Facile synthesis of corncob biochar via in-house modified pyrolysis for removal of methylene blue in wastewater

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Abstract
Low-cost biochar was derived from corncob Zea mays L. cultivated in Northern Thailand for animal feed by facile synthesis with in-house modified pyrolysis for 2 h at ∼500 °C, ∼10 °C min⁻¹ heating rate. Fixed-carbon, ash, %CHNSO and volatile contents of biochar were characterized and compared with pristine biomass. Thermal analysis was performed to monitor the transition of corncob biomass to biochar under the pyrolysis conditions. The physicochemical properties of biochar were investigated by scanning electron microscopy and FT-IR analysis, indicated honeycomb structure on the biochar surface with cylindrical pores and various functional groups, such as carbonyl and phenolic groups. Methylene blue adsorption in aqueous solution by biochar was studied at 25 °C. Without any chemical activation on biochar, the maximum removal efficiency of methylene blue by biochar was 16.50 mg g⁻¹. Effect of the initial concentration and the contact time on removal of methylene blue was studied to archive optimal conditions. The equilibrium adsorption of methylene blue on the biochar was well fit by the Langmuir isotherm. Kinetic of adsorption was perfectly fit by pseudo-second order dynamic model. The results suggest low-cost corncob biochar prepared by in-house modified pyrolysis could be utilized in wastewater treatment.

List of abbreviations
BET Brunauer–Emmett–Teller
C₀ Initial dye concentration (mg l⁻¹)
Cₑ Equilibrium concentration of dye (mg l⁻¹)
EIA Environmental impact assessment
qₑ Sorbed dye amount per gram of sorbent at equilibrium (mg g⁻¹)
qₑ,cal Calculated amount of dye sorbed per gram of sorbent at equilibrium (mg g⁻¹)
qₑ,exp Experimental amount of dye sorbed per gram of sorbent at equilibrium (mg g⁻¹)
qₜ Sorbed dye amount per gram of sorbent at time t (mg g⁻¹)
Kₑ Langmuir isotherm equilibrium constant representing the energy of sorption (L mg⁻¹)
Kₑ,F Freundlich constant representing sorption capacity (mg g⁻¹)(L mg⁻¹)n⁻¹
k₁ Pseudo-first order rate constant (1 min⁻¹)
Kₑ,F Pseudo-second order rate constant (g mg⁻¹ min⁻¹)
MB Methylene blue

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**1. Introduction**

Disposal of residual waste is a major concern in countries with strong agriculture. In recent years, there have been several studies dealing with these waste materials, in relation to ‘zero waste’ strategy [1, 2]. Biochar is a carbon–rich material obtained by pyrolysis of organic materials, such as agricultural wastes, under oxygen-free conditions [3, 4]. The specific properties of biochar, including porous structure of the carbonaceous solid with large specific surface enriched with functional groups and minerals, make biochar a potentially effective material for carbon storage, soil amendment, productivity enhancement, mitigation of global warming and adsorption of contaminants from wastewater [1, 5]. Further, biochar is considered an alternative approach to waste processing and disposal [6, 7]. There have been many reports on biochars produced from different low-cost biomass types, such as rice straw, pine, palm shell, seed, weeds and animal manure, having promising ability to adsorb dyes in aqueous solution [5, 8, 9]. The earlier studies of Wang et al 2015, assessed biomass materials with different components, even from different cultivation areas, and they had different elemental compositions, inorganic contents, volatile contents and moisture contents. These also affect the respective biochar properties [10]. Therefore, the physicochemical properties of biochar and its potential for dye removal are strongly influenced by the composition of raw material and the pyrolysis condition, especially pyrolysis temperature and heating time [11].

