

Article

Novel ZIF-67@Bentonite (ZIF-67@BNT) Nanocomposite for Aqueous Methyl Orange Removal

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Featured Application: 1. Developed highly efficient novel ZIF-67@BNT nanocomposite adsorbent. 2. The ZIF-67@BNT showed high MO adsorption capacity. 3. Advanced RSM and ML modeling were successfully used for process optimization.

Abstract: The indiscriminate discharge of synthetic dyes into wastewater streams poses a severe threat to the environment as well as to human well-being. Among all these dyes, methyl orange (MO) attracts attention due to its widespread use and persistence in industrial effluents. This study investigated the use of zeolitic imidazolate framework and bentonite (ZIF-67@BNT) nanocomposite material for the removal of MO from the aqueous phase. Various characterization techniques were employed such as FTIR, XRD, and TGA to verify the successful synthesis of the ZIF-67@BNT adsorbent, which was subsequently utilized to investigate the adsorption of MO. Batch adsorption studies demonstrated a high MO adsorption capacity of 187 mg/g. A response surface methodology (RSM)-based modeling exercise was used to optimize the adsorption process. While assessing the impact of various operational factors, the initial MO concentration followed by ZIF-67@BNT dose were noted to be important. Adsorption kinetics and isotherm studies were also completed. The ZIF-67@BNT nanocomposite after adsorption analysis indicated multiple mechanisms facilitating MO uptake. Additionally, various machine learning (ML) models such as ANN, SVR, RF, and GPR were also utilized to predict MO adsorption onto ZIF-67@BNT nanocomposite under a varying set of conditions.

Keywords: ZIF-67@Bentonite; methyl orange; adsorption; RSM and ML modeling



Academic Editor: Juan García Rodríguez

Received: 20 February 2025

Revised: 18 March 2025

Accepted: 19 March 2025

Published: 25 March 2025

Citation: Faheem, K.; Onaizi, S.A.; Vohra, M.S. Novel ZIF-67@Bentonite (ZIF-67@BNT) Nanocomposite for Aqueous Methyl Orange Removal. *Appl. Sci.* **2025**, *15*, 3562. <https://doi.org/10.3390/app15073562>

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1. Introduction

Human activities with an ever-increasing introduction of pollutants continue to diminish the availability of clean water [1,2]. Such aquatic pollution results from a range of inorganic and organic contaminants including heavy metals and dyes [2–16]. For example, the treatment of wastewater with dyes has been looked into to reduce the respective environmental concerns [2]. One such dye is methyl orange (MO). Its chemical structure is provided in Figure 1 and its IUPAC name is sodium-4-(4-dimethylamino phenyl diazenyl) benzenesulfonate [6]. MO dye is also noted in several industrial discharges, thus prompting the need for an effective treatment for its removal from wastewater streams.

Considering this, several techniques have been used for MO removal from wastewater, including photocatalysis and adsorption processes [8,13–16].

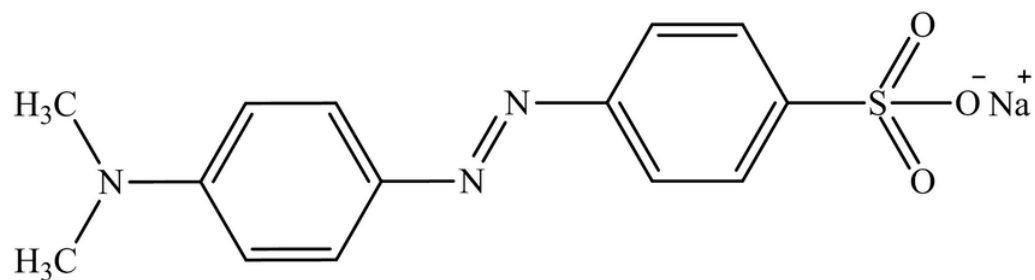


Figure 1. The chemical structure of methyl orange (MO).

Further, the adsorption capacity of a given adsorbent is contingent upon its inherent characteristics such as the specific surface area and surface functional groups [10]. Recently, there has been a surge of interest in novel materials known as metal organic frameworks (MOFs). MOFs have various types including zeolite imidazole framework-67 (ZIF-67). It comprises cobalt ions coordinated with imidazole ligands. This porous material is employed as an adsorbent for various treatments including wastewater treatment, and it is also used as catalyst [11,12]. Researchers have shown that different ZIFs can adsorb dyes, including methylene blue (MB), methyl orange (MO), and rhodamine B (RB) [13,14]. In one study, ZIF-67 with layered double hydroxide (ZIF-67@LDH) showed higher MO and MB removal compared to LDH-only systems [15]. Furthermore, several natural clay minerals have also been used for removing contaminants from the water phase [16] and the use of clay surface modification techniques to improve pollutant removal has also been reported [17–19]. Additionally, the response surface methodology (RSM) and artificial intelligence (AI)-based techniques have also been used for process optimization and environmental modeling [5,20]. Further, various ZIF-67-based materials have been explored for the removal of different pollutants and adsorption studies [21–30] and the aforementioned clay [17–20] materials' application for water decontamination show promising results that can be further explored for the application of nanocomposites of ZIFs with clay material. With this impetus, this study looked into the application of novel ZIF-67@BNT for aqueous methyl orange adsorption, which offers a viable solution for the treatment of aqueous waste streams. In summary, the aforementioned applications of ZIFs and clay-based materials for water decontamination applications support that both materials can be used as adsorbents for water decontamination. Furthermore, the literature review also indicates that the nanocomposite ZIF-67@BNT has not been used for the removal of MO from aqueous streams. Considering this, the present work investigated the use of ZIF-67@BNT-based adsorption for the removal of aqueous phase MO under a varying set of process conditions. Additionally, RSM and AI-based modeling were also employed for process optimization purposes, and the respective details are provided in the sections below.

2. Materials and Methods

2.1. Materials and Equipment

This investigation used pure bentonite (BNT) (Fisher, Waltham, MA, USA) and other chemicals of high purity, including ammonium hydroxide (NH_4OH), 2-methyl imidazole (2-MIM), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and methyl orange [$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=\text{N}=\text{C}_6\text{H}_4\text{SO}_3\text{Na}$]. All respective stock solutions were prepared using de-ionized water.

A Rigaku Miniflex-II diffractometer was used for X-ray diffraction (XRD) analysis to evaluate the crystalline structure of the synthesized ZIF-67@BNT. The respective materials were scanned at a rate of 7° per minute throughout a 2-theta angle range of 5° to 40° . Further, thermogravimetric analysis (TGA) was conducted using TA Instruments to evaluate the thermal stability of the synthesized nanocomposite within a temperature range of 25 to 800°C under an inert environment (i.e., in nitrogen) at a heating rate of 10°C per minute. Also, ZIF-67@BNT surface functional groups were determined by employing a Fourier transform infrared spectroscopy (FTIR) setup (Smart iTR NICOLET iS10). Furthermore, a Shimadzu UV-Vis spectrophotometer setup was used to determine the residual methyl orange (MO) concentration in aqueous samples (that had been duly pre-filtered using $0.2\ \mu\text{m}$ (Whatman, Dassel, Germany) filters to exclude the adsorbent particles) at 464 nm. Standards for MO ranged from 12.5 to 100 mg/L and the same were used to develop the calibration curve. Further details on the synthesis and application of ZIF-67@BNT for the adsorptive removal of MO from wastewater samples are provided in the sections below and also summarized in Figure 2.

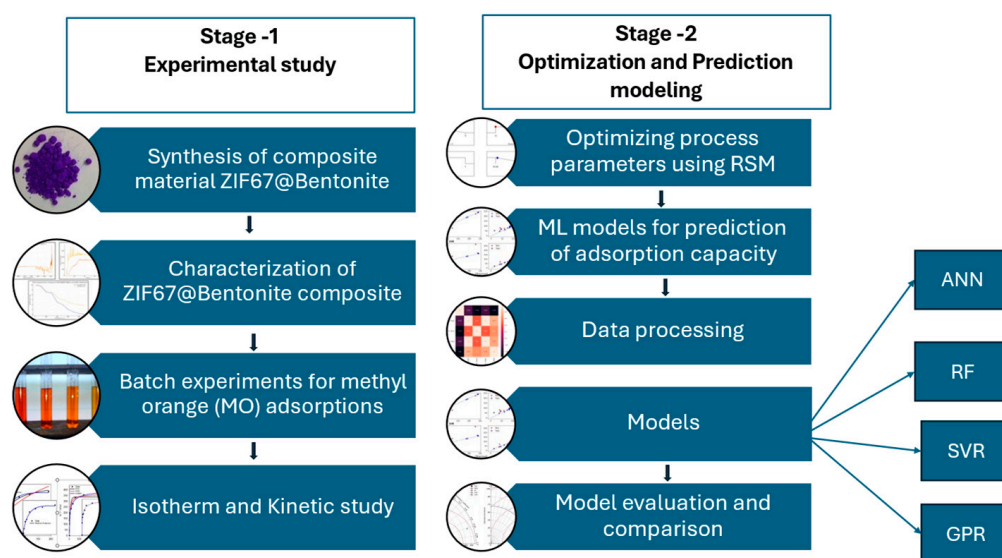


Figure 2. A general framework for evaluating MO adsorption using ZIF-67@BNT adsorbent along with the ML modeling.

2.2. Synthesis of ZIF-67 and ZIF-67@BNT

The ZIF-67@BNT nanocomposite synthesis procedure is sketched in Figure 3. First, a cobalt nitrate salt aqueous solution was prepared by dissolving 11.64 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 150 mL de-ionized water. To this solution, 0.24 g BNT was added, followed by stirring at room temperature for 10 min. To thoroughly disperse BNT in the cobalt solution, the mixture was sonicated at 50% amplitude for 30 min, with intervals of 30 s of pulse on and 3 s off. Meanwhile, in a separate beaker, 13.12 g of 2-methyl imidazole was mixed with 150 mL of 28% NH_4OH aqueous solution, maintaining a metal-to-linker ratio (i.e., Co:2-MIM) of 1:4. This was followed by pouring the imidazole-containing solution quickly into the bentonite–cobalt solution along with stirring the resulting liquid mixture continuously for 2 h. The produced ZIF-67@BNT nanocomposite was, then, recovered and purified through washing 5 times with de-ionized water. The ZIF-67@BNT nanocomposite was recovered after each washing cycle using 20 min of centrifugation at $6000 \times g$ rpm. The purified ZIF-67@BNT nanocomposite was dried at 50°C .

