Research Article

Cocoa Shell as Adsorbent for the Removal of Methylene Blue from Aqueous Solution: Kinetic and Equilibrium Study

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Abstract
Methylene blue (MB) adsorption from an aqueous solution onto activated carbon prepared from cocoa *(Theobroma cacao)* shell has been studied experimentally using batch adsorption method. Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration and contact time, pH and adsorbent dosage. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to examine the experimental data of different initial concentrations. Kinetics studies indicated that the adsorption followed pseudo -second order reaction. The high correlation coefficient of intraparticle diffusion model proves the pore diffusion plays a significant role for the adsorption of MB onto CSAC. Equilibrium data was analyzed using Langmuir, Freundlich and Tempkin isotherm models. The maximum monolayer adsorption capacity of Cocoa shell activated carbon (CSAC) was found to be 37.03 mg/g by using Langmuir model equation. On the basis of experimental results and the model parameters, it can be inferred that the activated carbon prepared from cocoa shell was effective for the removal of methylene blue from aqueous solution.

Keywords: Cocoa shell, adsorption, kinetics, equilibrium, activated carbon.

1. Introduction
The release of dyes into wastewaters from textile, cosmetic, paper and coloring industries poses serious environmental problems (Aysun, *et al.,* 2009). The coloration of the water by the dyes causes inhibitory effect on photosynthesis affecting aquatic ecosystems. The role of dyes in connection with variety of skin, lung and other respiratory disorders has been reported worldwide (Abd *et al.*, 2010). Color removal from textile effluents is a major environmental problem and the most popular treatment methods are electrocoagulation/electroflocculation (Mounir *et al., 2010*), ultrafilteration (Helene *et al.*, 2003), reverse osmosis (Bastaki, 2004), oxidation (Muthukumar *et al*., 2005) and adsorption (Chen and Zhao, 2009). Among these methods, adsorption using activated carbon is most widely used method 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 (Kadirvelu, *et al.,* 2003). Some agro waste materials studied for their capacity to remove dyes from aqueous solutions are coir pith (Namasivayam and Kavitha, 2002), pine sawdust (Mahmut and Ayhan, 2005), tamarind fruit shell (Somasekhara, 2006), bagasse (Tsai *et al.,* 2001), rice husk (Malik, 2003), orange peel (Ahmed *et al.,* 2009), palm kernel shell (Mak *et al.,*2009), cashew nut shell (Senthil *et al.,* 2010), wall nut shell (Sumanjit *et al*., 2008) etc. The present investigation is an attempt to remove Methylene blue from synthetic wastewater by adsorption process using a low cost activated carbon prepared from cocoa shell agro waste as an adsorbent.

2. Materials and Methods
2.1 Preparation of adsorbent: Cocoa shell collected from local agricultural field was air – dried in sunlight and carbonized with concentrated sulphuric acid in the weight ratio of 1:1(w/v). The resulting product was kept in muffle furnace maintained at 550°C for 7 hr. The carbon obtained was washed with distilled water until it became free from excess acid and dried at 110°C for overnight in a hot air oven. The carbonized material was taken out, grounded to fine powder

and sieved to 150µm size and stored in a vacuum dessicator. *Preparation of dye solution:* Stock solution of Methylene blue (Chemical formula: $C_{16}H_{18}N_3SCl$, M.W.:320, C.I. no. 52015) was prepared by dissolving 1g of dye in 1L of distilled water to give concentration of 1000 mg/L. The serial dilutions say 20, 40, 60 and 80 mg/L were made by diluting the dye stock solution in accurate proportions.

2.2 Batch adsorption experiments:

Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125 rpm at 35°C using 250 mL conical flasks containing 100 mg of CSAC with 50 mL of dye solutions. All the experiments (except the study of pH effect) were carried out at pH of 7.0. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks. The adsorbents were separated from the solution by centrifugation (REMI make) at 2000 rpm for 10 min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at $\lambda_{max} =$ 665 nm spectrophotometrically using Elico make UV-Visible spectrophotometer. The adsorption isotherms were specified at pH 7.0 for adsorption of MB onto CSAC at 35°C. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherm and kinetic equations, respectively.

