TREATMENT OF WASTE WATER BY ACTIVATED CARBON DEVELOPED FROM *BORASSUS AETHIOPUM*

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ABSTRACT
The use and effectiveness of granular and powdered activated carbon made from Borassus aethiopum shells in adsorption studies were investigated. The source material was carbonized at 500^0C and for a residence time of three hour in a muffle furnace, while 0.5M each of H_3PO_4 and $ZnCl_2$ were used for chemical activation at 750^0C and for 60m residence time. The adsorption of lead from aqueous solution by $ZnCl_2$ and H_3PO_4 activated carbons was evaluated for the possibility of using the source material for the removal of heavy metals from aqueous solution. The effect of varying the concentration of the solution and the type of activating agents on the adsorption capacity were assessed. The results indicated that $ZnCl_2$ activated carbons exhibited better adsorption capacity than H_3PO_4 activated carbons. This provides low cost method of producing activated carbons locally in developing country like Nigeria for use in water treatment.

Keywords*: Borassus aethiopum, Activated carbons, wastewater, carbonization, adsorption.*

INTRODUCTION

Borassus aethiopum is tropical unbranched palm specie found widely spread in Africa. This plant is used in alimentation (Glew *et al*., 2005), in technology (Nethaji *et al*., 2010) and in traditional medicine as source of antioxidants, antifungal and antibacterial activities (Cassou *et al*., 1997, Adesegun *et al*., 2000). In the last decade, public awareness over the quality of drinking water has attracted interest in the global world (Zang *et al*., 2005). This is reflected in the demand for home water filter designed to remove objectionable taste, odour and organic contaminant from water, which has experienced substantial growth. Activated carbon products are used for cleanup of off-gases containing volatile organic compounds, decolourisation, solvent recovery and purification, treatment of industrial waste, surface and ground water redemption, food processing, pharmaceutical and environmental remediation amongst other uses (Al – Qodah, 2006).

In Nigeria and similar developing nations, activated carbon requirements are met by importation in enormous quantity and at exorbitant price, whereas vast quantity of agricultural residues which can be used for its production to meet local demands and even for exportation are generated annually. The thrust of this study is to create wealth from waste, by converting these materials considered by-products into activated carbon adsorbents, which can be used for water and wastewater treatment (Tharepong *et al*., 1999). A lot of income can be generated from activated carbon production with the price of activated carbon at well above USD 450.00/Ton.

Activated carbon is a microcrystalline, non graphite form of carbon that has been processed to develop internal porosity, characterized by a very large specific surface area (Softel, 1985, Gummas and Okpeke, 2015). Activated carbon is a fine black odourless and tasteless powder made from wood or other materials that have been exposed to high temperature in an airless environment to exhaust contained gases, resulting in a highly porous form. It can be treated or activated to increase its ability to adsorbs various substances such as gases, liquids, or dissolved substance (adsorbates) on the surface of its pores by reheating with oxidizing agent or other chemicals to break it into a very fine powder (Tran, 2002). Activated carbon is cost effective in that the same high temperature process that is used to manufacture carbon can be used to reactivate the carbon for reuse. In the regeneration process, adsorbed organic chemicals are thermally destroyed, and the carbon can then be recycled for reuse.

To be technically effective in a commercial separation process, whether this be a bulk separation or purification, an adsorbent material must have a high internal volume which is accessible to the components being removed from the fluid. Such a highly porous solid may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstances may have molecular sieving properties. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. In most applications, the adsorbent must be regenerated after use. Therefore, it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties of the adsorbent. The raw materials and methods of producing adsorption must ultimately be inexpensive for absorption to compete successfully on economic grounds, with alternative separation process (Thomas and Crittendem, 1998). The most important attributes of an adsorbent for any application are: adsorptive capacity, selectivity, regenerability, kinetics, compatibility and cost.

Commercial production of activated carbon uses raw materials such as wood, refinery residuals, peat, coal, coke, pitches, carbon blacks and nutshells. The raw materials for this study *Borassus aethiopum* shell, is obtained after the edible outer fibrous pulp and albumen or seed found inside the kernel have been removed. *Borassus aethiopum* shell is akin to palm kernel shell. Obtaining the shell offers solution to the *Borassus aethiopum* processing industry as a means of its disposal and almost no cost is incurred in its acquisition. Many high carbon materials considered waste which can also be used for producing activated carbon include: used bamboo, old and worn out automobile tyres, sawdust and wood, shaving bagasse (sugarcane fibre residue), rice halls and husk, animal horns and bones, palm kernel shell, hard shells, cobs, pits, pods and capsules of nuts, fruits and seeds, including walnut, chestnut, hazelnut, corn, olive, peach, peanut, almond, hickory, pecan etc.