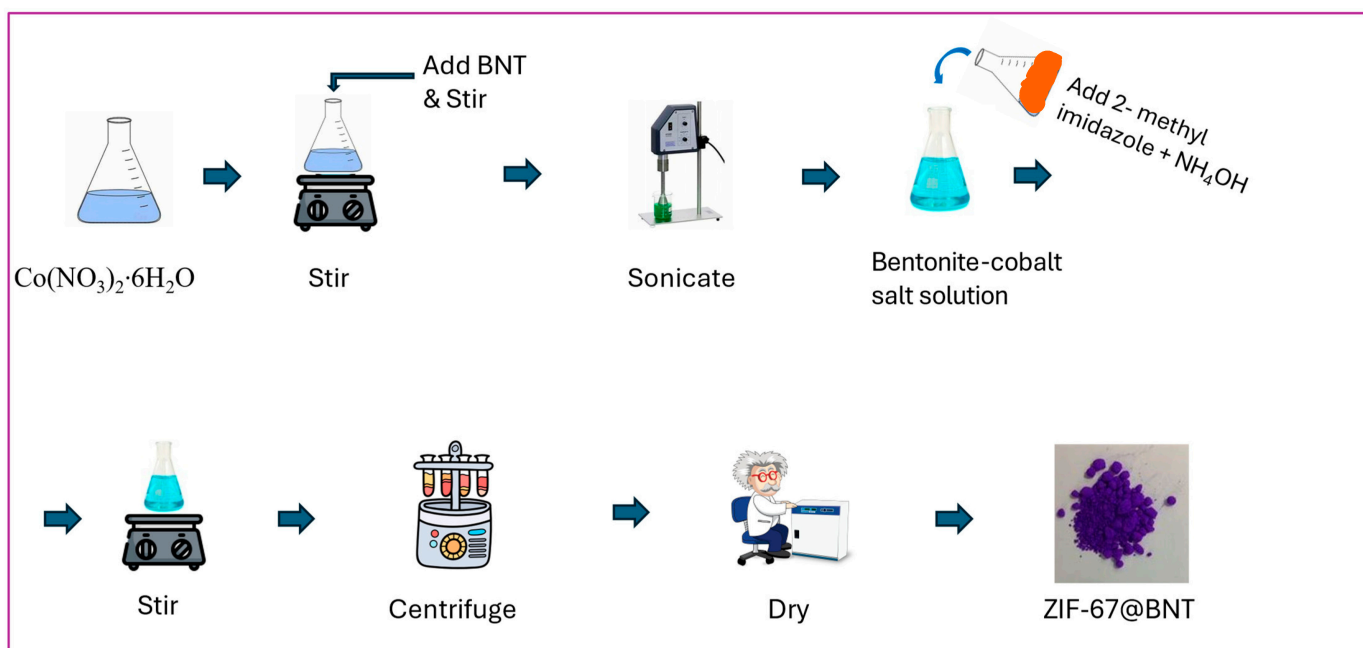


Figure 3. A schematic illustration depicting the preparation procedure of the ZIF-67@Bentonite (ZIF-67@BNT) nanocomposite.

2.3. Response Surface Methodology (RSM)

As shown in Equation (1), the response surface methodology (RSM)-based design of experiments and modeling facilitates the connections between input variables/factors (X_i) and the desired output/response (y) [31,32].

$$y = f(X_1, X_2, X_3, X_4, \dots, X_n) \quad (1)$$

Further, in RSM, the face-centered central composite design (FCCD) enables a comprehensive examination of all related system operation variables/factors in the desired response [33]. For the present MO adsorption work, the ZIF-67@BNT dosage, initial MO concentration, and contact time were the independent factors, whereas the ZIF-67@BNT MO adsorption capacity (mg/g) was the desired response. Table 1 lists those factors and the respective levels. The statistical parameters to assess the RSM model validity included coefficient of determination (R^2), adjusted R^2 , and projected R^2 along with the analysis of variance (ANOVA). The RSM modeling was completed employing Design-Expert software (version 13).

Table 1. The RSM modeling factors and levels used for design of experiments (DOE).

Factors		Levels		
		−1	0	1
A	Adsorbent dose (mg)	5	10	15
B	Methyl orange (mg/L)	10	20	30
C	Time (hours)	1	3	5

2.4. Batch Adsorption Experiment

The adsorption process is a complex sequence of events that begins with external diffusion, where the adsorbate migrates across the liquid film to the surface of the adsorbent. The final stage of the adsorption process involves the interaction between the adsorbate and the active sites of the adsorbent, leading to adsorption equilibrium. For this study,

each batch adsorption test a 150 mL MO solution was mixed with the desired ZIF-67@BNT adsorbent dose followed by placing it on a Bioevopeak mechanical shaker. All suspension samples were filtered using a 0.2 µm filter (Whatman, Dassel, Germany), followed by MO analysis and Equations (2) and (3) were then used to calculate the specific removal efficiency (%) and the adsorption capacity (mg/g), respectively:

$$R = \frac{C_0 - C_e}{C_e} \times 100 \quad (2)$$

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (3)$$

where the 'C₀' is the initial MO concentration (mg/L), 'C_e' is the MO concentration after adsorption at equilibrium, 'm' is the mass of the adsorbent in grams, and 'V' is the sample volume in liters. For the adsorption kinetics, the ZIF-67@BNT dose was 5 mg at an initial MO concentration of 100 ppm. For the adsorption isotherm tests, the starting initial MO concentration was varied from 5 to 125 mg/L at a ZIF-67@BNT dose of 5 mg.

2.5. Machine Learning (ML) and Artificial Neural Network (ANN) Modeling

Machine learning techniques are increasingly being used to forecast adsorbents to remove pollutants from aqueous streams [34,35]. However, due to operational and financial difficulties, there is still a lack of experimental data that support the application of machine learning and other artificial intelligence techniques in wastewater treatment. In order to assess the prediction capabilities of several machine learning algorithms, this study collected experimental data on batch adsorption. The machine learning (ML) modeling technique has been explored for adsorption work [36,37].

2.5.1. Artificial Neural Network

The ANN is another widely employed artificial intelligence (AI)-based modeling technique [38]. As shown in Figure 4A, the input layer, output layer, and one or more hidden layers make up the ANN structure and multiple neurons grouped as linked nodes make up each layer, which are trained as per the multi-layer perceptron (MLP) along with the experimentally acquired data and the final feedforward backpropagation (FFBP) calculated findings are used in order to improve model performance. Equation (4) displays the anticipated ANN output:

$$Y = f(W + B) \quad (4)$$

where Y stands for the output, B for the bias, W for the weight, and *f* for the activation function.

2.5.2. Support Vector Regression

Support vector regression (SVR) is an extension of support vector machines (SVMs) originally designed for classification but adapted for regression tasks. It maps input vectors into a high-dimensional feature space using a hyperplane to maximize the separation between data points, leading to accurate predictions. Various kernel functions can be used for this mapping, making SVR suitable for a wide range of applications, even with small datasets. Equation (5) produces the output and Figure 4B illustrates SVR operations [35,39].

$$y = \sum_{i=1}^n \alpha I_k(x_i, x_j) + b \quad (5)$$

where y is predicted output, n is number of support vectors, α is Lagrange multipliers, k is kernel function, b is bias term, and x_i and x_j are the support vectors and test inputs.

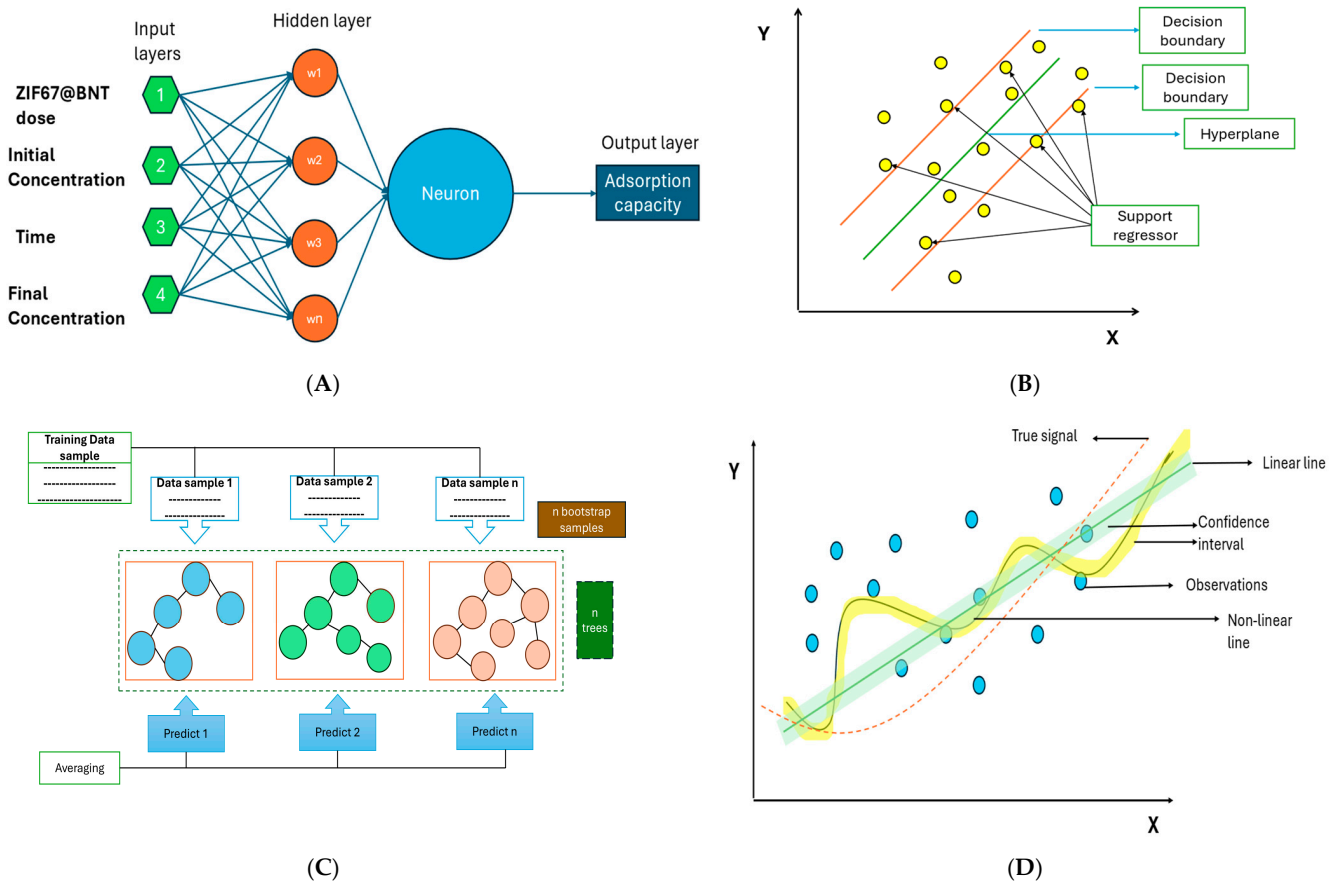


Figure 4. (A) ANN algorithm structure, (B) linear hyperplane-based SVR classification, (C) Random Forest algorithm architecture, and (D) Regressor for the Gaussian process.

