Carbon Adsorbents from Sugarcane Bagasse Prepared through Hydrothermal Carbonization for Adsorption of Methylene Blue: Effect of Heat Treatment on Adsorption Efficiency

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Abstract. A carbon hydrochar material (BG-230) has successfully been prepared by conversion of sugarcane bagasse through low-temperature hydrothermal carbonization (HTC) at 230 °C. BG-230 was subsequently subjected to further thermal treatment at 400 °C for 1 hour under air (BG-230/400). Both resulting materials were characterized using specific surface area analysis (BET), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), elemental analysis (C, H, N, O) and X-ray photoelectron spectroscopy (XPS). The characterization results showed that BG-230 possesses a higher number of acidic-oxygen functionalities than BG-230/400, indicating that the thermal treatment at 400 °C under air removed those functionalities. The adsorption properties were evaluated by the removal of methylene blue (MB) from aqueous solutions. The adsorption capacity of MB was found to be higher for BG-230 (~100 mg g⁻¹) than that for BG-230/400 (~25 mg g⁻¹). The investigation into the adsorption performance of both prepared adsorbents suggests that the oxygen functional groups on the prepared carbon materials are responsible for the adsorption mechanism.

Keywords: Adsorbent, sugarcane bagasse, hydrothermal carbonization, heat treatment

1. Introduction
Nowadays, organic dyes have been widely employed in textile, paper, printing industries, etc. The wastewater containing dyes is a serious problem to human health and the environment when being discharged without suitable treatment. Methylene blue (MB) is one of the most widely used synthetic dyes in the textile industry. MB is a toxic and carcinogenic compound [1]. Therefore, the elimination of MB from wastewater is necessary before releasing the treated water into environment. Many methods...
have been utilized to treat wastewater including adsorption [2,3], membrane filtration [4], chemical oxidation [5], and coagulation [6]. Among those methods, adsorption is one of the most popular methods for wastewater treatment because of its simplicity and high efficiency.

Activated carbon has mostly been employed as adsorbents in the removal of MB due to its high surface area, large pore volume, and high chemical stability. Furthermore, the resources for its production can easily be obtained from waste biomass. However, despite its high adsorption performance towards the MB adsorption, the preparation of activated carbons relies heavily on the use of toxic chemicals, e.g., KOH, ZnCl$_2$, or high-temperature treatment (>500 °C), which is considered to be the main drawback for industrial upscale. For this reason, alternative methods of preparing biomass-based adsorbents are desirable.

Hydrothermal carbonization or HTC is a green thermochemical process of converting organic feedstock into carbon-rich materials, with comparatively low CO$_2$ emissions [7,8]. HTC is performed at low-temperature (150-350 °C) by submerging biomass in water and heating in a confined system under high pressure. The final product from HTC is a dark-brown solid called ‘hydrochar’, which can be applied to several valuable applications in the industry and environment. Due to its oxygen-rich functionality, hydrochar has been employed as adsorbents for adsorption towards some toxic dyes [1,7]. Nevertheless, because of its low surface area (usually < 50 m$^2$/g), the hydrochar undergoes further activation at higher temperatures to improve porosity. Therefore, the oxygen-rich functional groups are likely to be removed during the heat treatment with high temperatures, leading to the loss of active functionality in spite of higher surface area. Moreover, direct comparisons in performance between the hydrochar and the high-temperature treated hydrochar are usually ignored.

Thailand is importantly an agricultural country, who grows sugarcane on a large scale per year. Therefore, sugarcane bagasse is among the most abundant of lignocellulosic material in agricultural crop residues. It is a residue produced in large quantities by the sugar industry [2]. The sugarcane bagasse is of low value; however, it is considered an interesting feedstock to be used in producing value-added chemicals or advanced materials [2,9]. Sugarcane bagasse contains around 40-45% cellulose, 30-35% hemicelluloses, and 20-30% lignin [9]; therefore, it is suitable to be used as a starting precursor in HTC. Accordingly, the sugarcane bagasse should be recovered in a way that they can be raised to valuable products in the industry.

In this study, the hydrochar derived from sugarcane bagasse is fabricated via a simple HTC at 230 °C, followed by a simple heat treatment at 400 °C. The HTC condition at 230 °C for 24 h was optimized in previous work [2], which provided the highest yield of hydrochar products. Also, the effect of the further heat treatment at 400 °C on the MB adsorption capability for both the sample has been investigated. Various characterization techniques were used to help correlate the relationships between the physicochemical properties and the MB adsorption efficiency. Therefore, the better insight into the adsorption mechanisms can be drawn.

