Efficient removal of methylene blue by low-cost and biodegradable highly effective adsorbents based on biomass in the fixed bed column

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Abstract. The adsorptive ability of sustainable biomass (spent coffee ground (SC) and water hyacinth (WH)) and activated biochar derived from WH to remove methylene blue (MB) from aqueous solution was evaluated under continuous fixed-bed column. Morphological structure and functional groups of WH and SC were determined by SEM and FTIR, respectively. The SEM showed the presence of porous structure of WH, whilst FTIR confirmed the presence of more hydroxyl groups at the WH surface, resulting in higher MB adsorption. A series of column experiments were performed with varying bed height and initial MB concentration. To determine the breakthrough curves and characteristic parameters for process design, Yoon-Nelson, Thomas and modified Dose-Response models were applied to experimental breakthrough data. The MB adsorption was dependent on the bed height and initial MB concentration. An increase in bed height resulted in improved adsorption capacity. With increasing initial MB concentration, the adsorption capacity decreased. The maximum adsorption capacity (Qe) of ~391 mg/g by WH (at 0.75 cm bed height and 300 mg/L initial MB concentration) and ~393 mg/g by its activated biochar (at 2 cm bed height and 200 mg/L initial MB concentration) was observed. The results showed that WH gave comparable MB adsorption capacity with a greater cost-effectiveness.

1. Introduction
Dyes are extensively used for several industries, e.g., textile. Methylene blue (MB) is a cationic dye that is most commonly utilized in textile industries. Approximately 10-15% of the dyes are released into the environment, causing significant health and environmental hazards. A lot of biological, physical and chemical techniques have been adopted for dye removal from wastewater. Among these methods, adsorption is regarded as an attractive and effective approach for water treatment due to its remarkable advantages, e.g., simple operation, low cost and no secondary pollution [1]. Generally, continuous flow adsorption process offers several advantages over batch process. The application is economic and practical as the operation is conducted continuously and the process is controllable [2]. Various types of adsorbents have been reported (e.g. metal oxide, activated carbon). Particularly, biomass has attracted increasing attention due to its cheap source and great potential to be modified as a highly efficient adsorbent [1]. In this study, WH and SC were selected for their abundance and economic significance. They are carbonaceous materials containing cellulose, lignin and some functional groups (hydroxyl,
carboxyl groups, etc) that make the adsorption process feasible [3]. Moreover, to avoid any environmental related issues for the poor WH management, WH was converted into activated biochar for using as an efficient and sustainable adsorbent material. Hence, this work focused on performing continuous column study for the MB removal and investigating the performance of WH and SC biosorbents and activated biochar under variation of bed height and initial MB concentration. Thomas, Yoon-Nelson, and modified Dose-Response models were applied to experimental data for evaluating the column adsorption performance and for predicting the scale-up of a unit plant for the MB removal.

2. Experimental

2.1. Materials and methods

WH was collected from Tha Chin River at Nakhon Pathom, Thailand. SC was obtained from coffee shop in Silpakorn University, Thailand. The raw materials were washed with distilled water to remove impurities and then dried at 70°C for 24 h. The dried WH and SC were ground and sieved to desired size (150-250 μm). The activated biochar was prepared from WH via a KOH activation and was denoted as ABW. Dried WH and KOH mixture with mass ratio of 1:1 was used. After mixing, the mixture was heated at 800°C for 1 h under N2 flow, followed by washing to reach pH 7 and drying at 80°C for 6 h. The resulting ABW was crushed and sieved to 75-106 μm. The BET surface area, total pore volume and average pore diameter of ABW were 911 m²/g, 0.50 cm³/g and 2.16 nm, respectively. The morphology was characterized using a Hitachi TM3030 SEM. To determine the functional groups, biomass powders were analyzed by a Bruker Vertex 70 FTIR spectrometer. For continuous column experiment, the lab scale fixed-bed parameters were applied for the actual large scale fixed-bed reactor design. A series of fixed-bed column tests were conducted in a plastic column (2 cm inside diameter, 10 cm long) for the simulation of adsorbents for MB adsorption.

