Mangosteen Peel-Derived Hydrochar Prepared via Hydrothermal Carbonization for Methylene Blue Removal

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Abstract. Hydrothermal carbonization (HTC) arises as an improved carbonization step developed to enhance the carbon porosity and reduce the production cost by thermally treating feedstock under milder operating conditions. This work aimed to generate hydrochar from mangosteen peel (MPHTC) via hydrothermal carbonization for the removal of methylene blue from aqueous solution. In the study, hydrochar was synthesized at an optimized carbonization temperature (200 °C) with a production yield of 82.75% and a methylene blue removal of 75.93%. The adsorption capacity of adsorbent enhanced with the increasing initial dye concentration due to high driving force for efficient mass transfer. The hydrochar was capable of attaining its maximum adsorption capacity at 131.58 mg/g. The derived hydrochar performed a higher uptake of dye molecules under basic conditions rather than acidic conditions owing to the presence of OH group for the attachment of cationic dye. It was determined that Freundlich isotherm and pseudo second order kinetic models best fitted the experimental data. External film diffusion was found to be the rate-controlling step for the batch adsorption process. The results revealed that MPHTC is a promising adsorbent for treatment of cationic dye for effluent wastewater.

1. Introduction

Mangosteen fruit thrives well in a warm and humid climate as in Malaysia. It is primarily eaten in fresh and also available as food complements such as dessert, fruit jam, canned fruit, fruity flavour sweet and etc. However, its wide range implementations in food processing industries are deteriorated by the massive generation of peel and stem waste. According to Malaysian Ministry of Agricultural and Agro-Based Industry, for every kilogram of mangosteen harvested, approximately 0.6 kg of mangosteen peel waste is generated. Simply dumping of the peel wastes into the landfills can be avoided by transforming the fruit wastes into valuable product such as hydrochar. Synthesis of activated carbon derived from mangosteen peel wastes has been studied previously via conventional pyrolysis method or microwave radiation method. Previously, study done by Cheok et al. (2018) discovered that around 43% of mangosteen peels were utilized in synthesizing activated carbon (AC) in the non-food application [1]. For instance, Foo et al. (2012) has synthesized activated carbon from mangosteen peel via microwave assisted $\text{K}_2\text{CO}_3$ activation with a carbonization temperature of 700 °C [2]. The carbon yield of mangosteen peel-derived activated carbon is roughly 80.95% with a carbon content of 78.45%. The mangosteen peel-derived activated carbon has a BET surface area of 1098.75 m$^2$/g, an average pore size of 22.25 Å and a total volume of 0.611 cm$^3$/g. Besides, by using single step $\text{ZnCl}_2$ activation process, Nasrullah et al. (2019) has derived an activated carbon from mangosteen peel waste with BET surface

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area, average pore diameter and total pore volume of 1621.8 m²/g, 4.4 nm and 1.805 cm³/g, respectively [3]. However, a great consumption of cost and energy has been induced owing to high carbonization temperature or long carbonization time. Therefore, the improved carbonization step, hydrothermal carbonization, is introduced to generate hydrochar with enhanced porosity and surface area from biomass precursor at milder operating conditions. Also, to ensure the yield and performance of derived hydrochar despite of cost and energy savings, the optimization on carbonization temperature shall be carried out accordingly. The hydrothermal carbonization step is getting more attention in recent due to its capability to stabilize the macro-cellular structure of organic wastes before pyrolysis and result in carbons with higher mesoporosity [4]. However, the main challenge for the application of hydrothermal carbonization in the industrial plant is the availability of a continuous reactor that can be operated under high temperatures and pressures since, in most literatures, batch reactors are preferably applied [5]. The production of hydrochar from various agricultural wastes via typical hydrothermal carbonization has been studied extensively, for instance, coconut shell-derived hydrochar [6], coffee husk-derived hydrochar [7], modified bamboo hydrochar [8] and etc. These agricultural waste-derived hydrochar have proven their suitability as an adsorbent after activation owing to their excellent adsorption capacity when tested with dye solutions. The synthesized hydrochar from mangosteen peels must able to suit its application on industrial scale. One of the great interests on hydrochar is its capability in adsorbing dye particles from wastewater. In this work, we report on the mangosteen peel-derived hydrochar via hydrothermal carbonization and its removal capability on methylene blue. Hydrochar were then used to adsorb methylene blue, which known as a dye, to determine the functionalization of the product as an adsorbent. The effects of operating conditions such as initial dye concentration and solution pH on the performance of hydrochar in adsorbing dye solution are evaluated as well. The kinetic and isotherm of adsorption process will be determined by using available mathematical model.

2. Materials and Methods
The experimental procedures were adapted and modified on the basis of study done by Islam et al. (2017) where mangosteen peels hydrochar was synthesized, activated by NaOH (aq) and tested on methylene blue removal [6]. The raw material, mangosteen peel, was dried at room temperature and crushed into smaller pieces by using an electric grinder. The small particles were collected from the grinder. The collection was subjected to a combination of sieves with openings of 2 mm and 1 mm, respectively, to obtain particles with sizes ranging from 1 – 2 mm.

