

Adsorption of Methylene Blue From Aqueous Solution by Banana Pseudo Stem Biochar

Noor Halini Baharim^{1*}, Fridelina Sjahrir², Rahmad Mohd Taib³,
 Norazlina Idris⁴, Tuan Azmar Tuan Daud⁵

^{1*}Faculty of Engineering and Life Sciences, Universiti Selangor, 45600 Bestari Jaya, Selangor, Malaysia
 halini@unisel.edu.my

²Faculty of Engineering and Life Sciences, Universiti Selangor, 45600 Bestari Jaya, Selangor, Malaysia
 fridelina@unisel.edu.my

³Faculty of Engineering and Life Sciences, Universiti Selangor, 45600 Bestari Jaya, Selangor, Malaysia
 rahmad@unisel.edu.my

⁴Faculty of Engineering and Life Sciences, Universiti Selangor, 45600 Bestari Jaya, Selangor, Malaysia
 azlinaidris@unisel.edu.my

⁵Faculty of Engineering and Life Sciences, Universiti Selangor, 45600 Bestari Jaya, Selangor, Malaysia
 azmardaud@unisel.edu.my

Abstract: In this study, the adsorption of methylene blue dye from aqueous solution onto banana pseudo stem biochar prepared via slow pyrolysis at 500 °C was examined. The influence parameter of solution pH, initial concentration of methylene blue solution, adsorbent dosage and contact time on the methylene blue removal and the amount of adsorbate adsorbed were determined by batch adsorption experiments. The highest removal efficiency was obtained at solution pH 6, initial methylene blue concentration of 25 ppm, adsorbent dosage of 0.25 g within 90 minutes. The amount of methylene blue adsorbed was increased from 6.77 – 52.04 mg/g as the initial concentration increases from 25 ppm to 150 ppm. The adsorption isotherm studies show the equilibrium adsorption experimental data was well fitted to the Freundlich isotherm model. Meanwhile the adsorption kinetics was excellent fitted to pseudo-second order model. The maximum adsorption capacity was found at 55.25 mg/g. The results indicate biochar derived from banana pseudo stem showed a great potential as an efficient adsorbent for removing methylene blue from aqueous solution.

Keywords: Banana pseudo stem, Biochar, Methylene blue, Adsorption

1. Introduction

Methylthioninium chloride or commonly known as methylene blue (MB) is one of the synthetic dyes that has been widely used for in textile, paper printing and other industries including pharmaceutical, cosmetics, paint, rubber, plastics and leather (Mohammed, Shitu & Ibrahim, 2014; Dabholkar et al., 2021). The discharges of MB dye pollutant create the undesirable colourations throughout the water bodies and cause a toxic carcinogenic environment towards the aquatic life (Tahir et al., 2016). Long term exposure of MB dye results in serious health problems to human being such as allergies, skin irritation, increasing heart rate, vomiting and dizziness (Ma et al., 2015). Therefore, the removal of MB dye contaminants from the water resources is mandatory to prevent the continuous environmental pollution.

As compared to other conventional treatment for the MB dye removal, adsorption has become the most prominent method due to its simplicity of the design, easy to operate, economical and high efficiency (Kumar, 2014; Fomina & Gadad, 2014). Studies on the development of adsorbents derived from natural sources and agricultural waste for the MB and other colourants removal have increased the interest among researchers (Hariz et al., 2015; Dabwan et al., 2015; Siquiera et al., 2020).

Banana pseudo stem wastes are abundantly left over in the plantation after harvesting, and most farmers are usually disposing of the stem by burning the waste openly, which

results in another environmental issue and air pollution problem. Research on the utilization of adsorbents derived from banana pseudo stem for removing colour pollutants are very limited as compared to banana peel and banana leaf which have been studied extensively (Amin, 2019; Gautam & Khan, 2016). Therefore, this study highlights in investigating the adsorption potential of banana pseudo stem derived biochar for the removal of MB from aqueous solution. The adsorption experiments were conducted by batch mode to determine the effect of solution pH, initial concentration, the amount of dosage and contact time parameters on the MB adsorption mechanism onto the prepared biochar.

