Equilibrium, Kinetics and Thermodynamic Studies on MB Adsorption Using Hamburger Seed Shell Activated Carbon

EJIKEME, EBERE M., EJIKEME, P. C. N., ABALU, BENJAMIN. N.

1Chemical Engineering Department, Enugu State University of Science and Technology, Enugu, Enugu State Nigeria.
2Chemical Engineering Department, Institute of Management and Technology, Enugu, Enugu State Nigeria.

Abstract-- Hamburger seed shell was activated and used as an alternative adsorbent for removing MB dye from aqueous solution. The kinetics study showed that MB dye adsorption followed the pseudo-second order kinetic model. Isotherm data fitted well to the Freundlich model in the pH and temperature ranges studied. The adsorption capacity was found to increase with temperature, which showed endothermic nature of MB dye adsorption. The negative value of the Gibb’s free energy confirmed the feasibility and spontaneity of the adsorption process. The magnitude of the enthalpy and Gibb’s free energy suggest that the MB dye adsorption occurred by both physical and weak chemical interaction.

Index Term-- Activated carbon, FTIR, Isotherm, Kinetics, Methylene blue,

I. INTRODUCTION
The residual dye molecules, even at very low concentrations in the wastewater are common water pollutant. Their presence in water is highly noticeable and undesirable and may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration [1] The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water which interferes with the growth of bacteria to levels insufficient to biological degrades impurities in water [2]. Dyes are chemicals which on binding with a material will give colour to the material [3]. The colour of a dye is provided by the presence of a chromophore group. Methylene blue (MB) is most commonly used for dying cotton, wood and silk [4]. Although, the dye is not regarded as a very toxic dye, MB can have various harmful effects on human being and animals. Once inhaled, it can cause heart rate increase, nausea and vomiting. It is environmentally important to remove them from waste streams before discharge to public water source. Adsorption process is the widely used method for treating waste water. Activated carbon is the main adsorbent used in adsorption processes [5], [6]. The adsorption capacity of the activated carbon and also the performance of the activated carbon adsorption system are usually predicted from equilibrium sorption isotherms [7]. The widely used isotherms by several researchers for different sorbate / sorbent systems are Freundlich [8], Langmuir [9] and Redlich and Peterson¹⁰ isotherms.

Adsorption kinetics involves the study of the rate at which pollutants are removed from aqueous solution unto adsorbent surface, which in turn controls the residence time of the adsorbate uptake at the solid – solution interface [11]. Several kinetic models are available to describe reaction order of adsorption processes, pseudo-first order [12], first order [13], second order [14] and pseudo-second order [15].

In this study, hamburger seed shell was used as the precursor in the preparation of activated carbon.

II. MATERIALS AND METHODS PRECURSOR

A. ADSORBATE
Methylene Blue (MB) (C1. 52015) with empirical formular C16H18N3SC1 and formular weight of 319.9g/mol was supplied by De Cliff Integrated LTD Ogbete Enugu, Enugu State Nigeria (97% purity). It has maximum absorbance at wavelength of 661nm.

B. Preparation of Activated Carbon
The preparation of the adsorbent was in accordance of the method used by [16] with slight modification.

C. Preparation of Methylene Blue Solution
Double distilled water supplied by Pymotech Research Center Abakpa Enugu State of Nigeria was used for the preparation of the solutions. A
1000mg/l stock solution was prepared and from there, necessary dilutions were made to obtain the desired concentration.

D. Characterization of Activated Carbon

The surface functional groups and structure were studied by fourier transform infrared spectroscopy [ Buck 530 IR ]. The FTIR spectra of the raw material and activated carbon were scanned at a wavelength of 600–4000cm⁻¹ to obtain its spectra lines.