3. Results and Discussion

3.1 Effect of Agitation Time and Initial Concentration

Figure 1 shows the effect of initial concentration of dye and contact time on adsorption uptake. The experiment was carried with initial concentrations 20, 40, 60 and 80 mg/L of MB solution (50 mL) and agitated with 100 mg of CSAC at 35ºC. The adsorption at different dye concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption. The uptake of MB onto CSAC nearly reaches equilibrium in 120 min. The time beyond no significant change in adsorption takes place has been fixed as equilibrium time (Necip and Asim, 2009). Based on the results, 120 min was fixed as equilibrium time throughout the study. The adsorption capacity at equilibrium increases from 9.48 to 36.08 mg/g with an increase in initial MB concentration from 20 to 80 mg/l.

More than 90% of MB adsorbed with initial concentrations ranging from 20-80mg/L for 2hr equilibrium time. The rate of percent removal and adsorption capacity are higher in beginning due to larger surface area of the adsorbents available for the adsorption of the dye. The percentage removal, however, decreased with increase in initial concentration of the MB dye. This may be attributed to lack of available active sites required for the high initial concentration of the dye. The adsorption sites took up the available solute more quickly at low concentrations.

3.2 Effect of Adsorbent Dosage

Figure 2 shows the effect of adsorbent mass on the adsorption. A series of adsorption experiments was carried out with different adsorbent dosages at initial concentration of 40 mg/L without changing the volume of dye solution (50 mL) with constant speed of 125 rpm for 2 hr. Similarly the pH (7.0) and temperature (35ºC) was kept constant. The results followed that the percentage of adsorption increased with increased adsorbent dosage. The increase in adsorption with increase in carbon dosage was due to increase in surface area or due to conglomeration of carbons at higher doses (Kannan, 1991)
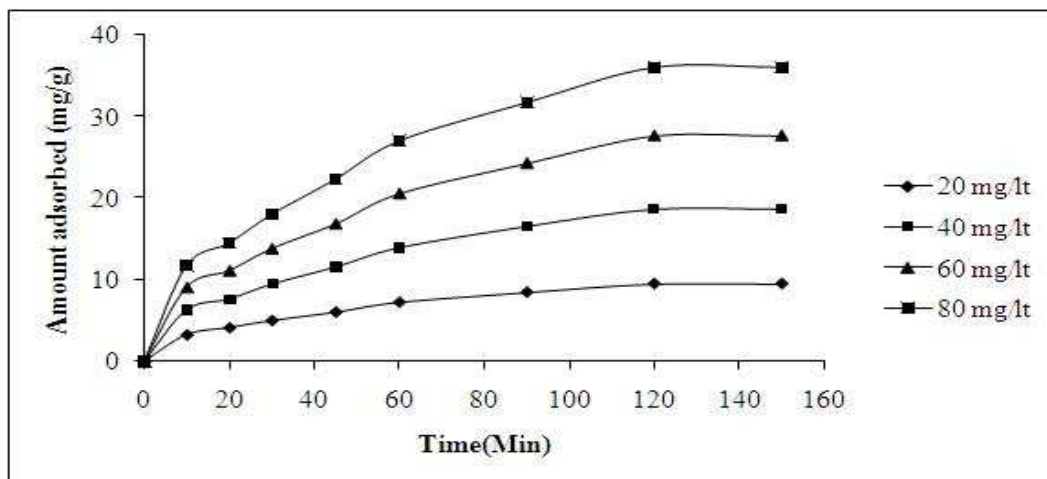

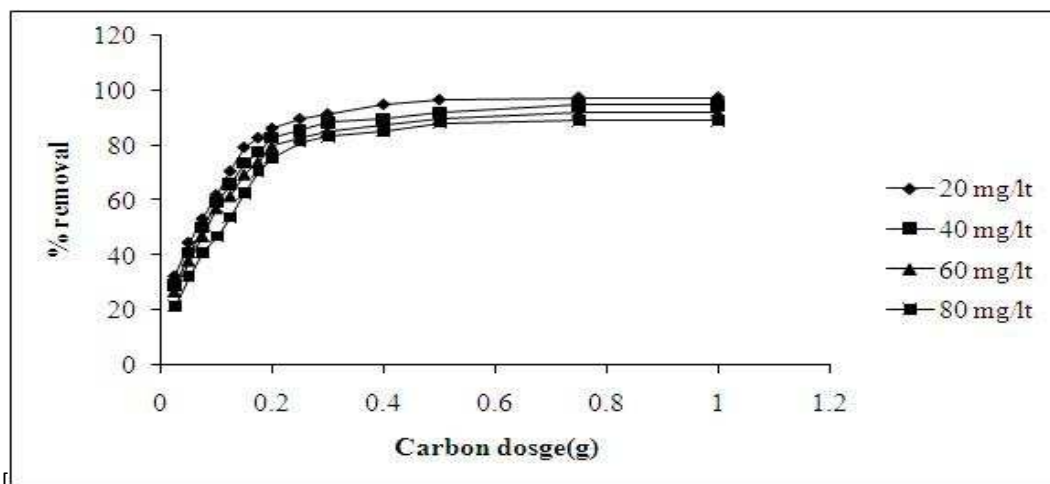**Figure 1: Effect of Agitation Time on Adsorption -Initial Concentration Variation**

