Equilibrium and kinetic studies of Methylene blue onto activated carbon prepared form Crescentia cujete fruit shell

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Abstract: The activated carbon prepared from agricultural waste has been investigated as an alternative to the expensive methods employed in the removal of dye form wastewater. The objective of current study is to explore the potential use of activated carbon prepared from the Thiruvottukai (Crescentia cujete) fruit shell for the removal of methylene blue from aqueous solution. The parameters studied include agitation time, initial dye concentration, carbon dose. The kinetic data were well modeled using pseudo first order and second order with isotherm studies. The adsorption–equilibrium was represented with Langmuir and Freundlich isotherms.
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1. Introduction

Water is an important natural resource for both natural ecosystem and human development. Wastewater from the chemical, textile, pulp and paper, printing, cosmetics, leather and food industries is polluted by dyes. These effluents are discharged to water bodies, causing it to be contaminated (Nazari Moghaddam 2009). Treatment of dye contaminated wastewater is very important because the presences of small amount of dyes are not only aesthetically displeasing but also toxic and even carcinogenic (Enamul Haque 2011). Several physical, Chemical and biological treatments are employed for the removal of dyes from the contaminated water waste. Among the proposed methods, adsorption is a simple, economic and effective separation process for the removal of both organic and inorganic pollutants form wastewater (Yamin Yasin 2007). Methylene blue is one of the most frequently used dyes in industries and presence of this dye in water leads to various health effects like eye burn, and irritation to the gastrointestinal tract and irritation to the skin(Yuh-Shun Ho 2009). Researchers have studied the production of activated carbon form agricultural wastes for the removal of dyes form aqueous solution. The waste materials include Delonix regia pods (Yuh-Shun Ho 2009) jute fiber (Senthil kumar 2005), Cocoa Shell (Theivarasu 2011), Khaya senegalensis fruits (Casmir 2009), olive-waste cakes (Bacaoui 2001), morinda coreia buch-ham bark (Arivoli 2010), Babul Seed(Sujatha 2008). In this study, Thiruvottukai (Crescentia cujete) fruit shell was selected as a raw material to produce the activated carbon. The carbon was prepared through carbonization and activated using concentrated sulphuric acid. The data obtained from kinetic and equilibrium studies were processed to understand the adsorption mechanism of Methylene blue dye molecule onto the activated carbon.

2. Methods and Materials

2.1. Preparation of Adsorbent

The Thiruvottukai (Crescentia cujete) fruit shell was cut into smaller pieces, washed with water and carbonized at 350°C for 2 hours and activated by 2N sulphuric acid at 1:1 ratio (weight of raw material/ volume of acid) for 24 hrs. The activated carbon was repeatedly washed with double distilled water until the pH of the washing solution reached 6-7. The carbon was then dried at 100°C for nearly 2 hours to remove the moisture.

2.2 Methlene Blue

Methylene blue (MB) ($C_{16}H_{18}N_3SCl$) supplied by merck was used as an adsorbate and was not purified further. A stock solution of 1,000 mg/L. Methylene blue was prepared and solutions of desired concentration were prepared by diluting the stock solution using double distilled water. Chemical structure of dye is shown in Appendix A.

2.3 Batch Equilibrium Experiments

Adsorption isotherms were performed using reaction bottles(100ml) where solutions of dye 50ml with different concentrations (50-250 mg/L) were

placed in these bottles. 0.1g of activated carbon was added to dye solution and kept in the shaker at room temperature for $2\frac{1}{2}$ hours to reach equilibrium. Similar procedure was conducted without activated carbon to be used as a blank. The bottles were then removed and the final concentration of dye in the solution was analysed. The amount of adsorption at equilibrium , q_e (mg/g) was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of adsorbent(g).

2.4 Batch Kinetic Studies

The procedure of kinetic experiment comprised triplicate glass bottles containing selected adsorbent (0.1g) and 50mL of adsorbate (100 mg/L) at solution pH. The bottles were kept in the mechanical shaker at constant temperature 30±2°C. The concentrations of the dye in the aqueous samples were measured at preset time intervals. The amount of adsorption q_t(mg/g), at time t, was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where C_0 and C_t are the initial and liquid-phase concentrations of dye at any time t of dye solution (mg/L), respectively. V is the volume of the solution (L), and W is the mass of adsorbent (g).

3. Result and Discussion

3.1 Batch Adsorption Studies

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to Freundlich and Langmuir isotherm models is an important step to find the suitable model that can be used for design purpose (Olugbenga Solomon Bello 2010).

