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Ethanol, Methanol, and Magnesium-Treated Palm Kernel Shell Biochar for Methylene Blue Removal: Adsorption Isotherms

Hasana NH, Wahi R, Yusof Y

Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia.

ABSTRACT

Introduction: Biochar's adsorbent attributes, for instance, surface area, porous structure, surface functionality, and adsorption capacity, can be enhanced via suitable chemical modification.

Objective: This work aimed to study the effect of ethanol (EtOH), methanol (MeOH), and magnesium (Mg) treatment on adsorbent properties of palm kernel shell (PKS) biochar.

Methods: The PKS biochar was obtained through fast carbonization in a rotary kiln (800 °C, 10 min) followed by steam activation (8 h). Both the EtOH and MeOH treated biochar were afforded via EtOH and MeOH treatment of PKS biochar, respectively, in the presence of HCl (6 h), followed by rinsing, filtering, and oven-drying. Mg treated biochar was obtained by soaking the PKS biochar with $MgSO_4 \cdot 7H_2O$ at 30 °C for 60 h. The EtOH, MeOH, and Mg treated biochars were characterized via proximate analysis, functional group analysis, surface area, and pore volume analyses. A batch adsorption study was conducted for adsorption of methylene blue (MB) by each EtOH, MeOH, and Mg treated biochar, respectively.

Results: Brunauer–Emmett–Teller (BET) analysis indicated that carbonization and chemical treatment has successfully enhanced the surface area with raw PKS (0.848 m^2g^{-1}), PKS biochar (592 m^2g^{-1}), EtOH-treated biochar (647 m^2g^{-1}), MeOH-treated biochar (663 m^2g^{-1}), and Mg-treated biochar (674 m^2g^{-1}). Batch adsorption studies showed that the highest methylene blue (MB) removal percentage for all studied biochar occurred at an initial concentration of 7 ppm (PKS biochar: 93.12%, EtOH-treated PKS biochar: 94.79%, MeOH-treated PKS biochar: 95.79%, and Mg-treated PKS biochar: 98.51%).

Conclusion: The EtOH, MeOH, and Mg treated PKS biochar gave high MB removal and thus, could potentially serve as efficient adsorbents for removal of dyes from wastewater.

Key Words: Carbonization, Biochar, Palm kernel shell, Chemical treatment, Engineered biochar

INTRODUCTION

Over 700 000 tonnes of commercial dyes are made per annum, for usage in fabrics, paper, plastic, leather, and chemical industries.^{1,2} Consequently, approximately 10–15% of dyes used in the afore-mentioned industries are discharged as industrial effluent annually.³ Severe dye pollution could cause coloured water that prevents solar radiation from entering water sources and inhibits the photosynthesis of aquatic biota.⁴ Considering the globally high volume of dye production and usage, proper treatments are needed in favour of reducing the ramification of dye pollution in the ecosystem.

Methylene blue (MB) is one of the basic dyes usually applied in industries such as colouring paper, hair dye, dyeing

cotton, wools, and others.⁵ MB (a thiazine cationic dye) can pose numerous detrimental effects such as complications in breathing, retching, nausea, gastritis, and diarrhoea, to living things.⁶ Moreover, MB can also cause permanent eye injury to humans and animals.⁷ Inhaling MB can lead to cyanosis, methemoglobinemia, dyspnoea, convulsions, and tachycardia.⁸ Hence, MB removal from wastewater before liberating it to water bodies is crucial in protecting human health.

Various techniques such as adsorption, ion exchange, reverse osmosis, and solvent extraction have been developed to remove dyes from wastewaters, including MB.^{5,9} Among these methods, adsorption is the most preferred approach in eliminating organic contaminants from aqueous solution as it has been proven to be effective, low cost, and gives high removal

Corresponding Author:

Rafeah Wahi, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia.

Email: wrafeah@unimas.my

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capacity.¹⁰ Adsorption of organic and inorganic pollutants, including dyes using biochar, has been applied for many years as its specific properties are fit for sorbent materials such as vast distinct surface area, porous structure, enhanced surface functionality, and mineral components.¹¹

However, biochar's adsorbent properties can be further enhanced via suitable chemical modification. Numerous studies have been accomplished on the usage of chemically modified biochar in removing MB. Jawad et al.¹ focused on the utilization of sulfuric acid-treated coconut leaf biochar to remove MB. Mohan and Chadaga¹² studied MB removal using cashew nutshell biochar, which was treated with sulfuric acid and hydrogen peroxide. Research has experimented using phosphoric acid-treated PKS biochar to adsorb MB from an aqueous solution.¹³ Most of the previous studies focused on treating biochar using acids or bases but rarely alcohols and minerals. Thus, this research aims to learn the nature of chemically treated palm kernel shell (PKS) biochar, namely the EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated biochar for the removal of MB from aqueous solution. The efficiency of MB removal from aqueous solution by the treated biochar was studied in the context of various adsorption isotherms (Langmuir and Freundlich isotherms).

