



Modelling of Methylene Blue Adsorption via Activated Carbon Derived from Indigenous Agricultural Solid Waste

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ABSTRACT

Conversion of indigenous agricultural solid waste into high quality activated carbon was a multi-fold strategy to counteract two major environmental problems; pollutant agricultural solid waste open burning and a partial solution for high-cost coloured industry effluents treatment, particularly in textiles and food processing plants by offering low-cost activated carbon. In this study, coconut shells were physiochemically treated at high temperature (850°C) in the presence of potassium hydroxide (KOH) with 1:1 impregnation weight ratio and carbon dioxide (CO₂) which acted as an oxidizing gas during activation stage. In order to evaluate the adsorption performance of prepared activated carbon (CS850A), a series of batch adsorption experiments were conducted at controlled parameters with initial concentrations of methylene blue ranging from 100 - 500 mg l⁻¹, temperature 30 ± 0.5°C, adsorbent loading 2.0 g and agitation speed of 100 RPM. It was found that the methylene blue adsorption on coconut shell-based activated carbon conformed to the Langmuir isotherm. The kinetic studies were well characterized by pseudo second order kinetic model. A suggestion has been made that the adsorption was favourable and was driven by a combination of physical and chemical adsorption forces. The monolayer adsorption capacity, Q₀ was found to be 222.0 mg g⁻¹.

Keywords: Activated carbon, methylene blue, batch adsorption, Langmuir, Freundlich

NOMENCLATURE

C_0	Initial adsorbate concentration	(mg l ⁻¹)
C_e	Equilibrium adsorbate concentration	(mg l ⁻¹)
C_t	Adsorbate concentration at time t	(mg l ⁻¹)
k_1	Rate constant of pseudo-first-order adsorption	(h ⁻¹)
k_2	Rate constant of pseudo-second-order adsorption	(g (h.mg) ⁻¹)
K_L	Langmuir isotherm constant	(l g ⁻¹)
a_L	Langmuir isotherm constant	(l mg ⁻¹)
K_F	Freundlich isotherm constant	((mg g ⁻¹) (l mg ⁻¹) ^{1/n})
$1/n$	Heterogeneity factor, dimensionless	
q_e	Amount of adsorbate adsorbed at equilibrium	(mg g ⁻¹)
q_t	Amount of adsorbate adsorbed at time t	(mg g ⁻¹)
R_L	Langmuir separation factor, dimensionless	
Q_0	Maximum adsorption capacity at monolayer	(mg g ⁻¹)
V	Volume of solution	(l)
w	Mass of adsorbent	(g)

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INTRODUCTION

Dyes have been regarded as major water pollutants since ages ago. Nowadays, dyes are widely used in textiles, food, rubber, paper, plastic and cosmetics industries (Lorenc-Grabowska and Gryglewicz, 2007). The presence of dyes in fresh water streams, even at low concentration can be easily detected through colour changes. Pollutant dyes discharged into fresh water stream may create unpleasant surroundings and decrease the esthetical value of the affected area. Besides, dyes can be very harmful to some aquatic life and reduce the light penetration into water thus affecting the photosynthesis capability of submerged green plants (Pearce *et al.*, 2003). In particular, methylene blue causes eye burns, inhalation difficulties, nausea, vomiting and methemoglobinemia (Ghosh and Bhattacharyya, 2002; Avom *et al.*, 1997). Therefore, the treatment of effluent containing such dye is necessary.

Adsorption techniques using activated carbon as adsorbent is the most popular approach to treat wastewater. The adsorption process is effective, cheap and flexible which makes it feasible in many wastewater treatment applications. Activated carbon is preferable due to its large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards (Ucer *et al.*, 2006). Most commercial activated carbons are produced from various types of coals; non-renewable material with limited source. In addition, the price of activated carbon has been increasing due to overwhelming demand. So, it is reasonable to seek a new activated carbon starting material which is cheap, renewable and a guaranteed steady supply throughout the year. The use of agricultural solid waste such coconut shell is rising in this context. Coconut trees are widely planted across Malaysia's coastal line for its oil, coconut milk and copra. It is estimated that 142,000 hectares of land was planted with coconut in 2006 (Agrolink, 2006). This huge planted area has resulted in higher harvest which apparently generates millions of tonnes of agricultural solid waste consistently. Typically, the shell is used as burning fuel or just being left to rot gradually. Coconut shell is very suitable to be converted into activated carbon due to its hardness and abrasion resistance. Further, the chemical composition of coconut shell is akin to hard wood which mainly composes of lignin and cellulose (Rodriguez and Pinto, 2007).

