



Adsorption of methylene blue on papaya bark fiber: Equilibrium, isotherm and kinetic perspectives

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ABSTRACT

Rapid population growth and industrial expansion lead us to be habitat of a polluted planet. One of the major pollutants that badly affect the ecosystem being organic dyes released from various chemical industries where cleaner production concept is straightway adopted. Papaya (*Carica papaya*) bark fiber (PBF) is a natural product used for Methylene Blue (MB) dye removal as a cost-effective adsorbent from aqueous solution by batch method. Several parameters as the effect of pH, initial dye concentration, contact time, and adsorbent dosage were studied and optimized for maximum dye recovery. Reaction kinetics of the process and Langmuir and Freundlich adsorption isotherms were investigated. Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) were used to confirm the surface properties of the PBF adsorbent. The maximum MB uptake capacity of PBF adsorbent was found to be 66.67 mg/g. Based on the results, the papaya bark fiber might be employed as a cost-effective bio-sorbent for the exclusion of dyestuffs from industrial effluent for cleaner production.

1. Introduction

Freshwater ecosystems and the resources they provide for people are under a lot of stress even in the absence of climate change as a result of rising water demand and deteriorating water quality [1]. Industrial pollution is contributing to growing freshwater shortages together with rising demand. The advancements made in science, have both positive and negative effects on the environment. Poor industrial effluent discharge practices into soil and water bodies, surface runoff from agricultural lands, untreated municipal waste disposal, and mining activities are all to threaten human health and life and deteriorate the environment's most important quality [2]. That explains why it is necessary to create and implement a sustainable clean production process. Efficient utilization of resources and energies plays role to get rid of toxic raw materials, and lower poisonous emissions and wastes [3]. This concept elucidates the need for developing and implementing a sustainable clean production approach [4]. Cleaner manufacturing looks forward and aims to foresee and avoid toxic chemical, e.g., formaldehyde in leather industries [5,6], vanadate ions [7,8], palm oil mill

effluent (POME) [9], etc. Thanks to the efficient removal of contaminants in the cleaner application of mesoporous boehmite, activated carbon and green surfactants [7–10].

Industrial sectors need to embrace a cleaner production strategy immediately. Up to 15% of industrial water contamination is attributed to the textile sector. One of the most environmentally destructive and dangerous components of the worldwide textile industry is the use of dyes that endanger human health [11]. More than 0.1 million commercially available dyes are generated yearly, with over 0.7 million tons of dyestuff produced out of which 5–10% of the dyestuff is wasted as industrial wastewater [12]. The discharge of colored waste materials destroys the aesthetic values of nature and at the same time reduces the photosynthetic activities of aquatic plants and weeds by interfering transmission of sunlight [13]. Varieties of dyes are attached to surfaces to give color and are recognized for their resistance to detergent action. Synthetic dyes are extensively utilized in a variety of sectors to add color to their goods, which include but are not limited to textiles, leather tanning, paper, carpet, cosmetics, plastic, and food [14]. Dyes are primarily chemical compounds made up of two key components:

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chromophore which provide color and auxochromes which increase the dye's affinity for fibers [15]. These dyes are frequently found in wastewater from industries, causing a dumping issue. Their effluent discharges are a significant source of pollution as a result of their obstinacy. They have a variety of chemical structures, most of which are based on substituted aromatic and heterocyclic groups, which are difficult to a breakdown in traditional wastewater treatment methods and higher the COD and BOD concentration harder the degradation of materials because of their resistance to sunlight, oxidizers, and microbes [16].

Methylene blue (3,7-bis (Dimethylamino)-phenothiazin-5-iumchloride) is a cationic thiazine dye which can produce a stable solution with water at room temperature [17]. It is usually utilized in the textile, paper, chemical, and pharmaceutical industries [18]. It is also used for biological staining and coloring of cotton, wool, and hair. Because of its toxicity, methylene blue (MB) is known to be a harmful chemical for human health, which includes but is not limited to nausea, vomiting, respiratory issues, eye burning and diarrhea [19]. It is difficult to biodegrade too. Thus, widespread utilization of MB results in an accumulation of this harmful chemical in industrial wastewater. Therefore, it is very important to develop an efficient and cost-effective method to remove MB from an aqueous solution.

Several physical, chemical, and biological methods are successfully developed to remove dyes and other pollutants from wastewater. The methods include adsorption, chemical oxidation, flocculation/coagulation, membrane separation, photocatalytic degradation, ion exchange, electrochemical, ozonization, aerobic/anaerobic treatments, and nano-filtration/reverse osmosis [20]. The efficiency, expense, and environmental consequences of each of these established approaches vary [21]. Among the aforementioned techniques, adsorption has been proved to be superior because of its simple operation process, low cost, availability, high effectiveness, easy recycling, and potential for scale-up of the process [22]. Moreover, the adsorption process neither generates any hazardous chemicals nor affects the treated water quality [21]. The adsorption efficiency is influenced by several factors including adsorbate-adsorbent interaction, adsorbent to adsorbate ratio, surface area and particle size of the adsorbent, concentration of the adsorbate, contact time, pH, and temperature [23]. Activated carbon (AC) is the most often utilized adsorbent in the industry because of its efficiency, large surface area, and strong surface reactivity [24]. The performance of AC is determined by the type of carbon employed and the specifications of the effluent. High running costs of AC, impact on the environment, and higher cost of regeneration limit its usage [25]. As a result, various nonconventional adsorbents, such as agricultural waste materials, natural biomaterials, etc. Have been utilized to extract MB from wastewater, owing to their increased effectiveness and simplicity. Such type of adsorbents include peat [25], rice husk [26], coconut husk [27], *Pteris vittata* root [28], sawdust [29], palm ash [30], neem leaf [31], clay [32], stone olives [33], sunflower seed shells [34], banana peel [35], tea dust [36], *Mangifera indica* (mango) seeds [37], *Artocarpus heterophyllus* (jackfruit) leaf powders [38], coconut leaves [39], *Citrus limetta* peels [40], potato peels [41], jute stick powder [42], sugarcane bagasse [43], maize stem [44], palm kernel fibre [45], pea shell [46], date palm leaves [47], etc. Were used for this purpose. In fact, there is always a demand of effective adsorbents, depending on low-cost, better-efficiency, ease of handling, and availability. Predominantly, the removal of recalcitrant dye MB from industrial and municipal effluents using papaya bark fiber (PBF) has not been demonstrated in details so far.