MATERIALS AND METHODS

Sample Pre-treatment

Raw PKS and PKS biochar were collected from Bravo Green Sdn. Bhd. The biochar was obtained through carbonization in a rotary kiln (800 °C, 10 min) followed by steam activation (8 h). The raw and biochar samples were washed, sun-dried, ground into powder, and sieved into 2.0 mm and 0.5 mm particle size.

EtOH and MeOH Treatment

PKS biochar (5 g, 0.5 mm) was added to MeOH (Sigma-Aldrich, Germany, 500 ml) and concentrated HCl (R&M Chemicals, Malaysia, 32%, 4.15 ml).^{14,15} The mixture was agitated on a rotary shaker (6 h, 130 rpm) before the treated biochar was rinsed, filtered off, and oven-dried (60 °C, 24 h).¹⁶ The method was repeated using ethanol (HmBG Chemicals, Malaysia, 500 ml).

Mg Treatment

The biochar was cleaned with distilled water to eliminate impurities and desiccated before Mg treatment. PKS biochar (20 g, 0.5 mm) were soaked in MgSO₄·7H₂O (Ajax Finechem Pty Ltd, Australia, 500 ml) at 30 °C for 60 h¹⁷. The PKS biochar was then vacuum-filtered, oven-dried (90 °C, 12 h), and pyrolyzed at 500 °C for 30 min.^{16,17} The cooled biochar was rinsed once again with distilled water to get rid of impurities.

Characterization of Adsorbent

The evaluation for moisture content, volatile matter, ash content, fixed carbon in PKS, and chemically treated biochar were determined through proximate analysis based on its applicable standards: ASTM D3173, ASTM D3174, and ASTM D3175. The surface area and pore volume of the biochar were determined using the Brunauer–Emmett–Teller (BET) technique via Surface Area Analyzer (Quantachrome® ASiQwin™, United States) with nitrogen adsorption technique.¹⁸ This method was executed by operating purified N₂ on the biochar followed by heating the sample (200 °C, 8 h) under vacuum conditions. The nitrogen gas was sanctioned to be aerated through the sample after the heating process. Then the surface area of biochar will be figured out by computing the isotherm of biochar towards the N₂.¹⁹ The functional groups of the PKS biochar were evaluated via Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Nicolet Is10, United States) analysis.

Adsorption Studies

Stock Solution Preparation: MB stock solution (Bendosen, Malaysia) was concocted by placing MB (1 g) in deionized water (1000 ml) to get 1000 ppm concentration.²⁰ The MB concentration was investigated by a UV/Vis spectrophotometer (JASCO V-730, Japan) at a wavelength of 665 nm. Calibration was conducted using 1, 2, 3, 4, 5, 6, and 7 ppm MB solution.²¹

Batch Adsorption Studies: The effects of MB initial concentration and adsorbent dosage on MB adsorption using untreated and treated biochars were studied using the batch adsorption method. The amount of MB absorbed at equilibrium, q_e (mg/g), was computed by using Eq. 1²²:

$$q_e = \left(\frac{(C_0 - C_e)V}{W} \right) \quad (\text{Eq. 1})$$

Whereas, the adsorption efficiency (%) of MB was determined by using Eq. 2²²:

$$\text{Percentage removal (\%)} = \left(\frac{(C_0 - C_e)}{C_0} \times 100 \right) \quad (\text{Eq. 2})$$

where C_0 = initial concentration of MB (mg/l), C_e = equilibrium concentration in liquid phase (mg/l), V = volume of solution, and W = mass of adsorbent

The effects of initial concentrations on MB removal were explored using MB solution (100 ml) at a different initial concentration (1, 2, 3, 4, 5, 6, and 7 ppm)²³ with no pH modification.²⁴ EtOH-treated PKS biochar (0.5 g), MeOH-treated PKS biochar (0.5 g), and Mg-treated PKS biochar (0.5 g) were added to MB mixtures, respectively. The effect of contact time on MB removal was planned at 5, 15, 30, 45, and 60 min. EtOH-treated PKS biochar (0.5 g), MeOH-

treated PKS biochar (0.5 g), and Mg-treated PKS biochar (0.5 g) were added to MB solution (3 ppm, 100 ml), respectively. The mixture was shaken (150 rpm, 30 min) to reach equilibrium and filtered. The final MB concentration was computed and obtained by using UV-Vis.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}} \quad (\text{Eq. 3})$$