This research investigated the adsorption properties of activated carbon prepared from coconut shell by using methylene blue as a model solute. Consequently, this paper reports adsorption equilibriums and isotherms, and kinetic modeling studies of the particular batch adsorption system.

MATERIALS AND METHODS

Preparation of Activated Carbon

The coconut shell used in this research was collected from local wet markets within the Kerian district in the state of Perak, Malaysia. As received, the material was washed, sun dried, and crushed to particle size of 1-2 mm. The shell was then carbonized at 700 °C under the influence of nitrogen flow ($150 \text{ cm}^3 \text{ min}^{-1}$) for 1 hour. An accurate weight of produced char then was impregnated with equivalent weight of potassium hydroxide at impregnation ratio of 1:1. The mixture was dehydrated in a drying oven at 110 °C overnight. The dried solid mixture was placed in a stainless steel vertical tubular reactor and pyrolysed in a vertical tube furnace under high purity nitrogen (99.995%) with flow

rate of $150 \text{ cm}^3 \text{ min}^{-1}$ till it reached the desired temperature of 850°C . The gas was subsequently switched to carbon dioxide and the activation was continued for 2 hours. The activated char was then cooled to room temperature under nitrogen influence and washed a few times with hot deionized water and hydrochloric acid (0.01 M) to unclog the pores from tar and other chemical residues. The washed activated carbon, named CS850A was finally dried and kept in air tight closed containers. Table 1 presents the physical properties of the prepared activated carbon from coconut shell.

TABLE 1
Surface area and pore volume properties of CS850A

Properties	
Total surface area ($\text{m}^2 \text{ g}^{-1}$)	1026.0
Micropore area ($\text{m}^2 \text{ g}^{-1}$)	943.2
Mesopore area ($\text{m}^2 \text{ g}^{-1}$)	82.5
Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.5768
Average pore diameter (nm)	2.249

Batch Adsorption Modelling

The stock solution of methylene blue was prepared by diluting 1 gram of the respective adsorbate with 1000 ml deionized water in a volumetric flask. The stock solution then was diluted to the desired initial concentrations ranging from 100–500 mg l^{-1} . An amount of 0.2 gram adsorbent was added into 250 ml conical flasks filled with 200 ml of adsorbates solution of known initial concentrations. The conical flasks were then covered with glass stoppers and placed inside the water bath shaker at room temperature, $30 \pm 1^\circ\text{C}$ and shaking speed of 125 rpm for 48 hours. The solution pH was adjusted by adding either a few drops of hydrochloric acid or sodium hydroxide (0.01 M). The samples were then withdrawn at appropriate time intervals using a glass syringe to determine the residual concentration of the adsorbate. The concentration of methylene blue in the aqueous solution was determined using a double beam UV spectrophotometer (Shidmadzu UV-1601, Japan) at wavelength 668 nm.

The amount of adsorbate adsorbed at time, q_t (mg g^{-1}) and at equilibrium condition, q_e (mg g^{-1}) was calculated according to the following equations:

$$q_t = \frac{V(C_0 - C_t)}{w} \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{w} z \quad (2)$$

where C_0 and C_e are initial and equilibrium adsorbate concentrations (mg l^{-1}), respectively. C_t is adsorbate concentration at time (mg l^{-1}). V is volume of solution (l) and W is mass of adsorbent (g).

