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Equilibrium Adsorption Studies Of Methylene Blue Onto Palm Kernel Shell-Based Activated Carbon

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Abstract: *This work investigates the adsorption capacity of activated carbon prepared from palm kernel shell for removing methylene blue from aqueous solution. The palm kernel shell was carbonized at 400^oC and then impregnated with KOH for 2 hours on a hot plate at 80^oC. The impreganated carbon was activated at 800^oC for 45mins in a furnace. The physicochemical parameters, ranging from the pH, SEM, BET surface area to surface functional group of the carbon surface were studied and indicate that palm kernel shell is a good precursor for preparation of activated carbon for methylene blue adsorption. The BET surface area as obtained from nitrogen gas adsorption was 127 g/m^2. The nitrogen gas adsorption also showed that the adsorption was characteristic of type 1 of IUPAC isotherm classification and indicative of a predominantly porous adsorbent. The micropore volume and the total pore volume were 0.11 and 0.12 cm^{3}g^{-1} respectively. The Langmuir adsorption capacity, Q^o, and the constant relating to the rate of adsorption, b, were 3.22 mg/g and -8.64 L/mg, respectively. This investigation has shown that the adsorption of methylene onto palm kernel shell based activated carbon can be best described by the Dubinin-Rushkevich model with a characteristic correlation coefficient of 0.98. The energy of adsorption obtained from this model shows clearly that the process is chemisorptions.***

Keywords*: activated carbon, adsorption, methylene blue, palm kernel shell.*

I. Introduction

More than 7,000 tons of approximately 10,000 different types of dyes and pigments are produced annually world wide of which 20 to 30 % are wasted in industrial effluents during finishing processes in the textile industries (Kannan and Meenakshisundaram, 2002). Dyes are also used in dyeing, paper and pulp, printing, plastics, leather, cosmetics and food industries. Some of these dyes are carcinogenic and highly toxic to living organisms and posses certain hazard and environmental problems (Yasin *et al*., 2007).

Methylene blue [3,7 bis(dimethylamino) phenazothionium chloride] is the most commonly used material for dyeing cotton, wool and silk (Hameed *et al*.,2006). Methylene blue specifically causes eye burn, which may be responsible for permanent injury to the eyes of humans and animals. It can give rise to short period of rapid or difficult breathing on inhalation while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating and mental confusion (Hameed *et al*., 2006).

Activated carbon is a carbonaceous material which is predominantly amorphous in nature and in which a high degree of porosity is developed by the process of manufacturing and treatment. Activated carbon can be manufacture from virtually all carbonaceous materials. However, agricultural wastes offer the most available and cheapest of all the known raw materials. Palm kernel shell which is an abundant agricultural solid waste that may be a good source of quality activated carbon. Activated carbon has been use extensively for the removal of undesirable odor, color, taste and other organic and inorganic impurities from domestic and industrial wastewater. Methods such as reverse osmosis, precipitation and ion exchange that have been used for the treatment of waste water are expensive. Activated carbon offers the most economical approach to wastewater treatment. This work investigates the adsorption capacity of activated carbon prepared from palm kernel shell for removing methylene blue from aqueous solution.

II. Materials and Methods

2.1 Sample Collection/ Sample Preparation

Palm kernel shell was collected from local palm oil producers. The palm kernel shell was removed, washed, dried and crushed using a locally made grinder. This was sieved to 1.18mm and carbonized at 400^{o}C for 1 hour. A portion of the carbonized material was mixed with KOH solution at impregnation ratio of 1:1(KOH pallet: Char). Impregnation was carried out at 80^{o}C on a hot plate equipped with a stirrer for 2 hours. The sample was filtered using a vacuum pump and dried overnight at 120^{o}C. The dried sample was then pyrolysed at a predetermined temperature and activation time of 800^{o}C 45 minutes in a furnace. The activated carbon was thoroughly washed and with 0.1 M HCl stirred for one hour to remove the alkali and alkaline earth metals and then washed with hot distilled water until the pH of the washing solution reached 7.0 to remove the

base and water soluble components in the carbon. The prepared activated carbons were dried at 120^{o}C overnight, cooled and stored for further studies.

