Sawdust as an Adsorbent for the Removal of Methylene Blue from Aqueous Solution: Adsorption and Equilibrium Studies

.   Suleiman Idris, Muhammed M. Ndamitso, Yahaya A. Iyaka and Etsuyankpa B. Muhammad

Abstract - **The present research indicated that activated carbon prepared from saw dust has been used to adsorb methylene blue (MB) from aqueous solution using NaOH as an activating agent at initial concentration of 10-50 mg/L. Percentage carbon yield decrease with increase in activation burn off time since more volatiles are release from the char. The pH range of 7.81±0.01 to 7.83±0.02 obtained by activated carbons prepared from saw dust is suitable for MB removal from aqueous solution since for most application, activated carbon pH of 6-8 is acceptable. Adsorption capacity at equilibrium (q_e) tend to increases with increases in initial concentration from 10 – 50 mg/L with higher MB removal of 99.67 % recorded. Adsorption isotherm which include Langmuir, Freundlich, Temkin and Harkin's – Jura were used to analysed the equilibrium data. Langmuir isotherm best described the adsorption data with higher correlation coefficient R^2 values ($R^2 = 0.982$, $R^2 = 0.996$ and $R^2 = 0.995$) and R_L values less than one ($R_L = 0.009$, $R_L = 0.001$ and $R_L = 0.001$) for SD/NaOH/5,   SD/NaOH/10   and   SD/NaOH/15 activated carbon respectively.**

Keywords- **Adsorption capacity, Correlation coefficient, Equilibrium, Harkin's-Jura.**

I.INTRODUCTION

Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula:

S. Idris is with the Department of Chemistry Federal University of Technology P. M. B. 65 Minna, Niger State Nigeria (+2348065699124;e-mail: suleimandrs@gmail.com).

M. M. Ndamitso is with the Department of Chemistry Federal University of Technology P. M. B. 65 Minna, Niger State Nigeria (e-mail: ndamitso@yahoo.com).

Y. A. Iyaka is with the Department of Chemistry Federal University of Technology P. M. B. 65 Minna, Niger State Nigeria (e-mail: iyaka07@yahoo.com).

E. B. Muhammad is with the Center for Preliminary and Exral Moral Studies, Federal University of Technology P.M. B.65, Minna, Niger State Nigeria (e-mail: myankpa@yahoo.com).

$C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odorless, dark green powder, that yields a blue solution when dissolved in water. MB is an important basic dye widely used for coloring paper, temporary hair colorant, coating for paper stock, dyeing, printing cotton and tannin, dyeing leather, used as an antiseptic and for other medicinal purposes (Methylene blue, 2011).

The release of dyes into wastewaters from textile, cosmetic, paper and coloring industries poses serious environmental problems. The coloration of the water by the dyes causes inhibitory effect on photosynthesis affecting aquatic ecosystems (Theivarasu *et al*.,2011). Adsorption of methylene blue from the aqueous phase is a useful toll for product control of adsorbents. Some kinds of sawdust have been studied as adsorbents for removal of methylene blue from aqueous solution (Rezal *et al*.,2011).

Adsorption using activated carbon is mostly widely used method to remove dyes from aqueous solution because of its low cost, ease of operation. But its use is limited because of high cost and associated problems of regeneration, there is a constant search for cheaper substitutes. Many efforts have been made to use low cost agro waste materials in substitute for commercial activated carbon. Some agro waste materials studied for their capacity to remove dyes from aqueous solutions are coir pith (Namasivayam and Kavitha, 2002), Cocoa Shell (Theivarasu *et al*.,2011) etc.

The present research is to remove methylene blue from aqueous solution using activated carbon prepared from sawdust. Adsorption isotherm which include Langmuir, Freundlich, Temkin and Harkin's- Jura were used to correlate the adsorption data.

II. MATERIALS AND METHODS

A. *Sample Collection and Preparation*

The sawdust was obtained from Maitumbi sawmill Kuta road Minna Niger State, Nigeria. The methylene blue dye effluent was purchased from Nahson medical equipment store, Hospital road,

Minna, Niger State, Nigeria. The experiment took place between April-September 2011.

The sawdust was sun dried, then oven dried at 100^oC until properly dried. The sample was ground and sieved with a 2 mm mesh size sieve. The less than 2 mm samples were stored in airtight container. Ash content was determined according to the method described by AOAC (1990).

B. Preparation of Adsorbent

Activation involving two steps activation process was adopted. 5 g of blended raw sample was weighed into clean and pre-weighed crucibles. They were introduced into a muffle furnace at 600^oC for 5 minutes after which they were poured from the crucible into a bath of ice water. The excess water was drained off then carbonized sample was washed, using 0.1 M HCl to remove surface ash, followed by hot water wash and further washing with distilled water to remove residual acid. The sample was then sun dried, and further dried in the oven at 100^0C for one hour. This process was repeated until a substantial amount of carbonized sample was obtained.

Thereafter, 5g of already carbonized sample was mixed with $5cm^3$ of activating agent (1M NaOH). The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800^0C for 5 minutes. The activated sample was cooled with ice-cold water, excess water was drained off and the sample dried at room temperature. The above procedure was repeated for different residual time (10 min and 15 min) until substantial amount of activated carbon was obtained. Washing was continue until the pH of sample solution fall within 6-8, then the sample was dried in an oven at 110^oC overnight and stored in air tight container (Rahman *et al*., 2005; Fan *et al*., 2005).

C. Activated Carbon Characteristic

Bulk density (g/cm^3) =

$$\frac{\text{Weight of dry activated carbon(g)}}{\text{Volume of packed dry material(cm}^3)} \qquad (1)$$

(Apipreeya *et al*., 2006)

$$\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \quad X100 \qquad (2)$$

W_0= weight of char after pyrolysis, washing and drying.