Equilibrium Adsorption Isotherms: Adsorption isotherms are applied to illustrate the correlation between the adsorbed concentration and the dissolved concentration at equilibrium and describe a particular interaction between adsorbent and adsorbate at a given environmental condition.^{24,25} In this study, the relevancy of Langmuir and Freundlich isotherms equations were contrasted by estimating the value of correlation coefficients, R^2 . The isotherm graph was plotted by using initial concentration data. Langmuir isotherm was initially introduced to illustrate gas-solid adsorption onto adsorbents, has been utilized to measure and compare the achievement of various adsorbents.²⁶ This isotherm operates based on the supposition that monolayer adsorption occurs with homogenous binding sites and energy levels and no interactions between adsorbed particles.²² Langmuir equation in linear form is as in Eq. 3:

where, C_e = equilibrium concentration in liquid phase (mg/L), q_e = equilibrium concentration in adsorbed phase (mmol/g), q_{max} = Langmuir constants representing the adsorption capacity (mg/g), and K_L : Langmuir constant (L/mg). A straight line with slope ($1/q_{max}$) and intercept ($1/K_L q_{max}$) could be achieved by plotting C_e/q_e versus C_e .²⁷

Freundlich isotherm is a factual equation that is dependent on a heterogeneous surface²⁷. This isotherm can depict the adsorption of organic and inorganic compounds on various adsorbents¹⁹. Freundlich isotherm can be conveyed in linear form (Eq. 4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{Eq. 4})$$

where, q_e = amount of MB adsorbed at equilibrium time (mmol/g), K_F , n = Freundlich constants, and C_e = Equilibrium concentration (mg/L). K_F indicates the adsorption capacity, and n indicates the adsorption intensity. Freundlich constants can be acquired from the slope ($1/n$) and intercept ($\log K_F$) of the linear plot by plotting $\log q_e$ vs. $\log C_e$.²⁷

RESULTS

Figure 1 shows the proximate analysis of the studied samples. All treated biochar showed higher moisture content compared to untreated biochar: EtOH-treated PKS biochar (17.56%), MeOH-treated PKS biochar (14.92%), and Mg-

treated PKS biochar (19.28%). Mg-treated biochar has the highest ash content (28.48%) compared to other treated biochars, which are likely due to the addition of Mg minerals in the biochar.¹⁷ The ash content percentage agrees with previous works on Mg-treated biochar for sugarcane bagasse biochar (20.64%)²⁸ and switchgrass biochar (28.4%).²⁹ Raw PKS displayed the highest volatile matter (75.58%) then followed by untreated PKS biochar (45.91%), EtOH-treated PKS biochar (26.87%), MeOH-treated PKS biochar (19.26%), and Mg-treated biochar (14.26%). The untreated biochar with the fixed carbon of 11.84% is significantly lower than the fixed carbon of treated biochar. EtOH-treated biochar exhibits the highest percentage of fixed carbon (41.90%), followed by MeOH-treated biochar (39.34%) and Mg-treated biochar (37.97%). Raw PKS has the lowest selected carbon content, which is 2.21%. The surface area of PKS biochar was notably amplified after carbonization, from 0.848 m^2g^{-1} to 592 m^2g^{-1} , and further increased after chemical treatment (Table 1). EtOH-treated biochar has a smaller surface area (647 m^2g^{-1}) than MeOH-treated biochar (663 m^2g^{-1}). Mg-treated PKS biochar was able to show the highest surface area, which is 674 m^2g^{-1} .

The simplified FTIR results of raw PKS, untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar are shown in Table 2. From the table, the band peaks at 3452.86 cm^{-1} , 3449.85 cm^{-1} , 3452.82 cm^{-1} , 3453.87 cm^{-1} , and 3455.23 cm^{-1} for raw PKS, untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar, respectively, correspond to O–H stretching vibrations demonstrating the existence of chemical complexes like alcohol, phenol, or carboxylic acid.³⁰ However, for the case of EtOH-treated PKS biochar and MeOH-treated PKS biochar, there is a significant shift for hydroxyl groups where after the treatment, from 3449.85 cm^{-1} (untreated PKS biochar), it increased to 3452.82 cm^{-1} and 3453.87 cm^{-1} , for EtOH-treated PKS biochar and MeOH-treated PKS biochar, respectively, indicating the multiplication of hydroxyl groups in both biochars¹⁴. A sequence of peaks at 800–400 cm^{-1} in the case of Mg-treated biochar can be attributed to Mg–O and O–Mg–O, which suggests the presence of Mg oxyhydroxides.¹⁷ EtOH-treated PKS biochar and MeOH-treated PKS biochar, the band peaks at 841.64 cm^{-1} and 840.03 cm^{-1} can be ascribed to C–H in aromatic rings of the biochar.^{31,32} Notably, the C–H ($-\text{CH}_2$ and $-\text{CH}_3$) bending vibrations at the peaks ranged from 1407.81 to 1388.26 cm^{-1} in all samples, possibly indicate the presence of alkanes components.