2. Methods
2.1. Preparation of the samples
Hydrochar carbon material (BG-230) was prepared via hydrothermal carbonization process with sugarcane bagasse precursor. In a preparation process, sugarcane bagasse (15 g) and deionized water (150 mL) were mixed in a Teflon-line stainless steel autoclave of 400 mL. The reaction mixture was heated at 230 °C for 24 h. After that, the products were cooled to room temperature. The obtained solid product was soaked in acetone (150 mL) for 1 h, filtered and dried at 110 °C for 3 h. Subsequently, the product was soaked in NaOH (0.1 M, 150 mL) at 70 °C for 2 h to remove all the base-soluble compounds, and then washed with DI water until the rinsed water became clear. The resulted material was labeled BG-230 after being dried for 3 h. For comparison, BG-230 was then treated at 400 °C for 1 h. The treatment product was cooled to room temperature. After that, the product was washed in HCl (0.1 M, 100 mL) for 30 minutes followed by washing with hot water (70-80 °C) until the rinsed water
was neutral. Finally, the obtained materials were dried at 110 °C for 3 h. The resultant material was labeled as ‘BG-230/400’.

2.2. Characterization of the samples
The carbon materials were characterized by using scanning electron microscopy (SEM, Quanta 400, FEI) to examine the surface morphology, elemental analyses to determine C, H, N, and O content. Nitrogen sorption analysis was performed at 77 K (Micromeritic ASAP2460) to calculate specific surface area (S\text{BET}). To determine functional groups on the surface of materials, Fourier transform infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer, US) was operated with the wavenumber range 4000 - 400 cm\(^{-1}\). The quantitative and qualitative analysis of functional groups on surfaces was specified by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos Analytical Ltd.).

2.3. Adsorption studies
The adsorption performance of methylene blue (MB) on BG-230 and BG-230/400 was studied by using 0.05 g of carbon materials in 25 mL of MB solution with various concentrations for 48 h. The determination of dye concentrations in the remaining solutions was directly calculated from the calibration curve prepared by measuring the absorbance of MB solutions with appropriated standard concentrations at \(\lambda_{\text{max}} = 664\) nm using a UV–vis spectrophotometer (UV 2600, Shimadzu). The adsorbed amount of MB (\(q_e\)) was calculated with equation (1) as follows

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(C_0\) and \(C_e\) stand for the initial and equilibrium concentrations of MB (mg/L), respectively, \(m\) is mass of the sample (g), and \(V\) is the volume of the MB solution (L).

3. Results and Discussion
The morphology of both BG-230 and BG-230/400 was investigated using SEM images and is shown in Figures 1 and 2, respectively. BG-230 contained aggregated microspheres with a diameter in the range of 0.1 - 3 \(\mu\)m (Figure 1 left). The microsphere appeared to be present throughout the whole sample surface, even in the macroporous channels (Figure 1 right). The presence of macropores in the resulted sample indicated that the macropores could be reserved during the HTC. After the heat treatment in air at 400 °C, the microspheres in BG-230/400 were slightly deformed and the sample surface became rougher. The rougher surface is consistent with the slight increase in BET surface area (\(S_{\text{BET}}\)) from 27.33 m\(^2\)/g (BG-230) to 35.47 m\(^2\)/g (BG-230/400).

![Figure 1. SEM images of BG-230: recorded on (left) the surface and (right) cross-section morphology.](image-url)
Figure 2. SEM images of BG-230/400: recorded on (left) the surface and (right) cross-section morphology.

Table 1. Elemental composition (%wt) of carbon materials

| Samples     | S$_{BET}$ (m$^2$/g) | Elemental composition (%wt) |
|-------------|---------------------|-----------------------------|
|             |                     | C   | H   | N   | O   |
| Bagasse     | 1.66                | 43.56 | 5.70 | 0.10 | 50.64 |
| BG-230      | 27.33               | 66.69 | 4.67 | 0.44 | 28.20 |
| BG-230/400  | 35.47               | 71.28 | 2.96 | 0.57 | 25.19 |

Figure 3. FTIR spectra of carbon materials

In order to confirm the functional groups of the carbon materials, FTIR measurements were carried out, and FTIR spectra are presented in Figure 3. The FTIR spectra of BG-230 and BG-230/400 appear to be similar but are different in the intensity of peaks. This indicates that the types of functional groups did not change after the heat treatment process although the amount of each functional group can be different. The broad FTIR band at 3300–3500 cm$^{-1}$ could be attributed to O-H stretching vibrations in hydroxyl or carboxyl groups. The bands appeared at 2850–2950 cm$^{-1}$ are assigned to the aromatic and aliphatic stretching (C-H) modes of benzene. The presence of aromatic rings is also evidenced by the band at 1620 cm$^{-1}$ attributed to C=C vibrations. The bands at 1710 cm$^{-1}$ (C=O) vibrations corresponding to carboxyl. The bands at 1000–1450 cm$^{-1}$ are assigned to C-O stretching vibrations in hydroxyl, ester or ether and O-H bending vibrations. The increase in the intensity of the bands at 1620 cm$^{-1}$ for BG-230/400 after heat treatment suggests the higher degree of graphitization. The decrease in the intensity of C=O at 1710 cm$^{-1}$ after the heat treatment reveals the lower amount of carboxylic functional group [1,9,10,11].
Figure 4. XPS spectra of BG-230: C 1s spectra (left) and O 1s spectra (right)

