

**NOVEL ZIF-67@BENTONITE (ZIF-67@BNT)
NANOCOMPOSITE FOR AQUEOUS METHYL
ORANGE REMOVAL**

BY

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I dedicate this work to my parents and siblings

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TABLE OF CONTENT

ACKNOWLEDGEMENTS	V
TABLE OF CONTENT	VI
LIST OF TABLES.....	VIII
LIST OF FIGURES	IX
LIST OF ABBREVIATIONS	X
ABSTRACT.....	XI
الملخص.....	XIII
CHAPTER 1	1
INTRODUCTION.....	1
CHAPTER 2	11
LITERATURE REVIEW	11
2.1. Bio-adsorbent	12
2.2 Activated Carbon	13
2.4. Clay and Minerals.....	17
2.5. Polymer and resins.....	17
2.6. Nanoparticles.....	24
2.7. Composite	25
CHAPTER 3	43
EXPERIMENTAL METHODS AND MATERIALS USED	43
3.1. Advanced instruments, chemicals and reagents used	43
3.2. Framework of studies	43
3.3. Synthesis of ZIF-67	44
3.4. Preparation of ZIF-67@bentonite	45
3.5. Central composite design.....	46
3.6. Analytical method	48
3.7. Batch Adsorption experiment	48
3.8. Machine learning.....	50
CHAPTER 4	54
RESULTS AND DISCUSSION	54
4.1. Material Characterization.....	54

4.2. Benchmarking the performance of the ZIF-67@BNT nanocomposite with its constituents	57
4.3. Experimental design and analysis of variance.....	59
4.4. Examine the impact of process parameters using ANOVA	64
4.5. Optimization of results based on RSM model	68
4.6. Adsorption kinetics and isotherm analysis	70
4.7. Analysis after adsorption and hypothesized adsorption mechanism.....	74
4.8. Predicting adsorption capacity with machine learning techniques	79
CHAPTER 5.....	85
CONCLUSION AND RECOMMENDATIONS.....	85
5.1. Conclusion	85
5.2. Recommendations.....	86
REFERENCES.....	89
VITAE	135

LIST OF TABLES

Table 1: Different types of dyes, their sources and health issues	2
Table 2: Advantage and Disadvantage of the contaminant removal techniques.....	7
Table 3: Distribution of the class according to the adsorbent type.	11
Table 4: Summary of different Bio-adsorbent, activated carbon and Biochar adsorbent and the dye removal efficiency.....	15
Table 5: Summary of different Clay and Minerals, Polymer and resins adsorbent and the dye removal efficiency	18
Table 6: Summary of different Nanoparticles and composites adsorbent and the dye removal efficiency	26
Table 7: Adsorbent ZIF-67 and different composites of ZIF-67.....	41
Table 8: RSM modeling renders utilization of independent variables and the levels that correspond to them.	48
Table 9: The RSM based DOE and the MO adsorption results using the ZIF-67@BNT nanocomposite adsorbent.....	61
Table 10: The respective statistical analysis of variance (ANOVA) for uptake of MO by ZIF67@BNT nanocomposite.....	62
Table 11: Constants of Kinetic models for MO adsorption by ZIF67@BNT composite	71
Table 12: Model parameters of isotherm model for MO adsorption by ZIF67@BNT composite	73
Table 13: Analysis of the response surface methodology data using descriptive statistics	80
Table 14: Analysis of the response surface methodology data using descriptive statistics	82

LIST OF FIGURES

Figure 1: The chemical structure of MO.....	5
Figure 2: Mass transfer steps in adsorption process.	6
Figure 3: Presents a summary of the adsorbent categories investigated in this study, together with the possible precursors used for their preparation.	12
Figure 4: Framework for evaluating ML models, optimizing adsorption, and synthesizing composite materials.	45
Figure 5: A schematic illustration depicting the preparation process of the ZIF67@Bentonite composite material for adsorption	46
Figure 6: (A) ANN algorithm structure, (C) linear hyperplane-based SVM classification, and (C) RF algorithm architecture (D) Regressor for the Gaussian process	51
Figure 7: FTIR (A) and XRD (B) analysis of ZIF67@BNT nanocomposite, ZIF67 and BNT ...	56
Figure 8: Thermogravimetric analysis of ZIF67@BNT nanocomposite	57
Figure 9: Benchmarking the adsorption of MO onto ZIF-67@BNT with its constituents (i.e., ZIF-67 and BNT). The adsorption took place from 100 ppm MO solution containing 50 mg/mL of each adsorbent.	59
Figure 10: Model adequacies check plots (a) Plotting of actual against anticipated or predicted adsorption capacity (b) Box-Cox plot for MO removal model (c) normality distribution lot (d) plot of residuals Vs order of run	64
Figure 11: Effect of (a) ZIF67@BNT dose (b) MO concentrations (c) adsorption time (d) Interaction between the Concentration dose and adsorption capacity with Maximum time.	66
Figure 12: 3D Surface plots interaction between (a) MO Concentration vs ZIF67@BNT Dose vs adsorption capacity (b) Time vs ZIF67@BNT dose vs adsorption capacity (c) ZIF67@BNT Dose vs MO Concentration vs adsorption capacity	68
Figure 13: Result of response optimization plot and 3D surface using design expert.....	70
Figure 14: Adsorption kinetic model for MO adsorption by ZIF67@BNT composite	72
Figure 15: Adsorption Isotherm model for MO adsorption by ZIF67@BNT composite	74
Figure 16: XRD Characterization of ZIF67@BNT Composite Before and After Adsorption of MO	76
Figure 17: FTIR Characterization of ZIF67@BNT Composite Before and After Adsorption	78
Figure 18: Taylor diagram for both testing and training.....	84

LIST OF ABBREVIATIONS

MOF	:	Metal Organic Framework
ZIF-67	:	Zeolite Imidazole Framework-67
BNT	:	Bentonite
MO	:	Methyl Orange
XRD	:	X-Diffraction Spectroscopy
FTIR	:	Fourier Transform Infrared Spectroscopy
TGA	:	Thermal Gravimetric Analysis
RSM	:	Response Surface Methodology
AI	:	Artificial Intelligence
ML	:	Machine Learning

ABSTRACT

Full name: Kashif Faheem

Thesis Title: Novel ZIF-67@bentonite (ZIF-67@BNT) nanocomposite for aqueous methyl orange removal

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The indiscriminate discharge of synthetic dyes into wastewater streams poses a severe threat to environmental as well as human well-being. Among all these dyes, methyl orange (MO) attracts attention due to its widespread use and persistence in industrial effluents. In response, this study advocates for a novel strategy utilizing zeolite imidazolate framework and bentonite (ZIF67@BNT), a nanocomposite material for the removal of MO from aqueous environment. Various characterization techniques were employed such as FTIR, XRD, and TGA to verify the successful synthesis of the ZIF67@BNT adsorbent, which was subsequently utilized to investigate the adsorption of MO from an aqueous system. Batch adsorption studies demonstrated a high MO adsorption capacity 187.26 mg/g with initial MO concentration 30 ppm at maximum time 5 hours with attributed to the precise optimization of process parameters. To optimize the adsorption process and assess the impact of various operational factors, the response surface methodology (RSM) was utilized. The most important of them was found to be the initial concentration, which was followed by the lowest ZIF67@BNT dose. The process fits well with several models, according to additional research on adsorption kinetics and isotherms under ideal conditions. The Langmuir isotherm model's shows maximum adsorption capacity ($q_{\max} = 528.7$ mg/g) suggests a complex and multidimensional adsorption mechanism. The ZIF67@BNT composite after post analysis identified as there are multiple mechanisms but π - π interaction as the primary mechanism

facilitating MO uptake onto ZIF67@BNT. Additionally, various machine learning (ML) models such ANN, SVR, RF and GPR, each employing distinct algorithms, were utilized to predict MO adsorption onto ZIF67@BNT composite. A gaussian process model, demonstrated the highest accuracy ($R^2 = 0.9629$) in predicting MO uptake. This was evidenced by its superior performance across multiple evaluation metrics and Taylor diagram.

الملخص

الاستخدام العشوائي للأصباغ الصناعية في مياه الصرف الصحي يشكل تهديدًا خطيرًا للبيئة وصحة الإنسان. من بين هذه، الانتباه نظرًا لاستخدامه الواسع وثباته في المخلفات الصناعية. استجابةً لهذا التحدي (MO) الأصباغ، يجذب ميثيل أورانج وهو (ZIF67@BNT) تهدف هذه الدراسة إلى تقديم استراتيجية مبتكرة تعتمد على إطار إيميدازولات الزيوليت والبينتونيت للتحقق من TGA و XRD و FTIR من البيئة المائية. تم استخدام تقنيات تحليل مختلفة، مثل MO مادة نانوية مركبة لإزالة من محلول مائي MO والتي تم استخدامها لاحقًا لدراسة امتزاز ZIF67@BNT النجاح في تحضير مادة

قدره 30 جزء MO بلغت 187.26 ملغ/غ بتركيز أولي لـ MO أظهرت دراسات الامتزاز الدفعي قدرة عالية على امتزاز في المليون خلال مدة قصوى بلغت 5 ساعات، ويُعزى ذلك إلى الضبط الدقيق لمتغيرات العملية. ولتحسين عملية الامتزاز وتقييم هو العامل الأكثر MO وجد أن التركيز الأولي لـ (RSM) تأثير العوامل التشغيلية المختلفة، تم استخدام منهجية سطح الاستجابة وأظهرت الدراسات الإضافية على حركية الامتزاز ونماذج التوازن تحت الظروف ZIF67@BNT أهمية، يليه أدنى جرة من (qmax =) المثلى أن العملية تتوافق بشكل جيد مع العديد من النماذج. وفقًا لنموذج توازن لانجمير، فإن أقصى سعة امتزاز (ملغ/غ) تشير إلى آلية امتزاز معقدة ومتعددة الأبعاد 528.7.

