International Journal of Modern Chemistry, 2013, 4(2): 90-103

Modern Scientific Press

International Journal of Modern Chemistry **ISSN: 2165-0128**

Journal homepage: www.ModernScientificPress.com/Journals/IJMChem.aspx *Florida, USA*

Article

Equilibrium and Adsorption Studies of Malachite Green onto Melon Seed Shell Activated Carbon

Suleiman Idris*, Jonathan Yisa, Ndamitso Muhammed Muhammed, Crystal Chioma Anyachukwu

Department of Chemistry, Federal University of Technology, P.M.B. 65 Minna, Niger State, Nigeria

* Author to whom correspondence should be addressed; E-Mail: suleman_drs@yahoo.co.uk; Tel.: +2348065699124.

Article history: Received 27 January 2013, Received in revised form 22 February 2013, Accepted 24 February 2013, Published 11 March 2013.

Abstract: The aim of the study is to produce activated carbon using melon seed shell which is harmless, cheaper, and abundant agricultural raw material with HNO_3 as an activating agent to remove malachite green from aqueous solution. Two step processes which involve carbonisation of the powder melon seed shell follow by activation of the carbon were used for the production of the activated carbon. Experimental data were analyse using Langmuir, Freundlich, Temkin and Harkin's-Jura adsorption isotherms. Characteristics of the activated carbon values are: pH = 6.18±0.02, 7.24±0.01, 7.12±0.01; conductivity (µS/cm) = 1.50±0.01, 1.60±0.01, 1.80±0.01; bulk density (g/cm^3) = 9.76±0.01, 9.15±0.06, 8.34±0.01; % yield = 56.63±0.02, 22.32±0.01, 13.54±0.03; % burn off = 43.41±0.01, 77.73±0.04, 86.50±0.02; for AC1 (activated carbon 1), AC2 (activated carbon 2) and AC3 (activated carbon 3) respectively. Isothetrm parameters obtained for Langmuir are R^2 = 0.9461, 0.9183, 0.9653 and R_L= 0.0468, 0.4640, 0.0712 for AC1, AC2 and AC3; for Freundlich are R^2 =0.9288, 0.8991, 0.9705 and n = 0.25, 0.41, 0.65 for AC1, AC2 and AC3; for Temkin are R^2 = 0.8273, 0.8430, 0.9019 for AC1, AC2 and AC3; for Harkin's-jura are R^2 = 0.8538, 0.8345, 0.8244 for AC1, AC2 and AC3. Adsorption capacity at equilibrium tends to increase as the initial concentration increases. Langmuir adsorption isotherm best described the adsorption processes because of the higher R^2 values.

Keywords: adsorption; malachite green; melon seed shell; activated carbon; effluent; dye; adsorbent; isotherm.

1. Introduction

Malachite green is an organic compound that is used as a dyestuff. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Although called *malachite green*, the compound is not related to the mineral malachite- the name just comes from the similarity of colour [1]. The textile industries are confronted with serious environmental problems associated with its immense wastewater discharge, substantial pollution load, extremely high salinity, alkalinity and heavy colored effluents. Different types of dyes are used in industries like textile, paper, rubber, plastic, leather, cosmetics, pharmaceutical and food stuff [2]. The effluents of these industries are composed of large amount of dye contents, which on mixing with water bodies causes severe problems such as increasing the chemical oxygen demand (COD) and reducing light penetration and visibility, thereby pose adverse effects on the marine life [3]. The presence of these dye stuffs in water bodies also makes water unfit for drinking due to toxic effects of different types of dyes on living cells [4].

Activated carbons are widely used as an adsorbent because of their high adsorption capacity, microporous structure, and high surface area. The preparation and effective utilization of activated carbon generated from natural plant materials have attracted worldwide attention in view of the large disposal problem detrimental to the environment [5].

The aim of this study is to see the possibility of using activated carbon of mellon seed shell which is harmless, cheaper, and abundant agricultural raw material in the northern part of Nigeria to remove malachite green from aqueous solution, and to use four adsorption isotherms namely Langmuir, Freundlich, Temkin and Harkin's-Jura for the adsorption studies.

2. Materials and Methods

2.1. Sample Collection and Preparation

The melon seed shell was collected from Lemu Gbako local government area of Niger state Nigeria. The collected samples were sun dried and oven dried at 100 ^{o}C overnight, ground and sieved with a 2 mm mesh size sieve. The powder sample was stored in an airtight container. The malachite green dye was purchased from Nahson hospital equipment store, hospital road, Minna, Niger State, Nigeria. Ash content was determined using the method described by the literature [6].

2.2. Activated Carbon Production

The 5 g of powdered sample was weighed into clean and weighed crucibles. The crucibles were introduced into a muffle furnace at 600 ^{o}C for 5 min after which the content of each crucible was poured into a bath of ice water. Excess water was drained off. The 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 ^{o}C for one hour. This process was repeated until a substantial amount of carbonized sample was obtained. Thereafter, 5 g of already carbonized sample was mixed with 5 cm^3 of 1 M HNO_3 activating agent. The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800 ^{o}C for 5 min. The activated sample was cooled with ice water, excess water was drained off and the sample was dried at room temperature. This was repeated until a substantial amount of activated carbon was obtained and the procedure was carried out for different residual time (10 min and 15 min). Washing of the activated sample was done with 0.1 M HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid. Washing was completed until the pH of 6-7 was obtained, then the sample was dried in oven at 110 ^{o}C overnight and stored in air tight container [7-10].

2.3. Characteristics of Activated Carbon

The bulk density was determined using the method of the literature [11].

