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Methylene Blue Adsorption by Acid Post-Treated Low Temperature Biochar Derived from Banana (*Musa acuminata*) Pseudostem
(Penjerapan Metilena Biru oleh Bioarang Bersuhu Rendah Selepas Dirawat Asid Dihasilkan daripada Batang Pseudo Pisang (*Musa acuminata*))

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ABSTRACT

The adsorption of methylene blue dye solution using low temperature biochar (PSB) and acid post-treated biochar (PT-PSB) derived from banana (*Musa acuminata)* pseudostem was investigated. The raw material was oven-dried at 105 °C for 24 h and then carbonized via slow pyrolysis at a low temperature of 300 °C for 1 h. The biochar was further treated with 1.0 M HCl for 24 h. At room temperature, batch adsorption experiments were conducted to determine the removal efficiency of methylene blue at different parameters; solution pH (3-10), adsorbent dosage (0.05-0.30 g) and initial concentration (25-150 mg/L). The results exhibited that the highest removal efficiency of methylene blue using PSB was 96.6% at optimum solution pH 6 with the adsorbent dosage of 0.20 g. Nevertheless, the better removal efficiency of methylene blue using PT-PSB was identified (99.3%) at optimum solution pH 7 and adsorbent dosage of 0.25 g. The initial concentration of 25 mg/L showed the maximum removal efficiency for both PSB and PT-PSB. The adsorption isotherm analysis showed that both PSB and PT-PSB were better fitted with the Freundlich isotherm model which indicates multilayer adsorption onto the heterogeneous surface of the adsorbents. Kinetic data showed that the adsorption of methylene blue onto PSB and PT-PSB was well fitted by the pseudo-second order model, indicating chemical adsorption. Banana pseudostem showed great potential to be used as an efficient low-cost and environmentally friendly adsorbent for the removal of methylene blue from aqueous solution.

Keywords: Acid post-treated biochar; adsorption; banana pseudostem; methylene blue

ABSTRAK

Penjerapan larutan pewarna metilena biru menggunakan bioarang bersuhu rendah (PSB) dan bioarang selepas dirawat asid (PT-PSB) yang berasal daripada batang pseudo pisang (*Musa acuminata*) dikaji. Bahan mentah dikeringkan dengan ketuhar pada suhu 105 °C selama 24 jam dan seterusnya dibakar melalui pirolisis perlahan pada suhu rendah 300 °C selama 1 jam. Bioarang seterusnya dirawat dengan 1.0 M HCl untuk 24 jam. Pada suhu bilik, uji kaji penjerapan kumpulan dijalankan untuk menentukan kecekapan penyingkiran metilena biru pada parameter pemboleh ubah yang berbeza; pH larutan (3-10), dos penjerap (0.05-0.30 g) dan kepekatan awal (25-150 mg/L). Keputusan menunjukkan kecekapan penyingkiran tertinggi metilena biru menggunakan PSB adalah 96.6% pada pH larutan optimum 6 dengan dos penjerap 0.20 g. Walau bagaimanapun, kecekapan penyingkiran metilena biru yang lebih baik menggunakan PT-PSB ditentukan (99.3%) pada pH larutan optimum 7 dan dos penjerap 0.25 g. Kepekatan awal 25 mg/L menunjukkan kecekapan penyingkiran yang maksimum bagi kedua-dua PSB dan PT-PSB. Analisis isoterma penjerapan menunjukkan kedua-dua PSB dan PT-PSB adalah lebih berpadanan dengan model isoterma Freundlich yang menunjukkan penjerapan berbilang lapisan ke permukaan heterogen penjerap. Data kinetik menunjukkan penjerapan metilena biru ke PSB dan PT-PSB adalah sangat berpadanan dengan model tertib kedua pseudo, menunjukkan penjerapan kimia. Batang pseudo pisang berpotensi besar digunakan sebagai penjerap berkos rendah yang cekap dan mesra alam untuk penyingkiran metilena biru daripada larutan akues.

Kata kunci: Batang pseudo pisang; bioarang selepas dirawat asid; metilena biru; penjerapan

Introduction

Industrial operations in textile, paper, pulp, plastic, leather, cosmetic, and pharmaceutical industries discharge various hazardous dye effluent that contaminates the water supply. According to a World Bank report, the textile industry is responsible for between 17 and 20% of the water contamination that occurs during texture dyeing and finishing operations (Saini 2017). The releasing of dyes effluent generates an undesirable quantity of coloured water that is perceptible to the human eye and consequently quite offensive on an aesthetic level. The majority of dyes are poisonous, mutagenic and carcinogenic, all of these which creates serious health problem for human. Additionally, the coloured dye effluent will prevent light penetration through the water body and may disrupt the biological metabolism processes of aquatic life. Dye concentrations as low as 1 mg/L are considered to be micropollutants and are evident in aquatic environments.

Methylene blue ($C_{16}H_{18}N_3SCl$, C. I. No. 52015) is one kind of common synthetic cationic dye that has been used extensively in the textile, paper and dyeing industries (Li et al. 2018). The discharges of methylene blue dye pollutants cause deterioration in human health and detrimental impacts on the aquatic environment. These dye effluents are toxic to aquatic organisms and the presence of dye in water hindered the transmission of sunlight thus reducing the photosynthesis activities of aquatic flora and oxygenation of water bodies. While from the human health angle, the common side effects of long-term exposure to methylene blue include headache, vomiting, confusion, shortness of breath, and high blood pressure (Bhatia et al. 2018). Therefore, the removal of this toxic dye from wastewater has become a main environmental challenge and there is a continuous need to have an effective procedure that can efficiently remove the pollutant economically.

Currently, a variety of traditional approaches, including chemical, biological, and physical processes, have been widely employed to treat dye wastewater. However, the majority of these techniques have drawbacks and some restrictions. For example, coagulation as a common chemical method produces a large amount of sludge which then needs to be treated and followed by disposing of treatment. The cost of disposal may increase due to the amount and toxicity of the sludge and the difficulty of dewatering it. Biological degradation methods, i.e., bioremediation using bacteria, algae and fungi are more economical, easier to be accomplished and environmentally friendly (Ali 2010). The main challenge with this approach is system instability to forecast the reaction and organism growth rate due to the application of these living organisms in its process. Besides that, this treatment is unable on its own to entirely eliminate hazardous components from dye effluent, yet coloured is still perceived throughout the water environment (Pan et al. 2017).

Membrane filtration, ion exchange, electrolysis, adsorption, and reverse osmosis are the typical physical method to treat dye wastewater. Among these treatments, adsorption currently appears as the most prominent method due to its simple design and operation, economical, and high efficiency (Katheresan, Kansedo & Lau 2018). The adsorption method has been proven to produce higher treated water quality compared to other dye removal conventional treatments (Katheresan, Kansedo & Lau 2018; Zhou et al. 2018). The selection of the adsorbents to be utilised is a major point to be considered in adsorption technology. Commercial activated carbon is the most often used adsorbent. Despite its efficiency and excellent adsorption capacity in eliminating dye from wastewater, the high cost of activated carbon production limits its widespread application (Crini 2006; Yuan et al. 2007). Therefore, it is necessary to discover the viability of using less expensive, effective and widely accessible materials as alternatives adsorbent for the dye treatment of wastewater.