كان الآلية الأساسية التي π - π تم تحديد وجود آليات متعددة، ولكن التفاعل ZIF67@BNT بعد التحليل اللاحق لمركب بالإضافة إلى ذلك، تم استخدام نماذج تعلم الآلة المختلفة مثل الشبكات العصبية ZIF67@BNT على MO تسهل امتصاص MO للتنبؤ بامتزاز (GPR) والانحدار الغاوسي (RF) والغابات العشوائية (SVR) والانحدار الداعم (ANN) الاصطناعية كما، MO في التنبؤ بامتصاص ($R^2 = 0.9629$) أظهر نموذج عملية التقدم الغاوسي أعلى دقة ZIF67@BNT على المركب. تم إثبات ذلك من خلال أدائه الفائق عبر عدة معايير تقييم ومخطط تايلور

CHAPTER 1

INTRODUCTION

It is impossible to overestimate the value of water for life support, it is abundant in all biomasses. Regrettably, human activities are diminishing the availability of clean water by introducing the pollutant in water sources [1], [2]. The ongoing industrial revolution has brought about numerous challenges for human civilization, with one of the most significant being the pollution of aquatic ecosystems by a range of synthetic organic compounds such as pesticides, dyes, poly chlorinated biphenyls, surfactants dispersing agents [2]. Organic dyes have extremely harmful effects, which lead to major human health as well as other living organisms and raise the risk of environmental issues when they are present in aquatic circumstances [3]. One such industry is the textile sector, which generates a lot of wastewaters into the environment due to its high-water consumption, particularly when processing wet materials [4]. A significant number of dyes are included in the effluent from the textile sector, which uses colorant extensively. Researchers have spent a lot of time and effort trying to mitigate the presence of these dyes in water bodies in an effort to reduce the environmental concerns associated with contaminated water [5]. Simple wastewater techniques have difficulty in eliminating complex molecules with distinct functional groups in organic dyes [6]. Typically, organic dyes have stable, resistant and aromatic molecule structure that impede their natural degradation and have harmful effects. Unfortunately, due to these reasons numerous dyes have carcinogenic or mutagenic consequences on both aquatic environments and humans, even at minimal concentrations. Industrial usage of dyes exceeds one hundred thousand types, with an average yearly production exceeding 7×10^5 tons [3]. Worldwide, the textile industry (TI) is predicted to release 2.8×10^5 tons of dyestuff into water bodies [7]. **Table 1** shows the different dyes and their health effects.

Table 1: Different types of dyes, their sources and health issues

Dyes	Chemical Structure	Characteristics	Sources	Health effect
Methyl Orange	Azo (-N=N-)	pH indicator, changes color in acidic/basic conditions, water-soluble	Textile industry, laboratory reagents, pH indicators	Cause skin and eye irritation, potential carcinogen with prolonged exposure
Methylene Blue	Thiazine	Cationic dye, commonly used in biology, water-soluble	Biological stains, textile industry, pharmaceuticals	Cause methemoglobinemia, skin irritation, and respiratory issues
Crystal Violet	Triarylmethane	Cationic dye, used in staining and microbiology, water-soluble	Textile industry, microbiology stains, printing inks	Possible carcinogen; can cause skin irritation and allergic reactions
Congo Red	Azo (-N=N-)	Anionic dye, used in textiles and as a pH indicator	Textile industry, paper printing, biological staining	Suspected carcinogen: prolonged exposure may

				cause liver and kidney damage
Rhodamine B	Xanthene	Fluorescent dye, used in biology and textiles, highly soluble in water	Textile industry, laser dyes, biological staining	May cause skin and eye irritation; toxic if ingested
Eosin Y	Xanthene	Fluorescent dye, used as a staining agent in microscopy	Ink manufacturing, biological staining, pharmaceuticals	May cause skin and eye irritation, potential mutagenic effects
Malachite Green	Triarylmethane	Cationic dye, used in microbiology and textiles, moderately soluble	Textile industry, leather dyeing, antifungal treatments	Toxic to aquatic life; potential carcinogen and irritating to skin and eyes
Basic Fuchsin	Triarylmethane	Basic dye, used in microbiology, moderate solubility	Textile industry, microbiology staining, histology	Possible carcinogen; causes skin irritation and respiratory issues

Brilliant Green	Triarylmethane	Cationic dye, used in microbiology and as an antiseptic	Textile industry, microbiology applications, antiseptics	Toxic if ingested; may cause skin and eye irritation
Acid Red 27	Azo (-N=N-)	Anionic dye, used in food coloring and textiles	Food coloring, textile dyeing, cosmetics	May cause skin irritation and allergic reactions, possible carcinogen

The methyl orange (MO) emerges as a prevalent dye within the textile sector and holds a significant position in analytical chemistry as one of the most frequently utilized indicators, because of its sharp color change occurring with a narrow spectrum. The chemical structure and health effects are displayed as follows in **Figure 1.** and **Table 1** [8]. A number of physical and chemical techniques have been used to separate and break down color molecules in wastewater discharges. Among these, a variety of techniques stand out as prominent methods for decolorizing MO dye from wastewater. These methods include coagulation-flocculation, biodegradation, solar degradation, adsorption, Fenton reaction, photocatalysis and ozone oxidation processes. **Table 2** shows the advantages and disadvantages of a variety of techniques. Amongst these methods, each characterized by specific constraints regarding design intricacies, dye removal efficacy, effectiveness, and economic viability, considered all the studies in the past have been directed towards the adsorption process as a means to eliminate the MO dye [9]. This validates the predominance of the adsorption techniques, which are increasingly commonly employed as an

attractive treatment method because of their excellent effectiveness, ease of use, and financial viability [10].

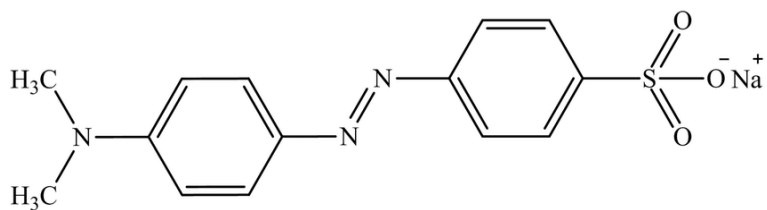


Figure 1: The chemical structure of MO.

Adsorption offers numerous advantages as a removal technique, many of which were highlighted in **Table 2**. It serves as a crucial advanced treatment method for the elimination of contaminants from water and wastewater. At the microscopic level, 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. This is followed by internal diffusion, in which the adsorbate penetrates the pores of the adsorbent, facilitating further interaction and adsorption. The final stage of the adsorption process involves the interaction between the adsorbate and the active sites of the adsorbent, leading to adsorption equilibrium. These sequential processes are illustrated in **Figure 2**. [11].

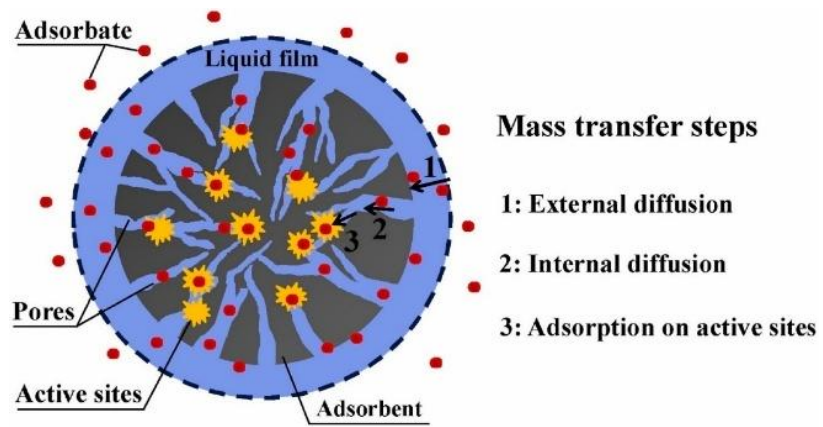


Figure 2: Mass transfer steps in adsorption process.

Table 2: Advantage and Disadvantage of the contaminant removal techniques

Technique name	Advantages	Disadvantages
Adsorption	Highly efficient for a wide range of contaminants; simple operation; cost-effective	Adsorbent regeneration or disposal required; performance decreases over time
Coagulation-Flocculation	Effective for removing suspended solids and organic matter; low cost	Produces sludge that requires disposal; efficiency depends on coagulant type
Membrane Filtration	Removes a broad spectrum of contaminants; produces high-quality water	High operational costs: membrane fouling is a major issue
Advanced Oxidation Processes (AOPs)	Highly effective in degrading organic pollutants; does not produce sludge	Expensive chemicals and high energy consumption require specialized equipment
Bioremediation	Environmentally friendly; can degrade a wide variety of contaminants	Slow process: effectiveness depends on microbial activity and environmental conditions
Electrocoagulation	High efficiency for metal and dye removal; lower chemical usage	High energy consumption: electrode passivation may occur
Ion Exchange	Selective removal of specific contaminants; regenerable resins	Expensive; requires periodic resin regeneration; limited to specific contaminants
Precipitation	Simple and cost-effective for heavy metal removal; widely used	Limited to specific contaminants; secondary pollution may occur
Photocatalysis	Utilizes renewable energy (solar); effective for organic pollutant degradation	Requires catalyst regeneration; dependent on light intensity
Activated Carbon Filtration	Highly effective for removing organic compounds, chlorine, and odor	Filters need periodic replacement; not effective for all contaminants
Solar degradation	Utilizes renewable energy; effective for breaking down organic pollutants; environmentally friendly	Dependent on sunlight availability; efficiency affected by weather conditions and catalyst stability

The widely recognized standard adsorbent is activated carbon, molecular sieves polymeric material and silica gel are extensively utilized for the effective removal of pollutants [12]. However, these standard adsorbents are characterized by their high costs, and their adsorption capacities are often limited by the absence of active sites [13]. The adsorption capacity of an

adsorbent contingent upon its inherent characteristics, such as specific surface area, the presence of functional group and the distribution of the pore size also depends on the adsorbent nature including factors such as polarity, hydrophobicity, molecular weight, solubility and size etc. as well as the solution condition (e.g., pH temperature, polarity of solvent and adsorbate concentration) [14]. Adsorbent from a wide range of materials have been utilized in adsorption separation procedures for environmental problems up to this point.