2.5.3. Random Forest

Further, the random forest (RF) is a tree-based ensemble learning model that improves upon the bagging tree approach. It constructs multiple decision trees using bootstrap sampling during training. Each decision tree consists of internal nodes (which assess predictions), branch nodes (which display evaluation results), and leaf nodes (which show class labels in regression). The RF model builds regression trees on bootstrap samples, selects attributes randomly at each branch node, and stops tree expansion once the mean squared error reaches an optimal level. Finally, the RF model aggregates predictions from multiple trees, averaging them to produce the final result. The RF model formulation is shown in Equation (6) [38].

$$\hat{f}_{rf}^N(x) = \frac{1}{N} \sum_{i=1}^N t_i(x) \quad (6)$$

where $t_i(x)$ is the individual regression tree algorithm, N is the number of regression algorithms, and $\hat{f}_{rf}^N(x)$ is the included regression tree. Figure 4C shows the RF method's graphical display.

2.5.4. Gaussian Process

The Gaussian process (GP) is a non-parametric probabilistic model used in machine learning for regression, classification, and uncertainty quantification. It models a collection of random variables with a joint Gaussian distribution, allowing for flexible data representation while providing predictions with uncertainty estimates. The key characteristics of the GP include handling non-parametric data, probabilistic predictions, interpolation, smoothing, and hyperparameter marginalization and the model is evaluated using N -fold

cross-validation, correlation coefficient (R), coefficient of determination (R^2), and RMSE. Figure 4D shows the visual presentation of the GP [40].

3. Results and Discussion

3.1. ZIF-67@BNT Characterization

3.1.1. X-Ray Diffraction Analysis

The X-ray diffraction (XRD) patterns of the ZIF-67@BNT nanocomposite, ZIF-67, and BNT are shown in Figure 5A. The diffraction pattern of BNT (shown in blue) shows some characteristic peaks related to the clay mineral structure. Major reflections seen at 2θ : 6.1° (001), 19.8° (110), 26.7° (020), 35.0° (220), 54.9° (240), and 68.1° (330) correspond to different planes of crystals existing in BNT [41]. The basal reflection determined close to 6.1° (001) is an indicator of the montmorillonite interlayer spacing, which is a fundamental structural property of BNT. Some peaks established near 20 – 30° correspond to quartz impurities predominating in natural BNT, while their broad character signifies an amorphous phase of BNT owing to its hydrated layered silicate structure. The calculated crystallite size of BNT is 2810.19 nm; therefore, it shows structural features in relatively large particle dimensions and a less defined crystalline nature than ZIF-67.

The X-ray diffraction (XRD) pattern of ZIF-67 (red pattern) can be assigned to characteristic peaks at $2\theta = 7.3^\circ, 10.4^\circ, 12.7^\circ, 14.7^\circ, 16.4^\circ, 18.1^\circ, 22.2^\circ, 24.5^\circ, 29.4^\circ$, and 33.5° , typical of the crystalline metal–organic framework (MOF) structure of ZIF-67 [42]. They are assigned as (011), (002), (013), (112), (222), (233), (044), (134), (244), and (235) crystal planes, respectively [43]. The calculated crystallite size of ZIF-67 and ZIF-67@BNT is 44.48 and 79.28 nm, respectively, with the ZIF-67@BNT nanocomposite being significantly larger than ZIF-67 alone, suggesting a structural reorganization upon composite formation. The decline in crystallinity in the composite might potentially point to surface changes and flaws, which would improve the adsorption capacity by raising the number of accessible active sites [44]. Furthermore, BNT in the composite is projected to increase the general structural stability of ZIF-67, hence avoiding its collapse in aqueous surroundings [45].

With all factors taken into account, the XRD study verifies the effective synthesis of the ZIF-67@BNT composite by maintaining the main structural characteristics of ZIF-67 and including modifications caused by interactions with BNT. The noted rise in crystallite size points to BNT's stabilizing action for ZIF-67, hence enabling better textural qualities. Moreover, the retention of unique ZIF-67 crystal planes in the composite shows that its crystalline structure stays intact; on the other hand, the addition of BNT brings structural changes advantageous for adsorption uses. The minimal shifting and widening of BNT's peaks point to exfoliation or intercalation, which improves ZIF-67 dispersion in the composite [46].

3.1.2. Fourier Transform Infrared Spectroscopy Analysis

Besides the crystallinity, Fourier transform infrared spectroscopy (FTIR) results of BNT, ZIF-67, and the ZIF-67@BNT composite are shown in Figure 5B, providing insight into the functional groups and interactions present between the components. BNT displays a wide O-H stretching band at 3100 cm^{-1} due to adsorbed water, as well as peaks at 2370 cm^{-1} (C-H stretching), 1408 cm^{-1} (C=N stretching), 1170 cm^{-1} (C=C stretching), and 970 cm^{-1} (Si-OH bending), which are a consequence of its layered silicate structure. These peaks indicate the presence of montmorillonite and silicate groups, responsible for the BNT's adsorption capacity [47,48].

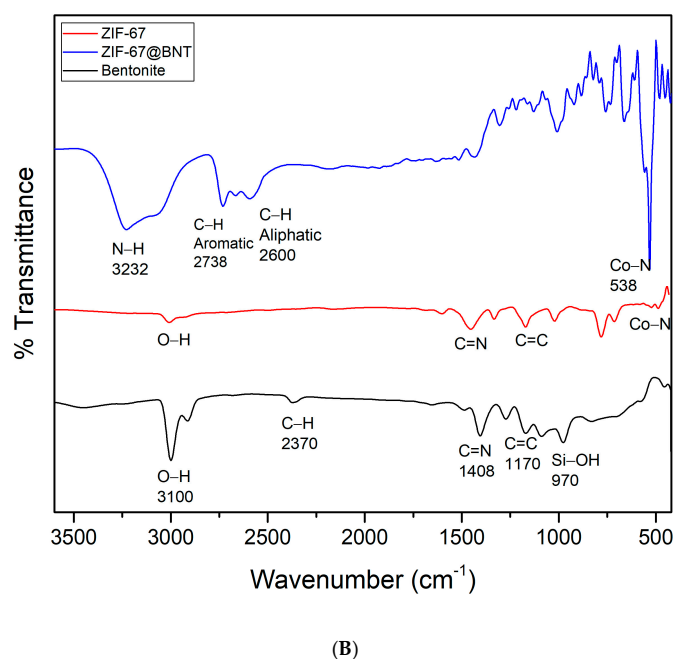
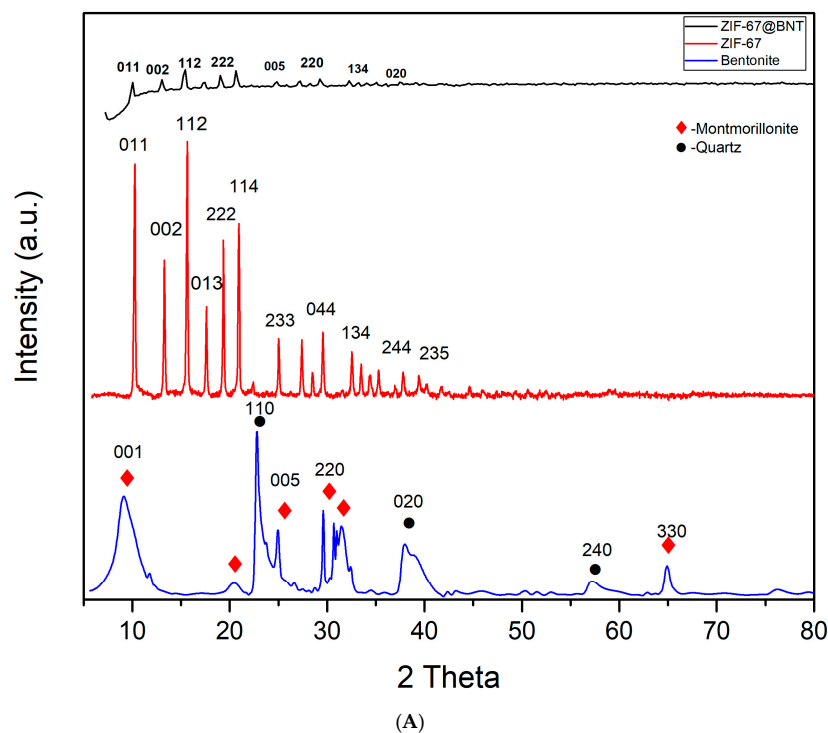


Figure 5. The ZIF-67@BNT nanocomposite's crystalline structure and functional group characterization are shown in (A) XRD patterns and (B) FTIR spectra, respectively.

The FTIR spectrum of ZIF-67 exhibits some characteristic vibrational modes related to its MOF structure. The Co-N stretching vibration coincides with a clear peak at 538 cm^{-1} , therefore verifying the coordination between cobalt ions and the 2-methylimidazolate linker. Strong O-H stretching vibrations imply the hydrophobic character of ZIF-67, which is anticipated from the non-polar imidazolate linkers. Since C=N and C=C stretching modes compose the fundamental structure of the MOF, their presence promotes the stability of the ZIF-67 framework even more. Crucially for preserving adsorption efficiency, the well-defined peaks of ZIF-67 point to a highly crystalline and stable framework [49].