Researchers are now more interested in utilizing natural sources and agricultural waste to produce biochar, an alternative adsorbent for treating dyes from wastewater (Abd-Elhamid 2020; Al-Mokhalelati et al. 2021; Deng et al. 2021; Hariz et al. 2015; Praveen et al. 2020). One of the most popular sources of feedstock for biochar preparation is banana (family: Musaceae) waste. Banana leaves (Kumar, Vibhute & Parikh 2021), banana peel (Amin Alazba & Shafiq 2019; Kapoor et al. 2022), banana stem (Baharim et al. 2022; Jadhav & Thorat 2022) and banana peduncle (Karim et al. 2015) derived biochar were economically and effectively in removing various types of dyes and heavy metal pollutant in wastewater. The application of agricultural wastes was also helping to resolve environmental concerns brought on by issues with agricultural waste disposal.

Biochar, a black carbonaceous solid product is prepared via the pyrolysis method where different biomass feedstocks are thermochemically decomposed at high temperatures under an oxygen-deficient environment (Zaman et al. 2017). To enhance the adsorption capability of biochar, it is often modified with physical or chemical treatment. Compared to physical, the advantages of chemical treatments are simple activation

reaction control, low activation temperatures and high prepared product performance (Nayak et al. 2017). Chemical treatments involved either pre-treatment or post-treatment methods employing various types of chemical reagents, such as basic or acid solutions. However, more literature highlighted the acid pre-treatment for enhancing the biochar adsorption capacity. For example, Liu et al. (2019) reported the adsorption capability of biochar prepared at 200 °C was improved from 87.28 to 146.23 mg/g at 45 °C with phosphomolybdic acid pre-treatment for methylene blue removal. Research conducted by Kim et al. (2020) found that phosphoric acid pre-treatment improved the physicochemical properties of biochar derived from banana peels, thus, improving the removal efficiencies of manganese and iron. Mahdi, Hanandeh and Yu (2019) investigated both methods of pre-treatment and post-treatment of date seed biochar using 1M HCl and 1M NaOH for the adsorption of Pb^{2+}, Cu^{2+}, and Ni^{2+}. The studies showed the HCl pre-treatment of biomass followed by pyrolysis at 550 °C for 3 h indicates the highest adsorption capacity and adsorption rate. The adsorption capacity of HCl pre-treated biochar for Pb^{2+}, Cu^{2+} and Ni^{2+} improved by 27%, 66%, and 98%, respectively, in comparison to unmodified biochar. Research using NaOH post-treated banana stem biochar reported by Kumar et al. (2022) showed that the removal efficiency of methylene blue was achieved at 96.6% as compared to 93.3% for untreated biochar.

To the best of our knowledge, the adsorption of methylene blue onto post-treated banana biochar produced at low temperatures has not yet been investigated. Since chemical modification using acid solution has a significant impact on the adsorption capabilities of biochar, thus, HCl was chosen due to its safety factor than the other acids and being more cost-effective for carbon activation. In this study, the banana pseudostem was used as the feedstock for the development of biochar via pyrolysis at 300 °C. The biochar was further treated with HCl solution and the effect of different variables parameters including pH, dosage, initial concentration and contact time on the removal efficiency and amount adsorbed of methylene blue was investigated. The isotherms and kinetic of the adsorption process were also evaluated. The same analysis and evaluation of the methylene blue removal efficiency were also performed using the untreated banana pseudostem for comparison with the synthesized HCl post-treated banana pseudostem biochar.

Materials and Methods

Chemicals

Methylene blue (analytical grade) was purchased from Sigma-Aldrich (M) Sdn. Bhd. Malaysia. A stock solution of 1000 mg/L of methylene blue was prepared by dissolving 1 g of methylene blue powder in 1000 mL of distilled water. The stock solution was diluted to the desired concentrations (25 mg/L to 150 mg/L) for the adsorption experiments. The chemical structure of methylene blue is presented in Figure 1.

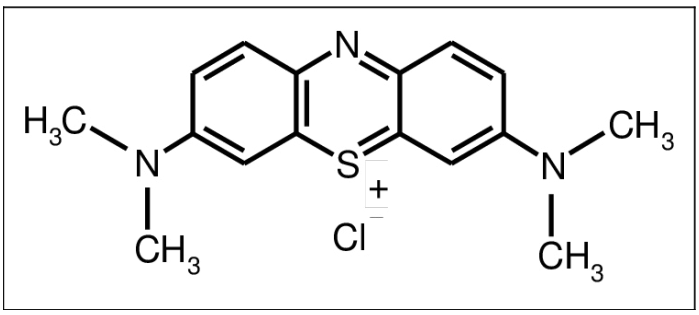


FIGURE 1. Chemical structure of methylene blue

Preparation of Biochar

The *Musa acuminata* pseudostem was collected from a local farmer at Bestari Jaya, Selangor, Malaysia. The stem was washed thoroughly several times with distilled water to remove impurities and cut into small pieces. The stem was then oven dried at 105 °C for 24 h for moisture content removal. Liu et al. (2019) reported that modification of biochar at low temperatures showed a better adsorption capacity for dye than biochar at a higher temperature. Thus, for this study, the biochar was

prepared by slow pyrolysis of the oven-dried stem in a muffle furnace (Protherm, Turkey) at 300 °C for 1 h and then cooled to room temperature. Later, the produced biochar was ground using a dry kitchen blender and sieved into the desired size of 200 µm. The biochar was stored in an airtight container and kept in a desiccator for further use. This untreated pseudostem biochar was labelled as PSB.

PREPARATION OF ACID POST-TREATMENT BIOCHAR

Acid post-treatment was conducted by mixing 50 mL of 1.0 M HCl solution with 10 g of BPS in a flask. The flask was stirred continuously on a rotary shaker (Protech SI 1000D, Malaysia) for 24 h at room temperature (Mahdi, Hanandeh & Yu 2019). Afterwards, the treated biochar was washed continuously with distilled water until the pH reached 6.0 - 6.5 to remove any chemical residue and then oven-dried for 24 h at 105 °C. The modified, acid post-treated biochar was labelled as PT-PSB, placed in an airtight container and stored in the desiccator for the next use.

BATCH ADSORPTION EXPERIMENTS

Batch adsorption experiments were performed to determine the effect of initial pH (3 to 9), different adsorbent dosages (0.05 g to 0.30 g) and various initial methylene blue concentrations (25 mg/L to 150 mg/L) on the removal efficiency and the amount adsorbed of methylene blue. The experiments were conducted at room temperature by adding the required amount of PSB and PT-PSB in a series of 250 mL Erlenmeyer flasks containing 100 mL of methylene blue solution. The pH adjustment of methylene blue solution was carried out with 0.1 M HCl and 0.1 M NaOH solution, using a pH meter (Sartorius, China). The mixture was agitated using an orbital shaker (Protech SI 1000D, Malaysia) at 120 rpm for 90 min (Tharaneedhar et al. 2016). Then, the mixtures were filtered using the Whatman 42 (pore size: 2.5 µm) filter paper. The concentration of methylene blue in each experiment was measured with UV-VIS-Spectrophotometer (Hitachi U2900, Japan) at the wavelength of 664 nm. All experiments were carried out in triplicates to minimize error and the average values with standard deviation were presented. The amount adsorbed, q_e (mg/g) and removal efficiency (R%) of methylene blue were calculated using Equation (1) and (2), respectively:

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

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where q_e is the amount of methylene blue adsorbed (mg/g); C_o and C_e are the initial and final concentration of methylene blue (mg/L) in the solution, respectively; V is the volume of methylene blue solution (L); and m is the mass (g) of the PSB and PT-PSB.

