Pak. j. sci. ind. res. Ser. A: phys. sci. 2025 **68A**(3) 235-251

Puffed Rice Biochar: Characterization and Adsorption Studies for Methyl Orange Dye Elimination

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(received January 31, 2024; revised October 5, 2024; accepted October 10, 2024)

Abstract. This study investigated the use of puffed rice biochar for the removal of methyl orange (MO) dye. The effects of various factors, including shaking duration, particle size, MO dye concentration and temperature, were examined. FTIR and SEM analyses were conducted to understand the mechanisms behind the effective removal of methyl orange (MO) dye using puffed rice biochar. Both techniques together offer a comprehensive view of the biochar's characteristics, combining chemical composition and surface morphology insights. Equilibrium in the adsorption process was reached within 60 min. Larger particle sizes are associated with lower Ce values, indicating that smaller particles are more effective at adsorbing MO, leading to higher yields. The adsorption process was efficient, especially at higher MO concentrations, with puffed rice biochar effectively removing methyl orange due to its porous structure and surface functional groups. However, at elevated MO concentrations, the biochar's adsorption capacity becomes limited. The thermodynamic study indicated that the process exhibited exothermic behaviour and was spontaneous within the temperature range of 20 °C to 30 °C. However, positive $\Delta G°$ values at higher temperatures suggested that the process became non-spontaneous and required the input of external energy. This implies that adsorption is more effective at lower temperatures, while higher temperatures may lead to desorption, affecting the overall colour removal efficiency. At a temperature of 313 K and with particles measuring 170 µm, nearly 96% of the dye was successfully removed by the system. FTIR and SEM analyses revealed the presence of several surface functional groups and a crystalline structure in the biochar, which are crucial for dye removal. The Langmuir model was found to better fit the adsorption isotherms, indicating that MO adsorption follows a monolayer pattern. The porous and crystalline structure of the biochar was also confirmed by SEM, suggesting potential for further enhancement.

Keywords: puffed rice biochar, methyl orange, adsorption, dye removal, langmuir, freundlich isotherm

Introduction

Asia, being one of the largest producers of paddy, generates approximately 45 million tonnes of rice husk annually; however, this byproduct of rice production predominantly lacks commercial value (Yadav *et al*., 2019; Bhattacharyya and Asia 2014). Rice husk biomass, primarily composed of cellulose, hemicelluloses and lignin, holds significant potential as an alternative energy source through thermochemical conversion processes (Zhao and Li, 2016). Puffed rice biochar, generated from the by-products of puffed rice, represents a novel approach to waste management and environmental remediation. By utilizing a by-product that might otherwise be discarded, it contributes to a circular economy. The elemental composition of the biochar from rice husk also shows the presence of N, Na, Mg, Si, Al, K and Ca with dominant contents of C, O and S. X-ray fluorescence spectroscopy (XRF) reveals that Si, Ca, K and P are the most abundant ash elements in rice husk biomass, with compositions of 87%, 2%, 9% and 0.9%, respectively (Armynah *et al*., 2018). The carbon, hydrogen and nitrogen contents ranged from 31.77% to 38.11%, 1.67% to 3.61% and 0.63% to 0.73%, respectively. The calorific value of the biochar ranged from 11.61 to 14.48 MJ/Kg (Hidayat *et al*., 2023; Armynah *et al*., 2018). Its specific physical and chemical properties make it a potentially effective adsorbent for pollutants like methyl orange (MO), an anionic azo dye. A certain group of azo dyes and their resulting substances, particularly aromatic amines, have been proven to be extremely carcinogenic based on their widespread use (Malik, 2004; Boeniger *et al*., 1980). Reactive azo dyes can induce genotoxic effects in adult fish, evidenced by an increase in erythrocytic

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micronuclei formation in a dose and time dependent manner. In fingerlings, these dyes lead to an increase in gill micronuclei formation in a time dependent manner (Sharma *et al*., 2022; Zheng *et al*., 2021).

Many sectors, including textiles, pulp and paper, dye stuffs and plastics, employ dyes, contributed for the generation of waste rich in vibrant hues. Plant-based biomass undergoes pyrolysis, often known as "Black Gold," through exposure to high temperatures. The material has a significant surface area, porosity, functional groups and cation exchange capability. Biochar improves soil fertility by altering its properties when it is added to the soil (Awad *et al*., 2018). The primary raw materials used for the production of biochar include agricultural waste, animal dung and paper based products. These waste products are crucial for the manufacture of biochar because they provide a realistic method of converting trash into a useful resource (Brewer *et al*., 2014). Biochar is a solid material created through the thermo-chemical conversion of biomass in an environment with limited oxygen. In addition to its use as a solid fuel (Liu *et al*., 2013; Kang *et al*., 2012) and as a bio-composite (Liu *et al*., 2015), biochar serves as an effective adsorbent for the removal of various contaminants from water (El-Nahas *et al*., 2019). It is also applied as a soil conditioner and carbon sequestrant in agriculture (Canlas *et al*., 2019; Salam *et al*., 2018). Furthermore, biochar offers a range of other potential applications. Adsorption is acknowledged as a potent technique for reducing environmental contamination and enhancing the quality of water and wastewater through treatment procedures (Derylo-Marczewska, 1993). Adsorption is an excellent strategy for mitigating environmental pollution and protecting water quality by efficiently treating water and wastewater (Wang *et al*., 1998).

MO is a commonly cited instance of an anionic azo dye that necessitates careful management prior to its discharge into the environment. Adsorption is a technique used to eliminate anionic dyes. Natural one-dimensional adsorption materials, such as nanotube minerals, possess a remarkable adsorption capacity due to their distinctive morphology and structure. Adsorption is an effective method for removing anionic dyes (Kali, 2022; Wu *et al*., 2021; Savci *et al*., 2019; Yagub *et al*., 2014). Dye compounds present challenges in handling due to their toxic and carcinogenic properties. Apart from their poisonous nature and long lasting effects, these discharges can also present a substantial risk to the physico-chemical characteristics of freshwater ecosystems and the organisms living in them. Consequently, it is necessary to employ appropriate wastewater treatment equipment, as it makes the water unsuitable for public consumption (Ali *et al*., 2022; Al-Tohamy *et al*., 2022; Almroth *et al*., 2021; Boeniger *et al*., 1980).

The researchers assessed the effectiveness of these adsorbents by exposing methyl orange contaminated water to them in order to recover the dye. Adsorption plays a crucial role in safeguarding the environment from pollutants during the treatment of water and wastewater (Derylo-Marczewska, 1993). Adsorption is a crucial process for eliminating harmful compounds, dangerous ions, and dyes from industrial waste which is necessary to safeguard the environment and public well-being. Moreover, solid adsorption diminishes the toxicity of wastewater and eradicates hazardous organic components from industrial effluents (Onganer and Temur, 1998; Wang *et al*., 1998). The removal of colour from textile effluents is a significant environmental issue due to the challenges of treating these streams using conventional physico-chemical and biological treatment methods (McKay, 1982). Adsorption has emerged as the prevailing method for wastewater treatment due to its straight forwardness, ability to be scaled up easily and effectiveness in removing minute water impurities (Sulaiman *et al*., 2020). The adsorptive activity of biochar is directly linked to its functional groups, surface area, cation exchange capacity and other properties. Applying acids, alkalis or oxidising agents can enhance the physical and chemical properties of biochar (Suganya *et al*., 2017; Jothirani *et al*., 2016).