Recently, there has been a surge of interest in novel material boasting an exceptionally high surface area, which is known as Metal organic frameworks (MOFs)[15]. MOFs have various types of categories, one of the types is zeolite imidazole framework-67 in short, we called ZIF-67. It is comprised of cobalt ions coordinated with imidazole ligands. This porous material is employed as an adsorbent for the various treatments including wastewater treatment, used as catalysis because of its high specific surface area, extra cobalt supply and topological structure. Nonetheless, the performance of straight forward ZIF-67 may at times fall short for tasks such as adsorption, photocatalysis, and electrocatalysts, primarily because ZIF-67 put the restriction on the presence of functional group on its surface area [16]. Researchers have shown that ZIF can absorb anionic dyes, however their capabilities alone are insufficient. One research by Yu Li et al. claims that triethylamine (TEA) and ammonium hydroxide were used in a mixed-based method to manufacture ZIF-8 and ZIF-67. Several ZIFs were used to investigate the adsorption of three popular dyes: cationic methylene blue (MB), anionic methyl orange (MO), and neutral rhodamine B (RB). ZIF-8 outperformed ZIF-67 in RB adsorption, while both ZIF-8 and ZIF-67 produced with TEA showed considerably increased RB adsorption, exhibiting 2.3 to 3.8 times greater capacity than those without TEA. ZIF-67 crystals performed better than ZIF-8 in terms of MO adsorption; however, ZIF-67 made with TEA demonstrated less MO adsorption [17] .

The adsorption of several azo dyes on ZIF-67 in single dye systems also showed that the removal efficiencies ranked as follows in a study by Zhan-hang Zhang et al. Methyl orange > methyl red > methyl blue > Congo red [18]. Additionally, Muhammad Altaf Nazir et al., In this work, they showed zeolite imidazolate frameworks (ZIF-67) may be synthesized in-situ on layered double hydroxides (LDH) to produce porous composites that are intended to eliminate methyl orange (MO) and methylene blue (MB). According to the results, ZIF-67@CoAl-LDH has a significant methylene blue adsorption capacity (q_m , 57.24 mg g⁻¹) in comparison to LDH (15.04 mg g⁻¹) and ZIF-67 by itself (57.14 mg g⁻¹). Similarly, compared to ZIF-67 (75.58 mg g⁻¹) and LDH (32.27 mg g⁻¹), ZIF-67@CoAl-LDH shown a significant adsorption ability for methyl orange (q_m , 180.5 mg g⁻¹). Furthermore, ZIF-67 and its composite absorbed 72.3% of MO within 90 minutes and 79.9% of MB within 100 minutes [19] . Detailed literature review shown in chapter 2

Recently, there has been a spike in interest in using natural clay minerals for eliminating organic contaminants from water and wastewater. This growing stems from several factors, including the low commercial value of clay minerals, their considerable cationic exchange capacity, and their widespread availability in nature. Consequently, they are increasingly perceived as a promising alternative for environmental remediation efforts [20]. Bentonite is a versatile clay mineral with a wide range of industrial and commercial applications. It is composed of montmorillonite, a type of smectite clay mineral. Bentonite typically forms soft, easily deformable masses when mixed with water, and it exhibits remarkable swelling properties due to its high-cation exchange capacity and ability to remove the pollutant from the water and wastewater. The structurally negative charge seen in the clay minerals is a consequence of isomorphic replacement of cations in their crystal lattice. These surface ions play a pivotal role in facilitating the adsorption process. Comprising constituents such as SiO₂, Al₂O₃, and various 5 oxides including those of Mg, Ca, and K, clay

minerals are believed to possess components that augment their adsorptive properties [21]. The use of surface modification techniques to improve the pollutant removal capabilities of clay minerals in wastewater treatment applications has been increasingly common in recent years [16].

In this study, we explore the use of the ‘zeolitic imidazolate framework @ bentonite (ZIF-67@BNT)’ nanocomposite for methyl orange (MO) removal. The ZIF-67@BNT nanocomposite is characterized using various techniques, including XRD, FTIR, and TGA, before assessing its adsorption capacity for MO. Furthermore, optimizing operating parameters is crucial for achieving maximum efficiency in chemical reactions. To this end, Response Surface Methodology (RSM) and Artificial Intelligence/Machine Learning (AI/ML) techniques are employed for process optimization. RSM modeling facilitates the statistical design of experiments tailored for multi-variable systems by systematically adjusting process components. The key advantage of these methods is their ability to generate comprehensive insights into the optimization of critical parameters, allowing for the simultaneous evaluation of their effects.

Thus, this study focuses on MO removal using the ZIF-67@BNT nanocomposite, coupled with process modeling and optimization through RSM and ML-based techniques.

CHAPTER 2

LITERATURE REVIEW

The increasing concern over water pollution has led to extensive research on efficient and sustainable wastewater treatment technologies. Among various pollutants, synthetic dyes, such as methyl orange (MO), pose a significant environmental threat due to their toxicity and persistence. This chapter provides a comprehensive review of existing literature on dye removal, focusing on the application of different adsorbents, for adsorption. The literature review consists of application of different adsorbents

The adsorbents have been classified into seven distinct categories based on their chemical composition or structural makeup for better understanding and analysis. These categories/classes are as follows in **Table 3**. There are various precursors utilized for the development of different adsorbents and the short description shown in **Figure 3**. Most of the precursors are inexpensive, easy to develop and readily available except the polymer and the nanoparticle precursors. The supply of precursors from agricultural residues may be constrained by the seasonal nature of farming and processing or by the suitability of the region's climate for cultivating the original crops [22].

Table 3: Distribution of the class according to the adsorbent type.

Category/Class	Adsorbent type
I	Bio-adsorbent
II	Activate carbon
III	Biochar
IV	Clays and Minerals
V	Polymer and resins
VI	Nanoparticles
VII	Composite



Figure 3: Presents a summary of the adsorbent categories investigated in this study, together with the possible precursors used for their preparation.

2.1. Bio-adsorbent

Biosorbents are biologically derived materials that undergo thermochemical decomposition and are utilized for pollutant sequestration from the environment via adsorption [23]. These materials are widely favored as adsorbents due to their low cost and abundant availability. Additionally,

biosorbents are advantageous because they do not generate intermediate products, and a diverse range of materials can serve this purpose [24]. In one study by El-Sayed and El-Sayed, it reports that Bio-adsorbent can be categorized into four major categories and all of them are employed for the removal of MO from aqueous solution. These categories include living biomass which consist of (1) fungi, (2) Agriculture waste, (3) dead biomass and (4) industrial solid waste [25], [26], [27], [28], [29], [30], [31], [32]. Various mechanisms involve in removal of the dyes through Bio-adsorbent which include physical and chemical sorption such as van der Waals force or ion exchange electrostatic interaction, micro-precipitation, complexation/chelation respectively [33]. The effectiveness of different biosorbents, both modified and unmodified, in the removal of methyl orange (MO) from solutions is summarized in **Table 4**.

2.2 Activated Carbon

Activated carbon (AC) materials are derived from a wide variety of carbon-rich sources such as lignite, peat, charcoal, wood, coal, and other plant-based residues, which undergo physical and chemical activation processes to significantly enhance their surface area and pore structure [34]. These modifications are intended to increase the material's adsorption efficiency. Typically, AC is synthesized at high temperatures often above 700 °C using activating agents like steam or flue gas to develop its porous architecture [35]. Owing to its high surface area, well-developed porosity, thermal stability, surface functionality, and chemical inertness, activated carbon has been extensively employed in the adsorption of methyl orange (MO) and other dyes from aqueous media [36]. Its remarkable adsorption performance is largely attributed to the presence of active sites and free valences that facilitate strong interactions with dye molecules. AC is widely available in two main formats: powdered activated carbon (PAC) and granulated activated carbon (GAC), each suited for specific treatment processes. Various raw materials such as coconut shells, coal, date

pits, eggshells, wood, and lignin-based compounds have been explored for the production of AC [37] [38]. Numerous studies have evaluated the adsorption efficiency of both modified and unmodified forms of activated carbon for MO removal, and a summary of their performance is detailed in **Table 4**.

2.3. Biochar

Biochar is a carbon-rich material derived from the thermal decomposition of biomass through pyrolysis, gasification, or carbonization under limited or no oxygen conditions [39]. It has gained significant attention as an adsorbent due to its porous structure, large surface area, and the presence of various functional groups that facilitate pollutant removal [40]. Compared to activated carbon, Biochar is produced at lower temperatures, typically below 700°C, resulting in a material with a lower surface area but a higher concentration of oxygen-containing functional groups that enhance adsorption efficiency. Different biomass sources, including agricultural residues, forestry waste, and animal manure [41], [42], [43], have been utilized for Biochar production to remove methyl orange (MO) from aqueous solutions. **Table 4** presents different Biochar's used for MO mitigation, arranged in decreasing order of adsorption capacity.

