Thermal Evaluation of Some Locally Sourced Activated Carbons from Agricultural Residues

Emmanuel O. Sangotayo [1*]   Olukunle E. Itabiyi [1]   Kasali A. Adedeji [2]

Oluwaseun A. Babarinde[1]   Michael O. Obasesan[1]

1.Department of Mechanical Engineering, Ladoke Akintola University of Technology, Ogbomoso,Nigeria.

2.Department of Mechanical Engineering, Lagos State University, Epe, Lagos State, Nigeria

Abstract

Activated carbons are progressively used as an economical and stable mass separation agent for eliminating surfactants to raise the final product property in many industrial processes. Activated carbon has various applications in different fields, and it performs differently at different temperatures; hence this paper presents a thermal experimental characterization of some locally produced activated carbon from agricultural residues. The experiment was done on the locally produced activated carbon from coconut shell, coconut husk, palm kernel shell, maize husk and imported activated carbons. The adsorbate used is Methylene Blue (MB), the samples were agitated in a water bath shaker at different concentration of adsorbate (50, 100, 150 and 200 ppm) and different temperatures (30 ºC, 40 ºC, and 50 ºC). Adsorption isotherm study is carried out on two well-known isotherms; Langmuir and Freundlich isotherm models. The results revealed that the adsorption capacity of the five samples increased with temperature and initial dye concentration. The adsorption in the samples follows the Langmuir Isotherm model that implies homogenous adsorption and Maize husk has the highest monolayer adsorption capacity at 40 ºC. Hence the carbons will perform satisfactorily under heat as the combination of adsorbent and adsorbate in adsorption refrigeration system. The locally produced activated carbons compared favourably with imported activated carbon, hence locally produced activated carbons can replace imported activated, to reduce dependency on foreign product and improve the economy of the country.

Keywords: Evaluation, Activated carbon,Adsorption Isotherm, Agricultural Residues

1. Introduction

The significance of activated carbon to an ever-growing society cannot be overstated considering its immense applications. Its utilizations range from liquid phase to gaseous phase applications. Activated carbons are highly porous and adsorbent materials. They have broad applications in domestic, commercial and industrial settings (Mendez *et al*., 2006). In the food industry, activated carbon is used in de-colourization, deodorization, and taste removal. It is used to remove heavy metals and organic contaminants from liquids. Activated carbon is used in water de-chlorination and processing of foods. It is also used in medicine for adsorption of harmful chemicals and drugs. In gas cleaning applications, activated carbon is extensively used in air filters at industrial level as well as in general air conditioning application (Oyo and Igbokwe, 2001, Diets, 1990, Inamullah *et al.,* 2008, and Elliot *et al.,* 1989).

Guo and Lua (2001) described the characteristics of activated carbon depend on the physical and chemical characteristics of the materials as well as activation technique used. The physical properties of carbon are essential in determining which form is best suited for specific application. The abrasion resistance or hardness of activated carbon will be vital if the coal is to be expended in use where many backwashing is required. Density characteristic is one of significant consideration for specific applications. Densities vary with the raw materials. A fewer quantity of carbon with a lower density will fit into a given container as compared to a coal with high density. This is significant because while a container may require less carbon weight of low density to make a fill, its contaminant removal performance may be severely reduced as compared to a high-density carbon. Iodine value is an essential characteristic of activated carbon. The iodine value gives the amount of the micropore volume of coal, and it approximates the total internal surface of the coal. The ash level reflects the purity of the coal. The ash content can be crucial in water filtration applications. Activated carbon with high phosphate ash can brings about cloudy water during usage because the ash combines with metal ions to form magnesium or calcium precipitates (Ecologix systems, 2008). The performance of activated carbon is indicated by its adsorptive characteristics, which is derived from the specific surface area, porosity of the carbon (Akinyemi and Taiwo, 2004). Micropores are formed in the interlayer spacing with widths in the range of 0.34 – 0.8 nm. It is the micropores in activated carbon which have the most significant influence upon gas adsorption while macropores and mesopores are essential in transport of fluids to and from the micropores (Hu and Srinivasan, 2001).

