

Article

Mesoporous Activated Carbon from Bamboo Waste via Microwave-Assisted K_2CO_3 Activation: Adsorption Optimization and Mechanism for Methylene Blue Dye

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Abstract: Bamboo waste (BW) was activated with a K_2CO_3 precursor in a microwave process for the adsorption of MB dye from an aqueous solution. The prepared bamboo-waste-activated carbon (BWAC) was analyzed by instrumental techniques such as FTIR, SEM, and BET analysis. The surface of the BWAC was mesoporous with a surface area of $107.148 \text{ m}^2/\text{g}$. The MB dye removal was optimized with the three variables of adsorbent dose, pH, and contact time using the Box–Behnken design (BBD) model. Up to 87% of MB was removed in the optimized conditions of adsorbent dose of $0.08 \text{ g}/100 \text{ mL}$, pH of 7.62, time of 8 min, and concentration of $50 \text{ mg}/\text{L}$. Here, the most effective parameter for MB removal was found to be adsorbent dose with an F-value of 121.70, while time and pH showed a smaller effect. The maximum adsorption capacity of BWAC in the optimized conditions was found to be $85.6 \text{ mg}/\text{g}$. The adsorption of MB on BWAC's surface was through chemisorption and a spontaneous process. The adsorption mechanism study showed that three types of interactions are responsible for the removal of MB dye from aqueous solutions by BWAC, i.e., electrostatic interactions, H-bonding, and π – π interactions. Hence, BWAC can be considered a highly efficient adsorbent for MB removal from wastewater.

Keywords: bamboo waste; microwave activation; Box–Behnken design; dye removal



Citation: Azlan Zahari, K.F.; Sahu, U.K.; Khadiran, T.; Surip, S.N.; ALOthman, Z.A.; Jawad, A.H. Mesoporous Activated Carbon from Bamboo Waste via Microwave-Assisted K_2CO_3 Activation: Adsorption Optimization and Mechanism for Methylene Blue Dye. *Separations* **2022**, *9*, 390. <https://doi.org/10.3390/separations9120390>

Academic Editor: Xinhua Qi

Received: 19 October 2022

Accepted: 16 November 2022

Published: 23 November 2022

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1. Introduction

The human population and rapid industrialization are the two key factors for water pollution, which becomes a major problem as the freshwater levels decrease day by day. Different types of pollutants such as heavy metals, dyes, pesticides, and organic compounds are directly discharged from industries, resulting in the water becoming unusable [1,2]. Compared to all these pollutants, the presence of dyes in the drinking water environments causes serious problems for animals and plant life, becoming a global issue. Dye-contaminated water is mostly discharged from the cosmetics, textiles, printing, and paper and dyeing industries, and every year, 7×10^5 metric tons of dye enters the natural water systems from these industrial sources [3]. Both the ecological system and human health are adversely affected as these man-made dyes are highly toxic, non-biodegradable, and carcinogenic in nature. Cationic organic dyes such as methylene blue (MB) (a heterocyclic compound) have properties of high organic matter, non-degradable nature, and higher chromaticity that can cause harm to the ecosystem, including the ultimate disturbance in photosynthesis by diminution of dissolved oxygen and creating toxicity, which ultimately

affects human beings [4,5]. The use of these MB dye-contaminated water resources in any way for lengthier times can cause carcinogenic, mutagenic, and micro-toxic effects in human beings and aquatic animals [6]. Hence, it is necessary to remove MB dye from wastewater using desirable cost-effective techniques for economic and practical application.

Therefore, scientists are trying to develop more efficient and bearable techniques for MB dye removal from water. The workable techniques available in the literature are membrane filtration [7], ion exchange [8], adsorption [9], reverse osmosis [10], and chemical precipitation processes [11]. However, most of these techniques show low performance with high operational cost; therefore, in many MB dye removal research studies, adsorption processes are applied and found to yield good results. In this technique, the operational cost is very low, removal is efficient, the process runs without electrical energy, there is no toxic by-product formation, and it is environmentally friendly [12]. In the adsorption process, adsorbent selection plays a crucial role, and it should not only be efficient but also easily available everywhere at low cost so that it can be applied in rural areas. Hence, for MB dye removal, adsorbents such as metal oxide nanoparticles [13], bimetal oxide [14], graphene [15], chitosan [16], and activated carbon [17] have been frequently used with good results. Compared to other materials, activated carbon has a high surface area, mesoporous structure, reusability, and good surface reactivity and is highly stable under acidic and basic conditions [18]. However, the available commercial activated carbon has a high cost, which limits its sequential application; therefore, agricultural wastes are used for activated carbon preparation, which is also the solution to the economic problem [19]. Agricultural by-products such as rice husk, tea waste, and coconut leaf have been applied for activated carbon preparation with a successful application for MB dye removal from wastewater.

The activated carbon prepared from the bio-waste sources is generally proceeded with chemical activation with an activating agent such as KOH, ZnCl₂, H₃PO₄, NaOH, K₂CO₃, and HNO₃ in an inert atmosphere at high temperature [20]. Compared to others, the activated carbon that is prepared with K₂CO₃ as an activating agent has a high surface area, a greater number of oxygen-carrier functional groups formed and is eco-friendly in nature [21]. Therefore, more consideration is given to produce activated carbon using K₂CO₃ for multipurpose applications such as pesticides removal [22], decolorization of dyes [23], and CO₂ capacitors [24].

Bamboo is a natural plant biomass that is under the Bambusoidae subfamily and Poaceae family. It is mainly grass and requires a very short time (a few months) for complete growth, so it is one of the fastest-growing plants found in nature [25]. Nearly 1500 bamboo species are grown in Asian countries such as Malaysia, Vietnam, India, Thailand, China, and Indonesia [26]. In Malaysia, bamboo is highly used in construction sites as it is easily available, low-cost, and very strong [27]. Hence, bamboo can be used as a raw material for activated carbon preparation, which will be a good step toward the recycling of bamboo waste and its reusability for MB dye removal.

Thus, the focus of this research work is to convert the bamboo waste (BW) into porous activated carbon to be a potential adsorbent for the removal of toxic cationic dye such as methylene blue (MB). In fact, the adsorption is controlled by different process parameters such as pH, adsorbate concentration, adsorbent dose, time, and temperature, and one-to-one analysis of these parameters would take a longer time with the loss of energy and resources. To solve these problems, adsorption studies are conducted according to the experimental designs, which give accurate output data and less consumption of valuable resources such as energy. Hence, the Box–Behnken Design (BBD), a theoretical model of the response surface methodology (RSM), has been used for wastewater treatment including toxic heavy metals [28], pharmaceutical waste [29], organic compounds [30], and dye removal [31] with the best removal results. In this study, bamboo-waste-activated carbon (BWAC) was prepared in the microwave synthesis process and used for MB removal using the Box–Behnken Design method. The properties of BWAC were analyzed with BET, FTIR, and FESEM studies. The adsorption kinetics, isotherms, thermodynamics, and mechanism for MB removal on the BWAC surface were also determined in this research study.

2. Materials and Methods

2.1. Materials

The chemicals used in this study were all analytical grade and could be used without any extra purification. Potassium carbonate (K_2CO_3), methylene blue (MB), and other reagents were bought from R & M Chemicals, Malaysia. Bamboo waste (BW) was supplied from the Forest Products Division, Forest Research Institute Malaysia (FRIM), 52109 Kepong, Selangor, Malaysia. The BW was repeatedly washed with deionized water several times, sundried for two days, then oven-heated for 24 h at 100 °C [32]. After that, the material was finely ground into a fine powder of size 1–2 mm.

