IOP Conference Series: Earth and Environmental Science

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To cite this article: Thevisri Hannanda Rao *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **596** 012029

IOP Conf. Series: Earth and Environmental Science **596** (2020) 012029 doi:10.1088/1755-1315/596/1/012029

Adsorption of Methylene Blue from Aqueous Solutions Using *Parkia speciosa* Pod-based Magnetic Biochar

Thevisri Hannanda Rao[a], Rosmawani Mohammad[1]*, Noor Fazliani Shoparwe[1]

[1]Faculty of Bioengineering and Technology, University Malaysia Kelantan, Jeli Campus, Locked Bag No100, Jeli, Kelantan, Malaysia.

E-mail: rosmawani@umk.edu.my

Abstract. This study was aimed to investigate the use of *Parkia speciosa* pod (petai pod) in the form of magnetic biochar as an efficient bioadsorbent to remove methylene blue (MB) in batch mode. The adsorption onto the magnetic biochar achieved about 99% of removal for all the initial concentrations studied (25 mg/L – 250 mg/L). The adsorption processes were studied using the adsorption isotherms, which were analysed using Langmuir and Freundlich model. The adsorption using magnetic biochar followed Freundlich model, indicating the heterogeneous surface of the magnetic biochar. Thus, the study showed that the *Parkia speciosa* pod (PSP) as agricultural waste has the potential to be used as a low-cost adsorbent.

1. Introduction

Adsorption is one of the efficient techniques in wastewater treatment. Contaminants, such as dyes, pesticides, metal ions and others in water can be removed using adsorption in a cost-effective manner. Textile dyes are the most polluting agent and are directly discharged into the water bodies by irresponsible industrialists [1]. Dye contaminations in the natural water bodies reduce the sunlight penetration into the water, impacting aquatic plants and animals. The water quality also decreases due to the synthetic dyes which contain harmful chemicals. Thus, this study focuses on the batch adsorption of methylene blue (MB) using *Parkia speciosa* pod-based (PSP; petai pod) magnetic biochar.

Recently, the utilisation of agricultural wastes reduces waste accumulation and follows the ‘waste to energy’ concept. One of the agricultural wastes is petai pods which are disposed pods after the seeds have been consumed [2]. To the best of our knowledge, there are few researches on the utilisation of the petai pods as adsorbents for dye removal [3]. Functional groups, like carboxyl, hydroxyl, sulfhydryl, and amino, and the components, such as hemicellulose, lignin, lipids, proteins, carbohydrates, water, hydrocarbon, and starch found in the agricultural wastes actually cause the binding of the contaminants’ ions on the surface of the adsorbent. However, based on some studies, petai pods and seeds have been utilised as bioadsorbents [4, 3]. Nevertheless, there are limited studies on adsorption onto magnetic biochar derived from petai pods.

In this work, petai pods were pretreated with $FeCl_3$ before carbonisation in order to produce magnetic biochar which had high reductive reactivity, large surface area and large surface adsorption sites. Magnetic biochar contains a metallic iron core and iron oxides layers or shells. The iron component of magnetic biochar helps improve the efficiency in adsorption. The iron oxides layer plays a positive role in enhancing the adsorption capacity of magnetic biochar [5]. The aim of the study is to investigate the potential use of magnetic biochar as adsorbents to remove MB dyes in aqueous solutions.

2. Methodology

2.1. *Preparation of Magnetic Biochar*

The petai pods were washed with distilled water to remove the dirt from the surface. Then, the petai pods were sun dried to eliminate the moisture content. The sun-dried petai pods were cut into small pieces and oven dried at 100°C for 24 hours to completely dry them. Then, the samples were grinded into powder. The powder was sieved in order to obtain 75 - 125 µm particles. Sieved petai pod powder was pretreated with 0.5 M $FeCl_3.6H_2O$. The ratio of powder and $FeCl_3.6H_2O$ was 1:8; 10 g of powder was mixed with 80 mL of 0.5 M $FeCl_3.6H_2O$ [6]. The mixture was stirred for 30 minutes and heated for 30 minutes at 70°C for aging process. Then, the liquid was filtered out and the resulting solid was dried in the oven for 17.45 hours at 70°C. Then, the dried samples were placed in crucibles and carbonized at 800°C for 2 hours at 10°C/min to produce magnetic biochar [7].