2.1 Characterization of Raw Materials
The characterization of raw mangosteen peel particles was determined based on ASTM D 3172 – 3175 standard method (ASTM, 1999). For moisture content, 5.0 g of clean and air-dried mangosteen peel powder was placed in a crucible covered with a lid and heated in an oven at 105 °C for 3 hours. After heating, the crucible was left to cool and the remaining sample was weighed. The difference in weights before and after heating corresponded to the moisture content of raw mangosteen peel.

\[
\text{Moisture Content (\%) = } \frac{W_0 - W_f}{W_0} \times 100\%
\]  

(Eq. 1)

where \(W_0\) = weight of sample before heating; \(W_f\) = weight of sample after heating.

2.2 Hydrothermal Carbonization
The hydrothermal treatment of mangosteen peel powder was conducted in a 100 ml stainless steel reactor. 5 g of mangosteen peel together with 50 ml of distilled water as reaction medium were added to the reactor and heated at 150 °C for 2 hours. After heating, the reactor content was allowed to cool to room temperature before subjected to filter paper for the removal of solid product from aqueous medium. Then, the obtained solid product was dried in an oven at 105 °C for 24 hours after thoroughly washing with distilled water for twice. The dried sample was weighed and the yield of hydrochar was calculated as formulated below:
Yield (%) = \( \frac{W_f}{W_0} \times 100\% \) \hspace{1cm} (Eq. 2)

2.3 Batch Adsorption of Methylene Blue

The 0.1 g of generated hydrochars using different carbonization temperatures were subjected to 100 ml of methylene blue solution at a concentration of 100 mg/L and neutral pH in 250 ml conical flasks, respectively. The conical flasks were then placed in a stirring water bath with a stirring speed of 100 rpm at room temperature for 3 hours. The UV-Vis spectrophotometer (Shimadzu UV-1601) was applied to determine the concentration of methylene blue solution at 15-minute time intervals based on its resulting absorbance. A concentration-time profile was generated for all hydrochar samples produced at varied temperatures and the respective removal efficiencies were determined after 3 hours of batch adsorption using the equation as stated below:

\[
\text{Removal Efficiency} (\%) = \frac{C_0 - C}{C_0} \times 100\% \hspace{1cm} (Eq. 3)
\]

where \( C_0 \) = initial concentration of methylene blue (mg/L); \( C \) = final concentration of methylene blue (mg/L).

0.2 g of samples from MPHTC were subjected to 200 ml of methylene blue solutions with varying concentrations of 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L at neutral pH in 250 ml conical flasks, respectively. The conical flasks were then placed in a stirring water bath with a stirring speed of 100 rpm at room temperature for 24 hours to attain equilibrium. The UV-Vis spectrophotometer was used to determine the concentration of methylene blue solution at time intervals by withdrawing the aqueous sample for measurement based on the resulting absorbance. The adsorption capacity (\( q \)) can then be computed as:

\[
q = \frac{V}{W} (C_0 - C) \hspace{1cm} (Eq. 4)
\]

where \( q \) = adsorption capacity (mg/g); \( V \) = volume of dye solution (L); \( W \) = weight of adsorbent (g); \( C_0 \) = initial concentration of methylene blue (mg/L); \( C \) = final concentration of methylene blue (mg/L).

Whereas, for the study on the effect of solution pH, similar experimental procedures were also applied on the chosen adsorbent by varying the pH of methylene blue solution at 3, 5, 7, 9 and 11 and keeping the solution concentration constant at 100 mg/L. The pH variations were done by the addition of 0.1 M of hydrochloric acid or 0.1 M of sodium hydroxide solution, accordingly. The weight of sample, volume of dye solution, stirring speed, contact time and contact temperature were held constant at 0.2 g, 200 ml, 100 rpm, 24 hours and room temperature, respectively. The adsorption capacity, \( q \), can then be computed using the similar equation as mentioned above.

2.4 Adsorption Isotherm, Kinetic and Mechanism

An adsorption isotherm is a curve relating the concentration of a solute on the surface of an adsorbent at equilibrium, \( q_e \), to the concentration of the solute in liquid phase, \( C_e \), with which it is in contact. Adsorption equilibrium is attained when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in dynamic balance with the interface concentration [2]. Adsorption isotherm is important in clarifying the interaction of adsorbates on the adsorbent surface and the surface phase may consider as monolayer and/or multilayer. Various models of equilibrium isotherm for adsorption process have introduced over the years and, among these developed models, Langmuir and Freundlich models serve as the most widely applied adsorption isotherms owing to their simplicity. To simplify the modelling application, the isotherm is further linearized into Equation (5):

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \hspace{1cm} (Eq. 5)
\]
where \( q_m \) and \( q_e \) (mg/g) are the adsorbate adsorbed per weight of adsorbent at saturation and equilibrium, respectively; \( C_e \) (mg/L) is the concentration of adsorbate in liquid phase at equilibrium; \( K_L \) (L/mg) is the Langmuir constant. The maximum adsorption capacity, \( q_m \), can then be deduced from the slope of plot between \( \frac{C_e}{q_e} \) and \( C_e \). On the other hand, the intercept of curve at vertical axis gives the Langmuir constant.