2.2. Preparation of Adsorbent

BW microwave activation was performed in a SAMSUNG solo 20 L microwave oven. Here, 1 g of BW powder was first treated with 2 g of K_2CO_3 solid powder (impregnation ratio 1:2) for 24 h at 110 °C. Then, the microwave activation was carried out in a quartz chamber sealed on both sides while N_2 gas flowed continuously through it at microwave irradiation power of 800 W for 15 min. After activation, the activated carbon from BW was rinsed several times with distilled water until neutral pH and then dried in an oven for 24 h at 100 °C. Finally, the formed material was labeled as bamboo-waste-activated carbon (BWAC) and stored in an air-tight container.

2.3. Characterization Techniques

The functional groups on the surface of BW and BWAC were analyzed by a FT-IR spectrophotometer (PerkinElmer, Spectrum RX I, Waltham, MA, USA) by using a KBr disc in the range of 4000 to 400 cm^{-1} with 60 scans per screening. The external surface morphology and elemental composition of the BWAC before and after MB dye adsorption were identified by scanning electron microscopy with energy-dispersive X-ray spectrometry by a Zeiss Supra 40 VP model, Jena, Germany. A Micromeritics ASAP 2060 BET instrument (Norcross, GA, USA) was used for the surface area and other porous analyses of BWAC. The point of zero charge (pHpzc) of BWAC was calculated based on a previously reported method [33]. The concentration of MB dye was measured using a spectrophotometer (HACH DR 3900) (Berlin, Germany) at 661 nm.

2.4. Design of Experiments

Design expert version 13 software (Stat-Ease, Inc, Minneapolis, MN, USA) was used for the data analysis of this study. The Box–Behnken Design (BBD) was statistically applied for process parameter optimization to remove the maximum amount of MB dye from aqueous solutions using BWAC within the ranges of experimental factors. Here, the independent variables were pH (A), adsorbent dose (B), and time (C), whereas the removal of MB dye (Y) was the dependent variable. The levels and ranges of experimental independent variables are summarized in Table 1. A response surface quadratic second-order polynomial regression equation (Equation (1)) was applied to measure the interactions of independent variables of adsorbent dose, pH, and time with MB removal (%).

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \quad (1)$$

where ϵ represents the error in the model; Y (%) shows the output response of the removal of MB; β_0 , β_i , and β_{ij} are the coefficients constant, linear parameter constant, and first-order coefficient constant of X_i and X_j , respectively.

Table 1. Different variables and their levels for MB removal.

Variables	Codes	Level 1 (−1)	Level 2 (0)	Level 3 (+1)
Dose (g/100 mL)	A	0.02	0.05	0.08
pH	B	4	7	10
Time (min)	C	2	5	8

The batch experiments were conducted in a 250 mL conical flask, where 100 mL of 100 mg/L initial-concentration MB dye solutions were taken and the required amount of adsorbent was added to it while constantly agitating inside a thermostat water bath shaker stirred for 30 min. The required pH of the solutions was achieved using 0.1 M NaOH and 0.1 M HCl solutions. After MB dye adsorption, the adsorbent was separated from the solution using a nylon syringe filter (0.45 µm). Then, the residual MB concentration was analyzed with the spectrophotometer (HACH DR 3900) at a wavelength of 661 nm. The percentage of MB removal and uptake capacity of BWAC were calculated using Equations (2) and (3), respectively.

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

where C_o and C_e = initial and equilibrium concentrations (mg/L), respectively; W = adsorbent weight (g); V = solution volume (L); R = removal percentage (%); lastly, q_e = uptake capacity (mg/g).

3. Results and Discussion

3.1. Characterization of Adsorbent

The SEM with EDX images of BW and BWAC (before and after adsorption) is presented in Figure 1. From Figure 1a, it was observed that the raw BW had a plane or smooth surface having no cavities and pores. The corresponding EDX image is presented in Figure 1b and it could be seen that the elements C, O, and N were present in the BW surface with elemental ratios (in wt.%) of 43.11, 51.17, and 5.72, respectively. Consequently, after activation of BW with K_2CO_3 , significant changes were observed, and from Figure 1c, a flake-type activated carbon was formed with numerous irregular pores with a mesoporous structure, which will be in high demand for MB dye adsorption. The corresponding EDX data (Figure 1d) indicated the presence of C, O, and N in the ratio (in wt.%) of 66.40, 25.01, and 9.60, respectively. After MB dye adsorption, the surface of BWAC was drastically changed, as seen in Figure 1e. BWAC's surface became a more compact and less porous surface due to the deposition of MB dye molecules on the BWAC surface. This observation was reconfirmed by EDX analysis (Figure 1e). The EDX analysis (Figure 1e) showed the elemental content of BWAC after MB adsorption as follows: C, O, N, S, and Cl with elemental ratios of (in wt.%) 68.66, 19.90, 10.92, 0.52, and 0.09, respectively. In fact, the obvious increment in carbon (C) content and detection of new elements such as sulfur (S) and chloride (Cl) indicating that the MB dye molecules were deposited in BWAC's surface caused an alteration to the surface morphology of BWAC and elemental content.

The information about the interaction of BWAC's surface functional groups with MB dyes is given in Figure 2. Before MB dye adsorption, the broad peak observed at 3400 cm^{-1} represents the $-OH$ groups' stretching vibrations [27]. The bend at 1203 cm^{-1} corresponds to C-O stretching vibrations of the carbonyl groups [34–36]. Lastly, one more peak was seen at 1571 cm^{-1} , and this bend corresponds to the C=C vibrations of the aromatic benzene ring of lignin [37]. After adsorption of MB on BWAC, the positions of the bends at 3396 cm^{-1} , 1212 cm^{-1} , and 1573 cm^{-1} were slightly shifted, which specified that $-OH$ groups on the carboxylic group and C-O groups of the carbonyl group and aromatic benzene ring present on BWAC are responsible for MB dye adsorption.