The choice of *Borassus aethiopum* shell over other waste raw materials is due to its availability all year round and low cost, its lack of alternative use, and its possession of advantageous properties such as high carbon content, low ash content, high yield, mechanical strength and resistance to attrition, which makes it the preferred source for activated carbon used in the treatment of wastewater. *Borassus aethiopum* shell is a highly carbonaceous material which can easily be processed into activated carbon that is widely used in liquid and gas face separation, purification of products and water cleaning operation (Therapong *et al*., 1999).

Even though all carbonaceous materials can be converted to activated carbon, *Borassus aethiopum* shells give a high-grade vapour adsorbent carbon due to the inherent high carbon content and mechanical strength (Korubalkaran *et al.,* 1991). Developed adsorbent from *Borassus aethiopum* shell and the like is economically friendly, cost effective and durable.

Chemical industries are one of the major industrial users of water. These industries have one of the wastes most difficult to treat satisfactorily. The high organic content of chemical industry effluent classifies it as very high – strength waste in terms of chemical oxygen demand from 1000 to 4000 *mg/L* and biochemical oxygen demand of up to 1500 *mg/L*. The treatment of chemical industries wastewater effluent is a costly task for the chemical industry in order to meet the government regulations and to practice environmentally friendly manufacturing. The untreated effluent discharged from these industries is coloured and highly intoxicating due to presence of residual chemicals and can be toxic to aquatic life in receiving wastewaters, hence the need for the treatment of chemical industries wastewater effluent before being discharged into water courses. However, the current problems in water and wastewater treatment stem from the increasing pollution of waters by organic compounds that are difficult to decompose biologically because these substances resist the self – purification capabilities of the rivers as well as decomposition in conventional waste water treatment plants. Consequently, conventional mechanical-biological purification no longer suffices and must be supplemented by an additional stage of processing. Among the physicochemical processes that have proved useful for this, adsorption onto activated carbon is especially important because it is difficult to decompose organic substances and heavy metals that can be selectively removed by activated carbon (Olaoadehan and Aribike; 2000; Pollard *et al*; 2005).

The objective of this study is to treat wastewater effluent from chemical industries in Nigeria using the manufactured activated carbon from *Borassus aethiopum* shells with a view to determining its efficacy. The production of activated carbon locally, which can treat industrial wastewater will not only reduce the cost of treating wastewater for local industries but also increase the Gross Domestic Product (GDP) of the nation which justifies this work.

MATERIALS AND METHODS

Pre – Treatment of *Borassus aethiopum* Shells

The waste *Borassus aethiopum* shell used in this study was obtained from Daura in Katsina State. Prior to the carbonization and activation experiments the *Borassus aethiopum* shells were crushed to pieces of 11–14 *mm*, washed with warm water, rinsed with distilled water, dried at 105^0C for three hours in the oven and allowed to cool in desiccators.

Production of Carbonized Carbon

The dried *Borassus aethiopum* shells were carbonized in a Carbolite Furnace at a temperature of 500^0C for three hours as shown in equation 1 and the charred product was allowed to cool to room temperature. The carbonized *Borassus aethiopum* shells were chemically activated using two difference activating agents.

$$Borassus\ aethiopum\ \text{shells} \xrightarrow{500^0C} Carbon + As\square + Volatile \ldots . Eq. 1$$

Production of Activated Carbon using $ZnCl_2$ and H_3PO_4

The carbonized carbon was impregnated with zinc (II) chloride (0.5*M* $ZnCl_2$), followed by heating in absence of air as shown in equation 2 below using the muffle furnance.

$$Carbonized\ carbon \xrightarrow{ZnCl_2 750^0C} Activated\ carbon + ZnCl_2 \ldots . Eq. 2$$

The resulting moist paste upon mixing the char with $ZnCl_2$ (50*g* carbonized carbon and 150*mL* of 0.5*M* $ZnCl_2$) was charged into the furnace and heated for 60 minutes to a final temperature of 750 ^0C. Cold water was used to quench the activated carbon produced and this was further dried for 60minutes at 110^0C in an oven till a constant weight of activated carbon was obtained. After the chemical activation, the activated carbon was rinsed thoroughly. Washing was used to remove the remaining of zinc chloride and ash in the adsorbent. This was accomplished by washing with distilled water. The activated carbon was then drained and spread on a tray at room temperature. The activated carbon was dried in an oven at a temperature of 110^0C for 3*h*. The weight of activated carbon produced was taken and yield calculated. The same process of activation was repeated for carbonized carbon impregnated with H_3PO_4.

