CHARACTERIZATION OF ADSORBENTS FOR THE PURIFICATION OF DRY – CLEANING EFFLUENT

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Abstract

The treatment of dry-cleaning effluent with locally developed adsorbent showed significant reduction in the concentration of pollutants. The surface area, bulk density, ash content, fixed carbon, pore volume, porosity and pH of the four locally developed adsorbents were estimated. The adsorbents were then used to treat effluent from a dry-cleaning centre. The limiting amount of solute (Xm) and the adsorption constant (K) for the four (4) developed adsorbent samples A, B, C and D were found to be 0.004 litre mg^{-1}; 0.05mgg^{-1}; 0.005 litres mg^{-1}; 0.327 mgg^{-1}; 0.004 litre mg^{-1}; 0.09 mgg^{-1} and 0.006 litre mg^{-1}; 0.219 mgg^{-1} respectively, while their fixed carbons are 0.90 (A), 0.92 (B), 0.81 (C), and 0.84 (D). The data obtained from the adsorption process were fitted in Langmuir isotherm. The calculated values of limiting amount of solute (adsorbate) and Langmuir's constant revealed that the coverage was of a monolayer type.

Keywords: Adsorbent, dry-cleaning, effluent, pollutant, carbonization, activation

Introduction

Activated carbon is an amorphous form of carbon which has been specially treated so that it possesses a very large surface area The large surface area obtained by developing the internal pore structure of carbon provides the activated carbon with the ability to adsorb gases and vapors from gases or dissolved and dispersed substances from liquids [Ejila and Tagang, 2001]. Two types of activated carbon known commercially are low density soft carbon, which are used for liquid phase adsorption and high density hard carbon, used for gas phase adsorption [Oyoh and Igbokwe, 2001]. Most of the activated carbons manufactured for liquid phase applications are used in powdered form. These carbons possess smaller surface area and lower degree of activation than the gas phase carbons, but the method of manufacture is such that to develop a surface character that has a greater capacity to remove substances from solution than is found in the more porous gas phase carbons [Oyoh and Igbokwe, 2001]. Activated carbons have a wide variety of Industrial uses and their potential applications come from the fact that activated carbon with desired internal surface area, porosity and adsorption characteristics can be manufactured virtually from any carbonaceous solid precursor both naturally occurring or synthetic [Dai, 1994]. Garcia – Garcia *et al* (1994) reported that numerous attempts to prepare activated carbons from solid waste have been undertaken with success. The approach to reuse waste materials is greatly desired and has great promises in the area of environmental pollution control especially when it is known that these solid waste materials are cheap, abundant and are easily converted into useful active carbons.

In an earlier study by Aneke and Okafor (2004), effluent from a dry - cleaning centre was purified using a locally prepared adsorbent and the result compared with the fresh solvent. The recovered solvent showed similar chemical and physical characteristics with the unused solvent.

Several equilibria models are in use to describe, understand and predict the behaviour of adsorption systems. The Langmuir isotherm model is used in this work to test and predict this liquid - phase adsorption system [Vasanth, 2004]. This present work therefore intends to characterise the locally developed adsorbent for the purification of dry-cleaning waste water and properties such as porosity, pore volume, bulk density, surface area, ash content and adsorption capacity were determined.

Materials and Method

Dry-cleaning effluent was obtained from Edison Dry-cleaning Services, No 23 E-close, FESTAC Town, Lagos State while bone and wood chippings were bought from New Market and Timber shed in Bida, Niger State.

Carbonisation: Carbonisation was carried out in a Muffle furnace (Model FSE 250-010-F/78-1171-D) which allowed a limited supply of air. Bone was carbonized at 900^oC while wood was carbonized at 800°C for 2 hours each. The charred products were allowed to cool to room temperature in three hours [Gimba et al, 2001].

Thermal Activation: The Muffle furnace was set at a temperature of 900^oC. A nickel crucible was cleansed and heated to a constant weight. A 25g sample of carbonized bone was charged and heated at the set temperature for three hours. [Gimba et al, 2001]. This w as named sample A. The procedure was repeated at 800^oC for half of the wood carbonized at 800^oC, and the resulting sample was named sample C.