2.2. *Preparation of Stock Solution*

The stock solution of MB at the 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 using the Thermo Scientific GENESYS 20 Visible Spectrophotometer [8].

2.3. *Batch Adsorption Studies*

The effects of adsorbent dosage were studied by using three different adsorbent dosages: 0.5 g, 1.0 g and 2.0 g. The optimum adsorbent dosage was used to investigate the effect of initial dye concentrations. The effect of initial dye concentrations was studied at 25, 50, 100, 150, 200, and 250 mg/L in a batch system. Then, 50 mL of dye was placed in contact with the optimum dosage of magnetic biochar in a conical flask. The mixture was stirred using glass rod. Based on the preliminary study, a duration of 50 minutes was fixed as the optimum time required to reach the optimum removal.

The adsorbed amount of dye or adsorption capacity was calculated using Equation 1 [9]:

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

Where C_o represents the initial concentration of dye, C_t is the concentration of dye at end time (mg/L), m indicates adsorbent mass (g) and V is the solution volume (L).

The percentage of dye removal was calculated using Equation 2 [9]:

$$\text{Removal Percentage} = 100 \text{ x } \frac{C_o - C_t}{C_o} \tag{2}$$

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

2.4. Adsorption Isotherm Models

2.4.1. Langmuir Isotherm. Langmuir isotherm model is usually applied to define the sorption process between the liquid and solid interface. To use the Langmuir model, an assumption needs to be made: the sorption occurs at specific homogenous sites on the adsorbent surface. No further sorption will occur when an adsorbate molecule occupies a site [9]. The equation describing the model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} \qquad (3)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e represents the equilibrium concentration of the adsorbate (mg/L), q_{max} defines the monolayer adsorption capacity of sorbent (mg/g), and K_L is the Langmuir constant (L/mg).

2.4.2. Freundlich Isotherm. In Freundlich isotherm, the adsorbent has a heterogeneous surface. The isotherm is applicable to multilayer sorption of the surface. In this case, infinite surface coverage is predicted, with no saturation [9]. The general equation involved is as follows:

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

Where K_F is a constant value related to adsorption capacity (mg/g) and 1/n is the empirical parameter related to the adsorption intensity which depends on heterogeneity.

3. Results and Discussion

3.1. *Effect of Adsorbent Dosage*

As mentioned in section 2.3, three different dosages were used. Figure 1 shows the removal percentage of MB at three different adsorbent dosages. The results indicated that the removal percentage of MB increased with the increasing adsorbent dosage due to the increased number of binding sites for dye molecules [10]. We chose 1.0 g of magnetic biochar as the optimum dosage since 1.0 g of magnetic biochar was able to achieve about 99% of removal.

