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Equilibrium isotherms and kinetic studies for the adsorption of Methylene blue onto biochar from *Parkia Speciosa Pod*

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Abstract: The ability of *Parkia Speciosa* pod (PSP) or commonly known as petai pod based biochar as bioadsorbent was investigated in order to utilise the waste generated. Methylene Blue (MB) dye was used as adsorbate and the adsorption was carried out in a batch system. The influence of various initial dye concentrations on the adsorption capacity was evaluated. Adsorption equilibrium data was best described by Langmuir isotherm model with R^2 of 0.997 and q_{max} of 1.175 mg/g. Overall, biosorption kinetics was found to fit well the pseudo- first order model. The maximum removal percentage of 99.06% was achieved at 25mg/L of initial concentration.

1. Introduction

In the last decade, wastewater treatment has been extensively studied due to harmful consequences as a result of illegal discharging of industrial effluents into water bodies. Synthetic pigments and dyes are widely used in many industries such as pulp and paper, food, cosmetics, textile and etc. Studies show that textile industries release more than 1 million kg of dyes into water bodies annually [1]. As non-biodegradable compounds, dyes are creating serious issues once discharged into water. These dyes are also known for their toxicogenic, mutagenic and carcinogenic effects. Thus, many chemical, physical and biological techniques are being studied in order to treat the water bodies which are dye contaminated. In the case, adsorption using carbon rich materials such as activated carbon and biochar is a well-known physical treatment to treat wastewater. High production costs of activated carbon lead to the development of biochar production which are cost effective and environmental friendly. Biomass and wastes such as corn cob, coconut husk, banana peels and etc are used for the production of biochar. Biochar or can be described as solid carbonaceous material is produced through carbonisation of biomass under limited oxygen. Biochar has high adsorption capacity due to the abundant functional active sites and surface pores [2]. Therefore, this study focused on utilisation of *Parkia Speciosa* pod (PSP) or commonly known as ‘petai’ pod for biochar production. Based on literature, PSP widely used in development of activated carbon and there are limited report on utilisation of PSP based biochar as pollutant removal [3 , 4]. Furthermore, PSP are considered as waste and lead to waste disposal problems in Malaysia as the country is one of the biggest producer of *Parkia Speciosa* [5]. Thus, this research is conducted in order to study the adsorption performance of PSP biochar in batch system on removal of a basic dye, Methylene Blue (MB). Furthermore, the study investigates equilibrium and kinetics of MB adsorption in a batch system.

2. Methods



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2.1. Preparation of PSP biochar

PSP are collected from restaurants located at Gurun, Kedah. PSP are washed with distilled water to remove the dirt on the surfaces. Then, PSP sample was cut into small pieces and sundried to eliminate the moisture content, followed by oven dried for 24 hour at 100 °C to completely dry. Then, the sample was grinded into powder and sieved to obtain desired particle size of 75 – 125 µm. The powder PSP was placed in crucibles and carbonised at 800°C with retention time of 2 hour at 10°C/min.

2.2. Preparation of stock solution of MB

The stock solution of MB at concentration of 1000 mg/L was prepared by dissolving 0.5 g of MB dye powder in 500 mL of distilled water. The concentration of the dye was determined at 660 nm [6]. In order to prepare desired initial concentrations the dye was diluted.

2.3. Batch experiment study

Batch adsorption was set up to investigate adsorption performance of MB at different initial concentrations (25 mg/L, 50 mg/L, 100mg/L and 150 mg/L) in term of equilibrium isotherm, kinetics and the removal efficiency onto PSP biochar. Based on preliminary studies, 1.0 g of biochar is used. 50 mL of dye at desired initial concentration was placed in contact with 1.0 g of biochar in a conical flask. The mixture was stirred for several minutes using glass rod. Absorbance reading of the dye concentration was taken for every 5 minutes and the total of 50 minutes was set as duration required to reach optimum removal. Adsorption capacity or adsorbed amount of dye can be calculated using following equation [7]:

$$q_e = \frac{V}{m} (C_o - C_t) \quad (1)$$

Where C_o represents the initial concentration of dye, C_t is the concentration of dye at time (mg/L), m indicates adsorbent mass (g) and V is the solution volume (L). The percentage of dye removal was calculated using following equation [8]:

$$\text{Percentage removal} = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

Where C_o represents the initial concentration of dye (mg/L) and C_t is the concentration of dye at time (mg/L).