ISOTHERM AND KINETIC ADSORPTION EXPERIMENTS

The adsorption isotherms experiment for the adsorption of methylene blue was conducted using the optimum dosage and pH condition (0.20 g and pH 6 for PSB; 0.25 g and pH 7 for PT-PSB) at temperatures of 25 °C, 30 °C, 40 °C and 50 °C. All samples were constantly stirred at a stirring speed of 120 rpm and a fixed contact time of 90 min. While for the adsorption kinetic experiments, methylene blue solution was prepared with three different concentrations (25 mg/L, 50 mg/L, and 75 mg/L). The experiments were carried out at optimum conditions (0.20 g and pH 6 for PSB; 0.25 g and pH 7 for PT-PSB) and constantly stirred at a stirring speed of 120 rpm for 90 min at 25 °C. For both isotherm and kinetic studies, the model fitting's suitability was evaluated according to the correlation coefficient values (R^2).

RESULTS AND DISCUSSIONS

EFFECT OF SOLUTION pH

The effect of solution pH on the amount adsorbed of PSB and PT-PSB and the percentage removal efficiency of methylene blue from aqueous solution is depicted in Figure 2. The experiments were carried out at room temperature, in pH ranging between 3 and 10, by using 25 mg/L of methylene blue solution (100 mL), the adsorbent dosage of 0.2 g and a contact time of 90 min. The amount adsorbed of PSB and PT-PSB and the removal efficiency of methylene blue were increased significantly from pH 3 to 4 and then gradually stabilized until pH 9. The amount adsorbed of PSB and PT-PSB was recorded in the range of 10.9-12.1 mg/g and 10.7-12.4 mg/g, respectively. Meanwhile, the removal efficiency of methylene blue was achieved between 86.8-96.6% for PSB and 85.4-99.3% for PT-PSB.

The aqueous solution pH plays as one of the major factors that influence the adsorption process and active sites on the surface charge of adsorbent particles and methylene blue (Ahmad et al. 2020; Tang et al. 2017). At acidic pH conditions, the presence of excess H^+ ions creates a more positive charge on the adsorbent surface. This causes for repulsion of electrostatic forces between cationic methylene blue dye and the positively charged adsorbent surface, subsequently reducing the adsorption rate (Chahm, Martins & Rodrigues 2018). Furthermore, higher competition for adsorption on the adsorbent surface actives sites among H^+ ion and dye

cations contributes to the lower adsorption of methylene blue at lower pH acidic conditions. As the solution pH increases, the adsorbent surface becomes negatively charged, thus resulting in higher adsorption capacity due to the increase of electrostatic attractive forces. As can be seen in Figure 2, both PSB and PT-PSB showed the maximum amount adsorbed and the highest removal efficiency was simultaneously achieved at the optimum pH of 6 and 7, respectively. Thus, further investigation of adsorption experiments was carried out at these optimum pH conditions. No significant changes in the amount adsorbed and removal percentage for both PSB and PT-PSB were observed as the studied solution pH increases to pH 9. Chahm, Martins and Rodrigues (2018) and Shoukat et al. (2017) reported a decreasing trend of methylene blue adsorption at higher solution pH (pH > 9). Under alkali conditions, the increasing of hydroxyl groups in the solution causing for the competition of the adsorbent active site, thus causing the decreasing trend of the adsorption process.

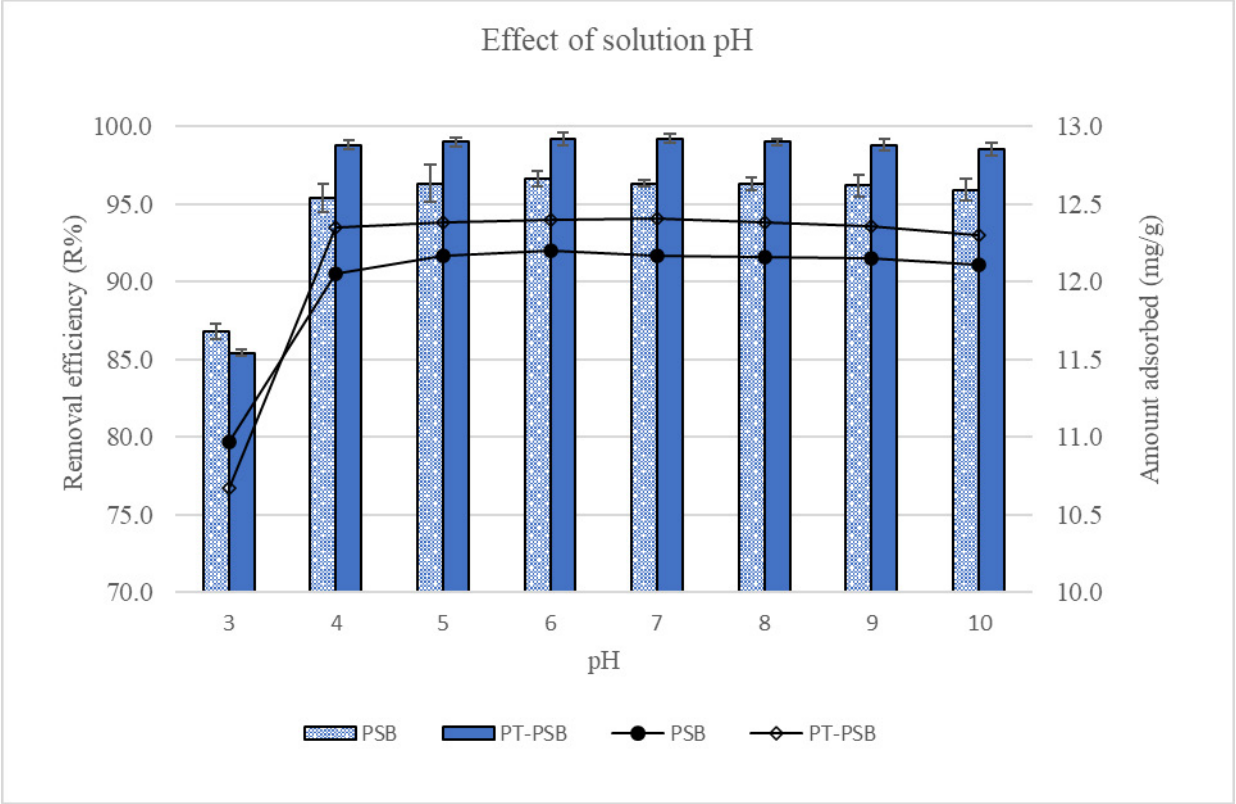


FIGURE 2. Effect of pH on removal efficiency and amount of methylene blue adsorbed for PSB and PT-PSB (0.2 g dosage, 25 mg/L methylene blue solution, contact time 90 min, room temperature)

EFFECT OF ADSORBENT DOSAGE

The effect of different dosages of PSB and PT-PSB (0.05 g to 0.30 g) on the amount adsorbed and the removal efficiency of methylene blue from the aqueous solution is presented in Figure 3. The solution pH was set at optimum pH of 6 for PSB and pH 7 for PT-PSB, respectively. The removal efficiency of methylene blue was increased with the increase of the amount of dosage and PT-PSB mostly exhibit higher removal percentage than PSB using the same dosage. Adding more adsorbent dosage would increase the potential surface areas and provides more accessibility to the active site for the adsorption site thus increasing the removal efficiency of the methylene blue (Da Silva et al. 2018).

Initially, the removal efficiency of methylene blue for both PSB and PT-PSB was drastically increased when the dosage was increased from 0.05 g to 0.10 g and continued to slightly increase with the increasing amount

dosage from 0.15 g to 0.30 g. This indicated that there were no significant changes in the removal efficiency when the quantity of the dose exceeded the critical amount since the adsorption of methylene blue reached equilibrium and saturation conditions. This observation was similarly described for the methylene blue removal using high-surface-area activated red mud (Hu & Gao 2017) and *Lagerstroemia indica* seed activated carbon (Kumar, Sivaprakash & Jayakumar 2017) where the percentage removal remained constant after the equilibrium achieved at a critical dosage quantity. As for this study, the highest removal efficiency of methylene blue was 97.7% and 99.4%, with the optimum dosage of 0.20 g and 0.25 g for PSB and PT-PSB, respectively.