RESULTS AND DISCUSSION

Equilibrium

Dye removal depends highly on concentration. The methylene blue uptake increased with increasing methylene blue initial concentrations. The trend is clearly elucidated in *Fig. 1*. This is due to a high driving force for mass transfer resulting from changes in concentration gradient within the solid-liquid bulk phase of the particular adsorption system. The equilibrium time was recorded after 5 hours for all ranges of initial concentrations. A steep slope in the first 3 hours indicates a rapid adsorption process. After a time lapse, the adsorption process got slower; the slope becomes less steep and eventually forming a plateau line; which is evidence that the whole adsorption system has achieved equilibrium state. The adsorption capacity at equilibrium increases from 99.38 to 227.0 mg g⁻¹ with an increase in initial dye concentration from 100 – 500 mg l⁻¹. It is evident that the activated carbon prepared from coconut shell is efficient at adsorbing methylene blue dye from aqueous solution. The adsorption of methylene blue dye may follow four sequential steps. First, the migration of dye from bulk solution to the surface of activated carbon. Second, the diffusion of dye through the boundary layer to the surface of activated carbon. Third, the attachment of dye on the active site at activated carbon surface and finally, the intra-particle diffusion of dye into the interior pores of activated carbon matrix (Kannan and Sundaram, 2001).

Isotherms

The adsorption isotherms depict the distribution of solute molecule between liquid-solid phases at equilibrium. *Fig. 2* shows the adsorption isotherm of methylene blue on coconut shell-based activated carbon, CS850A. The isotherm was a typical L-type in which describes a favourable adsorption process. The L or Langmuir isotherm shape means no strong competition between the solvent (water) and the adsorbate (methylene blue) to occupy the adsorbent sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface (Giles *et al.*, 1960).