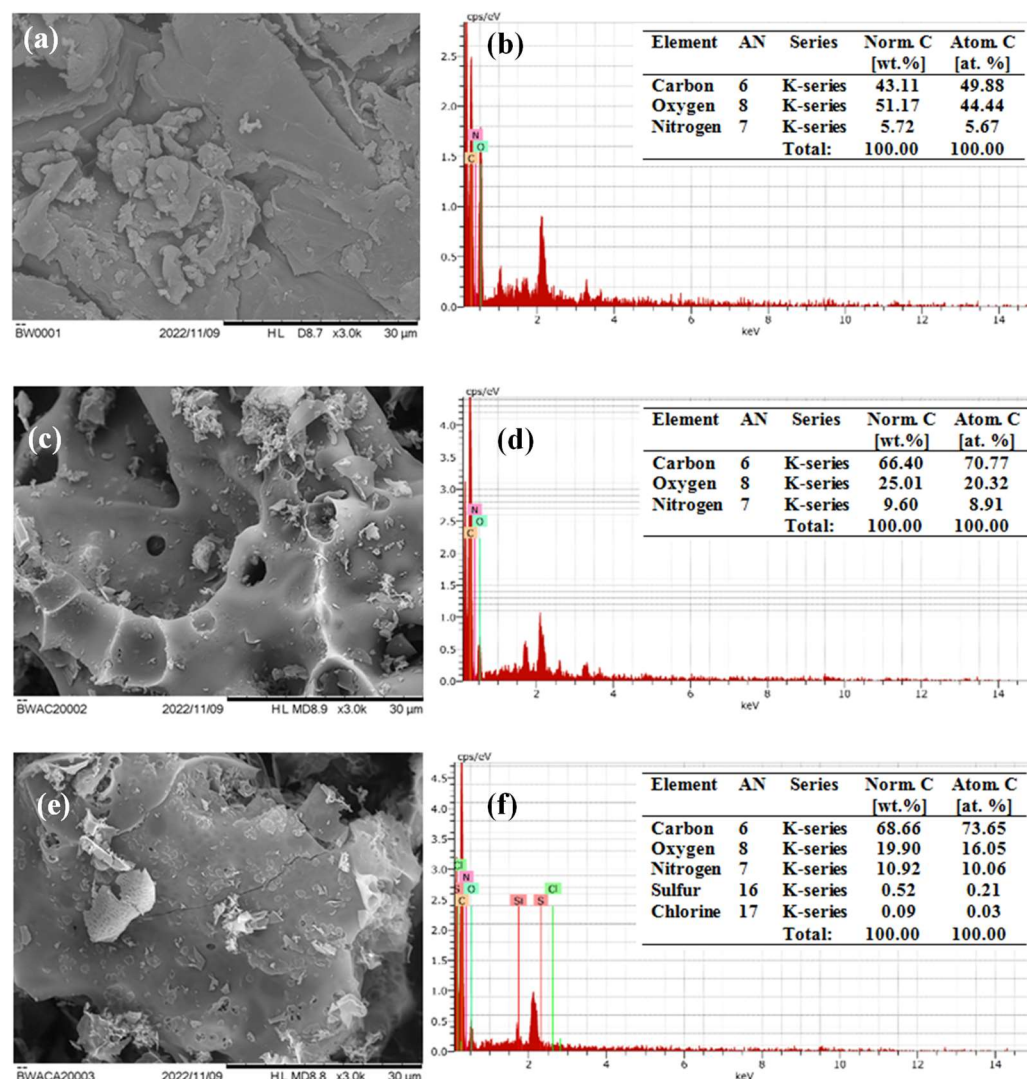


Figure 1. SEM and EDX images of (a,b) BW, (c,d) BWAC, and (e,f) BWAC after MB adsorption.

The BET analysis was conducted for the analysis of surface properties, and the obtained N_2 adsorption–desorption isotherm plot of BWAC is presented in Figure 3. Furthermore, the originated surface properties from BET analysis are presented in Table 2. Figure 3 illustrates a beautiful sigmoidal curve originating in between the relative pressure of 0.2 to 1, which suggests a type IV isotherm for BWAC, revealing that the BWAC's surface is mesoporous [38]. This suggested that K_2CO_3 activation resulted in the formation of a mesoporous material and, furthermore, the surface area of BWAC was $107.148 \text{ m}^2/\text{g}$ with a pore volume of $0.049 \text{ cm}^3/\text{g}$ and pore size of 2.91 nm . This high surface area provided a higher number of active pores or binding sites for MB adsorption. The expected dimensions of MB dye molecules are nearly equal to $0.7 \times 1.7 \text{ nm}$ [39] and, hence, within the pores of BWAC; MB dyes can be easily accommodated and adsorbed.

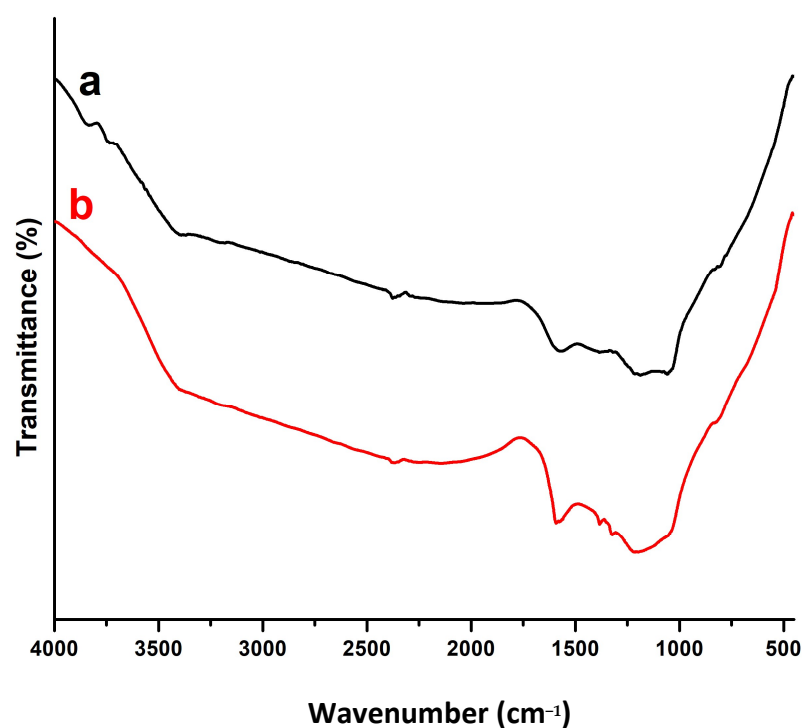


Figure 2. FTIR spectra of (a) BWAC and (b) MB-loaded BWAC.

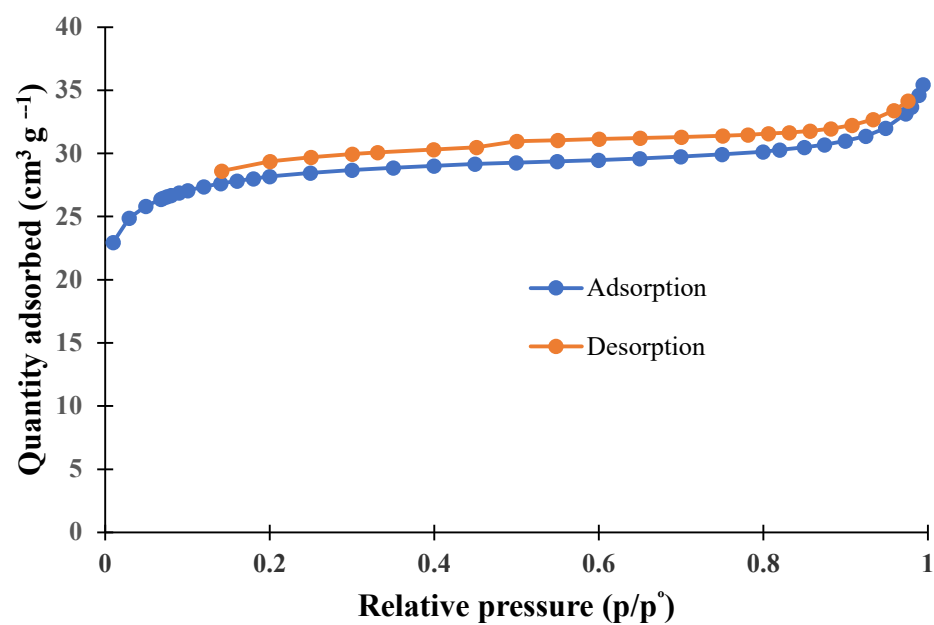


Figure 3. N₂ adsorption–desorption isotherms of BWAC.