The percentage removal of MB by untreated PKS biochar appeared to be steadily increasing, starting from the initial concentration of 2 ppm up to 7 ppm (Figure 2). For EtOH-treated PKS biochar, the percentage of removal increased from an initial concentration of 1 ppm to 2 ppm and became constant after that. On the other hand, percentage removal of

MB by MeOH-treated PKS biochar showed a slight increase from 1 ppm up to 4 ppm and remain constant until 6 ppm and slowly rise again to reach the highest percentage of 95.79%.

The initial concentration of 1 ppm displayed the lowest MB removal percentage for all biochars (untreated PKS biochar: 65.64%, EtOH-treated PKS biochar: 77.45%, MeOH-treated PKS biochar: 84.76%, and Mg-treated PKS biochar: 87.20%). The highest MB removal percentage for all studied biochars occurred at the initial concentration of 7 ppm (untreated PKS biochar: 93.12%, EtOH-treated PKS biochar: 94.79%, MeOH-treated PKS biochar: 95.79%, and Mg-treated PKS biochar: 98.51%). Based on the statistical analysis of variance (ANOVA), there is a substantial contrast between percentage removal between untreated biochar and treated biochar as the p-value is 0.0435 ($p < 0.05$). The percentage removal of MB by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar start to remain constant at 3 ppm, which indicates that the optimum initial concentration for all adsorbents is 3 ppm.

Figure 3 illustrates that MB removal percentage improved as the contact time increased for all treated PKS biochar. All treated biochar has succeeded in removing more than 90% of MB for the first 5 min with the same conditions applied to all samples (initial concentration of 3 ppm and dosage of 0.5 g). In contrast, the MB removal percentage for untreated biochar (87.73%) is less than 90%. This result follows the outcome for the effect of initial concentration where the MB removal percentage for untreated biochar (86.89%) is less than 90%, while treated biochar showed a high MB removal percentage of more than 90%. The repulsive forces between the ions could instigate the steep decrease, which occurred at 15 min, or the solution could be simply contaminated³³. The highest percentage of removal for untreated PKS biochar is 91.33% at 60 min. The highest removal percentages for EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar are 96.46%, 96.76%, and 96.86% at 60 min.

Langmuir constants, q_m (maximum adsorption capacity), and K_L can be obtained and computed from the slope and intercept of the graph, respectively. Based on Figure 4, the value of q_m for MB adsorption by untreated PKS biochar is -0.0863 mg/g, whereas the value of K_L is -1.9694 L/mg. Meanwhile, the value of q_m for EtOH-treated PKS biochar is -0.2776 mg/g, and the value of K_L is -2.2702 L/mg. The adsorption of MB by MeOH-treated PKS biochar revealed that the q_m has a value of -0.4773 mg/g and a constant K_L value of -2.1893 L/mg. On the other hand, Mg-treated PKS biochar has the maximum adsorption capacity constant, q_m , of 0.0613 mg/g and K_L value of -10.063 L/mg. The negative values of K_L mean that Langmuir isotherm does not fit with the trial data of this study. The value of the coefficient of determination, R^2 for MB adsorption by untreated PKS

biochar is 0.7124, whereas the value of R^2 for EtOH-treated PKS biochar is 0.3507. Adsorption of MB by MeOH-treated PKS biochar and Mg-treated PKS biochar displayed R^2 of 0.3806 and 0.5669, respectively.

Linear plot of $\log q_e$ against $\log C_e$ (Figure 5) was plotted to analyze the adsorption equilibrium of MB with untreated PKS biochar, Mg-treated PKS biochar, MeOH-treated PKS biochar, and EtOH-treated PKS biochar. K_F and n are Freundlich constants that signify adsorption capacity and adsorption intensity, respectively, while $1/n$ can be ascribed to heterogeneity factor.³⁶ Both constants can be determined based on the equation from the graph. The value of K_F for untreated PKS biochar is 69.231 mg/g, the value of n is 0.1766, and the $1/n$ value is 5.5926. On the other hand, the value of K_F , n , and $1/n$ for MB adsorption by EtOH-treated PKS biochar is 16.912 mg/g, 0.3808, and 2.6258, respectively. The adsorption of MB by MeOH-treated PKS biochar demonstrated that the value of K_F is 11.094 mg/g, and the value of n constant is 0.4944 with $1/n$ of 2.0226. Mg-treated PKS biochar has the adsorption capacity, K_F , 2.8536×10^{-6} mg/g, n value of -0.1764, and $1/n$ of -5.6699.

Table 3 shows that the adsorption characteristics of untreated PKS biochar can be described and explained by Langmuir and Freundlich isotherms since untreated PKS biochar has the highest determination coefficient, R^2 , in studied isotherm models.