In the ZIF-67@BNT, significant spectrum alterations noticed in the ZIF-67@BNT composite indicate robust interactions between ZIF-67 and BNT. N-H stretching at 3232 cm^{-1} points to interactions between the hydroxyl (-OH) groups of BNTs and the imidazolate linkers of ZIF-67. New C-H stretching vibrations at 2738 cm^{-1} (aromatic) and 2600 cm^{-1} (aliphatic) point to changes in the organic framework of the MOF, maybe resulting from surface alterations following integration with BNT or electrostatic interactions. Retention of the Co-N peak at 538 cm^{-1} guarantees composite structural integrity of ZIF-67 [41,50].

Due to the high interfacial interactions between the two adsorbent materials, ZIF-67@BNT exhibits additional distinctive peaks when compared to ZIF-67 and BNT. Electrostatic interactions between the Co^{2+} metal centers in the ZIF-67 framework and the negatively charged BNT surface cause structural modifications, while hydrogen bonding between the hydroxyl groups of BNT and the imidazolate linkers of ZIF-67 causes changes in vibrational frequencies. Spectral fluctuations may also be caused by the emergence of new functional groups or changes to the electrical environment of existing groups brought about by ZIF-67's integration into the BNT matrix. Alterations to the peak intensities and movement of the peaks point to altered adsorption sites, which may improve the composite's efficacy in pollutant removal [51–53].

3.1.3. Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of the ZIF-67@BNT nanocomposite as shown in Figure 6 reveals its thermal stability profile. The initial segment of the TGA curve, up to approximately $150\text{ }^{\circ}\text{C}$, shows minimal weight loss, likely due to the evaporation of surface-adsorbed moisture or other volatile components. However, a pronounced weight loss occurs between 150 and $600\text{ }^{\circ}\text{C}$, with the primary decomposition phase observed from around $300\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$. This substantial weight reduction is attributed to the degradation of the organic framework within ZIF-67 and possibly the release of structurally bound water associated with the BNT component. Beyond $600\text{ }^{\circ}\text{C}$, a slower rate of weight loss is noted, indicating the breakdown of more thermally resilient components within the nanocomposite, with stabilization occurring at around $800\text{ }^{\circ}\text{C}$ [54].

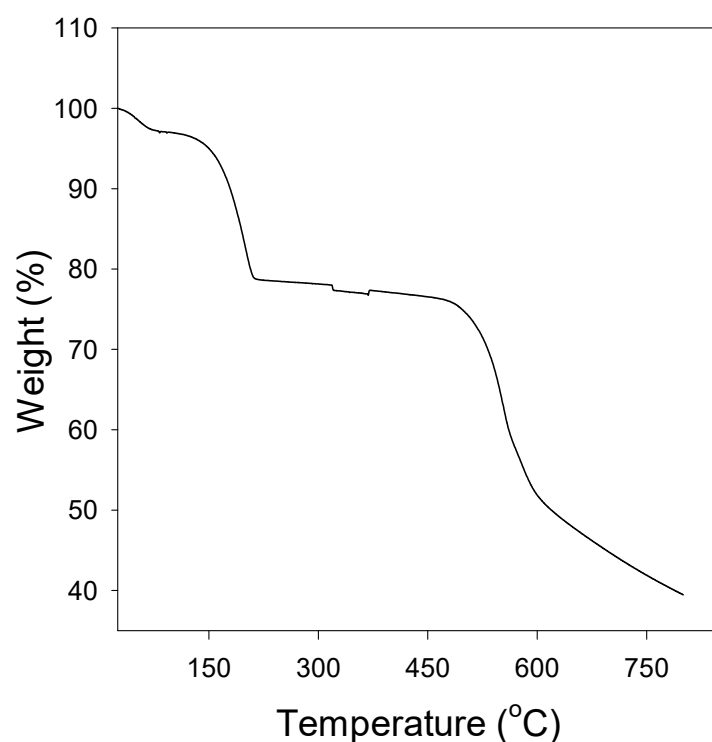


Figure 6. Thermogravimetric analysis results for the ZIF-67@BNT nanocomposite.

Hence, the characterization results given above, using XRD, FTIR, and TGA, regarding the structural, chemical, and thermal characterizations of the ZIF-67@BNT composite, confirm its successful synthesis. They also demonstrate that the ZIF-67 composite retains the crystalline integrity of ZIF-67, as it undergoes modifications because of its interactions with BNT and shows enhanced thermal stability. These characteristics make the composite a good material for uses in environmental remediation and adsorption systems.

3.2. Benchmarking the Performance of the ZIF-67@BNT Nanocomposite with Its Constituents

The results depicted in Figure 7 contrast the MO adsorption performance of ZIF-67@BNT nanocomposite with its parental materials (i.e., ZIF-67 and BNT). As shown in Figure 7, ZIF-67 exhibits an MO adsorption capacity of 222.9 mg/g. The ZIF-67@BNT nanocomposite, on the other hand, shows the highest MO adsorption capacity with a value of 275.3 mg/g. The enhanced performance of ZIF-67@BNT can be attributed to a synergistic effect between ZIF-67 and BNT, where the integration of BNT with ZIF-67 results in improved structural stability, increased active sites, or optimized interaction with the targeted pollutant (MO in this case). This superior capacity highlights the potential of nanocomposite materials to outperform their individual components by leveraging the strengths of their constituents. The superiority of nanocomposites generated from different materials has also been demonstrated in the literature [10,32,55–58]. Such superiority underscores the importance of material hybridization in developing advanced materials with enhanced properties, paving the way for further exploration and optimization in the wastewater treatment field.

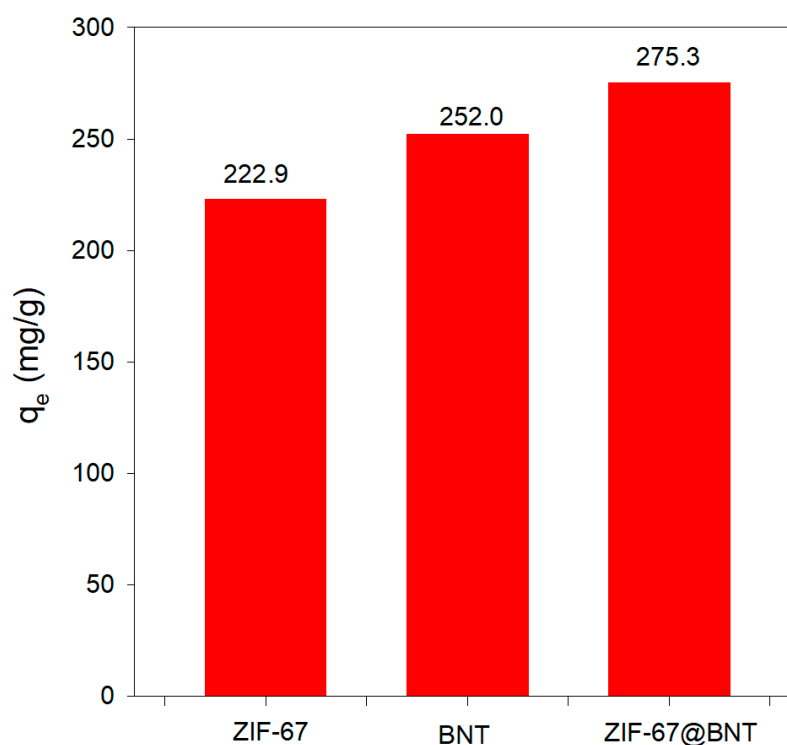


Figure 7. Benchmarking the adsorption of MO onto ZIF-67@BNT with its constituents (i.e., ZIF-67 and BNT). The adsorption took place from 100 mg/L MO solution containing 50 mg/mL of each adsorbent.

Based on the results presented in Figure 7, the ZIF-67@BNT nanocomposite offers a greater performance, making it a promising candidate for applications in water decoloring such as the MO removal reported herein. Thus, subsequent studies will focus on optimizing the performance of ZIF-67@BNT nanocomposite using RSM techniques, studying the

adsorption kinetics and adsorption isotherm of MO onto this nanocomposite, and developing predictive machine learning models. Plausible adsorption mechanism(s) will also be highlighted wherever applicable throughout the discussion in the subsequent sections.

3.3. Analysis of Methyl Orange Adsorption Using ZIF-67@BNT

3.3.1. Experimental Design and Analysis of Variance

Results from the MO adsorption experiments conducted using the ZIF-67@BNT nanocomposite are given in Table 2. The adsorption findings show that the uptake of MO by ZIF-67@BNT is a function of the process parameters. Also, the MO adsorption capacity using ZIF-67@BNT ranges from 38 to 187 mg/g, indicating that the MO removal can be significantly enhanced and optimized by varying the process conditions. Furthermore, among the various RSM-based models generated, the quadratic model fitted well to the noted MO adsorption results using ZIF-67@BNT, as given below (Equation (7)):

$$\text{Adsorption capacity (mg/g)} = 2.57351 + 0.185881A + 0.057277B + 0.115436C - 0.002436AB - 0.009655A^2 \quad (7)$$

Table 2. The RSM-based DOE and the MO adsorption results using the ZIF-67@BNT nanocomposite adsorbent.

Run	A: Adsorbent Dose (mg)	B: Methyl Orange (mg/L)	C: Time (Hours)	Adsorption Capacity (mg/g)
1	15	30	5	82
2	5	20	3	89
3	15	30	1	46
4	10	20	5	105
5	10	10	3	62
6	5	10	5	84
7	10	20	3	85
8	5	30	1	109
9	10	20	1	75
10	5	30	5	187
11	15	10	5	44
12	5	10	1	41
13	10	30	3	124
14	15	10	1	38
15	15	20	3	60

The R^2 , adjusted R^2 , and predicted R^2 values for the present RSM model were noted to be 0.953, 0.927, and 0.822, respectively. The quadratic model's (Equation (7)) suitability is thus demonstrated by less than 20% difference between the adjusted and predicted R^2 values [59]. This is also supported by the actual and predicted MO removal as given in Figure 8a. Further, some other statistical parameters for the suggested RSM model (Equation (7)) are also provided in Table 3. The ANOVA findings as shown in Table 3, with a p -value of 0.05 or less, also support the suggested RSM-based model for MO adsorption by ZIF-67@BNT. Furthermore, the Box–Cox plot for total MO removal (Figure 8b), Figure 8c that illustrates that the residuals have a normal distribution, and Figure 8d that reveals an absence of correlation between the run sequence and residuals (as shown by the random dispersion of points in the plot) also support the suggested RSM-based model's (Equation (7)) suitability to predict the MO uptake by the novel ZIF-67@BNT under a varying set of process conditions.