Meanwhile, linear form of Freundlich isotherm which assumes a multi-layer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface can be expressed into a natural logarithm equation as Equation (6):

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

(Eq. 6)

Adsorption kinetics is a quantification method in measuring the time-dependent adsorption uptake at a constant pressure or concentration and being employed to study the diffusion of adsorbates through pores. There are two most common models being applied to evaluate the dynamics of adsorption process by hydrochar which pseudo first order and pseudo second order.

\[\text{2.4.1 Pseudo First Order Kinetic Model}\]

A pseudo first order reaction can be defined as a second order reaction that behaves in a manner of first order reaction. It is the most widely utilized kinetic model in describing the adsorption of solute from aqueous solution and well-known as Lagergren model. The rate expression of pseudo first order kinetic model is highly based on the adsorption capacity of an adsorbent and may be written as Equation (7):

\[
\frac{dq}{dt} = k_1(q_e - q)^2
\]

(Eq. 7)

After the integration of differential equation with respect to time (t), the non-linear and linear relationship for the kinetic model can be expressed as Equation (8) and (9), respectively.

\[
q_t = q_e(1 - e^{-k_1 t})
\]

(Eq. 8)

\[
\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t
\]

(Eq. 9)

where \( q_e \) and \( q_t \) (mg/g) are the amount of sorbate molecules adsorbed at equilibrium and at any time instant, respectively; \( k_1 \) (min\(^{-1}\)) is the adsorption rate constant for pseudo first order kinetics. The slope of curve explaining the relationship between \( \ln(q_e - q_t) \) and \( t \) gives the desired rate constant (\( k_1 \)).

\[\text{2.4.2 Pseudo Second Order Kinetic Model}\]

A reaction with molecularity greater than two but only involves two molecules in the rate determining step is termed as pseudo second order reaction. The kinetic model is developed based on the adsorption capacity of solid phase and its differential equation may be expressed as Equation (10):

\[
\frac{dq}{dt} = k_2(q_e - q)^2
\]

(Eq. 10)

The integrated form of pseudo second order kinetic model can hence be written as Equation (11) and (12), respectively:

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t}
\]

(Eq. 11)
\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \tag{Eq. 12}
\]

where \(q_e\) and \(q_t\) (mg/g) are the amount of sorbate molecules adsorbed at equilibrium and at any time instant, respectively; \(k_2\) (min\(^{-1}\)) is the adsorption rate constant for pseudo second order kinetics. The adsorption capacity of model at equilibrium can be computed from the slope of \(t/q_t\) versus \(t\) and the adsorption rate constant is then deduced from the intercept at vertical axis.

Instead of solely explaining the solute-surface interactions of an adsorption process as kinetic model does, adsorption mechanism illustrates the diffusion, either inter-particle or intra-particle, process between solutes and adsorbents [9]. Therefore, it is useful to determine the rate-controlling step involved in an adsorption process with the application of diffusion models. In the study of dye adsorption, two most commonly used models are Weber-Morris intraparticle diffusion model and Boyd model.

### 2.4.3 Weber-Morris Model

Weber-Morris model suggests that the dynamic of adsorption process generally consists of three sequential steps which are: (i) diffusion of adsorbate from bulk solution to surface of adsorbent (film diffusion); (ii) transport of adsorbate through the pores of adsorbent at external surface (intraparticle diffusion); and (iii) sorption of adsorbate on pores’ interior surface of adsorbent [10]. The mathematical expression of Weber-Morris model is written as Eq. 13:

\[
q_t = k_{id}t^{1/2} + C \tag{Eq. 13}
\]

where \(q_t\) (mg/g) is the adsorption capacity at any time instant, \(t\) while \(k_{id}\) (mg/g.min\(^{1/2}\)) is the intraparticle diffusion rate constant and \(C\) is the intercept.

### 2.4.4 Boyd Model

Boyd model is normally applied to distinguish the rate-limiting factor, either film diffusion or intraparticle diffusion, by assuming the resistance on adsorption is concentrated at the boundary of adsorbent particle [10]. The model is represented by mathematical expressions as shown:

\[
F = \frac{q_t}{q_e} = 1 - \left(\sum_{n=1}^{\infty} \frac{1}{n^2} \right) e^{-n^2 B_t} \tag{Eq. 14}
\]

\[
B_t = -0.4977 - \ln(1-F); \quad F > 0.85 \tag{Eq. 15}
\]

\[
B_t = \left(\sqrt{\pi} - \left(\pi - \frac{\pi^2 F}{3}\right)\right)^2; \quad F < 0.85 \tag{Eq. 16}
\]

where \(F\) is the fractional attainment of equilibrium at different times, \(t\) while \(q_e\) and \(q_t\) (mg/g) are the adsorption capacities at equilibrium and at any time instant, \(t\), respectively with \(B_t\) as Boyd constant.

### 3. Result and Discussion

#### 3.1 Synthesis of Hydrochar

Multiple hydrochars derived from similar precursor, mangosteen peel, were generated at varied temperatures ranging from 150 °C to 200 °C. Whereas, other important parameters such as water to biomass ratio and carbonization time were kept constant during hydrothermal carbonization. Two parameters were applied to compare for the optimum carbonization temperature of hydrochar production, which are hydrochar yield and methylene blue removal efficiency of hydrochar.