Biochar has been proposed as a potential low-cost sorbent of various pollutants in wastewater. The textile-dyeing industry consumes a large quantity of water and produces a large volume of wastewater from different steps in the dyeing and the finishing processes. Dye wastewater disposal is a major problem, because the wastewater may contain acids, bases, toxic compounds, and has visible color [12]. Therefore, such wastewater streams need to be properly treated before release to the environment. Various techniques for treatment of dyes such as chemical precipitation, ion exchange, oxidation process, photocatalysis or membrane filtration have been used for elimination of dyes from wastewater streams. However, each of these techniques has its own limitations such as slow processing, low efficiency, high operating and costs [13–15]. And among the physical, chemical, and biological decolorization technologies available, physical sorption is an effective and attractive process for the treatment of dye-contaminated wastewater in large scale applications such as commercial or industrial. Adsorption by commercial activated carbon is effective in the removal of dyes from wastewater. Thus, the world consumption of activated carbon is steadily increasing because of its applications in pollution control [16–19]. Although processing to increase the specific surface is known, this would also increase the production costs and the use of energy and chemicals that impact the environment [12, 18, 20]. Moreover, the design of in-house biomass carbonizers, gasifiers or pyrolysers to create the low-cost, energy conservative and eco-friendly tools is the sustainable way to reduce the agricultural wastes in farm and return them to biochars [21].

Corncobs are an abundant biomass resource. They are often discarded as waste on producing animal feed and cause considerable environmental issues. Corncobs have high carbon content (>40 wt%) and a heterogeneous porous microstructure. They also contain a large fraction of hemicellulose, which can be considered appropriate high carbon content biomass for biochar [22].

The focus of this study was to assess the physicochemical properties of corncob biochar produced by facile synthesis in modified pyrolysis chamber and to evaluate the adsorption potential of corncob biochar produced in this technique to investigate the sorption property of the obtained corncob biochar for removing methylene blue dye (MB) in which MB can serve as a model of visible pollution with strong adsorption onto solids and toxicity to humans and animals [18]. During the carbonization, physical and chemical changes alter elemental composition, surface structure, and surface functional groups. A thermal analysis was further performed to the corncob biomass in order to follow the pyrolysis conditions. The resultant biochar was used as low-cost adsorbent without any chemical modifications. The adsorption of MB by corncob derived biochar was studied, and kinetic and equilibrium data were used to assess the adsorption mechanisms.
2. Experiments

2.1. Biochar preparation

Maize, *Zea mays* L., was cultivated in Northern Thailand for animal feed, and cob waste was obtained from a local company in Chiangmai Province, Thailand. The corncobs were separated manually and washed thoroughly with water to remove dirt, and were then dried in air for 2 days. The modified pyrolysis tool was created by preparing two different sizes of barrels and making 6–8 holes with diameter 1.0 cm and 1.5 cm around the bottom part of inner- and outer barrels, respectively, as shown in scheme 1. Samples of corncob biomass were placed in inner barrel (scheme 1(a)). The inner barrel was covered and then put upside down in the outer barrel (scheme 1(b)). We used two-layer chambers to control the inner chamber to oxygen limited condition. The agricultural wastes (∼2 kg) were placed on the bottom of inner barrel and then ignited to start heating process. For reducing the pressure in chamber, the cover of outer barrel was prepared by cutting 8 triangle holes zigzag around the cover. The outer barrel was covered and fitted with the chimney as shown in scheme 1(c). The pyrolysis process started from the top to the bottom of outer barrel. The temperature of pyrolysis process was controlled at ∼500 °C. The pyrolysis process was finished in 2 h and the biochar was then allowed to cool to room temperature. The biochar was finally crushed and sieved to a particle size less than 0.5 mm. The physicochemical characteristics of biochar was then analyzed. Adsorption properties of obtained biochar were tested using MB dye without any chemical modification on biochar adsorbent.