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Weight of dry activated carbon (g)}}{\text{Volume of packed dry material (cm}^3\text{)}} \quad (1)$$

Burn off refers to the weight difference between the original char and activated carbon divided by the weight of the original char with both weights on dry basis [12].

$$\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

W_0 = weight of char after pyrolysis, washing and drying, W_1 = weight of carbon after activation, washing and drying.

The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original precursor with both weights on a dry basis [11].

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

W_0 = original mass of precursor, W_1 = weight of carbon after activation, washing and drying.

The pH and conductivity of the activated carbon produced were determined using a pH meter (Model Kent EIL 7045/46) and a conductivity meter (Model Kent EIL 5013) at room temperature [13].

2.4. Batch Equilibrium Studies

The 2 g of each activated carbon was interacted with 40 cm^3 of malachite green dye solution of initial concentration of 10 ppm in a beaker, covered and allowed to stand for 1 hour. It was then filtered using Whatman filter paper (No. 42) and the filtrate was collected. The process was repeated at

different initial concentration of 20, 30, 40 and 50 ppm respectively [14]. 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, qe (mg/g) was calculated as follows:

$$qe = \frac{(Co - Ce)\ V}{W} \quad (4)$$

Co and Ce (mg/L) are the liquid-phase concentration of dye at initial and equilibrium, V (L) = volume of the malachite green dye solution, W (g) = weight of the activated carbon.

The percentage dye removal was calculated as follows [15]:

$$\% \text{ malachite green removal} = \frac{Co - Ce}{Ce} \times 100 \quad (5)$$

2.5. Adsorption Isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent, and is important in the design of adsorption systems [16].

2.6. Langmuir Isotherm

The linear form of Langmuir equation is

$$1/qe = 1/KaqmCe + 1/qm \quad (6)$$

Where Ka is binding constant related to the adsorption energy and qm is the sorbent binding capacity, that is, the maximum sorption upon complete saturation of adsorbent surface. Ka and qm values are calculated from the slope and intercepts of plot of 1/qe against 1/Ce.

2.7. Freundlich Isotherm

Freundlich equation gives a description of adsorption data over a restricted range of concentration, and is suitable for a multilayer adsorption. The linear form of Freundlich equation is

$$lnqe = lnKf + 1/n\ lnCe \quad (7)$$

Where Kf is a constant indicating the adsorption capacity and n is adsorption intensity and can be calculated from the slope and intercept of the plot of lnqe against lnCe.

2.8. Temkin Isotherm

The linear form of Temkin isotherm is given as

$$qe = BlnA + BlnCe \quad (8)$$

Where A (L/g) is maximum binding energy and B (J/mol) is heat of sorption. The value of A and B

can be calculated from the slope and intercept of plot of qe against lnCe [17].

2.9. Harkin's- Jura Isotherm

Harkin's-Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore distribution [18]. The linear form of the equation is

$$1/qe^2 = (B/A) - (1/A)\log Ce \quad (9)$$

where A and B are the isotherm constants which can be calculated from the slope and intercept of the plot of $1/qe^2$ versus logCe.

3. Results and Discussion

3.1. Characteristics of Activated Carbon

Ash content of the melon seed shell was found to be 0.04%. The sample ash content was very low, which is an indication of high carbon yield. The pH range of 6.18±0.02 to 7.24±0.01 was recorded for the activated carbons. For most applications activated carbon pH of 6-8 is accepted [19]. Percentage yield decrease as activation burn off increase which is as a result of more volatile being released from the char, that is, as the percentage burn off increases, the percentage yield decreases which is shown by this findings. Carbon with adequate bulk density helps to improve the filtration rate by forming an even cake on the filter surface. The adsorbents bulk density was recorded as 8.34±0.02 to 9.76±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 [20]. The 1.50±0.01, 1.60±0.01 and 1.80±0.01 µS/cm are the conductivity for the activated carbons which indicated that the adsorbents contain less leach able ash (Table 1).

Table 1. Characteristics of the activated carbon

Parameters	AC1	AC2	AC3
% Burn off	43.41±0.01	77.73±0.04	86.50±0.02
% Yield	56.63±0.02	22.32±0.01	13.54±0.03
Bulk density (g/cm^3)	9.76±0.01	9.15±0.06	8.34±0.01
pH	6.18±0.02	7.24±0.01	7.12±0.01
Conductivity (µS/cm)	1.50±0.01	1.60±0.01	1.80±0.01

3.2. Effect of Initial Dye Concentration

The plot of equilibrium data in Fig. 1 indicated that equilibrium adsorption capacity increases

as the initial concentration of the dye increases which implies that the adsorption is highly depend upon initial dye concentration. Also, at high initial concentration the available adsorption sites becomes much, hence the percentage removal of dye is dependent upon initial concentration.