Pyrolysis is a crucial heat process that affects the physico-chemical characteristics of biochar, including its surface area, pH and functional groups. The features of biochar have an impact on its performance as a soil amendment (Ding *et al*., 2014). The temperature of pyrolysis is intricately associated with changes in the molecular composition and physico-chemical properties of biochar (Jindo *et al*., 2014; Chen *et al*., 2008). Pyrolysis is recognised as the primary method for transforming biomass into charcoal through the thermochemical decomposition of biomass at elevated temperatures in an environment devoid of oxygen (Amini *et al*., 2019; Antonakou *et al*., 2006). Addressing the increasing global energy demand, which is fuelled by population growth and improved living standards, is one of the most urgent concerns of our era. Nevertheless, the dependence on fossil fuels, which were the main source of energy, results in the release of green house gases that contributed to the phenomenon of global warming (Popp *et al*., 2014).

Synthetic dyes are extensively used in various industries in the present era, such as the food, pharmaceutical, and textile sectors. Due to the growing demand for textile products, large quantities of dye effluent are being discharged into the environment, leading to the rapid emergence of environmental issues. The textile sector contributes approximately 5 to 15 percent of the total yearly dye production which amounts to 700,000 metric tonnes (Katheresan *et al*., 2018). Traditional textile firms seldom employ natural dyes as a result of the prevalence of synthetic dyes which are more affordable and offer superior quality (Orietta *et al*., 2018). The un-controlled discharge of chemical additives and artificial dyes presents a significant peril to the ecosystem. The inclusion of nitrogen and aromatic structures in dye functional groups adds complexity to the process of removing them from effluent streams (Zhai *et al*., 2018; Shajahan *et al*., 2017).

The study was conducted to analyze and evaluate the efficacy of puffed rice biochar as a viable alternative to traditional commercial adsorbents in the removal of MO dye from water based solutions. This research examined key variables, including the ideal period of shaking, greater surface area, concentration of MO and suitable temperature, in order to improve the effectiveness of dye removal. In addition, a comprehensive analysis of puffed rice biochar was conducted using FTIR (Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscopy) to examine its structural modifications before and after the adsorption of MO. This analysis provided valuable information about the changes in its composition and morphology.

Materials and Method

Collection of puffed rice. The puffed rice was obtained from the local market and immediately used, despite being pulverized into a fine powder. The item, known as Muri in the local area, was obtained from the nearby market and underwent extensive cleaning. Afterward, it was meticulously pulverized into a powdery state. Precisely 5 g of this powdered puffed rice were accurately measured and deposited into a ceramic crucible, which was subsequently introduced into a muffle furnace. It was utilized for the production of biochar.

Production of biochar from puffed rice. The 5 g of puffed rice which had been grounded and were initially placed in a muffle furnace that recently cleaned and devoid of impurities. Additionally, it should possess a vent or a minuscule aperture to allow for the release of gas throughout the pyrolysis procedure. The container was filled with puffed rice, leaving a small space at the top to prevent any leakage during the cooking process. Next, the container was placed directly above the heating element and covered with the lid. When the puffed rice is heated, the organic content will undergo pyrolysis, which is a chemical reaction that results in the formation of charcoal. Throughout the process of biochar synthesis, the temperature was consistently maintained at 573 K for one hour. The puffed rice biochar was then allowed to settle, sifted and divided into particle sizes of 120 μm and 170 μm.

Preparation of methyl orange solution. Methyl orange (MO) of analytical grade, obtained from Merck, Germany which has a chemical formula of $C_{14}H_{14}N_3NaO_3S$ and a mass of 327.33 g/mol. It has a purity of 99%. Various dilutions of MO solutions were prepared using de-ionized distilled water. In order to establish a linear relationship using Lambert-Beer's law, varying quantities of the MO stock solution were transferred into colourimetric tubes, diluted to a volume of 20 mL with de-ionized water and standardized solutions with concentrations of 2, 4, 5, 8 and 10 mg/L were prepared.

Analytical. During the batch sorption investigations, a 20 mL solution of methyl orange (MO) dye with a specific concentration was combined with different amounts of puffed rice biochar (0.5, 1 and 1.5 g) in 220 mL reagent bottles. The mixes were then hermetically sealed and agitated for 60 min using a shaking machine operating at a speed of 300 strokes per minute. The experiment was completed at various time intervals, except for the temperature dependence research, which was carried out at a controlled temperature of (303 ± 0.5) K using a thermostatic water bath. Following agitation, the solutions were further separated and

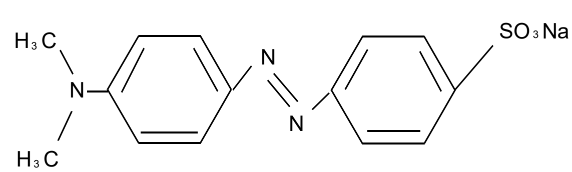

Fig. 1. Structural formula of MO.

filtered using ashless filter paper to determine absorbance values at 462 nm using a spectrophotometer (Shimadzu, Japan).

Isotherm studies. The Freundlich and Langmuir isotherms are the primary methodologies employed for determining the adsorption capacity of a substance.

During the batch adsorption tests, a 20 mL volume of synthetic effluent was utilized to investigate the effects of different factors, including phase contact time, particle sizes, MO concentration and temperature. After reaching equilibrium, the UV-visible spectrophotometer was used to quantify the optical density at 462 nm of the filtered samples. The provided data was utilized to ascertain the equilibrium concentration of MO (Ce), the quantity of MO adsorbed (q_e) and the percentage of adsorption.

Adsorption percentage or dye removal was calculated using the following equation (Le *et al.*, 2021)

$$\% \text{ Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \text{ .... (1)}$$

where:

C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of MO in the liquid phase, respectively.

Equilibrium Adsorption was measured by the following equation (Anisuzzaman *et al.*, 2015; Thilagan *et al.*, 2013).

$$q_e = \frac{C_0 - C_e}{M} \times V \text{ .... (2)}$$

Equilibrium studies. The Langmuir adsorption isotherm represents a process where a mono layer of molecules is adsorbed, while the Freundlich model depicts the ability of the material to adsorb many layers of molecules.

The Langmuir isotherm is a mathematical model used to describe the adsorption of a gas onto a solid surface.

Langmuir isotherm. The Langmuir adsorption isotherm is frequently utilized in the examination of gas-solid phase sorption. It facilitates comprehension of surface coverage by achieving a balance between the rates of adsorption and desorption at equilibrium. The adsorption capacity is directly related to the surface area of the adsorbent, while desorption depends on the coverage of the adsorbent surface (Ayawei *et al.*, 2017; Anisuzzaman *et al.*, 2015; Deng *et al.*, 2009). The adsorption isotherm data was analysed using the Langmuir isotherm model, resulting in the following linear form (Zhul-quarnain *et al.*, 2018; Hussaro *et al.*, 2014).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \text{ .... (3)}$$

$$RL = \frac{1}{1+K_L C_0} \text{ .... (4)}$$

Freundlich isotherm. The Freundlich isotherm is used to explain the adsorption process on surfaces that are not uniform. This isotherm presents an equation that describes the surface heterogeneity and the exponential distribution of energy and active sites (Ayawei *et al.*, 2017; Tay *et al.*, 2012). The Freundlich isotherm is represented in linear form as follows:

$$\log q_e = \log K_F + 1/n \log Ce \text{ .... (5)}$$

where:

K_F represents the Freundlich adsorption constant, indicating the maximum adsorption capacity of MO (mg/g) and 'n' denotes the adsorption intensity constant (dimensionless).