#### 3.1.1 Hydrochar Production Yield

Generally, the yield of mangosteen peel-derived hydrochar decreased from 89.71% to 82.75% with increasing carbonization temperature owing to a greater extent of biomass dissolution at higher temperatures as illustrated in Table 1. A similar trend can be observed from the findings of previous studies by [11] and [12]. In fact, a satisfactory hydrochar production yield (>80%) was attained at every...
studied temperature as compared to that derived from sugarcane bagasse (47.75%), hickory (54.60%) and peanut hull (50.55%) at 200 °C [11]. The relatively low initial moisture content (2.2%) of the feedstock observed from this study also contributed to the high production yield of hydrochar as a result of higher solid contents which is in-line with the previous work by [13]. According to Fakkaew et al. (2015), the solubility of feedstock and intermediate products is increased with the presence of high water content which acts as a solvent, thus, producing less hydrochar [14]. Eventually, the resulting yield has minimum impact on the selection of optimum carbonization temperature for the hydrochar production because of minor range being observed.

Table 1. Production yield of hydrochar at varied carbonization temperatures

| Carbonization Temperature (°C) | Initial Weight (g) | Final Weight (g) | Yield (%) |
|--------------------------------|--------------------|------------------|-----------|
| 150                            | 5.0082             | 4.4930           | 89.71     |
| 160                            | 5.0087             | 4.4275           | 88.40     |
| 170                            | 5.0094             | 4.3823           | 87.48     |
| 180                            | 5.0080             | 4.2565           | 84.99     |
| 190                            | 5.0063             | 4.2012           | 83.92     |
| 200                            | 5.0057             | 4.1422           | 82.75     |

3.1.2. Methylene Blue Removal

The removal of methylene blue by hydrochars carbonized at varied temperatures, ranging from 150 °C to 200 °C, is illustrated in Figure 1. A positive correlation was observed and the maximum removal capability was postulated by raw hydrochar generated at 200 °C with an efficiency of 75.93%. The performance of hydrochar derived from mangosteen peel on methylene blue removal is appreciable as compared to those produced from coconut shell (20.5%) and factory-rejected tea (52.4%) under similar adsorption conditions [6], [9]. The findings are in consistent with the demonstration of best adsorption performance on methylene blue by sewage sludge-derived hydrochar carbonized at 190 °C and 220 °C by [15]. However, the studies by Arellano et al. (2016) have shown a contradicting result where an inverse relationship being established [16]. Commonly, the surface area and pore volume of pyrolysis char display a proportional relationship with its production temperature [17]. According to Fang et al. (2015), hydrochar being produced at 200 °C has the highest surface area and pore volume regardless of feedstock [11]. Thus, the increasing trend of methylene blue removal is further supported as the higher surface area and pore volume increases the adsorptive capacity of hydrochars [18]. In short, the hydrochar carbonized at 200 °C was therefore selected as the best adsorbent for the following studies owing to its appreciable production yield and high removal capability.
3.2. Effect of Initial Methylene Blue Concentration

Adsorption of methylene blue by mangosteen peel-derived hydrochar was studied by subjecting an adsorbent dosage of 1.0 g/L to dye solutions with varying initial concentrations from 50 mg/L to 250 mg/L at neutral pH and 30 °C. The manipulation of initial concentrations aids in determining the suitability of hydrochar applications in various conditions and developing cost-effective process. The time-dependent interactions and uptake of methylene blue were illustrated in Figure 2. At the initial stage of adsorption, the availability of more active sites on the surface of hydrochar promotes a rapid uptake of adsorbates. The scenario is well-represented by steeper curves observed at the first 15 minutes for every studied initial concentration as shown in Figure 2. With the passage of time, the sites are gradually occupied through the competitive adsorption of dye molecules and few vacant sites are retained [6]. Therefore, the adsorption of methylene blue becomes slower until the equilibrium is attained. Also, the maximum adsorption capacity of hydrochar increased from 50.44 mg/g to 128.44 mg/g with the increasing initial concentration of methylene blue solution, ranged from 50 mg/L to 250 mg/L. The uptake of sorbate molecules seems to occur more readily at high initial concentrations owing to the presence of higher driving force required for the mass transfer of dye molecules. In addition, it can be noticed that a longer equilibrium time was required for solutions with high initial concentrations. The adsorption equilibrium was attained at 23rd hour for the highest initial concentration (250 mg/L) whereas, for the lowest initial concentration (50 mg/L), it was achieved at 5th hour. This is due to the fact that at the final stage of adsorption, most of the sorbate molecules diffuse into the porous structure of hydrochar as the adsorbent surface is saturated. The diffusion mechanism enhances the mass transfer resistance to the adsorption, and thus relatively longer contact time is necessary for high initial concentrations to achieve equilibrium with the adsorbent. The result is in agreement with the findings reported by Islam et al. (2015a) on adsorption by palm date seed-derived hydrochar [9].
3.3 Effect of Solution pH
In an aqueous solution, the solution pH has a significant impact on the adsorption process owing to its influence on surface chemistry as well as surface charge. To examine the effect of solution pH on methylene blue adsorption, 1.0 g/L dosage of hydrochar was subjected to 100 mg/L dye solution at varied initial pH ranging from pH 3 to pH 11 at 30 °C. The pH value was altered by the addition of hydrochloric acid or sodium hydroxide solution accordingly and the time-dependent adsorption profile was depicted as illustrated in Figure 3. The explanation on adsorption profile with sharp increment at the beginning stage and gradually flattened curves is identical to the discussion for effect of initial dye concentration. Similar to the study on effect of initial methylene blue concentration, the adsorption performance improved with contact time until the equilibrium state was attained. The uptake of dye molecules was relatively low under extremely acidic condition as hydrochar recorded the lowest adsorption capacity at equilibrium with a value of 60.89 mg/g. This is because the methylene blue dye molecules which are cationic in nature generates a strong electrostatic repulsion on the surface of hydrochar with high concentration of H⁺ ions under acidic environment. In addition, according to Islam et al. (2017), the presence of OH groups on hydrochar surface triggers the protonation of OH group and creates a competition between H⁺ ions and dye molecules to bind with the active sites, leading to a low uptake of sorbate molecules [6]. The adsorption capacity-time curves explained that the adsorption increased from acidic to basic condition with a maximum equilibrium adsorption capacity of 96.89 mg/g achieved at pH 11. In opposition to acidic solution, a raising solution pH enhanced the negatively-charged active sites in the presence of OH groups on the adsorbent surface and improved the adsorption performance. However, it can be noticed that there was no significant increment in adsorption capacity for solutions with pH 5 to pH 9. Similar phenomenon has been reported in the literatures of previous studies [3], [19]. It can be well explained that the H⁺ and OH⁻ ions are nearly balanced within these three pH values, and therefore no noticeable competitions being observed.
Figure 3. Methylene Blue uptake of MPHTC at different solution pH