Table 4: Summary of different Bio-adsorbent, activated carbon and Biochar adsorbent and the dye removal efficiency

Adsorbent Name	Method of qmax determination	Adsorbent type	pH	SSA (m ² /g)	Temp (°C)	qmax (mg/g)	Highest RE %	Ref.
Biochar from cellulose	Langmuir	Biochar	-	12.87	-	166.7	-	[44]
Biochar from hazelnut shell	Langmuir	Biochar	-	23.01	-	181.8	-	[44]
Pomelo peel-derived porous carbon	Langmuir	AC	3	1892	50	680.3	-	[45]
AC from aloe vera	Langmuir	Activated Carbon	3	-	25	196.1	-	[82]
AC from coffee waste	Dubinin-Radushkevich	AC	3	-	30	1017	-	[46]
Biochar from glucose	Langmuir	Biochar	-	5.44	-	147.1	-	[44]
Coffee waste/cetyltrimethyl ammonium bromide	Langmuir	Bio-adsorbent	3.5	-	25	58.82	-	[47]
Coffee waste/cetylpyridinium chloride	Langmuir	Bio-adsorbent	3.5	-	25	62.5	-	[47]
Polyethyleneimine-modified persimmon tannin	Langmuir	Bio-adsorbent	4	8.13	50	877.2	97.6	[48]

Epiphyton biofilm	-	Bio-adsorbent	7	-	30	-	99.8	[49]
AC from coconut shell	Experiments	AC	-	1640	25	3	100	[50]
Aminated pumpkin seed powder	Langmuir	Bio-adsorbent	3	-	45	200.3	-	[51]
AC from waste tire rubber	Langmuir	AC	3.6	-	23	588	80	[52]
Protonated amine-modified hydrochar	Langmuir	Biochar	-	11.76	-	909.1	-	[53]
AC from sugarcane mills boiler residue	Langmuir	AC	5	1073	25	161.8	-	[54]
AC from popcorn	Experiments	AC	-	3291	25	969	48.5	[55]
Biochar from chicken manure	Langmuir	Biochar	6.5	-	45	41.49	100	[56]
Sulfactant-modified pineapple leaf	Langmuir	Bio-adsorbent	3	-	-	47.62	-	[57]
Activated Biochar from pomelo peel waste	Langmuir	Biochar	3	75.32	25	163.1	99.9	[58]
Rayon-based AC fibers	Langmuir	AC	6	2126	-	7000	-	[59]

2.4. Clay and Minerals

Clays and minerals are widely utilized in environmental applications due to their unique physicochemical properties. Clays, a group of microcrystalline secondary minerals primarily composed of phyllosilicates, exhibit a layered structure with varying degrees of hydration[60]. These materials are not only abundant and cost-effective but also serve as highly efficient adsorbents in water treatment processes [61]. Their high surface area, cation exchange capacity, and ability to retain water within interlayer spaces make them ideal for pollutant removal [62]. Common clay minerals employed for methyl orange (MO) as well as other dyes adsorption include bentonite [63], montmorillonite [64], and kaolin [65], each offering distinct adsorption mechanisms and efficiencies. Additionally, zeolites, which are crystalline aluminosilicates with a porous framework, have been extensively studied for their ability to remove contaminants through ion exchange and molecular sieving [66]. The adsorption capacities of various clays and minerals used for methyl orange (MO) removal from solutions, are presented in **Table 5**.

2.5. Polymer and resins

Polymers and resins are versatile materials composed of macromolecules formed by repeating monomeric units, making them highly adaptable for various applications, including water treatment [67]. Polymeric adsorbents can be utilized in their natural, synthetic, or chemically modified forms, with their adsorption efficiency largely determined by the presence of functional groups within their structure [68]. These materials can be modified through cross-linking, which interconnects polymer chains to enhance stability, or grafting, which introduces new functional groups to increase active adsorption sites [69]. Compared to conventional adsorbents, polymeric materials offer advantages such as ease of processing, mechanical flexibility, and simple regeneration methods. Polymeric adsorbents can be broadly categorized as natural or synthetic

[70]. Natural polymers employed for methyl orange (MO) removal include polysaccharides such as chitosan, cellulose, starch, alginate, and cyclodextrin, while synthetic resins with tailored functionalization have also demonstrated high adsorption efficiency [71], [72], [73], [74]. The adsorption capacities of various polymers and resins for methyl orange removal are presented **Table 5**.

Table 5: Summary of different Clay and Minerals, Polymer and resins adsorbent and the dye removal efficiency

Adsorbent Name	Method of q _{max} determination	Adsorbent type	pH	SSA (m ² /g)	Temp (°C)	Q _{max} (mg/g)	Highest RE %	Ref.
Tungstosilicic acid/zeolites	-	Clay and Minerals	2.5	362	-	-	85	[75]
MgAl LDH	Experiments	Clay and Minerals	-	-	25	197.6	-	[76]
Ionic-liquid-crafted zeolite	Langmuir	Polymer and resins	-	-	-	38	-	[77]
Dimeric surfactant-modified Na montmorillonite	Langmuir	Clay and Minerals	3	10.72	20	313.3	-	[78]
Epibromohydrin-modified polyamine resin	Langmuir	Polymer and resins	-	-	-	358.3	99	[79]

CuAl LDH	-	Clay and Minerals	-	-	40	-	100	[80]
Poly(N-isopropylacrylamide)-based ionic hydrogels	Langmuir	Polymer and resins	-	-	25	64.8	-	[81]
Chitosan microspheres	Langmuir	Polymer and resins	3.1	-	-	207	-	[82]
CoAl/Cl LDH	Langmuir	Clay and Minerals	7	19.7	20	827.5	98.3	[83]
NiCO-LDH	Langmuir	Clay and Minerals	-	-	-	497	98	[84]
ZIF-67	Experiments	Polymer and resins	-	989	-	16.3	-	[85]
Polyaniline powder	Langmuir	Polymer and resins	7	11.8	29	147	-	[86]
Bimorphic Mg-Al mixed metal oxides	Langmuir	Clay and Minerals	-	-	25	182.8	99.7	[87]
UiO-66 MOF	Langmuir	Polymer and resins	12	1276	25	4545	-	[88]
3D scaffolds from thiol group-modified chitosan	Langmuir	Polymer and resins	7	-	-	305	90	[89]

Palygorskite	Langmuir	Clay and Minerals	7	-	25	109.4	-	[90]
Gemini surfactant-modified Na-montmorillonite	Langmuir	Clay and Minerals	300	6.7	-	282.4	-	[91]
Goethite	Langmuir	Clay and Minerals	3	4.37	25	55	-	[92]
Chitosan Schiff bases	Experiments	Polymer and resins	8	-	80	20	-	[93]
Mesoporous ZSM-5 zeolite	Langmuir	Polymer and resins	1	-	30	25	94.3	[94]
Uncalcined glycerol-modified nanocrystalline MgAl LDH	Langmuir	Clay and Minerals	4.5	71.4	25	443.5	93	[95]
Organosilica	-	Clay and Minerals	3	10	-	1708	-	[96]
Chitosan beads	Langmuir	Polymer and resins	3	10.81	25	73	-	[92]
Organic matter-rich clays from Egypt	Langmuir	Clay and Minerals	2	59.14	25	41.67	96.4	[97]
Cellulose from <i>Stipa tenacissima</i> L	Langmuir	Polymer and resins	3.7	-	25	16.94	-	[98]

Trimeric surfactant- modified Na montmorillonite	Langmuir	Clay and Minerals	3	7.75	20	368.6	-	[78]
Immobilised polyaniline	Langmuir	Polymer and resins	6.5	8.5	30	77.5	97.6	[99]
Flower-like NiAl LDH	Langmuir	Clay and Minerals	3	133	25	500.6	-	[100]
Biofunctional BiOCl ₃ I solid	Experiments	Clay and Minerals	-	29.34	-	5	100	[101]
Zirconium MOF (UiO-66)	-	Polymer and resins	2	-	25	-	31	[102]
Cadmium MOFs	-	Polymer and resins	-	-	-	-	39	[103]
Multifunctional Cd(II) MOFs	-	Polymer and resins	-	517	-	-	100	[104]
Amine-modified PIM-1 fibrous membrane	Langmuir	Polymer and resins	-	15	-	312.5	-	[105]
Polyvinylene fluoride/PEDOT mats	Langmuir	Polymer and resins	3	5.691	20	146.2	75	[106]
Salecan polyssacharides	Experiments	Polymer and resins	-	-	-	56.2	93	[107]

Protonated cross-linked chitosan	Langmuir	Polymer and resins	4.5	-	45	180.2	-	[108]
CoFe LDH	Langmuir	Clay and Minerals	7.5	108.8	25	1290	80	[109]
Cd-zeolite imidazolate framework (Cd-ZIF-8)	Langmuir	Clay and Minerals	2	1281	50	145.4	92	[110]
Cd-based MOF	Langmuir	Polymer and resins	7	384	25	166.7	-	[111]
Amino groups functionalised UiO-66 MOF	Experiments	Polymer and resins	5	9.527	25	148.4	87.4	[112]
Organo vermiculite	Langmuir	Clay and Minerals	6.9	-	55	157	-	[113]
Cetyltrimethylammonium bromide/H ₂ O ₂ -clay	Dubinin-Radushkevich	Clay and Minerals	3	21.16	25	268.7	98	[114]
Polyethyleneimine-functionalised graphene aerogel	Langmuir	Polymer and resins	3	-	-	3059	-	[115]
Fly ash	-	Clay and Minerals	8.5	1.18	25	-	66	[116]

Calcinated organic matter-rich clays from Egypt	Langmuir	Clay and Minerals	2	48.32	25	34.48	92.9	
Calcined glycerol-modified nanocrystallined MgAl LDH	Langmuir	Clay and Minerals	4.5	170.3	25	1062	95	[95]
CuMgAl LDH	Langmuir	Clay and Minerals	7	60	25	123.5	98	[80]
NiFe LDH	Langmuir	Clay and Minerals	-	17.85	-	205.8	96.5	[117]
MnOx-decorated MgAl LDH	Langmuir	Clay and Minerals	-	-	30	555.6	90.5	[118]
Zeolite imidazolate framework-8	Langmuir	Polymer and resins	-	1007	-	18	-	[119]
HDPy+-clay	Langmuir	Clay and Minerals	3	94.93	-	227.3	-	[120]
MOF-derived nanoporous carbon	Langmuir	Polymer and resins	6	1731	-	872	-	[121]
Viologen-based β -cyclodextrin polymer	Langmuir	Polymer and resins	-	22	-	370	77	[122]

Starch-modified ZnMgAl LDH	Langmuir	Clay and Minerals	-	76.8	25	1555	-	[123]
Zeolitic imidazolate framework-8 (ZIF-8)	Experiments	Polymer and resins	-	1007	-	9.2	-	[85]
N-acyl thiolated chitosan	Langmuir	Polymer and resins	7	10	26	588.2	88	[124]
Blast furnace slag acid-alkaline precipitate	Langmuir	Clay and Minerals	13	3.45	25	167	100	[125]
Hydrotalcite-like modified bentonite	Langmuir	Clay and Minerals	6.5	83.24	24	333.3	-	[126]
Stone-like NiAl LDH	Langmuir	Clay and Minerals	3	90	25	292	-	[100]
Poly-melamine formaldehyde	Experiments	Polymer and resins	-	979.9	-	81.2	-	[127]
Acid promoted UiO-66	Experiments	Polymer and resins	-	1090	-	84.8	-	[128]

2.6. Nanoparticles

Nanoparticles are ultrafine materials with at least one dimension measuring less than 100 nm [129], offering exceptional surface reactivity and high surface-area-to-volume ratios. These unique properties make nanoparticles highly effective for environmental applications, particularly in the adsorption of dyes and other pollutants from aqueous solutions [130]. Depending on their

composition, nanoparticles can be organic, inorganic, or hybrid, each exhibiting distinct adsorption mechanisms such as electrostatic interactions, hydrogen bonding, or surface complexation. Their small size, high functional group density, and tunable surface properties allow for enhanced pollutant removal efficiency [131]. Various nanoparticles, including metal oxides, carbon-based nanomaterials, and functionalized nanostructures, have been explored for methyl orange (MO) removal, often outperforming conventional adsorbents [132][133]. The adsorption capacities of different nanoparticles used for MO removal are presented in **Table 6**.