2. Methodology

2.1 Preparation of Solutions

All the chemicals are of analytical grade. Methylene blue (MB), HCl and NaOH were purchased from HmbG Chemicals. The stock solution of 1000 ppm MB was prepared in deionized water and then diluted to desired concentrations. All prepared MB solutions were adjusted to the required pH by using 0.1 N HCl or 0.1 N NaOH.

2.2 Preparation of Banana Pseudo Stem Biochar

Fresh banana pseudo stem collected from Kampung Bestari Jaya, Bestari Jaya, Selangor was washed with distilled water for removing external dirt. Then, the stem sample was cut into small sizes and followed by the drying procedure for 24 hours using an oven at 105 °C. Later the dried sample was pyrolyzed in a muffle furnace at 500 °C for 1 hour. The produced banana pseudo stem biochar was then crushed and followed by sieving to less than 200 µm for the homogenization of the particles. The biochar samples were stored in a cabinet desiccator for further adsorptive experiment.

2.3 Biochar Batch Adsorption Experiments

The effects of various adsorption parameters, including solution pH (3 – 9), initial MB concentration (25 ppm – 150 ppm), adsorbent dosage (0.05 g – 0.30 g) and contact time (10 – 120 minutes) were carried out by batch experiments. The experiments were performed by preparing a set of 100 mL Erlenmeyer flasks containing 100 mL of MB solution with the varied solution pH, initial concentration of MB solution, adsorbent dosage and contact time intervals. A pH meter (Sartorius PB-10, Germany) was used to measure the pH of the prepared MB solution. The mixtures were agitated at a constant speed of 120 rpm using a horizontal bench shaking incubator (Protech SI 1000D, Malaysia) at room temperature for the required time period. Then the mixtures were filtered and the MB concentrations in the supernatant were measured using the UV-VIS Spectrophotometer (Hitachi U2900, Japan) at 664 nm wavelength. To ensure the accuracy of the results, the experiments were performed in triplicates. The percentage MB removal efficiency, (%R) and the amount of MB adsorbed onto biochar, Q_e (mg/g) of the MB dye was calculated according Eq. (1) and Eq. (2), respectively.

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 and C_e are the initial and final MB concentration (mg/L), respectively. V is the volume (L) and m is the mass of the adsorbent (g).

3. Result and Discussion

3.1 Effects of Parameters on Methylene Blue Adsorption onto Banana Pseudo Stem Biochar

The effect of various process parameters on the adsorption of MB onto biochar, i.e solution pH, initial concentration of MB solution, adsorbent dosage and contact time were determined by adsorption experiments and the results are depicted in Figure 1.