In contrast, the amount adsorbed of PSB and PT-PSB gradually decreased as the dosage increased. At 0.05 g of dosage, the amount adsorbed of PSB was 45.2 mg/g and for PT-PSB was 42.5 mg/g, later reduced to about 8.1 mg/g at 0.30 g of dosage for both biochar. This could be attributed to aggregation of the adsorbents and particle interaction at a higher dosage subsequent to the reduction of the adsorption site, thus, resulting in a decrease in the amount of methylene blue adsorbed per unit mass of adsorbent (Abd-Elhamid et al. 2020).

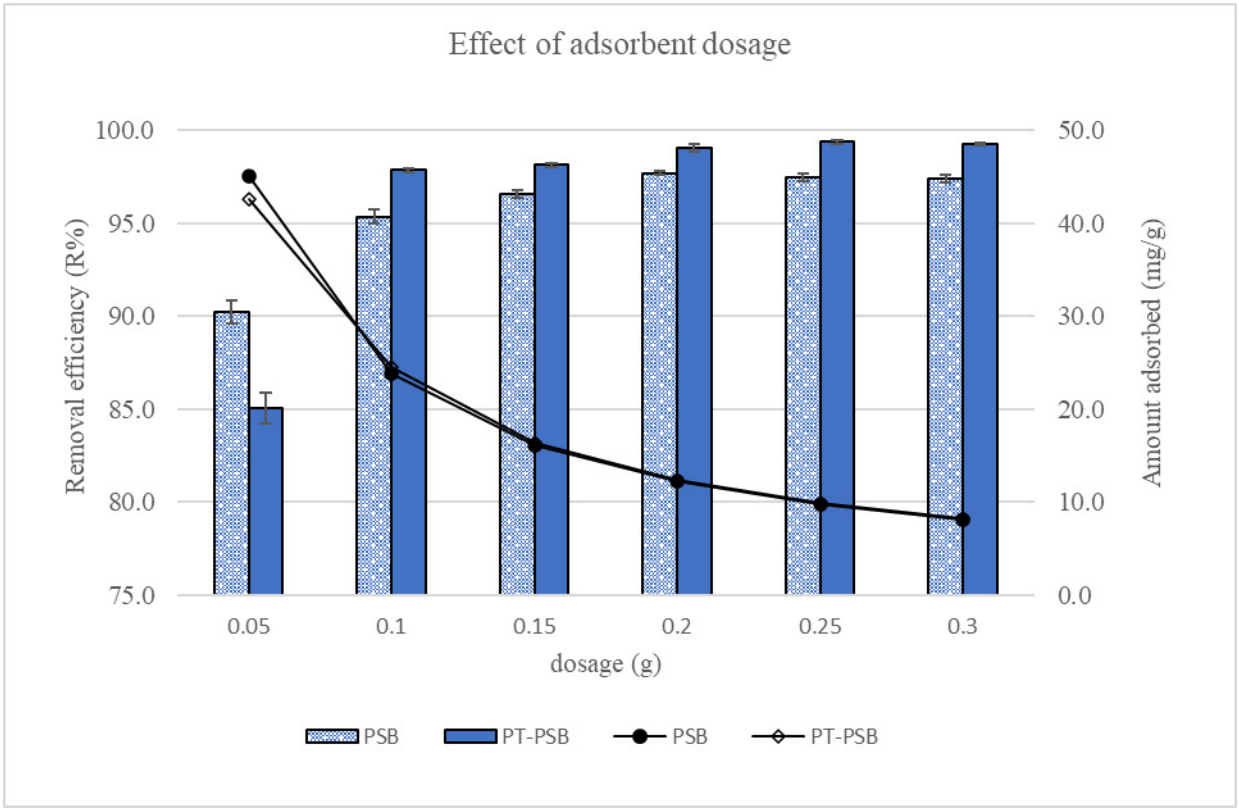


FIGURE 3. Effect of dosage on removal efficiency and amount of methylene blue adsorbed for PSB and PT-PSB (25 mg/L methylene blue solution, contact time 90 min, room temperature, pH 6 for PSB, pH 7 for PT-PSB)

EFFECT OF INITIAL CONCENTRATION

The initial concentration of adsorbate is another important factor that significantly influences the adsorption process. Figure 4 shows the effect of various initial concentrations of methylene blue solutions (25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 125 mg/L, and 150 mg/L) on the removal efficiency and the amount adsorbed by the PSB and PT-PSB. The batch experiment was performed using 0.20 g and 0.25 g dosages at pH solutions of 6 and 7 for PSB dan PT-PSB, respectively. It is observed that the removal efficiency was decreased from 96.4% to 91.7% for PSB and from 99.4% to 96.3% for PT-PSB with the further increase in the initial concentration of methylene blue solution from 25 mg/L to

150 mg/L. In contrast, the amount of adsorbed methylene blue increases from 12.1 mg/g to 68.8 mg/g for PSB and 12.4 mg/g to 72.2 mg/g for PT-PSB, when the methylene blue concentration increases as described. The optimum initial concentration for both biochars was achieved at 25 mg/L with the highest removal efficiency of 96.4% and 99.4% for PSB and PT-PSB, respectively. When the initial concentration of methylene blue increases, the limited availability of active sites was rapidly filled by the adsorbate, thus, causing the adsorption site on the adsorbent surface to become saturated. Consequently, the amount of adsorbed methylene blue increased with the increase of the dye concentration. Similar results were described earlier using activated red mud (Tang et al. 2017), magnetically activated biochar derived from wakame (Yao et al. 2020) and different biochar from three different plant feedstocks (Chen et al. 2019) that the removal efficiency of methylene blue was decreased with the increasing of methylene blue initial concentration. Additionally, a higher initial concentration of adsorbate provides a stronger driving force to overcome mass transfer resistance between adsorbent and aqueous solution (Khataee, Vafaei & Jannatkhah 2013). As a result, the removal efficiency of methylene blue decreases and the amount of dye adsorbed increases as the initial concentration of methylene blue increases.