3.4 Adsorption Isotherms
The adsorption isotherms describe the relation between the concentration of dye (adsorbate) molecules in aqueous phase and the degree of adsorbed molecules on adsorbent surface at equilibrium under constant temperature. To determine the interaction of adsorbed molecules on adsorbent surface, Langmuir (Equation 5) and Freundlich isotherms (Equation 6) were applied as the mathematical model on the experimental data. Equation 5 and 6 suggest the linearized form of mathematical expressions for Langmuir and Freundlich isotherms, respectively. Figure 4 depicts the graphical representation for both models based on their corresponding linear equations. To compare the analyses of both isotherms accurately, two statistical measures, namely R-squared ($R^2$) value and root mean square error (RMSE), were applied. The isotherm constants were tabulated along with the statistical measures as shown in Table 2. To ease the comparison of both isotherms, a combined non-linear plot for the experimental and theoretical data of the adsorption isotherms was plotted in Figure 4. From the tabulated result, it can be noticed that the maximum adsorption capacity, $q_m$, computed from Langmuir isotherm is close to the experimentally determined value (128.44 mg/g). Besides, the value of $1/n$ (0.1915) from Freundlich isotherm has proven that the adsorption process for methylene blue-hydrochar system is favourable as it is much lesser than unity [6]. In terms of regression coefficient, the experimental data has shown a good fitting to both models with values approaching unity ($R^2 > 0.99$). However, when comparing the resultant errors of root-mean square, Freundlich isotherm exhibits a relatively low RMSE which is highly preferable. The RMSE values are in consistent with the non-linear plot as shown in Figure 5. This is because the curve representing Freundlich isotherm is closer to the experimental data at every studied equilibrium concentration than that of Langmuir isotherm. Therefore, based on the non-linear statistical analysis result, it can be deduced that the system correlates better with Freundlich isotherm model. Coincidently, the findings are in agreement with the previous studies by other researchers, which reported that methylene blue adsorption showed a better fit for Freundlich isotherm as compared to Langmuir isotherm [9]. These studies suggested that the existence of some heterogeneity on adsorbent surfaces or pores were accounted for methylene blue adsorption.
Table 2. Adsorption isotherm parameters for methylene blue adsorption on MPHTC

| Isotherm        | Parameters                      | Values         |
|-----------------|---------------------------------|----------------|
| Langmuir        | $q_m$ (mg/g)                    | 131.58         |
|                 | $K_L$ (L/mg)                    | 0.1974         |
|                 | $R^2$                           | 0.9968         |
|                 | RMSE                            | 16.20          |
| Freundlich      | $K_F$ ((mg/g).(L/mg)$^{1/n}$)   | 52.59          |
|                 | $1/n$                           | 0.1915         |
|                 | $R^2$                           | 0.9938         |
|                 | RMSE                            | 3.17           |

Figure 4. Isotherm linear plots Langmuir isotherm [a] and Freundlich Isotherm [b] for methylene blue uptake of MPHTC
Figure 5. Non-linear plot of adsorption isotherms for methylene blue uptake of MPHTC