Table 2. BET textural data of BWAC.

Sample	Average Pore Size (nm)	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)
BWAC	2.91	107.148	0.049

3.2. Optimization Study

3.2.1. Regression Model Improvement

Calculated batch results of MB dye removal by BWAC from aqueous solutions, which were obtained from the 17 experimental runs conducted in different conditions, are presented in Table 3. The model recommended a quadratic model for MB removal and the obtained range of MB removal percentages was from 49% to 87%. The model was also explained by a second-order polynomial equation, which correlates the coded factors of independent variables with the response for MB removal, given in Equation (4):

$$Y = +34.78 + 18.18A + 14.00B + 14.73C + 10.47AB + 9.03AC + 7.88BC + 2.35A^2 + 5.50B^2 + 5.10C^2 \quad (4)$$

where the positive and negative signs indicate the synergetic and anti-synergetic effects of MB dye removal by BWAC, respectively. The R^2 (correlation coefficient) and Adj. R^2 (Adjusted correlation coefficient) values could better explain the model accuracy. Higher values for R^2 (approaching to one) would indicate the high accuracy and reliability of the model as well as its quality. Furthermore, Adj. R^2 can better explain the model accuracy as insignificant data are eliminated during the calculation process [40]. The model obtained through the experimental design shown in Equation (4) shows high accuracy with a high R^2 value nearing one, i.e., 0.98 indicating that 98% of the data can be explained by the model and only 2% of the data cannot be explained by the model, due to pure error.

Table 3. Three-variable BBD matrix and experimental data for MB dye removal.

Run	A: Dose (g)	B: pH	C: Time (min)	MB Removal (%)
1	0.02	4	5	49
2	0.08	4	5	73
3	0.02	10	5	63
4	0.08	10	5	73
5	0.02	7	2	61
6	0.08	7	2	65
7	0.02	7	8	61
8	0.08	7	8	87
9	0.05	4	2	51
10	0.05	10	2	63
11	0.05	4	8	72
12	0.05	10	8	65
13	0.05	7	5	61
14	0.05	7	5	62
15	0.05	7	5	63
16	0.05	7	5	63
17	0.05	7	5	58

Figure 4a,b show the actual versus predicted MB dye removal and normal probability of MB removal, respectively. Here, it can be observed that all the points were present near the diagonal line, suggesting that the batch adsorption data of MB removal fitted well with the model response. This confirmed that the model formulated for MB dye adsorption by BWAC is highly momentous. Figure 4c shows the Cook's distance of MB removal, and it can be seen that all the 17 points are present below 1, which further proves the statistical significance of the model [17]. These observations confirmed that the present developed model is adequately significant.

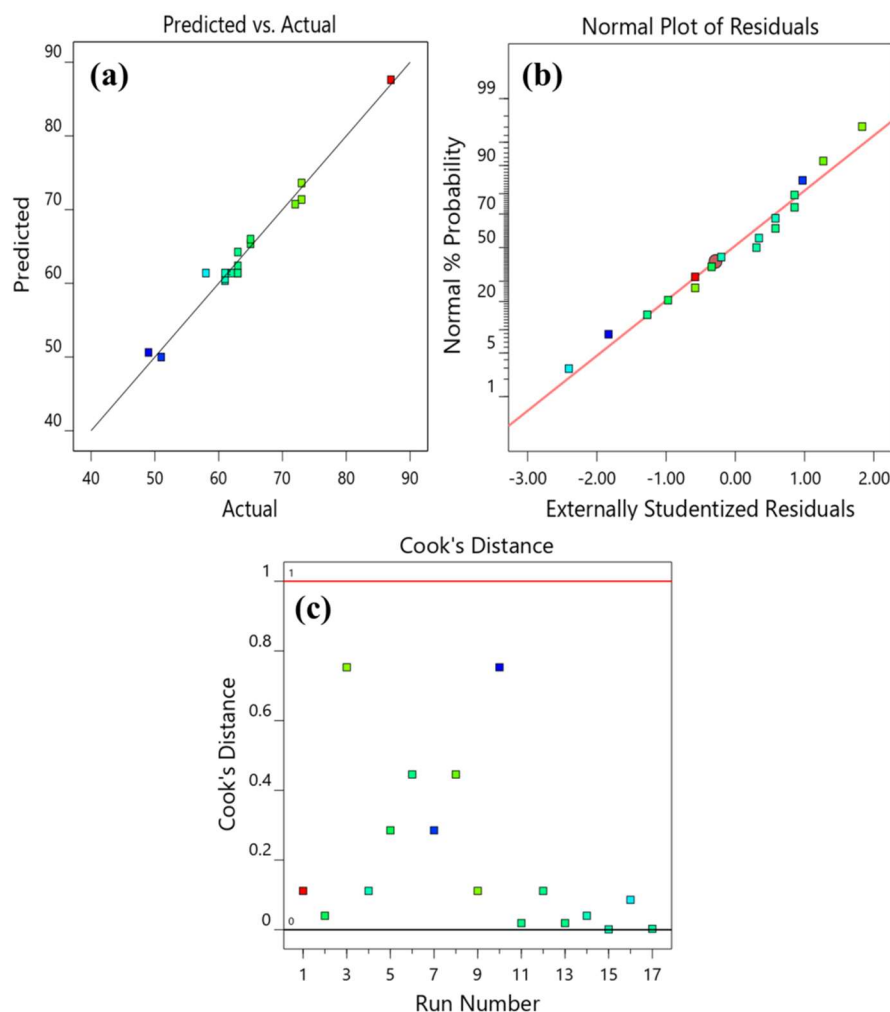


Figure 4. (a) Experimental and actual removal, (b) normal probability plot of MB (%), and (c) Cook's distance plot.

3.2.2. Analysis of Variance (ANOVA)

The ANOVA data for MB removal from aqueous solutions by BWAC are presented in Table 4. The ANOVA data are generally based on probability (p) and F-value, and p -values of lower than 0.05 indicate that the model is a statistically efficient, accurate, and significant one, where the findings are not random [41–44]. Here, the p -value of the model was less than 0.0001 with an F-value of 31.49, which confirms that the model was significant. Other terms such as the lack-of-fit test and coefficient of variation (CV) were also taken into consideration for model accuracy check. If the lack of fit test is non-significant and CV values are less than 10%, then the model results are good and accurate [42,45]. Here, the lack-of-fit test was non-significant with a CV of 3%, further confirming the significance of the model. In this design model, the effect of adsorbent dose showed a higher effect on MB removal as it had a high F-value of 121.70, followed by contact time with an F-value of 60.17. The solution pH had very little effect on MB removal with an F-value of 10.73. Except for the square of pH, all other model terms were significant, so the model had very high R^2 and Adj. R^2 values.

Table 4. Analysis of variance (ANOVA) for MB removal (%) by BWAC.