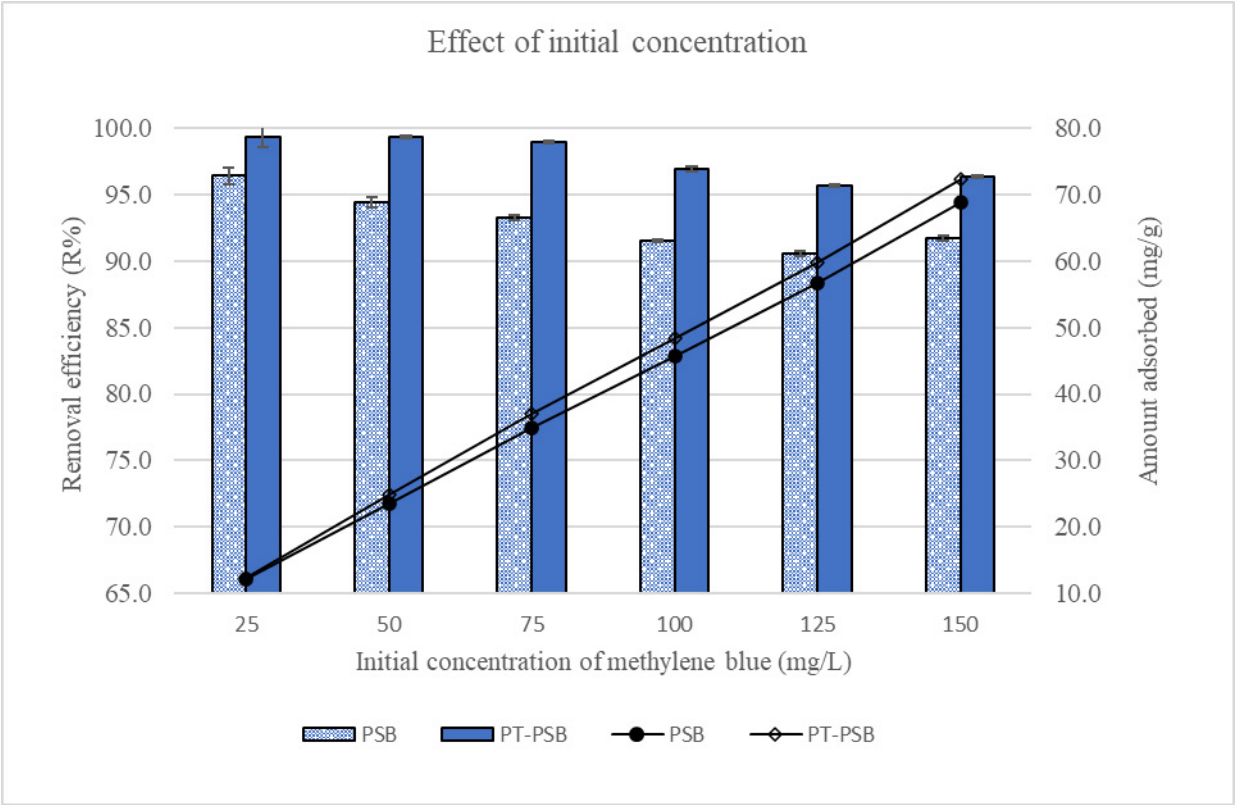


FIGURE 4. Effect of methylene blue initial concentration on removal efficiency and amount of methylene blue adsorbed for PSB and PT-PSB (Contact time of 90 min, room temperature, stirring speed 120 rpm, pH 6 and 0.20 g dosage for PSB, 0.25 g dosage and pH 7 for PT-PSB)

ADSORPTION ISOTHERM

Two recognized isotherm models; Langmuir and Freundlich were used to describe the equilibrium between the adsorption of methylene blue on the PSB and PT-PSB surface. Langmuir isotherms are usually applied to explain the monolayer adsorption process over the homogeneous surface, showing no interaction between adsorbed molecules existed (Amin 2009). The linear form of the Langmuir isotherm model is expressed as follows:

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

The value of K_L (L/mg) and q_{max} (mg/g) are indicated for the Langmuir constant (related to the energy of adsorption) and maximum adsorption amount, respectively. These two values were measured from the slope and intercept of the Langmuir plotting graph, $\frac{C_e}{q_e}$ versus C_e (Equation 3). C_e is the methylene blue concentration at equilibrium (mg/L) and q_e is the adsorption amount of methylene blue (mg/g). The Langmuir isotherm characteristics are confirmed to be favourable for the monolayer adsorption by the dimensionless separation factor, R_L as follows (Hu & Gao 2018):

$$R_L = \frac{1}{(1+ K_L C_0)} \quad (4)$$

where C_0 is the initial methylene blue concentration (mg/L). The value of R_L indicates 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 Freundlich isotherms are used to describe the multilayer adsorption on the heterogeneous surface and are expressed in a linearized form according to the following Equation (5) (Chen et al. 2018).

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (5)$$

From the Freundlich plotting graph, log q_e versus log C_e, the values of $\frac{1}{n}$ and K_F were determined from the slope and intercept of the graph. K_F is the Freundlich isotherm constant related to adsorption intensity ((mg/L)(L/mg)1/n) and $\frac{1}{n}$ is indicating the adsorption capacity. If $\frac{1}{n}$ = 1, the separation within the two phases is not dependent on the concentration. If the value of $\frac{1}{n} < 1$, it shows normal adsorption. If $\frac{1}{n} > 1$, it shows cooperative adsorption. Similar to the Langmuir model, C_e is the methylene blue concentration at equilibrium (mg/L) and q_e is the adsorption amount of methylene blue (mg/g).

The linearized plotting graph of Langmuir and Freundlich isotherms is shown in Figure 5 and isotherm parameters are listed in Table 1. Results showed that the adsorption capacity of methylene blue onto PSB dan PT-PSB significantly increased with the increase of methylene blue concentration. Nevertheless, there were no significant changes in the adsorption capacity of both PSB and PT-PSB when the temperature was raised, signifying the constant availability of the active adsorption site on the surface of the adsorbent (Liu et al. 2019). With the PSB adsorbent (Figure 5(a) and 5(b)), the correlation coefficient values (R^2) were recorded in the range of 0.8453-0.9794 and 0.9493-0.9901 for Langmuir and Freundlich isotherm, respectively. Meanwhile, the R^2 values of Langmuir isotherm are 0.8863-0.9952 and Freundlich isotherm is 0.9326-0.9924 for the PT-PSB biochar (Figure 5(c) and 5(d)). This shows that the adsorption isotherms were better fitted with the Freundlich model than the Langmuir model for PSB and PT-PSB, indicating the multilayer adsorption majorly contributes to the adsorption of methylene blue onto both adsorbent and biochar. Furthermore, the $\frac{1}{n}$ values are in the range of 0.554-0.698 and 0.418-0.549 for PSB and PT-PSB, respectively (Table 1). These results suggested the adsorption of methylene blue is favourable for both biochars. However, the adsorption of methylene blue on the PT-PSB surface is much easier than PSB and follows normal adsorption since the $\frac{1}{n}$ values are generally less than 0.5. The values of K_F and q_{max} also indicate better adsorption of methylene blue onto PT-PSB than PSB which corresponds to the obtained experimental data.

ADSORPTION KINETICS

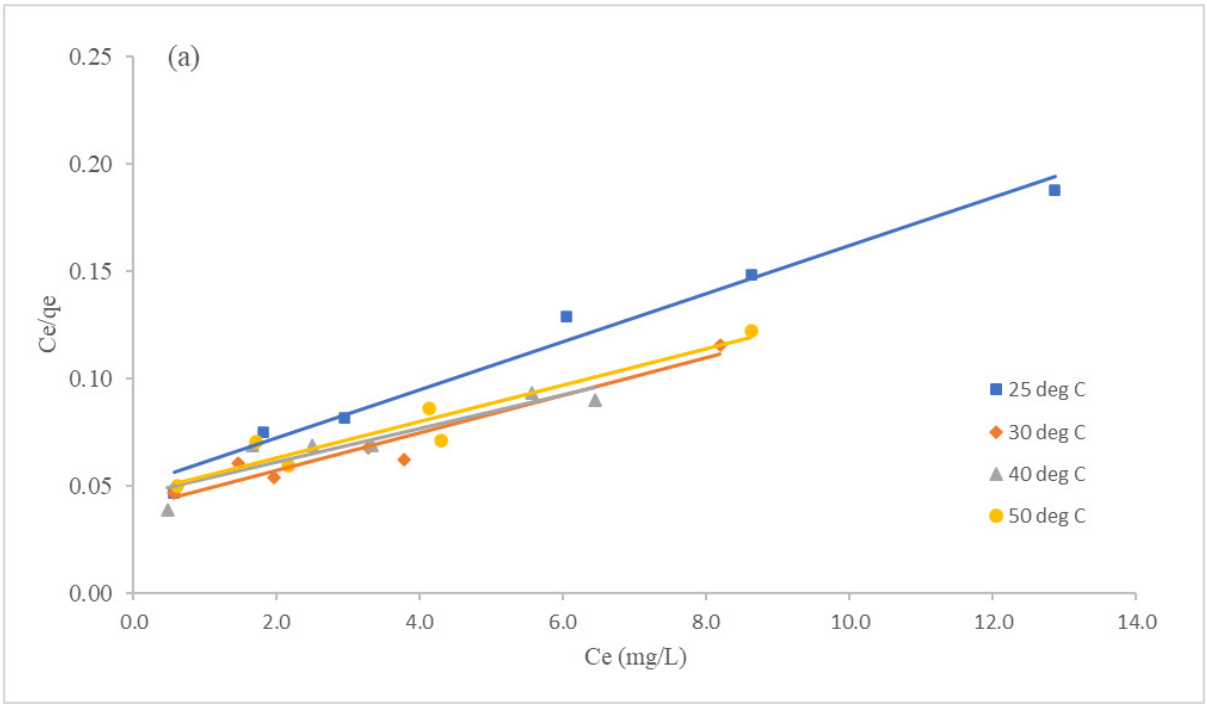
An adsorption kinetics study was conducted in order to predict the removal rate of methylene blue dye from an aqueous solution and to obtain related data for a better understanding of the adsorption reaction mechanisms. The kinetics of methylene blue dye adsorption was investigated using two common models, pseudo-first order (Equation 6) and pseudo-second order (Equation 7), as given in the following equations:

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

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

where q_e (mg/g) and q_t (mg/g) are the adsorption amount at equilibrium and time, respectively. The value of k_1 (g/(mg.min)) and k_2 (g/(mg.min$^{1/2}$)) are the first-order and second-order constants, respectively.

Figure 6 illustrates the fitting plots of ln (q_e - q_t) versus t for pseudo-first order and the plots of versus t for pseudo-second order of methylene blue adsorption on PSB and PT-PSB biochar with three different concentrations (25 mg/L, 50 mg/L, and 75 mg/L). The corresponding parameters for both kinetic models are summarized in Table 2. With PSB biochar, the correlation coefficient values (R^2) for pseudo-second order (ranging


(a)
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Ce (mg/L)
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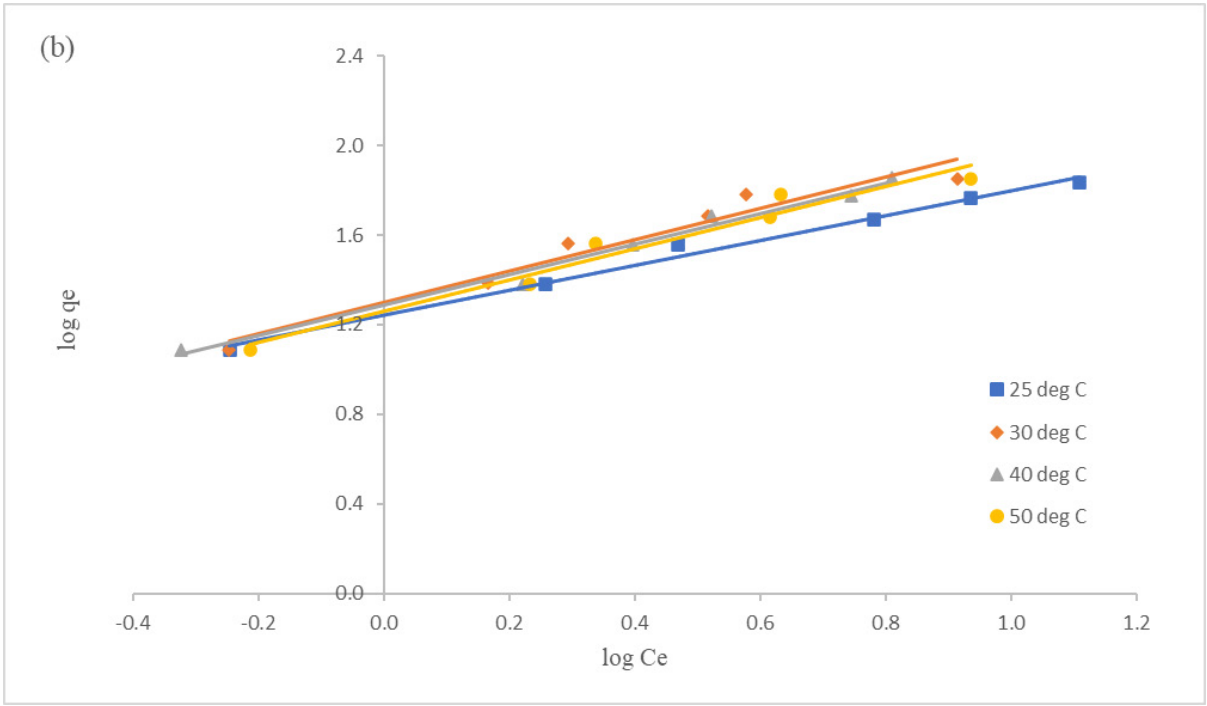
(b)
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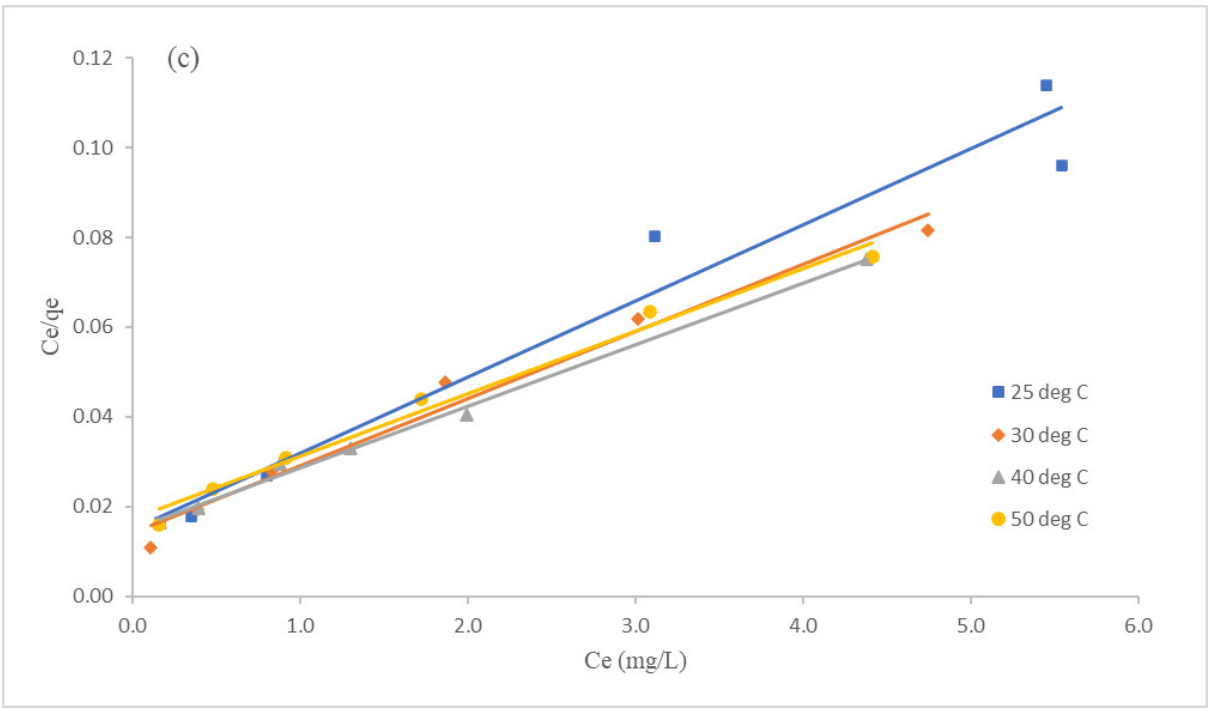
log Ce
25 deg C
30 deg C
40 deg C
50 deg C