Figure 2: Effect of Adsorbent Dose on the Removal of Mb onto CSAC

3.3 Effect of pH

Figure 3 shows the effect of pH on the adsorption of MB onto CSAC. The effect of solution pH was studied between 1 to 11, initial pH controlled by the addition of 0.1M HCl or 0.1M NaOH and agitated with 100 mg of CSAC for 2 hr, at initial MB concentration of 40 mg/L. As shown in figure, the adsorption of MB onto CSAC increased as the pH of the solution increases in acidic medium, and further decrease of pH in basic medium had no effect on the adsorption process. The % removal increased from 46% (at pH = 1) to 86.8% (at pH = 7). Lower adsorption in acidic pH was due to the presence of excess H^+ ions competing with dye cations for the adsorption sites (Ponnusami et al., 2009).

The pH of the solution is an important parameter for controlling the adsorption process. The interaction between adsorbate and adsorbent is affected by the pH of an aqueous medium in two ways: firstly, dyes are complex organic compounds having different aromatic rings and functional groups having different ionization potentials at different pH, resulting in the pH-dependent net charge on dye molecules. Secondly, the surface of adsorbent consists of many functional groups, so the net charge on adsorbent could be measured in the form of zeta potential, is also pH dependent. The influence of the solution pH on the dye uptake could be explained on the basis of pH zero point charge (pH_{zpc}). For amphoteric molecules which contain both positive and negative charges, the net surface charge is influenced by the pH of their surrounding environment. By either losing or gaining protons (H^+) they can become more negatively or more positively charged. At a higher pH the surface of the CSAC particles may get negatively charged, which enhances the positively charged MB dye cations through electrostatic attraction. So, for the further experiments neutral (pH=7) solutions were used for maximum removal.
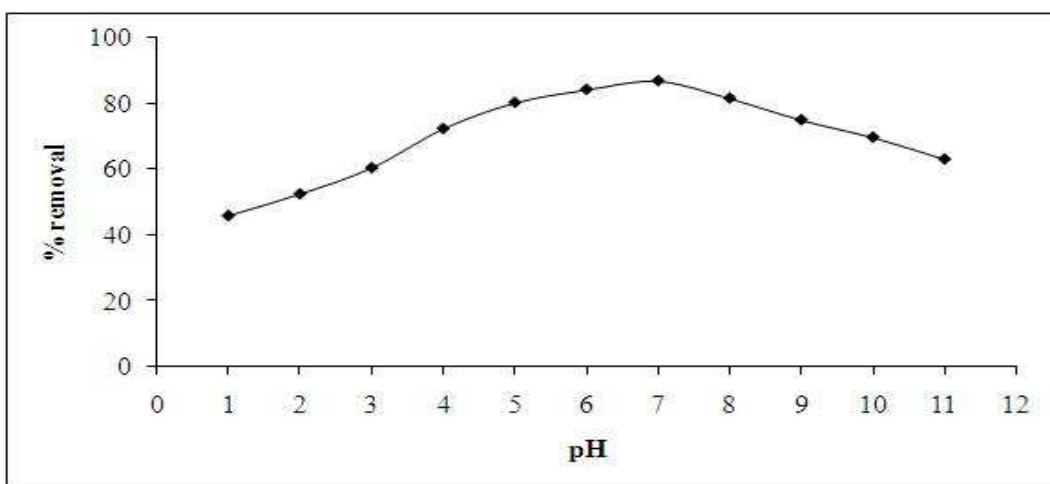

Figure 3: Effect of pH on the Removal of MB onto CSAC

3.4 Adsorption kinetics
3.4.1 Pseudo-first order kinetic model
The linear pseudo-first order equation is as follows (Krishnan *et al.*, 2010):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}). A plot of log (q_e-q_t) versus t gives a linear line (figure 4) from which the values of k_1 and q_e were determined from the slope and intercept respectively and presented in table 1.