2.7. Composite

The search for more effective and economical adsorbents has led to the development of a wide variety of hybrid adsorbents for the removal of environmental contaminants [134]. Hybrid adsorbents combine two or more distinct materials, leveraging their complementary properties to enhance adsorption efficiency, stability, and selectivity. These materials can integrate organic, inorganic, or polymeric components, optimizing their performance for specific applications [135], [136]. Various hybrid adsorbents have been investigated for methyl orange (MO) removal, offering improved pollutant capture through synergistic interactions. The adsorption capacities of different hybrid adsorbents used for MO removal are detailed in **Table 6**.

Table 6: Summary of different Nanoparticles and composites adsorbent and the dye removal efficiency

Adsorbent Name	Method of q _{max} determination	adsorbent type	Adsorbent Category	pH	SSA (m ² /g)	Temp (°C)	q _{max} (mg/g)	Highest RE%	Ref.
Reduced graphene oxide/NiCr–CO ₃ LDH	Langmuir	composite	C (IV-VI)	–	–	–	312.5	–	[137]
CuO nanoflakes	Langmuir	nanoparticles	-	2	69.27	–	158.7	93.2	[138]
Fe ₃ O ₄ /poly(styrene sulfonate)/ZIF-67	Experiments	composite	C (V-VI)	8	1042	25	738	92	[139]
Cu ₂ O NPs	–	nanoparticles	-	–	6.15	–	–	100	[140]
Chitosan/diatomitic	Langmuir	composite	C (IV-V)	5	–	20	35.12	88.4	[141]
Fe-based MOF/graphene oxide	–	composite	C (V-VI)	3	1602	30	–	98	[142]
Mesoporous carbon nanofibers	Langmuir	nanoparticles	-	7	392.3	45	126.6	–	[143]
Chitosan/PVA/zeolite electrospun membrane	Langmuir	composite	C (V-VI-VII)	–	–	–	153	–	[144]

Chitosan/ β -cyclodextrin polymer	Langmuir	composite	C (V-VI)	5	–	25	392	90.7	[145]
Magnetic hierarchical porous carbon sphere	Langmuir	nanoparticles	-	–	603	30	1523	99.9	[146]
Date palm ash/MgAl-LDH	Langmuir	composite	C (III-IV)	3	140.7	25	243	93	[147]
Zn–Al LDH/SiO ₂	Langmuir	composite	C (IV-VI)	–	–	–	266.5	88.9	[148]
Ag–N–ZnO/coconut husk AC	Experiments	composite	C (II-VI)	–	472	–	90.42	98.8	[149]
CuO NPs	Langmuir	nanoparticles	-	6.5	6.188	60	217.4	–	[150]
AC/polytetrafluoroethylene	Experiments	composite	C (II-V)	–	700	25	176	–	[151]
Biochar from waste walnut shells/TiO ₂	–	composite	C (III-VI)	–	66.06	–	–	96.9	[152]
Chitosan/bentonite	Langmuir	composite	C (IV-V)	3	–	25	136.8	99.7	[153]
Fe ₃ O ₄ /polydopamine	Experiments	composite	C (V-VI)	–	–	–	2.07	–	[154]

Fe3O4/graphene oxide nanocomposite	Langmuir	composite	C (VI- VII)	6	–	–	714.3	–	[155]
Amine/Fe3O4- resin	Langmuir	composite	C (V- VI)	5.5	–	45	416.7	–	[156]
Chitosan/polyvinyl alcohol (PVA)/zeolite	–	composite	C (V- V-V)	–	–	–	–	94	[157]
TiO2/pure calcium silicate	–	composite	C (IV- VI)	–	126	–	–	60	[158]
Starch/ascorbic acid-modified MWCNTs	Langmuir	composite	C (I- VI)	2	–	–	11.11	70	[159]
Chitosan/Al2O3/Fe 3O4	Experiments	composite	C (V- VI-VI)	6	21.8 7	25	419	96	[160]
Carbon nanostructure from Bengal gram bean husk	Langmuir	nanoparticl es	-	–	171 0	–	418.4	–	[161]
Silica daisogel/vinylbenz yl N,N-diethyl 2- hydroxyethyl ammonium moieties	Langmuir	composite	C (IV- V)	5.5	–	25	180.3	100	[162]

Amorphous CNTs	Langmuir	nanoparticles	-	–	–	–	21.39	95	[163]
Reduced graphene oxide	Langmuir	nanoparticles	-	7	–	–	243.9	–	[164]
Chitosan/H ₂ O ₂ activated anthracite	Langmuir	composite	C (IV-V)	3	–	25	297.3	98.8	[165]
Co ₃ O ₄ nanocube/polyaniline	Experiments	composite	C (V-VI)	7	43	25	107	94	[166]
Polyaniline nano-adsorbent	Langmuir	nanoparticles	-	10	10.44	65	75.9	98.2	[167]
Chitosan/graphene nanoplates	Langmuir	composite	C (V-VI)	3	–	25	230.9	96	[168]
Fe ₃ O ₄ /polypyrrole	Langmuir	composite	C (V-VI)	–	–	25	149.5	–	[169]
Fe ₂ O ₃ /Biochar	Langmuir	composite	C (III-VI)	2.86	15.3	25	16.05	100	[170]
Fe ₂ O ₃ /mesoporous carbon	Langmuir	composite	C (VI-VI)	3	69	20	26.5		[171]
β-Ni(OH) ₂ nanostructures	Experiments	nanoparticles	-	–	–	–	48.14	20.6	[172]
Mesoporous silica NPs	–	nanoparticles	-	3	–	70	–	91.1	[173]
NDA88 MOF/Cu	Langmuir	composite	C (V-VI)	–	370.4	–	398.8	–	[174]

Nitrogen-doped porous carbon	Langmuir	nanoparticles	-	7.1	1259	20	337.8	–	[175]
Polyaniline/AC	Langmuir	composite	C (B-E)	6.5	36	–	285	70	[176]
Bi ₂ O ₃ /TiO ₂ /powdered AC	Experiments	composite	C (II–VI)	–	83.3	–	16.33	–	[177]
Graphene oxide/NiFe LDH	–	composite	C (IV–VI)	–	145	–	438	–	[178]
Carbon dots/ZnFe ₂ O ₄	Langmuir	composite	C (VI–VI)	5	161.8	20	181.2	–	[179]
AgGaO ₂ nanocomposites	Experiments	composite	C (VI–VI)	7.5	23.35	25	11.39	–	[180]
Chitosan/PVA/TiO ₂	Langmuir	composite	C (V–V–VI)	–	–	–	425	–	[181]
Fe NPs/SiO ₂ –NH ₂ /glycerol	Experiments	composite	C (I–IV–VI)	3	171	25	3.02	100	[182]
Co ₃ O ₄ NPs	Langmuir	nanoparticles	-	6	–	–	46.08	–	[183]
Chitosan/PVA/TiO ₂ nanofiber	Langmuir	composite	C (V–V–VI)	–	–	–	314	94	[184]
Porous ZnO spheres	–	nanoparticles	-	–	114.6	–	–	96.3	[185]
p-CNTs/N,N-diethylethanol	Langmuir	nanoparticles	-	2	169.7	–	263.1	–	[186]

ammonium chloride									
Manganese ferrite/hausmannite NP	Langmuir	composite	C (VI– VI)	2	100. 6	25	303	97.4	[187]
Nitrogen-doped TiO ₂	Langmuir	nanoparticl es	-	–	232. 4	20.2	14.1	–	[188]
CoFe ₂ O ₃ /MgAl- hydrotalcite	Langmuir	composite	C (IV- VI)	6	–	25	1220	–	[189]
NiO NPs	Langmuir	nanoparticl es	-	8	78.3 7	60	370.4	–	[150]
Calcium ferrite/zirconia	Langmuir	composite	C (VI– VI)	2	95.3 2	30	370.4	98.9	[190]
Graphene/β- cyclodextrin	Experiments	composite	C (V- VI)	–	–	–	328.2	–	[191]
ZIF-67 nanostructure	Langmuir	nanoparticl es	-	–	593. 6	–	75.59	70.2	[192]
Chitosan/polyanilin e/copper(II) oxide	–	composite	C (V- V-VI)	4	–	–	–	98.9	[193]
Polyaniline/glass plates	Langmuir	composite	C (V- V)	7	3.7	29	93	100	[86]
ZnO/CuO	Experiments	composite	C (VI– VI)	–	–	25	341	93	[194]
Chitosan/chitosan- sodium zeolites	Langmuir	composite	C (V- V)	8	–	30	909	95.5	[195]

TiO ₂ /aluminosilicate zeolite (ZSM-5)	–	composite	C (V-VI)	7.5	1151		–	99.6	[182]
Fe NPs/SiO ₂ –NH ₂ /black tea extract	Experiments	composite	C (I-IV-VI)	3	89.1	25	2.97	100	[365]
Non-functionalised CNTs (p-CNTs)	Langmuir	nanoparticles	-	2	123.5	–	110.4	–	[186]
Starch/NiFe LDH	Langmuir	composite	C (I-IV)	3	–	25	387.6	99	[182]
Chitosan/rectorite/CNTs	Langmuir	composite	C (IV-V-VI)	5	8.303		50.75	80.5	[196]
MgAL-LDHs nanosheets	Experiments	nanoparticles	-	–	65.94	–	229.8	–	[[197]
Activated organic-bentonite/sodium alginate	Langmuir	composite	C (IV-V)	11	80	23	141.2	–	[198]
Chitosan/ethylene glycol diglycidyl ether beads	Langmuir	composite	C (V-V)	–	–	30	112.4	–	[199]
Magnetic pressler/chitosan/Fe ₃ O ₄	Langmuir	composite	C (V-VI-VI)	6	–	45	88.5	97	[200]
Scoria-Ni/TiO ₂ NPs	–	nanoparticles	-	7	–	–	–	95.9	[201]