A stock solution of MB was prepared by dissolving 0.5 g in 1000 cm^3 of distilled water. Serial dilutions were made to obtain the required lower concentrations. The concentration of MB in the aqueous solution was determined at λ_{max} of 660 nm, using UV-visible spectrophotometer (Helios γ). Methylene blue solution (25 cm^3) of known initial concentration and a 0.2 g (particle size of 855µm) of activated carbon were taken in a 150 cm^3 Erlenmeyer flasks with air tight stopper. This mixture was agitated in a temperature controlled shaker water bath, at a constant shaking speed for each experiment.

The percentage of methylene blue adsorbed and the amount adsorbed were calculated as (Hameed *et al.*, 2006):

% adsorbed = 100 (Co –Ce) / Co……..…….... (1)

where Co is the initial concentration of the adsorbate (ppm) and Ce is the equilibrium concentration (ppm).

Amount adsorbed (qe) = V (Co – Ce)/ m……..... (2)

where m (g) is the weight of activated carbon used for the adsorption studies and V (cm^3) is the volume of the adsorbate. Similar procedure was followed for another set of Erlenmeyer flask containing the same adsorbate concentration without activated carbon was used as blank.

The ash content, bulk density, pH, and conductivity were determined by the method of Rao *et al.* (2003). Oxygenated surface functional groups of the prepared activated carbon were determined by Boehm's titration method while the pHpzc was determined by the method of Sheng *et al.*, (2004).

III. Results and Discussions

Activated carbons were prepared from palm kernel shell as a precursor with chemical activation using potassium hydroxide as activating agent. Potassium hydroxide is a common activating agent in activated carbon manufacturing industries. The choice of this chemical in this work was informed by the fact that it is a cleaner production technology while compared to the use of $ZnCl_2$, H_3PO_4 and other chemical agent frequently being used. The activated carbon was characterized by standard methods. Scanning Electron Microscopy (SEM) was used to study the morphological structure on the prepared activated carbons (Figure 1).

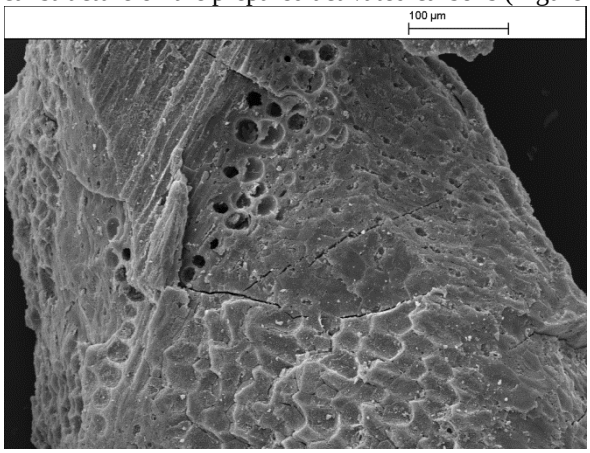

Figure 1: SEM of the prepared Activated sample

The surface structures of the activated carbons have burnt out pores with tunnel or honeycomb-like structures as shown in Figure 1. The sample is characterized by a smooth surface with many orderly pores developed. This is as a result of lack of tars and other impurities that could clog up the pores and inhibit the development of pore structures.

The BET surface area as obtained from nitrogen gas adsorption was 127 g/m^2. The nitrogen gas adsorption also showed that the adsorption was characteristic of type 1 of IUPAC isotherm classification (Figure 2). This is indicative of a predominantly porous adsorbent. The micropore volume and the total pore volume were 0.11 and 0.12 cm^3g^{-1} respectively. The pore size distribution is as shown in Figure 3.