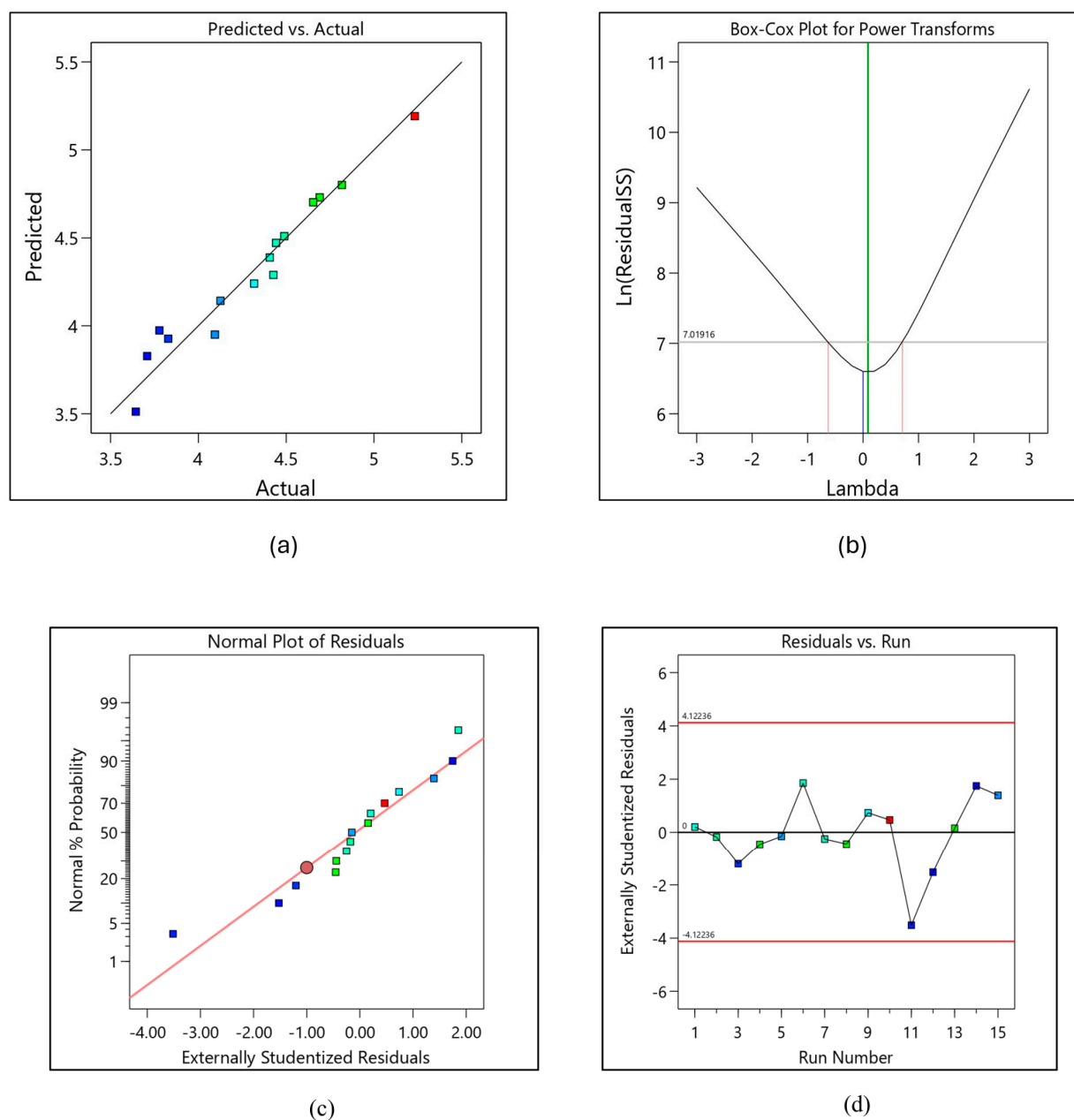


Figure 8. The RSM Model (for MO adsorption by ZIF-67@BNT) check plots. (a) Predicted Vs. Actual adsorption capacity, (b) Box–Cox plot, (c) Normality distribution plot, and (d) Residuals Vs. Run plot.

Table 3. The respective statistical parameters for RSM modeling.

Source	Sum of Squares	Degree of Freedom (df)	Mean Square	F-Value	<i>p</i> -Value	
Model	2.71	5	0.5424	36.79	<0.0001	Significant
A: Adsorbent dose	0.7823	1	0.7823	53.06	<0.0001	
B: Methyl Orange	1.08	1	1.08	73.49	<0.0001	
C: Time	0.5330	1	0.5330	36.15	<0.000	
AB	0.1187	1	0.1187	8.05	0.0002	
A ²	0.1942	1	0.1942	13.17	0.0195	
Residual	0.1327	9	0.0147		0.0055	
Core Total	2.84	14				

3.3.2. Examine the Effect of Process Parameters Using ANOVA

Additionally, the process variables could have a significant effect on the adsorption capacity [60] and Figure 9 illustrates the effect of the present process variables on MO adsorption capacity. To that end, it is noted that an increase in the MO concentration from 10 to 30 mg/L at an adsorbent dose of 5 mg increases the MO adsorption capacity. Such an enhancement in the MO uptake by ZIF-67@BNT is suggested to result from an enhanced driving force for the mass transfer of MO from the bulk aqueous phase to the bulk adsorbent surface. Figure 9 also shows that extended contact time delivers better MO uptake, as more process time permits more adsorbate molecules to diffuse to the adsorbent surface sites until reaching the adsorption equilibrium. Similarly, Figures 10 and 11 also indicate that the MO adsorption capacity ($Q_{\max}$) is affected by both the adsorbent ZIF-67@BNT dose and the methyl orange (MO) initial concentration; at higher MO concentrations (30 ppm) an increase in the ZIF-67@BNT adsorbent dose equilibrates more MO molecules on the adsorbent surface and significantly increases the $Q_{\max}$ [61]. Hence, these findings can be used to establish parameters for the enhancement of MO uptake by ZIF-67@BNT. Furthermore, this study also provides a comparison with the other adsorption studies on the removal of MO from aqueous solution as shown in Table 4.

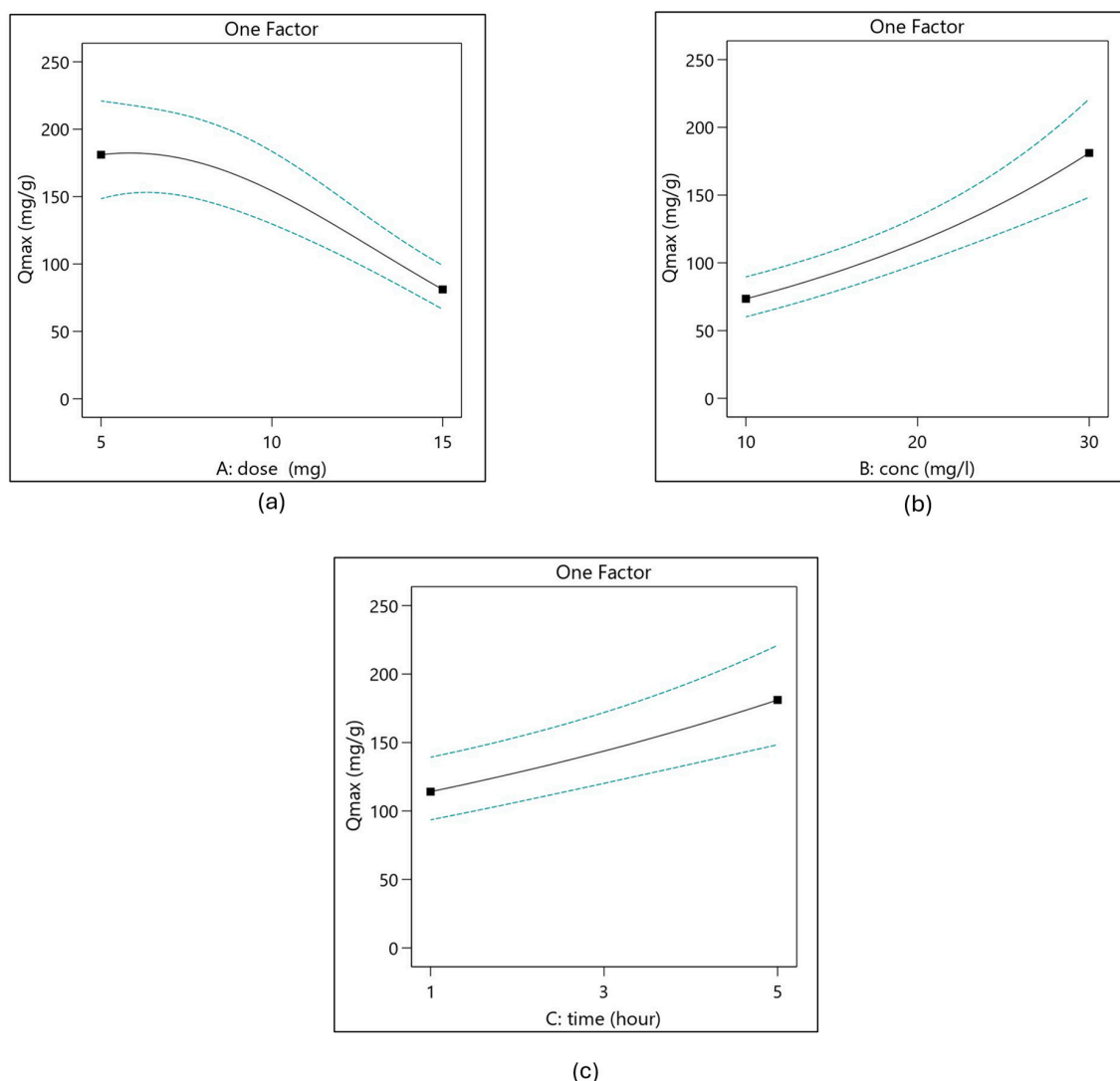


Figure 9. MO adsorption onto ZIF-67@BNT as a function of (a) ZIF-67@BNT dose, (b) MO concentration, and (c) Time.