3.4.2 Pseudo-second order kinetic model
The linear pseudo-second order equation is as follows (Ho and McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

k_2 is the rate constant of pseudo-second order adsorption (g/mg min). A plot of t/q_t versus t gives a linear relationship (figure 5), from which q_e and k_2 were determined from the slope and intercept of the plot respectively and presented in table 1. For both the systems studied, good correlation coefficients were obtained ($r^2 \approx 1$) by fitting the experimental data to pseudo-second order kinetics than that for the pseudo-first order kinetic model.
Intraparticle diffusion model: The intraparticle diffusion model is expressed as follows (Chen *et al.*, 2010):

$$q_t = k_d t^{1/2} + C \qquad (3)$$

k_d is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), C is the intercept (mg /g).
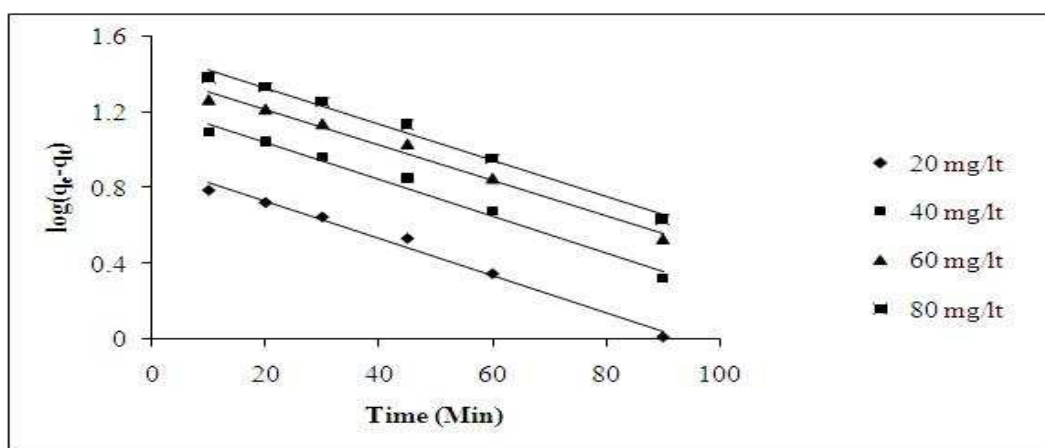

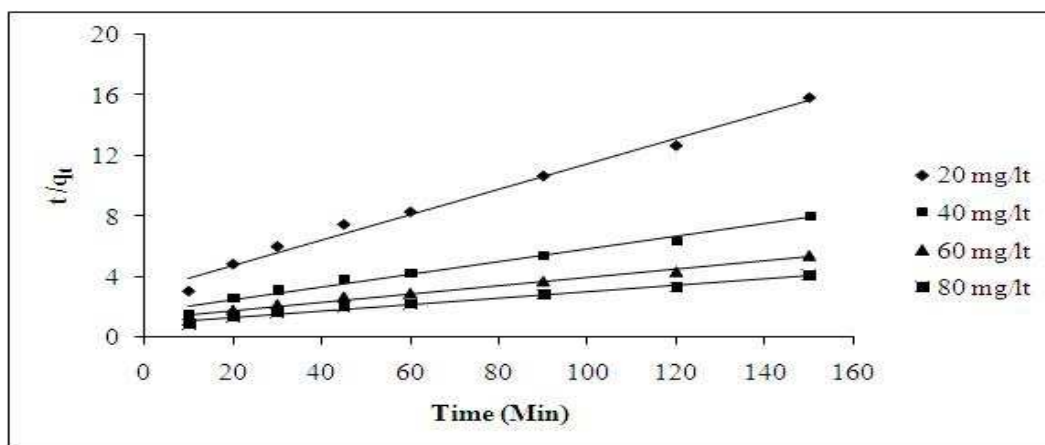**Figure 4: Pseudo- First Order Plot- Initial MB Concentration Variation**