2.4. Equilibrium isotherm and kinetics of MB adsorption onto PSP biochar

2.4.1. Equilibrium isotherm models. The MB adsorptions on PSP biochar at different initial concentrations were analysed using Langmuir and Freundlich equations. A Langmuir model assumes a monolayer sorption of dye molecules from aqueous medium. The Langmuir equation is given by Equation (3):

$$q_e = \frac{q_{max} K_c C_e}{1 + K_c C_e} \quad (3)$$

where q_{max} is the maximum specific uptake of dye molecules (mgL^{-1}), K_c is equilibrium constant (Lmg^{-1}). The parameters can be determined from a linearized form of Equation (4) [9]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_c} + \frac{C_e}{q_{max}} \quad (4)$$

where C_e is the equilibrium concentration (mgL^{-1}), q_e is the amount of dye molecules uptake at equilibrium (mgg^{-1}). The Freundlich model is based on sorption on a heterogeneous surface. Freundlich isotherm model is represented as Equation (5):

$$q_e = K_f C_e^n \quad (5)$$

The equation may be linearised and represented by Equation. (6) [9]:

$$\text{Log} q_e = \frac{1}{n} \text{Log} C_e + \text{Log} K_f \quad (6)$$

where q_e is the amount of dye molecules uptake (mgg^{-1}) at equilibrium, C_e is the equilibrium concentration (mgL^{-1}), K_f and n are the Freundlich constants indicative of adsorption capacity and adsorption intensity, respectively.

2.4.2. Kinetic modeling. Pseudo-first order model (Equation (7)) is used to examine the controlling mechanism involved in the biosorption of MB dye molecules onto PSP biochar such as mass transfer and chemical reactions [10].

$$\frac{dC}{dt} = k_1 (C_e - C_t) \quad (7)$$

In order to predict the parameter based on the experimental results, Equation (7) is integrated and derived into nonlinear form shown as an Equation (8):

$$q_t = q_e - \exp(-k_1 t)(q_e - q_o) \quad (8)$$

where k_1 is the adsorption rate constant, q_e and q_t are the amounts of adsorbed (mg/g) at equilibrium and at time (t), respectively.

2.4.3. Coefficient of correlation (R^2) determination and error analysis. The validity of each model was determined based on coefficient of correlation (R^2) and sum-of-squared errors (SSE). R^2 represent the degree of variability of dependent variable which is explained by all independent variables. Basically, it ranges from 0 to 1 and the values of R^2 which close to 1 shows a perfect fit. Meanwhile lower SSE indicates better fit to the respective model. Equation 9 is used for calculate SSE(%) [11,12]:

$$\text{SSE} (\%) = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} \quad (9)$$

where $q_{e,exp}$ and $q_{e,cal}$ are the values of the measured q_e and predicted q_e by the intended model respectively. N is the number of $q_{e,exp}$

3. Results and discussion

3.1. Adsorption equilibrium isotherms

Figure 1(a) and (b) show the fitting results of experimental data at different initial concentrations (25, 50, 100 and 150 mg/L) using Langmuir and Freundlich models respectively. The results showed that Langmuir isotherms was in good agreement with the experimental data compared than Freundlich model which gave R^2 value of 0.997 and 0.014, respectively. The parameters value obtained from the fitting of the adsorption equilibrium isotherms models is represented in Table 1. Based on Table 1, the negative value of the Langmuir constant (K_c) indicates the inadequacy of the model to explain the

adsorption process, since this constant is indicative of the surface binding energy [13]. The q_{\max} (mg/g) of langmuir model indicates adsorption capacity which is around 1.175 mg/g. Similar finding where the adsorption follows Langmuir isotherm was reported by [14] in the study of adsorption process using sawdust derived biochar for the removal of MB.