Chemical activation: Twenty-five grames of carbonized bone was put in a beaker containing $500cm^3$ of 0.5M $ZnCl_2$ and the content thoroughly mixed and heated to 100^oC until it formed a paste. The paste was then transferred to a crucible which was placed in a furnace and then heated at 900^oC for two hours. The activated sample was cooled to room temperature, washed with distilled water and dried on the hot place [NPL -600-010Q/Oc-4405-G] at 100^oC for three hours. The final product of chemical activation was kept in an air-tight vial ready for use [Gimba et al, 2001]. This was named sample B and the procedure was repeated for wood ashed at 800^oC which gave sample D. Four different types of the adsorbents were developed and labelled A, B, C and D.
A - thermally activated bone
B. chemically activated bone
C. - thermally activated wood
D. - chemically activated wood

Determination of pH: Two grams of the adsorbent sample was weighed using a weighing balance. The weighed activated carbon was washed several times with distilled water and the extract collected. The pH of the extract was measured using a pH meter [Madukasi et al, 2001].

Determination of pore volume: The pore volume was estimated by boiling 2g of the sample immersed in water. After the air in the pore had been displaced, the sample was superficially dried and weighed again. The increase in weight divided by the density of water gives the pore volume. Porosity was therefore calculated from pore volume by dividing the pore volume of the particle with the total volume of the particle [Smith, 2000].

Determination of bulk density: Twenty grams of each of the adsorbents was weighed in air with a balance and then completely immersed in water using an overflow can and the balance reading was noted. The density was determined by dividing the mass of the activated carbon by the volume of water displaced through the overflow can [Okeke, 1995].

Determination of surface area: Iodine method according to Okuo et al, (2001), was used to determine the surface area of the activated carbon. 0.5g of activated carbon was weighed and centrifuged in 0.095M iodine solution. 0.1M sodium thiosulphate solution was titrated against 20ml activated sample free aliquot solution using 5ml of freshly prepared starch solution as indicator. The volume of thiosulphate required to titrate 20ml of blank solution was also determined. All the titrations were made in triplicate and the average value recorded. The surface area of the activated carbon was calculated using the inverse of iodine value (I.V.) [Okuo et al, 2001].

Determination of ash content: Two grams of the activated carbon was weighed and ignited in a Bunsen burner flame and cooled in a dessicator. The crucible with its content (activated carbon) was heated in Muffle furnace at 900^{o}C for three hours and then allowed to cool down to room temperature and the weight taken again. Ash content was found by finding the difference in weight [Odebunmi and Okeola, 2001].

Determination of adsorption capacity: A carefully weighed 2.0g of adsorbent sample was added to 100ml of the effluent. The mixture was centrifuged for one hour. The mixture was later filtered and the concentration of the filtrate determined using a spectrophotometer [Odebunmi and Okeola, 2001].

Treatment of data

For each adsorbent sample the adsorption ability (i.e the amount of solute adsorbed per gram of the adsorbent) was found from the absorbance data. The linearized form of the Langmuir isotherm equation given below was used [Gimba et al, 2001; Venkata and Karthikeya, 1997].

$$\frac{1}{x} = \frac{1}{x_m} k \times \frac{1}{c} + \frac{1}{x_m} \qquad (1)$$

where

x = amount of solute adsorbed per unit mass of adsorbent, (g/g)

x_m = limiting amount of solute (adsorbate) adsorbed per unit mass of adsorbent (i.e mono – layer capacity), (g/g)

k = a constant, (cm^3/g)

c = concentration of the solute in the solution that is in equilibrium with the adsorbent.(g/cm^3)

The experimental data were fitted in Langmuir isotherm to obtain a linear graph from which the monolayer coverage, x_m, was determined.

Results and Discussion

Physical properties of the developed adsorbents are shown in Table 1

Table 1: Physical properties of the adsorbents

Sample	Surface area (cm^2/g)	Bulk density (g/cm^3)	Ash Content (g)	Fixed Carbon (g)	Pore Volume	Porosity εp	pH
A	$1.053x10^2$	6.52	0.10	0.90	0.82	$1. 76x10^{-1}$	7.0
B	$1.372x10^2$	5.89	0.089	0.92	0.90	$1.56x10^{-1}$	6.0
C	$2.152x10^2$	11.36	0.19	0.81	0.65	$2.14x10^{-1}$	5.0
D	$1.729x10^2$	10.12	0.16	0.84	0.35	$1.24x10^{-1}$	6.0

Table 2: Physical properties of dry-cleaning effluent before Treatment.