Adsorption thermodynamics. The provided equations were used to calculate the thermodynamic parameters for the adsorption of MO on activated carbon, as described by (Thilagan *et al.*, 2013; Ozer *et al.*, 2007).

$$Kd = qe/Ce \text{ .... (6)}$$

$$\Delta G^o = -2.303RT \log Kd \text{ .... (7)}$$

The values of Gibbs free energy (ΔG^o) at various temperatures were computed based on the experimental results.

Results and Discussion

Characterization of absorbent materials. ***Fourier transform infrared spectroscopy (FTIR) evaluation.*** The FTIR spectrum of puffed rice biochar in Fig. 2(a) and 2(b) facilitates the identification of surface organic functional groups. Long (2004) utilized infrared spectroscopy to monitor chemical alterations taking place on the surface of the adsorbent. Although the frequency values demonstrate some variation in different situations, as shown in Fig. 2(a and b), the spectra themselves remain relatively unchanged. The broad absorption peak observed at 3414.29/cm is attributed to the intense vibration of the main amine bond in hydroxyl functional phenolic groups. This vibration is accompanied by the formation of hydrogen bonds due to the adsorption of water. The presence of the absorption band at 2070.22/cm signifies the strong vibration of isothiocyanate, namely the stretching of the N=C=S bond. The band seen at 1638.27/cm, falling within the

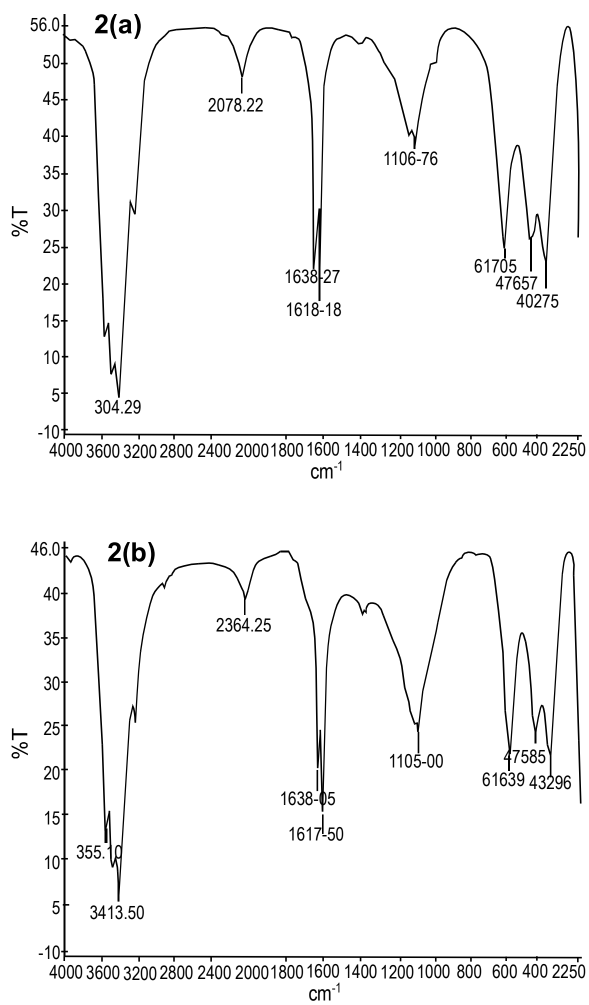

Fig. 2. **(a)** FTIR spectrum of puffed biochar at 303 K; Particle size = 170 μm; **(b)** = FTIR spectrum of puffed rice biochar with MO; Particle size = 170 μm; [MO] = 29.59 mg/L; Volume of MO = 20 mL; Equilibration time = 60 min.

range of 1638 to 1648/cm, is likely attributed to a prominent vibration of the C=C conjugated alkene, which is caused by the aromatic structure (Pezoti *et al*., 2014). The band seen at a wavelength of 1106.76/cm is attributed to the bending and severe stretching vibration of the C=O bond in the secondary alcohol phenol compound (Robert *et al*., 1997). Additionally, the presence of a peak at 617.05/cm is indicative of the intense stretching of the C-Br bond in the halogenated molecule. The peak remained rather stable both before and after the adsorption of MO which is essential for comprehending the distinctive qualities and possible uses of biochar, particularly in adsorption procedures such as wastewater treatment and environmental remediation. The biochar exhibited significant adsorption capacity, making it suitable for use in the removal of dyes from wastewater, particularly in the treatment of textile effluents. Nevertheless, the efficacy and appropriateness of puffed rice charcoal for this objective would also rely on more meticulous experimental findings and comparison analyses with alternative adsorbents.

Scanning electron microscope (SEM) evaluation. scanning Electron Microscopy (SEM) utilizes low-energy electron beams to examine and visualize materials in various modes, such as electron imaging and X-ray mapping. Fig. 3(a) presents an SEM image at a magnification of 170 μm, offering a detailed view of the puffed rice biochar's surface. This image reveals a complex morphology characterized by significant porosity, indicated by numerous voids and cavities within the structure. Such a highly porous material is essential for enhancing adsorption capacity, as the large pores facilitate the access of pollutants in aqueous solutions to the puffed rice biochar's internal surface, there by increasing the likelihood of adsorption. The irregular shapes and sizes of the pores contribute to a diverse surface area, further enhancing the biochar's effectiveness as an adsorbent. These micro-structural features are critical for optimizing performance in environmental remediation, particularly in removing contaminants like methyl orange from wastewater.

Figure 3(b), represents SEM at a magnification of 100 μm, reveals a densely packed arrangement of irregularly shaped particles. This configuration highlights a heterogeneous structure typical of biochar materials, characterized by numerous voids and gaps between particles, which indicate a porous nature. These interstitial spaces are vital for adsorption applications as they significantly increase the available surface area for molecular adhesion. The thin, plate-like shape of the particles contributes to an overall enhanced surface area that effectively interacts with various pollutants. The observed morphological variation with differing particle sizes and shapes, suggests that the biochar has not undergone extensive uniform processing, allowing for interactions with a broader range of contaminants. Overall, the SEM analysis provides essential insights into the puffed rice biochar's microstructure, indicating its potential effectiveness in adsorbing substances from aqueous solutions.

Figure 3(c) presents SEM analysis at a magnification of 2 µm, revealing finer details of the interaction between MO molecules and the puffed rice biochar surface. This scale retains the visible porous structure of the biochar, while highlighting individual or clusters of MO particles that may be attached to or filling the pores. The rough, uneven texture of the biochar show cases potential adsorption sites, with MO particles appearing as distinct or aggregated formations, confirming successful adsorption. This magnification further illustrates how effectively the biochar captures and retains MO molecules and indicates potential changes in surface morphology due to the adsorption process, such as occlusion of pores or alterations in surface texture caused by the attached MO molecules.

