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Production and evaluation of activated carbon from palm kernel shells (PKS) for economic and environmental sustainability

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Activated carbon (AC) was produced from palm kernel shells (PKS) by acid activation method at temperature of 600°C. The effects of carbonization and acid impregnation time on the adsorption potential of the ACs on purification of contaminated rain and flowing river water bodies were examined. The results were compared with results of similar analysis based on commercial AC purchased from a nearby chemical shop. The results show that the AC produced from PKS upon 2 days acid impregnation followed by 3 h carbonization periods, purified both water bodies better than the others on reduction of microbial and micro impurity contents of the water bodies. The implications of the results show that production of AC from PKS is value addition to oil palm processing, boost to the national economy and positive environmental impact to the people that produce and use PKS. Hence, multiple-product derivations, such as bioenergy and bio-char production for adsorption purposes from palm kernel shells, are encouraged in process industries as against the sole traditional combustion for heat production.

Key words: Adsorption, palm kernel shell, carbonization, acid impregnation, activated carbon, purification.

INTRODUCTION

In Africa and some other developing countries, availability of safe drinking water is a sustainability issue. Most domestic and industrial activities depend greatly on supply of clean water. Water sources available to most developing countries are rivers, natural ponds, crack rocks and rainfall. In few areas there are underground water supplies through boreholes and water distribution tankers. A common feature about these water bodies is that they are in some ways contaminated (polluted) by heavy metals discharged from industries (Tumin et al., 2008), as well as the rocky pathways through which they discharge to the open. Some identified water contaminants are summarized in the Table 1.

Contaminated water bodies can be purified for drinking, industrial processing activities and domestic cooking purposes. It has been recommended (Gleik, 1996) that water providers (international organizations, national and local government) should adopt a basic water requirement standard for human needs of 50 L per person per day (l/p/d) and also guarantee access to it regardless individual's economic, social, or political status. In order to ensure this effort should be made towards clean water from these common water bodies.

One of the major ways of cleaning contaminated water is by use of activated carbon (AC). Activated carbon is an industrial raw material obtained by carbonization of

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Table 1. Some identified water contaminants and their sources.

Contaminant	Source	Ref
Pesticides	Farm	Nkwonta and Ochieng (2009)
Fertilizer runoff	Farm	"
Sediments	Run off	"
Household waste	House	"
Unclassified chemical contaminants	Municipal and industrial discharges, urban and rural run-off, natural geological formations, drinking water distribution materials and the drinking water treatment process	Calderon (2000)

carbonaceous biomass materials within a temperature range of 300 to 600 °C in the absence of oxygen. It aims at removing most volatiles leaving behind carbon rich char whose surface area is larger than the original substance (Malik, 2003; Shepherd, 1992). Activated carbon can be produced in different ways such as steam (heat) activation and acid activation. It can be applied in pharmaceutical industries to remove odour; in vegetable oil for odour and colour removal; water treatment plants to remove odour, microbes, colour, heavy ions, hardness etc (Okochi et al., 1997; Matsunaga et al., 1994). According to Lartey et al. (1999) activated carbon is used in the gold mining industries to recover gold from cyanide while in the brewery and soft drink industries, activated carbon is used mainly to purify the water used in production. Similarly, Gamby et al. (2001) have studied the performance of different ACs in the manufacture of super capacitors for charge storage. The porosity measurements on the materials showed a better understanding of the electrochemical behaviors of the ACs. Hence, activated carbon has become an interesting active material for super capacitor manufacturing.

Activated carbon can be produced from carbonaceous materials such as coconut shell, saw dust, agricultural residues (Malik, 2003; Ogedengbe et al., 1985; Adewumi, 1999, 2006, 2009). It has been noted that effectiveness in impurity removal is a function of the material and the method of production (Gordon and Hissink, 2005; Grayson, 2005; Adewumi and Ogedengbe, 2005). In oil palm processing, palm kernel shell (PKS) is usually regarded as waste even though it is commonly used as fuel for cooking and in boiler firing during palm oil processing. Most times when individuals produce more PKS than they can immediately use, they heap up the remainder to decay over time in an open storage. By this the heating value is usually reduced thereby devaluing the PKS. An alternative use of PKS which is economically viable is the manufacture of good quality activated carbon due to its high density, high carbon and low ash contents (Arami-Niya et al., 2010).

