Carbonization of sludge biomass of water treatment plant using continuous screw type conveyer pyrolyzer for methylene blue removal

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Abstract. The wide and fast growth of the textile industry has become one of the contributors to the water pollution. In this study, carbonized sludge (CS) was produced as an adsorbent for removal of methylene blue (MB) dye from aqueous solution. Sludge biomass from water treatment plant as precursor was carbonized using continuous screw type conveyer pyrolyzer at different conveyer frequency of 5 Hz and 10 Hz. Batch adsorption studies were carried out by varying MB initial concentrations (25 - 300 mg/L) and contact time (0 - 24 hours). The CS5Hz sample shows the highest surface area and total pore volume of 88.73 m²/g and 0.1417 cm³/g, respectively. This sample exhibits average pore diameter of 3.84 nm, monolayer adsorption capacity of 45.68 mg/g and well develop of pores structure. Freundlich and pseudo second order models were revealed to fit the isotherm and kinetic data, respectively with film diffusion play a major role as rate limiting step.

1. Introduction
One of the largest established manufacturing sectors in Malaysia is the textile industry. However the wastewater produced form this industry contained high level of pollutants especially dyes which are hazardous to human, aquatic life and the ecosystem once they enter the water bodies [1]. A huge amount of dyes, 200,000 tons to be specific is lost to the effluents as the result of inefficient dyeing process in the industry [2]. Different type of methods namely physical, biological and chemical treatment is widely employed to treat contaminated dyes wastewater. Physical treatment includes adsorption process, coagulation, ion exchange, irradiation and membrane filtration whereas chemical treatment consists of electrochemical destruction, oxidation, ozonation and photochemical [3]. On the other hand, examples of biological treatment are exploitation of the microbial biomass for adsorption process, enzyme degradation, algae degradation and microbial cultures. Each one of these treatments has their own advantages and limitation.
Methylene blue (MB) dye is classified as cationic dye and it appears to be blue in colour and odourless [4]. Upon inhalation, it could cause difficulty in breathing, while through ingestion it could cause nausea, vomiting, diarrhoea and gastritis [5]. The dye discharge into water bodies can reduce the sunlight penetration under water, thus affecting the photosynthesis process of the aquatic plant. Adsorption process using highly porous adsorbent is preferred in treating wastewater. The only disadvantage of the adsorption method is that the high cost of the adsorbent’s precursor. The research for low-cost adsorbents has bloomed over the years [6]. Eco-friendly precursors have always been a good substitution for commercial precursors like bituminous coal and coke. The unutilized sludge biomass is an example of cheap and abundance precursor that has potential to be modified into adsorbent [7]. In this study, sludge biomass obtained from water treatment plant was selected as precursor and converted to adsorbent to treat MB dye from aqueous solution.

2. Methodology
2.1 Materials
Sludge collected from water treatment plant at Parit Buntar, Perak, Malaysia was used as precursor. Methylene blue (MB) from Sigma Aldrich Sdn. Bhd. used as an adsorbate has properties as given in Table 1. Deionized water was utilized to prepare the stock and MB dye solution.

| Dye name | Methylene blue |
|----------|----------------|
| Molecular formula | C₁₆H₁₈N₃SCl |
| Molecular weight, g/mol | 319.85 |
| Chemical structure | ![Chemical structure](image) |

2.2 Carbonized sludge (CS) preparation
The sludge was dried under sunlight for 8 hours for drying purposes. The dried sludge was fed into the conveyer belt of pyrolyzer as shown in Figure 1. Nitrogen gas was flows into the chamber with flow rate fixed at 150 ml/min and the furnace was turned on to increase the temperature of chamber until 600°C. Once the desired temperature had reached, the conveyer belt was turned on at the targeted frequency of 5 Hz (sample CS5Hz) and 10 Hz (sample CS10Hz). The CS product was continuously collected at the secondary chamber.

