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Removal of Methylene Blue via Adsorption using Magnetic Char Derived from Food Waste

Noor Raihan Izan[1], Muzakkir Mohammad Zainol[1]*, Abu Hassan Nordin[2], Mohd Asmadi[2], Syie Luing Wong[3], Muhammad Ammir Ilham Azhar[1] and Nur Hashimah Alias[1]
[1]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor Darul Ehsan, Malaysia
[2]School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81300 Skudai, Johor Darul Takzim, Malaysia
[3]Dpto. Matemática Aplicada, Ciencia e Ingeniería de Materiales y Tecnología Electrónica, Universidad Rey Juan Carlos, C/ Tulipán s/n, Móstoles 28933, Madrid, Spain.
*Corresponding author (e-mail: muzakkir@uitm.edu.my)

In this work, the char residue from hydrothermal liquefaction of food waste was chemically treated with potassium hydroxide and modified to prepare magnetic char (MC) adsorbent for removal of methylene blue (MB). The char was modified to prepare MC with improved surface properties and to enhance MB adsorption. The surface chemistry and textural properties of the developed modified char were analyzed by Fourier transform infrared spectroscopy, thermogravimetric analysis, vibrating sample magnetometry, and point of zero charge. Raw char and various treated char and MC prepared at different conditions were used for MB adsorption at selected conditions to identify the best performing adsorbent for further testing in the parametric study. The influence of pH (2–12), adsorbent dosage (0.05–0.15 g), and initial MB concentration (50–250 mg/L) was studied for 30 min at room temperature to determine the conditions for maximum adsorption capacity and removal efficiency of MB using MC. The results show successful impregnation of magnetic nanoparticles (MNP) on activated char for effective MB adsorption and also for MC separation after adsorption. The adsorption capacity of MB achieved approximately 59.8 mg/g with the maximum removal efficiency of 59.8% using selected MC at the conditions of pH 10 and 0.05 g of MC dosage for 30 min. The finding shows that MC has a potential as an effective adsorbent to remove dyes from wastewater and has an advantage to separate adsorbent using magnet.

Key words: Magnetic char; methylene blue; adsorption; food waste; cationic dye

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Industrial growth and increasing demand for dyes, particularly in the papermaking, textile, paint, and printing industries, have led to a large amount of toxic chemical discharge into water resources. Methylene blue (MB) is a common type of synthetic dye in coloring wood, silk, and cotton. This cationic dye with the chemical formula $C_{16}H_{18}N_3SCl{\cdot}3H_2O$ appeared deep blue when dissolved in water [1]. Due to their capacity to limit oxygen levels and inhibit light penetration, this highly colored effluent significantly impacts photosynthetic organisms and aquatic life. Long-term exposure to MB can cause allergic reactions, breathing problems, discomfort, vomiting, nausea, and diarrhea [2]. In general, dyes have the potential to be poisonous and cancerous. Therefore, the uncontrolled release of coloring compounds causes significant environmental contamination and negative consequences on human health.

Dye wastewater treatment is challenging due to its complex chemical structure, color resistance, and low biodegradability [3]. Throughout the growth of technology, numerous physical and chemical methods have been introduced, including membrane filtration, photodegradation, electrochemistry, ozonation, and adsorption. Although there are many solutions for wastewater treatment, most of these techniques require high operating costs and need further pretreatment phases before application. Therefore, these methods are less cost-effective. Adsorption has gained attention as a treatment option owing to its simplicity, high operational efficiency, environmentally friendly, and cost-effectiveness in comparison to other methods [4]. Besides, the essential feature of adsorption has made this technique favorable due to the absence of hazardous compounds generated during the operation [5].

Many studies have recommended porous materials, such as activated carbon (AC), as the most effective materials for dye removal [6,7]. As the environmental crisis arises from the abundance of

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food waste and agricultural by-products, this indirectly sparked the interest of researchers to use low-cost adsorbents as precursors in dye adsorption [8]. Biochar from hydrothermal liquefaction (HTL) of biomass, also known as hydrochar, is a valuable product with significant benefits other than the liquid water-immiscible product (i.e., bio-oil) [9]. Biochar liquefaction is well-known with the presence of several functional groups, including hydroxyl, phenol, and carboxyl [10]. Hydrochar produced from HTL of food waste has low alkalinity, indicating that acid-free and base-added reactions have a lower pH value (4.0 ± 0.1) [11]. Adsorptive forces may be created between the adsorbent and the cationic adsorbate for effective removal of organic dyes through the existence of surface functional groups and relevant properties.