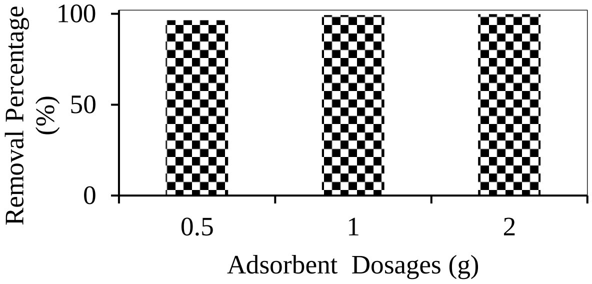

Figure 1. Effect of Adsorbent Dosage

3.2. *Effect of Initial Dye Concentrations*

Figure 2 shows the removal time profile of MB by the magnetic biochar. At low initial MB concentrations, such as 25 mg/L and 50 mg/L, the equilibrium was reached in the first five minutes. As the initial MB concentration increased, the time taken to reach the equilibrium also increased (Figure 2). However, zerovalent iron (ZVI), Fe_3O_4 and Fe_2O_3 formation on the magnetic biochar influenced the time taken to reach the equilibrium at high initial MB concentrations. The transformation process of iron into ZVI during pyrolysis and the quality of ZVI formation are influenced by the nature of biomass. However, the transformation process of iron into ZVI is still being studied, requiring further researches [11]. The formation of Fe_3O_4 and Fe_2O_3 (iron oxide layers) are the results of the spontaneous chemical reactions with limited oxygen, and high temperature during carbonisation. Studies have shown that the formation of Fe_3O_4 can be the dominant form of iron in the biochar during carbonisation at 700°C while evidence of ZVI formation has been observed for biochar produced at 700°C - 900°C [11]. Based on the previous studies, Fe_3O_4 has higher magnetic properties and adsorption capacity compared to Fe_2O_3 [12]. Thus, the biochar surrounded primarily by Fe_3O_4 adsorb dye molecules rapidly even at higher initial concentrations. The removal percentage of MB by the magnetic biochar as illustrated in Figure 3 remained at around 99% for all the initial concentrations, indicating high adsorption sites and adsorption capacity (Refer Figure 4) of the magnetic biochar even though the rate of reaction varied according to the magnetic biochars' composition. As illustrated in Figure 4, the adsorption capacity of the magnetic biochar increased with the increasing initial dye concentration. Similar trend was also reported in other studies [13]. The increase in the initial dye concentrations led to an increase in the amount of MB dyes adsorbed onto the magnetic biochar due to the inclining collision rate between the dye molecules and magnetic biochar [14].

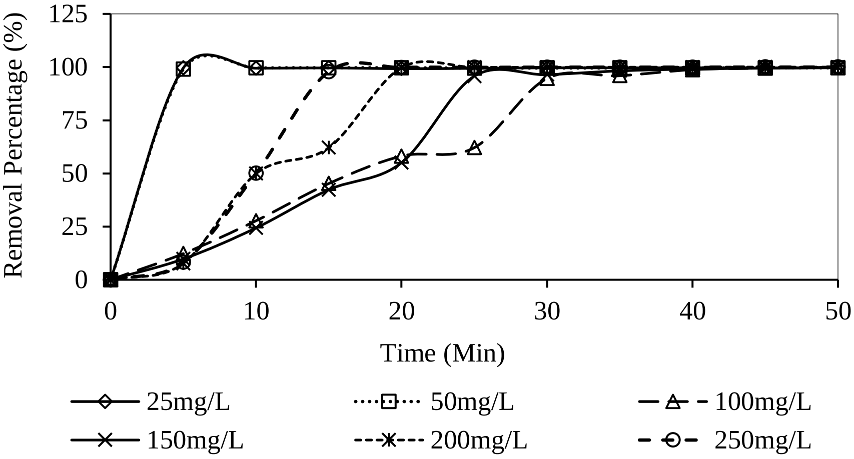

Figure 2. MB removal time profile by the magnetic biochar.

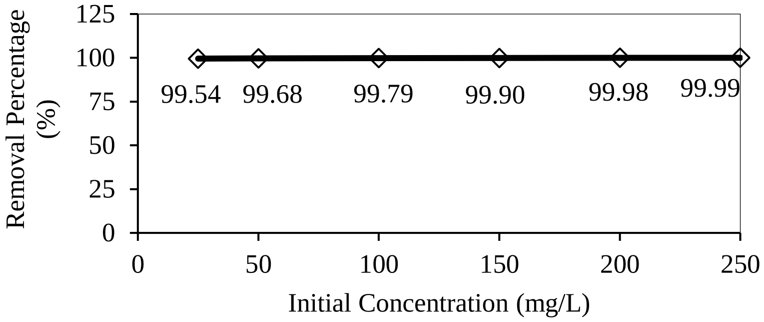

Figure 3. Removal percentage of MB using the magnetic biochar.