W_1 = weight of carbon after activation, washing and drying   (Ioannidou and Zabaniotou, 2006).

$$\% \text{ Yield} = \frac{W_1}{W_0} \quad X 100 \qquad (3)$$

$W_{0 =}$ Original mass of precursor

W_1 = weight of carbon after activation, washing and drying   (Yulu *et al*., 2001)

pH was determined using a pH meter and the conductivity was taken using a conductivity meter at room temperature (Okiemen *et al*., 2004).

D. Equilibrium Studies Using Batch Method

2g of activated carbon was interacted with 40 cm^3 of methylene blue dye 10 ppm solution in a beaker at 30^oC. It was covered and allowed to stand for 1 hour. It was than filtered using whatman filter paper (No.42). The process was repeated at different concentration (20, 30, 40 and 50 ppm). Each mixture was separately filtered and the filtrate was collected. The absorbance of the solution of standard series and each filtrate after interaction was taken using JENWAY spectrophotometer at 650 nm.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(C_o - C_e) \, V}{W} \qquad (4)$$

Co and Ce (mg/L) are the liquid-phase concentration of dye at initial and equilibrium.

V(L) = volume of the methylene blue dye solution.

W(g) = weight of the activated carbon.

The percentage dye removal was calculated as:

$$\% \text{ methylene blue removal} = \frac{C_o - C_e}{C_o} X100 \qquad (5)$$

(Hameed, 2009)

E. Adsorption Isotherm

Adsorption isotherm is basically important to describe how solutes interact with adsorbates, and is critical in optimizing the use of adsorbents.

Langmuir Isotherm

The Langmuir isotherm is based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent (Langmuir, 1918). This model also suggests that there is no lateral interaction between the sorbed molecules. Linear form of Langmuir isotherm is

$$1/q_e = 1/K_a q_m C_e + 1/q_m \qquad (6)$$

$K_a(L/mg)$ = Langmuir constant related to adsorption capacity.

$q_m(mg/g)$ = Langmuir constant related to energy of adsorption.

Langmuir constants K_a and q_m can be calculated from the slope and intercept of the plot of $1/q_e$ versus $1/C_e$.

Freundlich isotherm

The Freundlich isotherm is based on multilayer adsorption on heterogeneous surface (Freundlich,1906). The linear form of Freundlich equation is

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (7)$$

K_F (mg/g) = Freundlich constant indicating adsorption capacity.

n = adsorption intensity.

Freundlich constant K_F and n can be calculated from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$.

Temkin isotherm

The linear form of Temkin isotherm is given as

$$q_e = B \ln A + B \ln C_e \qquad (8)$$

$A(L/g)$ = Temkin constant related to maximum binding energy.

$B(J/mol)$ = Temkin constant related to heat of sorption.

The plot of q_e versus $\ln C_e$ enables the determination of the constants A and B (Temkin and Pyzhev, 1940).

Harkin's – Jura isotherm

Harkin's – Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore distribution (Gurses *et al.*, 2006). The linear form of the equation is given as

$$1/q_e^2 = (B/A) - (1/A(\log C_e)) \qquad (9)$$

Where A and B are the isotherm constants which can be calculated from the slope and intercept of the plot of $1/q_e^2$ versus $\log C_e$.

III. RESULTS AND DISCUSSION
A. *Characteristics of Activated Carbon*

The percentage ash content of the sample was low which is an indication of higher carbon yield by the sample. The pH of the activated carbons ranges from 7.81 ± 0.01 to 7.83 ± 0.02 respectively. For most application activated carbon pH of 6-8 is acceptable (Ahmedna *et al.*,2000). Percentage carbon yield is the amount of original precursor remaining after pyrolisis and activation treatment. Percentage yield decrease as activation burn off time increases which is as a result of more volatile being released from the char, that is, as the percentage activation burn off increases, the percentage yield decreases. Carbon with an adequate density also help to improve the filtration rate by forming an even cake on the filter surface. The American water work Association has set a lower limit on bulk density at 0.25 g/cm^3 for granular activated carbons (GACs) to be of practical use (American Water Works Association, 1991). The bulk density of the adsorbents fall within the range of 0.25 ± 0.02 to 0.28 ± 0.01 g/cm^3. The conductivity test is important because it shows the presence of leach able ash which is considered impurity and undesirable in activated carbon (Khadija *et al.*,2007). The activated carbons indicated the highest conductivity value of 5.80 ± 0.05 µS/cm which implies that the adsorbents contain less leach able ash (Table 1).

TABLE 1

CHARACTERISTICS OF ACTIVATED CARBON

Parameter	SD/NaOH/5	SD/NaOH/10	SD/NaOH/15
Activation burn off (%)	52.12 ± 0.02	56.00 ± 0.01	58.00 ± 0.01
Yield (%)	48.01 ± 0.01	44.11 ± 0.02	41.13 ± 0.01
Bulk density (g/cm^3)	0.27 ± 0.01	$0..28 \pm 0.01$	0.25 ± 0.02
Ph	7.81 ± 0.01	7.82 ± 0.01	7.83 ± 0.02
Conductivity (µS/cm)	3.60 ± 0.03	5.80 ± 0.05	4.70 ± 0.11