Chitosan/ethylene glycol diglycidyl ether biofilm	Langmuir	composite	C (V-V)	3	0.82	30	131.2	–	[200]
Flower-like MoSe ₂ microspheres	Langmuir	nanoparticles	-	–	25	–	36.91	–	[202]
Mesoporous MCM-41/microfiltration membrane	Langmuir	nanoparticles	-	4	1451	25	151.5	99	[203]
Amino-functionalised magnetic multi-MOF	Langmuir	nanoparticles	-	6	598	50	355.8	99.6	[204]
Nitrogen-doped nanoporous carbon	Langmuir	nanoparticles	-	6	1152	25	222.2	95.2	[205]
Cobalt hydroxide NPs	Langmuir	nanoparticles	-	5	–	–	234	87	[206]
α -Fe ₂ O ₃ NPs	Langmuir	nanoparticles	-	2	–	25	28.9	90	[140]
Cu ₂ O particles	Langmuir	nanoparticles	-	–	1.13	–	96.42	–	[207]
Nitrogen-doped mesoporous carbon	Langmuir	nanoparticles	-	–	968	25	202.4	–	[208]

Magnetic pectin/chlorella vulgaris	Langmuir	composite	C (I-VI)	–	–	30	109.1	–	[209]
Fe ₂ O ₃ /AC	Langmuir	composite	C (II-VI)	3	1110	20	362	80	[171]
NaX/MgO–TiO ₂ zeolite	Langmuir	composite	C (V-VI)	6.5	–	45	53.76	95	[210]
MnO ₂ deposited diatomic nanosheets	Langmuir	nanoparticles	-	3	–	25	420.2	95	[[211]
Chitosan/PVA/Na-titanate/TiO ₂	Experiments	composite	C (V-V-VI)	–	–	–	6.86	99.9	[212]
Polyanilined-based nanoadsorbent	Langmuir	nanoparticles	-	6	10.34	45	75.9	97	[213]
Spent tea leaves/polyethylene imine	Langmuir	composite	C (I-V)	3	2.33	25	62.11	91.1	[214]
Copper sulphide NPs/AC	Langmuir	composite	C (II-VI)	5	1286	25	122	99	[215]
pTSA-PANI/PLLA nanofiber mat	Langmuir	nanoparticles	-	6	1276	25	333	70	[216]
Bismuth nitrate NP	Langmuir	nanoparticles	-	–	5.29	–	730	97	[217]

LDH/Fe ₃ O ₄ /polyvinyl alcohol	Langmuir	composite	C (I-VI)	6	87	25	19.59	97	[218]
Immobilised chitosan/montmorillonite	Langmuir	composite	C (IV-V)	6.3	4.38	30	154.4	94.6	[20]
Pisum sativum peels/Fe ₃ O ₄ NPs	–	composite	C (I-VI)	6	17.6	–	–	96.2	[219]
γ -Fe ₂ O ₃ /2C nanocomposites	Langmuir	composite	C (VI-VI)	4.8	394.1	25	72.68	99.9	[220]
Mesoporous MCM-41	Langmuir	nanoparticles	-	2	1451	20	1000	92	[221]
TiO ₂ /slag-made calcium silicate	–	composite	C (IV-VI)	–	149	–	–	43.7	[158]
UiO-66/nanocellulose aerogels	Experiments	composite	C (VI-VI)	–	826	–	71.7	–	[222]
Chitosan/Co-MCM-15	–	composite	C (V-VI)	8	–	–	–	76	[223]
Palladium nanocubes/MWCNTs	–	nanoparticles	-	–	–	–	–	99.3	[224]
Fe ₂ O ₃ /polypeptidylated hemoglobin	Langmuir	composite	C (V-VI)		–	25	15.2	–	[225]

Nickel hydroxide nanocatalyst	–	nanoparticles	-	–	87	30	–	80	[226]
NiFe ₂ O ₄ /LDH composite	–	composite	C (IV-VI)	–	–	25	–	94.3	[227]
Porous Al-doped ZnO nanosheets	Langmuir	nanoparticles	-	7	34.3	25	74.57	99.3	[228]
Magnetic lignin-based CNPs	Langmuir	nanoparticles	-	5	82.8	20	113	90.7	[259]
Amorphous CNTs	Langmuir	nanoparticles	-	3		25	21.51	99.9	[229]
Graphene/Fe ₃ O ₄	–	composite	C (VI-VI)	–	–	–	–	99.2	[230]
CuO nanostructures	–	nanoparticles	-	–	24.1	65	–	100	[231]
Ni NPs/porous carbon-carbon nanotubes	Langmuir	composite	C (VI-VI)	–	999	–	274	–	[232]
Ni–Co–S/hexadecyltrimethyl ammonium bromide	Langmuir	composite	C (V-VI)	–	12.73	25	2355	99	[233]
Cellulose nanofiber/chitosan	Langmuir	composite	C (V-VI)	5	–	25	655.2	96.3	[234]
ZnO/polyaniline	Langmuir	composite	C (V-VI)	4	63.17	–	240.8	99.1	[235]

MnO ₂ deposited diatomic nanowires	Langmuir	nanoparticles	-	3	–	25	324.7	99	[211]
Chitosan/PVA electrospun nanofiber	Langmuir	composite	C (V-VI)	–	–	–	183	–	[236]
Graphene oxide	Langmuir	nanoparticles	-	3	1330	25	16.83	–	[237]
ZIF-67/CoAl-LDH	Langmuir	composite	C (IV-V)	–	274.3	–	180.5	72.3	[192]
Nitrilotriacetic acid/ β - cyclodextrin/chitosan	Sips	composite	C (V-V)	–	–	–	132.5	94	[238]
Cellulose acetate/polyurethane	Langmuir	composite	C (V-V)	–	–	–	0.185	25.5	[239]
Chitosan/Fe(OH) ₃ beads	Langmuir	composite	C (IV-V)	3	10.2	–	314.5	91.1	[240]
Nanofibrillated cellulose-based cryogel/N-doped TiO ₂	Langmuir	composite	C (I-V-VI)	–	–	20	17.6	99	[241]
Fe ₃ O ₄ /CNTs	Experiments	composite	C (VI-VI)	–	–	–	2.76	–	[154]

Sulfamic acid/Cr-MIL-101	Langmuir	nanoparticles	-	2	944	25	291.5	70	[10]
Polydopamine/polyethyleneimine/graphene oxide	Langmuir	composite	C (V-VI)	–	–	40	237.5	–	[242]
Graphene oxide/ZnO	Langmuir	composite	C (VI–VI)	7	–	–	714.3	75	[243]
Fe ₃ O ₄ /AC	Liu	composite	C (II–VI)	7	1200	25	150.4	–	[244]
Nanoporous carbon	Langmuir	nanoparticles	-	–	814	25	18.8	100	[245]
Ag ₃ PO ₄	–	nanoparticles	-	9	–	–	–	91.8	[281]
NiO nanoflakes	Langmuir	nanoparticles	-	2	9.72	–	165.8	84.6	[138]
Polydopamine/cellulose nanofibril/polyethylene-imine	Langmuir	composite	C (V–VI)	4	–	25	265.9	–	[246]
Fe NPs/SiO ₂ –NH ₂ /yerba mate extract	Experiments	composite	C (I–IV–VI)	3	113.1	25	2.84	100	[182]
Mesoporous ZIF-67/LDH	Langmuir	composite	C (IV–V)	6	172.3	30	1030	98	[247]

Magnetic nanoporous Fe/MCM-41	Langmuir	nanoparticles	-	2	1216	20	5000	96.7	[221]
Au/Cu ₂ O	–	composite	C (VI–VI)	–	16	–	–	98.8	[248]
Goethite/chitosan beads	Langmuir	composite	C (IV–V)	3	17.81	25	84	–	[92]
Amino-functionalised magnetic bacterial cellulose/AC	Langmuir	composite	C (II–VI)	3	–	45	103.3	82.8	[249]
Mesoporous carbon	Langmuir	nanoparticles	-	3	2944	–	9091	–	[250]
p-CNTs/chlorine chloride	Langmuir	nanoparticles	-	2	197.8	–	310.2	–	[186]
Zn–Al LDH/ZnO	Langmuir	composite	C (IV–VI)	–	–	–	276.6	96.9	[148]
Copper hydroxide nitrate nanosheets	Experiments	nanoparticles	-	–	–	–	428.8	–	[251]
Fe ₂ O ₃ /Mn ₃ O ₄ magnetic nanocomposites	Langmuir	composite	C (VI–VI)	2	178.3	25	322.6	97.7	[252]
Chitosan/Fe ₃ O ₄	Langmuir	composite	C (VI–VI)	7	–	25	758	95	[253]

nanodiamond	Experiments	nanoparticles	-	–	282	–	41.74	–	[254]
Al-doped CNTs	Langmuir	nanoparticles	-	4.5	118.8	–	69.7	99.4	[172]
Functionalised CNTs/TiO ₂	Langmuir	composite	C (VI–VI)	6.5	–	25	42.68	100	[220]
Waste straws/citric acid group/acrylamide	Langmuir	composite	C (II–V)	3	–	–	3053	80	[255]
NiFe LDH nanoflakes/montmorillonite	Langmuir	composite	C (IV–V)		103.9	25	108.8	91.8	[256]
Mg NP/modified nanosized SiO ₂ –Al ₂ O ₃	Sips	composite	C (IV–VI)	6.5	101	25	167.2	89.3	[257]
Al-doped MOF/graphene oxide	Langmuir	composite	C (V–VI)	8	1309	–	400	–	[258]
Cu ₂ O/Ag	Langmuir	nanoparticles	-	–	55.36	–	709.2	–	[259]
Silver NP/zeolite X	–	composite	C (V–VI)	5	552.6	–	–	100	[260]
Ni–Al LDH/AC	Sips	composite	C (II–IV)	4.5	1158	30	412.8	–	[261]