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	Significant
Model	1192.31	9	132.48	31.49	<0.0001	Significant
A-Dose	512.00	1	512.00	121.70	<0.0001	*
B-pH	45.13	1	45.13	10.73	0.0136	*
C-Time	253.13	1	253.13	60.17	0.0001	*
AB	49.00	1	49.00	11.65	0.0112	*
AC	121.00	1	121.00	28.76	0.0010	*
BC	90.25	1	90.25	21.45	0.0024	*
A ²	82.44	1	82.44	19.60	0.0031	*
B ²	7.39	1	7.39	1.76	0.2266	#
C ²	30.13	1	30.13	7.16	0.0317	*
Residual	29.45	7	4.21			
Lack of Fit	12.25	3	4.08	0.9496	0.4967	#
Pure Error	17.20	4	4.30			
Cor Total	1221.76	16				

R² = 0.9759, Adj-R² = 0.9449, * = significant, # = not-significant.

3.2.3. Interactive Effects on MB Removal

The 3D and contour plots were used for better explanation of MB dye removal where the combined effects of two independent parameters were studied while the third parameter was kept constant. Figure 5a,b present the interactive effect of BWAC dose and pH while the time was kept constant at 5 min. The interaction was significant with an F-value of 11.65. Here, it was observed that with greater values of BWAC dose from 0.02 g to 0.08 g, the MB removal drastically increased from 55% to 70%, respectively. A higher amount of dose provides more binding sites for MB dye molecules and increases the removal capacity [43]. On the other hand, the same observation was seen for pH, and it was seen that with an alteration in pH from 4 to 10, MB dye removal improved from 40% to 60%, respectively. Figure 5c shows that the point of zero charge (pH_{pzc}) for BWAC was at the pH value of 6.9; hence, below this pH, the surface of BWAC had a positive charge and, above this pH, it had a negative charge. As MB dye is a cationic dye and at higher pH, BWAC's surface becomes negatively charged, electrostatic attraction can occur between them, which leads to a higher adsorption of MB dye by BWAC. The same conclusion was reached for MB dye removal by watermelon-rind-activated carbon in a previous study [17]. Figure 5d,e explain the combined effect of BWAC dose and time, while the pH was kept constant at 7. The respective *p*-value was found to be 0.0010 with an F-value of 28.76. With the change in time from 2 to 8 min, the removal rate improved from 60% to 77% respectively. At the beginning of the adsorption process, the dye molecules were attached to the surface of the adsorbent, and with the increase in time, they would diffuse into the pores of the activated carbon. Therefore, the removal rate became higher with the increase in adsorption time. The effect of BWAC dose became the same as discussed above. Lastly, the effects of pH and time for MB dye removal at a constant BWAC dose of 0.05 g are displayed in Figure 5f,g. This was also a significant interaction with an F-value of 21.45. The observation for both was the same as discussed above and, in both cases, the removal rate was increased with an increase in pH and time, respectively.

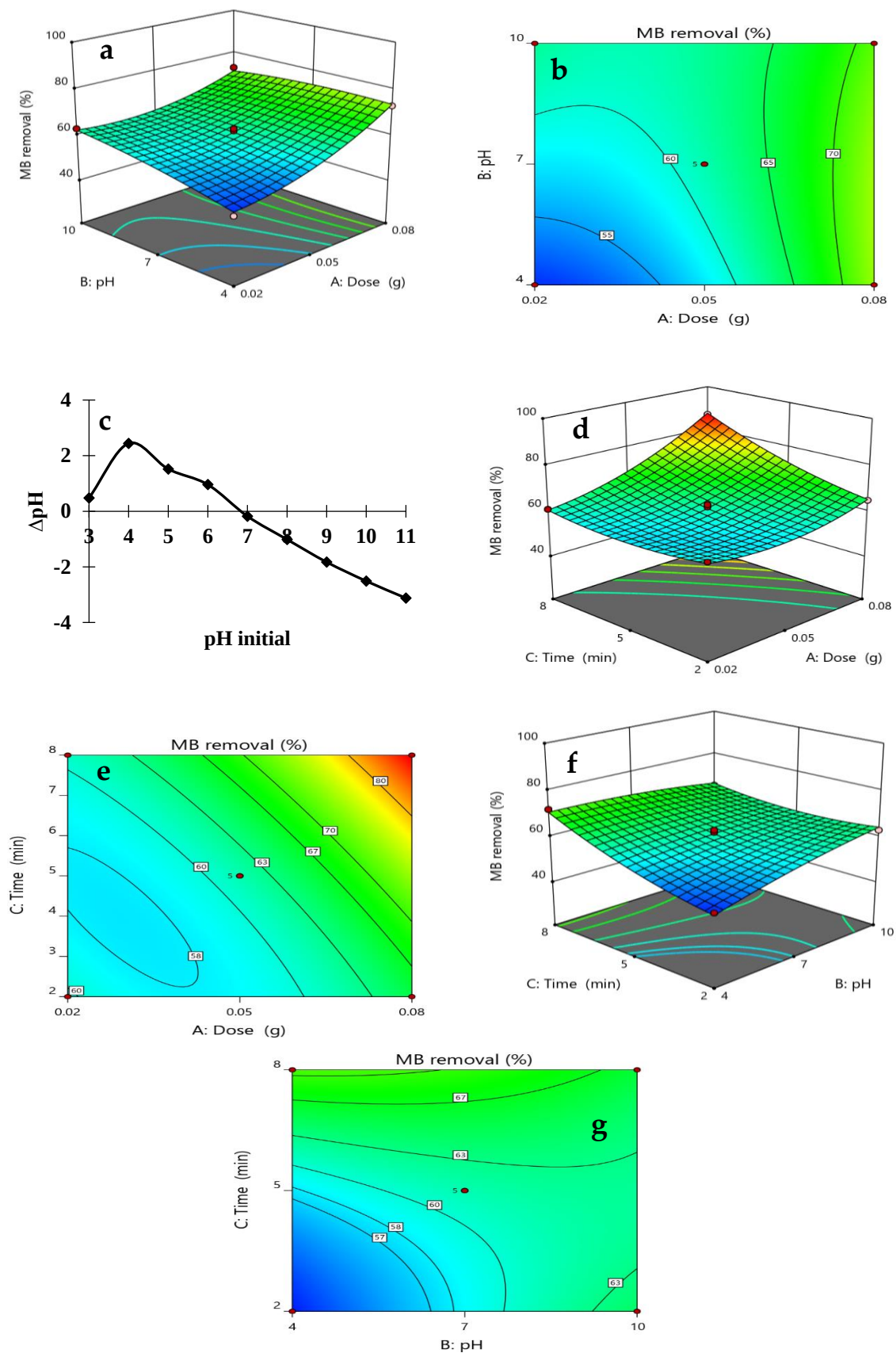


Figure 5. Three-dimensional response surface plot and contour plots showing the interactions between (a,b) dose and pH, (c) pHpzc of BWAC, (d,e) dose and time, and (f,g) pH and time for MB removal by BWAC.

3.2.4. Model Validation and Desirability Function for MB Removal

The BBD model accuracy for MB removal by BWAC was validated by the desirability function approach. Figure 6 presents the best desirability functions of the BBD model for maximum removal of MB by BWAC. Under these most desirable operational conditions of adsorbent dose, pH, and time, the batch adsorption studies were conducted three times and the results found are presented in Table 5. The results suggested that batch studies were significantly aligned with the desirability approach of the model. Hence, this confirmed that the BBD model was accurate and best to explain the desirable conditions of adsorbent dose, pH, and time for MB removal.