The percent ash of the palm kernel shell was determined to be 0.92%. This is lower than 1.10% reported in literature (Daud and Ali, 2004). The low ash content indicates that palm kernel shell is a suitable precursor for preparation of activated carbon. The ash content is a measure of the minerals as impurities in carbons, mainly derived from the carbon precursor (Reo *et al*., 2003). Ash consists mainly of minerals such as silica, aluminum, iron, magnesium and calcium that is not desired (Losso *et al.*, 2002). These metals can leach from the activated carbon, causing catalysis of adverse reactions or interference by competitive adsorption (Losso *et al.*, 2002).

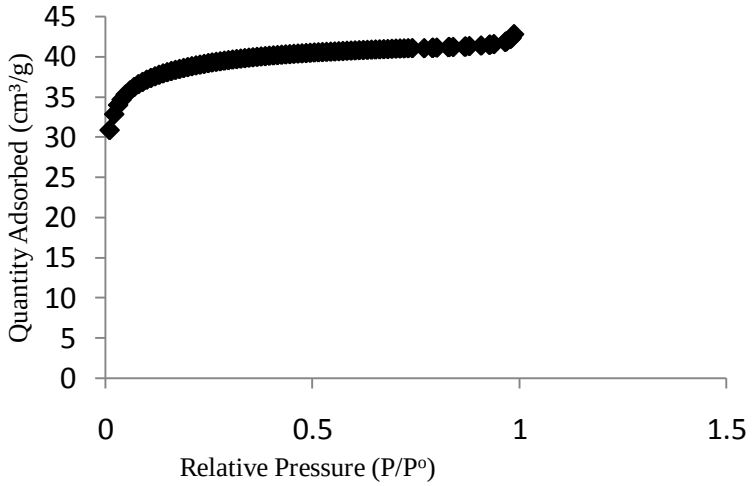

Figure 2: Nitrogen gas adsorption isotherm for the sample at 77 K.

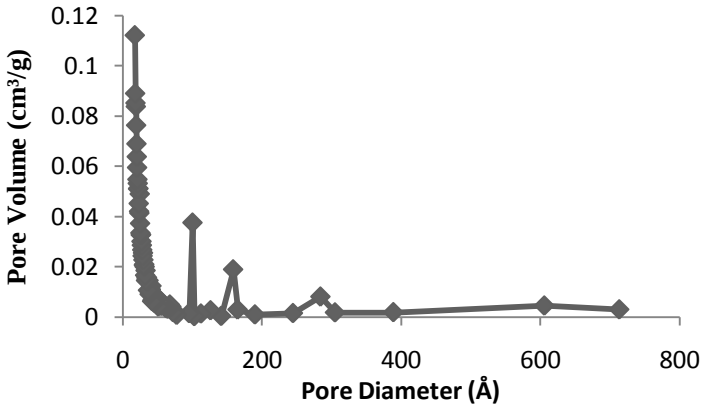

Figure 3: Pore size distribution of the sample

The sample is also characterized by a pH of 9.32, conductivity of 138µS and a pHpzc of 7. The pH, conductivity and ash constitute the chemical properties of activated carbon. The pH of 9.32 is slightly higher than the 7.4 reported for most commercial carbon in literature (Reo *et al*., 2003). The pH of the solution is an important factor that may affect uptake of the adsorbate. Yasin *et al*. (2007) and Santhy and Selvapthy, (2006), reported that the chemical characteristic of both adsorbate and adsorbent vary with pH and showed that the removal of methylene blue from aqueous solution increased with increase of pH of the solution. The pH of the carbon directly impacts the adsorption process and may affect the final pH of the treated wastewater. Therefore a neutral pH is generally preferred (Reo *et al*., 2003). A solution pH of 6.98-7.02 was therefore used throughout in this work.

The surface charge on the adsorbent is a function of pH. The pH with which the charge of the adsorbent surface is zero is referred to as the point of zero charge (pHpzc). According to Sheng *et al*. (2004), at pH < pHpzc, the carbon surface has a net positive charge, whereas at pH > pHpzc, the carbon surface has a net negative charge. The pHpzc of the activated carbon was 7.47 (Figure not Shown). Methylene blue is a cationic dye and its adsorption will be favoured at pH below the pHpzc. It is therefore preferable to work at pH slightly below the pHpzc which in this case was at neutral. High conductivity of the carbon is undesirable because it interferes with the adsorption process because of the leachable minerals associated with the carbon surface (Reo *et al.*, 2003). The prepared carbon has a conductivity of 138 µS. This is lower than 347 µS reported for CO_2 activated pecan shell (Losso *et al*., 2002).