HTL biochar produced from wastewater sludge and lignocellulose biomass exhibits slightly lower adsorption capacity than commercial AC [10]. For example, the biochar prepared from the pyrolysis of mixed municipal discarded material achieved low MB adsorption capacity of 7.2 mg/g [12]. Acknowledging these findings, there is still potential for char from food waste as an absorbent, and further improvement is required for better outcomes. Chemical treatment or activation can be applied to improve the surface chemistry of adsorbent. Chemical activation on adsorbent is typically favored due to its simplicity, low-temperature process, shorter activation time, and improved porous structure of the material [13]. Char can be modified via chemical treatment or activation using potassium hydroxide (KOH), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and potassium carbonate (K_2CO_3) on the precursor to improve the surface chemistry of adsorbent. According to a recent study on MB adsorption, the modification of AC from date stones with an alkali-type activator (i.e., NaOH) achieved a maximum value of 163.6 mg/g in improving the capacity of dye adsorption [14]. Similarly, the synthesis of KOH-AC from tea waste produced adsorbent with a higher surface area, which increased the effectiveness of MB adsorption to 357.14 mg/g [15] compared to NaOH as an activating agent, which recorded 33.33 mg/g of adsorption capacity [16]. Activated carbon from cellulose prepared using KOH as an activator received a great deal of interest due to its excellent ecologically beneficial properties, such as biodegradability [17].

A previous study demonstrated that HTL char has the potential to remove contaminants from wastewater as a high-performance magnetic composite [18]. The problem in the dissociation of hydrochar in aqueous solution can be resolved by converting the hydrochar into a magnetic material [19]. Magnetic separation is a promising technique for easy and quick recovery under an external magnetic field. According to recent research, magnetically-modified materials can be separated selectively, quickly, and easily from dye wastewater [20]. Well-distributed magnetic particles on the adsorbent surface can improve surface chemistry and adsorption performance. Hence, the modification of char via impregnation with magnetic nanoparticles (MNP) can be considered as one of the best approaches of low-cost adsorbent with higher adsorption capacity.

The char residue from HTL of food waste has a potential as an adsorbent for wastewater treatment (e.g., MB removal), but some modification on char is required to improve its surface properties. There are limited studies on the application of food waste char for MB adsorption, including the application of magnetic char (MC) adsorbent. Therefore, in this study, the char residue was treated with KOH solution and thermal treatment, followed by impregnation with MNP to prepare MC adsorbent. Raw char and magnetic-activated char were analyzed to study the adsorbent properties. The removal of MB was studied for raw char and various treated char and MC prepared at different conditions to choose an adsorbent for further parametric study.

METHODOLOGY

1. Materials

The char utilized as a precursor in this research is a solid residue obtained from the previous work of HTL of food waste containing rice, vegetables, and chicken, as described by [21]. The char was obtained after the HTL process in a batch reactor at 225 °C for 1 h. The magnetic nanoparticles (iron oxide, Fe_3O_4) were purchased from Merck Millipore, while other chemicals, including MB dye ($C_{16}H_{18}N_3SCl{\cdot}3H_2O$), KOH, NaOH, and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich. The purchased chemicals were utilized as received without further pretreatment or purification.

2. Preparation of Magnetic Char

Char was pretreated in a furnace at 200 °C for 2 h prior to chemical treatment with 2 M KOH at a specified ratio (1:4 g/mL of char:KOH) under stirring for 6 h, followed by washing with distilled water and drying in an oven at 80 °C for 24 h. The char was further heated in the furnace at 300 and 400 °C for 2 h, where the end products were named C-300 and C-400, respectively. The treated chars (C-300 and C-400) were washed with distilled water, filtered several times until pH 7.0–7.5, and dried in the oven at 80 °C for 24 h prior to further modification.

The precursor of MC was prepared and modified from the work of [22, 23] by mixing 2 g of activated char and MNPs through impregnation. Different loadings of MNP (X = 0.2, 0.6, 1.2, and 2.4 g) were applied for impregnation with treated char in distilled water for 1 h and labeled as MC-300-X or

MC-400-X. Then, MC was filtered and oven-dried at 80 °C for 24 h prior to adsorption testing.

3. Treated Char and Magnetic Char Characterization

The presence of surface functional groups and chemical interaction was identified for the treated char and MC by Fourier transform infrared (FTIR) spectroscopy using a Perkin Elmer Spectrum One spectrometer with universal attenuated total reflectance sampling for the range of 400–4000 cm^{-1}. The thermogravimetric analysis (TGA) was conducted to study thermal stability and degradation of MC were evaluated using Mettler Toledo TGA/SDTA 851 apparatus by heating from 30 to 950 ℃ under N_2 flow at 10 ℃/min. A vibrating sample magnetometry (VSM) analyzer from Lake Shore 7400 was used to study the magnetization value and hysteresis loop of the selected MC sample. Meanwhile, the point of zero charge (pH_{pzc}) was determined following previous studies by preparing a 0.01 M NaCl solution (50 mL) in conical flasks with pH ranging from 2 to 12 [24-26]. Then, 0.1 g of adsorbent was added to each flask and left for 48 h. The initial and final pH values were measured using a pH meter.