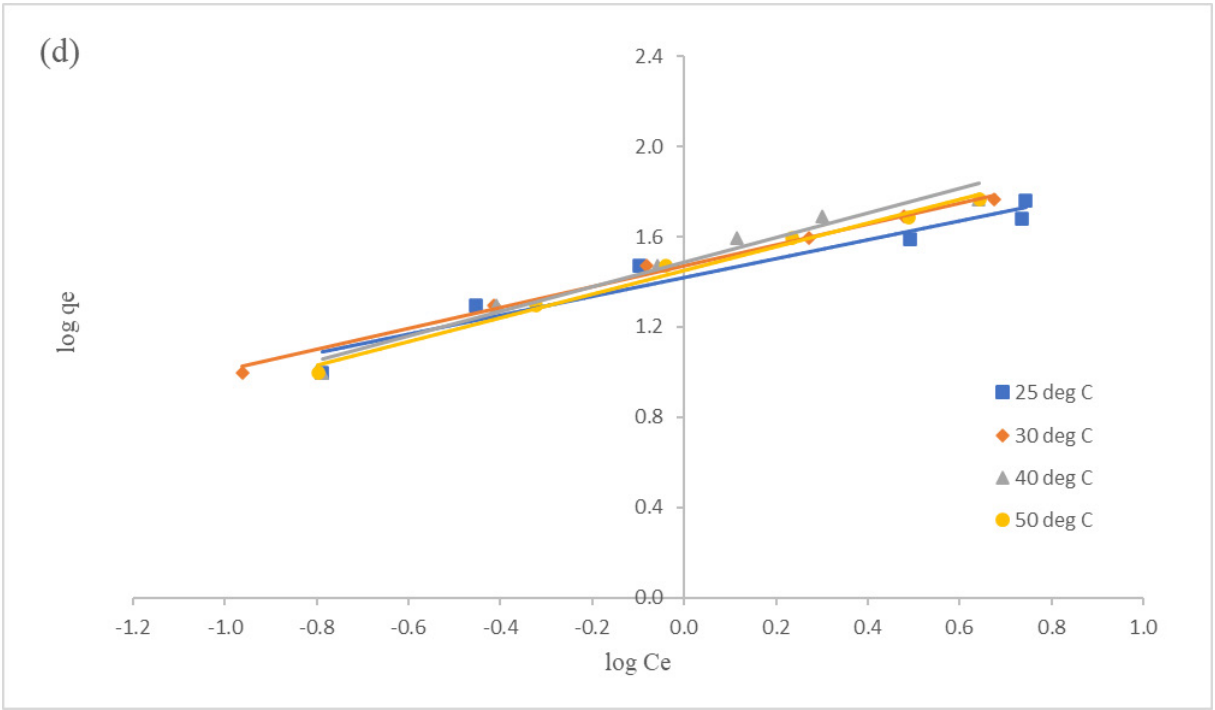
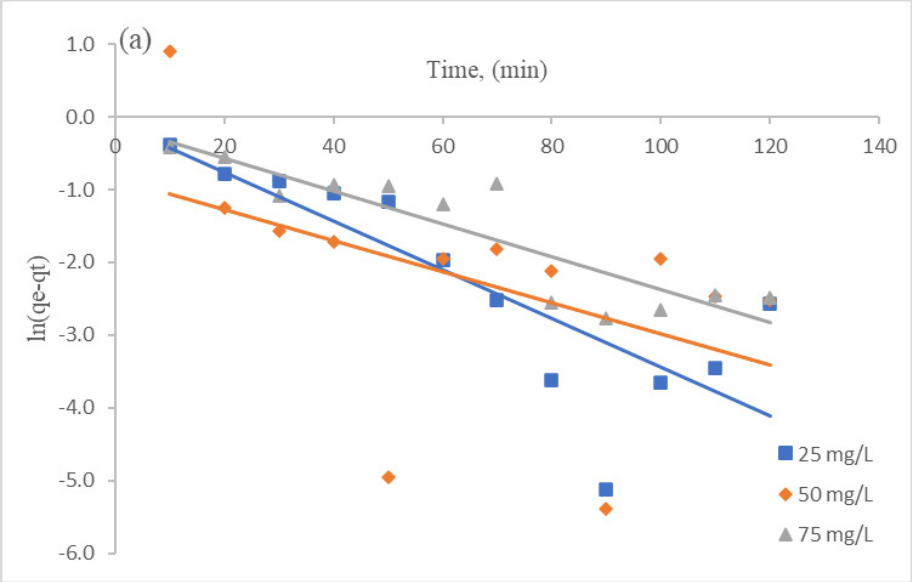
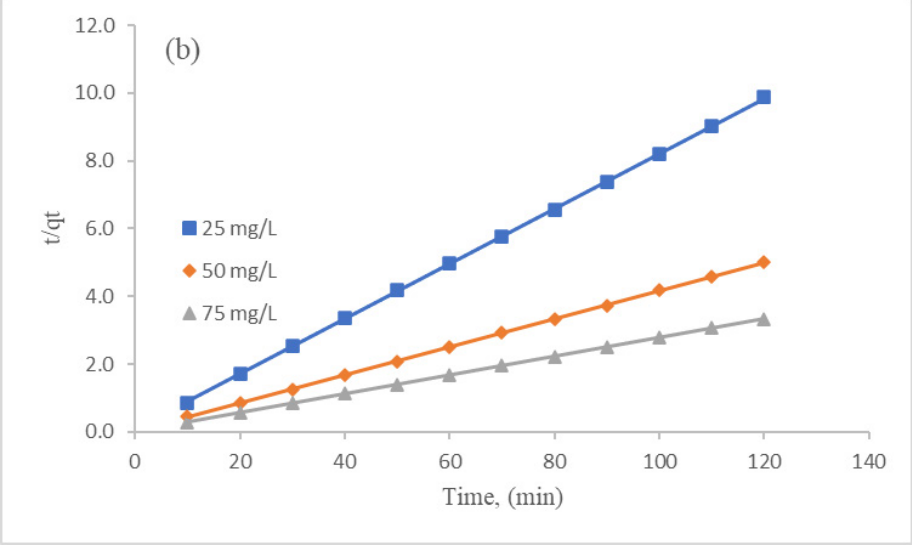


FIGURE 5. (a) Langmuir for PSB, (b) Freundlich for PSB, (c) Langmuir for PT-PSB, and (d) Freundlich for PT-PSB for adsorption of methylene blue

TABLE 1. Langmuir and Freundlich isotherm parameters for adsorption of methylene blue onto PSB and PT-PSB at various temperature

Biochar	Temperature (° C)	Langmuir				Freundlich		
		q_{max}	K_L	R_L	R^2	K_F	$1/n$	R^2
PSB	25	89.286	0.224	0.029	0.9794	17.547	0.554	0.9901
	30	113.636	0.222	0.029	0.9333	19.985	0.698	0.9493
	40	128.205	0.172	0.037	0.8453	19.436	0.681	0.9856
	50	117.647	0.184	0.035	0.9104	18.273	0.697	0.9582
PT-PSB	25	58.824	1.141	0.006	0.9314	26.430	0.418	0.9326
	30	66.667	1.056	0.006	0.9798	29.648	0.463	0.9924
	40	72.993	0.919	0.007	0.9952	30.761	0.549	0.9654
	50	71.429	0.814	0.008	0.8863	28.249	0.525	0.9887