Many ACs from carbonaceous biomass have been produced and evaluated using different methods. For instance, Adewumi and Ogedengbe (2005) analyzed

factors which have prominent effect on the quality of AC produced from raw or charred PKS carbonized at 400 or 600 °C, for 20 or 40 min. It was suggested that optimum quality will be obtained by carbonizing the charred shells at 500 °C for 20 min after cessation of fumes and quenching the shells in alkaline water medium. In addition, drying the shells and pulverizing them to the desired grain sizes and activating the pulverized shells at 800 °C for 15 min in alkaline steam medium would enhance the quality. Earlier, Adewunmi (2009) carried out a survey of the sources and users of AC in SW Nigeria. He found that all the ACs were imported from Europe and Asia. There was no evidence of local production of this high-demand engineering material. Secondly, there was no standardization of the imported ACs either. Solution to these is local manufacture and characterization of ACs.

Methods implored in the production of ACs affect their adsorption capacity. Chemical and physical methods are available as production methods with chemical method widely used because of lower temperature activation and higher carbon yield than the physical method. Phosphoric acid (H_3PO_4) and Zinc chloride ($ZnCl_2$) are used more predominantly on a larger scale than other chemicals (Baker, 2010). Because of this, Arami et al. (2010) produced AC from PKS using zinc chloride and phosphoric acid. The samples were treated with CO_2 flow at 850 °C at different activation time. It was found that the samples activated chemically with phosphoric acid showed higher surface area and pore volume compared to the samples activated using zinc chloride as chemical agent at the same duration.

Since most ACs sold in Nigeria and Ghana (Lartey et al., 1999) and probably West Africa are imported, the need to produce and characterize ACs locally becomes imperative. This will not only improve the water treatment technology of these countries but also reduce the foreign exchange spending on importation of this industrial raw material. Water bone diseases, epidemics and deaths would be abated. It is therefore the aim of this work to produce and characterize AC at laboratory scale) using palm kernel shell as feedstock and phosphoric acid activation. Different ACs produced at different acid soaking and activation periods would be characterized by

Table 2. Characteristics of the PKS and commercial AC.

Property	48 h acid impregnation		72 h acid impregnation		Control
	A	B	C	D	E
Pore volume (m ³)	0.82	1.00	0.46	0.78	0.60
Ash content (%)	6.36	5.20	8.14	6.80	7.30
Moisture content (%)	3.00	2.80	4.50	3.60	4.30
Fixed carbon (%)	88.40	89.60	86.90	88.10	87.70
Bulk density (Kg/m ³)	668	661	740	705	460

water filtration technique.

MATERIALS AND METHODS

All reagents were of analytical grade procured from BDH, England. Distilled water was used except otherwise stated. PKS samples were obtained from the Okoroigwe family palm plantation in Umueze 2 Ehime-Mbano, Imo State and were first crushed and passed through a set of sieves. Particles ranging from 1 to 2 mm were collected for this research. Two samples weighing 200 g each were put each in 1000 ml beaker. 60% phosphoric acid was added to submerge the samples. The first sample was left for 48 h while the second was left for 72 h after which each of the samples was divided into two and carbonized at 600°C for two and three hours separately. The samples were allowed to cool and washed with distilled water until a neutral pH was attained. These were dried, further crushed and stored in airtight plastic containers. The rain water was collected at the National Centre for Energy Research and Development, University of Nigeria, Nsukka, using open clean basin positioned at the top of a decked roof. It was lifted a little above the roof floor to make sure that only direct droplets of water were collected. The river water was collected from Ubu river in Ukpok town of Nnewi South local council, Anambra State which serves as one of the sources of domestic water for the people of that community.

The first AC samples were labeled A and B for 48 h acid impregnation, 2 and 3 h carbonization respectively. The second set of samples was labeled C and D for acid impregnation of 72 h, 2 and 3 h carbonization respectively. The commercial activated charcoal was labeled E which served as a control.

Samples A-E were analysed for pore volume, bulk density, ash, moisture and fixed carbon contents. They were thereafter packed in different columns maintained at equal length and diameter. Samples of the water bodies were passed through them at the same retention time. Their ability to purify the water bodies through adsorption was determined through the physico-chemical and microbial analysis carried out on the water bodies before and after purification.

