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Adsorption of Acetic Acid, Cadmium ions, Lead ions and Iodine Using Activated Carbon from Waste Wood and Rice Husks

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ABSTRACT: This paper presents the performance evaluation of locally prepared activated carbon from rice husk and saw dust. The raw materials were carbonized at different temperatures (600-800°C) using sodium hydroxide (NaOH) as the activating agent. The study includes moisture content determination of the raw materials used in the activation and carbonization processes. The effects of variations in carbonization temperature and concentration of activating agent on various performance indices for good quality absorbent were investigated. The percentage yield of the activated carbon from the raw materials as well as iodine number and adsorption of heavy metals from aqueous solutions were also determined. The experimental data which make a comparative assessment of activated carbon obtained from rice husk and saw dust were also presented. Preliminary examination of the raw materials showed that rice husk and saw dust had a moisture content of 14.6% and 5.8% respectively. Increase in carbonization temperature decreases yield of the active carbon. The highest yield of about 48% was obtained from rice husk at 600°C, with moisture content of 26%. The rice husk at 800°C gave a yield of 47.2% with moisture content of 26.5%. While the yields of the saw dust were 44% at 600°C and 40% at 800°C with moisture content of 17% and 19% respectively. A detailed study of mass transfer processes indicated that activated carbon from these materials show good performance. @JASEM

With the situation of the Nigerian economy and the population increase, the need has come for self sufficiency to achieve a stable and comfortable economy. A research on our waste materials can yield useful adsorbents, which have numerous uses and applications in our various industries land application of these materials may improve crop production. However, this practice can also degrade the environment with the introduction of potentially harmful substances such as traces of heavy metals into the soil.

Heavy metals have been applied to soil with pesticides, as plant nutrients and as a constituent of waste products. These heavy metals may include cadmium, zinc, lead etc. Thus taking into account the harmful effect of these heavy metals, it was considered of great extent to study the adsorption process of these metals from aqueous solution using locally prepared activated carbon which can be produced from wide variety of these carbon rich raw materials.

Over the decades there has been rapid population expansion and technological development in Nigeria. This leads to a more extensive and intensive use of available supplies of water, and ultimately to the pollution and degradation of the quality of these waters. Pollution is inevitable because domestic and industrial activities generate wastes, which are discharged into the environment. These wastes or effluent might contain non-biodegradable matter, toxic heavy metals, organic matter and also might give off some offensive odour (Webber and Vernana, 1967, Eckenfelder, 2000, Tchobanoglous et' al., 2003.). These can cause negative impact on the people living around those areas. Activated carbon is thus used as an effective adsorbent for the removal of these dissolved organic substances, heavy metals, obnoxious odour and colour from water and waste waters. Recent researchers studied the use of chemically modified and unmodified cassava waste for the removal of Cd, Cu, and Zn ions from solution (Abia et al., 2003). While sorption of Cd, Cu, and Zn ions from aqueous solutions by cassava waste biomass was investigated by Horsfall et al., 2004.

Recent reports indicate an escalating demand for and use of imported adsorbent on the developing countries, particularly Nigeria (Olafe and Bosch, 1996, Nwokoma and Anane, 2010, Okafor and Aneke, 2006, Emmanuel and Innocent, 2008). Thus in 1987, activated carbon worth ₦1,670,117 was imported from USA, Europe and Kuwait. In 1999, ₦5,096,999 worth of imports were made with brazil, China, and Taiwan (also developing countries) providing 98.9% of these imports, while the remainder was supplied by USA (Olafe and Bosch, 1996). Governments of these developing countries (Nigeria inclusive) are concerned with the amount of foreign exchange spent on importing these adsorbents, thus local substitutes are given some consideration. Amongst various substitutes considered, activated carbon has shown much potential. This is due to its versatilities and abundance of carbonaceous agricultural wastes.

Despite the work done so far, there still remains according to recent reports a dearth of rigorous and comprehensive chemical engineering information

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published on the process development of activated carbon sourced from these raw materials particularly palm kernel shells, animal bones, rice husks and saw dust (Balci and Dogu, 1992).