Green papaya is used as a popular vegetable and ripe papaya is used to make juice. The Indian subcontinent (Bangladesh, India, and a few neighboring countries) leads the annual papaya production in the world; whereas, only India produces about 3.0 million tons of papaya per annum [48]. Papaya cultivation in Bangladesh has become popular among farmers because of the availability of a high-yielding variety of papaya. A report revealed that in 2018–19 the commercial papaya produced about 1.5 million tons [49]. Therefore, the

bark of this available and low-cost agro-based product can be utilized for any innovative purpose. Papaya has been reported to be rich in hydroxyl (OH) functional groups because it contains cellulose (58.7%), hemicellulose (11.8%), and lignin (14.3%) [50,51]. This has opened an immense opportunity to modify papaya bark in such a way that it can be utilized as an adsorbent.

In the present study, the removal of MB from an aqueous solution using papaya bark fiber as an efficient, locally available, and low-cost adsorbent has been investigated. In this regard, various factors such as pH, initial dye concentration, adsorbent doses, and contact time were examined by several experimental conditions to find out an optimum adsorption conditions. Moreover, various physicochemical and surface properties were analyzed to confirm the statements provided in the article hereinafter.

2. Experimental

2.1. Materials and methods

2.1.1. Adsorbent preparation

The papaya plants were collected from Jashore, Bangladesh. The decaying piece of the bark was separated from it and dirt particles were rinsed away from the bark by washing with water. They were broken up into little bits and cleaned up by double distilled water (DW). The cut pieces were immersed in 40% HCl for 40 min. A blender was used to mix the tiny fragments. They were then filtered to remove the fiber. The filtrate was subsequently washed for three times. The result was then dried for 6 h at 105 °C before being processed in a mortar to produce fine PBF powder. The powder was then stored in an airtight storage container.

2.1.2. Adsorbent characterization

Spectrophotometric analysis of the PBF was carried out by FTIR spectroscopy (Model: FTIR 2000, Shimadzu, Kyoto, Japan). KBr disks of 150 mg holding roughly 2% of the samples were created just earlier. The FTIR spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . The spectra of 30 scans on an average were recorded for each run. Scanning electron microscope (SEM) analysis of the adsorbent was done by placing papaya ample on Leo 435 VP. Images of the fiber were produced by SEM through scanning it with a focused beam of electrons. Multiple magnifications were taken at 5 kV such as 100 × , 300 × , 500 × , and 1000 × for 10 μg .

2.1.3. Adsorbate preparation

Methylene blue (MW 319.85 g/mol), a basic dye, was purchased from Merck, India. To prepare the dye solution MB was dissolved in an appropriate quantity into water. To make 100 ppm solutions, 500 ml DW was placed in a beaker of 1 L. Then MB accurately weighed 50 mg by a digital weighing machine. Then the solution was shaken by a rotary flask shaker for 20 min. In this way, the multiple concentrations of solutions such as 25 ppm, 50 ppm, 75 ppm, 150 ppm, 200 ppm and 300 ppm were prepared.

2.2. Adsorption procedure

All of the trials were done at room temperature (27 ± 5 °C). Batch adsorption tests were carried out by consuming the required adsorbents in a 250 ml conical flask holding 100 ml dye solution at the correct pH value, multiple concentrations, contact time, and adsorbent dosage. The pH of the solution was accustomed as needed by 0.1 M HCl and 0.1 M NaOH. The needed amount of PBF was applied, and the samples in the flask were loaded on an electrically rotating flask shaker for the necessary contact time. The time it took to reach equilibrium was calculated by taking samples at regular intervals. Filter paper was used to filter the contents of the flask. The absorbance of these solutions was then measured at 668 nm by a HACH-DR-4000 UV-visible



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spectrophotometer. The equation applied to calculate the percentage removal of MB:

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Where C_o is the initial or starting concentration (mg/L) and C_t is the concentration at time t .

The capacity of adsorption at equilibrium, q_e (mg/g) calculated using the equation (Eq. (2)) mentioned below:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where, C_o and C_e are the primary and equilibrium liquid-phase concentrations (mg/L) of MB, respectively. The volume (L) of the solution and the dry adsorbent mass (g) employed is denoted by V and m , sequentially.