As a whole, the SEM tests demonstrate the biochar's strong ability to remove MO colouring from wastewater. It’s highly porous structure, with numerous gaps and irregular forms, improves adsorption capacity by allowing colour molecules to easily penetrate. The rough and heterogeneous surface has several active sites for effective binding, which promotes efficient adsorption. As a result, puffed rice biochar's distinct microstructural properties make it a viable adsorbent for MO elimination, as seen by its efficiency in wastewater treatment applications. Hence, the Fig. 3(c) demonstrated the best wastewater treatment effectiveness for MO dye removal using puffed rice biochar. It provides direct visual evidence of the adsorption process, showing how MO interacts with the puffed rice biochar surface and confirming its capability to effectively adsorb the dye.

Adsorption equilibrium studies. ***Effect of shaking time on the MO adsorption by puffed rice biochar.*** The time variation graphs are shown in Fig. 4(a) for the biochar particle size of 170 µm. The study explored time variations at intervals of 5, 10, 20, 40 and 60 min.

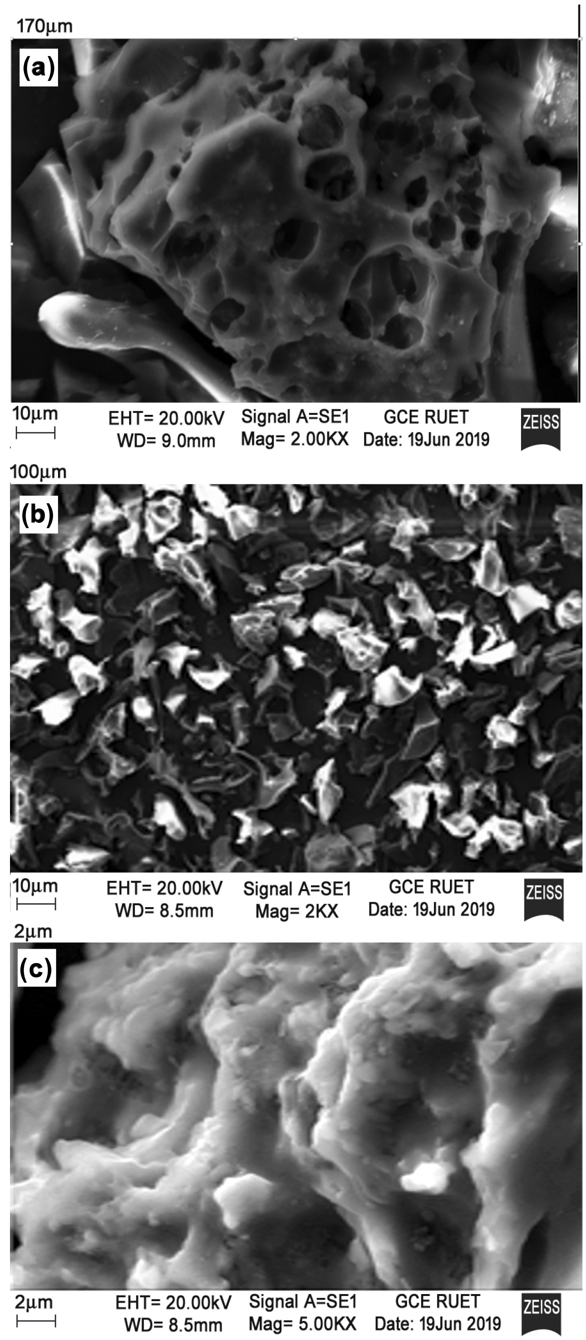

Fig. 3. **(a)** SEM of puffed rice biochar at 303K; Particle size = 170 µm; **(b)** SEM of puffed rice biochar with MO (Magnification 100 µm) and **(c)** SEM of puffed rice biochar with MO (Magnification 2 µm); [Particle size = 170 µm; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Equilibration time = 60 min; Temperature = 303K].

The time variation research has been graphed for both the Langmuir isotherm and Freundlich isotherm models. An investigation was conducted to determine the impact of shaking time on the equilibrium concentration of an aqueous solution containing 29.599 mg/L of MO and varying amounts (0.5 g, 1.0 g and 1.5 g) of biochar with particle sizes of 170 µm at a temperature of 303 K. It was observed that with extended shaking times, the concentration of MO decreases, indicating a reduction in the equilibrium concentration over time. The initial stage of adsorption occurs at a faster rate due to the presence of a greater number of active sites on the adsorbent surface for interaction. We have calculated the values of C_e and qe from equation (1) and observed that the duration of shaking rises, there is a clear reduction in the concentration of MO in the solution (C_e), which suggests that biochar has a stronger adsorption capacity. This is further supported by a consistent increase in adsorption capacity (q_e) as the shaking period is extended. Higher qe values indicate a correlation between increased biochar sample weight and improved adsorption. The yield, a metric that quantifies the amount of methyl orange that has been eliminated, provides insight into the efficacy of the adsorption process. Enhanced crop production indicates a higher capacity for capturing and retaining substances. The Ce/qe ratios indicate the ratio between the concentration and adsorption capacity, serving as a measure of the adsorbent's effectiveness. The value of K_d was determined using equation (6) which indicates a greater degree of adsorption, as K_d measures the affinity for adsorption. The results indicate that the duration of shaking and the weight of the sample have an impact on the amount of MO absorbed by puffed rice biochar. Specifically, longer shaking times and larger samples tend to lead to higher levels of adsorption. The provided data in real-world scenarios offers valuable insights for optimizing the adsorption process. Understanding K_d allows for the optimization of adsorption systems, such as in wastewater treatment by selecting adsorbents that exhibit higher K_d values for the pollutants of interest.

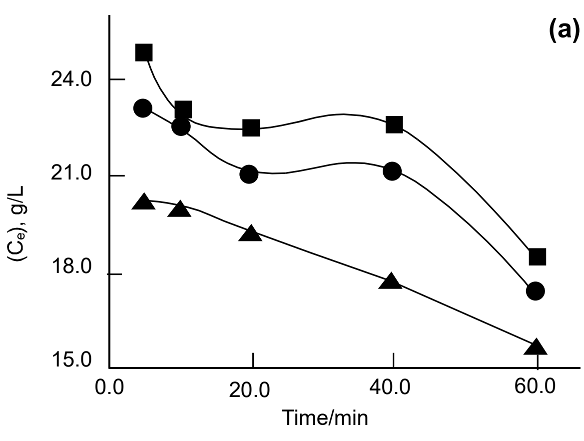

Fig. 4(a). Effect of shaking time on the adsorption of MO by puffed rice biochar [Particle size = 170 µm; Temperature = 303 K; [MO] = 29.599 mg/L; Volume of MO = 20 mL; (▲) 1.5 g (●) 1.0 g (■) 0.5 g].