Figure 5. XPS spectra of BG-230/400: C 1s spectra (left) and O 1s spectra (right)

XPS characterization confirmed the oxygen functional groups at the outer surface of BG-230 and BG-230/400. The C 1s spectra obtained for BG-230 in Figure 4 (left) and BG-230/400 in Figure 5 (left) with the peak fitting of their envelopes [8,9]. The spectrum was resolved into 5 individual component peaks; the main peak at 284.9 eV could be assigned to aliphatic or aromatic carbon group and other four peaks attributed to C-O (286.1eV), C-O-C (287.2eV), C=O (288.3eV), and O=C=O (289.3eV). The atomic concentration percentage of carbon was 83.70% for BG-230 and 88.78% for BG-230/400. This is consistent with the CHN analysis results and confirms the heated treatment after HTC as to decompose the oxygen and hydrogen content. The O 1s spectra of BG-230 in Figure 4 (right) is the spectrum composed of 4 individual component peaks. The main peak at 533.4 eV (44.4%) could be assigned to a carboxylic group and other three peaks attributed to C-O-C (531.3eV, 15.5%), C-OH (532.3eV, 28.9%) and Ar-OH (543.8eV, 11.2%). For BG-230/400 in Figure 5 (right), the result of O 1s showed that the spectrum fitted into 3 individual component peaks, the main peak at 534.1 eV (41.3%) could be assigned to carbonyl group and other two peaks attributed to C-O-C (531.9eV, 33.7%) and O*-C=O (532.3eV, 25.0%). For the O 1s spectra of both materials suggest that the percentage of carboxylic group was clearly reduced after heating treatment, also resulting in a decreased acidic functional group on the surface. The atomic concentration percentages of oxygen for BG-230 (15.04%) and BG-230/400 (11.22%) were also found to be different.

The adsorption performance of MB on BG-230 and BG-230/400 was investigated using 0.05 g of carbon materials in 25 mL MB solution containing various concentrations for 48 h. The results from adsorption isotherm (Figure 6) show that the maximum adsorption capacity of MB on BG-230 is as high as 100 mg/g. In contrast, the maximum adsorption capacity of BG-230/400 is 4 times lower than that of BG-230 (25 mg/g). Furthermore, the adsorption mechanism of BG-230 and BG-230/400 was also
demonstrated. Although, the BET surface area of BG-230/400 was slightly higher than that of BG-230 (Table 1), but the adsorption capacities of BG-230/400 was much lower than that for BG-230. It can be concluded that the surface area is not an important factor to determine the adsorption capacity of MB on our samples. Hence, the behavior of adsorption capacity is instead determined by the presence of oxygen functional groups on the surface of materials. The oxygen is possibly in the form of stable groups such as ether and quinone, whereas the oxygen functionalities may consist of more reactive or hydrophilic groups such as hydroxyl, carbonyl, carboxylic and ester which were identified by FTIR and XPS measurements. BG-230 contains a high content of reactive oxygen functionalities, especially the high percentages of the carboxylic group (44.4%). On the contrary, BG-230/400 include a significant amount of ether groups (41.3%) [11]. Therefore, the high adsorption capacity on BG-230 is resulted from its abundant reactive oxygen functional groups which are an acidic or anionic character on the surface. This acidic group is more favorable to the adsorption of cationic molecules. As a result, MB containing a cationic character could easily interact with anionic surface generated from the carboxylic group of BG-230 via electrostatic interactions. These results were in the higher MB adsorption capacity for BG-230 than that for BG-230/400 [10].

Figure 6. Adsorption isotherm of methylene blue on BG-230 and BG-230/400.

4. Conclusion
BG-230 was successfully prepared by hydrothermal carbonization process from sugarcane bagasse and could be used to adsorb cationic MB from aqueous solution. The possible factor for adsorption of this dye is an electrostatic interaction between adsorbent surface and MB molecules. Compared with BG-230/400, which was heat-treated at 400 °C, the adsorption capacity was dropped because of the decomposition of the active site on the surface after heating treatment. This finding indicates the importance of the HTC in maintaining the oxygen functionalities on the surface of the hydrochar.

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