To study the pH effect on adsorption experiments 50 ml 100 ppm aqueous solution was placed in each 250 ml beaker using a measuring cylinder. pH is regulated by the controlled addition of 0.1 M hydrochloric acid and 0.1 M sodium hydroxide in the range of pH 1–12 with a PBF dose of 0.2 g. Then 12 h of shaking were done. The effect of multiple dye concentrations was studied using a 100 ml dye solution of concentrations 25–300 ppm at pH 7, PBF dose 0.5 g, and a contact time of 12 h. The effect of adsorbent dose on 100 ppm 100 ml MB dye solution was found by applying various PBF doses in the range of 0.25–4.0 g. The pH of each sample was maintained at 7 and the contact time was 12 h. Adsorption experiments for the effect of contact time were performed by using 100 ml 100 ppm dye solution at pH 7 and 0.5 g PBF dose at various contact times in the range of 10–300 min.

2.3. Adsorption isotherm study

Adsorption isotherm studies were performed with six different starting dye solution concentrations ranging from 25 to 300 ppm at pH 7, a contact period of 100 min for 12 h, and an adsorption dose of 0.5 g. Then the mixture of dye solution and adsorbent was filtered and the filtrate was analyzed by UV-vis spectrometer.

2.3.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm depicts monolayer adsorption of adsorbate on the outer surface of the adsorbent, followed by no further adsorption. The model predicts homogeneous adsorption energies on the surface and no adsorbate transmigration in the plane of the surface. The equation presented by Langmuir:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (3)$$

The parameters of Langmuir adsorption were calculated by linearizing the Langmuir equation (Eq. (4)). The linear form of the model is:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (4)$$

Where, C_e , q_e , Q_o , and K_L correspond to the equilibrium adsorbate concentration (mg/L), the quantity of dye absorbed per gram of adsorbent at equilibrium (mg/g), the maximum monolayer coverage capacity (mg/g), and the Langmuir isotherm constant (L/mg).

The slope and intercept of the Langmuir plot of $1/q_e$ against $1/C_e$ were used to get the values of q_{\max} and K_L . The key characteristics of Langmuir isotherm can be described by the equilibrium parameter R_L , which is a dimensionless constant known as the separation factor.

$$R_L = \frac{1}{1 + (1 + K_L C_o)} \quad (5)$$

When $R_L < 1$, it is favorable; $0 < R_L < 1$, it is favorable; and $R_L = 0$, it is irreversible [52].

unfavorable; $0 < R_L < 1$, it is favorable; and $R_L = 0$, it is irreversible [52].

2.3.2. Freundlich adsorption isotherm

This is a model that is frequently used to describe the adsorption properties of a heterogeneous surface. The well-known non-linear Freundlich isotherm equation is:

$$q_e = K_f (C_e)^{1/n} \quad (6)$$

Where, K_f , n , C_e , and q_e respectively represent the Freundlich isotherm constant (L/mg), the adsorption intensity, the adsorbate equilibrium concentration (mg/L), and the quantity of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g). The linearized form of the equation (Eq. (7)):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

The constant K_f is a rough measurement of adsorption capacity, whereas $1/n$ is a function of the adsorption strength of the process. When $n = 1$, the partition between the two phases is unaffected by concentration [52].

2.4. Kinetics studies

Adsorption kinetic parameters of the adsorption were investigated for the batch system of 100 ppm of MB dye solution at pH 7. During the trial, the contact time varied from 10 to 300 min, and the percent dye removal was observed. The quantity of adsorption was estimated using Eq. 3 with q_e equaling q_t and C_e equaling C_t at time t . Both Lagergren pseudo-first and second-order kinetics were investigated to boost our knowledge of adsorption kinetics.

2.4.1. Pseudo-first-order

The following equation can be used to express the Lagergren pseudo-first-order model:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

Where, q_e and q_t (mg/g) are the amounts of the quantities adsorbed at equilibrium and at time t , respectively; k_1 is the equilibrium rate constant in the pseudo-first-order model (L/min). The linear graph of $\log (q_e - q_t)$ vs. t yields the value of k_1 [53].

2.4.2. Pseudo-second-order

The pseudo-second-order model shown in Eq. (10) can be used to characterize the adsorption kinetics.

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (9)$$

Where k_2 is the pseudo-second-order sorption rate constant (g/mg min). The following equation (Eq. 11) is the integral linearized form of the preceding one:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

The plot of t/q_t against t is used to calculate the quantity of adsorption (q_e) and the rate constant (k_2) [54].

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FTIR analysis

Fig. 1 shows the FTIR spectrum of the PBF to identify various functional groups present on its surface to remove MB dye. It can be seen from the figure that O–H bond stretching takes place at 3364 cm^{-1} [51].





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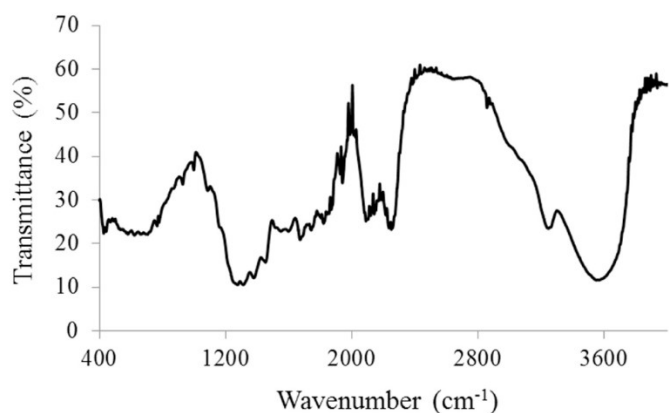


Fig. 1. FTIR spectrum of PBF.