2.2. Biochar characterization

The biochar sample was dried and kept in a desiccator. Elemental analysis was performed using a CHNS/O analyzer (Flash 2000, ThermoScientific, Italy). The mass fractions of moisture, volatile fixed carbon, and ash content were determined by ASTM D7582 standard test methods. The heating value of the dried samples was determined using a bomb calorimeter. TOC was determined using a Total Organic Carbon (TOC) method by multi EA® 4000 TOC Analyzer (Analytik Jena AG, Germany). The specific surface area and porosity were measured by Static volumetric N$_2$ gas adsorption method with an ASAP 2460, ASAP2060 surface area and porosity analyzer (Micrometrics, USA) and was calculated using the BET (Brunauer–Emmett–Teller) method. The biochar sample was characterized by FT-IR spectroscopy (Vertex70, Bruker, Germany). Infrared spectra were obtained in the range 400–4000 cm$^{-1}$ using potassium bromide (KBr) pellets. The specific surface area and porosity of biochar were measured by nitrogen adsorption at 77 K using a surface area and porosimetry system (ASAP 2020 M + C, USA). The surface characteristic of the biochar was imaged using a Quanta 400 Scanning Electron Microscope (FEI-SEM, Czech Republic). The thermal analysis of raw material for preparing the biochar included TGA, DTA, and DTG runs with a Simultaneous Thermal Analyser (STA8000, Perkin Elmer, USA) under N$_2$ flushing over the temperature range from 25 to 800 °C, with a heating rate of 10 °C min$^{-1}$. The
characterizations were performed on both biochar and corncob raw material, to assess the conversion of corncob biomass to biochar.

2.3. Adsorption experiments

The adsorption of MB by the biochar was assessed from batch experiments. MB as received from Aldrich, USA, was prepared to a stock solution at 100 mg l\(^{-1}\) concentration in distilled water. The test solutions were prepared by diluting the MB stock solution to select concentrations. The concentrations in adsorption experiments were determined from light absorbance by UV–vis absorption spectrophotometer (Lambda 35, Perkin Elmer, USA). The effects of initial MB concentration and contact time on adsorption by corncob biochar were investigated. 10 ml at a tested concentration (5–100 mg l\(^{-1}\)) of MB was transferred in a 50 ml centrifuge tube with 0.05 mg of biochar. The solution was agitated at 150 rpm in a thermostatic shaker water bath for a specified time (5 to 120 min) at 25 °C. The samples were withdrawn, and biochar was filtered off, and the supernatant concentration determined at 600 nm. The adsorption capacity \(q_e\) is calculated as follows:

\[
q_e = (C_{in} - C_e) m^1 \times V
\] (1)

2.4. Adsorption isotherm study

The equilibrium capacity to adsorb MB for corncob biochar is described by an adsorption isotherm, describing the ratio of MB adsorbed and that which remains in solution at equilibrium, at a fixed temperature \([23, 24]\). In this study, the MB dye adsorption was measured at optimum conditions, at 25 °C.

2.4.1. Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity, with complete monolayer coverage of the biochar surfaces, and is expressed by equation (2). The rearrangement in equation (3) makes this isotherm appear linear in a plot \([25, 26]\):

\[
q_e = (q_{max} K C_e)(1 + K C_e)^{-1}
\]

\[
C_e q_e^{-1} = 1 q_{max}^{-1} + C_e q_{max}^{-1}
\] (3)

The constants \(q_{max}\) and \(K_l\) can be determined from the slope and intercept of equation (3), respectively.

2.4.2. Freundlich isotherm

The Freundlich model is an empirical equation, here used to estimate the adsorption intensity by biochar of MB. The model assumes that the adsorbed molecules interact with a heterogeneous multilayer surface \([27]\) and is given by equation (4).

\[
q_e = K_F C_e^n
\] (4)

Here parameter \(n\) indicates the affinity of MB and biochar adsorbent. The linearized form is:

\[
\log q_e = \log K_F + n^{-1} \log C_e
\] (5)

If a plot of \(\ln C_e\) against \(\ln q_e\) yields a straight line, this indicates that the Freundlich adsorption isotherm matches the data. The constants \(n^{-1}\) and \(\ln K_F\) can be determined from the slope and intercept, respectively.