4. Adsorption Performance

A standard solution was prepared by dissolving 1 g of MB in distilled water to prepare a 500 mg/L stock solution. Other solution concentrations used in this work were prepared by diluting the stock solution. The removal efficiency of MB and corresponding absorption capacity by MC were used to assess the adsorption performance. For the standard test conducted, a 50 mL solution containing 100 mg/L of MB and 0.1 g of adsorbent was used for the adsorption test for 30 min at room temperature and under constant stirring (200 rpm). The removal of MB via the effect of different pHs (2–12), adsorbent dosages (0.05–0.15 g), and initial MB concentrations (50–250 mg/L) was studied using MC for 30 min at room temperature.

After the adsorption test, the adsorbent was filtered and the filtrate was further analyzed using an ultraviolet-visible (UV-Vis) spectrophotometer (Perkin Elmer, LAMBDA 750) at 665 nm. The final concentration of MB was determined based on the standard calibration curve of the MB solution. The removal efficiency (RE) of MB (%) and the adsorption capacity (AC, mg/g) were calculated following Equation (1) and (2), respectively:

$$RE\ (\%) = \frac{C_o - C_f}{C_o} \times 100\% \qquad \text{Equation 1}$$

$$AC\ (mg/g) = \frac{(C_o - C_f)}{m} \times V \qquad \text{Equation 2}$$

Where C_o and C_f represent the initial and final concentrations of MB dye (mg/L), respectively, V denotes the volume of dye solution (L), and m is the adsorbent dosage (g).

RESULTS AND DISCUSSION

1. Methylene Blue Adsorption

The initial study of MB adsorption was conducted to compare and select the suitable adsorbent for further testing. The study was conducted under different pH conditions (pH 2, 6, and 10) by fixing other parameters. Figure 1 shows the results of the percentage removal of MB dye. Significant removal was observed for MC-300-0.2 at pH values of 6 and 10 with removal efficiency and adsorption capacity of 57% (27 mg/g) and 79% (40.0 mg/g), respectively. Among all adsorbents, treated char (C-300) and magnetic char (MC-300-0.2) achieved excellent removal efficiency and adsorption capacity. The surface of char is chemically and thermally treated at 300 ℃ to improve the surface chemistry of the char. A previous work applied chemical treatment and thermal heating to create more pores on the adsorbent for MB adsorption [27]. KOH was used to treat the char as the surface is initially acidic, which is less effective for MB adsorption. This is because the proton formation on the surface reduces the attraction of MB cation and consequently the adsorption of MB cation, resulting in lower adsorption capacity of MB [23]. The impregnation of 0.2 g of MNP achieved the optimal loading by the incorporation with treated char, where the MNP distributed uniformly and homogeneously throughout the solution while maintaining an excellent adsorption capacity of MB. The result for MC-300-0.2 is slightly higher than C-300, highlighting the advantage of MC-300-0.2 as magnetic adsorbent without affecting adsorption performance after the impregnation of MNP. A similar approach was implemented by Nordin et al. [23] to prepare magnetic adsorbent with good adsorption capacity. A suitable loading of MNP can maintain the cationic dye adsorption performance, whereas a high loading of MNP can block active pore sites on the adsorbent surface. Therefore, MC-300-0.2 was selected for further adsorption study. The results also indicate that MC-300-0.2 has better performance in alkaline condition (high pH value) for the MB adsorption study. A further study was conducted to identify the optimum pH for MB adsorption using MC-300-0.2 and to relate with the results of pH_{pzc} analysis performed on MC-300-0.2.

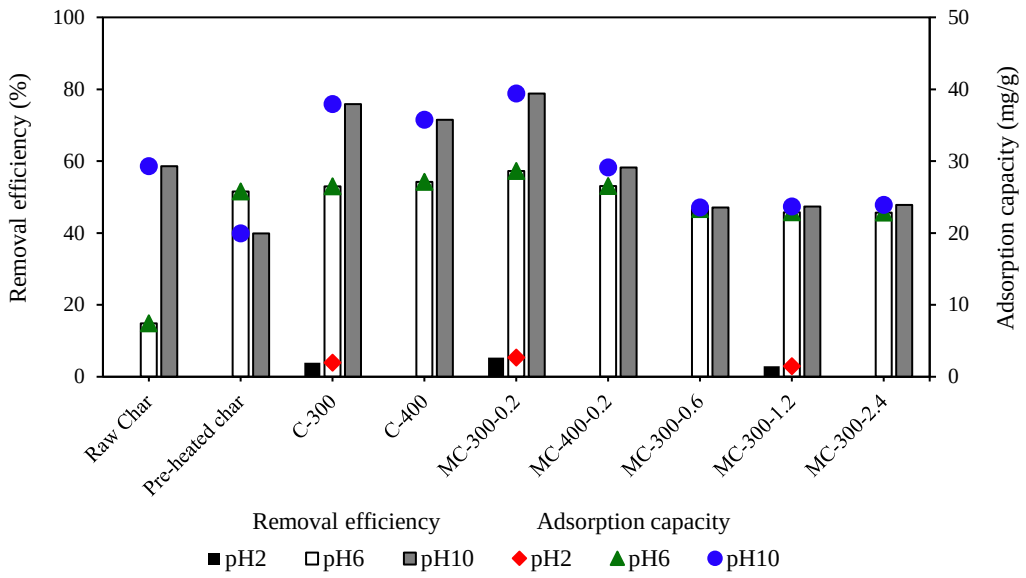

Figure 1. Removal efficiency and adsorption capacity of MB using various adsorbents at different pHs (0.1 g adsorbent, 100 mg/L, 30 min).