The surface functionalities obtained from result of Boehm titration are shown in table 1.

Table 1: Surface functionalities of the sample

Total acid sites	Phenolic	Carboxylic	Lactonic	Total basic sites
6.00	2.00	0.65	3.35	6.35

Table 1 show that the surface of the prepared activated carbon is heterogeneous with a variety of functional groups present; as such the adsorbent could be use effectively for adsorption of a variety of impurities from solution.

3.1 Effect of contact time and initial concentration on adsorption of MB onto the activated carbon:

Figure 4 shows the percent methylene blue adsorbed at different initial concentration at varying contact time. It is clear that the percent adsorbed increased with contact time but however decreased with increase in initial concentration. The adsorption characteristic indicates a rapid uptake of the adsorbate as shown by the curves. The adsorption rate however increased marginally after the first ten minutes to a near constant value with increase in contact time. This agrees with the report of other investigators in literature [Garg *et al*. (2003), Kadirvelu *et al.* (2000), and Kannam and Meenarshisundran (2002)]. The percent adsorbed was maximum at 50 minutes at most initial concentration, hence 50 minutes is the optimum contact time for the adsorption of methylene blue onto the prepared carbon. The percent adsorbed decreased from 94 to 80 percent after the first ten minutes of contact of the MB with the adsorbent as the initial concentration increased from 5 to 25 ppm.

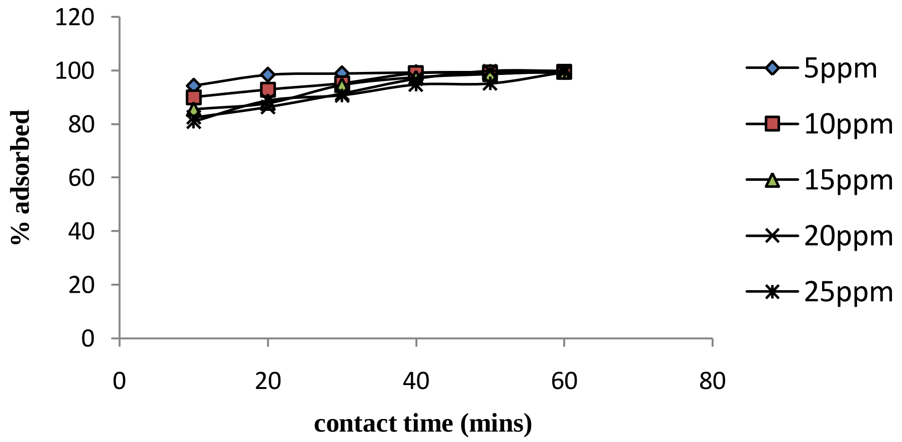

Figure 4: Effect of contact time and initial conc on adsorption of MB onto AC.

3.2 Adsorption isotherms

Two important physicochemical aspects for the evaluation of adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. The adsorption equilibrium usually presented as adsorption isotherm is useful for predicting the performances of activated carbon. According to Wang and Do (1999), adsorption capacity is a prime factor to be considered in the optimization of activated carbon. The equilibrium relationships between adsorbate and adsorbent are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium (Mohmmed *et al.*, 1998). The analysis of isotherm data by fitting them into different isotherm models is an important step to find the suitable model that can be used to reproduce the experimental result obtained and hence for design purposes.