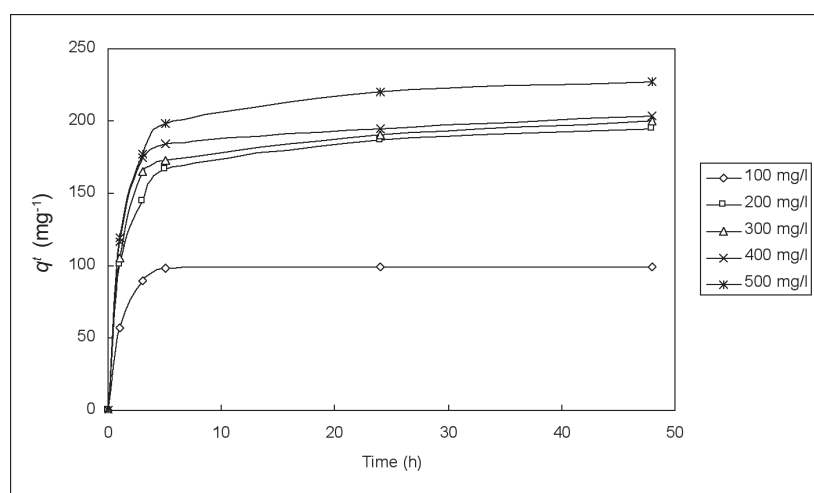


Fig. 1: Adsorption profiles of methylene blue-CS850A batch adsorption system

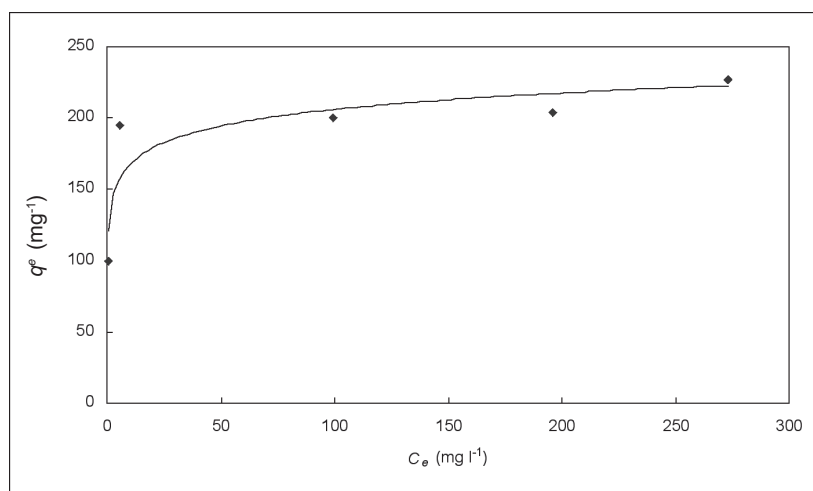


Fig. 2: Adsorption isotherm of methylene blue by CS850A

The analysis of the isotherm data by fitting them to different isotherm models is a crucial step to find the suitable model that can be used for design purpose (El-Guendi, 1991). Langmuir isotherm assumes monolayer formation of solute on the adsorption sites with homogenous energy distribution whereas; Freundlich isotherm assumes heterogenous energy distribution. Equations 3 and 4 represent Langmuir and Freundlich isotherm model, accordingly.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where q_e is amount of adsorbate adsorbed at equilibrium (mg g^{-1}), C_e is equilibrium concentration of the adsorbate (mg l^{-1}). K_L and a_L are Langmuir isotherm constants (l g^{-1}) and (l mg^{-1}), respectively. For Langmuir, plots of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the Langmuir constant related to maximum adsorption capacity at monolayer, Q_0 (mg g^{-1}). As for Freundlich, a plot of $\log q_e$ versus $\log C_e$ enables the determination of constant K_F and exponent $1/n$. K_F is Freundlich constant, ($\text{mg g}^{-1})(\text{mg l}^{-1})^{1/n}$ and $1/n$ is dimensionless heterogeneity factor. The Langmuir separation factor, R_L is defined as Equation 5.

$$R_L = \frac{1}{(1 + a_L C_0)} \quad (5)$$

where C_0 is the maximum initial concentration (mg l^{-1}). The adsorption is favourable if the value of R_L lies within 0 to 1.

Figs. 3 and 4 illustrate the methylene blue adsorption isotherm plots of Langmuir and Freundlich, respectively. The coefficient values for both Langmuir and Freundlich isotherm models are shown in Table 2. The linear correlation coefficient, R^2 for Langmuir and Freundlich were 0.994 and 0.762, respectively. Hence, it is evident that methylene blue adsorption onto coconut shell-based activated carbon used in this study is well-fitted to Langmuir isotherm model. Therefore, it can be concluded that the methylene blue adsorption was characterized by monolayer surface coverage. The monolayer adsorption capacity, Q_o was found to be 221.96 mg g⁻¹; an encouraging finding. High surface area of CS850A activated carbon (1026.0 m² g⁻¹) provides ample adsorption sites for dye molecule to attach on it; thus maximizing the uptakes. The average pore diameter (2.249 nm) is slightly larger than size of methylene blue dye molecule (≈ 1.5 nm), which simplifies the molecule to traverse beyond the internal pores. The adsorption process was favourable in nature as indicated by the R_L value.

Kinetics

Linear forms of pseudo-first and pseudo-second order kinetic equations are given in Equations 6 and 7, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where q_t is the amount of solute adsorbed per unit weight (mg g⁻¹) of adsorbent per time, k_1 is rate constant of pseudo-first order sorption (h⁻¹) and k_2 is rate constant of pseudo-second order sorption (g (h mg)⁻¹). Linear plots of pseudo-first and second order kinetic model for methylene blue adsorption onto CS850A are given in Figs. 5 and 6, respectively. The applicability of the models is verified through the sum of error squares (SSE). The mathematical equation of SSE is given in Equation 8.