The aim of this research is to determine the performance of activated carbon derived from rice husk and saw dust in the removal of heavy metals from aqueous solution of known concentration of the metal salts. And also to provide additional information relating to the process development of activated carbon from rice husks and saw dust using chemical activation method.

MATERIALS AND METHODS

Materials: The saw dust was collected from a saw mill which was close enough for research. It was obtained from a variety of woods which include chanomi, obeche, mahogany and iroko. . The rice husk was obtained from local rice farmers which appeared in its normal oblong shape. Other materials for the experiment include chloroform, ethanol, sodium hydroxide, phosphoric acid, acetic acid, iodine solution, sodium thiosulphate, cadmium and lead nitrates, indicator (Phenolphthalein and xylenol orange), sulphuric acid, hexamine, ethylene ditetra acetate solution (EDTA), ammonia solution, potassium cyanide, and sodium sulphide solution, pH meter.

Experimental Procedure: 2000g of each powdered sample (rice husk and saw dust) were mixed with 1500ml of 50% NaOH solution into a plastic bucket containing the powdered sample until a semi-fine paste was formed. The mixture was allowed to remain in the bucket for a minimum of 12hours before using it for further experiment. This impregnation process was carried out batch by batch for each required temperature (600^{o}C and 800^{o}C) for rice husk and saw dust. The paste obtained from the process of impregnation was sent immediately for carbonization. The paste was carbonised using furnace equipped with temperature control device. Each furnace crucible was pre-weighted before filling up with respective known weight of each paste and put inside the furnace. The timing of the carbonization was taken when the temperature of the furnace had reached the specific temperature (600^{o}C and 800^{o}C), with the aid of the thermostat control knob. This temperature was maintained for a period 3½ hours before it was switched off and allowed to cool down to room temperature. The crucible and the product were weighed together while the difference between the crucible plus product weight and the weight of the crucible gave the weight of product. Each product was thoroughly washed with water several times before neutralizing with 50% H_3PO_4 solution under a pH meter at a pH value of 7.0. The neutralized product was also washed again to remove the resulting salt of sodium phosphate due to the neutralization. The samples were then filtered and dried, and thereafter crushed to its powdered form. The following properties of the activated carbon from the rice husk and saw dust at the respective temperatures were also determined using ASTM standards and chemical engineering handbook (Perry *et* al., 1987, Babu and Ramakrishna, 2001).

- Yield, Moisture content, Adsorptive capacity of activated carbon by (CH_3COOH) aqueous phase
- Iodine number, Adsorbance of cadmium from aqueous solution, Adsorbance of lead from aqueous solution

RESULTS AND DISCUSSION

Figure 1 shows the effect of temperature on the adsorptive capacity of activated carbon obtained from rice husk (RH) and saw dust (SD). The adsorptive capacities of the four samples show a peculiar trend in acetic acid solution. RH 600^{o}C > SD 600^{o}C >RH 800^{o}C > SD 800^{o}C. This demonstrates the extend to which the pore surface developed within the matrix of the activated carbon. Using the principle, the greater the surface area, the higher the number of adsorptive site available. The results show that RH 600^{o}C, having the highest adsorptive capacity, will have the most developed surface area.

Table 1: Adsorption of Acetic Acid on activated carbon

Co (N)	RH 600^{o}C Sample 1		RH 800^{o}C Sample 2		SD 600^{o}C Sample 3		SD 800^{o}C Sample 4	
	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)
0.1	0.072	84	0.0845	46.5	0.098	6	0.0828	51.6
0.2	0.14	180	0.188	36	0.198	6	0.178	66
0.3	0.205	285	0.284	48	0.292	24	0.248	156
0.4	0.256	432	0.382	54	0.386	42	0.332	204
0.5	0.318	546	0.49	30	0.482	54	0.456	132

Key: C(N) Concentration of acetic acid, X/M Mass of acetic acid adsorbed per unit mass of adsorbent, SD Saw dust, RH Rice husk.

The results of the experiment are presented using log/log plots. The graph shows that the adsorptive capacities of the samples increase with increase in initial concentration of acetic acid with the exception of sample 2 (RH 800°C) which has almost equal adsorptive capacity with increase in initial concentration.