DISCUSSION

Mg-treated biochar showed the highest moisture content compared to other treated biochar, plausibly resulting from longer soaking time in $MgSO_4 \cdot 7H_2O$ solution (60 h) than methanol and ethanol treatment. The moisture content for all biochars is considered low moisture since the percentage is below 40%, whereas high moisture content is more than 40%.²⁷⁻²⁹ It can be perceived that the moisture content for the treated biochars in this study is measurably higher than other treated biochars such as treated cashew nut shells biochar with a moisture content of 9.83%^{30,31} and moisture content of coconut husk biochar treated with various chemicals which are ranged from 3.48 to 10.59%.³¹⁻³³ The most likely reason could be the long washing process after being soaked in chemicals. Ash content is incombustible minerals such as calcium, magnesium, iron, sodium, and potassium found in the biomass.^{34,35,38} The high temperature used during the carbonization process was responsible for the volatile matter to discharge from weaker bonds hence being released into the atmosphere.^{36,37,39} High release of volatile matter leads to biochar production with additional new pores, thus improving the surface area of the biochar.^{40,41} Fixed carbon is fundamentally carbon comprised of O_2 , H_2 , N_2 , and S, which are in small quantities. The fixed carbon in the biochar can

develop the structure of carbons into pores, which further denotes the potential improvement of the adsorption sites of the biochar.³⁰

The main characteristics that indicate cellulose, hemicellulose and lignin in the PKS biochar are when the functional groups as O–H, C–O, C=O, and C–H present in the spectra.³¹ The bands for all biochars shifted to higher wavenumbers indicating that the bond length of hydroxyl groups decreases.⁴² The decreasing bond length might occur due to environmental factors such as temperature and concentration.⁴² The peaks of Mg-treated biochar imply that Mg particles do not influence the structure of organic functional groups in Mg-treated biochar.⁴³ Extra OH was generated on Mg-treated biochar, which may be accountable for the adsorption ability of biochar.¹⁷

Surface area and pore volume are parts of the essential characteristics for any carbon adsorbents to reflect its adsorptive capacity.⁴⁴ Mg-treated PKS biochar was able to show the highest surface area, which might be due to several mechanisms that had occurred on the biochar surface⁴⁵. This research showed a similar result where MgO-treated corncob biochar ($26.56 \text{ m}^2\text{g}^{-1}$) has a higher surface area than corncob biochar ($0.07 \text{ m}^2\text{g}^{-1}$).⁴⁵

Volatile matters discharged during carbonization assist the pore formation in the biochar structure³⁹. Besides, chemical activation and high carbonization temperature affect the size of the surface area of biochar, which leads to the creation of additional biochar pores.³⁹ However, a few studies displayed different results. The surface area of Mg-treated biochars is smaller than the untreated biochar due to the accumulation of Mg elements on the biochar surface.^{29,43} Mg-treated biochar made from PKS displayed a relatively large surface area compared to other feedstocks such as corncob and wood chips, where at least numerous of them are below $< 500 \text{ m}^2\text{g}^{-1}$.¹⁷ All chemically treated biochar also presented a slight prominent increase in the pore volume, indicating that the ethanol, methanol, and magnesium treatment could increase the biochar porosity.

The differences in MB removal efficiencies for all biochars are notable as untreated PKS biochar has the lowest removal efficiency, followed by EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar with a probable reason due to the differences in surface areas and total pore volume (Table 1). Biochars that have large surface areas and pore volumes indicate that the biochar has more pores, leading to the formation of additional active sites for the adsorption to happen.⁴⁶ Other than that, the highest MB removal efficiency for all biochars took place at the highest initial concentration in this study^{46,47}, which is 7 ppm. The higher concentration is believed to supply a driving force to surmount all bulk transfer resistances between all particles in aqueous solution and solid phases.⁴⁷ The escalation in MB

removal percentage as the initial concentration increased might be instigated by the exchanges or interactions between MB ions and the active sites of biochar.⁴⁸ The higher the MB concentration, the higher the quantity of MB ions in the mixture. Thus, the greater the adsorption of MB takes place on the adsorbent's adsorption site.⁴⁹

However, the surface area is not the only biochar properties that influence MB removal efficiency. Surface functionality is also vital in facilitating the adsorption between the adsorbate and the adsorbent.⁴⁶ Adsorption of contaminants from aqueous solution by adsorbents is caused by chemical interactions such as electrostatic interaction, cation exchange, and surface precipitation⁴⁶. The bands that are slightly shifted to a new one (lower or higher wavenumber) in biochar, demonstrating that chemical interactions had occurred on the treated biochar surface.³²

The treatment of PKS biochar using EtOH and MeOH has altered and enhanced the O-containing functional groups on the biochar surface, which is following the study by Jing et al.¹⁴. In the case of EtOH-treated PKS biochar and MeOH-treated PKS biochar, one of the essential mechanisms that could happen between the positively charged MB and the negatively charged biochar is electrostatic interaction. Based on the adsorption experiment in the present study, the MB removal efficiencies for both EtOH-treated PKS biochar and MeOH-treated PKS biochar are higher than that of untreated PKS biochar hence, implying that the surface of EtOH-treated PKS biochar and MeOH-treated PKS biochar had been enriched with more carboxyl groups and hydroxyl groups for more chemical interactions to occur³². This can be seen in Table 2 where both MeOH-treated PKS biochar and EtOH-treated PKS biochar shifted to a higher wavenumber than untreated PKS biochar.