B. *Effect of Initial Dye Concentration*

Fig. 1 indicates that an increase in initial MB concentration leads to increase in the adsorption of MB on saw dust. The adsorption capacity at equilibrium increases from 0.20 to 0.99 mg/g with an increase in the initial dye concentration from 10 to 50 mg/L. It is indicated that the activated carbons prepared from saw dust yield better adsorption of MB dye from aqueous solution, the process attaining equilibrium gradually. This is due to the fact that activated carbon is composed of porous structure with large internal surface area. Similar process was obtained on the adsorption of MB on peanut hull (Gong *et al.*, 2005).
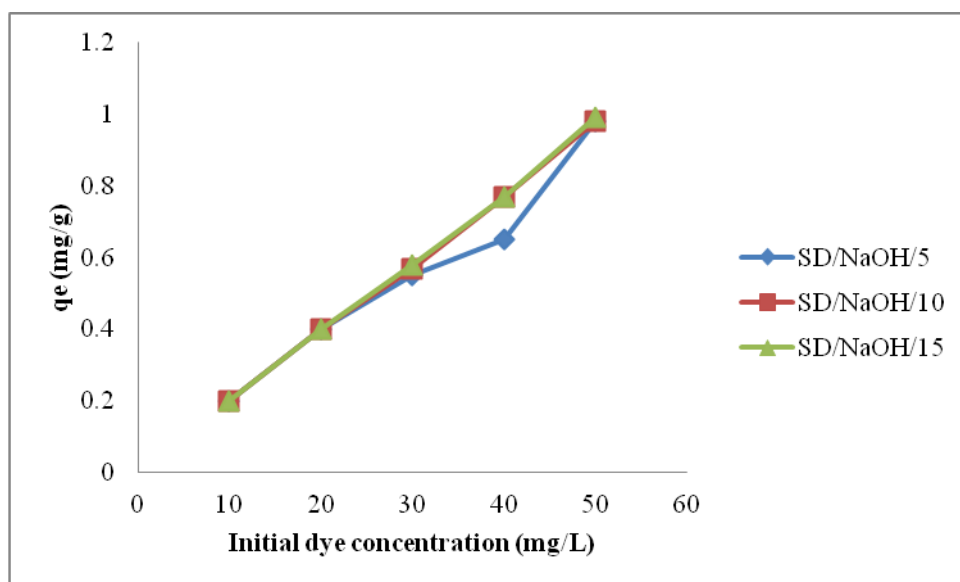
Fig.1. Effect of initial dye concentration on equilibrium adsorption capacity.

C. *Isotherm Analysis*

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems (Özer and Dursun, 2007). The equilibrium data for MB on saw dust were modelled with the Langmuir, Freundlich, Temkin and Harkin's-Jura models.

Langmuir Isotherm

The linear plot of specific adsorption $(1/q_e)$ against the equilibrium concentration $(1/C_e)$ (Fig. 2, Fig. 3 and Fig. 4) shows that the adsorption obeys the Langmuir model. Langmuir constants q_m and K_a were determined from the slope and intercept of the plot and are presented in Table II. The values of correlation coefficient ($R^2 = 0.982$, $R^2 = 0.996$ and $R^2 = 0.995$) obtained from Langmuir expression indicates that Langmuir expression provided a better fit to the experimental data of MB on saw dust. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption and is expressed as $R_L = 1/(1+K_aC_0)$. R_L values indicate the nature of adsorption to be either be unfavourable ($R_L > 1$), linear ($R_L=1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values for the adsorption of MB onto saw dust were 0.009, 0.001 and 0.001, indicating that the adsorption was a favourable process.

TABLE II

LANGMUIR ISOTHERM PARAMETERS

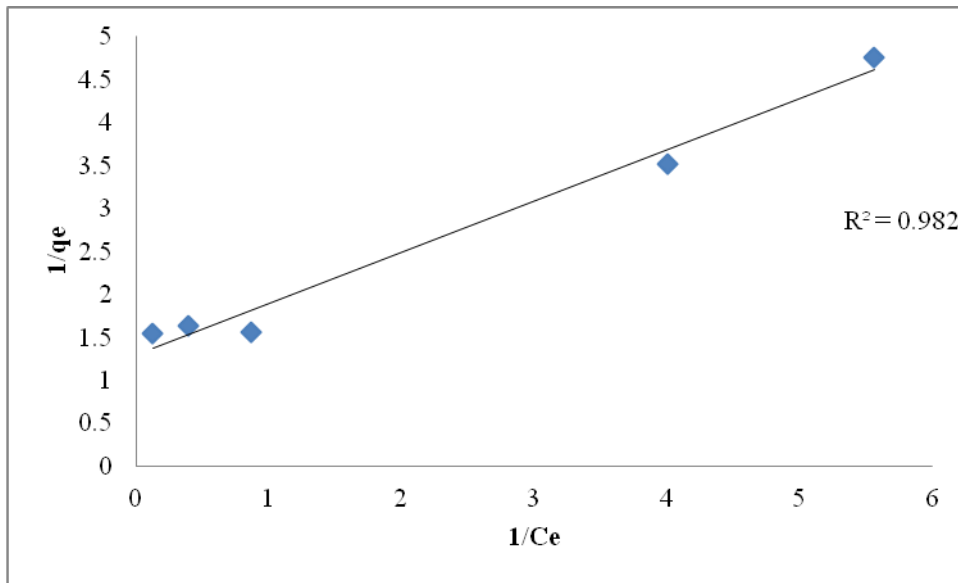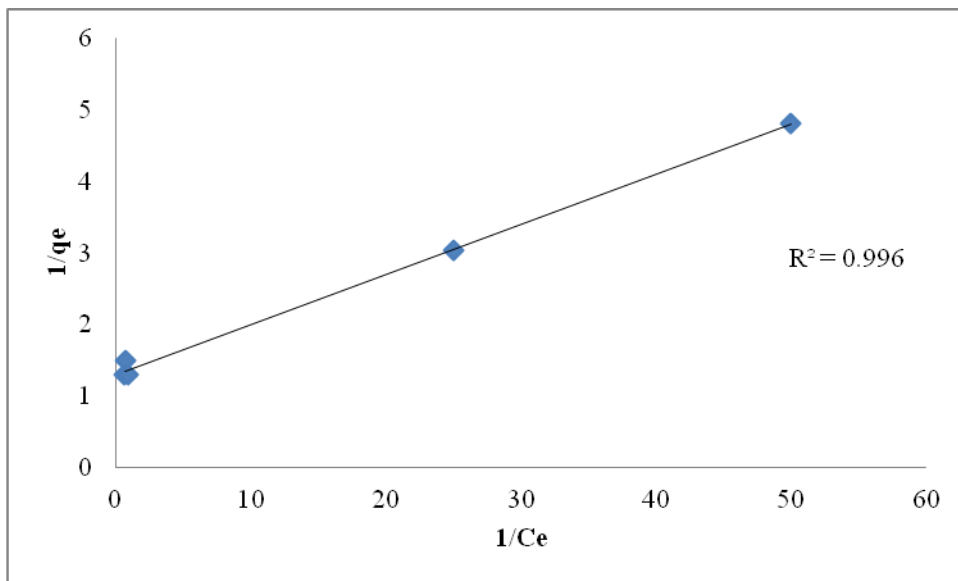| Parameters	SD/NaOH/5	SD/NaOH/10	SD/NaOH/15
q_m(mg/g)	0.76	0.76	0.67
K_a(L/mg)	2.18	18.94	13.95
R^2	0.982	0.996	0.995
R_L	0.009	0.001	0.001