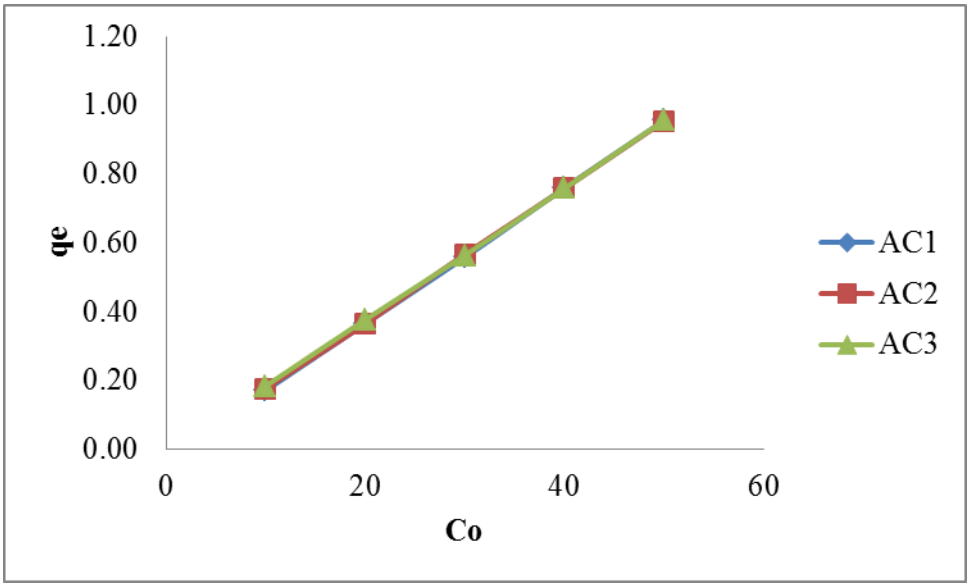

Figure 1. Effect of initial dye concentration on equilibrium adsorption capacity

3.3. Adsorption Isotherm

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems [21].

3.3.1. Langmuir Isotherm

A plot of 1/qe against 1/Ce (Figs. 2-4) indicated that the adsorption obeys Langmuir model. The qm and Ka were determined from the slope and intercept of the plot and represented in Table 2. R^2 values of 0.9461, 0.9183 and 0.9653 obtained from Langmuir expression indicated that the expression provided a better fit for the experiment. The favorability of the adsorption process was calculated from dimensionless separation factor (R_L) to determine high affinity adsorption and is expressed as $R_L = 1/(1+KaCo)$. R_L values indicates the nature of adsorption to be either unfavourable ($R_L > 1$), linear ($R_L=1$), favourable ($0 < R_L < 1$), or irreversible ($R_L=0$). The R_L values for these adsorptions were 0.0468, 0.4640 and 0.0712 which implies that the adsorption was a favourable process.

Table 2. Langmuir isotherm parameters

Parameters	AC1	AC2	AC3
qm(mg/g)	0.12	3.94	0.70
Ka(L/mg)	0.41	0.02	0.26
R^2	0.9461	0.9183	0.9653
R_L	0.0468	0.4640	0.0712