As for Mg-treated PKS biochar, since Mg is a positively charged compound similar to MB, repulsion might occur between Mg and MB. However, based on the removal efficiency result of Mg-treated PKS biochar (Figure 2), the biochar treatment using Mg has the highest removal efficiency. This further implies that electrostatic interaction might occur between Mg-treated PKS biochar and MB, which explained the bands' shifts. Apart from that, cation exchange might be one of the prominent mechanisms included in MB adsorption onto PKS biochar, which also shifted the bands.^{28,50} MB is widely used as a standard reagent for cation exchange determination in soil.⁵⁰ From Table 2, the band spectra representing the hydroxyl group shifted to higher wavenumbers with a plausible reason because of the increase in the interactions between the hydroxyl group of the biochar and MB.^{32,42} Adsorption of MB via cation exchange could happen when Mg compounds on the biochar surface are released and replaced with MB. Besides, intraparticle diffusion and pore diffusion might also occur during the adsorption of MB onto all chemically modified biochar.^{28,51}

Several previous studies show a similar increment trend for removing MB on the surface of biochar produced from numerous feedstocks.^{1,20,24} However, a few types of research displayed a declining trend for percentage removal of MB, probably due to different adsorbents and parameters used.²⁰ In terms of adsorption, the curves were smoothly increasing up to the point of saturation and started to remain stable afterward.^{1,34,35} This might be attributed to the great exposure of the adsorption spots on the adsorbents.³³ There is no remarkable contrast between MB removal percentages by all treated biochar at 30 min, 45 min, and 60 min though all percentages keep on increasing when the contact time increases. This, however, implies that the MB removal percentage can reach 100% if a longer contact time is taken.

Langmuir isotherm functions based on the supposition that monolayer adsorption occurs with homogenous binding sites and energy levels, with no interactions between adsorbed particles on the surface of adsorbents.⁵² In other words, the instant an adsorbate particle fills up a site, there would be no further adsorption can occur.⁵³ Langmuir isotherm was tested for MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar. A linear plot of C_e/q_e against C_e was drawn to evaluate the MB adsorption equilibrium with all biochar.

The R^2 value indicates that the adsorption data for MB removal by all adsorbents is not appropriate with the Langmuir model as R^2 values for all adsorbents are comparatively low and distant from 1. Hence, it is observed that Langmuir isotherm is unsuitable for defining adsorption characteristics of untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar. However, a few studies showed opposite results where the MB adsorption was able to fit Langmuir isotherm. An earlier study by Savran et al.^{52,53} exhibited that adsorption data for MB by *Paliurus Spina-Christi* fruits and seeds fitted well with Langmuir isotherm. Since all biochar from this study does not fit with the Langmuir isotherm graph, the adsorption of MB was said not to be limited to only monolayer adsorption.⁵⁴

The Freundlich isotherm was tested based on the adsorption experiment for MB. This model is primarily utilized in the heterogeneous system, particularly for extremely interactive molecules on the adsorbent's surface³⁶. Constant n suggests the favourability of the adsorption system³⁶. The adsorption is considered to be favourable when the value of n is between 1 and 10⁵⁵. When the n value is high, it is regarded as beneficial adsorption throughout the whole range of concentration. In contrast, a low value of n gives an implication of useful adsorption at high concentrations but less favourable at lower concentrations⁵⁶. In the current work, the values of n for all biochar are below 1. Therefore, it is implied that the adsorption of MB at low concentrations is unfavourable. $1/n$ is the measure of heterogeneity factor of the surface of

adsorbents, ranging between 0 and 1, where $1/n < 1$ suggests that normal adsorption or chemisorption has occurred while $1/n > 1$ provides implication of cooperative adsorption.⁵⁷ In the case of the current study, it can be observed that the value of $1/n$ for Mg-treated PKS biochar is -5.6699, indicating that the type of adsorption that might take place on the biochar surface is chemisorptions.^{56,57} The value of the coefficient of determination, R^2 for MB adsorption by untreated PKS biochar is 0.9306, and the value of R^2 for EtOH-treated PKS biochar is 0.7291. MeOH-treated PKS biochar and Mg-treated PKS biochar have R^2 of 0.6545 and 0.5370, respectively. From these results, Freundlich isotherm also is not fit to define the adsorption attributes of MB by PKS biochar as compared to Langmuir isotherm. However, there is a possibility for Mg-treated PKS biochar can be explained by other isotherms models such as Tempkin and Dubinin-Kaganer-Radushkevich.^{58,59}

CONCLUSION

The current study showed that PKS biochar treated using EtOH, MeOH, and Mg can be employed as a sorbent to eradicate MB from an aqueous solution. The surface area for all biochar, as shown in BET analysis, indeed increased after the carbonization and modification of biochar, ranging from 0.848 m^2g^{-1} to 674 m^2g^{-1} . The highest percentage removals of MB onto all biochar were 93.12%, 94.79%, 95.79%, and 98.51%, which occurred at an initial concentration of 7 ppm. Results suggested that the EtOH, MeOH, and Mg treated PKS biochar can potentially function as an adsorbent in removing dye from wastewater.