Sample RH 600°C has better adsorptive capacity than RH800°C at the respective concentrations, while the reverse is the case with activated carbon obtained from saw dust (SD). It can be conclusively stated that lower carbonization temperature increase the adsorptive capacity of activated carbon obtained from rice husk while higher carbonization temperature favours adsorptive capacity of activated carbon from saw dust.

Figure 2 shows the effect of temperature and concentration on the iodine number of activated carbon. Iodine number is a measure of the porosity (especially within the microspores) of activated carbon and is also the amount of iodine adsorbed (mg/g).

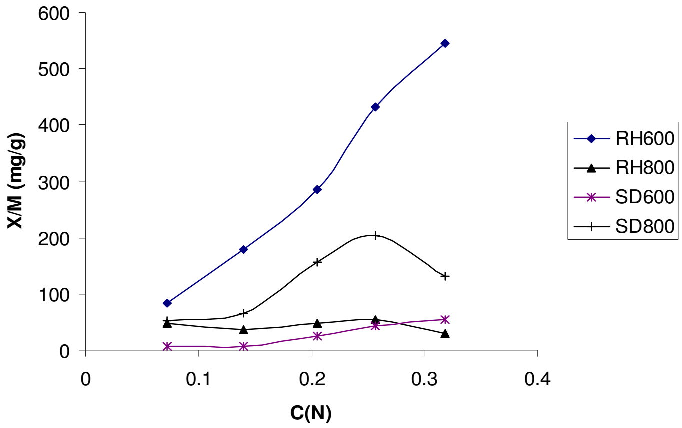

Fig. 1. Acetic acid adsorbance isotherm on activated carbo

Table 2: Result of Iodine Number Determination

Co (N) Initial conc. of Iodine	RH 600°C Sample 1		RH 800°C Sample 2		SD 600°C Sample 3		SD 800°C Sample 4	
	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)	C(N)	X/M (mg/g)
0.1	0.053	1058.6	0.0512	1108.9	0.072	528.03	0.0712	550.37
0.08	0.0312	969.7	0.0304	1477.5	0.0422	1064.2	0.043	1036.3
0.04	0.0048	680.34	0.0042	2248.2	0.0084	1952.2	0.0093	1890.8

Key: C(N) Concentration of iodine, X/M Mass of iodine adsorbed per unit mass of adsorbent, SD Saw dust, RH Rice husk.

It also shows the effect of concentration on the quantity of iodine adsorbed on activated carbon produced from rice husk and saw dust. The iodine number is the quantity of iodine adsorbed (X/M) at a residual iodine concentrations (c) of 0.02N. From figure 2 the iodine numbers of the various activated carbon samples were obtained as 60, 1780, 1650, and 1600 for RH600°C, RH800°C, SD600°C, and SD800°C respectively. There is considerable difference in iodine number between the activated carbon obtained from rice husk at the difference temperatures. But this is not the case for sample obtained from saw dust. However, it is noticeable that increase in carbonization temperature increases the porosity of the carbon.

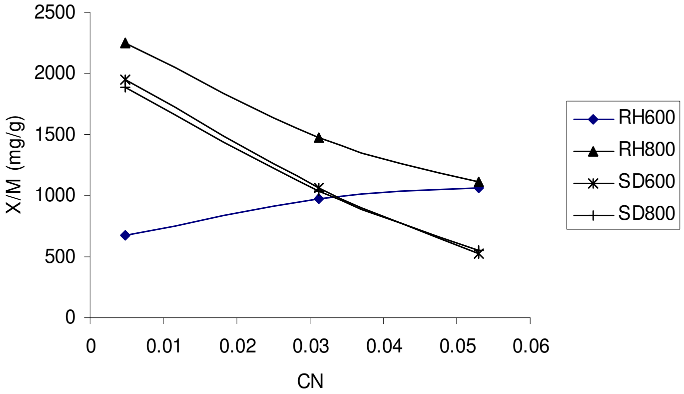

Fig 2: Iodine number determination

This is evident from the increase in iodine number for the samples (rice husk and saw dust) activated at 600°C and 800°C.