Activated carbons are used as an economic and stable mass separation agent for the removal of surfactants to improve the finishing product quality in many industrial processes. Activated carbons also play an essential role in many areas of modern science and technology such as purification of liquids and gases, separation of mixtures, and catalysis (Tay *et al*., 2001). Adsorption of activated carbon is regulated by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic (Rozada *et al*., 2003). Torregrosa-Macia

et al., (1997) given industrial application, a solid adsorbent with a comparatively wide pore size determination can be obtained solely through a chemical activation techniques. Physical activation can further enhance the adsorbent's pore structure due to a partial oxidation of the carbonized material by gases such as CO/CO_2 or steam (Molina-Sabio *et al.*, 1996, Rodriguez-Reinoso *et al.*, 1995). The study of the surface physical characteristics of the carbon includes determination of the total surface area, extent of microporosity, and characterization of the pore size distribution. The degree of the microporosity is commonly evaluated by applying low-pressure isotherm data to the Dubinin– Radushkevich (DR) equation. (Warhurst *et al.*, 1997).

Sangotayo *et al.*, (2017) described experimental analysis of the characterization of activated carbon produced from local materials which includes: activated carbon from coconut shell, coconut husk, maize husk and palm kernel shell. The mass of activated carbons produced from coconut shell, coconut husk, maize husk and palm kernel shell are 688.21 g, 539.89 g, 482.53 g and 707.37 g, respectively. The percentage composition of Iodine value obtained from the same quantity of imported activated carbon (12.143 %), coconut husk (60.1 %), maize husk (38.1 %), palm kernel shell (24.286 %) and coconut shell (63.571 %) and the percentage surface area of imported activated carbon (42 %), coconut shell (21 %), coconut husk (24.1 %), maize husk (33.1 %) and palm kernel shell (37 %). The higher the iodine number, the higher the rate of adsorption of activated carbon and locally produced carbon from agricultural residue can be used to replace the imported coal.

The knowledge of the physical and activity characteristics of activated carbons helps in determining where each can be better applied. From various studies and research, it was discovered that agricultural residue could be used to produce activated carbons which do not cost much as the imported ones; though they serve almost the same purpose but the cost of importation for various use results in low quantity purchased compared to the amount needed in multiple industries. Nevertheless, little or no work has been done on thermal characteristics of locally produced activated carbon because effectiveness of activated carbon is affected by temperature. Thermal performance of some locally produced activated carbon and foreign coal is presented in this work

2. Materials and Methods
2.1 Materials
The experiment was carried out on the activated carbons locally produced from agricultural residues which are abundant with little or no cost such as coconut shell, coconut husk, palm kernel shell, maize husk and costly imported activated carbon. The adsorbate used is Methylene blue (MB).

2.2 Physical Characterization of Available Activated Carbon
2.2.1 pH measurement
5 g of each adsorbent were mixed with 200ml of distilled water measured in different conical flasks. The solutions were shaken thoroughly until it dissolved. Then, the pH meter electrode was dipped into each solution, and then readings were recorded.
2.2.2 Conductivity determination
5 g of each adsorbent were mixed with 200ml of distilled water measured in different conical flasks. The solutions were shaken thoroughly until it dissolved. Then the conductivity meter electrode was dipped into each solution, and then readings were taken from the meter.
2.2.3 Bulk density
The weight of the empty measuring cylinder was firstly recorded using an electric weighing balance. Then, the weights of the samples (10ml each) together with the measuring cylinder were taken. The mass and volume were recorded, and the bulk density was calculated using the equation (1.0).

$$\rho = \frac{m}{v} \qquad (1.0)$$

Where m is the mass in gramme and v is the volume occupied in cubic metre, (Yosiyuki and Yukata, 2003, Aziza *et al.* 2008).
2.2.4 Moisture Content Determination
5 g each of the adsorbent were weighed in clean dried and pre-weighed Petri dishes. The sample were thinly spread in the dishes and then dried in air- circulated oven at 105 ºC for 5 hours. The dry samples were cooled in a desiccator for 30 minutes. In order to ascertain constant weight, the percentage moisture content (Percentage loss in weight) was calculated using equation (2.0). (Aziza *et al.* 2008).

$$Moisture(\%) = \frac{\left(w_i - w_f\right)}{w_i} \times 100\% \qquad (2.0)$$

Where w_i and w_f are weight of sample before drying and after drying respectively.