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Authors' Contributions:

NHH: Conducting laboratory work, data analysis, and drafting the article

RW: Conception of the work and critical revision of the article

YY: Data interpretation, and critical revision of the article.

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Table 1: Surface area and total pore volume for raw PKS, untreated PKS biochar, MeOH-treated PKS biochar, EtOH-treated PKS biochar and Mg-treated PKS biochar

Sample	Raw PKS	Untreated PKS biochar	EtOH-treated PKS biochar	MeOH-treated PKS biochar	Mg-treated PKS biochar
Surface area (m ² g ⁻¹)	0.848	592	647	663	674
Total pore volume (cm ³ /g)	0.003	0.353	0.394	0.404	0.424

Table 2: FTIR spectra band assignments

Wavenumber (cm ⁻¹)	Assignments	Wavenumber of samples (cm ⁻¹)				
		Raw PKS	Untreated PKS Biochar	MeOH-treated PKS biochar	EtOH-treated PKS biochar	Mg-treated PKS biochar
3500–3200	O–H stretching indicative of alcohol, phenol or carboxylic acid	3452.86	3449.85	3452.82	3453.87	3455.23
1700–1600	C=O or C=C stretching in aromatic ring or alkenes	1650.47	1646.50	1649.94	1649.67	1646.46
1500–1300	C–H (CH ₂ and CH ₃) bending in alkanes	1407.81	1389.21	1389.47	1388.26	1390.22
900–600	C–H bending vibrations in aromatic compounds	612.14	672.03	841.64 672.51	840.03 611.81	605.57

Table 3: Adsorption isotherms parameters for MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar

Isotherm models	Parameters	Adsorbents			
		Untreated PKS Biochar	EtOH-treated PKS Biochar	MeOH-treated PKS Biochar	Mg-treated PKS Biochar
Langmuir	q _m (mg/g)	-0.08628	-0.2776	-0.4773	0.06126
	K _L (L/mg)	-1.9694	-2.2702	-2.1893	-10.0635
	R ²	0.7124	0.3507	0.3806	0.5669
Freundlich	1/n	5.5926	2.6258	2.0226	-5.6699
	n	0.1766	0.3808	0.4944	-0.1764
	K _F (mg/g)	69.2309	16.9122	11.0943	2.8536×10 ⁻⁶
	R ²	0.9306	0.7291	0.6545	0.5370

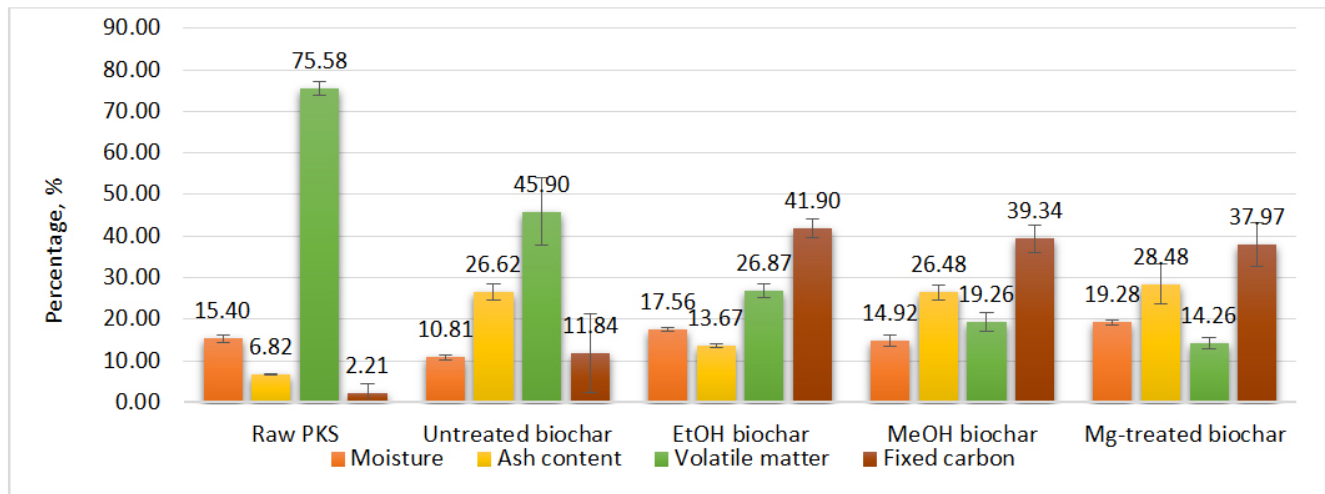


Figure 1: Proximate analysis of raw PKS, untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar.