2.5. Adsorption dynamics study

As opposed to an equilibrium isotherm, adsorption kinetics describe the rates at which the equilibria are approached. In practice, the processing capacity depends on the rate, and we would prefer rapid equilibration to slow. In this work, pseudo-first order and the pseudo-second order kinetic models were tested to describe the adsorption of MB (initially 10 mg l\(^{-1}\)) by corncob biochar at 25 °C \([24, 28]\).

2.5.1. Pseudo-first-order model

The pseudo-first-order kinetic model is given by equation (6).

\[
\log (q_e - q) = \log q_e - (k_1 2.303^{-1})t
\] (6)

2.5.2. Pseudo-second-order model

The sorption data were also analyzed in terms of the pseudo-second order model, given by equation (7).

\[
t q_e^{-1} = 1(k_2 q_e^{-5})^{-1} + (1 q_e^{-5})t
\] (7)
3. Results and discussion

3.1. Characterization of biochar

From in-house modified pyrolysis technique, corncob biochar was obtained at 24.43 ± 5.28% yield. The physical characteristics and chemical composition of biochar were determined with elemental analysis, BET sorption, SEM, and FT-IR techniques. Thermal analysis of the conversion of biomass to biochar was also done to follow the physicochemical property at pyrolysis temperature. In this experiment, the biochar was produced in a modified pyrolysis chamber and the temperature was detected at ~500 °C with a heating rate in the range of ~10 °C min⁻¹ (~2 h pyrolysis process). Low-temperature pyrolysis at 400 °C–500 °C gave a higher biochar yield with more volatile-matter components than high-temperature pyrolysis, so increasing the pyrolysis temperature reduced biochar yield and its volatiles content [29]. The elemental composition and physical parameters of the corncob biomass and the biochar are given in table 1. The results show that carbon is the major constituent (C 80.60%wt) of corncob biomass, which confirms its carbonaceous nature compared to previous carbonized corncob prepared using acid (C 49.87%wt) [30]. The obtained biochar has a high fix-carbon content of 76%wt and a small ash content of 5%wt, which is low among plants biomasses [31, 32]. The previous work of Lonappan et al. 2016, suggested that biochar with high ash content exhibited subdued adsorption potential for organic pesticides, such as carbaryl and atrazine, because adsorption sites of organic moieties can be masked by the ash [5, 33, 34]. Dehydration and decarboxylation removed oxygen and hydrogen from the biomass material in H₂O, and CO₂ forms, so oxygen and hydrogen contents in biochar were dramatically decreased from those in the biomass [35]. The nitrogen content is higher in biochar than in the raw material, because of only slight loss of nitrogen in the forms NOₓ and NH₃, so nitrogen largely remained in the carbon structure at the current pyrolysis temperatures, and is seen in the C–N peak of IR spectrum of the biochar [36]. The volatile matters contribute to the bio-oil remaining after pyrolysis of corncob biomass. The TOC is the total organic carbon content, which was increased by pyrolysis. The chemical composition observed is comparable to prior studies on pyrolysis of corncob to biochar [37–39].

The BET surface area relates to porosity as shown in table 2 and figure 1. The specific surface of corncob biochar was 655.79 m² g⁻¹, and the pore volume was 0.26 cm³ g⁻¹, and these depend on the pyrolysis conditions, including temperature and heating rate. The biochar was considered mesoporous structure [10]. The adsorption average pore diameter was estimated as 1.58 nm by BET technique [19, 40]. These results can be

| Parameter     | Unit      | Corncob biomass | Biochar |
|---------------|-----------|-----------------|---------|
| C             | %wt       | 44.01 ± 0.22    | 80.60 ± 0.38 |
| H             | %wt       | 5.87 ± 0.23     | 2.08 ± 0.01  |
| N             | %wt       | 0.38 ± 0.02     | 0.58 ± 0.01  |
| S             | %wt       | 0.07 ± 0.01     | 0.01 ± 0.00  |
| O             | %wt       | 45.86 ± 0.39    | 6.72 ± 0.27  |
| Net heating   | value     | 3356.80 ± 77.85 | —        |
| Moisture content | %wt   | 7.76 ± 0.02     | 7.61 ± 0.06  |
| Volatile      | %wt       | 74.06 ± 0.23    | 10.94 ± 0.41 |
| Fixed carbon  | %wt       | 16.93 ± 0.21    | 76.43 ± 0.43 |
| Ash           | %wt       | 1.25 ± 0.03     | 5.02 ± 0.07  |
| TOC           | g kg⁻¹    | 385.31          | 700.60     |
compared with the previous result of Ma et al 2015 which reported the adsorbent of biochar prepared by hydrothermal carbonization using ZnCl₂ [41].