![Image](image)

**Figure 1.** Continuous screw type conveyer pyrolyzer.
2.3 Characterization analysis
Volumetric adsorption analyzer (Model: Micromeritics ASAP 2020) was used to give several characteristics of the samples including surface area, pore volume and average pore diameter. The surface area was measured from the adsorption isotherm using Brunauer-Emmett-Teller (BET) equation. Scanning electron microscope (Model: Quanta 450 FEG, Netherland) was operated to obtain the surface morphology of the samples. Finally, FTIR spectrometer (Model: IR Prestige 21 Shidmazu, Japan) was useful in providing the surface chemistry of the samples.

2.4 Batch adsorption system
Series of 0.20 g of the prepared adsorbent were added into each of the test tubes filled with 200 mL of dye solutions. The test tubes were then sealed and placed in the isothermal water bath shaker.

2.4.1 Production of MB dye solution. MB dye with different initial concentrations of 50, 100, 150, 200, 250 and 300 mg/L were prepared via dilution method of 1000 mg/L stock solution using deionized water in volumetric flask. The dilution was done using the equation as follows:

\[ M_1V_1 = M_2V_2 \]  

where \( M_1 \) and \( M_2 \) are concentration of stock solution and desired adsorbate solution (mg/L), respectively whereas \( V_1 \) and \( V_2 \) are the volumes of stock solution and desired adsorbate solution (mL), respectively.

2.4.2 Adsorbate analysis. Sample was collected at identified time interval by using 3 mL of syringe. The respective MB dye concentration was determined by operating UV-visible spectrometer at wavelength of 665 nm. Calibration curve was constructed based on the fact that absorbance of dye changes linearly with concentration of dye solution.

2.5 Batch equilibrium, isotherm, kinetic and mechanism studies
For equilibrium studies, the amount of MB adsorbed at the state of equilibrium and the MB removal were calculated as follows:

\[ q_e = \frac{(C_o - C_e)V}{M} \]  \hspace{1cm} (2)

Removal (%) = \( \frac{(C_o - C_e)}{C_o} \times 100\% \)  \hspace{1cm} (3)

where \( q_e \) represents the amount of MB dye adsorbed at the state of equilibrium, \( C_o \) and \( C_e \) denote the MB concentration at the state of initial and equilibrium, respectively, \( V \) refers the volume of MB dye solution and \( M \) is the weight of samples used. Three models of Langmuir, Freundlich and Temkin were used in adsorption equilibrium studies. Determination on which model fit the data the best was made by comparing the correlation coefficients, \( R^2 \) value. Equation of Langmuir, Freundlich and Temkin in linear form are given by Equations 4, 5 and 6, respectively:

\[ \frac{C_e}{q_e} = \frac{1}{K_LQ_m} + \frac{C_e}{Q_m} \]  \hspace{1cm} (4)

where \( q_e \) is the amount of MB dye adsorbed by samples at the state of equilibrium, \( Q_m \) indicates Langmuir monolayer coverage adsorption capacity, \( C_e \) represents concentration of MB dye at the state of equilibrium and \( K_L \) is the constant associated with free energy adsorption.

\[ \ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \]  \hspace{1cm} (5)
where $q_e$ denotes the amount of MB dye adsorbed by samples at the state of equilibrium, $K_F$ indicates constant linked to bonding energy (mg/g (L/mg) $1/n$), $C_e$ represents MB dye concentration at the state of equilibrium and $1/n_F$ is the adsorption intensity.

$$q_e = B \ln A_T + B \ln C_e$$

(6)

where $q_e$ denotes the amount of MB dye adsorbed by samples at the state of equilibrium, $C_e$ represents concentration of MB dye at the state of equilibrium, BT is the constant linked to heat of adsorption and AT is constant associated with equilibrium binding.