Fig. 2. Langmuir adsorption isotherm of MB on activated carbon (SD/NaOH/5)

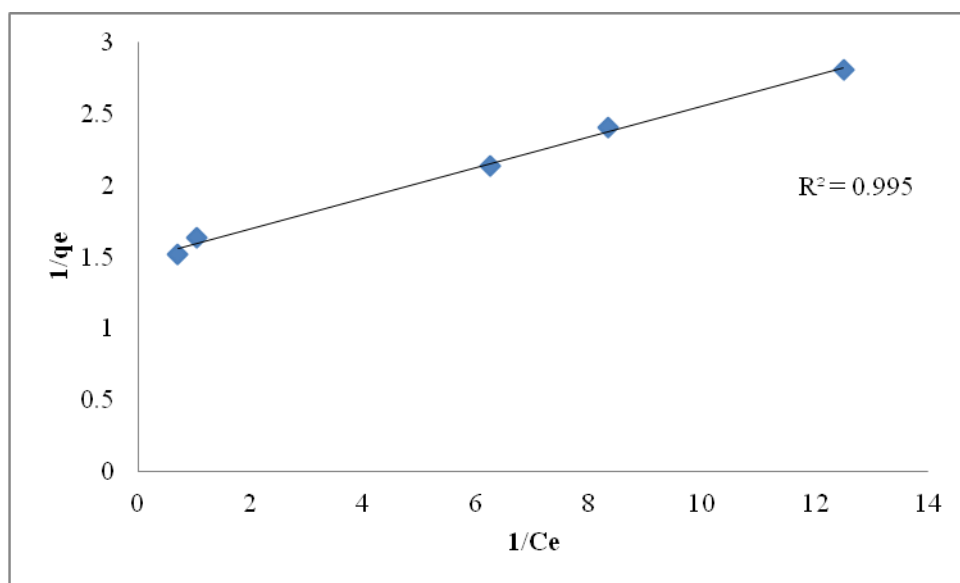Fig. 3. Langmuir adsorption isotherm of MB on activated carbon (SD/NaOH/10)

Fig. 4. Langmuir adsorption isotherm of MB on activated carbon (SD/NaOH/15)

Freundlich Isotherm

The equilibrium data were analyzed using the linear form of Freundlich isotherm, by plotting ln q_e versus ln Ce (Fig.5, Fig.6 and Fig.7). The Freundlich isotherm constants and the corresponding correlation coefficient (R^2) are shown in Table III. The R^2 values were higher (R^2 = 0.948, R^2 = 0.948, R^2 = 0.997) showing a good linearity. n values show the type of isotherm to be either favourable n >1 and unfavourable n < 1 (Alley, 2000). The findings revealed that the values of n were greater than one (n = 4.85, n = 3.70 and n = 4.07) indicating that the dye adsorption is favourable.

TABLE III

FREUNDLICH ISOTHERM PARAMETER

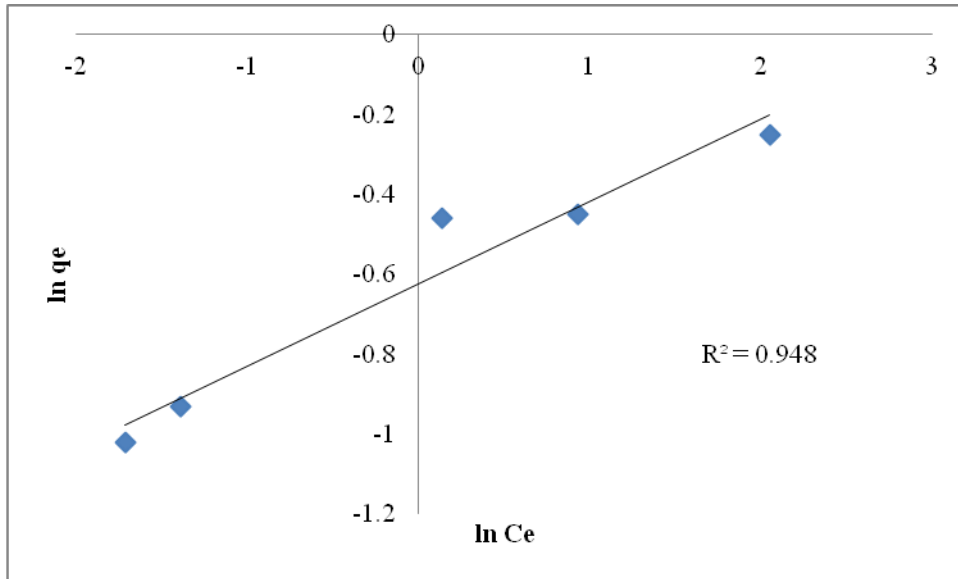| Parameters	SD/NaOH/5	SD/NaOH/10	SD/NaOH/15
K_F (mg/g)	0.54	0.77	0.65
n	4.85	3.70	4.07
R^2	0.948	0.948	0.997