The effect of the initial pH of MB solution (between pH 2 and 12) is significant on MB adsorption by MC-300-0.2. Based on the results in Figure 2, the adsorption efficiency of MC-300-0.2 increased with the increase of the initial pH of MB solution. This suggests that the negative charge developed on the MC surface potentially enhanced MB removal. The MB uptake by MC-300-0.2 increased significantly as the initial pH increased from 2 to 4, but decreased slowly for the adsorption between pH 4 and 9. The acidic condition makes the proton formation competes with MB cation for adsorption on the active sites of MC-300-0.2, resulting in lower adsorption capacity [23]. Meanwhile, pH near neutral conditions resulted in a buffering mechanism on the surface of MC-300-0.2, which describes the slow increase in MB adsorption [28]. As the pH of the solution shifts to a high range of 10–12, high adsorption of MB is noticeable, which is likely due to the high cation exchange capacity on MC-300-0.2. The alkaline condition of the solution indicates that more negative charges are present on the adsorbent surface [19]. The negative charge on the surface of MC-300-0.2 results in electrostatic attraction to cationic MB for high adsorption efficiency and capacity, which is around 80% (~40 mg/g). Thus, it can be concluded that MC-300-0.2 requires a basic condition for high adsorption efficiency. Therefore, the solution with pH 10 was applied for subsequent adsorption studies.

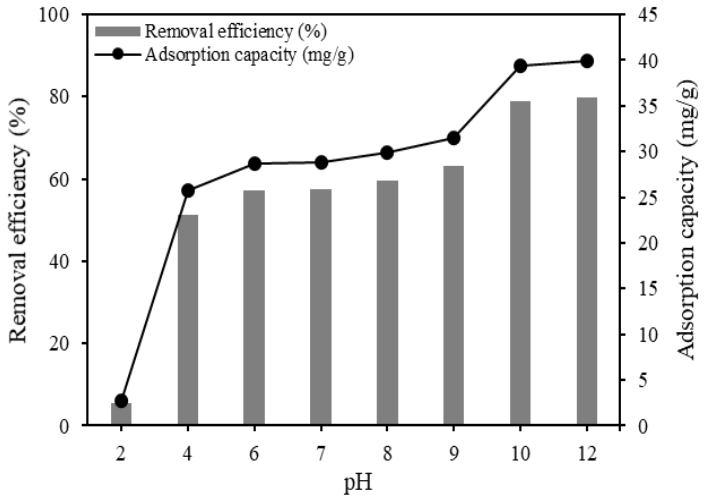

Figure 2. The effect of pH values on the removal efficiency and adsorption capacity of MB using MC-300-0.2 (0.1 g adsorbent, 100 mg/L, 30 min)

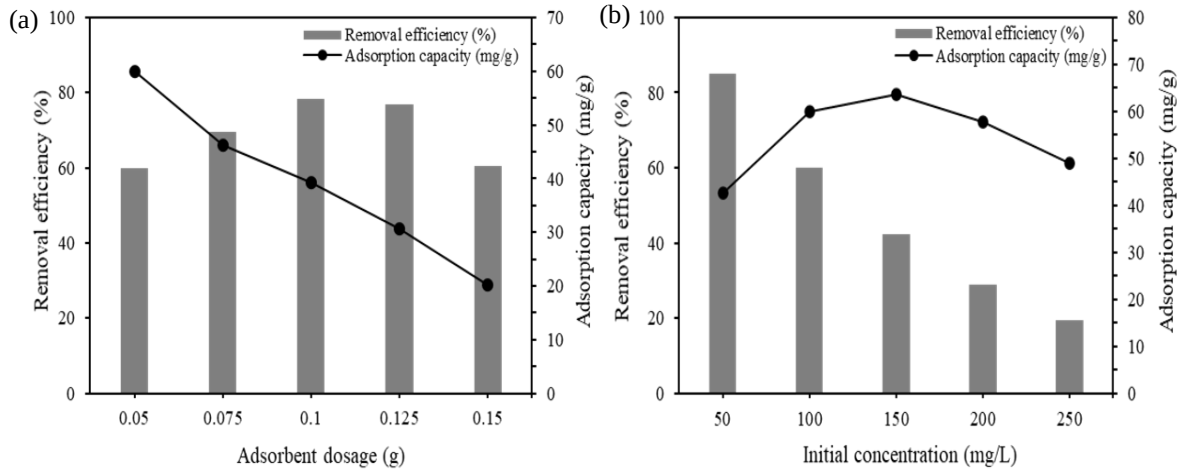

Figure 3. The effect of (a) adsorbent dosage (pH 10, 100 mg/L, 30 min) and (b) initial concentration (pH 10, 0.05 g adsorbent, 30 min) on the removal efficiency and adsorption capacity of MB using MC-300-0.2.