E. Adsorption Isotherm

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323K and 343K on an Isothermal shaker for 6 hours to ensure equilibrium. 0.02g of the adsorbent was mixed with 50ml of 30mg/l, 50mg/l, 80mg/l and 110mg/l of the solution at different pH of 4, 8 and 10. The pH was adjusted using 0.1M HCl or 0.1M NaOH before addition of the adsorbent. At the end of equilibrium time of 6 hours, the reaction mixture was centrifuged and the residual MB concentration analysed. The amount of MB adsorbent at equilibrium qₑ(mg/g) was calculated from the following equation (1).

\[ qₑ = \left( \frac{C₀ - Cₑ}{W} \right) V \]  

(1)

F. Adsorption Kinetic Model

The kinetic experiments were performed using a procedure similar to the equilibrium studies. 50mls of known concentration of MB was mixed with 0.02g of the adsorbent in a flask. Then, the flask was agitated in a shaker incubator for a contact time varied in the range 0-240mins at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed by the same procedure as batch equilibrium studies. The amount of MB adsorbed at each time interval per unit mass of the adsorbent, qₜ (mg/g), was calculated by equation 2:

\[ qₜ = \left( \frac{C₀ - Cₜ}{W} \right) V \]  

(2)

Where C₀ (mg/L) is initial MB solution, Cₜ (mg/L) is its concentration at time t, V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

The kinetics of methylene blue adsorption was analysed using pseudo-first order model, pseudo-second order model, and intra particle diffusion model.

III. RESULTS AND DISCUSSIONS

A. Infrared Spectroscopy Analysis

The well known activity, reactivity and adsorption efficiency of activated carbon and other carbonaceous sorbents are mainly based and dependent on the various loaded functional groups on the surface of these sorbents [17]. FTIR spectroscopy is an important technique used to identify characteristics surfaces functional groups on the adsorbent, which in some cases are responsible for the binding of the adsorbent molecules. The functional groups on the adsorbent surface were identified by analyzing the spectra using available literature [18], [19], [20], [21], [22].

Fig. 1 shows the FTIR spectra of the activated carbon and it’s precursor in the range of 600-4000cm⁻¹. Several distinct and sharp absorption bands were observed as well as relatively low intensity peaks for all sample spectra. The raw hamburger-shell shows indication of various surface functional groups. The wide peaks between 3185.033 – 3803.987 cm⁻¹ indicates 0-H stretching vibration of hydroxyl functional groups including hydrogen bonding or adsorbed water. The peak at 2972.8 can be ascribed to C-H stretching which described the presence of –CH and ≡CH groups present in the lignin structure of the hamburger shell. The trichotomous peaks at 2743.85325, 2628.28106 and 2531.97435 cm⁻¹ are attributed to C-OH stretching vibrations in carboxylic acid derivatives. The peaks in the ranges of 2266.137 – 2425.026cm⁻¹ can be linked to the C≡C stretching vibration in alkyne groups. The peak at 1794.616cm⁻¹ depicts C = O stretching from carboxylic acid group. The band located at 1678.955cm⁻¹ corresponds to the formation of oxygen functional groups based on highly conjugated C = O stretching in carboxylic or carboxylate group as well as carbonyl group. The skeletal C=C vibration in aromatic rings cause band at 1438.687cm⁻¹. The appearance of a band at 1364.761cm⁻¹ can be attributed to C = O stretching vibration in carboxylic groups. The band at 1140.975cm⁻¹ and band at about 1008.632cm⁻¹ can be assigned to C-O stretching vibration in alcohols, phenols, or ether or ester groups. The bands at 867.4942cm⁻¹
and relatively intense band at 773.2506 cm\(^{-1}\) are C-H out of plane bending of benzene derivatives. Finally, the band caused by O-H out of plane bending vibrations band is located at 672.5205 cm\(^{-1}\). The FTIR spectra of activated carbon are equally shown in fig. 1. Fewer functional groups were detected, indicating that the surface functional groups of hamburger shell experienced chemical changes during carbonization. Many peaks present in the raw hamburger shell spectrum absolutely disappeared in the activated carbon spectrum while those remaining were weak to a great extent. This is consistent with the breaking of many bonds in the KOH impregnated raw hamburger shell leading to the libration and elimination of volatile species and partial aromatization during carbonization [19], [23]. Compared with the raw hamburger shell, the C-H vibrations is methyl and methylene groups at 2977.829 cm\(^{-1}\) became much weaker after activation, suggesting the carbonization of the material is almost complete [18].