2.2 Application of empirical models for breakthrough curves

The breakthrough curves were analyzed using Thomas, Yoon-Nelson, and modified Dose-Response models. These models are given, respectively, by the following equations [4]:

\[ \frac{C_t}{C_0} = \left( 1 + \exp \left( \frac{k_mq_{0}m}{Q} - k_mC_0 \tau \right) \right)^{-1} \]
\[ \frac{C_t}{C_0} = \left( 1 + \exp (k_{YN}\tau - k_{YN} t) \right)^{-1} \]
\[ \frac{C_t}{C_0} = 1 - \left( 1 + \frac{C_0q_{0}a}{Q_{0}m} \right)^{-1} \]

where \( k_m \) is the Thomas kinetic coefficient (mL/min mg), \( k_{YN} \) is the Yoon-Nelson rate of constant (1/min), \( C_0 \) is the concentration of initial time (mg/L), \( C_t \) is the concentration at arbitrary time \( t \) (mg/L), \( Q_s \) is the maximum adsorption capacity of adsorbent (mg/g), \( \tau \) is the time required for 50% adsorbate breakthrough (min), \( Q \) is the flow rate (mL/min), \( m \) is the mass of adsorbent (g), and \( a \) is the constant.

3. Results and discussion

The morphological structure of SC and WH biosorbents is analyzed by the SEM analysis (Figure 1(a)-(b)). SC particles presented denser morphology than WH particles. The sponge-like rough surface morphology with high porosity was observed in WH. This surface roughness may possibly be useful in MB adsorption. The FTIR spectra of WH and SC are shown in Figure 1(c). The strong band at 3400 cm⁻¹ indicates the stretching vibrations of OH groups. The band at 2920 cm⁻¹ corresponds to the C-H stretching. The peaks at 1631 and 1731 cm⁻¹ are related to the adsorbed water in WH and either acetyl or ionic ether linkages of carboxylic group in the ferulic and p-coumeric acids of lignin [5]. The peaks of SC at 1744, 1654, and 1543 cm⁻¹ correspond to the C=O stretching of hemicellulose and chlorogenic acids, and stretching of caffeine CN bonds [6]. This suggests that functional groups, particularly hydroxyl groups, may potentially act as the active sites for the binding of MB. To predict the breakthrough curves and determine the characteristic column parameters, Yoon-Nelson, Thomas and modified Dose-Response models were compared with the experimental points and exhibited in Figure 1(d)-(f). All the models predicted the column performance parameters by including the bed height (0.5 and 0.75 cm) and initial MB concentration (200 and 300 mg/L) of the column system reported in Table
1. The experimental data were well described by three models in different column conditions (R² > 0.95), suggesting their suitability to be used for the design and scale-up. On studying the effect of bed height, it was observed that at a fixed initial MB concentration (300 mg/L), the maximum adsorption capacity (Q₀) and breakthrough time (tₜₚ at C/C₀ ≈ 0.1) increased with bed height of WH (Table 1). At higher bed height, the amount of adsorbent in the column is increased, therefore there is an increased number of biosorbent active sites. This leads to increased adsorption capacity at higher bed height, and the breakthrough times are longer as well since more active sites available would become slowly saturated. For the effect of initial MB concentration, it was found that the tₜₚ and Q₀ values decreased with increasing adsorbate concentration as the binding sites became more quickly saturated. At higher concentration, more dye molecules are left unadsorbed in the solution, probably because of the saturation of binding sites resulting in decreased adsorption capacity. Similar trend has also been observed by other researchers [1,7]. The highest Q₀ of ~391 mg/g was obtained at 0.75 cm bed height and 300 mg/L initial MB concentration. At the same bed height (0.5 cm) and initial concentration (300 mg/L), the Q₀ value of WH was higher than that of SC by 51%. This may be due to the presence of more hydroxyl groups at the surface of WH, resulting in the formation of surface hydrogen bonds between the hydroxyl groups on the WH surface and the nitrogen atoms of MB [8].