2.3 Batch Adsorption Experiment
2.3.1 Preparation of Adsorbate
The adsorbate used in this work is Methylene Blue (MB), the solution of the dye was prepared by dissolving 1 g of the dye in distilled water 1000 cm³ (1dm³) volumetric flask and then made up to the mark with distilled water. This gives 1000 mg/L (1000 ppm) of the solution.

2.3.2 Effect of Contact Time on Dye Adsorption
1 g each of the adsorbent was measured into different glass flasks. A 20ml volume of 50mg/L solution of the dye was added to each of the adsorbents. The adsorbent were agitated for different time intervals (60, 120, 150 and 180 minutes) at room temperature. At each time interval, it was filtered, and the filtrates were analyzed at a wavelength of 664 nm using Bio base (B-UV1080OPC) Spectrophotometer in order to determine the equilibrium time for each adsorbents.

2.3.3 Effects of Temperature on Dye Adsorption
Solutions of the dye (20ml) in mixture together with the adsorbents (1g each) were agitated at 30 ℃, 40 ℃ and 50 ℃ keeping other equilibrium parameters constant at the optimum values. It was then filtered at each predetermined equilibrium time for the adsorbents and filtrates were analyzed.

2.3.4 Effects of Initial Dye Concentration on Dye Adsorption
A 20ml solution of different initial concentrations (50, 100, 150 and 200 mg/L) of each dye in single dye system prepared from the stock solution by serial dilution was added to 1g each of the adsorbents in the glass flasks, keeping other parameters constant. The mixture was agitated at room temperature until equilibrium was reached, it was then filtered, and the filtrates were analyzed for the residual dye content.

2.3.5 Effects of Temperature and Initial Dye Concentration on Adsorption Capacity
A 20ml solution of different initial concentrations (50, 100, 150 and200 mg/L) of each dye in single dye system prepared from the stock solution by serial dilution was added to 1g each of the adsorbents in the glass flasks, keeping other parameters constant. The mixture was agitated 30 ℃, 40 ℃ and 50 ℃ until equilibrium was reached, it was then filtered, and the filtrates were analyzed for the residual dye content.

2.3.6 Adsorption Measurement
Adsorption isotherm study is carried out on two great- known isotherms: Langmuir and Freundlich isotherm models. The applicability of an isotherm model is judged by comparing the closeness of its correlation coefficients, R^2 values, to 1 (Bello *et al.,* 2008). The linear form of Langmuir isotherm model is given by the equation (2.0)

$$\frac{c_e}{q_e} = \frac{c_e}{q_0} + \frac{1}{q_0 b} \qquad (2.0)$$

Where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the quantity of adsorbate absorbed per unit mass of adsorbent (mgg⁻¹). q_o and b are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively (Bello et al., 2008). The well-known logarithmic form of Freundlich isotherm model is obtained using equation (3.0)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3.0)$$

K_f is rough indicator of the adsorption capacity related to the bond energy and $\frac{1}{n}$ is the adsorption intensity of dye onto the adsorbent or surface heterogeneity (Prasad and Santhi, 2012).

3. Results and Discussions
3.1 Physical Characterization of Available Activated Carbon
Figure 1.0 presents pH measurement results of the five activated carbon samples used such as Coconut shell, Coconut husk, Palm Kernel shell, Maize Husk and an Imported Activated Carbon. It was seen that Coconut Husk has the highest pH value of 10.35 (Alkaline) followed by the imported sample with value 10.00 (Alkaline). The sample with the lowest value is Palm Kernel shell with a pH of 7.14. However, from a study, it is known that the rate of removal decreases as pH increases, i.e., the adsorptive capacity of a sample decreases as the pH increases. Therefore, Palm Kernel Shell has more adsorptive capacity than any of the samples.
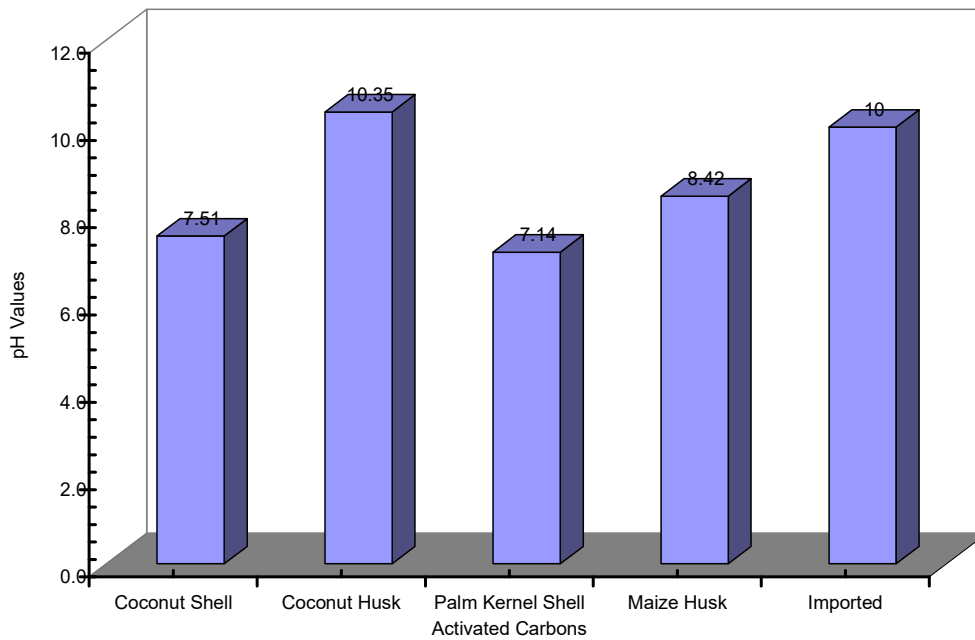
Figure 1.0 pH values of the five activated carbon samples