SEM micrographs of corncob biochar (figure 1) indicate rough honeycomb pattern with the heterogeneous pore size distribution of cylindrical pores (figures 1(a), (b)). The rough texture of porous biochar provided a large specific surface, see figure 1(c). All the micrographs and BET results indicate the excellent structure of the corncob biochars prepared by the in-house pyrolysis technique for an low-cost and environmental-friendly adsorbent (without chemical modification on surface of obtained biochar).

The FT-IR spectra showed functional group changes on the surfaces of the corncob biochar compared to original surfaces of biomass. The functional groups observed by FT-IR in biomass and biochar are listed in figure 2. For biomass, the broad peak at 3400 cm⁻¹ is attributed to H–bonded O–H stretching vibrations of hydroxyl groups from water content, alcohols, phenols, and organic acids; and also to N–H stretching in a small amount of NHₓ in corncob. The peak at 2920 cm⁻¹ indicates C–H stretching of alkyl structures. The peaks at 1620–1690 cm⁻¹ are from vibrations of aromatic and olefinic C=C bond, and of C=O in amide and ketone groups. The peaks at 1190–1220 cm⁻¹ were assigned to the C–O, C–N and C–S stretching. A strong dependence of carbonization on temperature was observed for corncob biomass, by changes in the FT-IR spectrum. The differences in FT-IR spectra reflect organic matter degradation, water loss, and changes in mineral components from the heat-induced mass losses [42].

Figure 3 shows a thermal analysis of the preparation of biochar. The DTG curve of corncob biomass shows weight loss peaks at 56, 290 and 336 °C. The first peak is due to degradation of volatile compounds. The peaks at 290 and 336 °C show degradation by release of remaining water from crystalline phases, and removal of volatiles CₓHᵧOz and CₓHᵧ related with change in FT-IR spectrum of biomass to biochar, with the transition ending around 400 °C [43]. The small transition around 700 °C shows loss of carbon (C=C, C–N, C–S, C–O) leaving only ash. TGA graph is related to the DTG curve with a weight loss of 36% at 308 °C. The results suggest that pyrolysis at ~500 °C is proper for corncob biomass.

| Sample | Parameter                        | This work (m² g⁻¹) | [41] (m² g⁻¹) |
|--------|----------------------------------|--------------------|--------------|
| Biochar| BET Surface area                 | 655.80             | 153.89       |
|        | Mean pore diameter (nm)          | 1.6                | 8.4          |
|        | Pore volume (cm³ g⁻¹)            | 0.27               | 0.18         |

Degas temperature of sample cleaning at 150 °C.

Figure 1. Scanning electron microscopy images of surface, in 20 (a) and 500 (b and c) microns, showing surface area and pores of corncob-derived biochar.

Table 2. BET results showing surface area and porosity of corncob-derived biochar.
3.2. Adsorption Study

The adsorption time and the initial concentration of MB are important factors influencing the adsorption capacity, as shown in Figure 4. The removal efficiency of MB by biochar increased consistently with time. Furthermore, increasing the initial MB concentration increased adsorption. The kinetic study showed that the adsorption of MB with different initial concentrations (5, 10, 50 and 80 mg l$^{-1}$) by corncob biochar reached the
equilibrium at different times. Absorption capacity and equilibration time increased with initial concentration. Rapid adsorption was observed in the first stage (0–5 min).