The prominent peak at 1730 cm^{-1} has been observed for the strong C=O bond stretching. This C=O bond confirms the presence of aldehyde [44]. The band at 1594 cm^{-1} is responsible for the carbonyl bond (C=O) that confirms the existence of lignin [45,46]. The band in the area of $1034\text{--}1029\text{ cm}^{-1}$ indicates the presence of carbohydrates (cellulose and lignin) with C–O–C as well as C–O stretching [46]. The peak observed at 1242 cm^{-1} specifies the existence of strong C–O stretching for the ester and tertiary alcohol groups [44]. The peaks in the range of $2887\text{--}2910\text{ cm}^{-1}$ were observed for C–H bond stretching [46].

3.1.2. SEM analysis

Fig. 2 represents the surface morphology (SEM) of PBF for the adsorption of MB dye at different magnifications such as $100\text{--}1000\times$ for $100\text{--}10\text{ }\mu\text{g}$ at 5 kV (Fig. 2a, b, 2c, and 2d). Additionally, original papaya bark is shown in inset of Fig. 2a. It can be seen from the figure that the fibers in papaya bark have a lot of pores and irregular surface structure

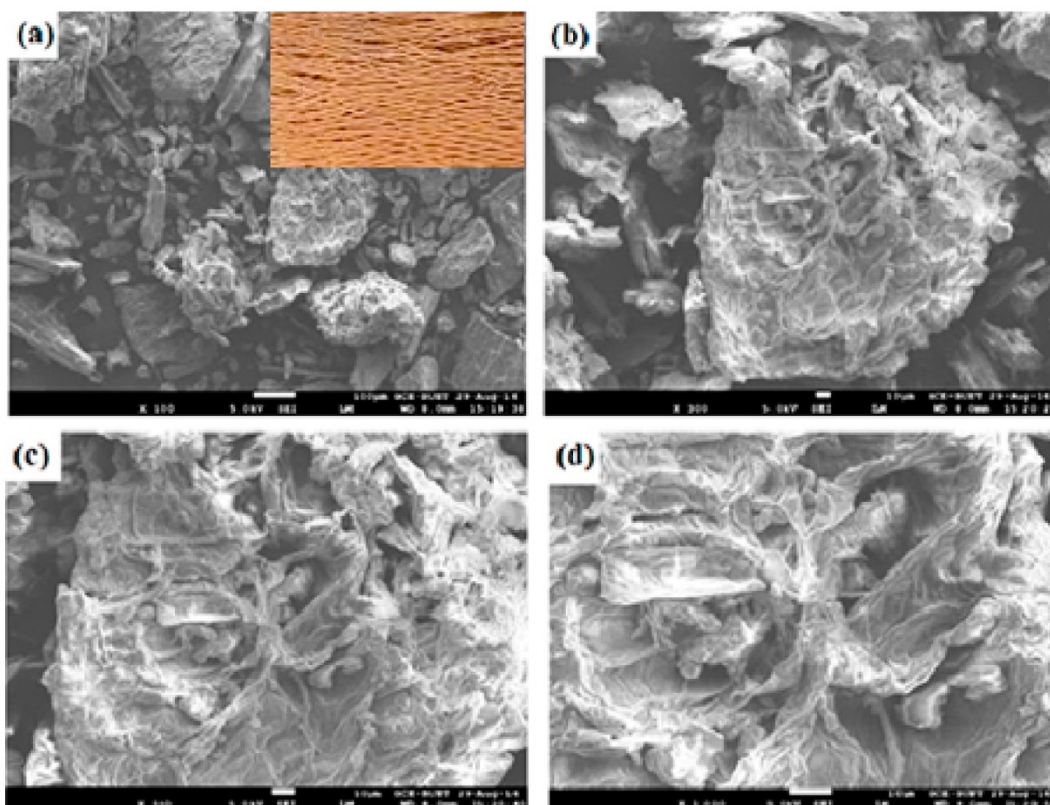


Fig. 2. SEM images of PBF for $100\text{ }\mu\text{g}$ and original papaya bark (inset) (b) $300\times$ for $10\text{ }\mu\text{g}$ (c) $500\times$ for $10\text{ }\mu\text{g}$ (d) $1000\times$ for $10\text{ }\mu\text{g}$.

[46]. The increased adsorption capacity will be supported by this surface feature of the fiber.

3.2. Consequence of pH

Different types of parameters affect the adsorption capacity in wastewater treatment projects, of them, pH is a predominant factor. The degree to which the absorptive molecules are ionized, so as the surface characteristics of the adsorbent due to the impact of the solution pH [55]. The maximum dye removal of 81.17% was recorded at pH 11, whilst the least dye removal was found at pH 1. MB is a basic dye that gives positive charges when it is ionized in an aqueous solution [51]. In an acidic solution, electrostatic repulsion occurs between the positively charged sorbent and sorbate which phenomenon is responsible for the poor adsorption at lower pH. On the other hand, when pH starts to increase, electrostatic attraction occurs between the positively charged sorbate and oppositely charged sorbent because the sorbent surface gains a positive charge with increasing pH value. Fig. 3 explains the consequence of the pH effect on the adsorption of MB dye by PBF powder with standard deviation. However, a moderate pH 7 has been considered for further experiments. Table 1 shows the adsorption capacity of various low-cost adsorbents for MB removal at different pH point out that the maximum removal observed at basic pH values.