3.1.1 Langmuir Isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place on a homogenous surface, where all sorption sites are identical and energetically equivalent. The linear form of Langmuir model is expressed by the following equation

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + (1/q_m)\, C_e \quad (3)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1}), and q_m and b are the Langmuir constants related to the monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively (Rawle Wayne Webster 2012). The Langmuir constants b and q_m were determined form slop and intercepts of the plot of C_e/q_e against C_e and their values are given in the Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L), is expressed by

$$R_L = \frac{1}{(1 + bC_0)} \quad (4)$$

Where C_0 is the initial solute concentration (mg/L) and b is the Langmuir's adsorption constant. The R_L value lies between 0 and 1 for a favorable adsorption, While the adsorption operation is irreversible if R_L=0. In the present work, the R_L values, has been found to be 0.087, indicating that the adsorption was a favorable process.

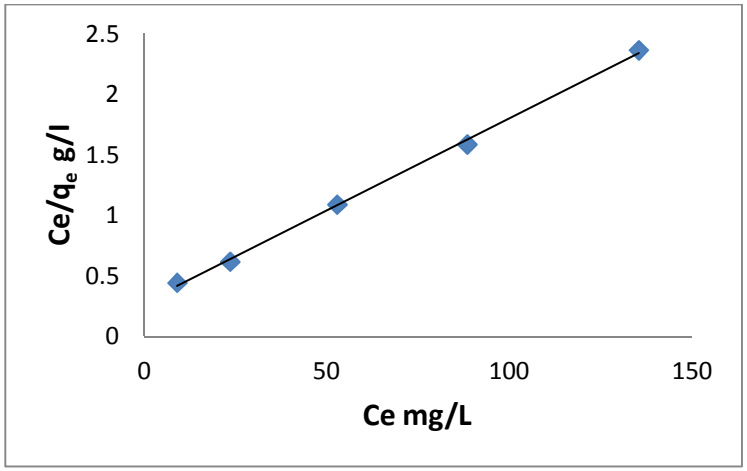


Figure 1: Langmuir isotherm for adsorption of methylene blue onto CCSC

3.2.2 Freundlich Isotherm

The linear from of the Freundlich expression is derived assuming a heterogeneous surface of adsorption capacity and adsorption intensity with a non-uniform distribution of heat of adsorption. The Freundlich equation can be given by:

$$q_e = K_F C_e^{1/n} \quad (6)$$

Rearranging equation 6.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where K_F and 1/n are Freundlich isotherm constant, n related to adsorption capacity. A plot of log q_e vs log C_e yields a straight line, with a slope of 1/n and intercept of ln K_F(Nasuha 2011). The values of K_F and n given in the Table 1.

Table 1 Langmuir and Freundlich isotherm constants for methylene blue adsorption

Langmuir				Freundlich		
q_m mg/L	b (L/mg)	R_L	R^2	K_F	1/n	R^2
66.6666	0.05415	0.0687	0.998	10.0	0.378	0.925

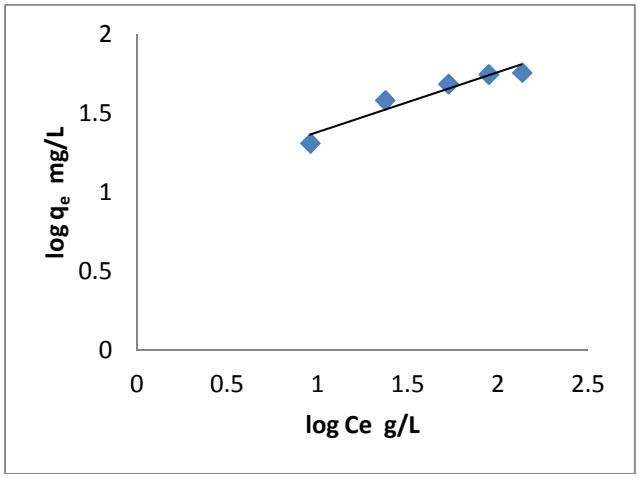


Figure 2: Freundlich isotherm for adsorption of Methylene blue onto CCSC

3.3 Adsorption Kinetics

The adsorption kinetic data of methylene blue are analyzed using two kinetics models, pseudo-first-order and pseudo-second-order. The best model is selected based on the linear regression correlation coefficient, R^2, values.

3.3.1 Pseudo-First Order Model

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation. The non linear form of the equation is expressed as follows (Okoye 2010):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

Integrating Eq. (8) and applying the initial conditions qt =0 at t=0, we obtain:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

Where k_1 is the adsorption rate constant (min^{-1}) for the first order adsorption, q_e and qt are the adsorption capacity at equilibrium and at time t, respectively(mg/g).