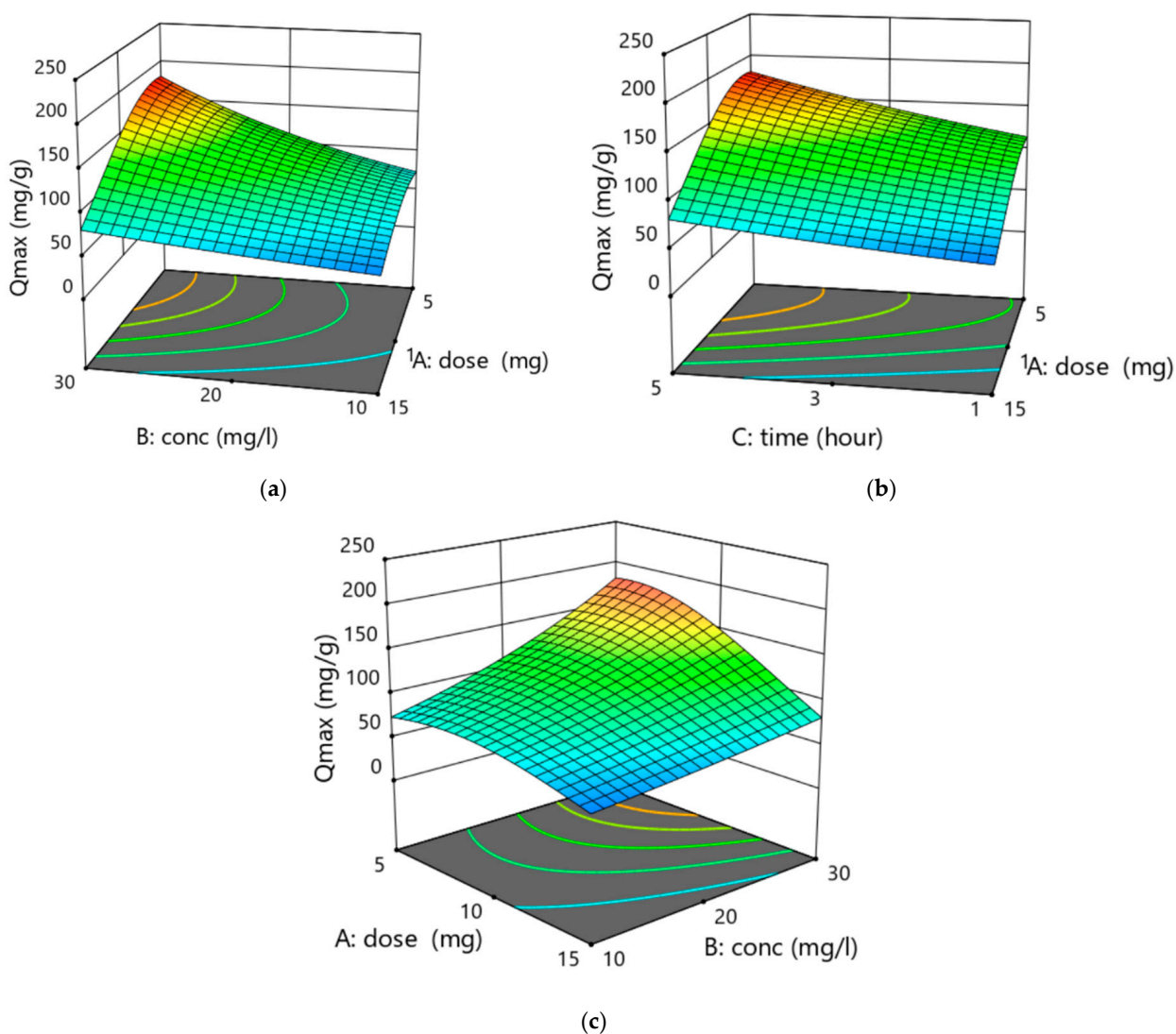


Figure 10. The 3D interaction plots for MO adsorption capacity: (a) MO concentration vs. ZIF-67@BNT dose, (b) Time vs. ZIF-67@BNT dose, (c) ZIF-67@BNT dose vs. MO concentration.

Table 4. Comparison with the other known adsorbent materials for the removal of MO.

Adsorbent	Initial Concentration	Adsorbent Dose	Initial pH	Temperature	Time	Adsorption Capacity	Reference
Ni@ZIF-67	40	20	6	Room	180	33.17	[21]
Ag@ZIF-67	200	20	6	30	180	994.6	[24]
ZIF-67@LDH		20	6	30	500	663.4	[30]
CGAC	300	50	3	40	90	658	[62]
AC/NiFe ₂ O ₄	100	300	3	30	180	182.82	[63]
CS-MT Composite	40	320	6.3	30	60	154.4	[17]
CTAB@GO	300	50	4	Room	1440	1301.5	[64]
ZnO/GO	40	20	4	60	50	296.73	[65]
Nanocomposite							
Cd-ZIF-8 Composite	200	50	5	25	120	425.8	[66]
This Study	30	5	-	Room	300	187	-

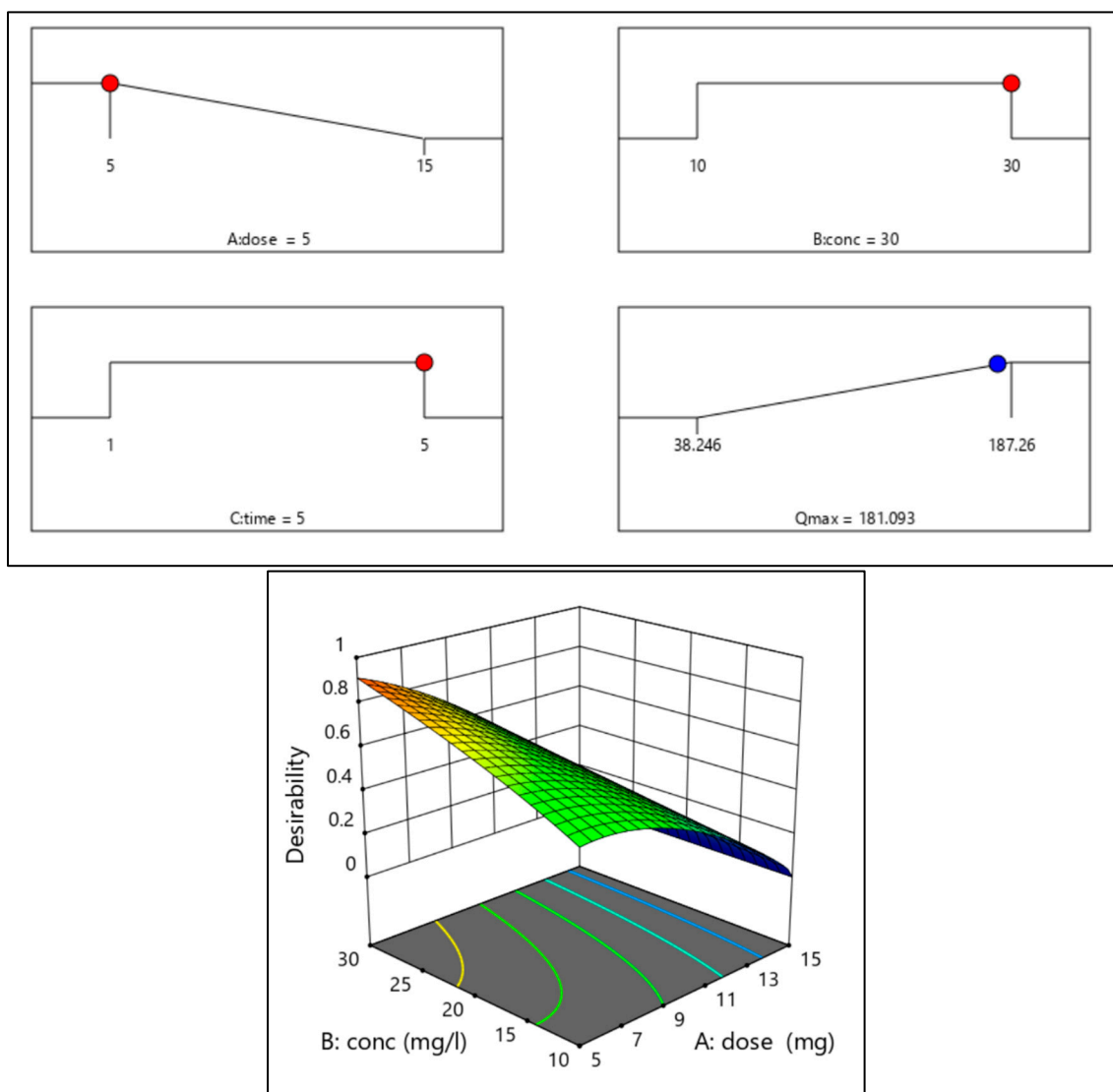


Figure 11. Results from the RSM-based response optimization exercise for MO adsorption using ZIF-67@BNT.

3.3.3. Adsorption Kinetics and Isotherm Analysis

The pseudo-first order (PFO), pseudo-second order (PSO), and Avrami models were also employed for the kinetic modeling. Out of these three kinetic models, the Avrami model showed the highest R^2 value of 0.9949 (Figure 12 and Table 5). This suggests that MO adsorption by ZIF-67@BNT involves a potential variation in the adsorption mechanism with the Avrami model indicating a non-linear kinetics and a better capturing of the overall MO adsorption trend as a function of time.

Table 5. Kinetic modeling parameters for MO adsorption by ZIF-67@BNT nanocomposite.