Immobilised Fe/chitosan	Langmuir	composite	C (V- VI)	4	–	50	205	–	[58]
MgO/carbon nanocomposites	Langmuir	composite	C (VI- VI)	–	59.3 4	–	101.8	–	[262]
Polyethyleneimine/ β - cyclodextrin/Fe ₃ O 4	Langmuir	composite	C (IV- V)	1	17.5 1	30	192.2	–	[263]

Table 7: Adsorbent ZIF-67 and different composites of ZIF-67

Pollutant	ZIF type	Reference
Methyl orange	Ni-doped ZIF-67	[264]
Congo red	ZIF-67	[265]
Congo red	ZIF-67	[266]
Methyl orange	Ag@ZIF-67	[267]
Direct Blue-86, Reactive Yellow, Congo Red	ZIF-8@ZIF-67	[268]
Eriochrome black T	ZIF-67-OAc	[269]
Methyl orange	ZIF-67@CoAl-LDH	[192]
Congo red	ZIF-67	[265]
Congo red	ZIF-67	[270]
Nitrophenol	Magnetic ZIF-67	[271]

Methyl orange	ZIF-67@LDH	[247]
Orange II, Methylene blue, Rhodamine B.	ZIF-67@PVDF	[272]
Malachite green (MG) dye from colored wastewater	PES/ZIF-8LZIF-67 beds	[273]
U(VI)	HAP/ZIF-67	[274]
tetracycline hydrochloride (TCH)	Mn-ZIF-67)	[275]
Strontium	ZIF-67- K ₄ Fe (CN) ₆	[276]
Tetracycline	ZnO@ZIF-67	[277]
methyl orange (MO), Minocycline (MC)	Ag@ZIF-67	[267]
malachite green (MG) and fuchsin acid (FA)	Hybridized ZIF-67 with polyvinylidene fluoride (PVDF)	[278]
Ciprofloxacin	N@ZIF-67/peroxymonosulfate	[279]
ZIF-67@ZIF-8@MIL-125-NH₂	Bacterial Bio film	[280]
Malachite green	ZIF-67@GO	[281]
Methylene blue (MB) and Methyl orange (MO).	ZIF-67 on layered double hydroxides (LDH)	[282]
Tmidacloprid and thiamethoxam	ZIF-67/CS@C	[283]
Phosphate	Fe ₃ O ₄ @ZIF-67	[284]
Humic Acid (HA)	ZIF-67-Cl, ZIF-67-OAc, ZIF-67-NO ₃ , and ZIF-67-SO ₄	[285]

CHAPTER 3

EXPERIMENTAL METHODS AND MATERIALS USED

3.1. Advanced instruments, chemicals and reagents used

This investigation used pure bentonite (BNT) samples as well as reagent-grade compounds with purity levels exceeding 95%. All of the chemicals were of high-purity reagent grade, 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 $[(\text{CH}_3)_2\text{NC}_6\text{H}_4:\text{N}_6\text{H}_4\text{SO}_3\text{Na}]$. All solution preparations, serial dilutions, and sample preparations were carried out using de-ionized water (CORNING Mega PureTM), and all glassware was meticulously cleaned and washed.

X-ray diffraction (XRD) analysis was used to evaluate the crystalline structure of the synthesized material, ZIF-67 and ZIF-67@bentonite. A Rigaku Miniflex-II diffractometer was used to scan the material at a rate of 7° per minute throughout a 2-theta angle range of 5° to 40° . Employing TA Instruments, thermogravimetric analysis (TGA) was used to evaluate thermal stability throughout a temperature range of 30°C to 800°C in an inert environment at a heating rate of 10°C per minute. ZIF-67@Bentonite's surface functional groups were determined by employing Fourier-transform infrared spectroscopy (FTIR) with the Smart iTR NICOLET iS10. Furthermore, a Shimadzu UV-V spectrophotometer was used to detect the amount of methyl orange (MO) in aqueous samples that had been diluted for accuracy and pre-filtered using $0.2\ \mu\text{m}$ Whatman filters to exclude adsorbent particles. The OAKTON[®] pH 700 was used to measure the pH values of the samples.

3.2. Framework of studies

Several essential steps compose the approach described in this work, which is depicted in **Figure**

4. To predict the removal efficiency and learn more about the adsorption mechanisms, these

include synthesizing a ZIF67@Bentonite composite material, characterizing it, assessing its adsorption performance, optimizing and evaluating this performance through RSM, and then using and comparing various machine learning models.

3.3. Synthesis of ZIF-67

Several methods of ZIF synthesis were discussed in previous studies. Considering that the solvothermal method is the most widely adopted technique, its steps will be briefly highlighted here. Metal solutions will be prepared by dissolving appropriate amounts of metal salt in an organic solvent. A separate solution of imidazole linker dissolved in organic solvent will also be prepared and will then be mixed with the metal solution. The resulting mixture will then be put into an autoclave reactor and then placed in an oven at the appropriate temperature. After allowing for sufficient growth time, the synthesized ZIF will be washed several times with organic solvent and remove impurities that may have formed during the synthesis [286].

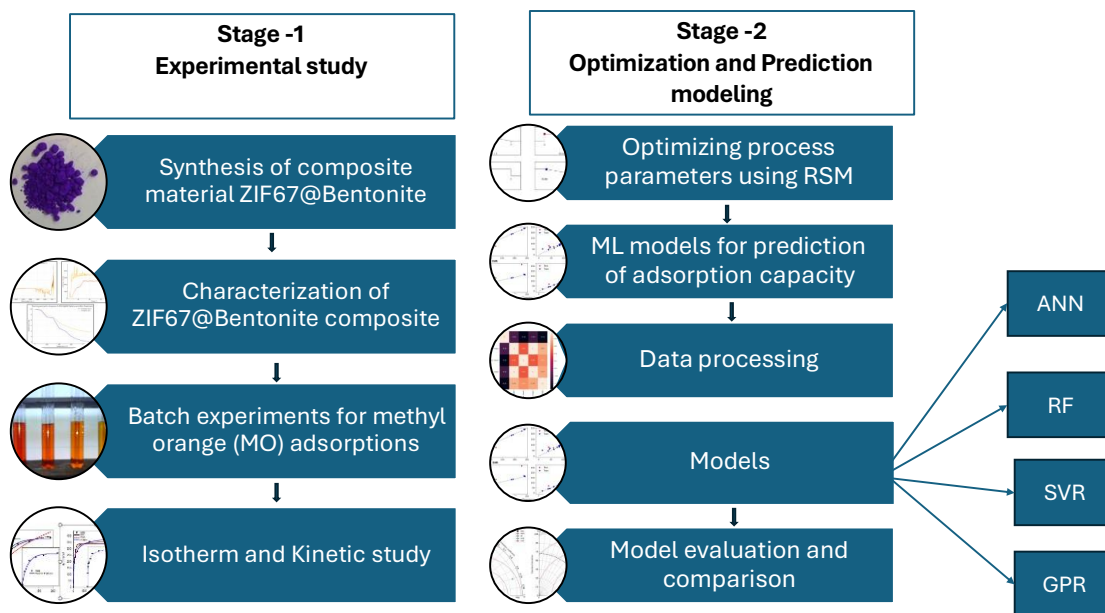


Figure 4: Framework for evaluating ML models, optimizing adsorption, and synthesizing composite materials.

3.4. Preparation of ZIF-67@bentonite

To initiate the synthesis, an aqueous cobalt nitrate solution was prepared by dissolving 11.64 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 150 mL of distilled water, followed by stirring for 5–10 minutes until complete dissolution of the salt was achieved. Subsequently, 0.24 grams of bentonite was introduced into the cobalt solution and stirred at ambient temperature for an additional 10 minutes to ensure uniform dispersion. The resulting mixture was then subjected to ultrasonic treatment at 50% amplitude for 30 minutes, using a pulsed mode of 30 seconds on and 3 seconds off to enhance dispersion. Simultaneously, a separate solution was prepared by dissolving 13.12 grams of 2-methylimidazole in approximately 150 mL of ammonium hydroxide (NH_4OH), maintaining a metal-to-ligand molar ratio of 1:4. Once both solutions were ready, the imidazole solution was rapidly poured into the bentonite-cobalt mixture under continuous stirring. The combined solution

was stirred for 2 hours to facilitate the in-situ formation of the composite. The resulting Bentonite@ZIF-67 material was isolated by centrifugation at 6000 rpm for 20 minutes, repeated five times, with intermediate washing using distilled water to remove residual reagents. The collected solid was then dried in an oven at 50–70 °C. After drying, the product was scraped from the vessel and ground, if needed, to obtain a uniform fine powder. The complete synthesis procedure is illustrated in **Figure 5**.

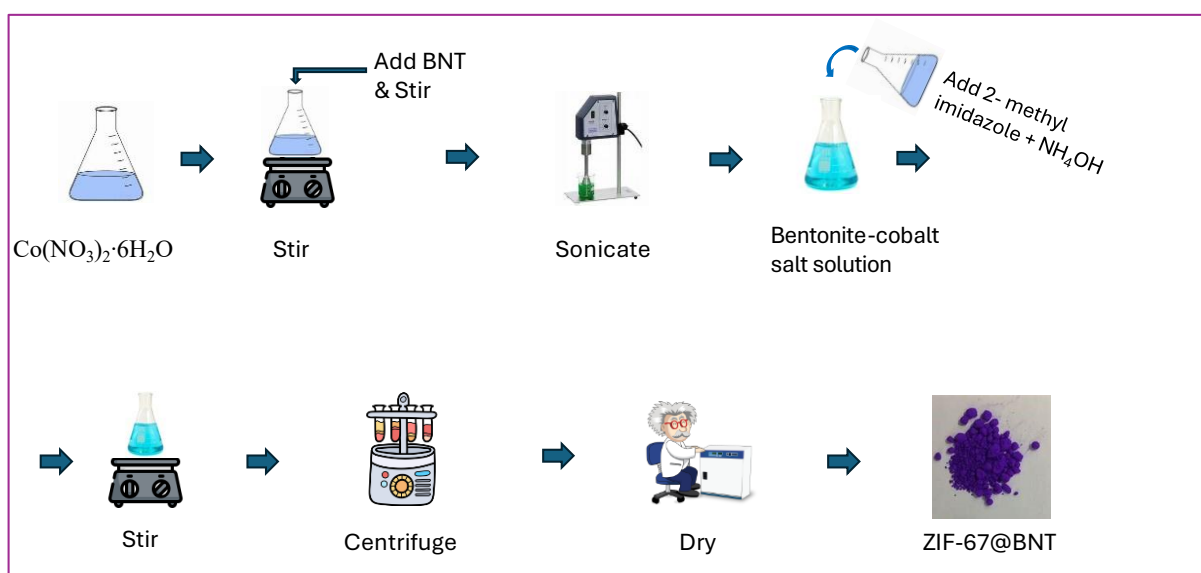


Figure 5: A schematic illustration depicting the preparation process of the ZIF67@Bentonite composite material for adsorption

3.5. Central composite design

Instead of using the conventional univariate strategy, the study used a multivariate approach to perform experiments. Conducting statistically planned tests, estimating coefficients in a mathematical model, and forecasting responses while evaluating model appropriateness are the three basic phases in this optimization process. Response surface methodology (RSM) facilitates

the identification of the connections between input variables (X_i s) and output variables (y) [287] [288].