Figure 5: Pseudo-Second Order Plot- Initial MB Concentration Variation

A plot of q_t versus $t^{1/2}$ gives a linear relationship (figure f), from which k_d values determined from the slope was presented in table 1.The intercept of the plot reflects the boundary layer effect. If the regression of the plot is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin, indicates the intraparticle diffusion was not only a rate controlling step. The high correlation coefficient proves the pore diffusion plays a significant role for the adsorption of MB onto CSAC.
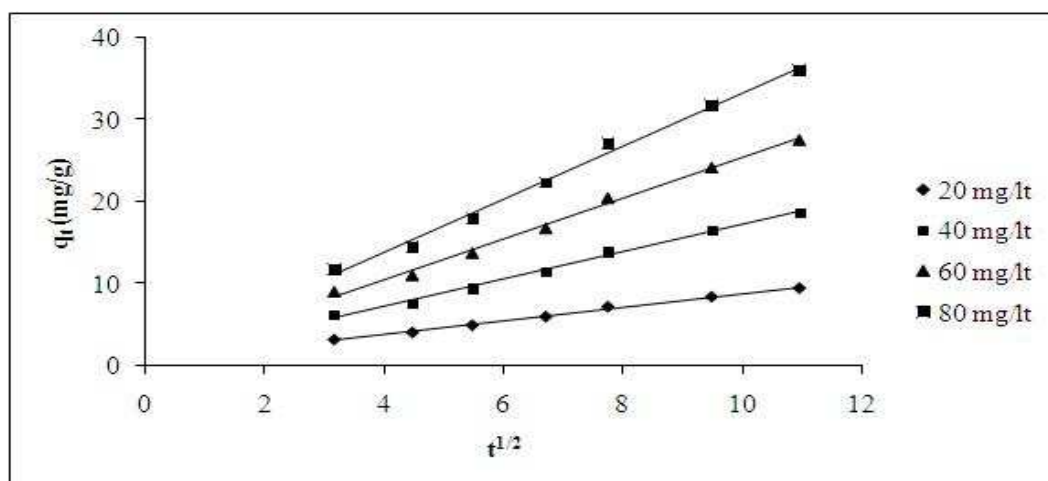
Figure 6: Intraparticle Diffusion Plot for the Removal of MB onto CSAC

Table 1: Results of Kinetic Plots for the Adsorption of MB onto CSAC

Concentration (mg/L)	20	40	60	80
Pseudo-first order				
$k_1 \times 10^{-2} (min^{-1})$	2.07	2.07	2.07	2.07
$q_e cal(mg/g)$	8.51	17.3	25.5	33.4
$q_e exp(mg/g)$	9.48	18.68	27.64	36.08
r^2	0.987	0.982	0.980	0.980
Pseudo-second order				
$k_2 \times 10^{-3}(g/mg\ min)$	2.2	1.0	0.7	0.5
$q_e cal\ (mg/g)$	11.49	23.26	35.71	47.6
r^2	0.987	0.983	0.981	0.983
Intraparticle				
$K_d(mg/\ g\ min)$	0.82	1.66	2.48	3.25
C (mg/g)	0.582	0.620	0.616	0.758
r^2	0.995	0.994	0.994	0.994

The study of adsorption kinetics describes the solute uptake rate and this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of MB adsorption onto CSAC was analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The experimental data and the model predicted values are expressed by the correlation coefficients, r^2. A relative high r^2 value indicates the model successfully describes the kinetics of dye adsorption. Therefore, the adsorption of MB onto CSAC was more favorably by pseudo-second order kinetic model, which was based on the assumption that the rate limiting step may be chemisorptions (Wong *et al.,* 2009)

involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. Weber and Morris (1963) proposed the intra-particle diffusion model to explain the transient behavior of dye adsorption. Accordingly, if a plot of dye uptake versus $t^{1/2}$ is a straight line passing through the origin, then the effect of external film resistance is negligible. On the other hand, if the intercept deviates from the origin, this shows the importance of the external film resistance. In the present study, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only a rate controlling step.

3.5 Adsorption Isotherms

3.5.1 Langmuir isotherm

Linear form of Langmuir model (Langmuir, 1918) is expressed by

$$\frac{C_e}{q_e} = \frac{1}{b}Q_0 = \frac{C_e}{Q_o} \quad (4)$$

where C_e is equilibrium concentration of dye (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), Q_0 and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of C_e/q_e versus C_e was shown in figure 7. The constants Q_0 and b can be calculated from slope and intercept of the plot and the values are tabulated in table 2. The maximum monolayer adsorption capacity of CSAC was found to be 37.03 mg/g. The shape of

the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption. R_L was calculated as follows:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) (or) unfavorable ($R_L > 1$) (Weber and Chakravorthi, 1974). In the present investigation, the R_L values were less than one for MB concentration range studied, which shows the adsorption process was favorable.