Langmuir adsorption isotherm for the effect of shaking time study. The Langmuir model proposes that the surface of the adsorbent is homogeneous and has a finite number of sites for adsorption. It argues that following the formation of a monolayer, further adsorption takes place (Kareem, 2016; Mulugeta and Lelisa, 2014). Equation (3) represents the Langmuir isotherm model and Fig. 4(b) displays the Langmuir adsorption isotherm for biochar particles of 170 µm in size. The q_m (mg/g) and K_L values (L/mg) were calculated using equation (3) based on the slope and intercept obtained from Fig. 4(c), along with the corresponding R^2 values. For a particle size of 170 µm, the computed qm values were found to be 0.08, 0.05 and 0.06 for dosages of 0.5 g, 1.0 g and 1.5 g, respectively. The estimated q_m and K_L values were used to calculate the appropriate R_L values. The K_L values were measured as -0.06, -0.07 and -0.09 for dosages of 0.5 g, 1.0 g and 1.5 g, respectively. The Langmuir isotherm demonstrates that the process is very efficient, indicating that the surface area has been fully utilized. The adsorption process preference was found by computing the separation factor (R_L) using equation (4). The R_L values for particles with a diameter of 170 µm were -1.16, -0.87 and -0.59 for gravitational forces of 0.5 g, 1.0 g and 1.5 g, respectively. The R_L values for 170 µm indicate that the biochar particles have a negative size, suggesting that the MO adsorption process is highly efficient. The R_L value provides information on the adsorption process. It is considered unfavourable when R_L is greater than 1, linear when R_L is equal to 1, favourable when R_L is between 0 and 1 and irreversible when RL is equal to 0 (Kareem, 2016; Mulugeta and Lelisa, 2014). Therefore, it is recommended that the MO adsorption process in the examined system adhere to the Langmuir isotherm.

Freundlich adsorption isotherm for the effect of shaking time study. This isotherm characterizes the spatial arrangement and energy levels of the active spots on the surface. Fig. 4(c) depicts the graph of the logarithm of C_e (mg/L) against the logarithm of q_e

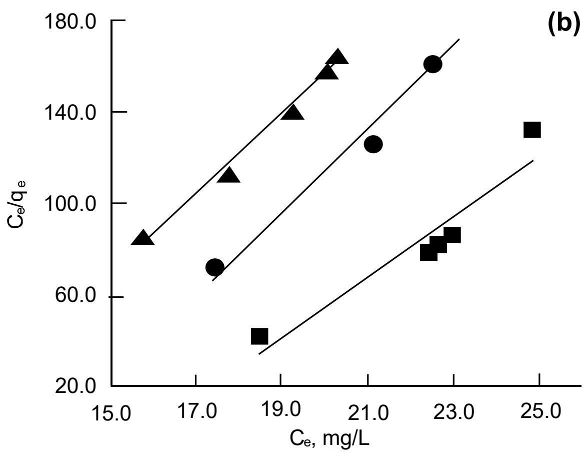

Fig. 4(b). Impact of shaking duration on MO adsorption by puffed rice biochar (Langmuir plot) [Particle size = 170 μm; Temperature = 303 K; [MO] = 29.599 mg/L; Volume of MO = 20 mL (▲) 1.5 g; s = 17.33; I = -190.49, R^2 = 0.99 (●) 1.0 g; s = 18.26; I = -252.17, R^2 = 0.96 (■) 0.5 g; s = 13.18; I = -209.36, R^2 = 0.90].

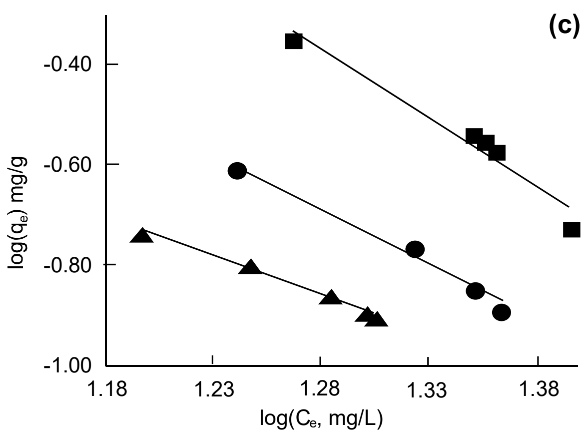

Fig. 4(c). Influence of shaking duration on MO adsorption by puffed rice biochar (Freundlich plot) [Particle size = 170 μm; Temperature = 303 K; [MO] = 29.599 mg/L; Volume of MO = 20 mL; (▲) 1.5 g; s = -1.57; I = 1.16; R^2 = 0.99 (●) 1.0 g; s = -2.18, I = 2.09, R^2 = 0.98, (■) 0.5 g; s = -2.74, I = 3.13, R^2 = 0.96].

(mg/L). The Freundlich isotherm model, as determined by equation (5), enables the calculation of the parameters K_F (adsorption coefficient) and 1/n (a measure of surface heterogeneity or adsorption intensity) based on the intercepts and slopes of the plots, respectively. The R^2 values are also noted. The K_F values obtained for adsorbent masses of 0.5 g, 1.0 g and 1.5 g were 1348.96, 123.03 and 14.45 respectively, when the particle size was 170 μm. The parameter 1/n generally falls within the range of 0 to 1 with values closer to zero indicating higher surface heterogeneity. Kareem (2016) and Ayawei *et al.* (2017) have found that a 1/n ratio less than 1.0 indicates a regular Freundlich isotherm, but a ratio greater than 1.0 suggests collective adsorption. When the logarithm of C_e (mg/L) is plotted against the logarithm of q_e (mg/g) for particles with a size of 170 μm, straight lines are obtained. The slopes of these lines are -1.57, -2.18 and -2.74 for masses of 1.5 g, 1 g and 0.5 g, respectively. Hence, the adsorption of methyl orange by puffed rice biochar does not adhere to the Freundlich isotherm under the investigated conditions.

Effect of particle sizes of the puffed rice biochar on the adsorption of MO. Figure 5(a) demonstrates the impact of particle size variations on MO adsorption. In order to examine the experiment, a 20 mL solution containing 6.800 mg/L of MO was used. This solution was combined with 0.5 g, 1 g and 1.5 g of biochar in separate reagent bottles. The reagent bottles were agitated for 60 min in a water bath held at a constant temperature

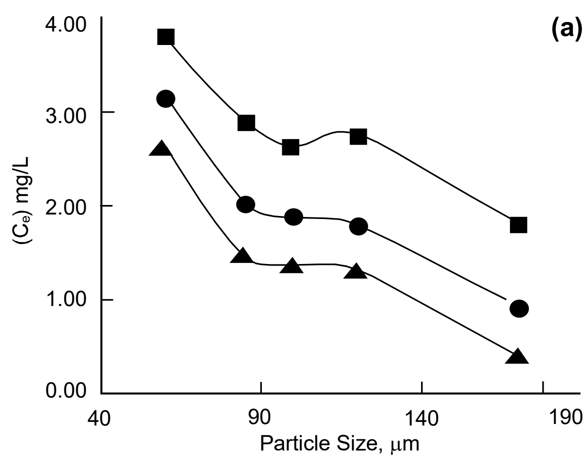

Fig. 5(a). Effect of biochar particle sizes on MO adsorption by puffed rice biochar [Temperature = 303 K; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g, (●) 1.0 g (■) 0.5 g].

of 303 K. The particle size varies between 60 µm and 170 µm. The reagent bottles were linked to a shaker and positioned inside a water bath.