The crushing process is required to crush or refine the activated carbon produced with crusher wood or mortar to size of 100 meshes. This provides the activated carbon with a large surface area required for gas or liquid adsorption. Activated carbon, with smaller particle size adsorbs better than large particles. This is the final process required for development of activated carbon from *Borassus aethiopum* shells after which packaging into sealable air-light polythene bags or plastics follows:

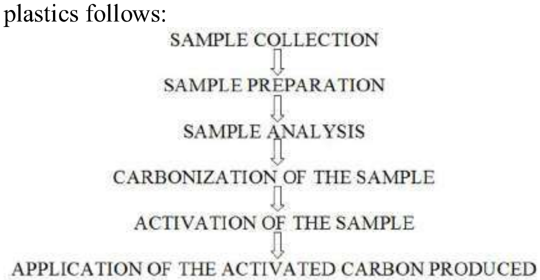

Figure 1: Flow sheet for the development of activated carbon from Borassus aethiopum shells.

Characterization of Activated Carbon from *Borassus aethiopum* Shells

pH Determination

2.0*g* of the absorbent was weighed out using a sensitive weighing balance. The weighed activated carbon was washed thoroughly for 5 *m* with 30 *ml* distilled water and filtered using a filter paper and pH of the filtrate was measured using a pH meter. This procedure was repeated in triplicate for each of the activated carbon.

Ash Content Determination

2.0 *g* of the adsorbent was placed into a crucible, and reweighed with its content, heated in a furnace at 900 ^0C for three hours. The sample was cooled to room temperature and weighed. The same procedure was repeated in the triplicate for the adsorbent. Ash content was calculated between the differences in weight.

$$Ash\ (\%) = \frac{Ash\ weight\ (g)}{Oven\ dried\ weight\ (g)} \times 100$$

Moisture and Dry Matter Content Determination

2.0 *g* of the adsorbent sample was placed into a crucible and reweighed with its content and dried in an oven at 110 ^0C for three hours, until weight of sample was constant. The same procedure was repeated in triplicate for the adsorbent. The Moisture content was calculated using the equation:

$$X\ (\%) = \frac{W_1 - W_2}{W_1} \times 100$$

where % X = percent moisture content on wet basis, W_1 = initial weight sample in grams, W_2 = Final weight of Sample in grams after drying.

$$Dry\ matter\ (\%) = \frac{Oven\ dried\ weight\ (g)}{Initial\ sample\ weight\ (g)} \times 100$$

Adsorption Test using Pb^{2+}

1.0 *g* of the activated carbon sample was weighed into 250 cm^3 conical flash and 50 cm^3 each of the 20, 40, 60, 80 and 100 *ppm* standard solution of Pb^{2+} was added. The mixture was shaken thoroughly with a Griffin model electric shaker for an hour to attain equilibrium. Thereafter, the supernatants were filtered and the concentration of the Pb^{2+} remaining in the filtrate was determined using Jenways Atomic absorption spectrometer (AAS 500).

RESULTS AND DISCUSSION

Results

Table1: Results of physicochemical parameters of activated *Borassusaethiopum*shells

Parameters	*B. aethiopum* Shells AC
Moisture content (%)	8.96
Dry matter (%)	91.03
Ash content (%)	4.01
pH	5.93

Table 2: Percentage adsorption of Pb^{2+} by *Borassusaethiopum* shells activated with H_3PO_4

Initial Conc. of Pb^{2+} (*ppm*)	Actual Conc. of Pb^{2+} (*ppm*)	Amount adsorbed by Pb^{2+} (*ppm*)	% Pb^{2+} Adsorbed (*ppm*)
20.00	19.32 ± 0.00	18.88 ± 0.11	97.72 ± 0.55
40.00	29.40 ± 0.00	26.83 ± 0.37	91.27 ± 126
60.00	42.38 ± 0.00	39.59 ± 0.37	93.41 ± 0.87
80.00	51.19 ± 0.00	48.58 ± 1.27	94.91 ± 2.47
100.00	57.83 ± 0.00	37.43 ± 13.96	64.72 ± 6.84