Models									
Pseudo-First Order $q_t = q_e (1 - e^{-k_1 t})$			Pseudo-Second Order $q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$			Avrami $q_t = q_e \left(1 - e^{-\frac{(k_a t)^n}{n}} \right)$			
q_e (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2	q_e (mg/g)	k_a (min ⁻¹)	n	R^2
338	0.0216	0.8837	360.7	9.464×10^{-5}	0.9585	386.8	0.0013	0.401	0.9949

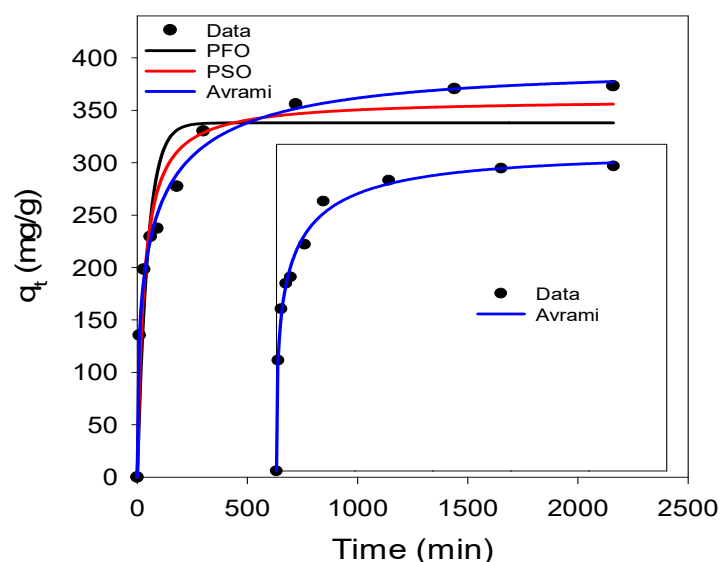


Figure 12. Adsorption kinetic model for MO adsorption by ZIF-67@BNT nanocomposite.

The interactions between the MO adsorbate and ZIF-67@BNT adsorbent were further evaluated using the adsorption isotherm approach. To that end, the respective MO adsorption isotherm results were fitted to the Langmuir isotherm, Freundlich isotherm, and Redlich–Peterson isotherm and the output was analyzed for possible adsorbate–adsorbent interactions as described earlier [67]. The respective experimental and modeling findings as given in Figure 13 and Table 6 indicate that the three-parameter Redlich–Peterson (R–P) isotherm shows a good match to the experimental MO adsorption isotherm results, which is also confirmed by the “ g ” parameter value of more than 1 [68]. This finding indicates that, instead of a plateau, the adsorption capacity would tend to increase with the mass transfer driving force, i.e., the MO aqueous phase concentration, though the change at higher equilibrium MO concentrations is low.

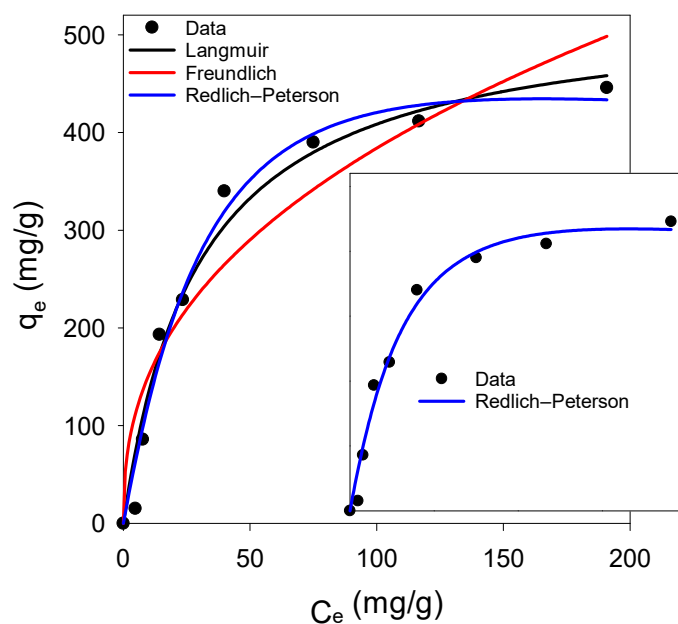


Figure 13. Adsorption Isotherm model for MO adsorption by ZIF-67@BNT nanocomposite.

Table 6. Adsorption isotherm modeling parameters for MO adsorption by ZIF-67@BNT nanocomposite.

Models									
Langmuir Adsorption Isotherm $q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$			Freundlich Adsorption Isotherm $q_e = K_F C_e^{1/n}$			Redlich–Peterson Adsorption Isotherm $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$			
$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2	K_R (L/g)	a_R (L/mg)	g	R^2
528.7	0.034	0.9746	2.48	59.8	0.9024	14.06	0.0081	1.23	0.9823

This also indicates a complex adsorption mechanism with several adsorbent surface parameters (including the type of surface functional group) initiating the MO adsorption. This topic is probed further.

3.3.4. Post-Analysis of MO Adsorption on ZIF-67@BNT Nanocomposite

Fourier transform infrared (FTIR) spectra of ZIF-67@BNT before and after methyl orange adsorption were analyzed to investigate the changes in functional groups and interactions involved in the adsorption process. The findings as shown in Figure 14 exhibit the effects of methyl orange adsorption on the nanocomposite's functional groups. The spectrum before adsorption exhibited a broad peak around 3400 cm^{-1} , corresponding to the stretching vibrations of hydroxyl (-OH) groups, which are typically associated with adsorbed water molecules and surface hydroxyl groups in BNT [69]. Peaks observed from $2900\text{--}3100\text{ cm}^{-1}$ can be attributed to C-H stretching vibrations from organic components in the ZIF-67 framework [58,70], while the band around $1600\text{--}1700\text{ cm}^{-1}$ corresponds to C = O stretching or H-O-H bending vibrations [71]. Additionally, strong peaks in the range of $1000\text{--}1500\text{ cm}^{-1}$ are characteristic of metal-oxygen (Co-O, Al-O-Si) stretching and bending vibrations from the BNT structure and ZIF-67 framework. The region below 1000 cm^{-1} represents metal-ligand interactions, specifically Co-N stretching in ZIF-67 [72,73]. After methyl orange adsorption, notable spectral changes were observed, confirming the interaction between the adsorbent and the dye molecules. A shift and reduction in the intensity of the hydroxyl (-OH) peak at $\sim 3400\text{ cm}^{-1}$ suggest possible hydrogen bonding between the dye and surface hydroxyl groups of ZIF-67@BNT [74]. The emergence of new peaks and enhanced intensities in the $1500\text{--}1650\text{ cm}^{-1}$ region correspond to the aromatic C=C stretching and sulfonate ($-\text{SO}_3^-$) vibrations of methyl orange, indicating its successful attachment to the surface of ZIF-67@BNT [75]. Furthermore, broadening and shifts in the $1000\text{--}1200\text{ cm}^{-1}$ region suggest interactions between the BNT structure and methyl orange functional groups, likely through electrostatic attractions or coordination interactions with Co^{2+} sites in ZIF-67. Additionally, changes in the fingerprint region (below 1000 cm^{-1}) indicate modifications in the metal-ligand framework due to adsorption. The observed spectral changes suggest that the adsorption of methyl orange onto ZIF-67@BNT occurs through multiple mechanisms, including electrostatic interactions between the negatively charged sulfonate ($-\text{SO}_3^-$) groups of methyl orange and the positively charged Co^{2+} or Al^{3+} sites in ZIF-67@BNT and hydrogen bonding between hydroxyl groups of BNT and methyl orange molecules [76].

These interactions validate the effectiveness of ZIF-67@BNT as an adsorbent for methyl orange, highlighting its potential utility in applications aimed at removing organic dyes from contaminated water. Furthermore, the noted stability and adsorption efficiency support the nanocomposite's reusability and robustness, making it a promising candidate for practical environmental remediation efforts [75].

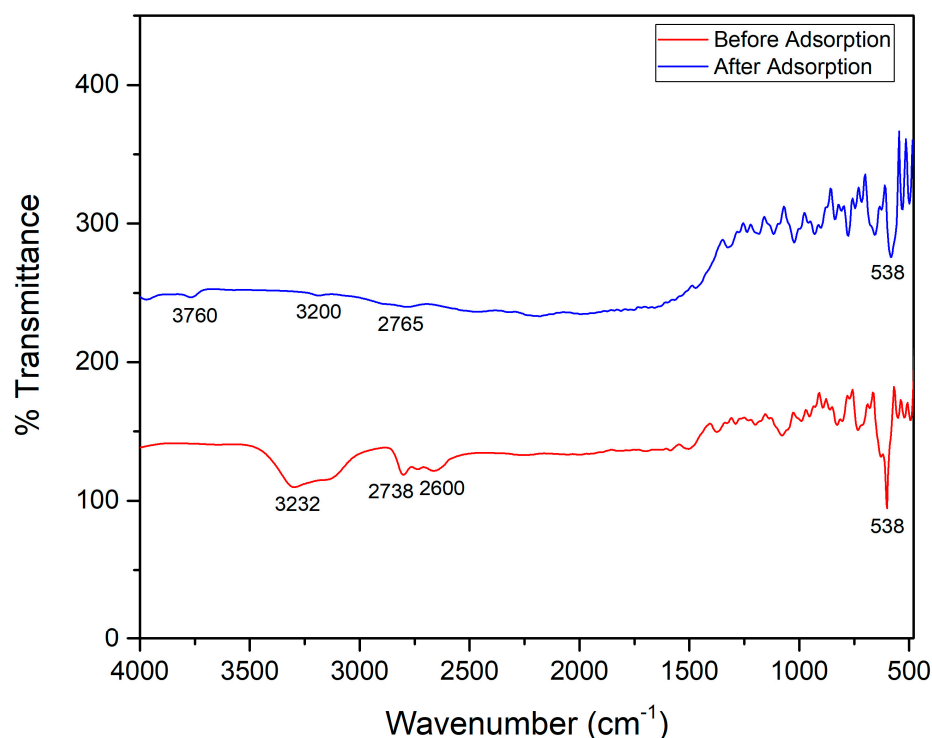


Figure 14. FTIR Characterization of ZIF-67@BNT nanocomposite Before and After Adsorption.