The effect of MC-300-0.2 dosage was evaluated for the adsorption of 100 mg/L of dye solution at pH 10, and the results are shown in Figure 3(a). As can be seen, the plot shows that the adsorption efficiency of MB increased from 60.0% to 78.4% for MC-300-0.2 dosage from 0.05 to 0.1 g, respectively. This is due to the increasing availability of unoccupied adsorption sites and the surface area of adsorbent for adsorption [29]. High adsorbent dosage may translate into high removal efficiency. However, the increasing dosage reduces the adsorption capacity. Further increase of adsorbent dosage may affect the condition of the solution as its alkalinity (initial pH) might not be sufficient to provide negative charges for MB adsorption. Thus, the removal efficiency could decline at this condition. Therefore, an adsorbent dosage of 0.05 g was used for the subsequent parametric study of MB adsorption due to its high adsorption capacity of 59.8 mg/g.

Figure 3(b) presents the effect of the initial concentration of MB solution on adsorption performance using MC-300-0.2. The results show a significant decrease in the percentage removal of MB as the initial concentration increases. However, the MB uptake increases from 42.6 to 63.7 mg/g. This indicates that at a higher initial MB concentration, the collision between MB cation and MC surface occurs more frequently, resulting in increased MB adsorption capacity [6]. This interaction initiates the competitive adsorption of MB onto the surface of adsorbent up to the optimum concentration. The MB uptake begins to decline as the concentration is raised above 150 mg/L. This implies that at a high MB concentration, the availability of adsorption sites decreases as the MC surface is already occupied by MB [4]. Therefore, the maximum concentration of 100 mg/L is considered due to the small difference in adsorption capacity compared to MB removal at 150 mg/L.

2. Treated Char and MC Characterization

The effect of pH on MB adsorption was examined as it is a crucial parameter related to surface charge and ionization of adsorbate molecules [23]. The influence of pH on the removal of MB can be supported using the pH_{pzc} of the adsorbent surface. Figure 4 depicts the plot used to determine the pH_{pzc} value of raw char, preheated char, C-300, and MC-300-0.2. This analysis is conducted to have a better understanding of the effect on adsorption performance with the change of surface properties. Generally, the adsorbent is positively charged when the pH of the solution is less than the pH_{pzc}. As the pH of the solution exceeds the value of pH_{pzc}, the surface of the adsorbent increases its intensity of negative charge, which is very effective for cationic dye adsorption [30]. The analysis shows that the pH_{pzc} of C-300 and MC-300-0.2 is pH 10, which can be considered as the optimal pH. The results also indicate that C-300 and MC-300-0.2 are suitable in alkaline solutions due to the developed negative charge, resulting in electrostatic attraction to cationic MB. Hence, this result supports MB removal at different pHs (as in Figure 2) and the use of MC-300-0.2 to obtain optimum adsorption at pH 10.

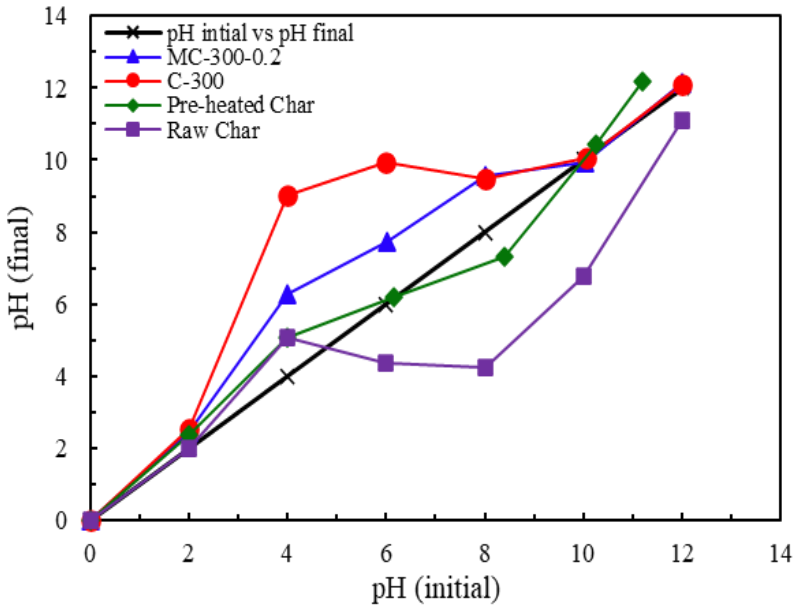

Figure 4. A plot for the determination of point of zero charge of raw char, preheated char, C-300, and MC-300-0.2.