3.2.1 The Langmuir Isotherm

The Langmuir isotherm is given as:

$$q_e = \frac{bCQ^o}{1+bC} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where, q_e is amount of adsorbate adsorbed per unit weight of carbon, Q^o is a constant relating to monolayer adsorption capacity, b is a constant which measures the surface energy of the adsorption process, C is

equilibrium concentration of the adsorbate in solution. Two convenient linear forms of the Langmuir equations are:

$$\frac{C}{q_e} = \frac{1}{bQ^o} + \frac{C}{Q^o} \quad \ldots (4)$$

$$\frac{1}{q_e} = \frac{1}{Q^o} + \left[\frac{1}{bQ^o}\right]\left[\frac{1}{C}\right] \quad \ldots (5)$$

Figure 5 is the Langmuir isotherm plot for the adsorption of methylene blue onto the prepared activated carbon. The Langmuir isotherm constants, separation factor and the correlation coefficient are shown in Table 2. The value of adsorption capacity, Q^o, and the constant relating to the rate of adsorption, b, as obtained from the slope and intercept of the plot were 3.22 mg/g and -8.64 L/mg, respectively (Table 2). A correlation coefficient, as high as 0.71 was observed, indicating that the experimental data fit to the Langmuir model.

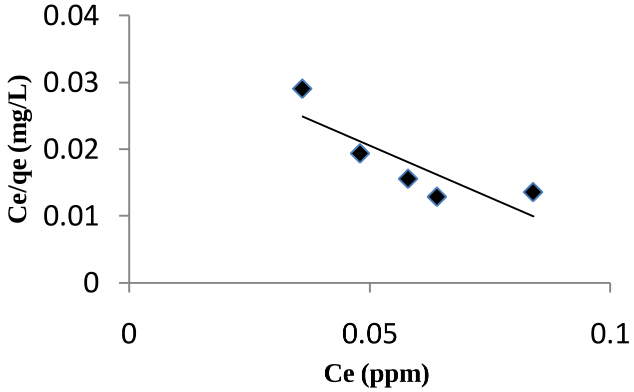

Figure 5: Langmuir isotherm for the adsorption of MB by the AC at 30°C

Table 2: Adsorption isotherm constant parameters

Langmuir	
Q^o (mg/g)	3.22
b.	-8.64
R_L	0.0046
R^2	0.71
Freudlich	
Kf	950.61
1/n	1.97
R^2	0.96
Temkin	
b_T. (kJ/mol)	406.77
K_T (dm^3/g)	32.82
R^2	0.97
Dubinin-Rushkevich (D-R)	
X_m' (mg/g)	61.31
E (kJ/mol)	3162.28
R^2	0.98

An important characteristic of the Langmuir model is a dimensionless parameter called the separation factor, R_L and expressed as (Hameed *et al.*,. 2006):

$$R_L = \frac{1}{1 + bC_o} \quad \ldots (6)$$

where b is the Langmuir constant expressing the adsorption rate and C_o is the highest initial concentration. The R_L parameter is considered as a reliable indicator of adsorption characteristic. It indicates the shape of the isotherm and the nature of the adsorption process as given below (Kannan and Meenkshisundran, 2002):

R_L values	Nature of the process
RL > 1	Unfavorable
RL = 1	Linear
0 < RL < 1	Favorable
RL = 0	Irreversible

The R_L value was 0.0046. The R_L value for the studied system was found to be between 0 and 1which is indicative of favorable adsorption of methylene blue onto the adsorbent.

3.2.2 Temkin Adsorption Isotherm

The Temkin isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is therefore, characterized by a uniform distribution of the binding energy (Hameed *et al.*, 2008). The Temkin isotherm is given as:

$$qe = \frac{R_T}{b_T} InK_T + \frac{R_T}{b_T} InCe \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where, $1/b_T$ is the adsorption potential of the adsorbent (kJ mol^{-1}) and K_T is Temkin isotherm constant (dm^3g^{-1}). A plot of InCe versus qe gives a straight line of slope R_T/b_T and intercept of R_T/b_T InK_T. The Temkin isotherm plot for the adsorption of MB from aqueous solution onto the palm kernel shell based activated carbon is shown in Figure 6. The high correlation coefficient (0.97), characterized by the plots indicates a fit into the model. The high value indicates a strong interaction between the adsorbate and the adsorbent. The Temkin isotherm constant (Table 2) shows that the value of b_T, which is related to heat of adsorption was 406.77 kJ/mol. This value is indicative of chemisorptions. The Temkin adsorption potential, K_T of the adsorbent was 32.82 (dm^3/g).