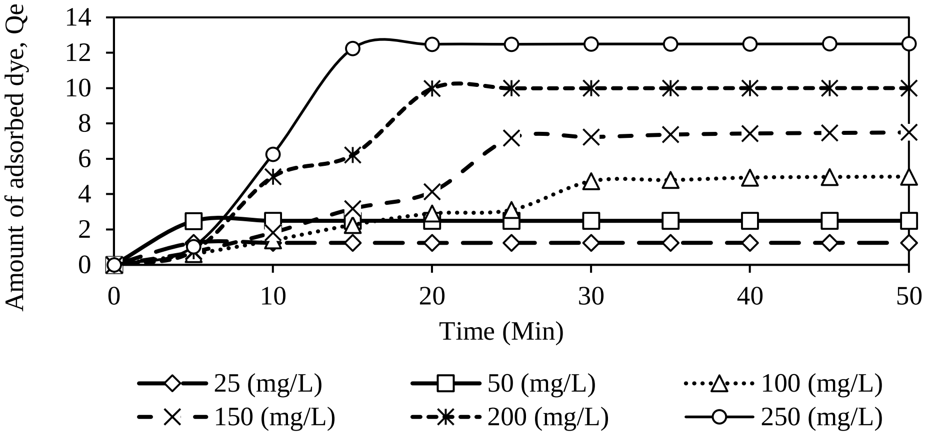

Figure 4. Adsorption capacity of the magnetic biochar.

3.3. Adsorption Isotherm Models.

Figure 5 (a) and (b) show the Langmuir and Freundlich isotherms, respectively. Based on the R^2 values as shown in Table 1, the experimental data fitted well to the Freundlich isotherm, indicating that the magnetic biochar had heterogeneous solid surfaces. Based on the literature, the Freundlich equation is used for data fitting related to the adsorption of cations on iron oxides [15]. The Freundlich constants, K_F and n are defined as the adsorption capacity and adsorption intensity, respectively [16]. The adsorption capacity obtained from the Freundlich model was good compared to Langmuir's and the adsorption intensity of $n < 1$ meant that the adsorption was a chemical process [16].

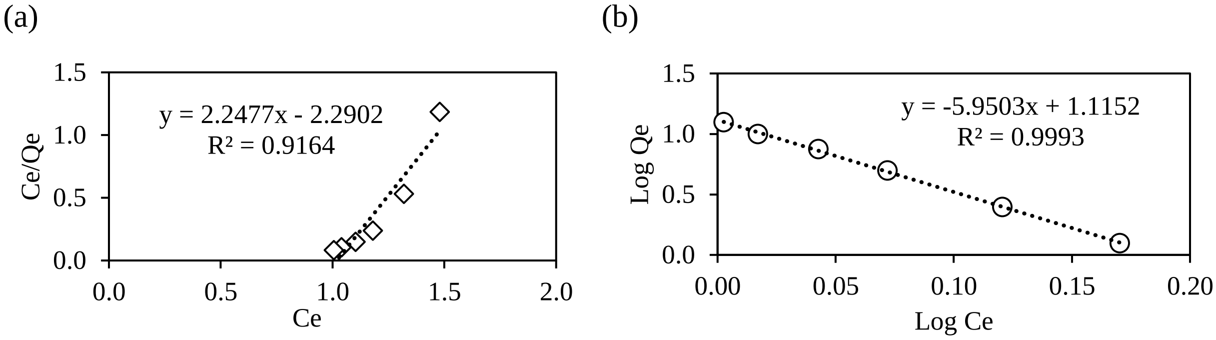

Figure 5. Adsorption isotherm linear plot of (a) Langmuir and (b) Freundlich.

Table 1. Adsorption isotherm parameters of MB onto the magnetic biochar of PSP.

Isotherm Model	MB adsorption
Langmuir	
q_{max} (mg/g)	0.44
K_L (L/mg)	-0.98
R^2	0.9164
Freundlich	
K_F (mg/g)(mg/L)$^{1/n}$	13.04
n	-0.17
R^2	0.9993

4. Conclusion

This study has demonstrated a promising eco-friendly and cost-effective technique for the removal of MB. The removal percentage of MB using magnetic biochar showed 99% of removal even at high initial dye concentrations. The adsorption of MB using the magnetic biochar followed the Freundlich model, indicating the heterogeneous surface of the magnetic biochar. This study indicates that PSP or petai pod is a viable bioadsorbent for the removal of MB from aqueous solutions.

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