Table 2: Results of isotherm plots for the adsorption of RO16 onto CSAC

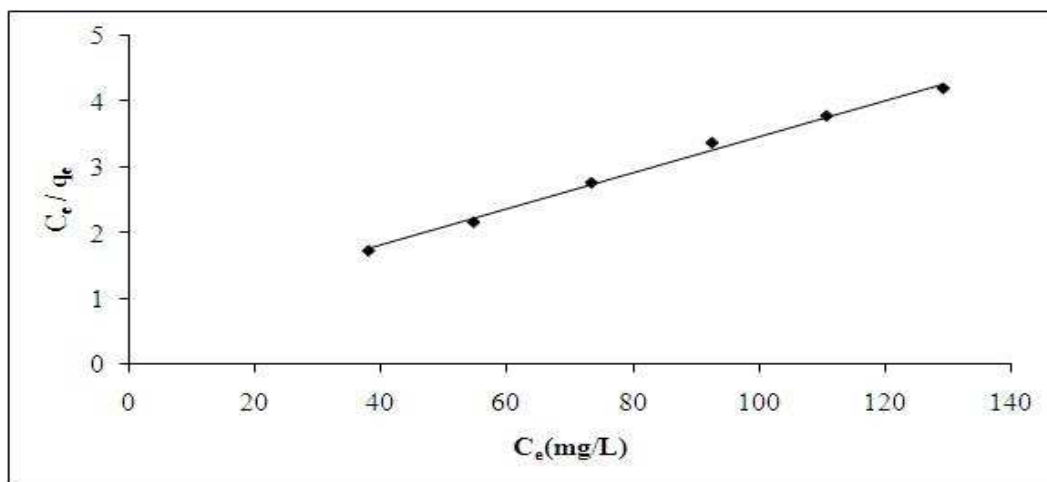| Langmuir				Freundlich			Tempkin		
Q_0(mg/g)	b(L/mg)	R_L	r^2	K_f(mg/g)	1/n	r^2	A(L/mg)	B(J/mol)	r^2
37.03	0.34	0.1416 - 0.3054	0.995	8.66	0.259	0.975	6.77	0.69	0.977

Figure 7: Langmuir Plot for the Removal of MB onto CSAC

3.5.2 Freundlich isotherm

Linear form of Freundlich model (Freundlich, 1906) is expressed by

$$\log C_e = \log k_f + \frac{1}{n}\log C_e \quad (6)$$

where k_f is measure of adsorption capacity (mg/g) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0),

favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$) (Bell, 1998). The linear plot of $\log q_e$ versus $\log C_e$ was shown in figure 8. The values of 1/n and k_f can be calculated from the slope and intercept respectively and the results are given in table 2. From the experimental data the value of 1/n was less than one indicating the favorable adsorption.
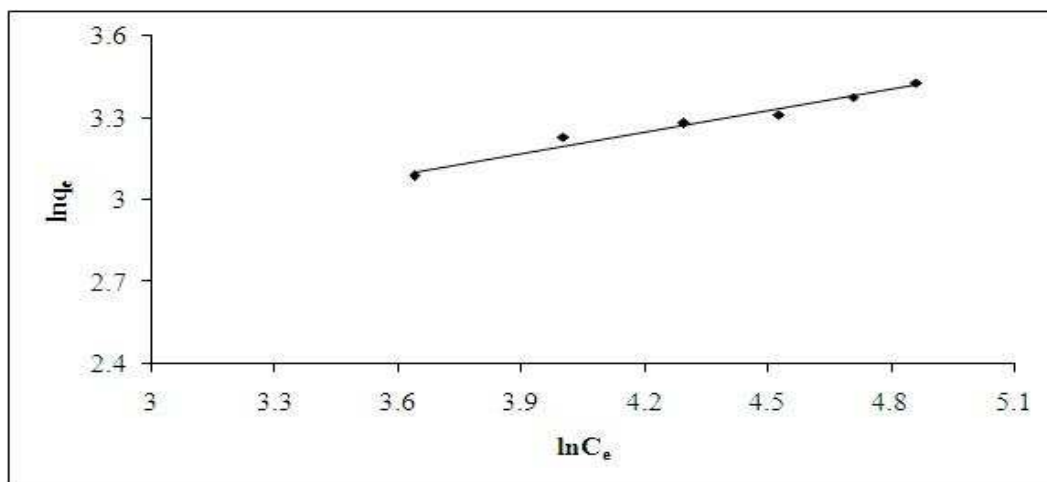
Figure 8: Freundlich Plot for the Removal of MB onto CSAC