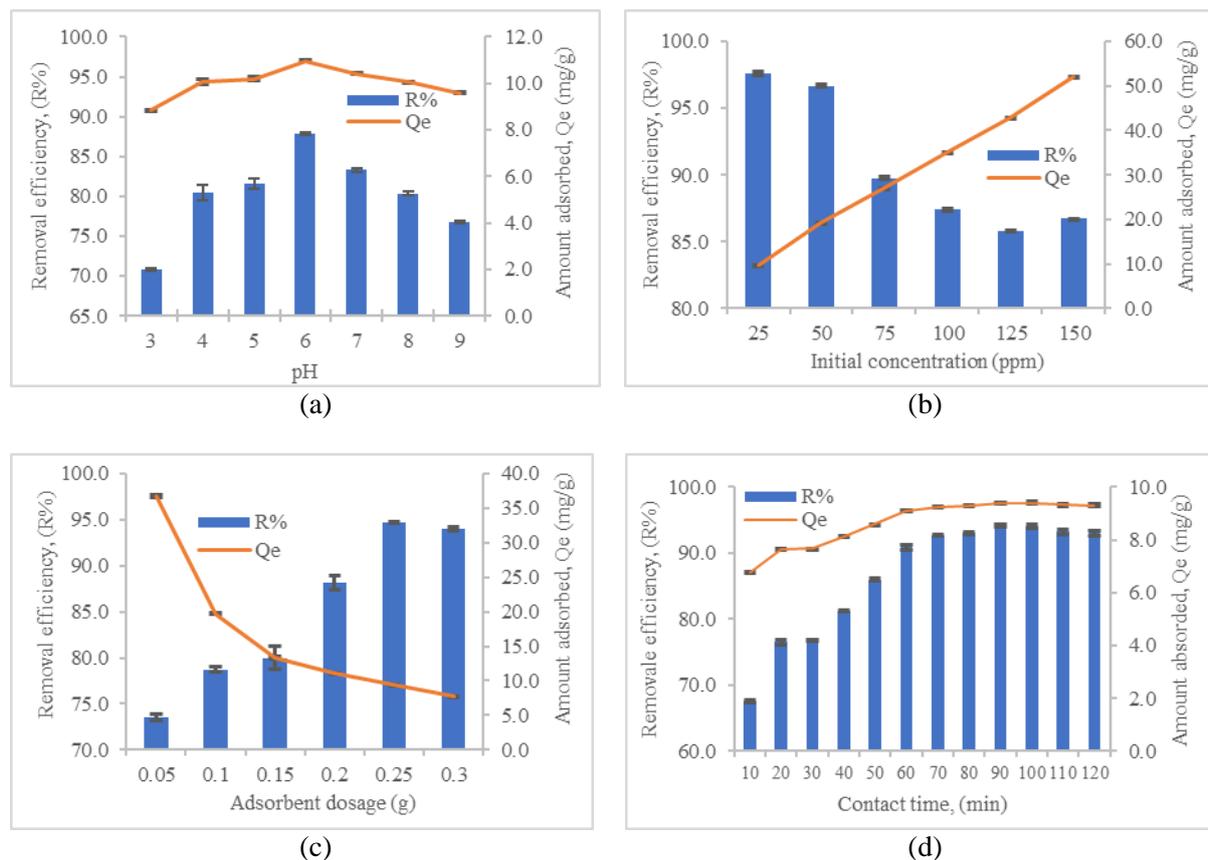


Figure 1. Evaluation of removal efficiency and amount of MB adsorbed onto biochar with the influence (a) pH of solution, (b) initial concentration of MB solution, (c) adsorbent dosage, (d) contact time of reaction.

The adsorption of MB onto biochar is greatly influenced by the pH of the dye solution. Figure 1(a) shows the profile of solution pH and it was found that both highest removal of MB (87%) and highest amount of MB adsorbed (10.9 mg/g) were at pH 6. These outcomes and the characteristic of MB as cationic dyes confirmed that the biochar is a positive-charged adsorbent.

The effect of initial concentration of MB (25-150 ppm) exhibited almost 10 fold of increment in the amount of MB adsorbed, which was from 6.77 to 52.04 mg/g as illustrated in Figure 1(b). The removal of MB was found highest at 25 ppm of initial concentration with percentage removal of nearly 98%. On top of that, the amount adsorbed was found to increase with an increase of initial concentration of MB, however no significant removal of

MB was observed. This may be attributed to the increasing mass transfer and higher interaction between the metal ions and sequestering sites of adsorbent caused by the increasing MB concentration (Pathania, Sharma & Singh, 2017; Elsherif, Haider & El-Hashani, 2019).

It was observed in Figure 1(c) that MB removal efficiency improved when the adsorbent was increased with highest removal efficiency of 95% detected at 0.25 g of MB dosage. The elevated trend in the removal of the MB was related to the availability of active sites for adsorption and additional adsorbent surface as the dosage increases (Pathania, Sharma & Singh, 2017). However, the amount of MB adsorbed was decreased with the increasing dosage used in the experiment. This declining trend in the amount of MB adsorbed may be due to the unsaturated active site of the adsorbent during the adsorption process and the overlapping and aggregation of biochar (Gazin & Bahri Rasht Abadi, 2017).

The adsorption process was also influenced by the contact time of the experiments. It can be seen in Figure 1(d) that the adsorption rate was a bit slow at the first 30 minutes of reaction and gradually increased until it reached equilibrium. Two steps of adsorption might be involved in this reaction. The first step was surface adsorption followed by the intraparticle transport between solution and porous surface of the BPS-biochar adsorbent (Nsami and Mbdcam, 2013). Approximately, 90% of the removal of MB was achieved in 60 minutes and the equilibrium was reached after 70 minutes with the highest removal efficiency of 94% at 90 minutes.