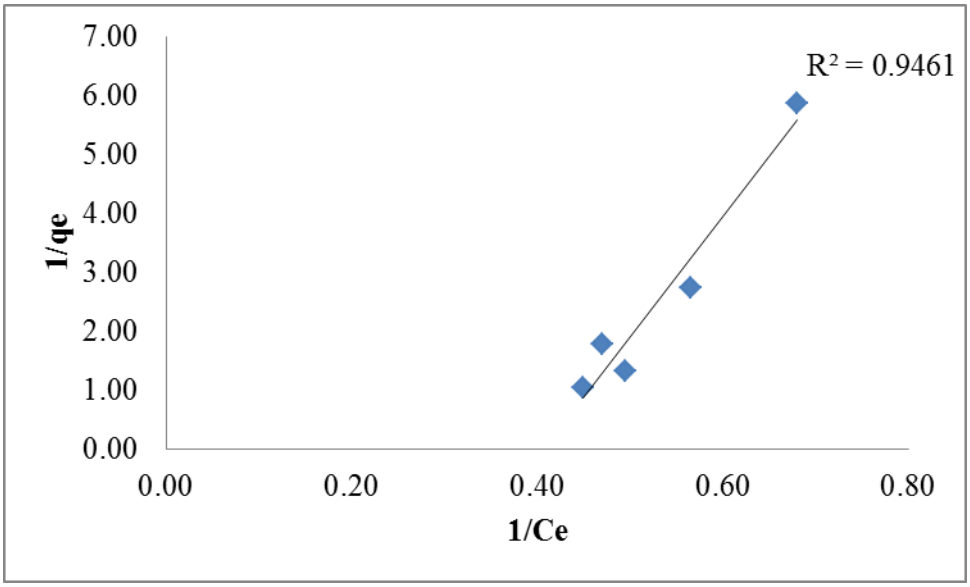

Figure 2. Langmuir adsorption isotherm of malachite green onto AC1

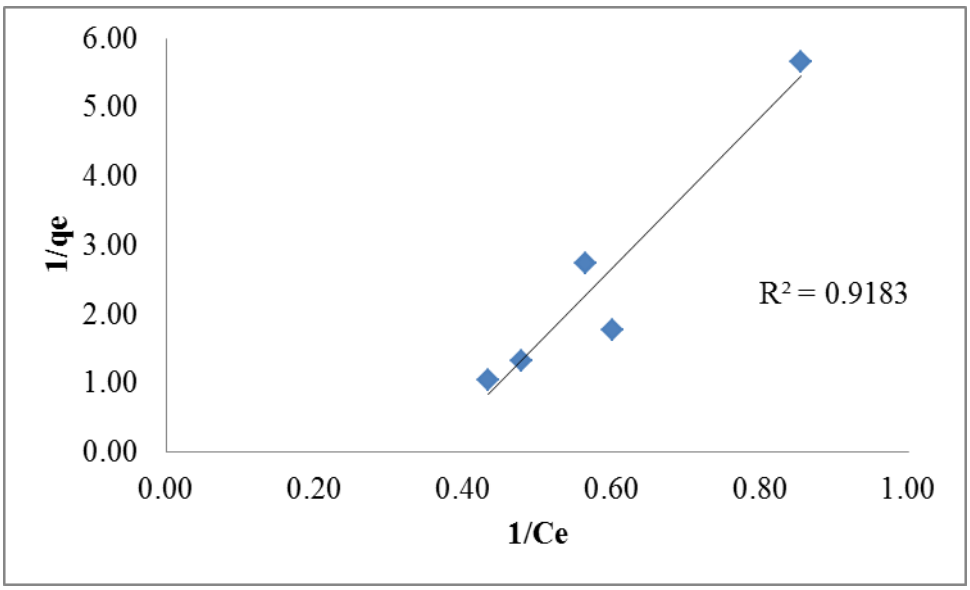

Figure 3. Langmuir adsorption isotherm of malachite green onto AC2

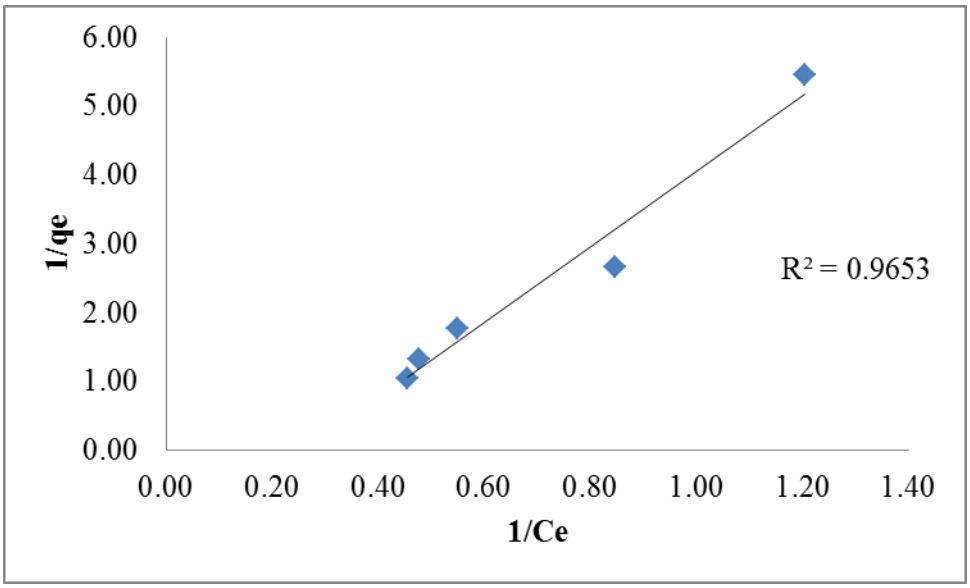

Figure 4. Langmuir adsorption isotherm of malachite green onto AC3

3.3.2. Freundlich Isotherm

Freundlich equation was used for the adsorption process by ploting lnqe versus lnCe (Figs. 5-7). The Freundlich isotherm constants and the higher R^2 values which show a good linearity were presented in Table 3. The intensity of adsorption is an indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption. The findings showed that the n values are less than one, that is, physisorption is much more favourable indicating that the dye adsorption is unfavourable [22-23].