B. KINETIC MODELS
The adsorption kinetic produces valuable information about the reaction pathways and mechanism of the reactions.

PSEUDO-FIRST ORDER
The pseudo-first order parameters at different pH along side with their correlation coefficients \(R^2\) are shown in table 2. The \(R^2\) values obtained were small at all the pH studied, and the experimental \(q_e\) values did not agree with the calculated values obtained from the linear plots.

PSEUDO SECOND ORDER
The values of the rate constants, correlation coefficients, the experimental and calculated values are shown in table 2.

It can be seen that the correlation coefficients for the linear plot of the pseudo second order increased from 0.988 to 1 as the pH increased, which is higher than the correlation coefficients of all other models studied. Also, there is a good agreement between the experimental \(q_e\) values and the calculated \(q_e\) values. This indicates that the adsorption kinetic is better represented by the pseudo-second order model. This was in agreement with the work done by Dalis et al on basic dye adsorption using Kenaf fiber char [24], A. Gil et al on dye removal using pillsed clay [25], Emmanuel I. et al on MB adsorption on defatted carica papaya seeds [26], Mehmet Ulas et al on Methylene blue adsorption on activated carbon from posindonia oceanic dead leaves [27], Andre Cazetta et al on methylene blue adsorption on NaOH-activated carbon from coconut shell [28], M. Auta and B. Hameed on MB removal using modified mesoporous clay [29] and so many others.

The high initial sorption rate, \(h\), obtained showed that the adsorption was rapid. The uptake of adsorbate by adsorbent has been observed to occur in two stages: the first rapid and quantitatively predominant and the second slower and quantitatively insignificant [26], [30]. The rapid adsorption of MB by this adsorbent is probably due to the abundant availability of active sites on the biomass, and the perceived porous and mesh structure of the adsorbent which provides ready access and large surface area for the adsorption of MB dye on the binding sites [31], [32].

INTRA PARTICLE DIFFUSION
The intra particle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step. The intra particle diffusion model usually includes three steps. The first portion is the external surface adsorption or boundary layer diffusion. The second portion is the gradual stage of adsorption which is the intra particle diffusion. If the plot of \(q_t\) versus \(t^{1/2}\) is linear and passed through the origin, then the intraparticle diffusion is the rate-controlling step [32]. The third portion is the final equilibrium stage in which the intra particle diffusion starts to slow down due to the extremely low dye concentration left in the solution [32].

The plot in fig. 2 shows that the linear plot did not pass through the origin which indicated that the intra particle diffusion was not only the rate controlling step and the boundary layer diffusion controlled the adsorption to some extent [32]. This deviation may be due to the difference in mass transfer rate in the initial and final stage of adsorption [24], [33].

This was in line with a work done by Dalis et al on basic dye adsorption using treated Kenaf fiber char [24], Hameed and Hakimi on acid dye removal using durian peel [33], A. Tan et al in basic dye adsorption by oil palm fiber activated carbon [34] and many others. The values of C and Kid are given in table 1. The values of the intercept \(C\) increased with an increase in pH, which showed that boundary layer effect increased as pH increases.

The correlation coefficients for intra particle diffusion were lower than that for the pseudo second order kinetics. This showed that the present system may be followed by intra particle diffusion, but is not the only rate controlling step.
C. ISOTHERM MODELS

Isotherm studies help to understand the nature of the interaction between the adsorbate and adsorbent used for the adsorption.

LANGMUIR MODEL

The value of the separation factor \( R_L \) indicates the nature of adsorption process. \( R_L \) values indicates the type to be irreversible \((R_L = 0)\), favourable \((0 < R_L < 1)\), linear \((R_L = 1)\) or unfavourable \((R_L > 1)\). The linear plot of \( ce/qe \) vs \( c_e \) indicated the applicability of Langmuir adsorption isotherm. Consequently, suggested the formation of mono layer coverage of the adsorbate on the surface of the adsorbent [35]. Langmuir constants, \( q_0 \) and \( K_L \) were calculated from the slopes and intercepts and are given in table 3 along with the correlation coefficient \( s(R^2) \) and separation factor \( R_L \). From the table, it is clear that the \( K_L \) values were higher at higher temperature, which showed endothermic nature.
Fig. 1. FTIR of the raw and activated Hamburgar seed shell
Table I