3.2 Adsorption Isotherm and Kinetics

The distribution of adsorption molecules onto the solid phase of the biochar at equilibrium condition can be determined using the adsorption isotherm studies. While adsorption kinetics explains the adsorption rate and mechanism of the reaction. Analysis on the adsorption process was carried out using two common isotherm models, Langmuir and Freundlich. Langmuir isotherm indicates for the monolayer adsorption on a homogenized surface with a finite number of adsorption sites, whereas Freundlich isotherm describes for the multilayer adsorption on heterogeneous surface. Kinetics of MB adsorption onto biochar were investigated using pseudo-first order model and pseudo-second order model. The linearized equation for all the models is tabulated in Table 1.

Table 1. Adsorption isotherm and kinetic equation

	Models	Linearized equation	
Isotherm	Langmuir	$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$	Eq. (3)
	Freundlich	$\log q_e = \frac{1}{n} \log C_e + \log K_F$	Eq. (4)
Kinetics	Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	Eq. (5)
	Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	Eq. (6)

Where

- q_e = amount of MB adsorbed (mg/g)
- C_e = MB concentration at equilibrium (mg/L)
- b = Langmuir isotherm constant (L/mg)
- q_m = maximum adsorption capacity (mg/g)
- K_F = Freundlich isotherm constant related to adsorption capacity ((mg/L) (L/mg)^{1/n})
- $1/n$ = adsorption intensity. If $1/n = 1$, the separation within the two phases is not dependent on the concentration. If the value of $1/n < 1$, it shows normal adsorption. If $1/n > 1$, it shows cooperative adsorption (Fytianos, Voudrias & Kokkalis, 2000).
- q_t = adsorption capacities at time, respectively
- k_1 = pseudo-first order constant (g/(mg.min))
- k_2 = pseudo-second order constant (g/(mg.min^{1/2}))

The separation factor, R_L , for the prediction of the affinity between adsorbate and adsorbent is calculated from Langmuir isotherm constant according to Eq. (7).

$$R_L = \frac{1}{1 + bC_o} \quad (7)$$

where, C_o is the initial MB concentration (mg/L). The values of R_L indicate the type of the isotherm to be either unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$), Irreversible ($R_L = 0$) or linear ($R_L = 1$).

The adsorption isotherm parameters and kinetic parameters are listed in Table 2.

Table 2. Adsorption isotherm and kinetic parameters

Isotherm	Models	Parameters			
	Langmuir	$R^2 = 0.899$	$b = 0.22$ L/mg	$q_m = 55.25$ mg/g	$R_L = 0.029$
Freundlich	$R^2 = 0.958$	$K_F = 13.12$ mg/L	$1/n = 0.418$		
Kinetics	Pseudo-first order	$R^2 = 0.888$	$k_1 = 0.037$	$Q_e = 3.98$ mg/g	
	Pseudo-second order	$R^2 = 0.998$	$k_2 = 0.015$	$Q_e = 9.97$ mg/g	

From Table 2, it is evidence that the adsorption isotherm was better fitted to the Freundlich model ($R^2 = 0.958$) than the Langmuir model ($R^2 = 0.899$). Additionally, the calculated maximum adsorption capacity, q_m , is 55.25 mg/g. The separation factor value, $R_L = 0.029$ indicates the favourable adsorption of MB onto biochar at the applied experimental conditions. The adsorption of MB onto the biochar can be defined as normal and easy according to the $1/n$ value from the Freundlich model.

Results on the adsorption kinetic models showed that the kinetics mechanism is well fitted for pseudo-second order models as the R^2 value (0.998) is larger than the R^2 value (0.888) for pseudo-first order. Furthermore, the adsorption capacity of the experiment, q_{exp} (9.41 mg/g) is closely to the calculated value of q_e (9.97 mg/g). Thus, it can be concluded that the adsorption of MB onto biochar is described as a chemical adsorption mechanism and an excellent fitted to pseudo-second order model.

4. Conclusion

From the batch experiment, it was found out that MB adsorption on the prepared biochar achieved the highest percentage of MB removal at solution pH of 6 while the initial concentration was at 25 ppm for the highest removal efficiency of 87.8% and 97.6% respectively. Excellent performance was recorded when MB concentration was gradually decreased after contacting with the adsorbent for 90 minutes with 0.25 g of adsorbent dosage at 94% of removal efficiency. Thus, banana pseudo-stem biochar at temperature 500 ° C was successfully utilized and a promising adsorbent in removing methylene blue from the aqueous solution.

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6. References

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