Tempkin isotherm: The linear form of Tempkin isotherm (Franca *et al.*, 2009) is expressed as

$$q_e = B \ln A + B \ln C_e \qquad (7)$$

where B is a constant related to the heat of adsorption (J/mol) and A is the Tempkin isotherm constant(L/mg). The constants A and B are calculated from the slope and intercept of q_e versus $\ln C_e$ (figure 9) and parameters are given in the table 2. Based on the correlation coefficient from all the three isotherm models, Langmuir model gave the highest r^2 value showing that the adsorption of MB onto CSAC was best described by this model.
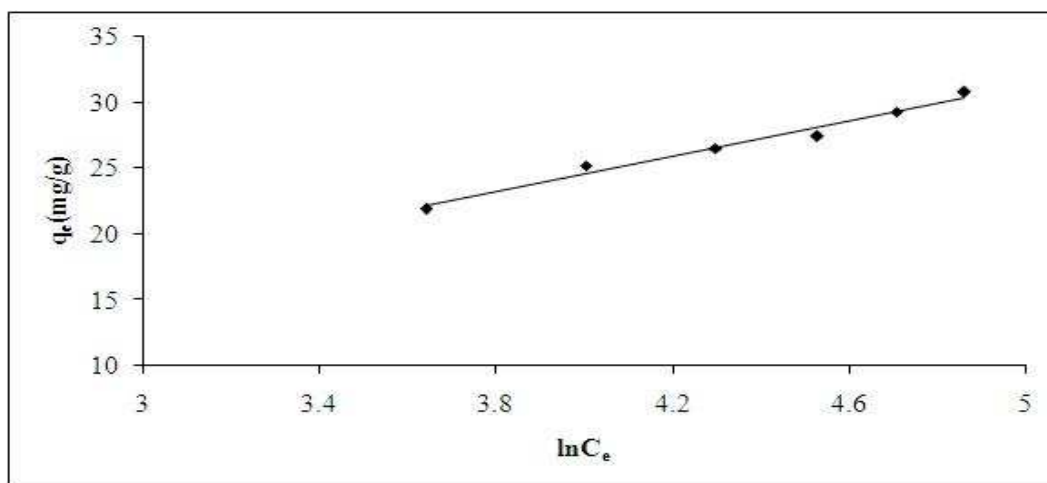

Figure 9: Tempkin Plot for the Removal of MB onto CSAC

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model for the case studied. The Langmuir, Freundlich and Tempkin models were used to describe the data derived from the adsorption of MB by CSAC. The Langmuir model assumes homogenous adsorption and it is used successfully in monomolecular adsorption processes. The Freundlich model assumes the adsorption intensity of the adsorbate on the adsorbent surface. The Tempkin model is based on the assumption that the heat of adsorption would decrease linearly with coverage due to adsorbate –

adsorbent interactions. The applicability of three isotherms was compared by evaluating the correlation coefficients, r^2. The equilibrium data fitted well for the Langmuir model with a correlation coefficient(r^2) of 0.995 while the Freundlich and Tempkin is not suitable to describe the adsorption process with an r^2 of only 0.975 and 0.977, respectively. The higher correlation coefficient for the Langmuir model predicts the coverage of MB may be monolayer and homogenous adsorption (Bulut and Aydin, 2006). Moreover the R_L values were less than one which shows the adsorption process was favorable.

4. Conclusion

In conclusion, activated carbon prepared from cocoa shell has been used successfully as an adsorbing agent for the removal of Methylene blue dye from aqueous solutions. Adsorption experiment carried out as a function of initial dye concentration and contact time, initial pH and dose of adsorbent. The maximum adsorption of MB dye by CSAC occurred at a pH of 7.0. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. The adsorption data was well described with Langmuir isotherm model. It was shown that the adsorption of MB onto CSAC best fitted by pseudo-second order model. An intraparticle diffusion model was used to calculate the intraparticle diffusion coefficients. The adsorption data was properly controlled by both external mass transfer and intraparticle diffusion. The present study indicated that CSAC could be employed as a low cost adsorbent for the removal of MB from aqueous solution.

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