Figure 2.0 presents a conductivity value obtained for the five activated carbon samples. The conductivity carried out on the five samples used in the experiment; it was discovered that Coconut husk as the lowest rate of conductivity and the sample with the highest is Palm Kernel Shell (PKS) followed by the Maize Husk. This result shows that PKS tends to conduct faster than any of the considered samples.
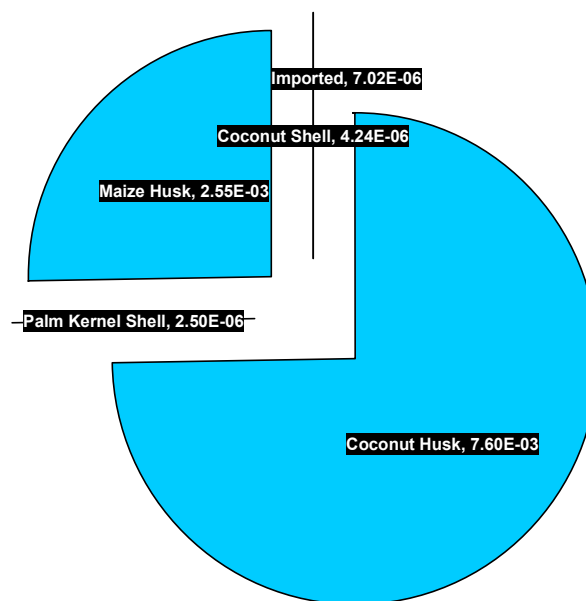

Figure 2.0 Conductivity values of the five activated carbon samples

Figure 3.0 presents bulk density values for the five activated carbon samples used in the experiment. It was discovered that Coconut shell has a large density than any of the considered examples with a value of 0.674 followed by the imported one with a value of 0.569 and the instance with the least amount is Maize Husk with 0.15. Less dense materials have low adsorption rate which means Maize Husk has the highest rate of adsorption.
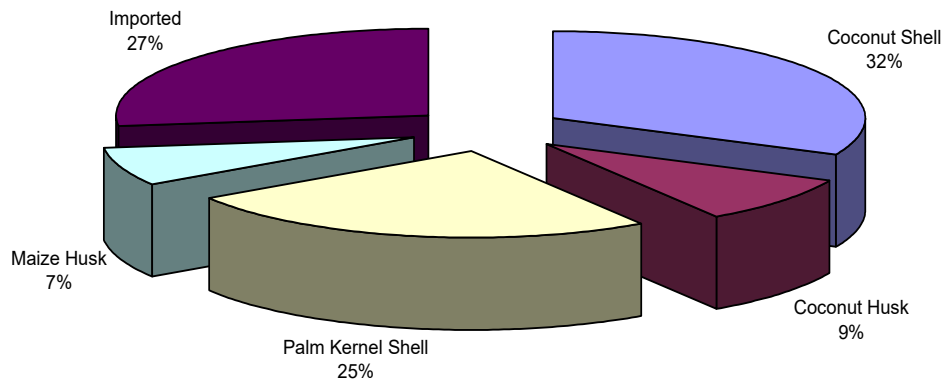
Figure 3.0 Bulk density values of the five activated carbon samples