Figure 1. SEM images of (a) SC and (b) WH, (c) FTIR spectra of SC and WH, (d) Yoon-Nelson, (e) Thomas and (f) modified Dose-Response non-linear breakthrough modeling.

Table 1. Parameters of three models for SC and WH in fixed-bed column (flow rate: 10 mL/min).

| Sample | C₀ (mg/L) | h (cm) | tₜₚ (min) | kÑN (1/min) | τ (min) | kTH (mL/mg·min) | Q₀ (mg/g) | R² | Q₀ (mg/g) | a | R² |
|--------|----------|--------|-----------|-------------|--------|----------------|----------|----|----------|---|----|
| SC     | 300      | 0.5    | 15        | 0.278       | 22.171 | 0.999          | 0.911    | 198.993 | 0.999 | 197.007 | 5.639 | 0.998 |
|        | 200      | 0.5    | 30        | 0.097       | 53.374 | 0.998          | 0.460    | 362.720 | 0.998 | 352.551 | 4.889 | 0.998 |
| WH     | 300      | 0.5    | 20        | 0.171       | 31.119 | 0.999          | 0.573    | 304.931 | 0.999 | 297.516 | 5.245 | 0.996 |
|        | 300      | 0.75   | 30        | 0.058       | 67.267 | 0.994          | 0.179    | 413.322 | 0.994 | 391.101 | 3.571 | 0.998 |

For a preliminary study of activated biochar from WH (Table 2), the analysis of the applicability of three models for predicting MB adsorption on ABW revealed that the correlation coefficient (R²) value
was between 0.996-0.998 for modified Dose-Response as compared with 0.995-0.9996 for Yoon-Nelson and Thomas model data fittings. The MB adsorption on ABW can best be predicted by modified Dose-Response. The \( Q_0 \) values increased with the increase in bed height and the decrease in initial MB concentration. The same observation has been reported by previous researchers [9]. The highest \( Q_0 \) of \( \sim 393 \, \text{mg/g} \) was found at 2 cm bed height and 200 mg/L initial MB concentration. Column tests of other activated biochars will be reported in future.

Table 2. Three model parameters for ABW in fixed bed column (flow rate: 10 mL/min).

| Sample | \( C_0 \) (mg/L)(cm) | \( h \) (min) | \( h_b \) (min) | \( \tau \) (min) | \( k_{YN} \) (l/min) | \( R_2 \) | \( k_{TH} \) (mL/mg min) | \( Q_0 \) (mg/g) | \( R_2 \) |
|--------|---------------------|---------------|----------------|---------------|-------------------|------|-----------------|----------------|------|
| AC-800 | 300                 | 1.0           | 25             | 0.109         | 41.389            | 0.996 | 0.359           | 308.238        | 0.996 |
|        | 300                 | 2.0           | 50             | 0.041         | 94.518            | 0.985 | 0.136           | 354.633        | 0.985 |
|        | 300                 | 4.0           | 110            | 0.021         | 204.508           | 0.987 | 0.068           | 383.663        | 0.987 |
|        | 300                 | 2.0           | 90             | 0.028         | 161.267           | 0.992 | 0.133           | 412.481        | 0.992 |
|        | 300                 | 2.0           | 35             | 0.065         | 67.557            | 0.995 | 0.160           | 335.540        | 0.995 |

4. Conclusions

The effectiveness of WH and SC as biosorbents and biochar obtained from WH was tested in the MB removal from aqueous solution in continuous fixed-bed column system by varying bed height and initial MB concentration. The breakthrough times were increased with increasing bed height and decreasing initial MB concentration. The adsorption capacity of MB on WH was higher than that of SC by 51%. In terms of adsorption capacity and economic efficiency, the use of a WH-packed column has demonstrated potential for the remediation of MB contaminated wastewater. For both biosorbents, all three models provided a satisfactory correlation of experimental column data with \( R_2 > 0.95 \), suggesting its suitability for the design and large-scale process. The modified Dose-Response model was found best fitted for biochar and could be applied to scale up the process to an industrial operation.

5. References

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Acknowledgement

The authors would like to thank the Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, and the Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University.