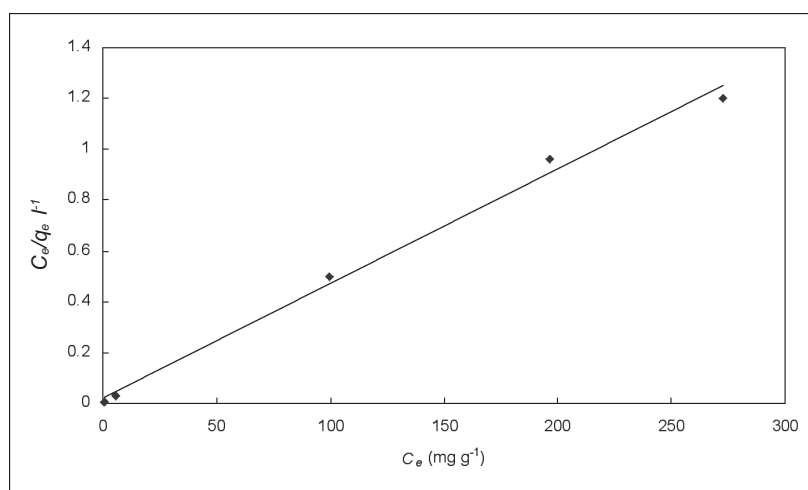


Fig. 3: Langmuir adsorption isotherm of methylene blue onto CS850 at 30°C

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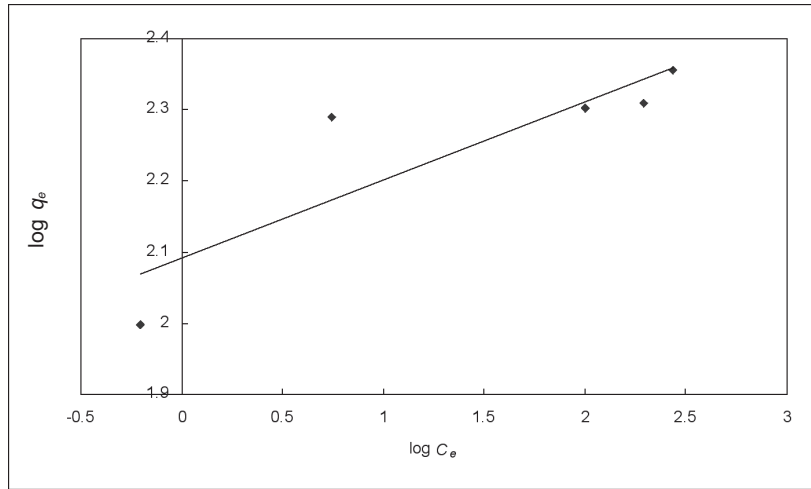


Fig. 4: Freundlich adsorption isotherm of methylene blue onto CS850 at 30°C

TABLE 2
Langmuir and Freundlich coefficients for methylene blue-CS850A batch adsorption system

Adsorbent	Langmuir isotherm parameters				Freundlich isotherm parameters			
	Q_0 (mg g ⁻¹)	K_L (l g ⁻¹)	a_L (l mg ⁻¹)	R_L	R_2	K_F (mg g ⁻¹)(l mg ⁻¹) ^{1/n}	n	R_2
CS850A	221.96	49.505	0.223	0.009	0.994	123.34	9.107	0.762

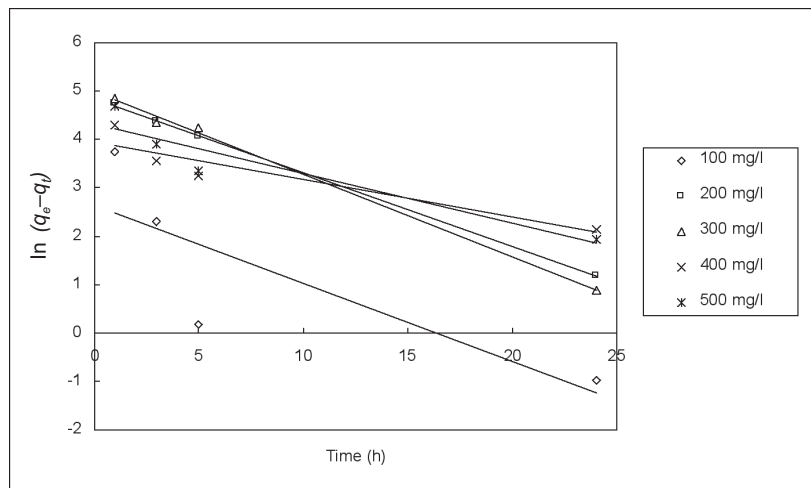


Fig. 5: Plots of Pseudo-first order kinetic model of methylene blue adsorption onto CS850A