Figure 4.0 presents the moisture content values for the five activated carbon samples. It revealed that both Palm Kernel shell and the imported example has a low content of moisture in it with a value of 4 while Maize Husk has the highest which is 16 followed by Coconut Husk with an amount of 14. The sample with low moisture content has a higher rate of adsorption than all other samples which is Palm Kernel Shell and the imported sample.
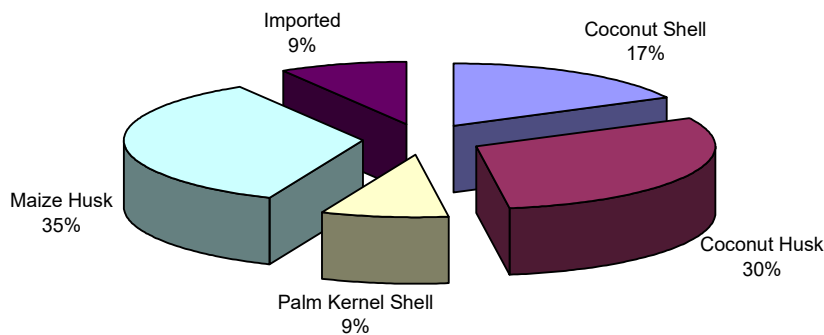

Figure 4.0 Moisture content values of the five activated carbon samples

The effect of contact time on dye adsorption in all the five activated carbon samples is presented in Figure 5.0. The adsorption of methylene blue increased with increasing contact time. As time increased from 60 – 180 minutes, the adsorption capacity, q_e (mg/g) also increased. q_e remains constant for all the dye systems. For the adsorption of Methylene blue on each adsorbent, q_e increased with time and then reached equilibrium at a point after which it becomes constant. This is because as time increases, the surface of the adsorbent has more extended contact with the dye thereby attracting more dye molecules. But at equilibrium, the surface of the adsorbent has been saturated (occupied). Therefore after stability, q_e becomes constant. The equilibrium time for each adsorbent is as shown in Figure 5.0. Similar reports were given by Hameed (2009) and Jabli *et al.*, (2011).
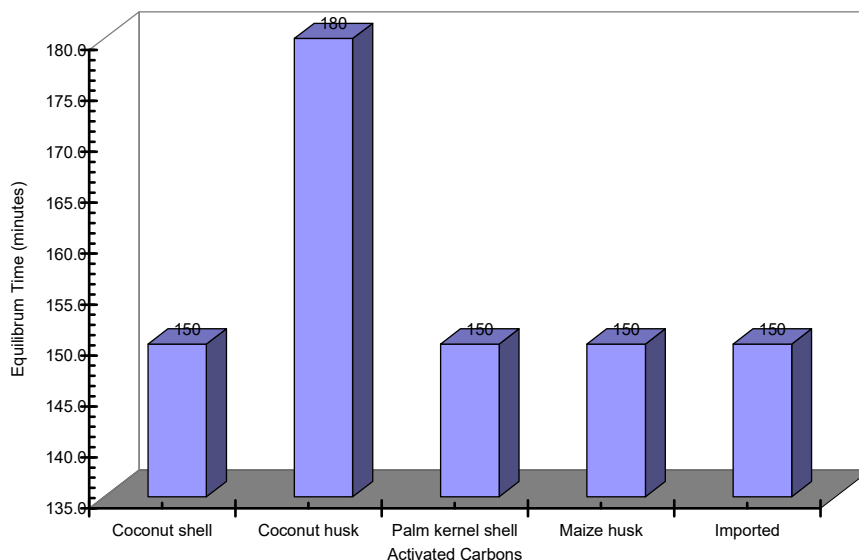