The adsorption isotherms for MB adsorption by corncob biochar at 25 °C are shown in figure 5, along with the fits by Langmuir and Freundlich models. The fitting parameters are listed in table 3, with coefficients of determination for Langmuir (R² = 0.9998) and Freundlich (R² = 0.9522) models. The Langmuir model gave a better fit suggesting that the adsorption of MB by biochar was mainly to a monolayer. From table 3, the K_L is larger than 0.5 and less than 1 (K_L = 0.524), so the adsorption of MB by corncob biochar was favorable [44]. Fan et al. 2017, also suggested that the factor (n⁻¹) in the Freundlich isotherm model can reflect the heterogeneity factor, the heterogeneity of site energies, and the adsorption intensity. Values of n⁻¹ smaller than 0.5 indicate that the adsorbate is easily adsorbed, while values of n⁻¹ larger than 2 indicate the adsorbate is hardly adsorbed [3]. In this study, the value of n⁻¹ for MB adsorption onto corncob biochar was −0.276 (<0.5), which indicates that MB was easily adsorbed by the corncob biochar.

The adsorption kinetics of MB in solution by corncob biochar at 25 °C are shown in figure 6. The fits of the pseudo-first and pseudo-second order kinetic models to MB adsorption by corncob biochar, at different initial MB concentrations, are summarized in table 4. At the lowest initial concentration of MB (10 mg l⁻¹), the pseudo-first models can fit adsorption data with the R² values of 0.9687. At a higher initial concentration of MB (50 mg l⁻¹), the adsorption of MB by corncob biochar becomes diffusion-controlled, so that the pseudo-second order model fits well because it can account for external liquid film diffusion, surface adsorption, and intra-particle diffusion of MB in corncob biochar. This model provides a more accurate and comprehensive interpretation of the adsorption mechanisms than the pseudo-first order model [45, 46]. The rate-limiting step and the linear form of pseudo-second order kinetic model confirm chemisorption in which liquid film diffusion, intra-particle diffusion and surface adsorption affected MB adsorption rates. On increasing the initial MB concentration, the molecules gradually disperse into the interior of the corncob biochar particles. Hence, the adsorption of MB on corncob biochar is very well fit by the pseudo-second order model, with coefficient of determination close to 1; and the calculated adsorption capacity (q_e = 16.69 mg g⁻¹) agrees well with the experimental adsorption capacity (16.50 mg g⁻¹).

The proposed mechanism of MB adsorption on corncob biochar is attributable to the functional groups and bonds presented on adsorbent surface. FT-IR result was therefor used for preliminary qualitative analysis of the change in major functional groups present on pristine biochar surface after MB adsorption. FT-IR spectra of pristine biochar and MB-adsorbed biochar were presented in figure 7, and the presented functional groups were listed in table 5. The broad peak at 3623 cm⁻¹, assigned to the stretching of O—H group was due to intermolecular hydrogen bonding of methylene blue and functional groups of biochar, such as alcohols, phenols and carboxylic acids [47]. The weaken C—H stretching band at 2877 cm⁻¹ and C—H bending band at 872 cm⁻¹ of MB-adsorbed biochar indicate hydrogen bonds (N—H—C or S—H—C) of C—H with phenothiazine moiety in MB. The weaken peaks of C==O stretching observed at 1551 cm⁻¹ and C—O stretching observed at 1002 cm⁻¹ were due to intermolecular hydrogen bonding of oxygen-containing group on biochar with N—H bonds of —NH₃ group of MB [48]. Moreover, The arising peak observed at 1222 cm⁻¹ on MB-adsorbed biochar was interpreted to C—N stretching of methylene blue moiety. A comparison of adsorption capacities of the biochar.
with literature data on some adsorbents is shown in Table 6. Without any chemical activation, the adsorption capacity of MB by corncob biochar is significantly low from the other referred studies even a very large BET surface area (655.8 m² g⁻¹) in the present work. However, the surface areas is not always the only factor that affect the adsorption capacity of an adsorbent. The surface chemistry, such as functional group and acid/base character, and the type of pores on biochar surface influenced from the different carbonization temperatures and activations are also the important factors driving the adsorption property in large extension [49].
4. Real-field applicability of this work