3.3. Consequence of concentration

The consequence of initial MB dye concentration on removal efficiency of PBF is presented in Fig. 4 with increasing concentration from 25 ppm to 300 ppm with standard deviation by considering the other parameters at constant values. From the graphical representations, it can be observed that the removal percentage started to decrease with increasing initial MB concentration as the fixed amount of adsorbent dosage was employed. There are active vacant sites on the adsorbent surface at low concentrations and with rising the initial MB dye





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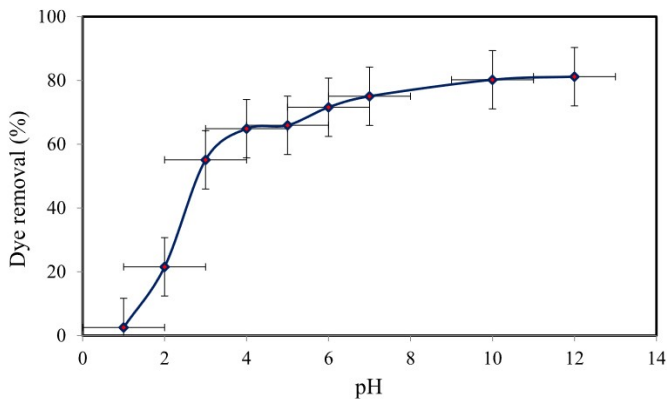


Fig. 3. Effect of the initial pH of solution on adsorption of MB on PBF powder ($C_0 = 100$ ppm, $W = 0.5g$, $V = 50$ ml and $t = 12$ h).

Table 1
Removal percentage of MB dye at different operating pH values.

Adsorbent	pH	Removal (%)	Reference
Rice husk	8	48.47	[26]
Jackfruit (<i>Artocarpus heterophyllus</i>) leaf	6.8	83.67	[38]
Coconut (<i>Cocos nucifera</i>) leaf	8.65	86.38	[39]
Coconut tree bark	10	92	[52]
Potato (<i>Solanum tuberosum</i>) peel	9	78.85	[41]
Tuberose sticks	11	80	[56]
Papaya bark fiber	11	81.17	Present work

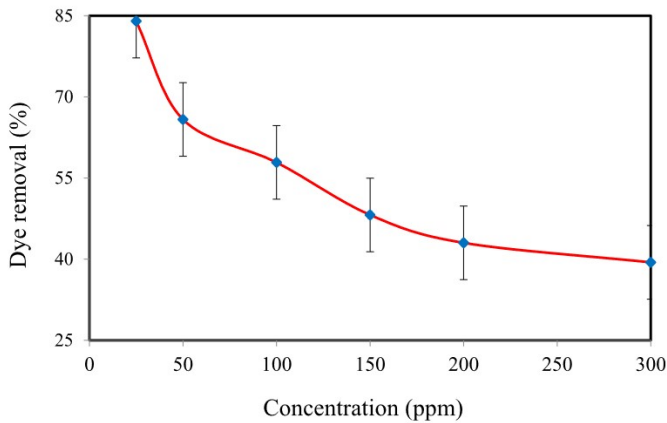


Fig. 4. Effect of initial dye concentration on the adsorption of MB on PBF powder ($pH = 7$, $W = 0.5g$, $V = 50$ ml and $t = 12$ h).

concentration, the necessary active sites for dye molecule adsorption become fewer. Besides, the higher driving force is required to overcome all mass transfer barriers of dye ions between the aqueous and solid phases, resulting in a greater chance of dye ions colliding with adsorbents. The moderate dye concentration was found to be 100 ppm with 57.88% removal capacity in this investigation. Similar phenomena are also found in the studies [52,58,59].

3.4. Effect of dosages

By altering the adsorbent dosages from 0.25 to 2.5 g/L, the MB dye removal efficiency was studied which is graphically represented with standard deviation in Fig. 5. Increasing the adsorbent dosages from 0.25 to 2.5 g/L, MB dye removal percentage increased at the fixed dye concentration as the amount of adsorbent increased the active sites for

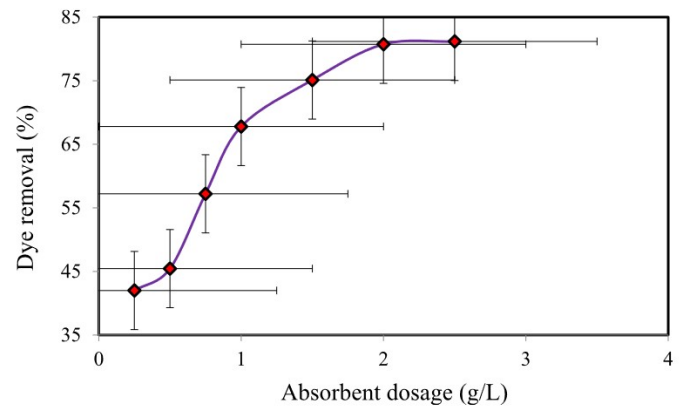


Fig. 5. Effect of adsorbent dosages on the adsorption of MB on PBF powder ($C_0 = 100$ ppm, $pH = 7$, $V = 50$ ml and $t = 12$ h).

2.5 g/L dosages and the removal efficiency was ~80%.