The adsorption capacity (q_e) exhibited a notable decline as the particle size increased across all three sample weights. This demonstrates that smaller particles exhibit greater adsorption effectiveness. Greater C_e values are associated with larger particle sizes, indicating that the ability of biochar to adsorb MO reduces as the particle size increases. The percentage yield decreases as the particle size increases, indicating that smaller particles are more effective in adsorbing MO. The C_e/q_e ratios suggest that smaller particle sizes were more efficient in attaining equilibrium between the solution and biochar. The value of K_d has been determined from equation (6) and data demonstrated that smaller particles had better adsorption performance, as seen by the negative connection between log K_d and particle size. This is further supported by the inverse correlation between the logarithm of K_d and the size of the particles. Following 60 min of agitation, the concentration of MO at equilibrium declined as the particle size decreased. The higher adsorption was a result of the augmented surface area of the particles. The particle size variation of the experimental system was assessed by employing Langmuir and Freundlich adsorption isotherms at varying MO concentrations and adsorbate weights.

Langmuir adsorption isotherm for the effect of particle size study. Equation (3) presents the relationship, and the Langmuir plot (C_e, mg/L *vs*. C_e/q_e) is displayed in Fig. 5(b). From this plot, a linear association has been observed for each experimental condition, as stated. The values of q_m (mg/g) were calculated based on the slope and intercept. The determined values of q_m were 0.09, 0.06 and 0.05 for puffed rice biochar weights of 0.5 g, 1.0 g and 1.5 g, respectively. The K_L (L/mg) values obtained for 0.5 g, 1.0 g and 1.5 g of puffed rice biochar were -0.87, -1.64 and -3.21, respectively. The R_L values were determined using the calculated values of qm and K_L, as obtained from equation (4). The R_L values were determined to be -0.20, -0.09 and -0.05 for 0.5 g, 1.0 g and 1.5 g, respectively. The value of R_L was calculated using equation (4) that indicates the examined solution is highly conducive to the adsorption of MO. Thus, it is evident that a larger concentration of MO is advantageous, whereas a lower concentration of MO is disadvantageous for the analyzed system.

Freundlich adsorption isotherm for the effect of particle size study. The Freundlich isotherm describes the process of adsorption on surfaces that have different energy levels, enabling interactions between adsorbed molecules that go beyond the development of a single layer (Haitham *et al*., 2014). Fig. 5(c) displays a linear correlation graphed as the logarithm of C_e (mg/L) *vs*. the logarithm of q_e (mg/L). The equation (5) represents

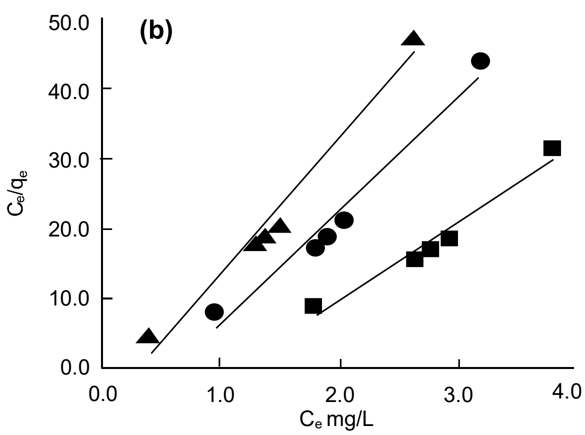

Fig. 5(b). Consequence of particle sizes on the adsorption of MO by puffed rice biochar (Langmuir plot) [Temperature = 303 K; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g; s = 19.47; I = -6.07; R^2 = 0.98; (●) 1.0 g; s = 16.27; I = -9.92; R^2 = 0.97 (■) 0.5 g; s = 11.31; I = -13.02; R^2 = 0.97].

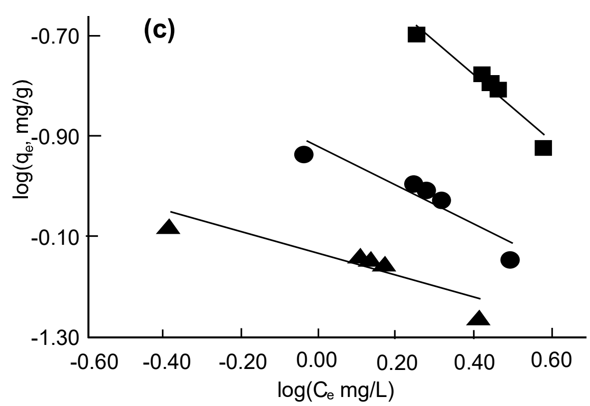

Fig. 5(c). Impact of particle sizes on the adsorption of MO by puffed rice biochar (Freundlich plot) [Temperature = 303 K; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g; s = -0.21; I = -1.13; R^2 = 0.85 (●) 1.0 g; s = -0.38; I = -0.92; R^2 = 0.91 (■) 0.5 g; s = -0.66; I = -0.51; R^2 = 0.95].

the Freundlich isotherm model. The values of the parameters K_F (L/g) and 1/n are obtained by calculating the intercept and slope of the plot, respectively. K_F denotes the adsorption coefficient which quantifies the quantity of dye that is adsorbed onto the activated carbon adsorbent per unit of equilibrium concentration. The K_F values for 0.5 g, 1.0 g and 1.5 g of puffed rice biochar were 0.31, 0.12 and -0.07, respectively, indicating a negative slope in each instance. Similarly, the values of 1/n were -0.21, -0.38 and -0.66 for 1.5 g, 1 g and 0.5 g of puffed rice biochar, suggesting different levels of surface heterogeneity or adsorption intensity. A smaller value of 1/n suggests a higher level of surface heterogeneity. Have found that a 1/n ratio below one indicates a normal Freundlich isotherm but a ratio above one indicates cooperative adsorption which is reported by (Ayawei *et al*., 2017; Kareem, 2016; Doke *et al*., 2013). These experimental observations lead to the conclusion that the system does not adhere to the Freundlich isotherm model.

Effect of various MO concentrations onto puffed rice biochar. Studies were done at a temperature of 303 K using aqueous solutions containing methyl orange at concentrations ranging from 5 to 25 mg/L as stated in Fig. 6 and adsorption was determined using equation 1. Additionally, puffed rice biochar with particle sizes of 170 μm was added to the solutions in amounts of 0.5, 1.0 and 1.5 g. The purpose of these studies was to study the effect of concentration on equilibrium adsorption. Each bottle included 20 mL of MO solution with different concentrations and quantities of biochar for the equilibrium investigation. The reagent bottles were linked to a shaker and positioned inside a water bath. The temperature of the water bath was being maintained at a constant 303 K showing the amount of MO adsorbed onto the puffed rice biochar at equilibrium also increased. This suggests that higher concentrations of MO in solution lead to greater adsorption capacity of the biochar under constant conditions. The continuous observation of this trend was noted in all experimental situations throughout the investigation. The adsorption process was efficient, especially at higher MO concentrations, with puffed rice biochar effectively removing methyl orange due to its porous structure and surface functional groups.

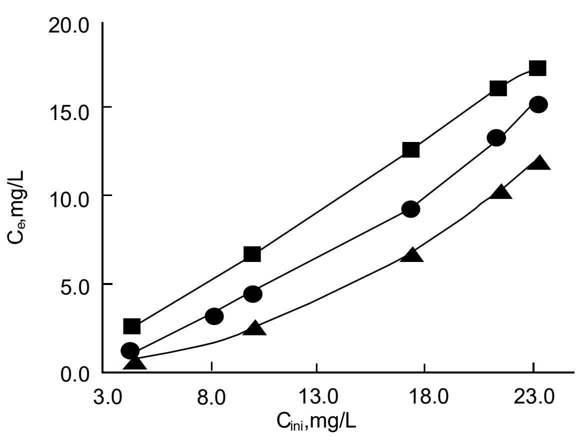

Fig. 6. Impact of various MO concentration on the adsorption by puffed rice biochar [Particle size = 170 μm; Temperature = 303 K; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g, (●) 1.0 g , (■) 0.5 g].