Fig. 5.0: Equilibrium Time for Each Adsorbent

The influence of temperature on the adsorption of dye in all the five activated carbon samples is presented in Figure 6.0. The adsorption capacity of each adsorbent for Methylene Blue (MB) increased as temperature increased (Fig. 6.0). It is due to an increase in the number of molecules that become mobile and acquire sufficient energy to undergo an interaction with active sites at the surface. Also, an increase in temperature produces a swelling effect with the internal structure of the adsorbent enabling large dyes to penetrate further (Verma and Mishra, 2009). A similar report was given by Singh and Srivastava (2001).
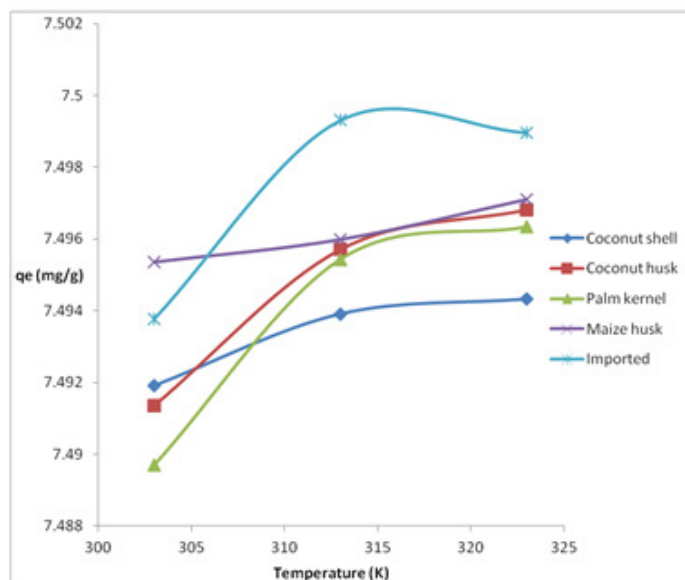

Fig. 6.0 Effect of Temperature on Adsorption of Methylene Blue on each Absorbent

The effect of initial dye concentration on dye adsorption in all the five activated carbon samples is presented in Figure 7.0. It was revealed that the adsorption of Methylene blue (MB) increased with increasing initial dye concentration at equilibrium. The observed increase in the dye specific uptake for the dye with increasing initial dye concentration may be because, at low levels, the number of dye molecules present is small, but at higher frequencies, the number of dye molecules available is high enough to overcome resistance to mass transfer. Similar reports were given by Bello et al., (2012) and Giwa et al., (2013).
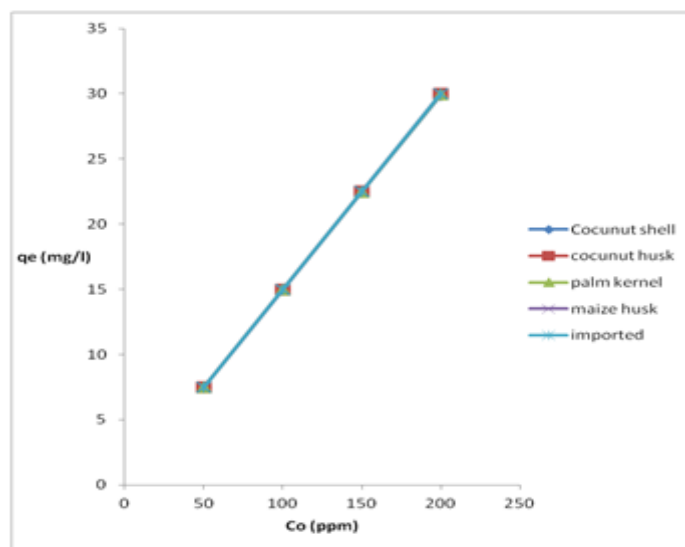

Fig.7.0: Effects of Initial Dye Concentration on Adsorption of Methylene Blue for each Adsorbent.

Adsorption of Methylene Blue on the five Activated Carbon samples has R^2 values for Langmuir Isotherm greater than R^2 values for Freundlich isotherm as presented in Table 1-5. Hence, the adsorption follows Langmuir isotherm which implies that adsorption is homogenous. Figure 8.0 presents Langmuir Isotherm plot for Adsorption of Methylene Blue on Coconut Shell (CS), Coconut Husk (CH), Palm Kernel Shell (PK), Maize Husk (MH) and Imported (IM) samples

Table 1.0: Isotherm Parameters for Adsorption of Methylene Blue on Coconut Shell

Temperature(K)	Langmuir			Freundlich		
	R^2	q_o	b	R^2	1/n	K_f
303	1.00	33.003	7.10	0.853	0.3944	35.60
313	0.9986	35.211	5.826	0.9869	0.5056	39.20
323	0.9997	37.313	5.411	0.9909	0.5282	36.72