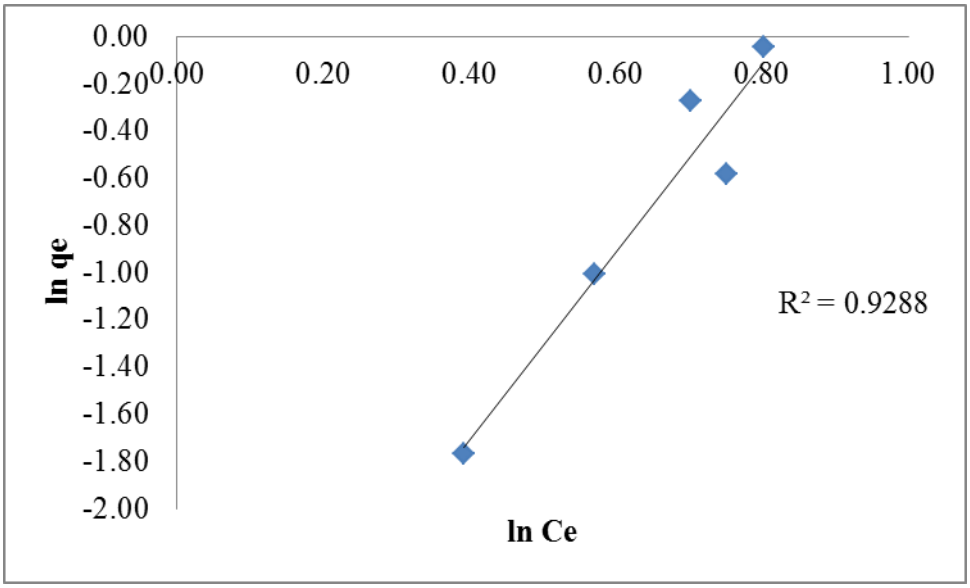

Figure 5. Freundlich adsorption isotherm of malachite green onto AC1

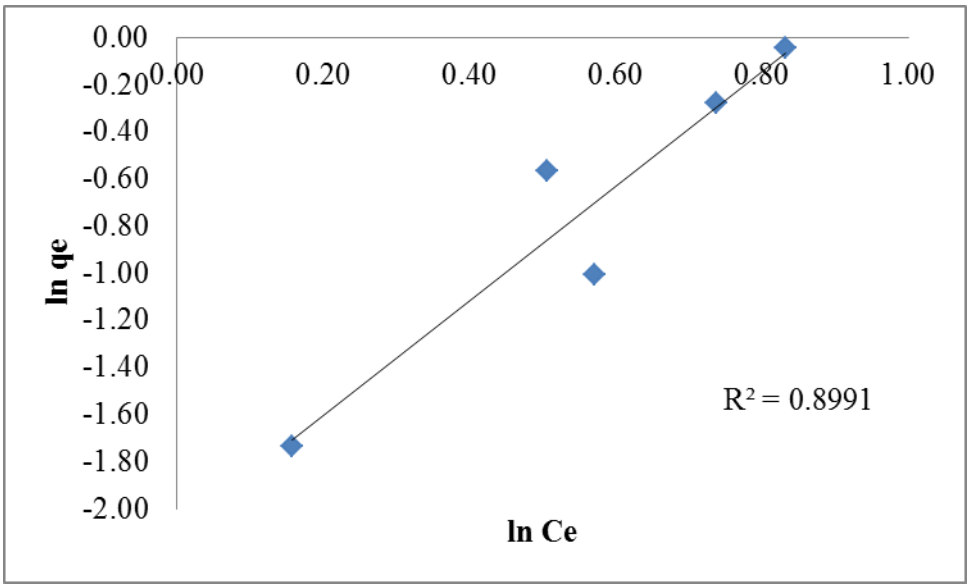

Figure 6. Freundlich adsorption isotherm of malachite green onto AC2

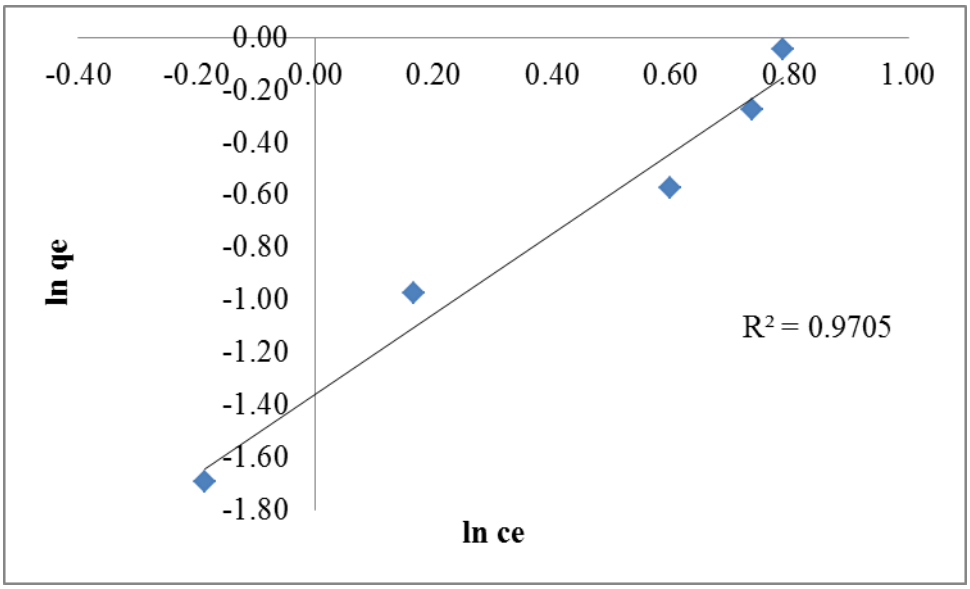

Figure 7. Freundlich adsorption isotherm of malachite green onto AC3

Table 3. Freundlich isotherm parameters

Parameters	AC1	AC2	AC3
Kf (mg/g)	0.04	0.12	0.26
n	0.25	0.41	0.65
R^2	0.9288	0.8991	0.9705

3.3.3. Temkin Isotherm

The adsorption data were analysed by plotting qe against lnCe (Figs. 8-10). The parameters of Temkin isotherm were presented in Table 4. The higher R^2 values indicated a good linearity.

Table 4. Temkin isotherm parameters

Parameters	AC1	AC2	AC3
A (L/g)	0.73	0.96	1.49
B (J/mol)	1.71	1.09	0.69
R^2	0.8273	0.8430	0.9019