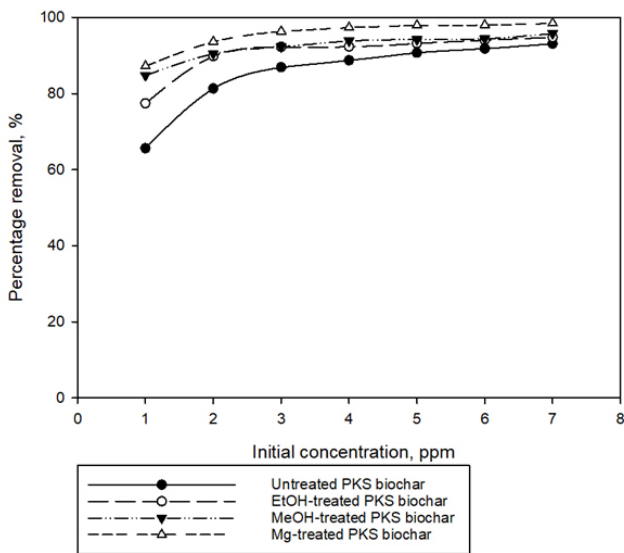


Figure 2: Effect of initial concentration on MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar.

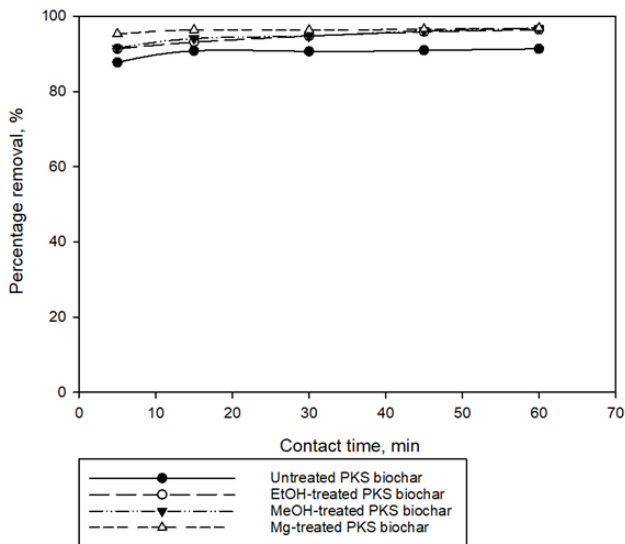


Figure 3: Effect of contact time on MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar.

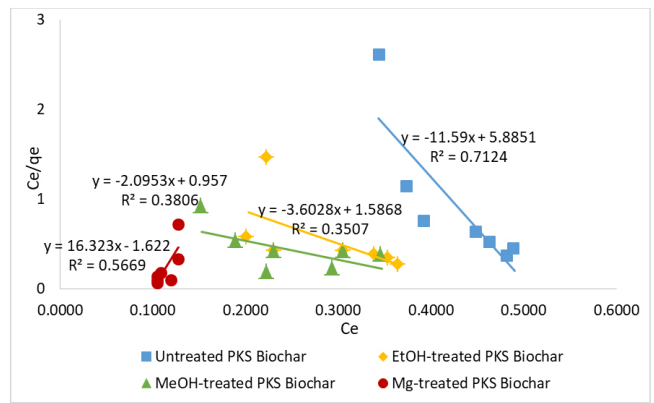


Figure 4: Langmuir isotherm plot for MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar.

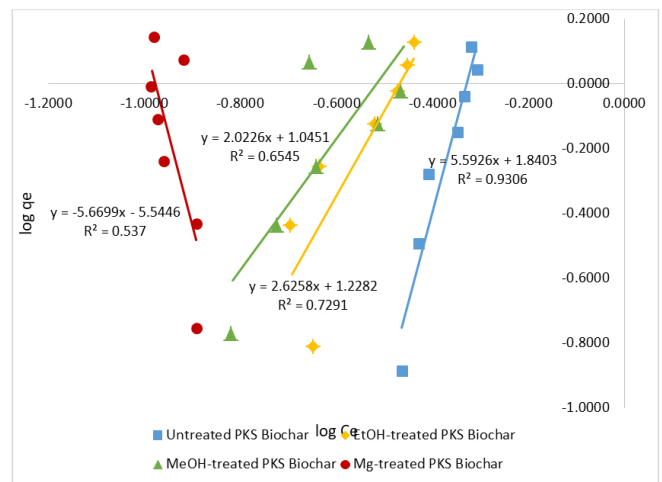


Figure 5: Freundlich isotherm plot for MB removal by untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar and Mg-treated PKS biochar.