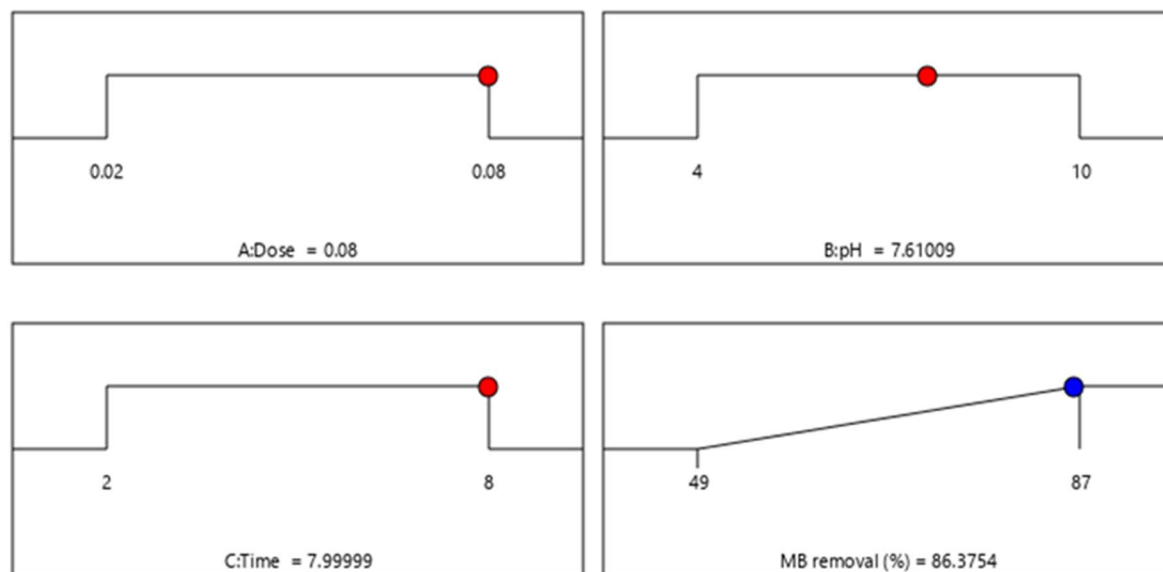


Figure 6. Input and output MB removal (%) responses in desirability ramp. Input variables (red point) and output response (blue point) MB removal (%) in desirability ramp.

Table 5. Experimental and model-optimized values of parameters.

Process Parameters	Optimized Values (Predicted by Disability Function)	Confirmation Values (Experimental)
BWAC Dose (g)	0.08	0.08
pH	7.61	7.62
Time (min)	7.99	8
MB removal (%)	86.37	83.5 ± 3

3.3. Adsorption Experiments

The adsorption study for MB was carried out preferring the optimum investigational conditions as given in Table 5 (BWAC dose = 0.08 g and pH = 7.62) at various initial MB dye concentrations from 20 to 100 mg/L versus the variation in contact time as given in Figure 7. From the figure, it can be seen that with an increase in concentration from 20 to 100 mg/L, the adsorption capacity of BWAC was increased from 23.83 mg/g to 107 mg/g. Hence, it is suggested that MB dye molecules entered and infused into the pores of the BWAC adsorbent surface by a driving force in the higher concentrations, which can allow the adsorbent to better display its adsorption capacity at any given time [42,45].

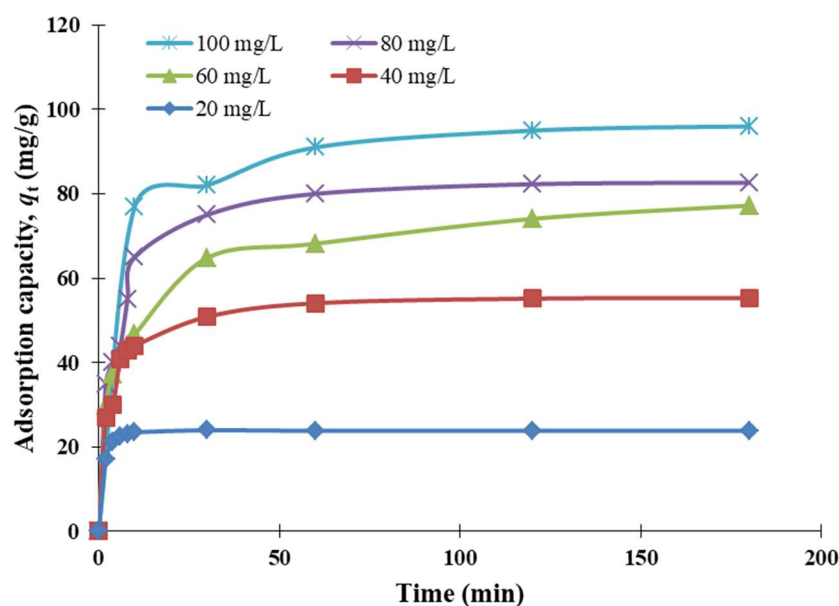


Figure 7. Effect of contact time on MB removal.

3.4. Adsorption Kinetics

The study of kinetics is an essential step in the process of adsorption as it can directly account for the feasibility of the process and the rate of the reaction. The MB dye adsorption experimental data were examined using the pseudo-first-order kinetic model (PFO) and pseudo-second-order kinetic model (PSO). The nonlinear PFO and PSO equations are given as Equations (5) and (6), respectively.

$$q_t = q_e \left(1 - \exp^{-k_1 t} \right) \quad (5)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (6)$$

where the rate constants for PFO and PSO models are k_1 (1/minute) and k_2 (g/mg minute), respectively; q_e and q_t (both mg/g) represent the quantity of the adsorbed MB dye at equilibrium and at time t , respectively. Table 6 represents the kinetics parameters including rate constants and correlation coefficients. In the case of the PFO model, a straight line was observed with a notable deviation in the calculated and experimental data. The PSO model was well fitted to the experimental results of MB with an R^2 value of 0.99 and a good agreement between the calculated q_e and q_e experiment. The rate constant k_2 was also higher than k_1 in all the concentrations, which also suggested that the PSO model was best fitted to the experimental data than the PFO kinetic model. One more thing was observed here with the increase in the initial concentrations: both k_1 and k_2 values decreased because the adsorption process was concentration-dependent and, at higher concentrations, the removal capacity decreased as a result of which the observed and calculated adsorption capacities showed a deviation and mismatch in the kinetic model with experimental data, respectively [44]. This concludes that the adsorption systems studied can be categorized under the PSO kinetic model, based on the assumption that the rate-limiting step is mainly due to chemisorption [45].

Table 6. PFO and PSO kinetic parameters for MB dye adsorption on BWAC.