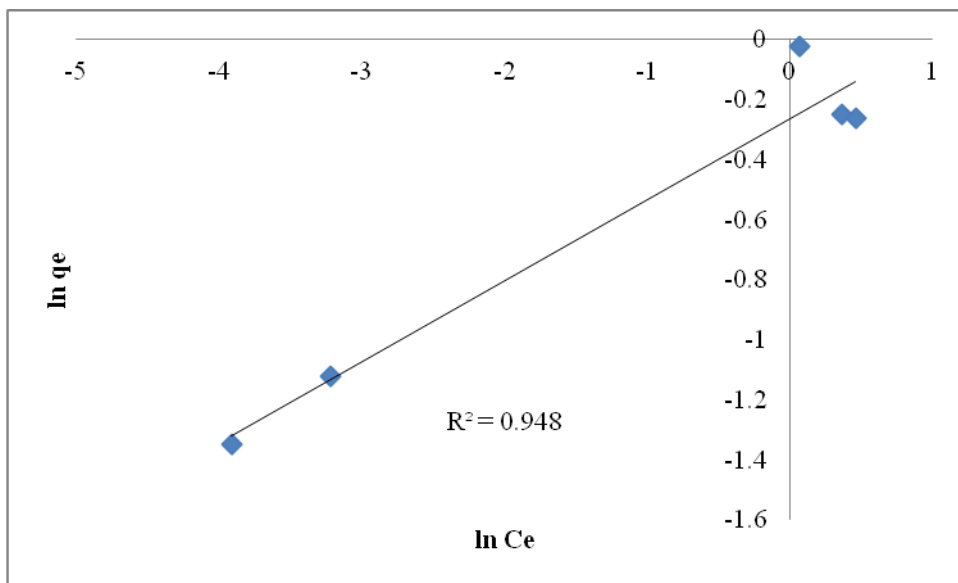Fig. 5. Freundlich adsorption isotherm of MB on activated carbon (SD/NaOH/5)

Fig. 6. Freundlich adsorption isotherm of MB on activated carbon (SD/NaOH/10)
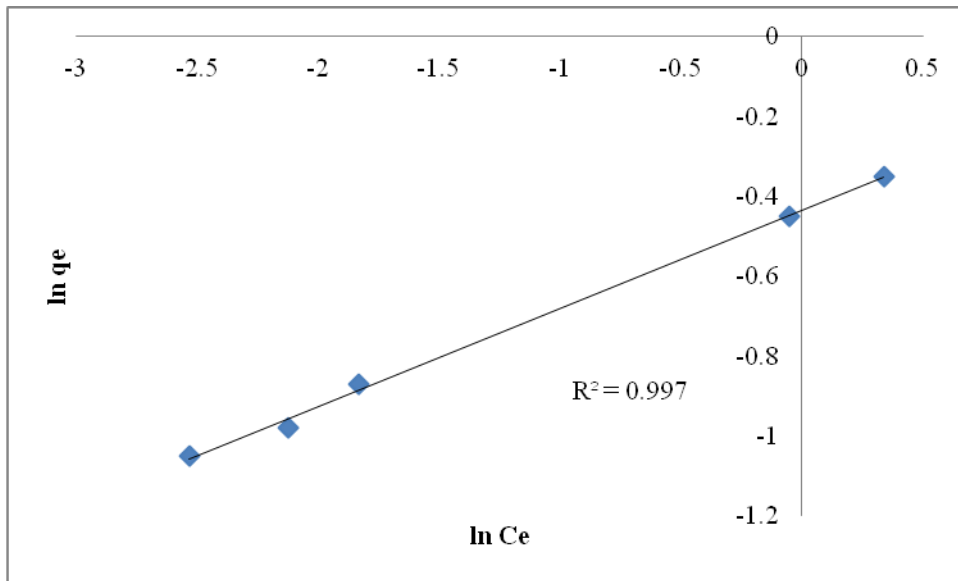
Fig. 7. Freundlich adsorption isotherm of MB on activated carbon (SD/NaOH/15)

Temkin Isotherm

The adsorption data were analysed by plotting q_e against $\ln C_e$. The parameter of Temkin isotherm were presented in Table IV. The R^2 values were also high ($R^2 = 0.915$, $R^2 = 0.905$ and $R^2 = 0.955$) indicating a good linearity.

TABLE IV

TEMKIN ISOTHERM PARAMETERS

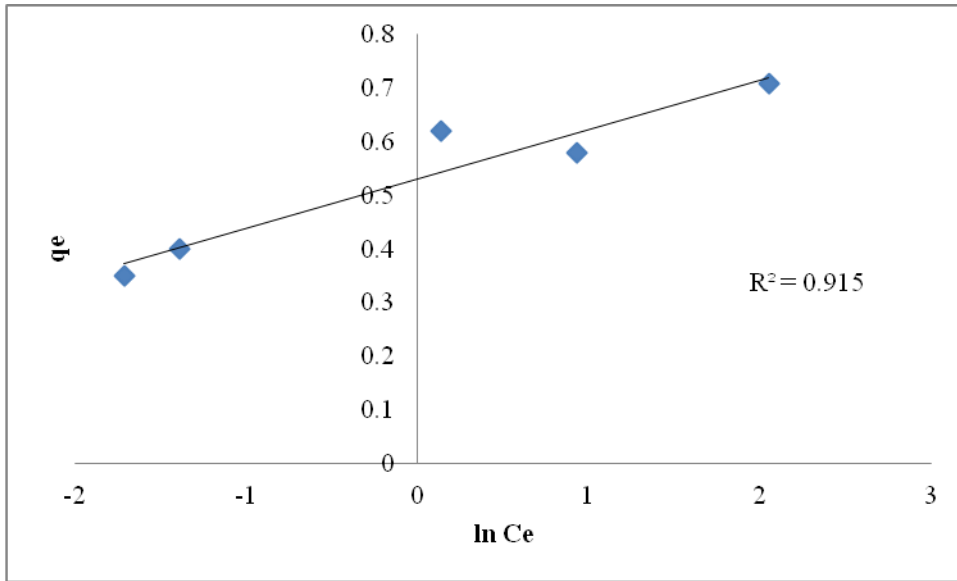| Parameters	SD/NaOH/5	SD/NaOH/10	SD/NaOH/15
A (L/g)	321.10	368.92	333.56
B (J/mol)	0.092	0.123	0.114
R^2	0.915	0.905	0.955