For kinetic studies, adsorption uptakes at any time $t$, $q_t$ was determined as follows:

$$q_t = \frac{(C_o - C_t)V}{W}$$

(7)

where $q_t$ represents the amount of MB dye adsorbed at the time $t$, $C_o$ and $C_t$ denote the concentration of MB dye solution at the state of initial and at the time $t$, respectively, $V$ refers the volume of MB dye solution and $M$ is the weight of samples used. Pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models were employed in kinetic studies and their equations are given in Equations 8 and 9, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

(8)

$$t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$$

(9)

where $q_e$ and $q_t$ denote the amount of MB dye adsorbed at the state of equilibrium and at the time $t$ (mg/g), respectively, $k_1$ and $k_2$ refer to rate constant for PFO (1/min) and PSO (g/mg.h), respectively.

Further analysis of mechanism was carried out by employing the intraparticle diffusion plot as given as follows:

$$q_t = K_p t^{1/2} + C$$

(10)

where $q_t$ denotes the amount of MB dye adsorbed at the time $t$ (mg/g), $C$ indicates constant associated with boundary layer thickness and $K_p$ refers to constant linked to intraparticle diffusion rate (mg/g.h$^{1/2}$). A plot of $q_t$ against $t^{1/2}$ yields a straight line and this is an indication of intraparticle diffusion. The rate limiting step can be confirmed to be governed by intraparticle diffusion if the straight line passing through the origin.

3. Results and discussion
3.1 Characteristics of carbonized sludge
3.1.1 Surface area and pore characteristics. Surface area of samples, both BET and mesopores together with total pore volume and average pore diameter are presented in Table 2. The sludge was noticed to produce small amount of surface area whereas after carbonization took place, the BET surface was found increased to 88.73 m$^2$/g and 73.29 m$^2$/g for CS5Hz and CS10Hz, respectively. The increased in surface area as well as total pore volume were contributed by the water and volatile matter which evaporated and leaves the raw during carbonization step. The average pore diameter for CS5Hz and CS10Hz were 3.84 and 3.71 nm, respectively which lies in the mesopores range and suitable for wastewater adsorption application.
Table 2. Surface area and pore characteristics of the samples.

| Sample | BET surface area (m²/g) | Mesopore surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) |
|--------|-------------------------|------------------------------|---------------------------|---------------------------|
| Sludge | 3.53                    | 0.63                         | 0.0001                    | 3.08                      |
| CS5Hz  | 88.73                   | 45.50                        | 0.1417                    | 3.84                      |
| CS10Hz | 73.29                   | 37.20                        | 0.1328                    | 3.71                      |

3.1.2 Surface morphology. The SEM images of the samples were shown in Figure 2. The raw sludge was observed to have rough and uneven surface textures. Upon carbonization process, the evaporation of volatile matter leads to well development of pores network and increase in surface area. The pores developed on the CS surface were also led by the breakdown of lignocellulosic material at high carbonization temperature [8].

![Figure 2. SEM images for (a) sludge, (b) CS5Hz and (c) CS10Hz (magnification 1000x).](image)

3.1.3 Surface chemistry. The peaks in FTIR spectrums can divulge important information including the reduction, disappearance and the development of new functional groups on the sample [8]. The functional groups appeared in carbonized sludge are strong and broad peak at 3414.00 cm⁻¹ that associated with the presence of an O-H group (alcohols) as shown in Figure 3. Besides that, there are peaks at 2555.58 cm⁻¹, 1587.47 and 1568.13 cm⁻¹, 1431.18 cm⁻¹ and 1037.70 cm⁻¹ to represent the existence of aromatic ring (C=C), O-H group (carboxylic acid) and C-O (ester).

![Figure 3. FTIR spectrums for (a) sludge and (b) CS5Hz.](image)

3.2 Batch equilibrium study

Figures 4 (a) and 4 (b) respectively show the MB dye adsorption uptakes and MB removal of CS5Hz against adsorption time. The adsorption capacity of CS5Hz increased rapidly in the initial 2 hours and a slow increase in adsorption capacity can be observed until the 20th hour. The adsorption has reached equilibrium after the 20th hour. In the early process of adsorption, big amount of active sites was vacant
and accessible on CS5Hz [9]. As the time passed, the number of unoccupied active sites decreased, thus causing the adsorption process to occur at slower rate [10]. At higher MB initial concentration, higher driving force was developed to triumph the mass transfer resistance between MB dye in bulk phase and in solid phase, leading to higher adsorption capacity [11]. On contrary, MB removal decreased when MB initial concentration increased due to ratio of MB molecules to available active sites was high.