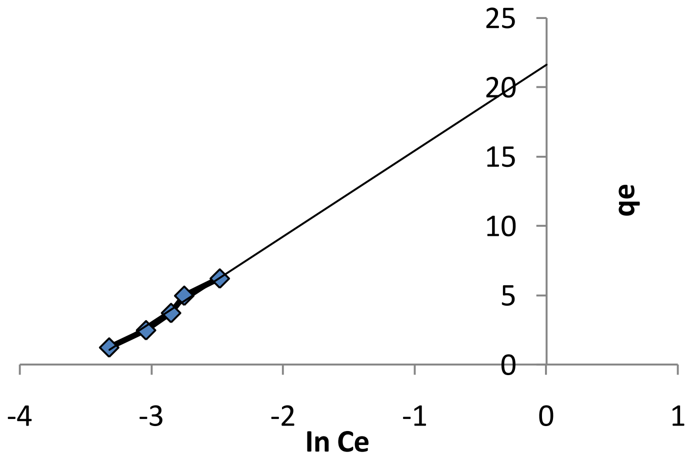

Figure 6: Temkin isotherm plots for adsorption of MB by AC at 30°C.

3.2.3 The Freundlich Isotherm

The Freundlich equation has the general form expressed as (Thomas and Crittenden, 1998):

$$q_e = K_f C^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where, n is a constant related to adsorption efficiency and energy of adsorption, K_f is a constant measuring adsorption capacity, q_e is amount of adsorbate adsorbed per unit weight of carbon. It describes adsorption processes on surface sites that are energetically heterogeneous. The logarithm form of the Freudlich equation can be written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

A plot of log q_e versus log C gives a straight line with the slope $1/n$ and the intercept log K_f. The K_f value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The numerical value of n is a useful index of adsorption efficiency and is related to the energy of adsorption. This means that the intercept is roughly an indicator of sorption capacity and slope indicates adsorption intensity (Ribeiro *et al*., 2001). The fitting of the experimental data into Freundlich model is shown in Figure 7. The Freundlich isotherm parameters, K_f and 1/n which measure the capacity of the adsorbent and adsorption intensity/ surface hetergeneity are obtained from the intercept and the slope of the plot, respectively, and are shown in Table 2. The K_f value was 950.61 while the value of 1/n was 1.97. Generally, $1<1/n<10$ is characteristic of cooperative adsorption and indicative of favourable adsorption process as reported in literature (Hameed *et al*., 2006; and Shabudeen *et al*., 2006). In cooperative adsorption, the formation of second layer is ruled out as there is no obvious phase change (Kipling, 1965). Freundlich model also yields a good fit with a correlation coefficient value of 0.96.

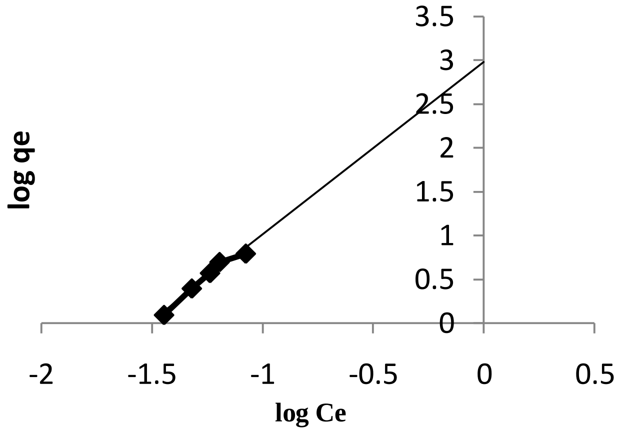

Figure 7: Freundlich isotherm plots for adsorption of MB at 30°C

3.2.4 Dubinin-Rushkevich (D-R) Model

The D-R adsorption isotherm is expressed as: (Kannan and Rengasamy, 2005).