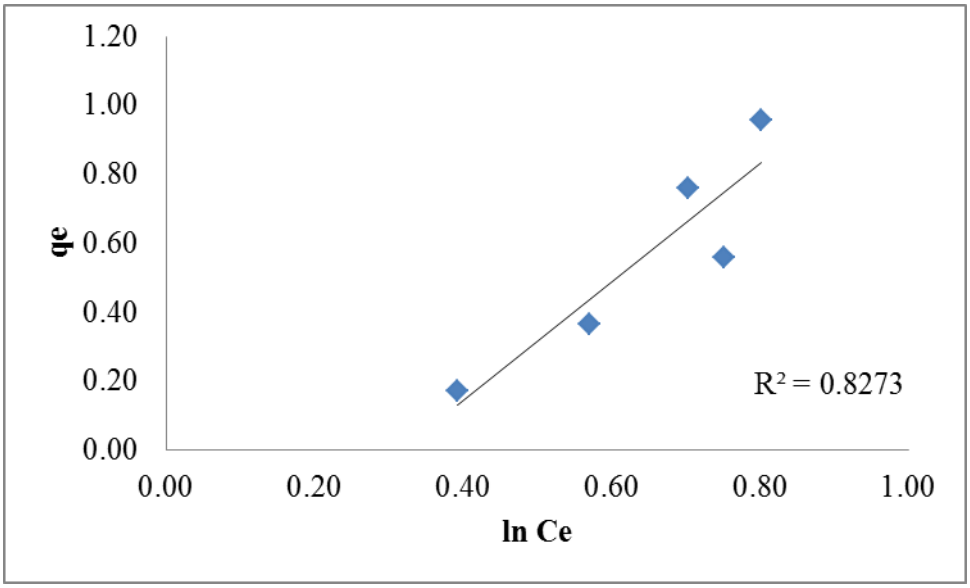

Figure 8. Temkin adsorption isotherm of malachite green onto AC1

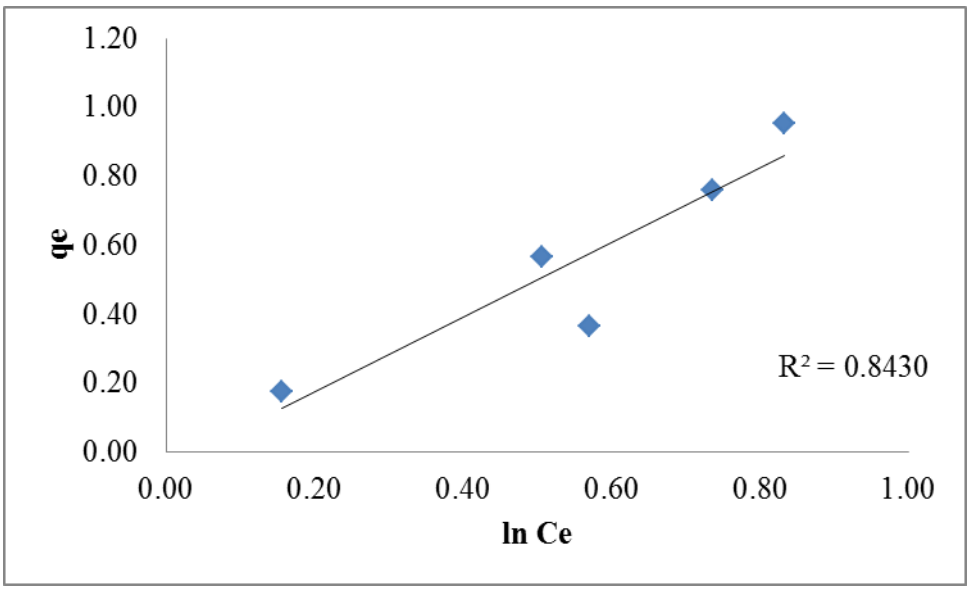

Figure 9. Temkin adsorption isotherm of malachite green onto AC2

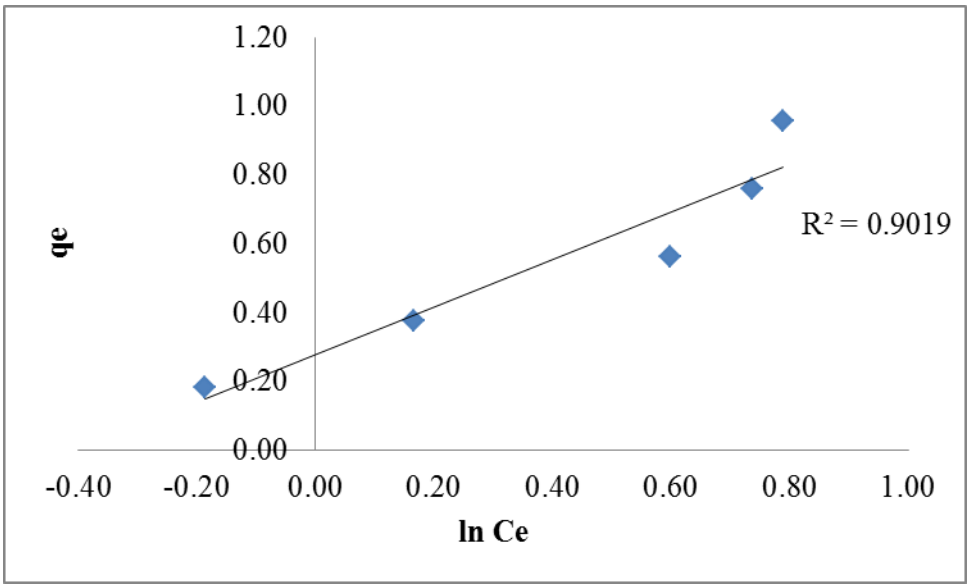

Figure 10. Temkin adsorption isotherm of malachite green onto AC3

3.3.5. Harkin's-Jura Isotherm

Equilibrium data was analysed by plot of $1/qe^2$ versus logCe (Figs. 11-13). Isotherm parameters with corresponding higher R^2 values showing a good linearity are presented in Table 5.

Table 5. Harkin's-Jura isotherm parameters

Parameters	AC1	AC2	AC3
A	0.006	0.010	0.017
B	0.33	0.33	0.32
R^2	0.8538	0.8345	0.824