Nowaday, the air pollutions and PM 2.5 problems are the increasingly serious problems in the Northern Thailand and nearby countries. Thailand is predominantly an agricultural country, especially in the northern region, and the main crops include corn, rice and pineapple. After crop harvesting, these crop wastes have been eliminated by burning process in the open air causing redundant problems and irreparable damage to human health in many areas. In order to disseminate the low-cost method to eliminate these wastes and to return the wastes to biochar, in-house modified pyrolysis tool is reported in this work. This modified tool can be a simple
and low-cost model for people who want to dispose of agricultural wastes in their house beside making fertilizer and landfill. Moreover, the demand for biochar is increasing, either for soil amendment as fertilizer or as an adsorbent. With this technique, the farmers can prepare biochar by themselves. The physicochemical properties including %CHNO content, mesoporous pore size and pore volume of corncob biochar prepared by in-house modified pyrolysis method is comparable with biochar prepared using chemicals activation or by furnace machine. The obtained characteristics is helpful in adsorbing the fertilizers for slowly releasing of adsorbed fertilizers into the soil and removing of toxic agents from wastewater. Although biochar is a suitable alternative material for various applications, the diversity of physicochemical properties of biochar was significantly related to the origin of the agricultural residues and carbonization process. These can encourage Thai farmers to install simple technology and monitor the quality of the obtained products which are the important advantages to quality control criteria during bio-production. Long-term field trials are essential to support environmental impact assessment (EIA) for future defined recycling situations.

**Table 5. Functional groups of biochar before and after MB adsorption.**

| Assignment                          | Biochar, cm⁻¹ | Biochar+MB, cm⁻¹ | Difference, cm⁻¹ |
|-------------------------------------|---------------|------------------|-----------------|
| Before adsorption                   | After adsorption |                   |                 |
| −OH stretching | 3431 | 3623 (broad) | 192 |
| Aliphatic C−H stretching | 2919 | 2877 | −42 |
| Aromatic C=C stretching, C=O stretching | 1613 | 1551 | −62 |
| C−N stretching | — | 1222 | — |
| C−O stretching | 1143 | 1002 | −141 |
| C−H bending | 882 | 872 | −10 |

**Table 6. Comparison of sorption property of MB dye by various biochars.**

| Biomass   | Carbonization Temperature, °C | Heating rate, °C/min | Time, min | Co, mg/L | qe, mg g⁻¹ | References |
|-----------|-----------------------------|----------------------|-----------|----------|------------|------------|
| Barley malt bagassea | 800 | 10 | 60 | 50 | 32.42 | [50] |
| Corncob b | — | — | — | 50 | 39.10 | [27] |
| Corncob c | 180 | 360 | 55.86 | [38] |
| Corncob d | 500 | 10 | 60 | 50 | 16.69 | Present work |

*The biomass was pyrolyzed in furnace followed by CO₂ activation.

* The biomass was carbonized by chemical activation with H₂SO₄.

* The biochar was prepared by hydrothermal carbonization using ZnCl₂.

* The biochar was prepared in house modified pyrolysis chamber without any chemical modification.
5. Conclusion

An investigation of physicochemical characteristics and chemical composition showed good properties of the corncob biochar prepared by in-house modified pyrolysis in terms of a specific surface, active sites of functional groups, texture and morphology. Thermal analysis indicated that pyrolysis at ~500 °C is proper to produce biochar from corn biochar biomass with high carbon contents. And the biochar residues from corn (Zea mays L.) could serve as raw material for the preparation of biochar for the removal of methylene blue dye from aqueous solutions, over a wide range of concentrations. Methylene blue dye was found to be strongly adsorbed by the biochar from corncob biomass with high carbon contents. And the corncob residues from corn production process as reported in earlier studies. Hence, corncob biochar prepared by in-house modified pyrolysis can be a viable alternative for a low-cost adsorbent in wastewater treatment.

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