3.5 Adsorption Kinetics
The two mostly applied kinetic models, namely, pseudo first order and pseudo second order kinetic models, were utilized to evaluate the adsorption kinetics of methylene blue-hydrochar system at various dye concentrations. The mathematical expressions, linearized and non-linearized form, of both kinetic models were stated as in Equation 8, 9, 10 and 11. The statistical measures such as regression coefficient ($R^2$) and standard deviation ($\sigma$) were used to examine the goodness of fit for the studied kinetic models on experimental data. The computed kinetics data from the mathematical models was tabulated along with the statistical parameters as shown in Table 3. Both linear and non-linear plots of kinetic models can be found as in Figure 6 and Figure 7, respectively. Based on the linear fitting results of the kinetic models, the kinetic equation of pseudo second order model (Figure 6 [b]) established a higher correlation coefficient ($R^2$) and lower standard deviation ($\sigma$) than that of pseudo first order model (Figure 6 [a]) at every measured concentration. The maximum $R^2$ value (0.9999) and minimum standard deviation (7.77) were both observed from pseudo second order model at the lowest studied concentration (50 mg/L). Also, with referring to the non-linear plot, it can be clearly spotted that the dotted-lines representing pseudo first order model were totally out of the range of experimental data. Therefore, it can be justified that pseudo second order kinetic model expressed the kinetics data of methylene blue adsorption on mangosteen peel-derived hydrochar in a better quality. Unlike boundary diffusion-controlled adsorption as suggested by pseudo first order model, the pseudo second order model proposes the governing of adsorption rate by chemisorption which includes the complex adsorption reactions such as film diffusion, surface adsorption and intraparticle diffusion [10]. The identical trend can be observed in the adsorption profiles of methylene blue-hydrochar system. Eventually, either theoretically or practically, the pseudo second order kinetic model has shown a good agreement with the dynamics of methylene blue adsorption. Multiple findings proposed by previous researchers for the kinetic study of methylene blue adsorption by various hydrochars were in-line with the results obtained, such as coconut shell-derived hydrochar [6], rice straw-derived hydrochar [20] and sewage sludge-derived hydrochar [15].
Table 3. Adsorption kinetics parameters for methylene blue adsorption on MPHTC

| Parameters          | $C_0$(mg/L) | 50   | 100  | 150  | 200  | 250  |
|---------------------|-------------|------|------|------|------|------|
| $q_{exp}$ (mg/g)    |             | 50.44| 89.11| 110.89| 120.00| 128.44|
| $q_{cal}$ (mg/g)    |             | 21.67| 55.51| 68.87| 72.87| 82.91|
| $k_1$ (min$^{-1}$)  |             | 0.0076| 0.0078| 0.0067| 0.0069| 0.0074|
| $R^2$               |             | 0.8949| 0.9563| 0.9762| 0.9674| 0.9821|
| $\sigma$            |             | 66.08| 49.15| 51.88| 53.12| 48.14|

Pseudo First Order

| $q_{cal}$ (mg/g)    |             | 51.81| 92.59| 114.94| 125.00| 135.14|
| $k_2$ (g/mg.min)    |             | 0.0005| 0.0002| 0.0001| 0.0001| 0.0001|
| $R^2$               |             | 0.9999| 0.9994| 0.9987| 0.9985| 0.9983|
| $\sigma$            |             | 7.77| 13.32| 17.17| 17.30| 17.40|

Pseudo Second Order

Figure 6. Kinetics linear plots pseudo-first order [a] and pseudo-second order [b] for methylene blue uptake of MPHTC
3.6 Adsorption Mechanisms

Unlike the kinetic studies focusing on solute-surface interaction during adsorption process, the adsorption mechanism helps on the understanding of step-by-step diffusion mechanism and rate-controlling step that affects the adsorption kinetics. The experimental results were fitted to Weber-Morris model intraparticle diffusion model and Boyd diffusion model. The equations from 13 through 16 have represented the essential mathematical expressions required for both diffusion models. As shown in Figure 8, the methylene blue adsorption by mangosteen peel-derived hydrochar was separated into three phases, which were coincidently in agreement with the three-step theoretical adsorption proposed by Weber-Morris model. According to Weber-Morris model, the dye molecule diffused through the bulk liquid phase to the adsorbent surface at the beginning stage [10]. A relatively low resistance resulted a quick adsorption rate and steep increment. The resistance increased for the diffusion of molecules from adsorbent surface to the active sites on inner surface owing to the saturation of external surface [10]. Therefore, the rate adsorption deceased at the second stage. In the final stage, the adsorbent was saturated, the adsorption process tended to be balanced and process equilibrium was said to be achieved at this stage. However, the plots of Weber-Morris model do not seem to be linear throughout the time range. Thus, the intraparticle diffusion step was not the only rate-controlling step of the adsorption process and other adsorption mechanisms exhibited [10].