3.5. Consequence of contact time

Fig. 6 presents the results of an experiment assessing the influence of contact time on batch MB dye adsorption by varying contact time with standard deviation and setting other parameters at a moderate level ($pH = 7$, MB concentration 100 ppm, and adsorbent dosage 2.0 g/L). It is clear from the figure that by increasing the contact time from 10 to 200 min; MB dye removal percentages were greatly increased and the maximum value was 63.32%. For the first 10 min, the MB removal (%) capacity was sluggish. The time it took to attain equilibrium was influenced by the type of the adsorbent and the quantity of accessible active adsorption sites [28]. The optimum contact time is considered 100 min herein for further experiment.

3.6. Isotherm study

The isotherm data will aid in determining the characteristics of adsorbate MB dye adsorption on the surface of PBF. Figs. 7 and 8 represent the graphical analyses of Langmuir and Freundlich isotherms, respectively and Table 2 shows the isotherm parameters extracted from the plots of the isotherms.

The values of maximum adsorption capacity (Q_{max}) and Langmuir isotherm constant (K_L) were determined from the plot of $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$. The key characteristics of the Langmuir isotherm might be described in terms of the equilibrium parameter R_L . The maximum coverage capacity from the

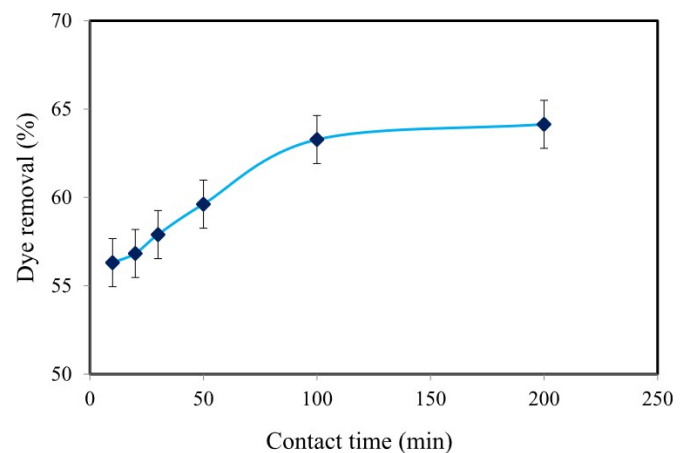


Fig. 6. Effect of contact time on the adsorption of MB on PBF powder ($C_0 = 100$ ppm, $pH = 7$, $W = 0.5g$ and $V = 50$ ml).





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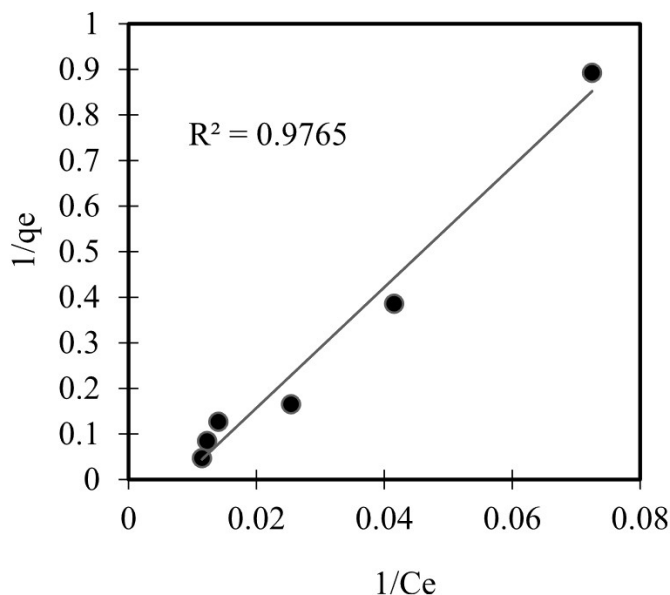


Fig. 7. Langmuir adsorption isotherm.

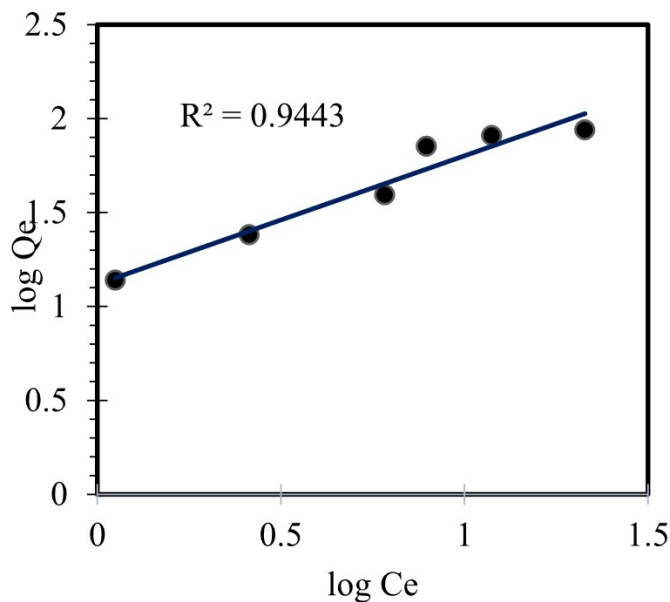


Fig. 8. Freundlich adsorption isotherm.

Langmuir isotherm model was calculated to be 66.67 mg/g and corresponding K_L , R_L , and R^2 values are 0.850 L/mg, 0.0114851, and 0.976 indicating that the equilibrium adsorption is promising. The adsorption capacity of several kinds of adsorbents employed to remove MB dye is compared in Table 3.