3.4. Predicting MO Adsorption Capacity with Machine Learning Techniques

In this study, we also used ML modeling using the four-regression model, namely GPR, SVR, ANN-based MLP, and RF, to optimize and analyze the obtained adsorption data and the descriptive analysis shown in Table 7. The MLP Regressor model with two hidden layers (65 and 42 neurons) and the ReLU activation function effectively captures non-linear patterns in regression tasks. Using the L-BFGS solver ensures faster convergence, while the adaptive learning rate optimizes performance dynamically. Further improvements can be made by fine-tuning hyperparameters, exploring alternative activation functions, and integrating feature selection techniques. The RF model used 100 estimators, a minimum of three samples for splitting nodes, a squared error threshold, and a maximum depth of six. This collection of parameter combinations was chosen to maximize the model's performance while balancing complexity and general applicability of results. SVR used a 5-degree polynomial kernel with an auto gamma and regularization parameter ($C = 1.0$). The GPR was set with a given kernel with 20 optimization restarts, a learning rate of 0.014 for regularization, and target value normalization enabled.

Table 7. Descriptive statistics for the machine learning dataset.

Index	Adsorbent Dose (mg)	Methyl Orange (mg/L)	Time (Hours)	Adsorption Capacity (mg/g)
Count	22	22	22	22
Mean	8.40	26.81	9.68	112.49
Median	5	20	5	85.41
Mode	5	10	24	-
Minimum	5	5	1	15.18
Maximum	15	100	24	241.80
Range	10	95	23	226.61
Standard deviation	4.19	22.60	10.10	73.91
Sample variance	17.58	510.82	102.13	5463.98

Metrics including coefficient of determination (R^2), root mean square error (RMSE), and mean absolute error (MAE) for both training and testing were analyzed and compared in order to assess the model fit, as seen in Table 8. The actual and predicted outcomes showed a very significant connection with the enhanced models, indicating R^2 values for training and testing as follows: GPR achieved 0.996 and 0.962, RF reached 0.955 and 0.927, while SVR had 0.998 and 0.907, and finally ANN had 0.999 and 0.872, respectively. With the highest R^2 and the lowest RMSE and MAE scores, as demonstrated in Table 8, the GPR model outperforms the other three models on testing datasets, demonstrating its superior accuracy in forecasting the MO adsorption capacity of the synthesized ZIF-67@BNT. The validation observations validate that the models generalize well to new data and underline the effectiveness of the measures taken to avoid data leaking. This suggests that, in comparison to the ANN, RF, and SVR models, the GPR model offers the greatest fit, the most precise forecasts, and the most efficiency in outcome prediction. Figure 15 provides a visual comparison of the performance of each model.

Table 8. Performance of machine learning models for the adsorption capacity by ZIF-67@BNT.

Algorithm	R^2	Testing RMSE	MAE	R^2	Training RMSE	MAE
ANN	0.872	25.582	21.143	0.999	0.833	0.553
Random forest	0.927	38.835	33.888	0.955	18.822	13.374
Support vector regression	0.907	110.956	96.385	0.998	3.997	1.476
Gaussian process regression	0.962	21.687	14.989	0.996	4.179	3.051

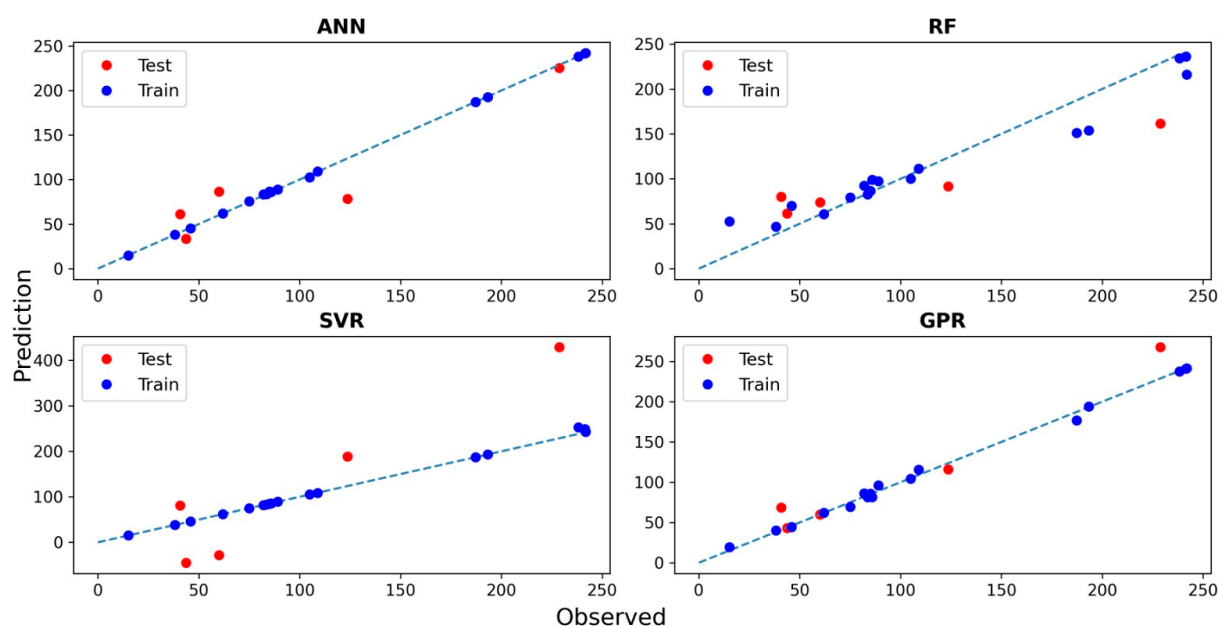


Figure 15. Actual vs. predicted machine learning models.

A Taylor diagram was used in this work for both training and testing datasets in order to identify the best model and assess its dependability. The standard deviation, root mean square error (RMSE), and correlation coefficient of the prediction models are all graphically depicted in the Taylor diagram (Figure 16). The GPR model (represented by the violet circle) is positioned closest to the observed data point in the Taylor diagram displayed in Figure 16, whereas the ANN model exhibits overfitting with high accuracy for the training dataset and comparatively moderate accuracy for the testing dataset. These assessment techniques provided convincing proof that the GPR model is the best option for adsorption capacity prediction, outperforming the independent MLP-based ANN, RF, and SVR models.

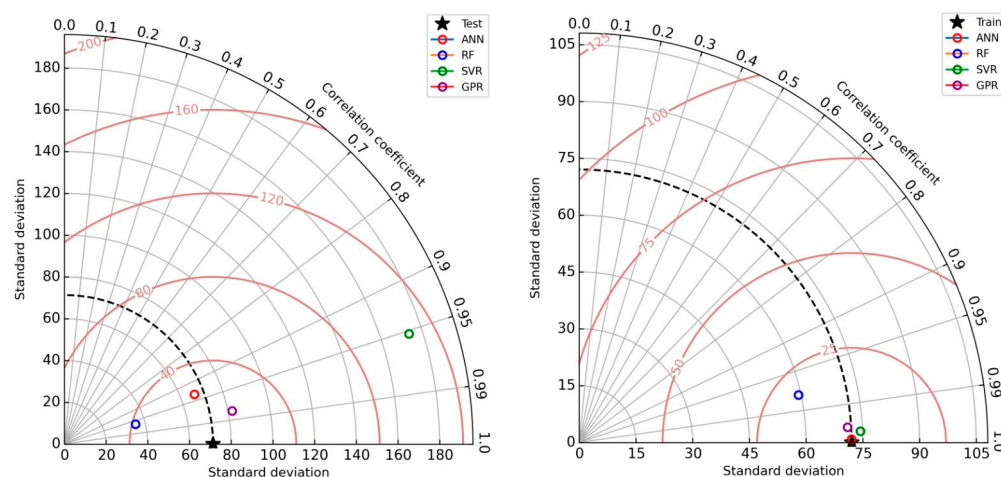


Figure 16. Taylor diagram for both testing and training.

The results suggest that machine learning algorithms offer useful insights into adsorbent efficiency for contaminant removal in water systems. Increasing the dataset used for training these models may further improve their accuracy in predicting adsorbent performance for water purification applications.

4. Conclusions

This study examined the removal of MO dye from polluted water through adsorption using a ZIF-67@Bentonite nanocomposite (ZIF-67@BNT). The synthesized ZIF-67@BNT was characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Furthermore, the batch adsorption studies demonstrated ZIF-67@BNT has a high MO adsorption capacity of 187 mg/g at an initial concentration of 30 mg/L, 5 mg dosage, and a 5 h duration. The response surface methodology (RSM)-based modeling exercise was used to optimize the adsorption process. While assessing the impact of various operational factors, the initial MO concentration, followed by ZIF-67@BNT dose, was noted to be important. Adsorption kinetics and isotherm studies were also completed. The adsorption kinetics results were best described by the Avrami model, whereas the MO adsorption isotherm data fitted well to the Redlich–Peterson (R-P) model. The ZIF-67@BNT nanocomposite ‘after adsorption analysis’ indicated multiple mechanisms facilitating MO uptake onto ZIF-67@BNT, including electrostatic and π – π interactions. Additionally, various machine learning (ML) models, such as ANN, SVR, RF, and GPR, were also utilized to predict MO adsorption onto ZIF-67@BNT nanocomposite under a varying set of conditions. In conclusion, the novel ZIF-67@BNT adsorbent can effectively treat MO-contaminated water, and both the RSM- and ML-based modeling approaches yielded good optimization results.

Author Contributions: Conceptualization, S.A.O. and M.S.V.; Methodology, K.F.; Software, K.F., S.A.O. and M.S.V.; Validation, K.F., S.A.O. and M.S.V.; Formal analysis, K.F., S.A.O. and M.S.V.; Investigation, K.F., S.A.O. and M.S.V.; Resources, S.A.O. and M.S.V.; Data curation, K.F., S.A.O. and M.S.V.; Writing—original draft, K.F., S.A.O. and M.S.V.; Writing—review & editing, K.F., S.A.O. and M.S.V.; Visualization, K.F., S.A.O. and M.S.V.; Supervision, S.A.O. and M.S.V.; Project administration, M.S.V.; Funding acquisition, M.S.V. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Interdisciplinary Research Center for Construction and Building Materials (IRC-CBM) at the King Fahd University of Petroleum & Minerals (KFUPM) under Research Grant # INCB2420.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors would like to thank the Civil and Environmental Engineering Department and the Chemical Engineering Department at King Fahd University of Petroleum & Minerals (KFUPM) for providing the lab facilities.

Conflicts of 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.

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