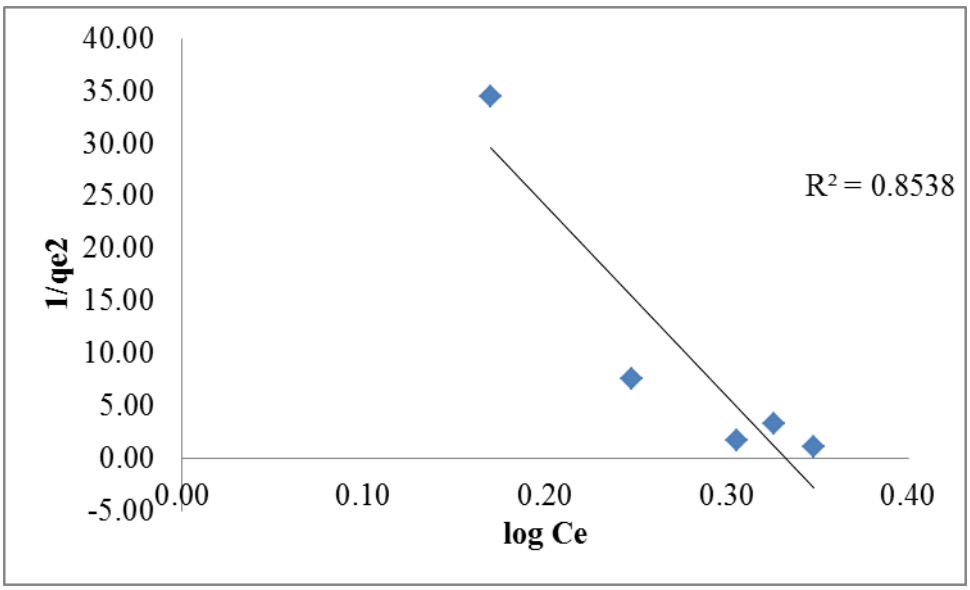

Figure 11. Harkin's-Jura adsorption isotherm of malachite green onto AC1

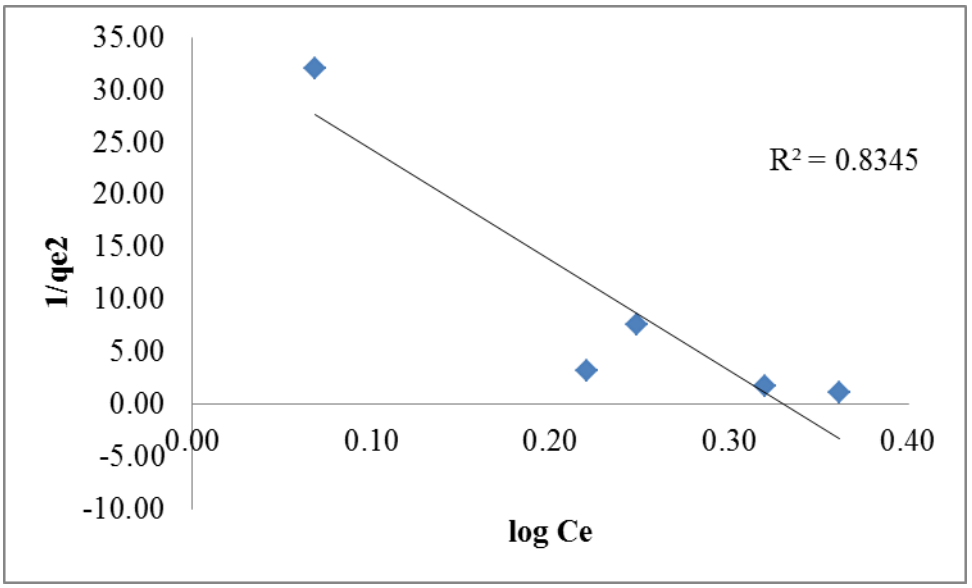

Figure 12. Harkin's-Jura adsorption isotherm of malachite green onto AC2

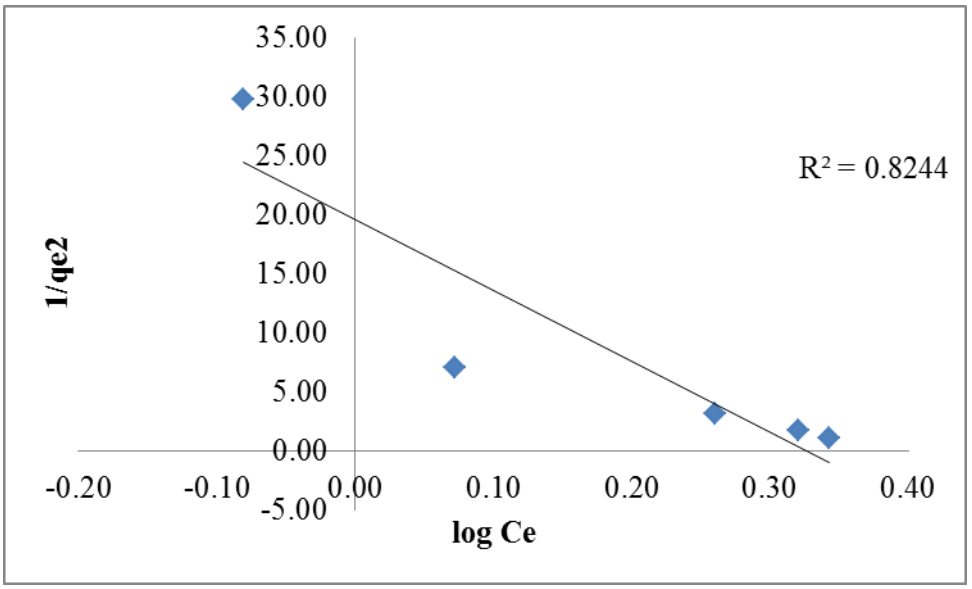

Figure 13. Harkin's-Jura adsorption isotherm of malachite green onto AC3

4. Conclusions

The research indicated that activated carbon was produce from melon seed shell for malachite green removal from aqueous solution. Equilibrium batch method was adopted at the initial concentration of 10-50 mg/L. The adsorption capacity at equilibrium tends to increase as the initial concentration increases. Four adsorption isotherms namely Langmuir, Freundlich, Temkin and Harkin's-Jura were used for the data but the Langmuir model is more suitable because of the high R^2 values of 0.9461, 0.9183 and 0.9653 respectively. Furthermore, the research revealed that melon seed shell which is cheaper and freely available could be employed as a low cost adsorbent for malachite

green removal from aqueous and other solution.