<table>
<thead>
<tr>
<th>KINETIC EQUATION</th>
<th>pH</th>
<th>KINETIC PARAMETERS</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intra – Particle Diffusion Model</td>
<td>2</td>
<td>K_{id} = 1.9267 (min⁻¹), C = 38.917</td>
<td>0.8365</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>K_{id} = 0.5807 (min⁻¹), C = 65.187</td>
<td>0.7186</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>K_{id} = 0.3089 (min⁻¹), C = 70.297</td>
<td>0.8198</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>K_{id} = 0.0986 (min⁻¹), C = 73.352</td>
<td>0.8959</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>K_{id} = 0.0919 (min⁻¹), C = 73.362</td>
<td>0.822</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>pH</th>
<th>Q_{exp}(mg/g)</th>
<th>Q_{calc}(mg/g)</th>
<th>K_1(min⁻²)</th>
<th>R²</th>
<th>KP2(min⁻¹)</th>
<th>h</th>
<th>Qe(mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>64.549</td>
<td>20.09</td>
<td>0.0161</td>
<td>0.767</td>
<td>KP2 = 0.001</td>
<td>5.102</td>
<td>71.429</td>
<td>0.998</td>
</tr>
<tr>
<td>4</td>
<td>72.687</td>
<td>3.313</td>
<td>0.0092</td>
<td>0.364</td>
<td>KP2 = 0.005</td>
<td>29.586</td>
<td>76.923</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>74.3575</td>
<td>1.5922</td>
<td>0.0046</td>
<td>0.132</td>
<td>KP3 = 0.009</td>
<td>53.28</td>
<td>76.923</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>74.7223</td>
<td>0.5688</td>
<td>0.0023</td>
<td>0.030</td>
<td>KP3 = 0.024</td>
<td>42.012</td>
<td>76.923</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>74.5688</td>
<td>0.3515</td>
<td>0</td>
<td>0.006</td>
<td>KP3 = 0.034</td>
<td>201.183</td>
<td>76.923</td>
<td>1.0</td>
</tr>
</tbody>
</table>

of MB adsorption. The average values of R_L for each of the temperature and pH used were between 0 and 1, which indicated the favorable adsorption of MB. This was in agreement with the work done by Dalia Khalid et al on the batch adsorption of basic dye using acid treated kenaf fiber [34], and work done by I.A.W Tan et al on equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon [43].

FREUNDLICH ISOTHERM

The values of Freundlich constants and correlation coefficients (R²) are given in table 3. The values of K_F and n changed with the rise in temperature. The value of n showed an indication of the favorability of adsorption. Values of n larger than 1, showed the favorable nature of the adsorbent [35], [37], [38]. The value of n suggested that MB was favorably adsorbed by the activated carbon prepared from Hamburger seed shells. The correlation coefficients greater than 0.980, showed that the data fitted well with Freundlich equation. This was statistically confirmed by giving greater R² values closer to unity (0.85 – 0.999). This implies that Freundlich model may better describes an adsorption isotherm for the adsorbent. This adsorptive behaviour indicates that the adsorption takes place on a heterogeneous surface, which may be attributed to the various active sites on the adsorbent surfaces [39]. This was in line with the work done by Hui Deng et al on adsorption of methylene blue on adsorbent materials produced from cotton stalk [4].
Table III

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_o (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td>303</td>
<td>500</td>
<td>1.0</td>
</tr>
<tr>
<td>313</td>
<td>500</td>
<td>2.0</td>
</tr>
<tr>
<td>323</td>
<td>500</td>
<td>2.0</td>
</tr>
<tr>
<td>333</td>
<td>500</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table IV

<table>
<thead>
<tr>
<th>Concentrations (mg/ls)</th>
<th>ΔG(KJ/mol)</th>
<th>ΔH(KJ/mol)</th>
<th>ΔS(Jmol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
</tr>
<tr>
<td>30mg/l</td>
<td>-15.424</td>
<td>-16.464</td>
<td>-17.504</td>
</tr>
<tr>
<td>50mg/l</td>
<td>-13.642</td>
<td>-14.652</td>
<td>-15.662</td>
</tr>
</tbody>
</table>
D. ADSORPTION THERMODYNAMICS