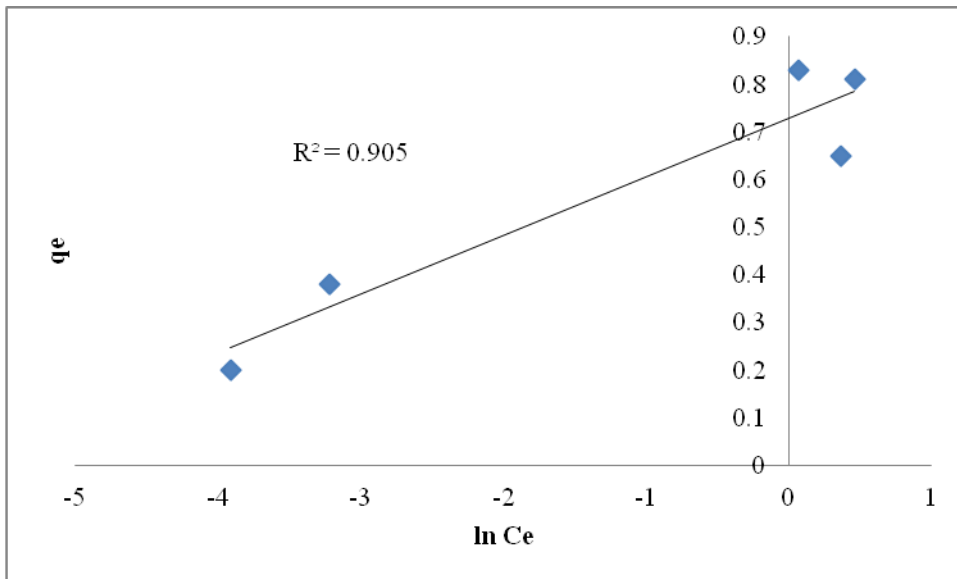Fig. 8. Temkin adsorption isotherm of MB on activated carbon (SD/NaOH/5)

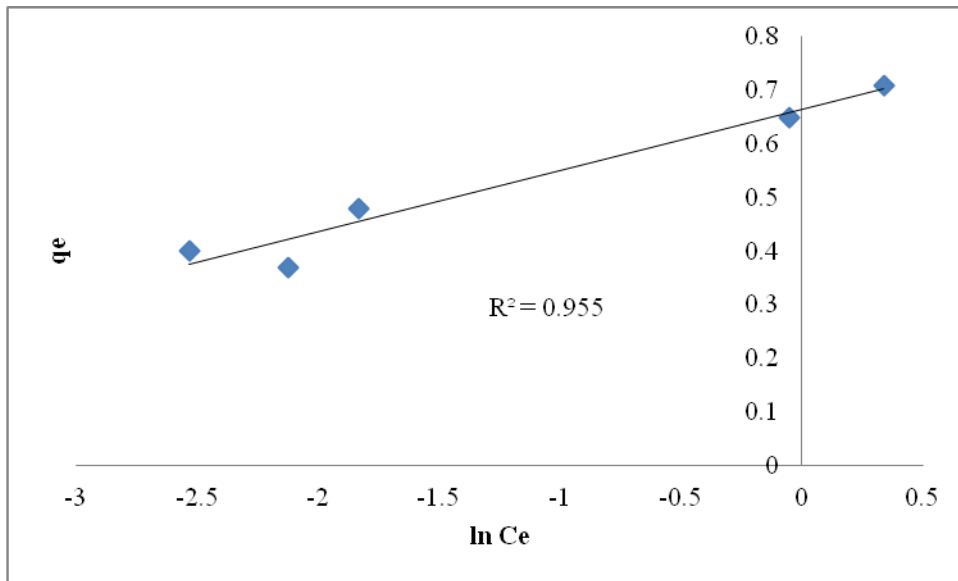Fig. 9. Temkin adsorption isotherm of MB on activated carbon (SD/NaOH/10)

Fig. 10. Temkin adsorption isotherm of MB on activated carbon (SD/NaOH/15)

Harkin's – Jura Isotherm

The equilibrium data were also analysed by plot of $1/q_e^2$ versus log C_e. The parameters were presented in Table V. The R^2 values were also high showing good linearity.

TABLE V

HARKIN'S-JURA ISOTHERM PARAMETERS

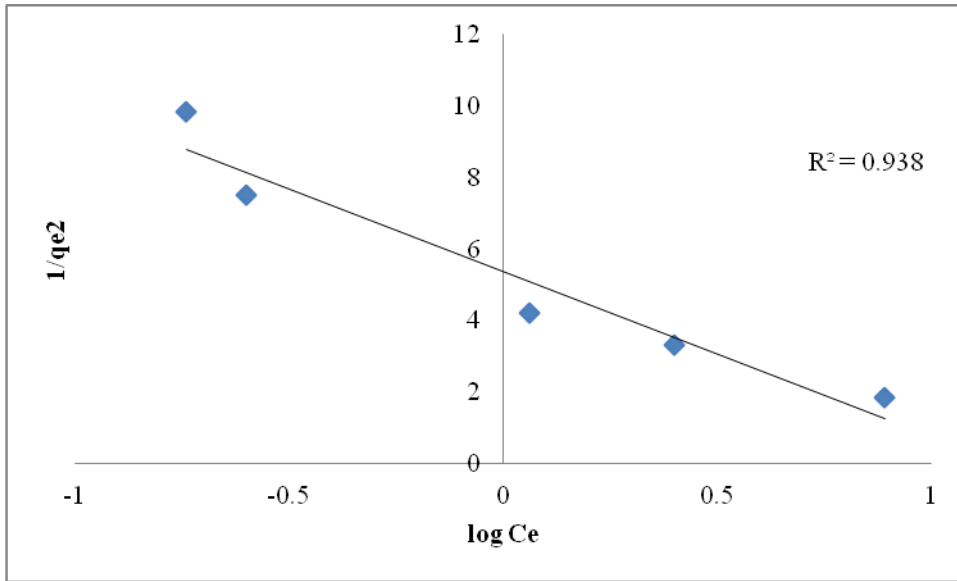| Parameters	SD/NaOH/5	SD/NaOH/10	SD/NaOH/15
A	0.22	0.09	0.26
B	1.18	0.29	0.71
R^2	0.938	0.925	0.977