Colour, taste and odour were analyzed by organoleptic method while pH was done by electrometric method, iron and lead contents were determined by atomic absorption spectrophotometric method. The total and calcium hardness were determined by complexometric method, Mohr's argentometric titration was used for chloride determination. Nitrate, sulphate, total dissolved and total suspended solids determination were done by spectrophotometric, turbidimetric and gravimetric methods respectively. Microbial analyses were done by total viable count method. The results were compared with Nigerian Industrial Standard (NIS) specification for drinking water quality (NIS, 2007).

RESULTS AND DISCUSSION

The physical properties of the produced activated carbon and the purchased commercial sample are presented in Table 2. From the table it could be observed that the duration of carbonization increased the pore volume of the test samples while impregnation period decreased the pore volume. The values are within the accepted range of 0.4 to 1.1 for standard commercial activated carbon. The higher the pore volume, the better the absorption capacity (Fapetu, 2000). However, the laboratory samples have larger pore volume than the commercial sample. The pore volume is an indication of adsorbability of ACs. Similarly, the carbonization period reduced the ash content of the samples. This is true as further heating, in the temperature regime used, will lead to devolatilization of lignin content of carbonaceous biomass material. The ash content was highest in sample C. since the same samples of biomass were used, the action of acid in decomposition of cellulose and hemicelluloses could leave more lignin exposed which will result in more ash in C than in A. This is also an indication of the level of impurity present in it and must have contributed to its poor performance in terms of water purification (Meites, 1963; Zadok, 1985).

The effect of carbonization period was obvious in the amount of carbon content represented by fixed carbon in Table 1. Acid impregnation period decreased the fixed carbon content between A and C, and B and D. However, the commercial sample's fixed carbon content is close to the values for the laboratory samples produced in this work although its parent feedstock and production parameters are not known. The reduction in bulk density due to increase in carbonization period resulted from further release of volatiles thereby reducing the unit weight of the samples. However, the values are within the standard range of 240 to 780 kg/m³ for standard activated carbon as reported by Dietz (1944).

Tables 3 and 4 present the physical and chemical properties of the river and rain water bodies before and after purification with the produced and commercial ACs. According to the NIS standard for safe water, domestic and industrial water should be tasteless and odourless (unobjectionable) but both water bodies were objectionable (not in the acceptable condition). The rain

Table 3. Physico-chemical analyses of the river water body before and after purification.

Parameter	NIS limit for safe water	Raw water	AC treated water				
			A	B	C	D	E
Colour	Colourless	Light brown	Colourless	Colourless	Colourless	Colourless	Colourless
Taste	Uo	Ob	Uo	Uo	Uo	Uo	Uo
Odour	Uo	Ob	Uo	Uo	Uo	Uo	Uo
pH	6.5-8.5	8.2	7.8	7.5	7.6	7.9	8.0
Fe ²⁺ (mg/l)	0.3	1.84	0.76	0.29	0.80	0.78	0.36
Total Hardness as CaCO ₃ (mg/l)	150	120	36.18	7.60	42.26	39.45	40.33
Ca ²⁺ (mg/l)	75	98.06	24.11	5.22	28.80	26.36	26.25
Cl ⁻ (mg/l)	250	300.45	6.92	3.20	9.41	8.68	9.06
Nitrate (mg/l)	50	13.28	7.5	5.6	9.2	8.5	8.2
Sulphate (mg/l)	100	456.28	19.25	13.48	32.80	29.36	20.42
T.D.S (mg/l)	500	620.11	92.44	49.90	105.70	98.66	97.48
T.S.S (mg/l)	Nil	40	0.11	Nil	0.26	0.21	0.16
Lead (mg/l)	0.01	0.05	No trace	No trace	No trace	No trace	No trace
Cyanide	0.01	0.03	No trace	No trace	No trace	No trace	No trace

Uo = Unobjectionable, Ob = Objectionable, TDS = total dissolved solids, TSS = total suspended solids.

Table 4. Physico-chemical analyses of the rain water body before and after purification.