Similarly, the values of Freundlich isotherm parameters were calculated from the plot of $\log q_e$ vs. $\log C_e$ (Fig. 8). The affinity of the MB adsorbate towards the PBF adsorbent was calculated from the isotherm model and K_F was found to be 13.14014 L/mg. The adsorption intensity n (1.463486) indicates good adsorption because the value is in the range

Table 2
Various adsorption isotherm parameters of MB dye adsorbed on PBF.

Langmuir isotherm			Freundlich isotherm				
q_m (mg/g)	K_L (L/mg)	R_L	R^2	$1/n$	N	K_F (L/mg)	R^2
66.67	0.850	0.0114851	0.976	0.6833	1.463486	13.14014	0.9443

of $1 < n < 10$ [57]. By comparing the R^2 values from Table 2, it can be pointed out that the sorption process is better fitted with the Langmuir isotherm model than the Freundlich model [51, 60].

3.7. Adsorption kinetics

To explain the kinetics of MB dye adsorption by PBF under several experimental conditions, two models were studied namely Lagergren's first order kinetic model and second order model which are graphically represented in Figs. 9 and 10, respectively. From the Lagergren plot of $\log (q_e - q_t)$ against t , nearly a linear relationship has been observed (Fig. 9). The linear least square approach was used to compute the rate constant (K_1) for each system and the value of the correlation coefficient (R^2) was quite satisfactory (0.899).

Similarly, from the plot of $\frac{t}{q_t}$ vs t , a linear relationship has been obtained. Graphical analysis based on the slope and intercept, the values of second order rate constant k_2 (0.0398) and R^2 (0.9999) were extracted from the fitting. In comparison to the values of the correlation coefficient (R^2), it can be found that the pseudo-second-order kinetic model indicates a better matching than the first one. Similar observations were noticed elsewhere [51, 52, 60, 63, and 66–68].

4. Mechanism of interaction of MB dye with PBF

The active sites on the surface of PBF are revealed by FTIR spectroscopy (Fig. 1). The three primary components of the PBF are

Table 3
Maximum monolayer coverage capacity for MB dye adsorption by various low-cost bio-sorbents.

Adsorbent	Maximum Monolayer Coverage (mg/g)	Reference
Orange peel	103.95	[51]
Coconut tree bark	14.92	[52]
Wheat shells	21.50	[57]
PAN/ β -CD membrane	109.90	[60]
Date palm leaves	58.14	[47]
Banana peel	28.10	[58]
Papaya bark fiber	66.67	Present Work

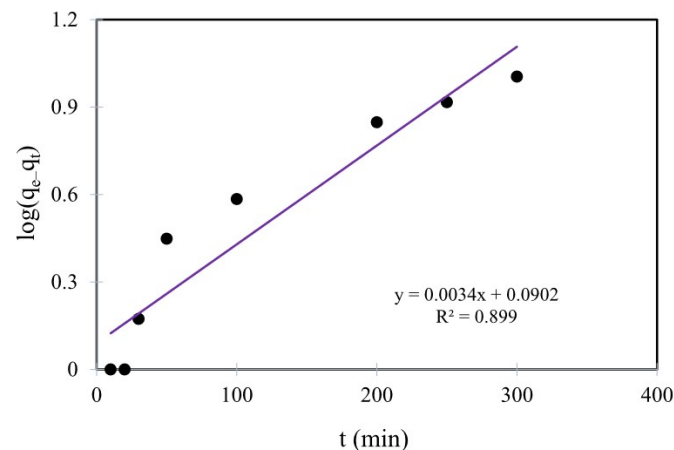


Fig. 9. Lagergren plot of a first-order kinetic model for the adsorption of MB dye by PBF.



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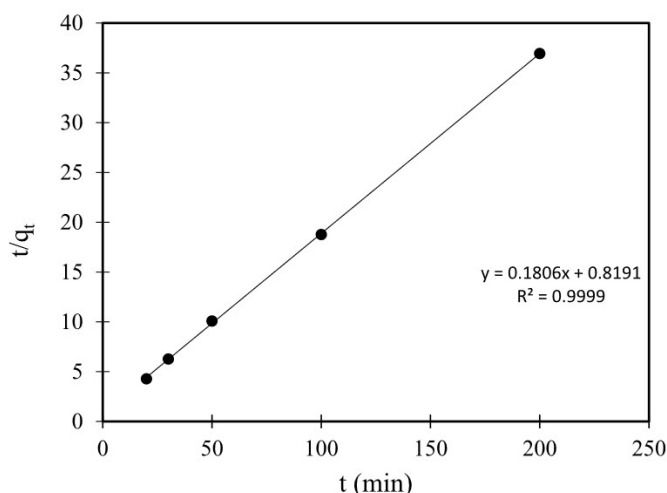


Fig. 10. Lagergren plot of second order kinetic model for the adsorption of MB dye by PBF.