Fig. 11. Harkin's – Jura adsorption isotherm of MB on activated carbon (SD/NaOH/5)
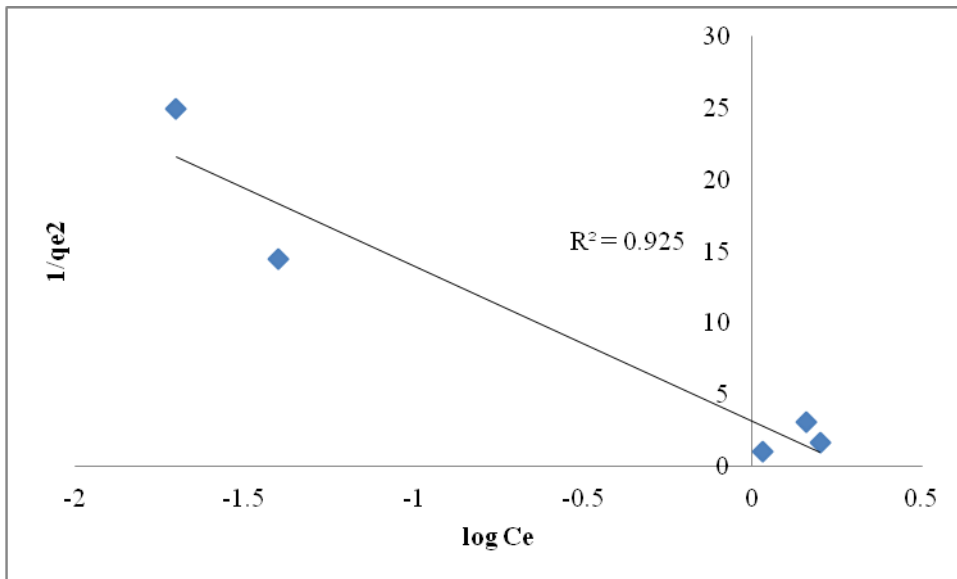

Fig. 12. Harkin's – Jura adsorption isotherm of MB on activated carbon (SD/NaOH/10)
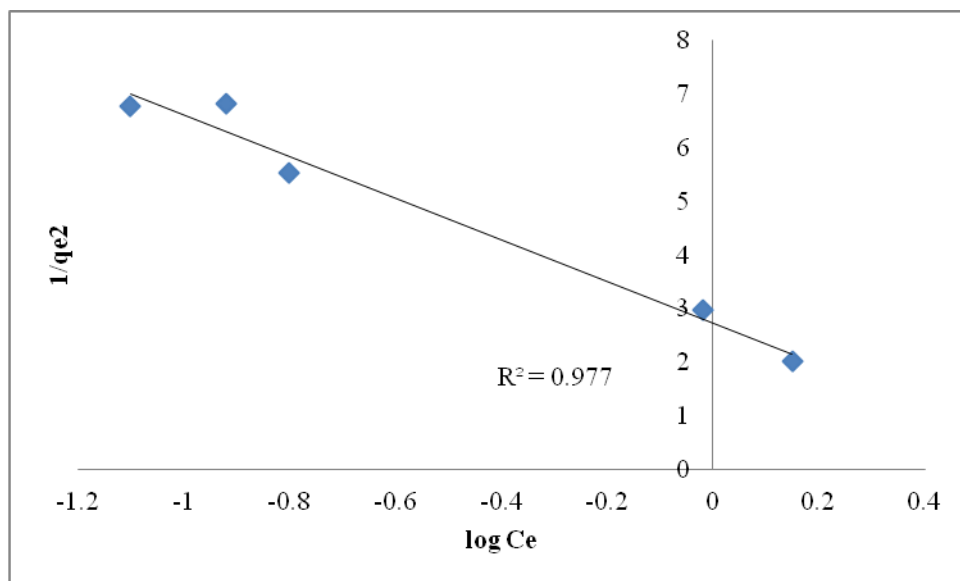
Fig. 13. Harkin's – Jura adsorption isotherm of MB on activated carbon (SD/NaOH/15)

Furthermore, the results revealed that the Langmuir isotherm model was more suitable for the experimental data than other isotherms because of the high value of correlation coefficient ($R^2 = 0.982$, $R^2 = 0.996$ and $R^2 = 0.995$). This showed that the adsorption of MB onto activated saw dust occur as a monolayer adsorption on the adsorbent surface. Demir *et al*. (2008) and Theivarasu and Mylsamy, (2010) reported similar phenomenon.

IV. CONCLUSION

The findings revealed that methylene blue was removed from aqueous using activated carbon prepared from saw dust. Batch adsorption was carried out at initial concentration of 10-50 mg/L. Percentage carbon yield tend to decrease with increase in activation burn off time since more volatiles are release from the char. Adsorption capacity at equilibrium also increases with increases in initial concentration which result to about 99.67 %   MB removal. Langmuir, Freundlich, Temkin and Harkin's – Jura adsorption isotherm were used to describe the equilibrium data. Langmuir isotherm best described the adsorption data with higher correlation coefficient R^2 values ($R^2 = 0.983$, $R^2 = 0.996$ and $R^2 = 0.995$) and R_L values less than one ($R_L = 0.009$, $R_L = 0.001$ and $R_L = 0.001$) for SD/NaOH/5, SD/NaOH/10 and SD/NaOH/15 activated carbon respectively. The research further confirmed that saw dust a low cost adsorbent could be employed for the removal of MB with greater percentage uptake.