Parameters	Effluent value	WHO Standard Values
pH	6.00	6.5-8.5
Turbidity (FTU)	630.00	0.40
Colour (Hazen)	200.00	5.00
Refractive Index	1.498	-
Conductivity (μs/cm)	140.00	750.50
Total dissolved Solids (ppm)	0.932	500.00
Temperature (°C)	30.00	21
Density (kg/m^3)	1375	-
Total suspended solids (ppm)	0.80	0.06
Total solid (ppm)	0.40	0.04
Odour	Pungent	Unobjectionable

Table 3: Physical and Biochemical properties of dry-cleaning effluent after treatment

Parameters	Wood based adsorbent		Bone based adsorbent	
	Thermally activated	Chemically Activated	Thermally Activated	Chemically Activated
pH	7.09	7.03	7.08	7.02
Turbidity (FTU)	220.00	87.00	106.00	73.00
Colour (Hazen)	130.00	45.00	110.00	30.00
Refractive Index	1.45	1.45	1.45	1.45
Conductivity (μs/cm)	1.32	1.26	1.28	1.14
Total dissolved solids (ppm)	0.88	0.84	0.85	0.76
Temperature (^oC)	29.50	29.00	29.00	29.00
Density (kg/m^3)	1372.00	1370.00	1370.00	1370.00
Total suspended solids (ppm)	0.02	0.06	0.07	0.04
Total solids (ppm)	0.09	0.10	0.10	0.09
Odour	Partially Removed	Fairly Removed	Partially Removed	Totally Removed

Table 2 shows the summary of physical properties of dry-cleaning effluent sample before treatment while Table 3 shows the results obtained for these physical properties after treatment with the developed adsorbents.

Analyses of the physical properties of developed adsorbents show that sample C has the largest surface area which favours adsorption processes followed by sample D while sample A had the lowest surface area [Odebunmi and Okeola, 2001].

Adsorbent C has the highest bulk density followed by adsorbent D. The bigger the bulk density of the adsorbent, the more suitable it becomes for adsorption because it will permit a more intimate contact with the effluent. [Carpsenter, 1985)]. The value of ash content and therefore fixed carbon for the adsorbents agree with those of the commercial activated carbon (CAC) [Gimba *et al*, 2001]. Adsorbent samples A and B (i.e. thermally and chemically activated bone respectively) exhibit the lowest ash content and the highest fixed carbon while adsorbents C and D (thermally and chemically activated wood) have approximately the same ash content and lowest fixed carbons.

A correlation had been shown to exist between fixed carbon and adsorption capacity. Activated carbons with high fixed carbon are found to have high adsorption capacity [Odebunmi and Okeda, 2001]. The presence of high ash content indicates low presence of fixed carbon in the adsorbent which is not desirable, hence adsorbent A would be preferred to wood based adsorbent. The pore volume of adsorbent A was bigger than that of adsorbent B while that of adsorbent C was greater than that of adsorbent D. Adsorbent D had the smallest value of the pore volume. Pore volume represents the presence of a cylindrical pore which may be either bidispersed or monodispersed in distribution. Adsorbent B is therefore the best out of the four samples.

Adsorbent C possess the highest porosity while adsorbent D has the least. Adsorbent A also had greater porosity than adsorbent B. Porosity indicates the atomic intragranular and intergranular arrangement of the adsorbent molecules. That is the space between each atom of the adsorbent and is characterized by porosity values. All pH values after treatment with the various adsorbents restored their pHs within admissible limit (6.5 – 8.5).

On using these developed adsorbents to treat dry-cleaning effluent, chemically activated bone (Sample B) was found to remove these pollutant indicators more effectively (85.0 – 88.4 %) while the other 3 samples achieved 35 – 86.2% effluent purification.
Table 4 was used in plotting $\frac{1}{x}$ against .$\frac{1}{c}$
and the graphs are shown in Figures 1 and 2

Table 4: Adsorption capacity data for thermally and chemically activated bone and wood

Samples	Thermally activated				Chemically activated			
	Bone		Wood		Bone		Wood	
	1/X	1/C	1/X	1/C	1/X	1/C	1/X	1/C
A	243.90	111.11	222.22	200.00	240.39	119.05	218.34	238.10
B	332.23	208.33	315.46	400.00	326.80	423.90	311.53	555.56
C	403.23	2500.00	406.50	1250.00	416.67	500.00	408.16	1000.00
D	502.51	5000.00	505.05	2500.00	510.20	1000.00	505.05	1666.67

Figures 1 and 2 confirm the formation of monolayer coverage of pollutant molecules on the surface of the thermally and chemically activated bone and wood.