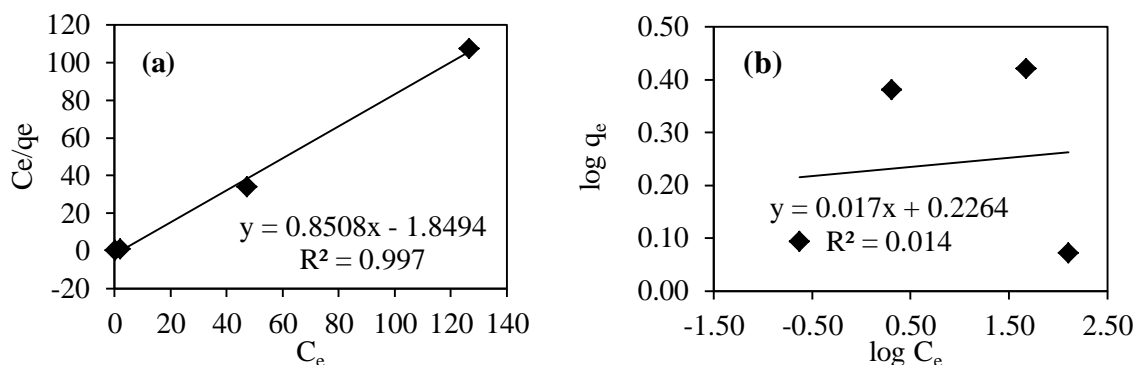


Figure 1. (a) Langmuir isotherm and (b) Freundlich isotherm for MB removal at various initial concentrations using PSP biochar

Table 1. R^2 and isotherm constants of PSP biochar for Langmuir and Freundlich isotherms for MB sorption

Adsorbate	Isotherm	R^2	Langmuir Constants		Freundlich Constants	
			q_{\max}	K_c	n	K_f
MB Dye	Langmuir	0.997	1.175	-0.460	-	-
	Freundlich	0.014	-	-	58.824	1.684

Since, this study fitted to Langmuir isotherm, it can be said that the adsorption was monolayer [15]. Thus, the adsorption of MB dye molecules occurred at a fixed number of definite localized sites. The adsorption also can refer as homogenous adsorption due to the constant enthalpies of molecules and activation energy of adsorption. Besides that, during homogenous adsorption all of the binding sites will shows equal affinity for the dye molecules [16].

3.2. Biosorption kinetics modeling and removal efficiency

Figure 2 illustrated the graphs of Pseudo first order model with experimental (Exp) and calculated (Cal) data for various initial MB concentrations and Table 2 summaries data for the biosorption kinetics –Pseudo First order model of MB dye onto PSP biochar.

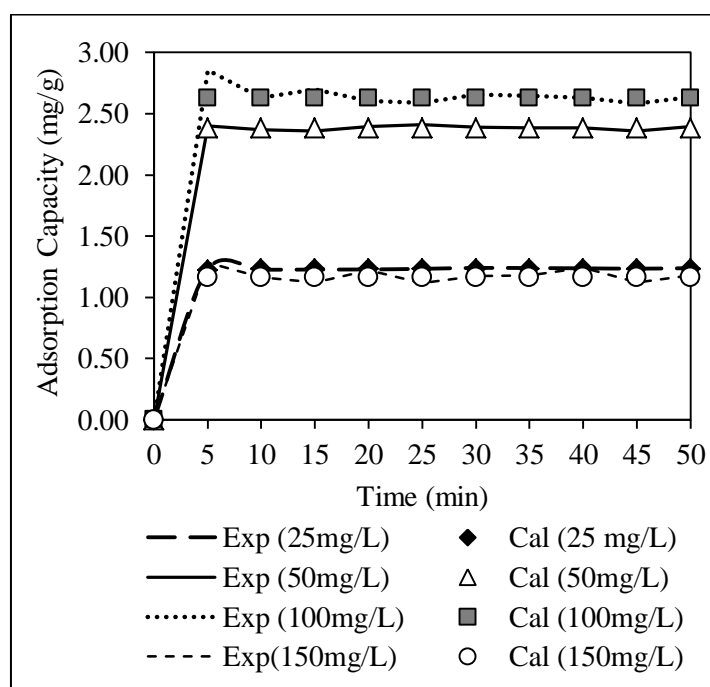


Figure 2. Experimental (Exp) and calculated (Cal) profile of pseudo first order kinetic model for various initial concentrations of MB adsorptions on PSP biochar