APPENDIX

SD/NaOH/5, SD/NaOH/10 and SD/NaOH/15 are saw dusts activated using NaOH as an activating agent at the residual time of 5, 10 and 15 minutes respectively.

Residual time is the time the activated carbon spend in the furnace at $800^{o}C$ to increase the porosity and better adsorption site for the activated carbon.

REFERENCES

[1] M. Ahmedna, W. E. Marshall, and R. M. Rao, "Granular

    activated carbons from agricultural by-products:

    Preparation, properties and application in came sugar

     refining" *Bulletin of Lousana State University Agricultural*

    Centre, pp. 54, 2000

[2] E. R. Alley," Water quality control handbook, McGraw

    Hill," 8, pp.125-141, 2000

[3] American Water Works Association, "AWWA standards for granular activated carbons, American Water Works Association," ANSI/AWWA B604-90 Denver Co, 1991.

[4] AOAC," Association of Official Analytical Chemist. Official method of Analysis," 14th ed. Washington DC, pp.140-147, 1990.

[5] K. I. Apipreeya, P. Phussadee, and P. Prasert, " Removal of metal ion from synthetic waste water by activated carbon from *Eucalyptus Camaldulensis Denn* Bark," *The 2nd Joint Int. Conf. on "Sustainable Energy and Environment (SEE 2006)"* E – 041, pp.1-9,2006.

[6] H. Demir, A. Top, D. Balköse, and S. Ülkü, " Dye adsorption behaviour of *Luffa cylindrical* fibers," *J. of Haz. Mat.*,vol. 153, pp.389-394,2008.

[7] M. Fan, W. Marshall, D. Daugaard, and C. Brown, " Steam activation of chars produced from oat hulls," *Bioresource Tech.*, vol. 93, no.1 , pp. 103 – 107, 2005.

[8] H. M. F. Freundlich," Over the adsorption in solution," *J. of Phy. Chemistry*, vol.57, pp.385-470, 1906.

[9] R. Gong, M. Li, C. Yang, Y. Sun, and J. Chen, " Removal of cationic dyes from aqueous solution by adsorption on peanut hull," *J. of Haz. Material*, B121, pp.247- 250, 2005.

[10] A. Gurses, C. Dogar, M. Yalc-in, M. Acikyildiz,R. Bayrak, and S. Karaca, " The adsorption kinetics of the cationic dye methylene blue onto clay" *J. of Haz. Mat.*,vol. 131,pp. 217-228, 2006.

[11] B. H. Hameed," Evaluation of papaya seed as a novel non-conventional low-cost adsorbent for removal of methylene blue," *J. of Haz. Mat.*,vol. 162, pp.939- 944,2009.

[12] O. Ioannidou, and A. Zabaniotou, " Agricultural precursors for activated carbon production," *Renewable and Sus. Ener. Review*,vol. 11, no.1, pp. 1966-2005, 2006.

[13] Q. Khadija, B. Inamullah, K. Rafique, and K. A. Abdul, "Physical and chemical analysis of activated carbon prepared from sugarcane bagasse and use for sugar decolorisation," *World Academy of Sci., Eng. and Tech.*, vol.34, pp.194-198, 2007.

[14] I. Langmuir, " The adsorption of gases on plane surface of glass. mica and platinum.," *J. of America Chem. Soc.*, vol. 40, pp. 1361, 1918.

[15] Methylene blue (2011, December). Wikipedia, the free encyclopedia, http://en.wikipedia.org/wiki/methylene_blue.

[16] C. Namasivayam, and D. Kavitha," Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste," *Dye Pigments*,vol. 54, pp.47-58, 2002.

[17] F. E. Okiemen, F. I. Ojokoh, C. D. Okiemen, and R. A. Wuana, " Preparation and evaluation of activated carbon from rice husk and rubber seed shell," *Chem. J., pp.*191-944, 2004.

[18] A. Özer, and G. Dursun, " Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon" *J. of Hazar. Mat.*,vol. 146, pp.262-269, 2007.

[19] I. A. Rahman, B. Said, S. O. Shadier, and E. S. Syarizal, "Adsorption characteristic of malachite green on activated carbon derived from rice husk produced by chemical thermal process," *Bio. Tech.*,vol. 95, no.14, pp. 1578-1583,2005.

[20] A. Reza, M. Zehra, B. K. Mohammed, and M. K. Ali, "Adsorption of cationic dyes from aqueous solutions using polyaniline conducting polymer as a novel adsorbent," *J. of Advan. Sci. Res.*,vol. 2, no.2, pp. 27-34, 2011.

[21] M. J. Temkin, and V. Pyzhev, " Recent modifications to Langmuir isotherms, Acta Physiochim. URSS," vol. 12, pp. 217-222, 1940.

[22] C. Theivarasu, and S. Mylsamy, " Equilibrium and kinetic

adsorption studies of Rhodamine-B from aqueous solutions

using cocoa (*Theobroma cacao*) shell as a new adsorbent,"

International J. of Eng. Sci. and Tech., vol 2, no.11,

pp.6284- 6292, 2010.

[23] C. Theivarasu, S. Mylsamy, and N. Sivakumar, "Cocoa

Shell as adsorbent for the removal of methylene blue from

aqueous solution: Kinetic and Equilibrium Study,"

Universal J. of Envi. Res. and Tech.,vol. 1, pp.70-78,2011

[24] D. Yulu, W. Walawender, and L. Fan, " Activated carbon

prepared from phosphoric   acid activation of grain

sorghum," *Bio. Tech.*, vol. 81,no.1,pp. 45-52, 2001.

ABOUT THE MAIN AUTHOR

NAME: Idris Suleiman

ADDRESS: Department of Chemistry Federal University of Technology Minna Niger State Nigeria.

Research Area: Adsorption of heavy metals using activated carbon produced from animal and plant waste.