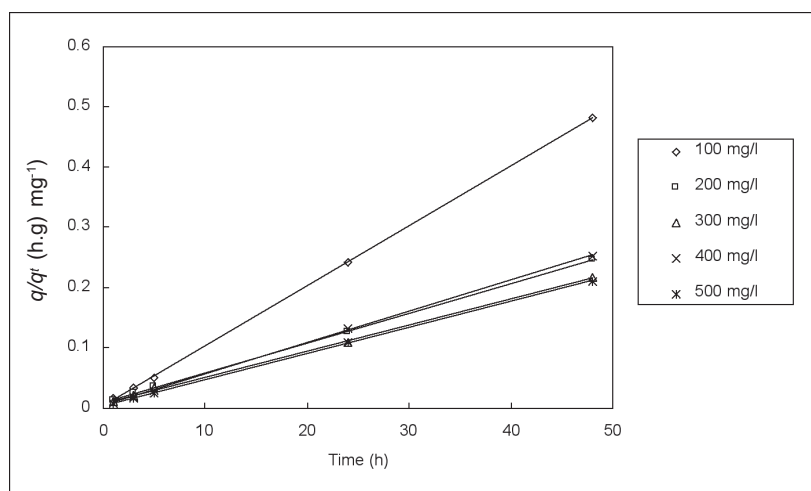


Fig. 6: Plots of Pseudo-second order kinetic model of methylene blue adsorption onto CS850A

$$SSE, \% = \sqrt{\frac{\sum (q_{e,exp} - q_{e,calc})^2}{N}} \quad (8)$$

where N is number of data points, $q_{e,exp}$ is amount of adsorbate adsorbed at equilibrium obtained from experiment (mg g^{-1}) and $q_{e,calc}$ is amount of adsorbate adsorbed at equilibrium obtained from the models (mg g^{-1}).

Figs. 5 and 6 elucidate the plots of pseudo- first and pseudo-second order kinetic models for methylene blue adsorption onto CS850A, respectively. It is a proof that the methylene blue adsorption onto CS850A is well-agreed to pseudo-second order kinetic model; indicating chemical reaction as a rate controlling parameter. The R^2 values are near unity. The model applicability was validated by small SSE values ($< 5.6\%$) throughout various ranges of initial dye concentration. The coefficient values for both kinetic models are given in Tables 3 and 4, accordingly. No strong agreement was shown by the pseudo-first order kinetic model due to poor R^2 values and higher SSE values.

TABLE 3
Pseudo-first order kinetic constants for methylene blue-CS850A
batch adsorption system

Concentration (mg l^{-1})	k_1 (h^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	SSE (%)
100	0.163	14.9	0.6691	42.24
200	0.154	128.3	0.9996	33.10
300	0.171	145.4	0.9972	37.99
400	0.078	52.4	0.8696	68.78
500	0.102	75.2	0.8902	75.92

TABLE 4
Pseudo-second order kinetic constants for methylene blue-CS850A batch adsorption system

Concentration (mg l ⁻¹)	k ₂ (g (h.mg) ⁻¹)	q _{e,cal} (mg g ⁻¹)	R ²	SSE (%)
100	2.439	100.0	0.9999	0.31
200	0.500	200.0	0.9995	2.70
300	0.551	232.6	0.9994	5.58
400	1.182	192.3	0.9997	1.15
500	1.049	232.6	0.9999	2.78

CONCLUSIONS

Coconut shell based-activated carbon can be effectively used as a high performance adsorbent for removal of methylene blue dye from aqueous solution. The adsorption isotherm is well-fitted to Langmuir isotherm indicating the formation of monolayer solute coverage on the adsorbent surface. A conformation to pseudo-second order kinetic model signifies chemical reaction as a rate controlling parameter. It is suggested that the adsorption was favourable in nature and was driven by a combination of physical and chemical adsorption forces. The monolayer adsorption capacity, Q , (221.96 mg g⁻¹) is encouraging.

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