PSO			PFO			$q_{e \text{ exp. (mg/g)}}$	Concentration (mg/L)
R^2	$k_2 \times 10^2$ (g/mg min)	$q_{e \text{ cal (mg/g)}}$	R^2	k_1 (1/min)	$q_{e \text{ cal (mg/g)}}$		
0.99	5.107	24.89	0.99	0.62	23.51	23.83	20
0.96	1.412	53.54	0.90	0.46	50.07	55.29	40
0.97	0.289	76.83	0.93	0.17	72.21	78.55	60
0.94	0.263	84.18	0.86	0.13	83.64	83.01	80
0.93	0.088	94.75	0.85	0.07	81.25	107.5	100

3.5. Adsorption Isotherm

The most frequently used adsorption isotherm models are Langmuir, Freundlich, and Temkin. The Langmuir isotherm model relates to the monolayer coverage of homogenous distribution, where the adsorption and desorption rates depend upon the covered and uncovered surfaces of the adsorbent [46]. The adsorption process is homogeneous and multilayer adsorption occurs in the case of the Freundlich isotherm model [47]. The Temkin isotherm model explains the binding energy of the adsorbing molecules where there is a linear decrease in heat of adsorption for all the molecules [48]. The non-linear Langmuir, Freundlich, and Temkin isotherm models can be explained by Equations (7), (8), and (9), respectively.

$$q_e = \frac{q_{\max} K_a C_e}{1 + K_a C_e} \quad (7)$$

$$q_e = K_f C_e^{1/n} \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (9)$$

where C_e = equilibrium concentration (mg/L); $q_{\max}$ = maximum adsorption capacity (mg/g); q_e = adsorption capacity (mg/g); K_a (L/mg) and K_f (mg/g (L/mg)^{1/n}) = Langmuir and Freundlich model constants, respectively; b_T (J/mol) and K_T (L/mg) = Temkin constants; R and T = universal gas constant and temperature, respectively.

Figure 8 shows information about the adsorption isotherm models and the respective parameters are tabulated in Table 7. The Langmuir isotherm model was favorable with the experimental data, which had an appropriate R^2 value of 0.95 as compared to the Freundlich isotherm model with an R^2 value of 0.84 and the Temkin isotherm model with an R^2 value of 0.87. According to the Langmuir isothermal model, the adsorption process of MB dye on the surface of BWAC had a homogenous distribution by the presence of a polar oxygen group and graphemic group on the surface [17]. The maximum adsorption capacity of BWAC was found to be 85.6 mg/g. The comparison of the adsorption capacity of BWAC with other biomass-based activated carbon materials prepared by different types of chemical activators can be found in Table 8. For the potential application of removing the cationic MB dye, BWAC can be considered an efficient and low-cost adsorbent.

Table 7. Isotherm parameters and correlation coefficient of different models.

Model	Parameter	Values
Langmuir	$q_{\max}$ (mg/g)	85.6
	K_a (L/mg)	5.74
	R^2	0.95
Freundlich	K_F (mg/g (L/mg) ^{1/n})	57.5
	N	8.33
	R^2	0.84
Temkin	K_T (L/mg)	816.1
	b_T (J/mol)	282.8
	R^2	0.87

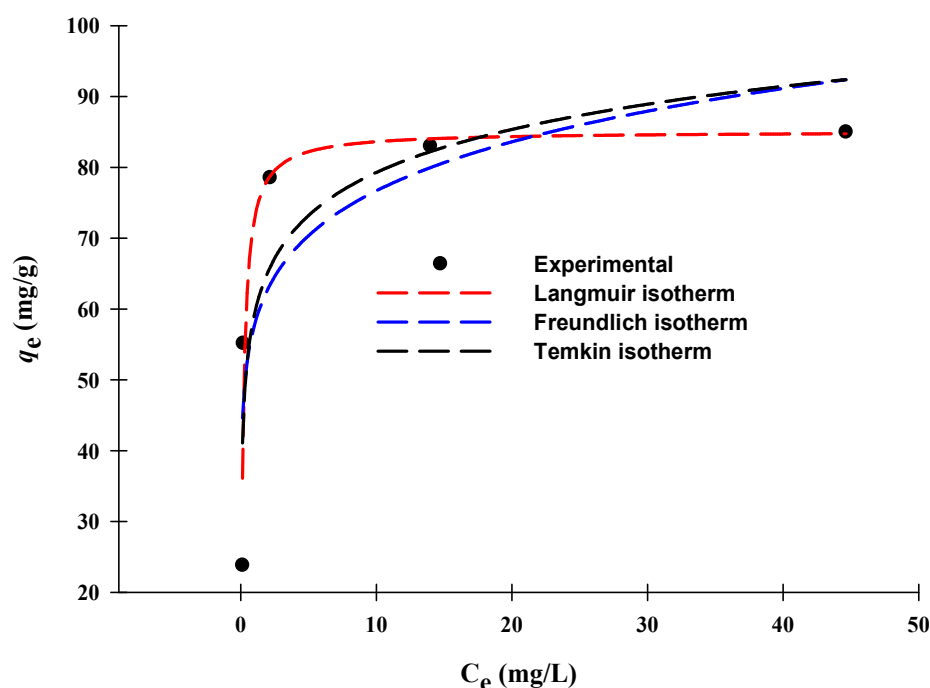


Figure 8. Langmuir, Freundlich, and Temkin nonlinear adsorption isotherms for MB adsorption by BWAC.

Table 8. Comparison study of activated carbon prepared from different materials.

Initial Material	Adsorption Capacity (mg/g)	Reference
Pineapple peel waste	462.10	[49]
Grass waste	364	[50]
Bamboo	298.82	[51]
African almond leaves	263.95	[52]
Nutshells	261	[53]
Coconut leaves	250	[54]
Agriculture wastes	148.8	[55]
Bamboo waste	85.6	This Study
<i>Elaeagnus Angustifolia</i> seeds	72	[56]
Rice agricultural waste	62.5	[57]
Pine cone	60.97	[58]
Corn cob	28.65	[59]
Pineapple waste	9.61	[60]

3.6. Thermodynamics Study

Adsorption studies were carried out at temperature conditions ranging from 25 to 55 °C, to investigate the effect of temperature on the adsorption of MB dye on BWAC. The standard change in Gibb's free energy ΔG^0 (kJ/mol), enthalpy ΔH^0 (kJ/mol), and entropy ΔS^0 (kJ/mol K) are adsorption functions that provide information about the process and adsorption behavior of an isothermal system, which were calculated using Equations (10)–(12) accordingly.

$$\Delta G^0 = -RT \ln K_d \quad (10)$$

$$K_d = \frac{q_e}{C_e} \quad (11)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

where ΔG^0 = free energy change; ΔH^0 = enthalpy change; K_d = thermodynamic distribution coefficient; ΔS^0 = entropy change. The thermodynamic studies were conducted according to operational conditions in Table 5 with the change in temperature from 25 to 55 °C. The relative thermodynamic output from the Van't Hoff plot (Figure 9) is presented in Table 9. Parameters such as ΔS^0 (0.13 kJ/mol K) and ΔH^0 (35.67 kJ/mol) had positive values, which confirms that the adsorption process was successful and endothermic [61]. On the other hand, the -ve values of ΔG^0 (−5.08, −5.94, −8.96, and −9.98 kJ/mol) indicate that the adsorption of MB dye on the BWAC surface was a spontaneous process.