Adsorption isotherms are essential for evaluating the adsorption capability of an adsorbent. The Langmuir and Freundlich models, widely utilized in this investigation which are recognized methodologies for analyzing aqueous solutions. Sorption mechanisms consist of two processes that is physisorption and chemisorption. These processes include the attachment of metallic or organic molecules to the adsorbent. Equilibrium is attained when the adsorbent becomes saturated, suggesting a state of equilibrium between the rates of adsorption and desorption (Payne *et al*., 2011). The concentration of adsorbate remaining in wastewater at equilibrium typically varies depending on the type and concentration of activated carbon used (Krishnaiah *et al*., 2013).

Impact of the temperature on the adsorption of MO. Equal volumes (20 mL) of these solutions were divided into individual reagent bottles, with each bottle holding different amounts of biochar. The reagent bottles were connected to a shaker and the equilibrium adsorption capacities for MO adsorption onto puffed rice biochar were studied at temperatures of 20, 30, 40, 50 and 60 °C. The sample weights used were 0.5 g, 1.0 g and 1.5 g. An investigation was conducted to assess the impact of temperature on the adsorption of methyl orange by biochar derived from puffed rice, using a particle size of 170 μm, as shown in Fig. 7(a). The concentration of MO (C_e) in the solution, adsorption capacity (q_e), percentage yield and distribution coefficient (K_d) were determined using equation 1, 2 and 7 respectively. In general, there was a decline in the adsorption capacity for all sample weights as the temperature increased. These findings indicate that there is a process of releasing molecules from a surface upto

40 °C which is then followed by an increase in the number of molecules being attracted to the surface at higher temperatures (Muinde *et al*., 2017; Islam *et al*., 2016). Remarkably, a substantial reduction in adsorption capacity was detected at a temperature of 60 °C, regardless of the weight of the samples. This implies that elevated temperatures could hurt the ability of biochar to adsorb efficiently. In addition, the adsorption behavior was influenced by differences in sample weight, where higher sample weights resulted in increased adsorption capabilities. This suggests that the quantity of the sample plays a significant role in the adsorption processes. The results highlight the need to take into account temperature and sample weight when trying to optimize the adsorption efficiency of puffed rice biochar for the removal of MO.

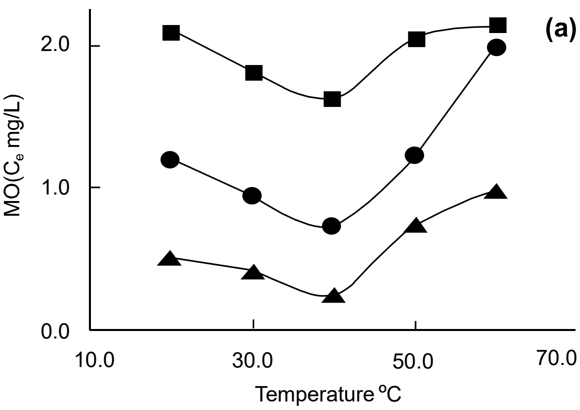

Fig. 7(a). Influence of temperatures on the adsorption of MO by puffed rice biochar [Particle size = 170 µm; [MO] = 6.800 mg/L, Volume of MO = 20 mL; Time = 60 min. (▲) 0.5 g (●) 1.0 g (■) 1.5 g].

Langmuir adsorption isotherm for the effect of the temperature on the adsorption of MO. Figure 7(b) demonstrates the Langmuir adsorption isotherm graph, showing the impact of temperature on the adsorption of MO by puffed rice biochar. It demonstrates the linear correlation for each group of experimental conditions being studied. The qm values (mg/g) were determined by calculating the slope and intercept. The values obtained were 0.14, 0.08 and 0.07 for 0.5 g, 1.0 g and 1.5 g of puffed rice biochar, respectively. The K_L (L/mg) values for 0.5 g, 1.0 g and 1.5 g of puffed rice biochar were determined to be -1.93, -3.85 and -20.95, respectively. The R_L values were determined using the calculated values of q_m and K_L, as described in equation (4). The resulting R_L values were found to be -0.08, -0.04 and -0.06, respectively. These values indicate the types of isotherms: unfavourable (R_L>1), linear (R_L= 1), favourable (0<R_L<1) and irreversible (R_L= 0). The

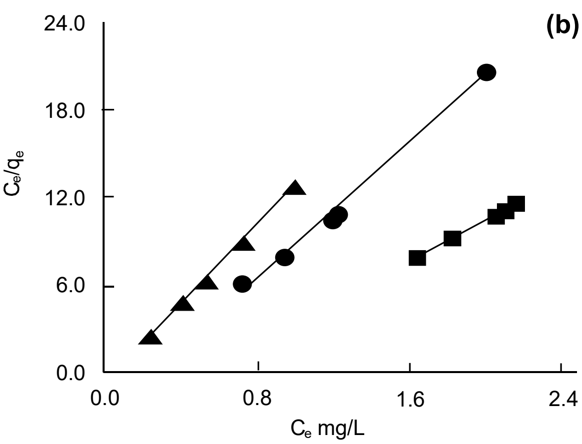

Fig. 7(b). Impact of temperatures on the adsorption of MO puffed rice biochar (Langmuir plot) [Particle size = 170 µm; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g; s = 13.41, I = -0.64, R^2 = 0.99 (●) 1.0 g; s = 11.80, I = -3.07, R^2 = 0.99 (■) 0.5 g; s = 7.07, I = -3.67, R^2 = 0.99].

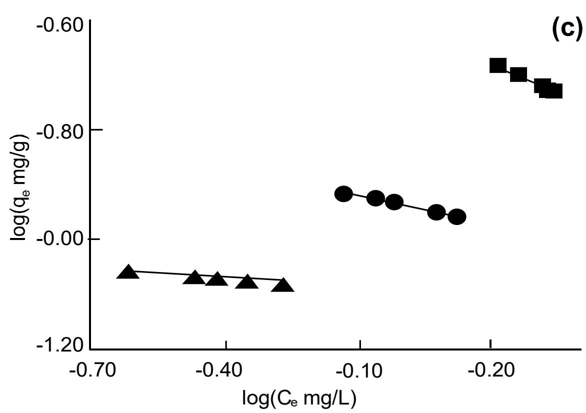

Fig. 7(c). Impact of temperatures on the adsorption of MO by puffed rice biochar (Freundlich plot) [Particle size = 170 µm; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Time = 60 min. (▲) 1.5 g; s = -0.06, I = -1.09, R^2 = 0.98 (●) 1.0 g; s = -0.17, I = -0.94, R^2 = 0.99 (■) 0.5 g; s = -0.38, I = -0.60, R^2 = 0.99].

presence of a positive slope suggests that the system being studied adheres to the Langmuir adsorption isotherm. Similar observations have been found for Reactive orange-16 dye which followed the Langmuir isotherm model, indicating monolayer formation without interaction among molecules (Butt, 2024).