Whereas, a plot of Boyd constant ($B_t$) versus time ($t$) was plotted as shown in Figure 9 to illustrate the fitting of experimental data on Boyd diffusion model. In fact, Boyd model was commonly used to determine the rate-limiting step of adsorption process, either film diffusion or intraparticle diffusion [9]. According to Boyd diffusion model, it suggests that the resistance on adsorption process is concentrated at the boundary of adsorbent particle. Based on Figure 9, it can be noticed that the model fitting lines didn’t show a good agreement with the experimental data. Also, all the fitting lines didn’t seem to pass through the origin as proposed by Boyd model. Thus, it can be concluded that the film diffusion exhibited as the adsorption rate-controlling step in the methylene blue-hydrochar system [10]. A similar methylene blue adsorption mechanism was also reported by Li et al. (2016) using activated carbon prepared from sugar beet pulp as adsorbent [10].
3.7 Comparison of Biomass Based Hydrochar on Adsorption of Methylene Blue

Table 4 depicts the maximum adsorption capacity of methylene blue for mangosteen peel based hydrochar and hydrochars produced from other biomasses such as rice straw [20], coffee husk [7], hickory [11], peanut hull [11], walnut shell [21], chilli seed [22], sewage sludge [15] and wastewater sludge [23]. The comparison illustrated that the hydrochar generated from mangosteen peel in the present work has a relatively higher adsorption capacity of methylene blue as compared to other hydrochars derived from various sources. Also, the synthesis conditions of the present work were comparatively milder in terms of carbonization temperature and time which, in turns, indicated a cost- and energy-effective process. The results serve as a reference for further development of hydrochar including activation, composite manufacturing and etc. to enhance the functionalization of hydrochar as a powerful and marketable adsorbent.
Table 4. Comparison of maximum methylene blue adsorption capacity for MPHTC and other biomass based hydrochars

| Source of Raw Hydrochar | Synthesis Conditions | $q_m$ (mg/g) | Reference |
|-------------------------|----------------------|-------------|-----------|
| Cellulose (Rice Straw)  | 180 °C; 20 hours     | 100.0       | [20]      |
| Coffee Husk             | 210 °C; 2 hours      | 34.9        | [7]       |
| Hickory                 | 200 °C; 6 hours      | 34.5        | [11]      |
| Lignin (Rice Straw)     | 180 °C; 20 hours     | 40.0        | [20]      |
| Peanut Hull             | 200 °C; 6 hours      | 38.4        | [11]      |
| Walnut Shell            | 180 °C; 24 hours     | 82.0        | [21]      |
| Wastewater Sludge       | 260 °C; 1 hour       | 63.3        | [23]      |
| Chilli Seed             | 215 °C; 2 hours      | 53.2        | [22]      |
| Sewage Sludge           | 190 °C; 3 hours      | 70.5        | [15]      |
| Mangosteen Peel         | 200 °C; 2 hours      | 131.6       | Present Work |

4. Conclusion
Mesoporous hydrochar has been successfully synthesized from mangosteen peel waste via hydrothermal carbonization at a relatively shorter time and lower temperature as compared to that of pyrolysis. Increasing carbonization temperature was able to, simultaneously, decrease the hydrochar production yield but enhance the methylene blue removal. Hydrochar being carbonized at 200 °C has been chosen as the studied adsorbent owing to its better performance on methylene blue removal (75.93%) and satisfactory production yield (82.75%). A higher uptake of dye molecules was shown in dye solution with higher initial concentration. The maximum adsorption capacity of MPHTC was determined as 131.58 mg/g. The methylene blue-hydrochar system required a longer contact time to attain its equilibrium state at high initial concentration. Derived hydrochar has demonstrated a comparatively greater performance on methylene blue adsorption under basic conditions rather than that under acidic conditions. The hydrochar was found to exhibit the highest adsorption capacity in solution at pH 11 under similar operating conditions. Langmuir isotherm and pseudo second order kinetic models were both favourably selected to describe the kinetic and equilibrium data of the system. In addition, external film diffusion step has been confirmed as the adsorption rate-controlling step of the system with the application of Weber-Morris and Boyd diffusion models. These exhibited results have proven the potential of low cost agricultural waste (mangosteen peel) to serve as a good adsorbent for the removal of synthetic dyes from wastewater.

References
[1] Cheok, CY., Mohd AN., Abdul RR and Nur HZA. 2018 ‘Current trends of tropical fruit waste utilization’, *Critical Reviews in Food Science and Nutrition*, 58(3), pp. 335–361.
[2] Foo, KY and Hameed, BH. 2012 ‘Factors affecting the carbon yield and adsorption capability of the mangosteen peel activated carbon prepared by microwave assisted K$_2$CO$_3$ activation’, *Chemical Engineering Journal*, 180, pp. 66–74.
[3] Nasrullah, A., Saad, B., Bhat, AH., Khan, AS., Danish, M., Isa, MH and Naeem, A. 2019 ‘Mangosteen peel waste as a sustainable precursor for high surface area mesoporous activated carbon: Characterization and application for methylene blue removal’, *Journal of Cleaner Production*, 211, pp. 1190–1200.
[4] Mbarki, F., Selmi, T., Kesraoui, A., Seffen, M., Gadonneix, P., Celzard, A. and Fierro, V. 2019 ‘Hydrothermal pre-treatment, an efficient tool to improve activated carbon performances’, *Industrial Crops and Products*, 140, pp. 1–10.

[5] Heidari, M., Dutta, A., Acharya, B. and Mahmud S. 2019 ‘A review of the current knowledge and challenges of hydrothermal carbonization for biomass conversion’, *Journal of the Energy Institute*, 92(6), pp. 1779–99.