It can also be noted that RH samples have a better developed pore structure than the SD samples at the respective temperatures (great difference in iodine number). The iodine number for the RH is satisfactory compared with the commercial activated carbon. The saw dust samples were still developing, thus the need for higher carbonization temperatures.

Figures 3 and 4 shows the effect of concentration on the adsorbance of lead and cadmium from aqueous solution. It is seen that there is considerable adsorption of cadmium from its aqueous solution with RH600 showing better performance than RH800. The plot of sample SD 800 demonstrated some degree of adsorption but not up to the acceptable limit. This could be attributed to the fact that the pore surface area and pore structure were not fully developed. Thus comparing the performance of the samples, it is clearly seen that RH600 > RH800 > SD800 > SD600.

Table 3: Test on adsorbance of lead (II) ion from aqueous solution

$Pb(NO_3)_2$ (Mg/l)	Pb Initial Con. (mg/l)	RH600		RH800		SD600		SD800	
		Pb Con. (mg/l)	X/M (mg/g)	Pb Con. (mg/l)	X/M (mg/g)	Pb Con. (mg/l)	X/M (mg/g)	Pb Con. (mg/l)	X/M (mg/g)
5	3.13	0.075	0.31	0.105	0.298	0.120	0.286	0.225	0.291
25	15.63	0.105	1.56	0.125	1.55	0.125	1.523	0.325	1.53
50	31.27	0.1175	3.18	0.150	3.112	0.225	3.015	0.375	3.095
75	46.90	0.125	4.68	0.175	4.67	0.250	4.628	0.415	4.655
100	62.54	0.225	6.28	0.225	6.25	0.275	6.20	0.420	6.23

Table 4: Tests on adsorbance of cadmium (II) ion from aqueous solution

Cd $(NO_3)_2$ (mg/l)	Cd2+ (mg/l)	RH600		RH800		SD600		SD800	
		Cd (mg/l)	X/M (mg/g)	Cd (mg/l)	X/M (mg/g)	Cd (mg/l)	X/M (mg/g)	Cd (mg/l)	X/M (mg/g)
5	2.37	0.112	0.125	0.28	0.12	0.25	0.105	0.365	0.11
25	11.86	0.562	1.21	0.34	1.158	0.275	0.511	0.393	0.793
50	23.73	0.660	2.317	0.41	2.261	0.362	1.81	0.478	1.895
75	35.59	0.740	3.475	0.45	3.39	0.365	2.997	0.562	3.194
100	47.46	0.860	4.634	0.48	4.605	0.381	4.071	0.675	4.465

The same scenario was observed with lead from aqueous solution. However, the adsorbance of cadmium from aqueous solution is better than lead. Saw dust activated at 800°C showed better adsorbance of lead than saw dust at 600°C. Whilst for rice husk samples, it is seen that adsorbance increases with increase in initial concentration of lead samples.

The moisture content of the raw materials (rice husk and saw dust) were 14.6% and 5.8% respectively. Whilst the moisture content of the produced samples were 26% (RH 600), 26.5% (RH 800), 17% (SD 600) and 19% (SD 800). The moisture content of the active carbon is a measure of the hydrophilic tendencies of carbon samples and this is related to the surface properties of the carbon. Thus samples with increase moisture content have better developed pore structure and internal surface area.