A plot of log ($q_e - q_t$) versus t should give a straight line. k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

Table 2 Kinetic model values for adsorption of methylene blue

Initial concentration (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-First order model			Pseudo-Second order model		
		k_1 min^{-1}	$q_{e,cal}$ (mg/g)	R^2	k_2 min^{-1}	$q_{e,cal}$ (mg/g)	R^2
100	36.4258	2.99 x 10^{-2}	29.107	0.954	1.374 x10^{-3}	41.666	0.993

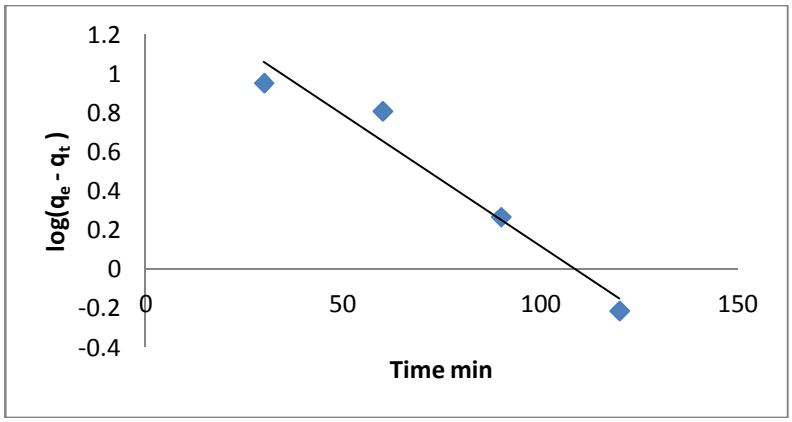


Figure 3: Pseudo–first-order model for adsorption of Methylene blue onto CCSC

3.3.2 Pseudo-Second Order Model

The pseudo-second-order adsorption kinetic rate equation is expressed as follows(Ho 2000):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

Where, K_2 is the rate constant of pseudo second order adsorption **(mg/g/min)**.

Integrating Eq. (10) and applying the boundary conditions t=0 to t=t and qt=0 to qt=qt, we obtain:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 \qquad (11)$$

Eq. 11 can be rearranged to obtain Eq. 12 which has a linear form.

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \qquad (12)$$

A plot of t/q_t versus t should give a straight line, if this model is obeyed by the sorption process. From the slope and intercept of the plots, q_e and k_2 are determined, respectively.

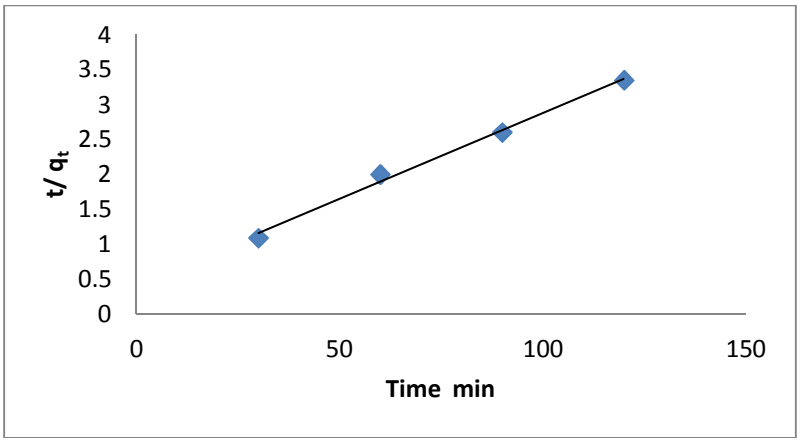
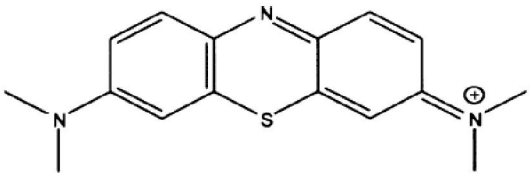


Figure 3: Pseudo – Second order model for adsorption of methylene blue onto CCSC

Conclution:

The present investigation showed that the activated carbon prepared form Thiruvottukai (Crescentia cujete) fruit shell can be used as an adsorbent for the removal of methylene blue from aqueous solution. Adsorption behavior of methylene blue onto CCSC is described by a mono layer Langmuir type isotherm. Langmuir constant confirms that adsorption process was favorable. The kinetic data obtained is described by Pseudo-Second order model.

Appendix A: Chemical Structure of methylene blue



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