was any significant difference between the properties obtained for activated carbon derived from water weeds and CAC. A null hypothesis was formulated, thus; there is no significant difference between the surface properties of CAC and activated carbon derived from water weeds. The null hypothesis was tested by assuming that the mean of the set of results is equal to the true or accepted value (that is,  $\bar{x} = \mu$ ) by using equation (10)

$$\pm t = (\bar{x} - \mu) \sqrt{\frac{n}{s}} \quad (10)$$

Where;  $\bar{x}$  = mean value of water weed activated carbons,  $\mu$  = true or accepted value (Commercial activated carbon in this case), n = number of measurement, s = standard deviation from the mean. To test the null hypothesis ( $H_0$ ), the experimental t-values ( $t_{exp}$ ) for any degree of freedom at any confidence level is compared with the critical t-value ( $t_{crit}$ ). If  $t_{exp} > t_{crit}$ , Reject  $H_0$  and conclude that there is a significant difference between X and  $\mu$  and If  $t_{exp} < t_{crit}$ , accept  $H_0$  and conclude that there is no significant difference between X and  $\mu$ . The calculated ( $t_{exp}$ ) values are given in table 4.

**Table 4:**  $t_{exp}$  values for the surface properties of the activated carbon samples derived from water hyacinth and water spinach

Property	$t_{exp}$					
	WHAA	WHAP	WHBA	WSAA	WSAP	WSBA
pH	2.251	2.062	2.853	3.090	1.944	1.734
Porosity	0.990	1.051	0.467	2.503	0.800	0.674
Density	0.733	0.643	0.569	0.423	0.422	0.823
Moisture content	7.110	9.761	8.690	9.162	3.661	3.132
Ash content	19.999	15.742	15.303	21.300	15.672	20.47
Surface Area	20.13	16.91	171.44	10.72	14.12	41.27
Iodine number	540.37	485.39	517.98	646.85	528.51	516.52

$$t_{critical} = 3.182$$

From table 4, it is seen that, for all the activated carbon samples;  $t_{exp} < t_{crit}$  for the properties pH, porosity and density. This shows that there is no significant difference between the mean values of pH, porosity and density of the activated carbon samples derived from water weeds and those of the CAC. While for the properties moisture content, surface area, ash content and iodine number;  $t_{exp} > t_{crit}$  which shows that there is a significant difference between these properties of the activated carbons from water weeds and those of CAC. For WSBA the  $t_{exp} < t_{crit}$  for moisture content, which shows that there is no significant difference between moisture content of CAC and the activated carbon derived from water weeds.

## CONCLUSION

This study demonstrates that water hyacinth and water spinach could be used as novel raw materials for the production of effective activated carbons for the adsorption (removal) of contaminants from aqueous solution. They can be used as adsorbents in batch and column reactors for the treatment of industrial waste waters.

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