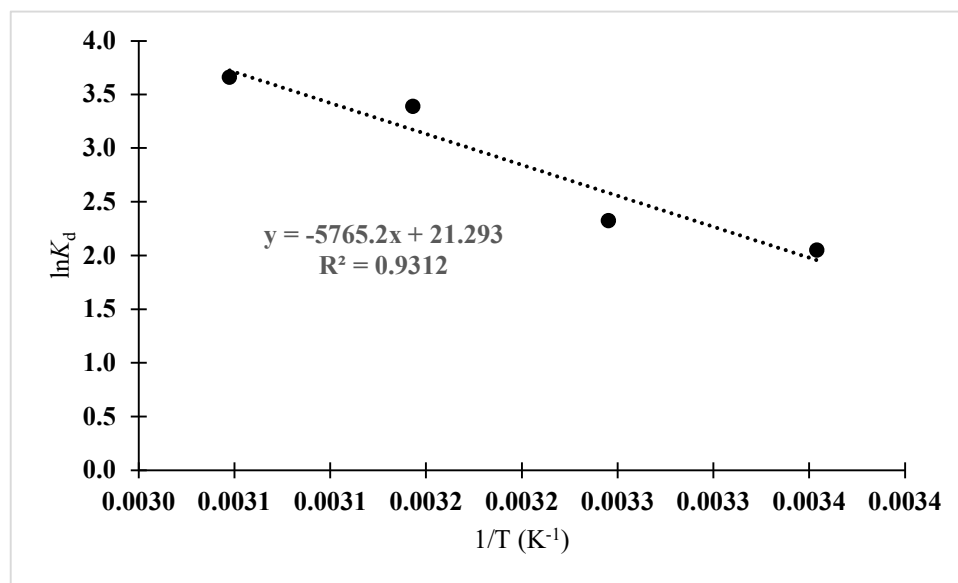


Figure 9. Van't Hoff plot for MB dye removal by BWAC.

Table 9. Thermodynamic parameters for the adsorption for MB dye by BWAC.

T (K)	Ln K _d	ΔG ⁰ (kJ/mol)	ΔH ⁰ (kJ/mol)	ΔS ⁰ (kJ/mol K)
298.15	2.05	−5.08	35.67	0.13
308.15	2.32	−5.94		
318.15	3.39	−8.96		
328.15	3.66	−9.98		

3.7. Adsorption Mechanism

The adsorption of MB on BWAC's surface was explained in the basics of FTIR studies. FTIR results displayed that −OH vibration of the −COOH groups and C=O vibrations of the carbonyl groups were changed after MB adsorption on BWAC's surface. Hence, these functional groups were involved in MB adsorption. The probable adsorption mechanisms for MB were electrostatic attractions, H-bonding, and pi–pi interactions, or hydrophobic to hydrophobic interactions. At higher pH levels, the surface of BWAC can become negatively charged and electrostatic attractions can take place with the positively charged MB dye molecules. Secondly, the −COOH and carboxyl groups present on BWAC's surface can interact with the N atoms of MB dye molecules through H-bonding. The last one is the benzene rings or hexagonal structures of BWAC that were involved in the adsorption process as there was a change observed in the FTIR studies; hence, hydrophobic–hydrophobic interactions (π–π interactions) occurred between aromatic rings of MB dye species with the aromatic hexagonal structures of BWAC. Similar types of results have been observed in our previous works [17,42]. The probable adsorption mechanism of MB dye on the surface of the adsorbent (BWAC) is presented in Figure 10.

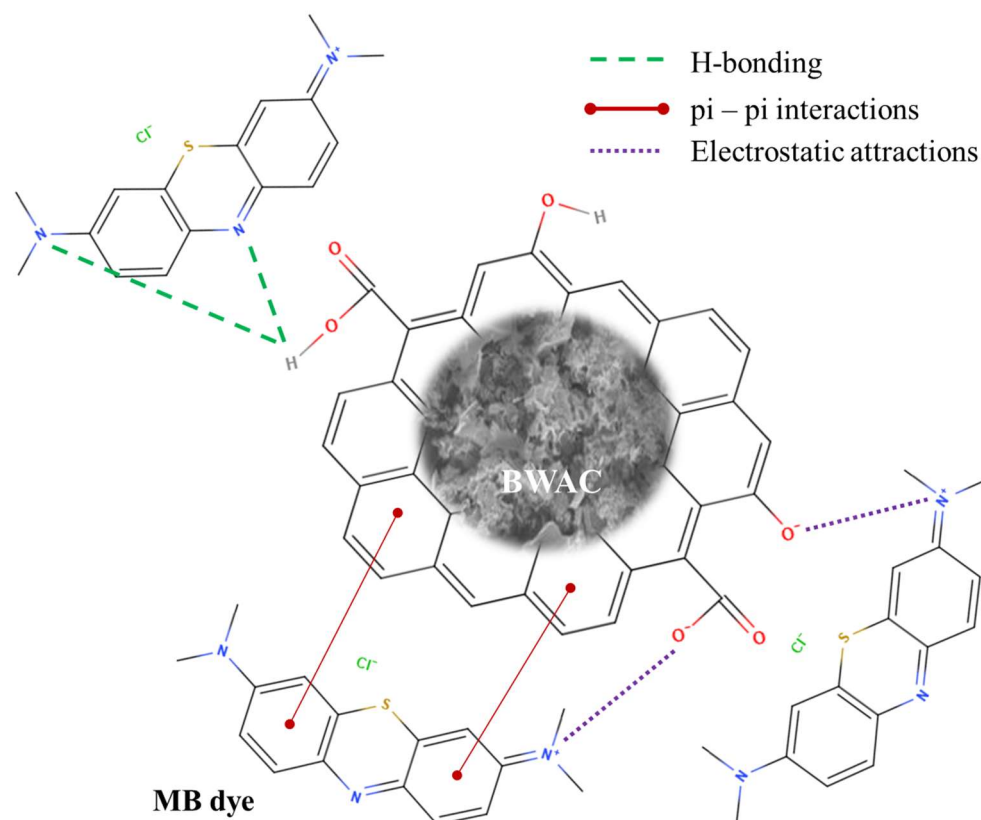


Figure 10. Illustration of the possible interactions between BWAC's surface and MB including electrostatic attractions, hydrogen bonding, and pi-pi interactions.

4. Conclusions

Bamboo-waste-activated carbon (BWAC) was successfully synthesized by the microwave heating process where activation of bamboo waste was carried out with K_2CO_3 as the activating agent. BWAC had good mesoporous pores with a surface area of $107.15 \text{ m}^2/\text{g}$. The optimized conditions for maximum MB removal (87.36%) of 50 mg/L of MB using BWAC obtained from the BBD model were 0.08 g/100 mL of adsorbent dose, pH of 7.62, and contact time of 8 min. From ANOVA studies, it was found that the adsorbent dose showed the highest effect on MB removal with an F-value of 121.70 followed by contact time and pH. The Langmuir model was able to explain the experimental data and BWAC had an adsorption capacity of 85.6 mg/g. The MB adsorption on the surface of BWAC was endothermic and maximum removal took place at 25°C . The pseudo-second-order model fitted to the experimental data, which suggested that chemisorption occurred between MB dye molecules and BWAC. Hence, from the above results, it can be concluded that BWAC can be used as a potential adsorbent for MB-dye-contaminated water treatment.

Author Contributions: K.F.A.Z.: Conceptualization, Data curation, Formal analysis, Investigation, Methodology. U.K.S.: Validation, Visualization, Writing—original draft. T.K.: Methodology Resources, Supervision. S.N.S.: Validation, Resources. Z.A.A.: Validation, Resources, Funding acquisition. A.H.J.: Conceptualization, Methodology, Resources, Software, Supervision, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Saudi Arabia Project No. (RSP-2021/1). King Saud University, Riyadh.

Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Acknowledgments: The authors are thankful to the Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM) Shah Alam, Malaysia for the research facilities. The author (Zeid A. ALOthman) is grateful to the Researchers Supporting Project No. (RSP-2021/1), King Saud University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

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