Appendix

AC1, AC2, and AC3 are carbon activated using HNO_3 as an activating agent at the residual time of 5, 10 and 15 min respectively. Residual time is the time the activated carbon spends in the furnace at 800 ^oC to increase the porosity and better adsorption site for the activated carbon.

Acknowledgements

The author is grateful to all laboratory technologists, Department of Chemistry, Federal University of Technology, Minna, Niger State, Nigeria, for their support during the research period.

References

[1] Malachite, G. Wikipedia, the free encyclopaedia. Available at: mlitml:file://c:\user\desktop\ malachite green-wikipedia (accessed 28/02/2011).

[2] Reed, B. E.; Matsumoto, M. R.; Jensen, J. N.; Viadero, R.; Lin, W. Physico-chemical processes. *Wat. Environ. Res.* **1998**, *70*: 449-473.

[3] Murray, C. A.; Parsons, S. A. Advance oxidation processes: Flowsheet options for bulk natural organic matter removal. *Wat. Sci. Tech.* **2004**, *4*(4): 113-119.

[4] Hajira, T.; Uzma, H.; Muhammad, S.; Qazi, J. Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent. *Afri. J. of Bio. Tech*. **2010**, *9*(48): 8206-8214.

[5] Arivoli, S.; Hema, M.; Prasath, P. M. D. Adsorption of malachite green onto carbon prepared from borassus bark. *Arab. J. Sci. Eng*. **2009**, *34*(2A): 31-38.

[6] AOAC. *Official Method of Analysis*. Association of Official Analytical Chemist, 14th ed. Washington DC, 1990.

[7] Rahman, I. A.; Said, B.; Shadier, S. O.; Syarizal, E. S. Adsorption characteristic of malachite green an activated carbon derived from rice husk produced by chemical thermal process. *Bioresour. Tech*. **2005**, *95*: 1578-1583.

[8] Fan, M.; Marshall, W.; Dangaard, D.; Brown, C. Steam activation of chars produced from oat hulls. *Bioresour. Tech*. **2005**, *93*: 103-107.

[9] Ahmedna, M.; Marshall, W.; Rao, M. Production of granular activated carbon from selected agric by products. *Bioresour. Tech.* **2000**, *71*: 113-123.

[10] Abdulrahman, F. W.; Hassan, L. G.; Idris, S.; Itodo, U. A.; Ladan, M. J. Assessment of shea nut

shell activated carbon in biochemical oxygen demand removal: A kinetic approach. *Int. J. Nat. Appl. Sci.* **2009**, **5**: 107-113.

[11] Apipreeya, K. I.; Phussadee, P.; Prasert, P. Removal of metal ion from synthetic wastewater by activated carbon from *Eucalyptus camaldulensis* Denn Bark. *The 2nd Joint International Conference on Sustainable Energy and Environmental (SEE 2006)*, **2006**, E-041: 1-9.

[12] Ioannidou, O.; Zabaniotou. A. Agricultural precursors for activated carbon production. *Renew. Sust. Ener. Rev.* **2006**, *11*: 1966-2005.

[13] Okiemen, F. E.; Ojoku, F. I.; Okiemen, C. D.; Wuana, R. A. Preparation and evaluation of activated carbon from rice husk and rubber seed shell. *Chem. J.* **2004**, *23*: 191-196.

[14] Baskaran, P. K.; Venkatraman, B. R.; Arivoli, S. Adsorption of malachite green dye by acid activated carbon- kinetic, thermodynamic and equilibrium studies. *E. J. Chem*. **2011**, *8*: 9-18.

[15] Hameed, H. B. Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. *J. Harz. Mat*. **2009**, *162*: 939-944.

[16] Santhi, T.; Manonmani, S.; Smitha, T.; Mahalakshmi, K. Adsorption of malachite green from aqueous solution onto a waste aqua cultural shell powders (prawn waste): Kinetic study. *Rasayan J. Chem*. **2009**, *2*: 813-824.

[17] Temkin, M. J.; Pyzhev, V. Recent modification to Langmuir isotherms. *Acta Physiochim. URSS.* **1940**, *12*: 217-222.

[18] Gurses, A.; Dogar, C.; Yalc-in, M.; Acikyildiz, M.; Bayrak, R.; Karaca, S. The adsorption kinetics of the cationic dye methylene blue onto clay. *J. Harz. Mat*. **2006**, *131*: 217-228.

[19] Ahmedna, M.; Marshall, W. E.; Rao, R. M. Granular activated carbon from agricultural by-products: Preparation, properties and application in cane sugar refining. *Bulletin of Lousana State University Agricultural Center*, **2000**: 54.

[20] Khadija, Q.; Inamullah, B.; Rafique, K.; Abdul, K. A. Physical and chemical analysis of activated carbon prepared from sugarcane bagasse and use for sugar. *World Acad. Sci. Eng. Tech.* **2007**, *34*: 194-198.

[21] Ozer, A.; Dursun, G. Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. *J. Harz. Mat*. **2007**, *146*: 262-269.

[22] Arivoli, S.; Hema, M. Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid low cost carbon. *Int. J. Phy. Sci.* **2007**, *2*: 10-17.

[23] Arivoli, S.; Venkatraman, R. B.; Rajachandrasekar, T.; Hema, M. Adsorption of ferrous ion from aqueous solution by low cost activated carbon obtained from natural plant material. *Res. J. Chem. Environ.* **2007**, *17*: 70-78.