$$\boldsymbol{In\ qe = In\ X_m{}' - K'\varepsilon^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{10})$$

where, X_m'= adsorption capacity (mg/g), K' = constant related to energy of adsorption ($mol^2\ kJ^{-2}$), ε = Polanyi potential = RT In [1+ (1/Ce)], R = universal gas constant ($J\ deg^{-1}\ mol^{-1}$), and E = mean energy of adsorption and can be computed from the K' value as

$$\boldsymbol{E = (-2K')^{-0.5}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{11})$$

A plot of $\boldsymbol{In\ qe\ vs\ \varepsilon^2}$ gives slope = K' and intercept = In X_m'. The value of mean energy E, provide information about the nature of adsorption process.

Figure 8 depict the linear plots of the Dubinin-Rushkevich (D-R) isotherm. The correlation coefficient 0.98, indicating the model best describes the experimental data. The slope and intercept of the plots were used to calculate the isotherm constants shown in Table 2.

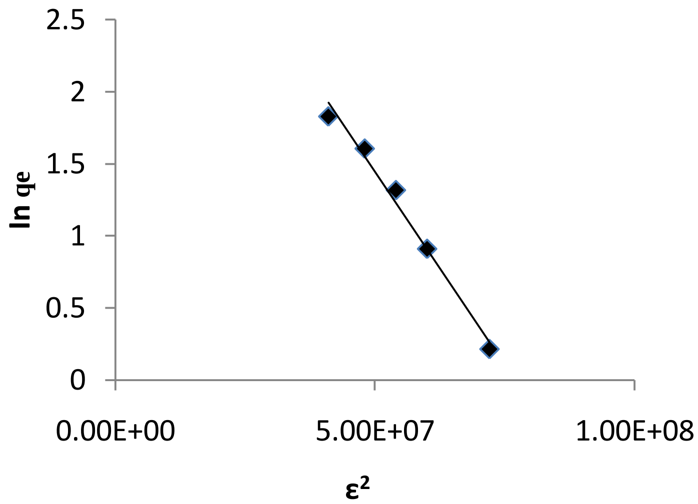

Figure 8: Dubinin-Radushkevich plot for the adsorption of MB

The adsorption capacity X_m as obtained from the intercept of the plots was 61.31 mg/g. The D-R isotherm is best employed to determine the adsorption energy. The energy of adsorption as estimated from the D-R plots was 3162 kJ/mol. The energy value suggests that the process is chemisorptions.

IV. Conclusion

This investigation has shown that palm kernel shell could be a good precursor for preparation of a low cost activated carbon for removal of dye from wastewater. This is shown by the results of the physicochemical

properties analysis of the prepared activated carbon. The pH, ash content are low; the BET surface area is adequate and SEM analysis shows development of adequate pores during the activation process. The carbon is therefore suitable for the adsorption of methylene blue from aqueous phase.

It is also observed that the surface of the prepared activated carbon is heterogeneous with a variety of functional groups present; as such the adsorbent could be effective for adsorption of a variety of impurities from solution. The Langmuir adsorption capacity, Q^{o}, and the constant relating to the rate of adsorption, b, for adsorption of methylene blue were 3.22 mg/g and -8.64 L/mg, respectively.

This research has established that the adsorption of methylene onto palm kernel shell based activated carbon can be best described by the Dubinin-Rushkevich isotherm model with a characteristic correlation coefficient of 0.98. The energy of adsorption obtained from this model shows clearly that the process is chemisorptions. This is buttressed by the fact that the nitrogen gas adsorption also showed that the adsorption was characteristic of type 1 of IUPAC isotherm classification and indicative of a predominantly porous adsorbent. It is observed that the adsorption characteristic indicates a rapid uptake of the adsorbate, the optimum contact time for the adsorption of methylene blue onto the prepared carbon being 50 minutes. This evidence also point to chemisorptions process.

V. Acknowledgement

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