Parameter	NIS limit	Raw water	Treated water				
			A	B	C	D	E
Colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Taste	Uo	Ob	Uo	Uo	Uo	Uo	Uo
Odour	Uo	Ob	Uo	Uo	Uo	Uo	Uo
pH	6.5-8.5	6.6	6.5	6.5	6.6	6.5	6.5
Fe ²⁺ (mg/L)	0.3	1.20	0.62	0.21	0.75	0.69	0.71
Hardness CaCO ₃ (mg/L)	150	236	93.42	15.28	96.90	94.36	95.20
Ca ²⁺ (mg/L)	75	120.5	89.36	12.11	92.60	90.48	90.50
Cl ⁻ (mg/l)	250	28.60	4.36	2.68	5.92	5.14	5.20
Nitrate (mg/L)	50	16.92	7.05	5.32	8.48	7.74	8.4
Sulphate (mg/L)	100	530.16	24.76	18.89	36.14	29.88	30.75
T.D.S (mg/L)	500	428.70	76.90	50.36	85.92	80.17	81.02
T.S.S (mg/L)	Nil	29.68	Nil	Nil	0.07	0.05	0.05
Lead (mg/L)	0.01	0.14	No trace	No trace	No trace	No trace	No trace
Cyanide	0.01	0.05	No trace	No trace	No trace	No trace	No trace

Uo = Unobjectionable, Ob = Objectionable, TDS = total dissolved solids, TSS = total suspended solids.

water developed some odour after being stored for some time before use due to the presence of coliform and *Klebsiella aerogens* microbes (Table 6). The use of the ACs including the commercial sample improved the quality of the water bodies by the removal of these bacteria as well as removing colour. Comparing the quality and action of the samples in removing the ferrous ion content of the water bodies, the sample B showed a better quality than others in reducing the ion within the NIS acceptable limit for safe water. Similarly, sample B

totally removed the total suspended solids (TSS) in river water while the rest only reduced the quantity (Table 3). In rain water, both samples A and B removed TSS to bring the water to the expected standard. It could be because of the quantity present in both water bodies. It implies that the quantity of TSS present can affect the adsorbity of activated carbons.

The sample B could reduce chloride ion to 1% level in the river water even though all the samples drastically reduced the ion to such level that falls within the

Table 5. Result of microbial analyses of river water before and after purification.

Parameter	NIS limit	Raw water	AC treated water				
			A	B	C	D	E
Total Coliform (cfu/ml)	10	23,600	420	360	510	480	400
E.Coli (cfu/ml)	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fungi (cfu/ml)	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Klebsiella aerogens (cfu/ml)	Nil	Present	Present	Present	Present	Present	Present

Table 6. Result of microbial analyses of rain water before and after purification.

Parameter	NIS limit	Raw water	AC Treated water				
			A	B	C	D	E
Total Coliform (cfu/ml)	10	440	86	80	92	89	90
E.Coli (cfu/ml)	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fungi (cfu/ml)	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Klebsiella aerogens (cfu/ml)	Nil	Present	Present	Present	Present	Present	Present

acceptable limit for safe water by NIS. The rain water can be classified naturally hard (Table 4) by the amount of total hardness compared to the limit expected. However, the PKS AC produced upon 48 h acid impregnation and 3 h carbonization absorbed more of the CaCO_3 and reduced its level to 6.5% even though others reduced the hardness to acceptable limit. Both the PKS activated carbon samples and the commercial bought out sample adsorbed in the other physico-chemical parameters in the Tables 4 and 5 but the sample B adsorbed more.

The Tables 5 and 6 are the results of the microbial analyses of the two water bodies before and after treatment with the ACs. The Ubu river naturally contained very large amount of Coliform bacteria because of its exposure to community activities and natural deposits due to weathering activities. However, the ACs could reduce this to some level. By the NIS standard, these samples could not reduce the microbes to the acceptable level. This implies that after filtration using the ACs, heating or boiling can be recommended to completely reduce the Coliform and *K. aerogenes* found present in all the test water samples.

Conclusion

The present investigation showed that palm kernel shell can be effectively used as a raw material for the preparation of activated carbon for use as water treatment material. The degree of purification however depends on time of soaking in phosphoric acid and carbonization duration. The production of AC from PKS is value addition to palm oil processing which is a veritable economic activity of people of southern Nigeria. The AC produced upon soaking the feedstock in acid for 48 and 3

h carbonization at 600 °C is better than others and can be further optimized to determine its most valuable production parameters.

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