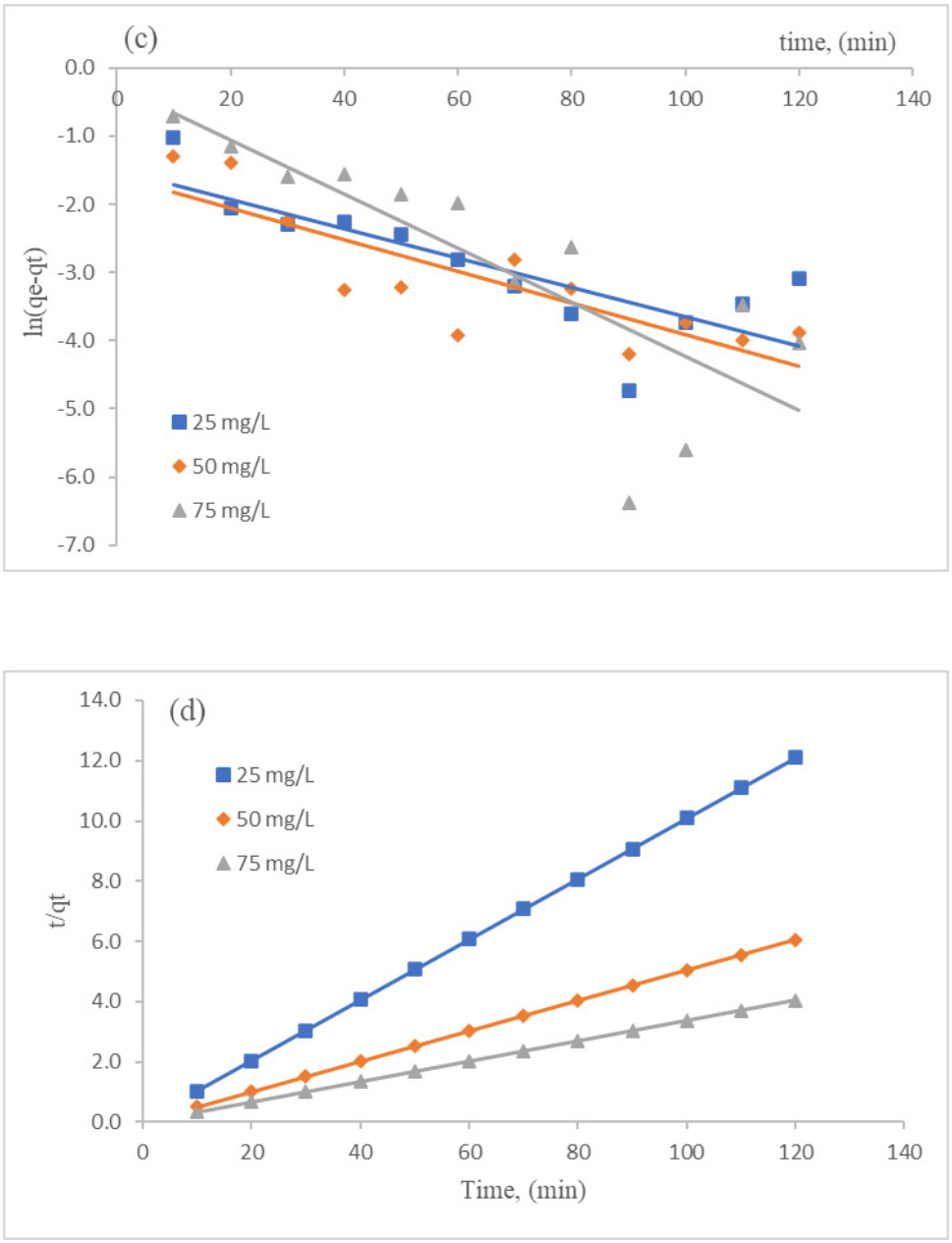


FIGURE 6. (a) Pseudo-first order for PSB, (b) Pseudo-second order for PSB, (c) Pseudo-first order for PT-PSB, and (d) Pseudo-second order for PT-PSB for the adsorption of methylene blue

0.998-0.999) were higher and nearly 1 as compared to the R^2 for pseudo-first order (ranging from 0.2227-0.7965). The pseudo-second order model showed the adsorption amount at equilibrium 12.300 mg/g, 24.155 mg/g, and 36.101 mg/g were closely to the experimental amount of 12.216 mg/g, 24.097 mg/g, and 36.030 mg/g, respectively. A similar trend was observed with PT-PSB biochar the pseudo-second order showed a higher R^2 value of 0.9999, while the pseudo-first order with R^2 values of 0.6481-0.7091. The calculated adsorption amount at the equilibrium of pseudo-second order model was 9.930 mg/g, 19.881 mg/g, and 29.762 mg/g, which were close to the experimental amount of 9.935 mg/g, 19.860 mg/g, and 29.680 mg/g, respectively. Therefore, it is suggested that the adsorption kinetics of methylene blue adsorption on PSB and PT-PSB were excellently fitted to

TABLE 2. Kinetic parameter of the adsorption of methylene blue on the PSB and PT-PSB

Biochar	Concentration of methylene blue (mg/L)	Pseudo-first order			Pseudo-second order		
		R^2	k_1 (min^{-1})	$q_{e,calc}$ (mg/g)	R^2	k_2 (min^{-1})	$q_{e,calc}$ (mg/g)
PSB	25	0.6719	0.034	1.091	0.9998	0.078	12.300
	50	0.2227	0.021	2.322	0.9998	0.085	24.155
	75	0.7965	0.023	1.119	0.9999	0.069	36.101
PT-PSB	25	0.6481	0.022	4.473	0.9999	0.308	9.930
	50	0.7091	0.023	4.937	0.9999	0.301	19.881
	75	0.6515	0.039	1.312	0.9999	0.121	29.762

pseudo-second order model. These results indicate that the overall adsorption of methylene blue on both adsorbents was mainly through the chemisorption mechanism (Aysan et al. 2016). Previous studies reported comparable adsorption kinetics of methylene blue using various adsorbents from different types of biomasses, rice husk (Ahmad et al. 2020), walnut shell (Tang et al. 2017), corncob (Choi & Yu 2019) and red mud (Hu & Gao 2018).

Conclusions

The utilization of low-temperature banana pseudostem biochar (PSB) and acid post-treated banana pseudostem biochar (PT-PSB) for the removal of methylene blue from an aqueous solution was investigated via batch adsorption experiments. At ambient room temperature, PT-PSB showed a higher removal efficiency of methylene blue as compared to PSB. The maximum removal efficiency of methylene blue with PT-PSB and PSB was achieved at pH 7 and pH 6 and adsorbent dosages of 0.25 g and 0.20 g, respectively. Both PSB and PT-PSB showed the same highest removal efficiency with the initial concentration of 25 mg/L. The adsorption experiments indicated the acid post-treated banana stem biochar demonstrated more effective removal of methylene blue from aqueous solution when compared to untreated banana stem biochar. The adsorption isotherm was determined by fitting the Langmuir and Freundlich models with the experimental data. Results showed that both PSB and PT-PSB were better fitted to the Freundlich isotherm model. The adsorption kinetics for both PSB and PT-PSB were excellently fitted to the pseudo-second order model, indicating the adsorption was majorly governed by chemical adsorption. In conclusion, the banana pseudostem is potentially to be used as a good alternative, efficient low-cost and commercially eco-friendly adsorbent for removal of methylene blue from aqueous solution.

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