![Figure 4](image)

**Figure 4.** (a) MB dye adsorption uptakes and (b) MB removal at different initial dye concentration: 50mg/l (Δ), 100mg/l (○), 150mg/l (□), 200mg/l (▲), 250mg/l (●) and 300mg/l (■) by CS5Hz sample.

From Figure 5, the adsorption capacity increased when the initial MB dye concentration increased. The amount of MB dye adsorbed increased from 4.82 mg/g to 28.03 mg/g (raw sludge), 4.98 mg/g to 29.38 mg/g (CS5Hz) and 4.96 mg/g to 29.16 mg/g (CS10Hz) for the increased in initial MB dye concentrations from 50 to 300 mg/L.

![Figure 5](image)

**Figure 5.** MB adsorption uptakes for different conveyor frequency at different initial concentration.

### 3.3 Isotherm study

Isotherm studies is important in revealing the interaction behaviour between adsorbate with adsorbent. Table 3 and Figure 6 show the parameters for all of the isotherms applied and plots of the linearized equation, respectively. Based on R² value, Freundlich isotherm was found to best fit all adsorption systems. The monolayer adsorption capacities were 36.41, 45.68 and 41.89 mg/g for sludge, CH5Hz and CH10Hz, respectively. Adsorption capacity of CH5Hz was the highest since it has the highest surface area and pore volume as active site for adsorption process.
Table 3. Isotherm values for adsorption of MB by samples.

| Isotherms | Samples | Constants | R²  |
|-----------|---------|-----------|-----|
|           |         | Q_m       | k_L |
| Langmuir  | Sludge  | 36.41     | 0.07| 0.9196 |
|           | CS5Hz   | 45.68     | 0.30| 0.5880 |
|           | CS10Hz  | 41.89     | 0.18| 0.6710 |
|           |         | k_F       | n_F |
| Freundlich| Sludge  | 3.70      | 1.47| 0.9707 |
|           | CS5Hz   | 10.14     | 2.33| 0.8786 |
|           | CS10Hz  | 7.70      | 1.80| 0.9377 |
| Temkin    | Sludge  | 0.87      | 9.03| 0.9611 |
|           | CS5Hz   | 10.87     | 5.27| 0.6851 |
|           | CS10Hz  | 3.49      | 7.09| 0.7980 |

Figure 6. Linearized plot of (a) Langmuir, (b) Freundlich and (c) Temkin at 350°C for MB-raw sludge (△), MB-CS5Hz (○) and MB-CS10Hz (□).

3.4 Kinetic study

Figures 7(a) and (b) show the linearized plots of PFO and FSO kinetic models for MB dye adsorption onto CS5Hz, respectively. Table 4 summarizes the parameters of the kinetic models employed in this study. Based on R² value, MB-CS10Hz adsorption system was found to be best represented by PSO kinetic model. It is also observed that the rate of coefficient, k₂ of the PSO decreased with the increasing of initial dye concentration.

Table 4. Kinetic model parameters for the MB-CS5Hz adsorption system.

| Initial dye concentration, C₀ (mg/L) | qₑ,exp (mg/g) | Pseudo-first order | Pseudo-second order |
|-------------------------------------|---------------|--------------------|--------------------|
|                                     | qₑ,calc (mg/g) | k₁ | R² | qₑ,calc (mg/g) | k₂ | R² |
| 50                                  | 4.99          | 2.12 | 2.07 | 0.9104 | 5.14 | 1.95 | 0.9971 |
| 100                                 | 9.80          | 2.92 | 0.91 | 0.9661 | 9.76 | 0.96 | 0.9998 |
| 150                                 | 14.62         | 4.15 | 0.75 | 0.9382 | 14.24 | 0.71 | 0.9999 |
| 200                                 | 19.57         | 7.58 | 0.71 | 0.9901 | 18.88 | 0.34 | 0.9985 |
| 250                                 | 24.39         | 8.96 | 0.67 | 0.9649 | 23.29 | 0.31 | 0.9994 |
| 300                                 | 29.38         | 12.21 | 0.63 | 0.9650 | 28.23 | 0.21 | 0.9992 |
Figure 7. Plot of (a) PFO and (b) PSO for MB-CS5Hz adsorption system: 50mg/l (Δ), 100mg/l (○), 150mg/l (□), 200mg/l (▲), 250mg/l (●) and 300mg/l (■).