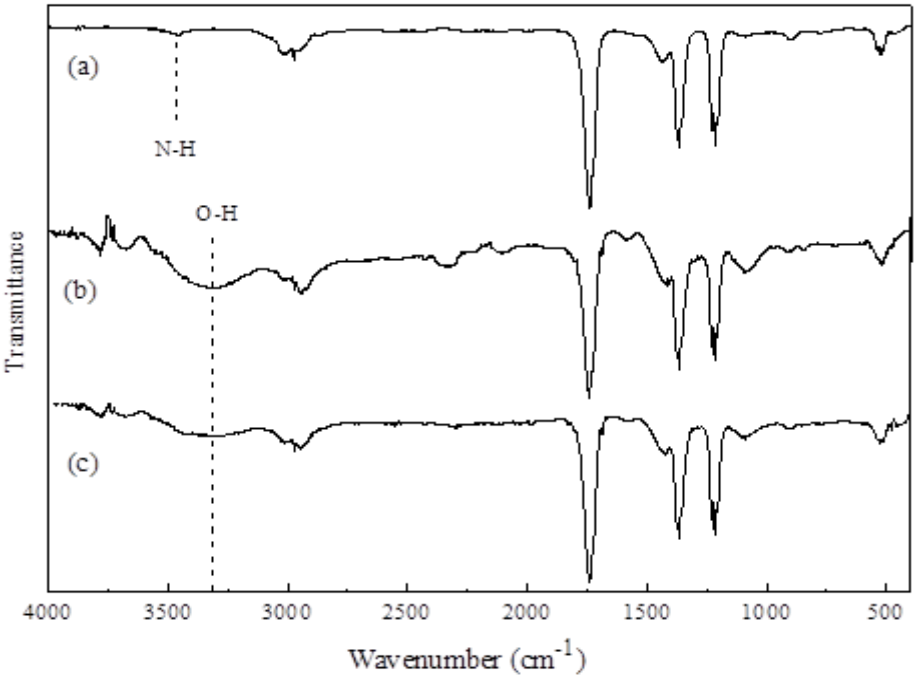

Figure 5. FTIR spectra of (a) preheated char, (b) C-300, and (c) MC-300-0.2.

Figure 5 shows the functional groups and chemical bonding of preheated char, C-300, and MC-300-0.2 studied using FTIR spectra. The broad peak at 3100–3500 cm^{-1} is detected, which refers to O-H stretching (e.g., moisture), as well as N-H stretching (e.g., protein structure) in the char structure [21]. As observed for the preheated char, a small peak of N-H stretching is observed around 3400–3450 cm^{-1}. The broad peak O-H stretching is observed for C-300 and MC-300-0.2 due to the effect of alkaline treatment and the presence of moisture in the samples after washing and drying. C-H stretching of -CH aliphatic in the char structure is detected around 2800–2900 cm^{-1}. The strong frequency peak detected at approximately 1700–1750 cm^{-1} is related to C=O stretching and possibly related to carboxylic acid, phenol, ketone, and/or aldehyde in the food waste char structure. The small peak refers to O-H bending around 1420 cm^{-1},

and the strong stretching around 1350–1370 cm^{-1} refers to C-N stretching and possibly S=O stretching. The stretching around 1200–1230 cm^{-1} is referred to the C-O functional group in the char structure. Semaan et al. [31] also reported that the frequency of C-O stretching for wood char and tire char is at approximately 1200–1230 cm^{-1}. A small peak at 1090 cm^{-1} is possibly related to S-O vibration or other C-O vibrations (e.g., aliphatic ether or alcohol). Comparing the IR spectra of MC-300-0.2 with those of C-300 and preheated char, the increasing peak intensity and sharp peak are observed around 500–600 cm^{-1}, which refers to Fe-O bonding of magnetic particles on the surface of char. The increasing peak intensity of C-O and O-H for MC-300-0.2 and C-300 show that the surface chemistry of the char improved after chemical and thermal treatments. These functional groups may be responsible for a possible binding mechanism with MB (cationic) dyes. The Fe-O bonding, which refers to MNP, provides a small effect on enhancing the removal of MB dye in this work, but shows an advantage as an alternative method for separating adsorbent using magnet.

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of preheated char, C-300, and MC-300-0.2 are presented in Figure 6. The preheated char and C-300 indicate high thermal stability up to 400 °C and further degraded until the final weight around 40–50 wt. % at 950 °C. Higher stability is shown by MC-300-0.2, where 70 wt. % of the sample can be retained up to 950 °C due to the presence of magnetic particles in the structure. The DTG peak shows the major mass loss from initial up to 950 °C, which can be divided into three major regions. The first region is below 200 °C, which shows major degradation of moisture and light components in char structure [25]. The second region is considered from 200 to 750 °C, where high degradation of sample is observed for preheated char due to the de-composition of major organic compounds of char. As discussed by Mahssin et al. [21], food waste contains organic compounds, such as protein, carbohydrate, and lipid, which are available in the solid residue (char) structure and decomposed in this region. However, small degradation between 200 and 400 °C for C-300 and MC-300-0.2 samples are observed due to the preparation and treatment of char conducted at 300 °C.