Freundlich adsorption isotherm for the effect of the temperature on the adsorption of MO. The Freundlich isotherm is suitable for describing adsorption processes that take place on surfaces with varying properties (Thilagan *et al*., 2013). The relationship is represented by equation (5) and illustrated in Fig. 7(c). The gradients of the graphs were calculated as -0.06, -0.17 and -0.38 for 1.5 g, 1 g and 0.5 g of puffed rice biochar, respectively. The values of K_F (L/g) and 1/n were determined based on the intercepts and slopes, resulting in values of 0.25, 0.11 and 0.08 for puffed rice biochar weights of 0.5 g, 1.0 g and 1.5 g, respectively. The adsorption coefficient, K_F, measures the quantity of dye that is adsorbed per unit of equilibrium concentration onto the activated carbon adsorbent. The parameter 1/n varies between 0 and 1 and represents the level of adsorption intensity or surface heterogeneity. Values closer to zero indicate higher levels of heterogeneity. A ratio of 1/n less than one indicates a conventional Freundlich isotherm, whereas a ratio greater than one shows cooperative adsorption (Ayawei *et al*., 2017; Kareem 2016).

The presence of a negative slope in the observed linear relationship suggests that the system being studied does not conform to the Freundlich adsorption isotherm. Consequently, after conducting this research, it can be deduced that the adsorption behaviour of this specific system does not adhere to the Freundlich model.

The Langmuir model accurately characterizes the adsorption process, depicting puffed rice biochar as a highly efficient adsorbent for MO. The departure from Freundlich's behaviour indicates that the adsorption takes place on a reasonably uniform surface. This study provides useful insights into maximizing the removal of MO by utilizing puffed rice biochar. It highlights the importance of controlling the temperature to optimize the effectiveness of this method.

Thermodynamics for MO adsorption. The thermodynamics of the adsorption system were characterized by the changes in Gibbs free energy (ΔG^0), enthalpy ($\Delta H^{\pm}$), and entropy ($\Delta S^{\pm}$). The values of Gibbs free energy (ΔG^0) at different temperatures were computed using equation (7) and are presented in Table 1 which is based on the experimental results.

The analysis of thermodynamic characteristics based on many conclusions about the adsorption of methyl orange (MO) by puffed rice biochar. The Gibbs free energy change (ΔG^0) is a reliable measure of spontaneity.

Table 1. Evaluation of thermodynamic parameters

Weight of biochar	T(°K)	ΔG° (J/mol)	$\Delta H^{\pm}$(kJ/mol)	$\Delta S^{\pm}$(kJ/mol/K)
Weight of sample = 0.5 g	293	5876.971	-4.02	-56.87
	303	5542.884		
	313	5373.913		
	323	6381.724		
	333	6777.912		
Weight of sample = 1.0 g	293	2505.712	-0.42	-18.96
	303	2273.392		
	313	2024.969		
	323	2319.973		
	333	2970.590		
Weight of sample = 1.5 g	293	1970.520	0.44	1.84
	303	1635.634		
	313	1154.626		
	323	1626.153		
	333	2011.508		

Particle size = 170 µm; [MO] = 6.800 mg/L; Volume of MO = 20 mL; Shaking time = 60 min.

A lower ΔG^0 value indicates a more spontaneous adsorption process, while a positive ΔG^0 value suggests non-spontaneous adsorption. Furthermore, the enthalpy change ($\Delta H^{\pm}$) can determine whether the adsorption process is exothermic (negative $\Delta H^{\pm}$) or endothermic (positive $\Delta H^{\pm}$), offering valuable information about heat variations during adsorption. Moreover, the entropy change ($\Delta S^{\pm}$) indicates alterations in disorder during adsorption, where negative $\Delta S^{\pm}$ values indicate reduced un-predictability and potentially enhanced intra-particle diffusion.

The adsorption process is greatly affected by temperature, as indicated by the decrease in ΔG^0 with increasing temperature. This suggests that the adsorption becomes more spontaneous at higher temperatures, regardless of the sample weights. Furthermore, the impact of sample weight on ΔG^0 values demonstrates that increased weights generally result in decreased ΔG^0 values, suggesting higher adsorption effectiveness per unit mass of biochar. At a temperature of 313 K, the 1.5 g sample demonstrates the most advantageous circumstances for MO adsorption, as indicated by the lowest ΔG^0 value (1154.626 J/mol) compared to the other parameters that were evaluated. These findings indicate the ideal circumstances for efficiently eliminating methyl orange by utilizing puffed rice biochar.

Conclusion

This study investigated the potential of puffed rice biochar for the removal of methyl orange (MO) dye, evaluating the effects of shaking duration, particle size, dye concentration and temperature on adsorption efficiency. Characterization techniques such as SEM and FTIR identified key functional groups and revealed the porous structure of the biochar, which is critical for adsorption.

The results indicated that particle size significantly impacted adsorption capacity and with finer particles exhibiting greater efficiency due to their larger surface area and improved access to active sites. The adsorption characteristics were analyzed using the Langmuir and Freundlich isotherms and with the Langmuir model demonstrating a superior fit, suggesting monolayer adsorption on a surface with finite active sites.

Thermodynamic analysis revealed that the adsorption process was endothermic, with estimated parameters (ΔG^0, $\Delta S^{\pm}$ and $\Delta H^{\pm}$) indicating non-spontaneous adsorption and exergonic reactions. The Gibbs free energy change (ΔG^0) for puffed rice biochar across varying temperatures further supported the findings, highlighting the significance of temperature in influencing adsorption and desorption behaviuors. The thermodynamic study established that the adsorption processes were endergonic and exothermic.

Finally, the use of puffed rice biochar for the removal of MO dye was shown to be effective, economical and environmentally safe for wastewater treatment applications. Optimizing temperature and particle size emerged as crucial factors to enhance adsorption efficiency, contributing to sustainable practices in textile wastewater treatment, while the Freundlich model did not fit the data well, the negative slope values of 1/n suggested varying degrees of adsorption intensity and surface heterogeneity, warranting further investigation into the mechanisms at play.

Future research directions. Future research on puffed rice biochar for methyl orange (MO) removal should focus on enhancing and expanding its applicability. One strategy is to optimize the biochar production process to improve its adsorption characteristics. This involves exploring various activation conditions, including temperature and chemical treatments. To gain a comprehensive understanding of biochar's versatility, it is essential to evaluate its performance against a wider range of pollutants and types of wastewater. Additionally, assessing the impact of environmental factors such as pH and ionic strength on adsorption will be crucial for adapting biochar to diverse conditions.

Utilizing advanced analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and detailed surface area measurements can provide deeper insights into the interactions between biochar and pollutants. Furthermore, investigating methods to modify or combine biochar with other materials could enhance its performance and regeneration efficiency.

Eventually, validation of laboratory outcomes through real-world applications and pilot-scale investigations is required to assess the practical and economic feasibility of employing puffed rice biochar in large-scale wastewater treatment operations.

Acknowledgement

Mst. Fahima Khatun (one of the authors) expresses her gratitude to the Ministry of Science and Technology, Government of the People's Republic of Bangladesh, for awarding her a one-year National Science and Technology (NST) fellowship which enabled the completion of this research.

Conflict of Interest. The author declare that thay have no conflict of interest.

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