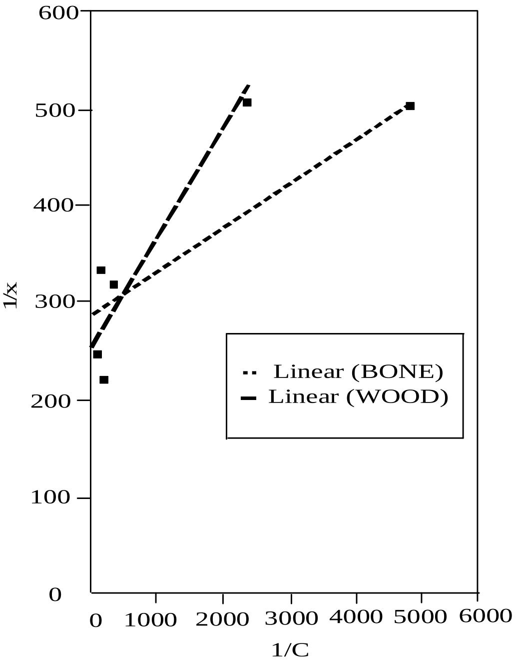

Fig. 1.0 Plot of 1/x against 1/C for thermally activated bone and wood

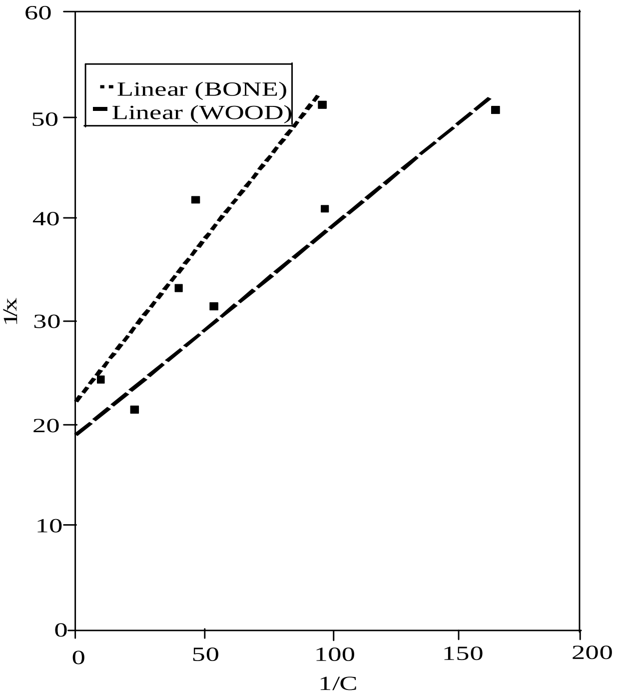

Fig. 2.0 Plot of 1/x against 1/C for Chemically activated bone and wood

The values of k and x_m were calculated from the slopes and intercept and were found to be 0.05 mgg^{-1}, 0.004 $litremg^{-1}$ for adsorbent A and 0.09 mgg^{-1}, 0.004 $litreg^{-1}$ for adsorbent C while the values for adsorbent B were 0.327 mgg^{-1}, 0.005 $Iitreg^{-1}$ and 0.219 mgg^{-1}, 0.006 $litreg^{-1}$ for D. Similar results were reported by Venkata and Karthikeya (1997) for sorption of azo dyes on activated carbon.

Fitting of the data to a linear form of Langmuir isotherm model indicates that the sorbent surface is uniform and homogeneous and that the sorption reaction results in the formation of a monolayer of adsorbed molecules.

Conclusion

The waste water from the dry-cleaning centre was highly polluted but these pollutants were drastically reduced after it was treated with the locally made adsorbents. These adsorbents labelled A, B, C and D were characterized by measuring the pore volume, porosity, bulk density, surface area, ash content and percentage fixed carbon. The experimental data fitted well into Langmuir isotherm model shows that the coverage is monolayer. Sample B was found to be very suitable in the treatment of dry-cleaning wastewater before discharge into the environment.

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