[6] Islam, MA., Ahmed, MJ., Khanday, WA., Asif, M. and Hameed, BH. 2017 ‘Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption’, *Journal of Environmental Management*, 203, pp. 237–244.

[7] Ronix, A., Pezoti, O., Souza, L.S., Souza, I.P.A.F., Bedin, K.C., Souza, P.S.C., Silva, T.L., Melo, SAR., Cazetta, AL and Almeida, V.C. 2017 ‘Hydrothermal carbonization of coffee husk: Optimization of experimental parameters and adsorption of methylene blue dye’, *Journal of Environmental Chemical Engineering*, 5(5), pp. 4841–49.

[8] Qian, W.C., Luo, X.F., Wang, X., Guo, M. and Li, B. 2018 ‘Removal of methylene blue from aqueous solution by modified bamboo hydrochar’, *Ecotoxicology and Environmental Safety*, 157, pp. 300–6.

[9] Islam, MA., Benhouria, A., Asif, M. and Hameed, B.H. 2015b ‘Methylene blue adsorption on factory-rejected tea activated carbon prepared by conjunction of hydrothermal carbonization and sodium hydroxide activation processes’, *Journal of the Taiwan Institute of Chemical Engineers*, 52, pp. 57–64.

[10] Li, X and Li, Y. 2019 ‘Adsorptive removal of dyes from aqueous solution by KMnO₄-modified rice husk and rice straw’, *Journal of Chemistry*, 2019, pp. 1–9.

[11] Fang, J., Gao, B., Chen, J. and Zimmerman, A.R. 2015 ‘Hydrochars derived from plant biomass under various conditions: Characterization and potential applications and impacts’, *Chemical Engineering Journal*, 267, pp. 253–9.

[12] Jaruwat, D., Udomsap, P., Chollacoop, N., Fuji, M. and Eiard-ua, A. 2018 ‘Effects of hydrothermal temperature and time of hydrochar from Cattail leaves’, *AIP Conference Proceedings*, 2010.

[13] Danso-Boateng, E., Holdich, RG, Shama, G., Wheatley, AD, Sohail, M. and Martin, SJ. 2013 ‘Kinetics of faecal biomass hydrothermal carbonisation for hydrochar production’, *Applied Energy*, 111, pp. 351–7.

[14] Fakkaew, K., Koottatep, T., Pussayanavim, T and Polprasert, C. 2015 ‘Hydrochar production by hydrothermal carbonization of faecal sludge’, *Journal of Water Sanitation and Hygiene for Development*, 5(3), pp. 439–447.

[15] Ferrentino, R., Ceccato, R., Marchetti, V., Andreottola, G. and Fiori, L. 2020 ‘Sewage sludge hydrochar: An option for removal of methylene blue from wastewater’, *Applied Sciences*, 10(10), 3445, pp. 1–22.

[16] Arellano, O., Flores, M., Guerra, J., Hidalgo, A., Rojas, D. and Strubinger, A. 2016 ‘Hydrothermal carbonization of corn cob and characterization of the obtained hydrochar’, *Chemical Engineering Transactions*, 50, pp. 235–240.

[17] Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottnner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H. and Soja, G. 2012 ‘Characterization of slow pyrolysis biochars: Effects of feedstocks and pyrolysis temperature on biochar properties’, *Journal of Environmental Quality*, 41(4), pp. 990–1000.

[18] Alhashimi, H.A. and Aktas, C.B. 2017 ‘Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis’, *Resources, Conservation and Recycling*, 118, pp. 13–26.

[19] Dai, J., Sun, J., Xie, A., He, J., Li, C. and Yan, Y. 2016 ‘Designed preparation of 3D hierarchically porous carbon material via solvothermal route and in situ activation for ultrahigh-efficiency dye removal: Adsorption isotherm, kinetics and thermodynamics characteristics’, *RSC Advances*, 6(5), pp. 3446–57.

[20] Mohamed, G.M., El-Shafey, O.I. and Fathy, N.A. 2017 ‘Preparation of carbonaceous hydrochar adsorbents from cellulose and lignin derived from rice straw’, *Egyptian Journal of Chemistry*, 60(5), pp. 793–804.

[21] Duan, X., Hong, W., Srinivasakannan, C. and Wang, X. 2018 ‘Hydrochar silicate composite
sorbent via simple hydrothermal carbonization and its application to methylene blue removal’, 
*Materials Research Express*, **6**(3), pp. 1–25.

[22] Parra-Marfil, A., Ocampo-Pérez, R., Collins-Martínez, V.H., Flores-Vélez, L.M., Gonzalez-Garcia, R., Medellín-Castillo, N.A. and Labrada-Delgado, G.J. 2020 ‘Synthesis and characterization of hydrochar from industrial Capsicum annuum seeds and its application for the adsorptive removal of methylene blue from water’, *Environmental Research*, **184**, pp. 1-50.

[23] Khoshbouy, R., Takahashi, F. and Yoshikawa, K. 2019 ‘Preparation of high surface area sludge-based activated hydrochar via hydrothermal carbonization and application in the removal of basic dye’, *Environmental Research*, **175**, pp. 457–467.

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