cellulose, hemicellulose and lignin. The major portion of oxygen-containing functional groups found in lignocellulosic material (e.g., hydroxyl, carbonyl, and ether) found in both cellulose and hemicellulose. This is crucial information to grasp to comprehend the MB adsorption mechanism on PBF. The mechanism of solute adsorption on solid surfaces must be understood for removing impurities from aqueous solutions. MB dissociates in the aqueous phase and produces MB^+ and Cl^- . The influence of pH on PBF adsorption is modest at lower pH according to the results of the experimental batch. Budnyak et al., 2018 reported the electrostatic interaction between the positively charged nitrogen atoms of the dye molecule and the dissociated carboxyl (COOH) and hydroxyl groups (OH) of sorbents is the fundamental mechanism for MB dye adsorption [59]. The interaction of MB with the PBF surface can be explained by the pH effect. Decreasing the pH (addition of H^+ ions) of the solution increases the positive charges at the PBF adsorbent surface via protonation of the functional groups [59]; as a

result, the positive charges of the PBF adsorbent surface creates less prone to interact with the positively charged MB dye molecules and hence less adsorption indicates low adsorption capacity of the adsorbent to remove the dye from the solution. This low adsorption may correspond to the hydrogen bonding and π - π interaction between the adsorbent and MB molecules. In contrast, at increasing pH, the PBF surface would facilitate the negative charges (Fig. 11) via de-protonation and/or dissociation of functional groups which could effectively attract the positive MB dye molecules; resulting in high adsorption. Furthermore, hydrogen bonding and π - π interaction may be a plus point to increase the adsorption (Fig. 11) [59]. The expected results have been observed in our work where increasing the pH of the solution increased the adsorption capacity and the maximum adsorption capacity was found at a higher pH value of 11 (Fig. 3).

5. Conclusions

The current study has demonstrated the effectiveness of PBF as a potential adsorbent for removing MB dye from an aqueous solution. To ascertain adsorption properties of PBF and quantify its capacity, various adsorption parameters were examined. The following deductions can be drawn based on the current research:

- (i) The morphologic characteristics of papaya bark fiber, which showed a well-distributed pore structure, large pore and volume, and high specific surface suggested the material's potential to adsorb MB.
- (ii) MB removal is pH-reliant with the greatest removal occurring at pH 11.
- (iii) The pseudo-first-order and pseudo-second-order kinetic parameters were analyzed. With a higher correlation coefficient, the rate of sorption was shown to match the pseudo-second-order kinetic model.
- (iv) Equilibrium data were characterized using Langmuir and Freundlich models. Freundlich isotherm model have better fit than Langmuir isotherm model. The highest capacity of sorption was determined to be 66.67 mg/g.

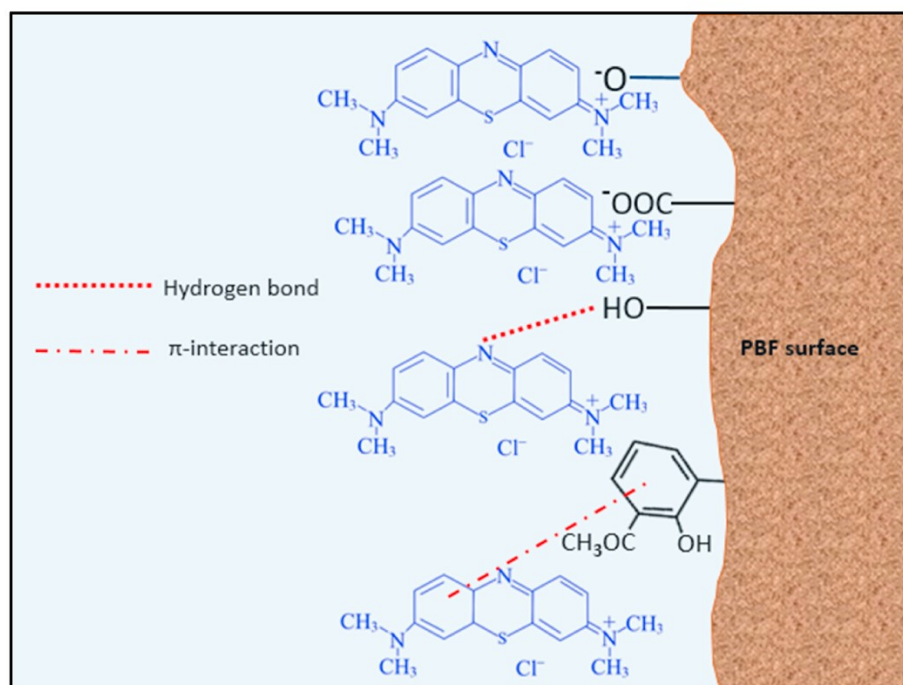


Fig. 11. Presumed adsorption mechanism of MB onto PBF.





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In a nutshell, PBF is a potential cost-effective adsorbent as it is prepared from natural resources. For cleaner concept, the as prepared biosorbent materials are highly preferable due to environmentally benign and it is expected that PBF will be prepared for real-world application in the near future.

Author contribution

Sumaya Tarannum Nipa: Investigation, Methodology, Writing; **Nawrin Rahman Shefa:** Investigation, Writing; **Shahanaz Parvin:** Conceptualization, Analysis, Writing; **Most. Afroza Khatun:** Conceptualization, Writing; **Md. Jahangir Alam:** Visualization, Software, Validation; **Sujan Chowdhury:** Software, Validation, Editing; **M. Azizur R. Khan:** Validation, Visualization, Reviewing and Editing; **Sk Md Ali Zaker Shawon:** Visualization, Reviewing and Editing; **Biplob K. Biswas:** Visualization, Reviewing and Editing; **Md. Wasikur Rahman:** Conceptualization, Supervision, Funding acquisition, Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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