3.5 Mechanism study

Figure 8 gives the plots of intraparticle diffusion model for CS5Hz. It was found that there are three stages of adsorption mechanism. The first stage with sharper region for the first 0.25 h of adsorption indicating an instantaneous adsorption caused by a strong electrostatic attraction between MB dye and the external surface of CS5Hz [12]. The second stage which is also known as gradual adsorption process occurred from 0.5 h to 1 h indicating the intraparticle diffusion of MB dye molecules through the pores of the CS5Hz. The third stage is the final equilibrium stage where adsorption process had slowed down since extremely less active sites available.

Figure 8. Intraparticle plot for MB-CS5Hz adsorption system: 50mg/l (Δ), 100mg/l (○), 150mg/l (□), 200mg/l (▲), 250mg/l (●) and 300mg/l (■).

The slope of the plotted lines in each stage is defined as the rate parameters; $k_{p,1}$, $k_{p,2}$ and $k_{p,3}$ [13]. The constants of the intraparticle diffusion model are listed in Table 5. The rate parameter values for the three stages of adsorption increased with the increasing MB initial concentration, indicating the increasing in dye diffusion rate. The values of intercept of the plotted lines; $c_1$, $c_2$ and $c_3$ increased with the increasing MB initial concentration range for the three stages, indicating the thickening of boundary layer [14]. The boundary layer gets thicker will decrease the external mass transfer, but will increase the internal mass transfer.

Table 5. Intraparticle diffusion model constants for MB-CS5Hz adsorption system.

| MB initial concentration (mg/L) | $k_{p,1}$ | $k_{p,2}$ | $k_{p,3}$ | $c_1$ | $c_2$ | $c_3$ | $R^2,1$ | $R^2,2$ | $R^2,3$ |
|-------------------------------|-----------|-----------|-----------|-------|-------|-------|---------|---------|---------|
| 50                            | 8.32      | 0.52      | 0.0070    | 0     | 3.96  | 4.95  | 1       | 0.9976  | 0.9975  |
| 100                           | 14.21     | 2.71      | 0.15      | 0     | 6.08  | 9.08  | 1       | 0.9995  | 0.9956  |
| 150                           | 21.08     | 3.71      | 0.30      | 0     | 9.22  | 13.19 | 1       | 0.9971  | 0.9962  |
| 200                           | 25.70     | 6.17      | 0.57      | 0     | 9.90  | 16.91 | 1       | 0.9997  | 0.9796  |
| 250                           | 31.92     | 7.75      | 0.75      | 0     | 12.52 | 20.85 | 1       | 0.9976  | 0.9847  |
| 300                           | 36.15     | 11.51     | 0.96      | 0     | 12.52 | 24.82 | 1       | 0.9959  | 0.9829  |

*$k_p$ is in mg/h$^{1/2}$
4. Conclusion
Carbonized sludge of CS5Hz sample shows the highest surface area and total pore volume of 88.73 m$^2$/g and 0.1417 cm$^3$/g, respectively. This sample exhibits average pore diameter of 3.84 nm, monolayer adsorption capacity of 45.68 mg/g and well develop of pores structure. Increasing the conveyer frequency causing less contact time between the sample and heat treatment, thus explained the better performance of CS5Hz compared to CS10Hz as adsorbent. Freundlich and pseudo second order models were revealed to fit the isotherm and kinetic data, respectively. Mechanism studies confirmed that film diffusion play a major role as rate limiting step in MB-CS5Hz adsorption system.

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