Table 2. Pseudo First Order Kinetic Model Parameters for MB adsorption on PSP biochar at various initial concentrations

Initial Concentration of MB (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	SSE (%)
25	1.24	1.23	1.02	0.999	0.00483
50	2.40	2.38	46.94	0.999	0.01648
100	2.63	2.63	50.05	0.991	0.07404
150	1.18	1.17	24.25	0.977	0.05198

Based on Table 2, R^2 values of pseudo first order model for adsorption of MB at various initial concentrations on PSP biochar are between 0.977 – 0.999 and SSE values are also considered low. This indicates pseudo first order model fits well for the experimental data. Adsorption system that follows pseudo first order indicates the adsorption of MB using PSP biochar is based on physisorption [17]. Based on literature, there are many adsorption processes which are following pseudo first order rate mechanisms [17]. Pseudo first order is chose to analysis the experimental data because according to [10] adsorption using coal based adsorbents mostly will follow pseudo first order mechanisms. Based on Table 2, amount of adsorbate adsorbed per unit mass of adsorbent, q_e (mg/g) and rate constants, K_1 are showing same trend where both are increasing until reach optimum initial concentration and after that both are decreasing. These are due to more availability of unoccupied active sites on the surface of PSP biochar at lower initial concentrations. Thus, the amount of dye molecules adsorbed increases until reaches equilibrium. Further increase in dye concentration decreases amount of dye adsorbed and also increases the driving force of mass transfer. Moreover, above optimal dye concentration, the active sites needed for the adsorption of dye molecules will be less and this will retard the adsorption process [18]. Rate constant, K_1 is coefficient of proportionality relating the rate of a chemical reaction to the concentration of reactant. Thus, as the initial concentrations increases, the frequency of the dye molecules colliding increases and results in high

rate of reaction. However, at above optimal concentration the driving forces of mass transfer increase and retards the adsorption mechanism and slows the rate of reaction which also reduces rate constant [17, 10].

As the initial concentration increases the removal efficiency of MB decreases due to the driving force provided by the increased solute concentration (Figure 3). This driving force is strong enough to overcome the resistance to mass transfer between the solid and liquid phase [19].

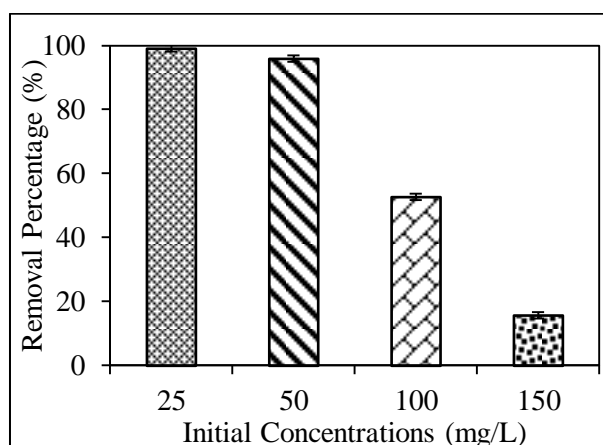


Figure 3. Removal Percentage of MB using PSP biochar as adsorbent at various initial concentrations.

4. Conclusion

The adsorption performance of MB dye onto PSP biochar has been analysed using equilibrium and kinetics study. The following results were obtained:

- Langmuir isotherm model fitted well the experimental data
- The kinetics of MB sorption onto PSP biochar at different initial concentrations of MB was best described using pseudo-first order, thus, indicated that physical reaction involved in the adsorption of MB dye molecules onto PSP biochar.
- Initial MB concentrations are highly affected the adsorption performance in term of removal efficiency.
- The maximum removal percentage was observed at 25mg/L.

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