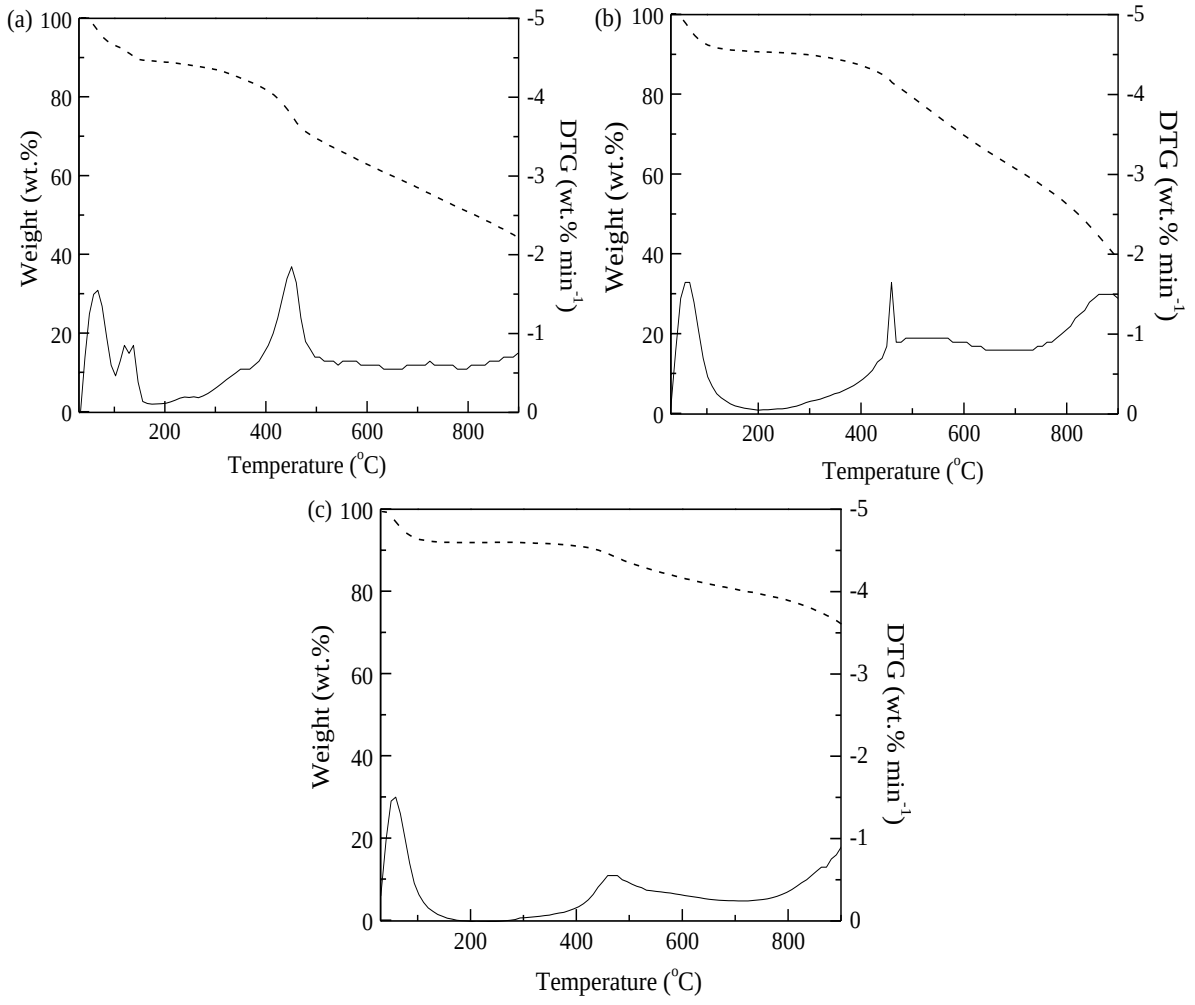

Figure 6. TG-DTG curves of (a) preheated char, (b) C-300, and (c) MC-300-0.2.