Table 3: Percentage adsorption of Pb^{2+} by *Borassusaethiopum* shells activated with $ZnCl_2$

Initial Conc. of Pb^{2+} (*ppm*)	Actual Conc. of Pb^{2+} (*ppm*)	Amount by adsorbed Pb^{2+} (*ppm*)	% Pb^{2+} Adsorbed (*ppm*)
20.00	19.32 ± 0.00	19.22 ± 0.05	99.46 ± 0.27
40.00	29.40 ± 0.00	29.25 ± 0.00	99.52 ± 0.00
60.00	42.38 ± 0.00	42.24 ± 0.11	99.67 ± 0.25
80.00	51.19 ± 0.00	51.05 ± 0.00	99.72 ± 0.00
100.00	57.83 ± 0.00	57.50 ± 0.26	99.43 ± 0.46

Discussion

The experimental results of characterization of activated carbon from *Borassus aethiopum* shells are shown in Table1. The moisture content is the amount of water physically bound to the activated carbon under normal condition. The moisture content of the *Borassus aethiopum* shell was 8.96%. Generally the yield and quality of activated carbon produced can be improved by removal of moisture (Omeiza, 2011). This value (value for *Borassus aethiopum* shells) is generally low than values obtained from powdered corn cobs and activated carbon from *Carica papaya* seeds (Adie *et al*., 2010, and Omeiza, 2011). Studies have shown that lower moisture content increase the rate of adsorption of contaminants (Rangaraj *et al*., 2002).

The percentage ash content of the *Borassus aethiopum* shells as shown in Table1 was 4.01%. Ash in activated carbon is not desirable and is considered an impurity. Ash may also interfere with carbon adsorption and catalysis of adverse reactions. However, the *Borassus aethiopum* shells have very low percentage ash (OMRI, 2002).

The pH of the activated carbon from Borassus aethiopum shells is 5.92 (Table 1). The pH of activated carbon may influence colour by changing the sensitive fraction of solution colourant causing unreliable colour measurements (Lafi, 2001). The activated carbon with pH of 6-8 is acceptable for most applications (Akash and Obrien, 1996).

Tables 2, and 3 show the percentage adsorption of Pb^{2+} by *Borassus aethiopum* shells carbonized at 500 ^0C and activated at 750 ^0C using 0.5*M* $ZnCl_2$ and 0.5*M* H_3PO_4 respectively. The percentage of Pb^{2+} adsorbed by *Borassus aethiopum* shells activated with 0.5M H_3PO_4 ranged from 64.72 to 97.72 *ppm* (Table 2) and the percentage of Pb^{2+} adsorbed by *Borassus aethiopum* shells activated with 0.5*M* $ZnCl_2$, ranged from 99.43 to 99.72 *ppm* (Table 3) at the various concentrations of $Pb^{2+.}$ This adsorption studies show that $ZnCl_2$ has better activating activity than H_3PO_4. The small size of $ZnCl_2$ molecule or its hydrate explains the small and uniform size of the micropores created. This does not happen for H_3PO_4 because there are no phosphoric acid molecules, but a mixture of molecules from the small H_3PO_4 and $H_4P_2O_5$ to $H_{13}P_{11}O_{34}$ in the proportion. The porosity developed in the *Borassus aethiopum* shells activated carbon is due to the impregnation of the doping agents ($ZnCl_2$ and H_3PO_4). This is because the chemical reaction caused by hydrolysis of the carbonized and the doping agents weaken the structure of the carbonized *Borassus aethiopum* shells and release volatile matter which is responsible for the porosity and adsorption capacity of the carbon.

CONCLUSION

The results of this study show the promising potential of developing activated carbon from *Borassus aethiopum* shell which is abundant as agriculture by-product in Northern Nigeria for industrial wastewater treatment. The adsorption studies conducted shows that $ZnCl_2$ has better activating activity than H_3PO_4. The outcome of this study showed that produced activated carbon from *Borassus aethiopum* shells can be used for removal of heavy metals from industrial wastewater, achieving 99% Pb^{2+} removal efficiency. This would be of immense benefit not only to the industries but also minimize the impact of heavy metals and reduce wastes generated for this plant on the environments.

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