Table 2.0: Isotherm Parameters for Adsorption of Methylene Blue on Coconut Husk

Temperature(K)	Langmuir			Freundlich		
	R^2	q_o	B	R^2	1/n	K_f
303	0.6848	3.880	28	0.773	-2.7452	0.00424
313	0.9982	14.88	3360	0.0164	-0.0427	14.648
323	0.3697	13.83	1032.85	0.292	-0.4782	2.597

Table 3.0: Isotherm Parameters for Adsorption of Methylene Blue on Palm Kernel Shell

Temperature(K)	Langmuir			Freundlich		
	R^2	q_o	B	R^2	1/n	K_f
303	0.7071	40.984	7.87	0.8271	0.5442	60.23
313	0.9957	34.13	11.72	0.8435	0.4245	42.45
323	0.8518	41.32	5.26	0.6815	0.5039	45.07

Table 4.0: Isotherm Parameters for Adsorption of Methylene Blue on Maize Husk

Temperature(K)	Langmuir			Freundlich		
	R^2	q_o	b	R^2	1/n	K_f
303	0.89	15.243	656	0.0297	0.1347	23.52
313	0.0007	270.27	2.47	0.1139	0.7979	328.09
323	0.0087	43.29	16.5	0.0017	0.1649	29.60

Table 5.0: Isotherm Parameters for Adsorption of Methylene Blue on the Imported sample

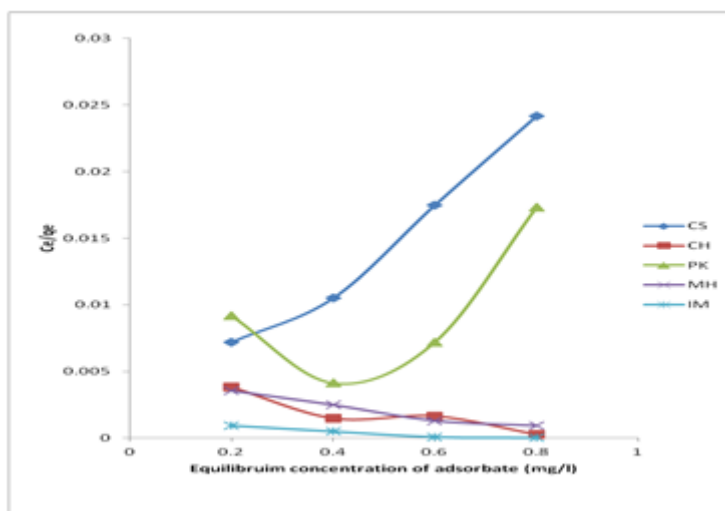| Temperature(K)	Langmuir			Freundlich		
	R^2	q_o	b	R^2	1/n	K_f
303	0.9563	5.45	79.74	0.8909	-1.1154	0.229
313	0.2423	17.09	9750	0.0042	-0.266	8.602
323	0.7766	9.83	254.25	0.7541	-0.5108	0.862

Fig 8.0: Langmuir Isotherm plot for Adsorption of Methylene Blue on Coconut Shell (CS), Coconut Husk (CH), Palm Kernel Shell (PK), Maize Husk (MH) and Imported (IM) samples

4   Conclusions

This work presented an experimental thermal characterization of some locally produced activated carbons from agricultural residues such as coconut shell, coconut husk, palm kernel shell, maize husk and imported activated

carbons. Coconut Husk has the highest pH value of 10.35 (Alkaline) followed by the imported sample with value 10.00 (Alkaline). The sample with the lowest value is Palm Kernel shell with a pH of 7.14. The adsorption of methylene blue increased with increasing contact time. Adsorption capacity for the five samples increased with an increase in temperature and initial dye concentration. Adsorption of methylene blue (MB) on locally produced activated carbon and an imported sample follow the Langmuir Isotherm model which implies homogenous adsorption. Maize husk has the highest monolayer adsorption capacity at 40 °C. Hence the carbons will perform well under heat as the combination of adsorbent, Activated carbon and adsorbate in adsorption refrigeration system. The locally produced activated carbons compared favourably with imported activated carbon, therefore locally produced activated carbons can replace imported activated, to reduce dependency on foreign AC and improve the economy of the country.

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