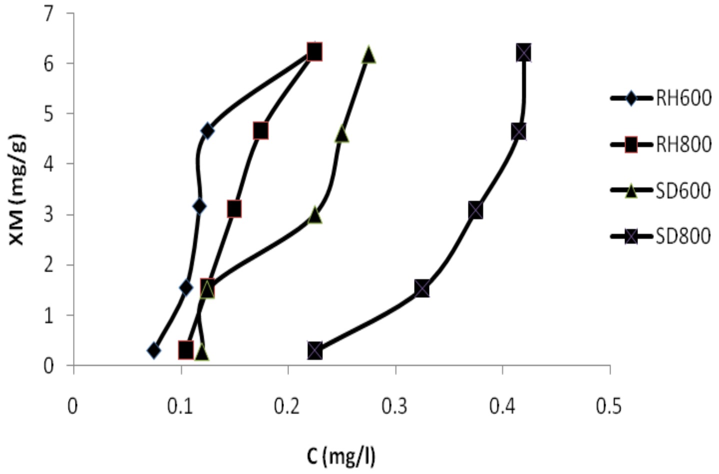

Figure 3: Adsorbance of lead (II) ion from aqueous solution

The yields of the various samples carbonized are presented in Table 6. It can be discerned that the yields of the two different raw materials at the respective temperatures fell within the same range with rice husk samples having the higher yield.

This might be due to presence of more organic components and impurities on the saw dust since the impurities are burnt off during carbonization. Since rice husk had higher yield it means that rice husk had a lower burnt off than that of saw dust. Yield for rice husk was 48% for RH600^{o}C, which is higher than that of saw dust which was 44% for SD600^{o}C.

It was further observed that the activated carbon obtained using rice husk as raw material was black and that obtained using saw dust as starting material was greyish. Though the rice husk carbon was black, it had some shades of black different from that of commercial grades. This clearly explains that the rice husk has higher carbon content.

Preliminary examination of the raw materials showed that rice husk and saw dust had a moisture content of 14.6% and 5.8% respectively. Increase in carbonization temperature decreases yield of the active carbon. The highest yield of about 48% was obtained from RH at 600^{o}C, with moisture content of 26%. The rice husk at 800^{o}C gave a yield of 47.2% with moisture content of 26.5%. Whilst the yield of the saw dust were 44% at 600^{o}C and 40% at 800^{o}C with moisture content of 17% and 19% respectively. Saw dust sample had lower adsorptive capacity and iodine number than rice husk samples. The RH600 showed the highest absorptive capacity. From the performance test carried out, it was sedn that the rice husk samples showed better performance in the adsorption of heavy metals (cadmium and lead). Taking the samples individually, and comparing their performance it can be stated that RH600 > RH800 > SD800.

Table 5: Moisture content of the Activated Carbon at different Temperatures

	RH 600	RH 800	SD 600	SD 800
Weight of crucible (g)	96.29	91.08	90.33	94.81
Weight of sample (g)	1.00	2.00	2.00	2.00
Total weight (g)	97.29	93.08	92.33	96.81
Total weight after heating (g)	97.03	92.55	91.99	96.43
Moisture content (%)	26%	26.5%	17%	19%

Table 6: Yield of the Activated Carbon after Carbonization of Raw Material at different Temperatures

	RH 600	RH 800	SD 600	SD 800
Initial weight (g)	250	250	250	250
Weight obtained (g)	120	118	110	100
Yield (%)	48	47.2	44	40

It can be concluded that the saw dust samples were still in the stage of development and their carbonization temperature requirement would be greater than 800^{o}C. Their porous structures were not fully developed. This is obvious from the results of the iodine number. Hence carbonization of these waste materials does not only manage the environment but is also a means of providing cheaper raw material for our growing chemical and allied industries.

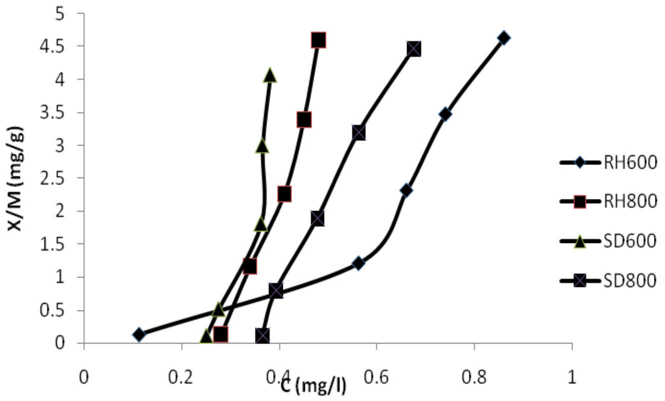

Figure 4: Adsorbance of cadmium (II) ion from aqueous solution

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