Thermodynamic studies are useful for interpretation of adsorption behaviors especially as it concerns equilibrium of the process [29], [40]. The adsorption of MB on the hamburger shell activated carbon thermodynamic studies were carried out at various temperatures of 30, 40, 50 and 60°C. Temperature is a significant parameter affecting adsorption capacity of adsorbents and transport/kinetic process of the dye adsorption. Thermodynamic reactions of the adsorption process can be determined via thermodynamic parameters, such as the changes in the standard free energy ($\Delta G^\circ$), the enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) associated with the adsorption process, using the following relation:

$$\Delta G^\circ = H - T\Delta S$$  \hspace{1cm} (3)

$$\Delta G^\circ = -RT\ln K_c$$  \hspace{1cm} (4)

Taking advantage of the two equations, the Van’t Hoff equation can be written as

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$  \hspace{1cm} (5)

Where $K_c$ is the equilibrium constant, which is the ratio of the equilibrium concentration of the dye ion on the adsorbent to the equilibrium concentration of the dye ions in solution. $R$ is the universal gas constant (8.314J/kmol), $T$ (k) is the absolute temperature.

The values of $\Delta S^\circ$ and $\Delta H^\circ$ were obtained from intercept and slope respectively of plot of $\ln K_c$ against $\frac{1}{T}$.

The negative values of $\Delta G^\circ$ (table 4) indicated the feasibility of the process and the spontaneous nature of the adsorption. Moreover, the standard free energy change for the adsorption was more than -20kJ/mol and less than zero. The magnitude of $\Delta G^\circ$ values is in the range of multilayer adsorption which occurs by both physical

adsorption and weak chemical interaction [1], [41], [42], [43]. This is confirmed with the results of the isotherm of adsorption which followed the Freundlich expression. The value of $\Delta G^\circ$ became more negative with increasing temperature. This showed that increase in temperature was favourable for the removal process. The results also showed that both enthalpy and entropy values were positive at different concentration, signifying that the adsorption process was endothermic and the degree of dispersion increased with increase in temperature. The endothermic behaviour observed from enthalpy value further confirmed the trend of adsorption of MB on the adsorbents which were found to increase as temperature was increased. The nature of the adsorption process was equally confirmed by the magnitude of the $\Delta H^\circ$ values. It is accepted that if magnitude of enthalpy change is less than 84kJ/mol, adsorption is physical, however, chemisorptions takes place from 84 to 420kJ/mol. The range of values of $\Delta H^\circ$ from table 4 showed that the nature of adsorption is physical. This equally confirmed the multilayer adsorption which can occur by both physical adsorption and chemical adsorption.
IV. CONCLUSION
Activated carbon was prepared from hamburger seed shell by chemical activated with KOH. This study investigates the adsorption of MB dye on activated carbon prepared conventionally from hamburger seed shell. The effects of temperature and pH on the isotherm and kinetics of the adsorption process were studied. The following results were obtained:

1. Hamburger seed shell was successfully used as an adsorbent for the removal of MB dye from aqueous solutions.
2. The pseudo-second-order kinetic model agreed very well with the experimental data at the pH studied.
3. Adsorption parameter for Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms were determined and the equilibrium data fitted well with Freundlich model of adsorption for MB dye. The uptake of the MB dye increased with the increased in temperature.

4. The thermodynamics properties such as $\Delta G^0, \Delta H^0$ and $\Delta S^0$ studied, confirmed the adsorption process as spontaneous and endothermic in nature which is favoured at higher temperature. The magnitude of the enthalpy and Gibbs free energy suggested that the adsorption occurs by both physical and weak chemical interactions.

ACKNOWLEDGEMENT

The authors wish to thank PYMOTECH RESEARCH CENTRE AND LABORATORIES ENUGU, ENUGU STATE NIGERIA for all their facilities used throughout the research work.

REFERENCES