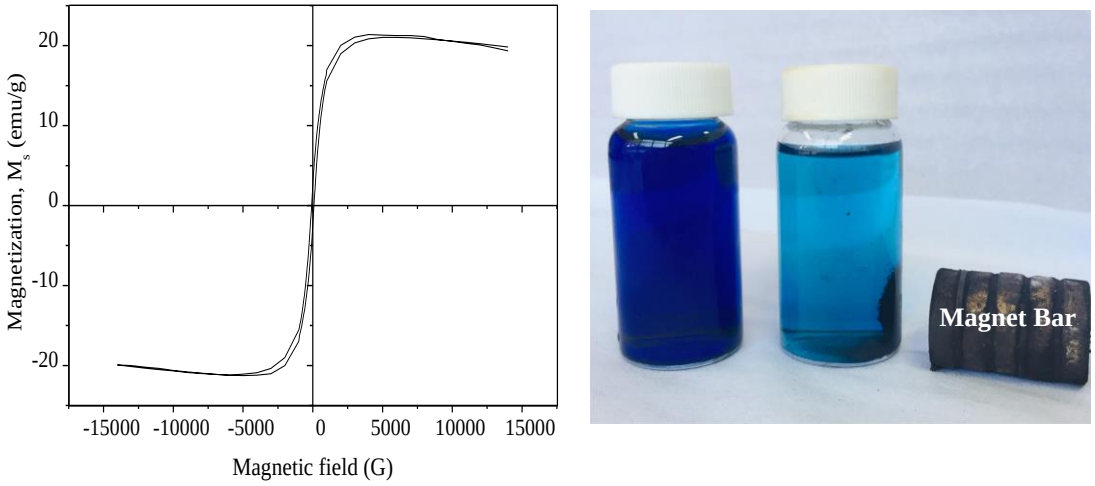

Figure 7. Magnetization curve of MC-300-0.2 and image of MB removal.

The final region, which is around 750–950 °C, shows that C-300 and MC-300-0.2 have higher degradation in this range of temperature. This explains that the chemical and thermal treatment of char has rearranged the char structure. The treated char becomes more thermally stable as the degradation peak of char shifts to high temperatures. After heat treatment, the char structure has changed due to the rearrangement of carbon structure, resulting in a more stable structure. This situation can be related to heat treatment of lignin polymer, which becomes more thermally stable due to changes in its aromatic structure and degree of condensation [32]. Yousef et al. [33] reported that the thermal treatment has caused the decomposition of all volatile compounds into carbon compounds with high thermal stability due to a large amount of ash and carbon in the sample. The presence of magnetic particles on the char structure also affects thermal stability. Based on the TG curve of MC-300-0.2, the recorded weight loss is different to the C-300 sample, which is due to the presence of magnetic particles in the char structure. A similar finding was observed for the impregnation of magnetic particles on oil palm frond activated carbon [26]. The results show increased thermal stability of magnetic adsorbent after the impregnation of magnetic particles due to the small weight loss observed for MC-300-0.2 compared to the C-300 sample.

The magnetic properties of the selected MC adsorbent (i.e., MC-300-0.2) determined through VSM analysis are shown in Figure 7. The magnetic behavior of MC can be analyzed from the magnetization curve. The plot shows that the magnetization value increased with increasing field strength until magnetic saturation was reached, and there is a very small hysteresis loop, which explains the presence of remanence. In addition, there is also a low coercivity, which refers to the intensity of the applied magnetic field required to obtain zero magnetization [26]. The analysis of MC-300-0.2 shows the presence of a very low coercivity and remanence. Based on the results, MC-300-0.2 achieved a saturated magnetization value of 21.33 emu/g. In comparison to previous work, magnetic adsorbents such as oil palm frond activated carbon magnetic particles (OPFAC-MP) recorded a magnetization value of 2.76 emu/g [26], oil palm shell activated carbon magnetic particle (CAC-MP) achieved a magnetization value of 9.01 emu/g [25], cellulose with polyethyleneimine magnetic particles (MCPEI) obtained a magnetization value of 3.3 emu/g [23], and magnetic adsorbent nano-composites (CH-EP@Fe_3O_4/AC) demonstrated a magnetic saturation value of 17.3 emu/g [34]. The high dispersion of magnetic particles on char during impregnation provides a high magnetization value of MC-300-0.2. As stated by Nordin et al., [23], the magnetic properties of MC allow the separation and recovery of the adsorbent for regeneration purposes.

CONCLUSION

Magnetic char was prepared in this work for MB adsorption. The investigation of the effect of pH, adsorbent dosage, and dye concentration on the adsorption capacity and removal efficiency provides a significant output in determining the selected conditions for adsorption using the chosen MC, which is MC-300-0.2. The selected optimal pH, adsorbent dosage, and MB concentration are selected at 10, 0.05 g, and 100 mg/L, respectively which results an adsorption capacity of 59.8 mg/g. The selected MC also demonstrates good surface chemistry and thermal stability for MB adsorption, and the magnetic properties provide an alternative separation method of adsorbent using a magnet. The C-O and O-H functional groups of the MC may be responsible for the interaction with MB as cationic dyes. The Fe-O bonding and the magnetic properties show that the magnetic adsorbent was successfully prepared in this work. The thermal stability of the MC explained by

TGA results shows the ability of the MC as an adsorbent without thermal degradation during adsorption. In order to improve the adsorption and efficiency of MB in future work, the char can be prepared with other chemical modifications or conducted via thermal activation at high temperatures. The magnetic char obtained from this work can serve as a potential adsorbent for MB and possibly other organic pollutants.

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