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

In RSM, a quadratic surface may be fitted using the Central Composite Design (CCD) to optimize important parameters and investigate variable contributions and interactions with the fewest possible experiments. When n is the number of variables, the CCD usually consists of factorial runs, 2^n axial runs, and central runs [289] [290]. An estimate of experimental error and data reproducibility can be obtained by replicating the center point. Consequently, conducting experiments enables a comprehensive examination of all regions in the study.

The tests were set up with three components in a typical face-centered central composite design, and the RSM approach was used to investigate the impact of process parameters and their interactions [291]. The ZIF-67@bentonite dosage, initially MO concentration, and duration or contact time were the study's independent factors; the MO's adsorption capability was the dependent variable (response). **Table 8** lists the factors and the levels that correlate to them. To anticipate the response, a number of regression models were created. Quality criteria including the coefficient of determination (R^2), adjusted R^2 , and projected R^2 were used to determine which model best suited the experimental data. Analysis of variance (ANOVA) was also performed to confirm the models' performance and validity. For RSM modeling and ANOVA, Design Expert version 13 software was utilized.

Table 8: RSM modeling renders utilization of independent variables and the levels that correspond to them.

Factors		Levels		
		-1	0	1
A	Adsorbent dosage(g/L)	0.005	0.01	0.015
B	Concentration (ppm)	10	20	30
C	Time (hour)	1	3	5

3.6. Analytical method

The dye analysis will be performed utilizing UV-spectroscopy, a reliable method for determining the concentration of substances based on their absorbance of ultraviolet light. Before commencing the analysis, it is imperative to calibrate the UV-spectrophotometer. This calibration process involves using various standards prepared from the pollutant stock solution. These standards serve as reference points, allowing for accurate and precise measurements during the analysis. Once the equipment is properly calibrated, the absorbance spectrum of the dye can be measured and analyzed against the established standards, facilitating the determination of its concentration and the result shown in **Table 9**.

3.7. Batch Adsorption experiment

The forthcoming study scrutinizes the adsorption dynamics of the synthesized material across diverse operational parameters. A determined quantity of methyl orange will be dissolved in ultrapure water to create a stock solution of 1000 ppm. This will be followed by sequential dilutions using ultrapure water to establish a spectrum of contaminant concentrations, which are 10 ppm, 20 ppm, and 30 ppm. According to the DOE, batch adsorption tests were carried out in a

sequence of 250 mL Pyrex bottles, each holding 150 mL of a solution with the designated MO concentration and ZIF-67@bentonite adsorbent dosage. To ensure uniformity, the bottles were positioned on a Bioevopeak mechanical shaker with a regulated ambient temperature and a mixing speed of 250 rpm.

Each experiment was run for 5 hours in line with the RSM-based adsorption methodology. Control samples will be extracted to ascertain the reduction in contaminant levels attributed to the incorporation of the adsorbent. Upon reaching equilibrium, the solution will be sieved through a 0.2 μm filter, and the resultant limpid solution will undergo meticulous analysis for each sample iteration. The specific efficiency of heavy metal removal may be calculated using Equation 2, and the adsorption capacity can be obtained using Equation 3.

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

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

In the provided context, 'Co' symbolizes the initial concentration, while 'Ce' denotes the concentration post-equilibrium, both measured in mg/L. 'Qe' represents the uptake subsequent to equilibration, quantified in mg/g, where 'm' denotes the mass of the adsorbent in grams and 'V' denotes the sample volume in liters.

A ZIF-67@bentonite dose of 0.0050 g/L at room temperature, an initial pH of 6.35, and an initial MO concentration of 100 ppm were utilized in the adsorption kinetics testing. After several samples were collected, adsorption was allowed to proceed until equilibrium was achieved. Similar circumstances were used in adsorption isotherm tests, where the starting MO concentration varied from 5 to 125 ppm and the adsorption process lasted for more than 24 hours.

3.8. Machine learning

Machine learning techniques are increasingly being used to forecast how well adsorbents would remove pollutants from aqueous streams [39] [40]. However, due to operational and financial difficulties, there is still a lack of experimental data that supports 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. **Table 13** provides a statistical overview of the dataset utilized in this investigation. The algorithms employed in this study also have brief explanations of their underlying ideas given below.

3.8.1. Artificial Neural Network

The artificial neural network (ANN) is a popular artificial intelligence technique. The mathematical modeling of the nervous system put forward by McCulloch and Pitts in 1943 served as the model for this approach [294]. The input layer, output layer, and one or more hidden layers positioned in between are the three separate layers that make up the ANN structure. Multiple neurons grouped as linked nodes make up each layer. The training technique for the used artificial neural network was multi-layer perceptron (MLP). The experimentally acquired data and the final FFBP calculated findings were contrasted. After that, errors were computed and MLP to modify each neuron's weight appropriately. A suitable cost function can be used to modify the weights across nodes in order to improve model performance. Activation functions like the rectified linear unit (ReLU) and sigmoid are used in nonlinear calculations [295]. Equation 4 displays the anticipated ANN output, and **Figure 6A** shows how the feed-forward ANN operates.

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

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

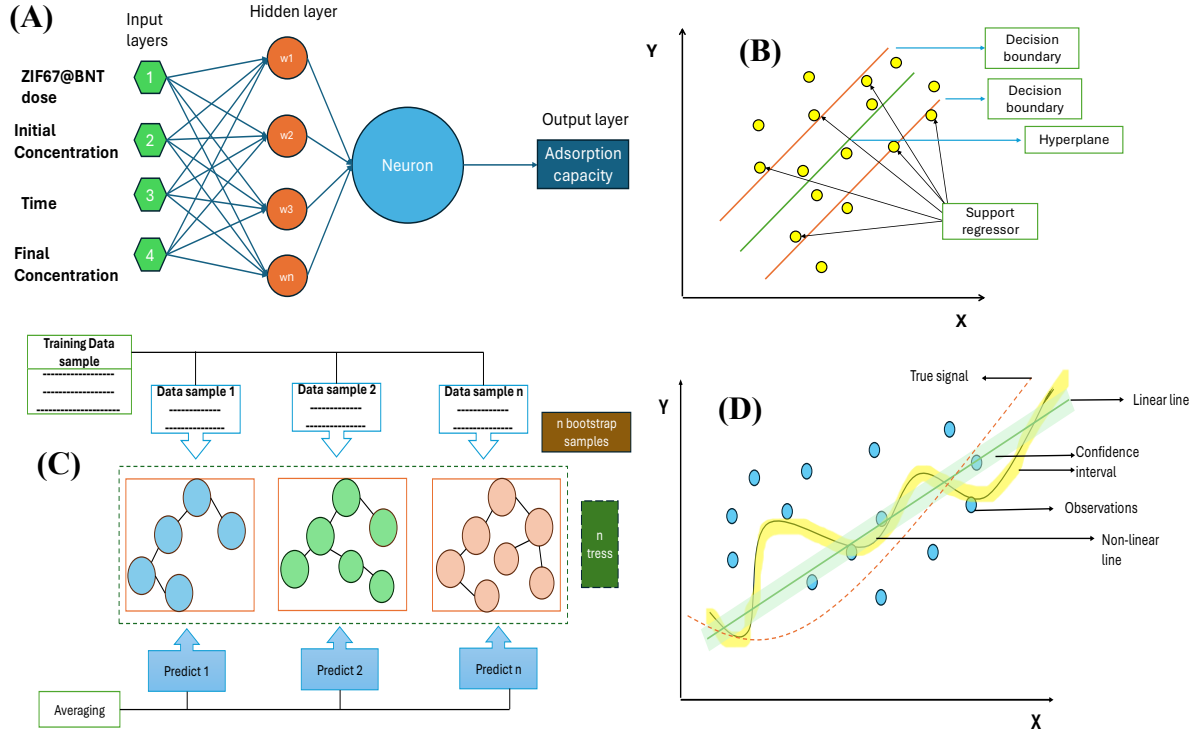


Figure 6: (A) ANN algorithm structure, (C) linear hyperplane-based SVM classification, and (C) RF algorithm architecture (D) Regressor for the Gaussian process

3.8.2. Support vector regression

The Support vector regression (SVR) method has now been improved to perform well on regression tasks, even with tiny datasets, but originally created for classification tasks,[296], [297]. The capacity of SVR to map input vectors into high-dimensional feature space using a hyperplane to divide classes makes it suitable for a wide range of applications. The gap between different classes is maximized by this separation, which frequently produces forecasts that are quite accurate

[298]. There are several kernel functions that may be used to do this mapping. Equation 5 produces the output in **Figure 6B**, which illustrates how SVR operates.

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

3.8.3. Random Forest (RF)

A tree-based model called Random Forest (RF) was presented by [299], [300] as an advancement over the bagging tree approach. RF is an ensemble tree technique that creates many decision trees using a bootstrap sampling technique carried out during the training stage. The internal node, branch, and leaf node are the three parts of a single decision tree. An internal node indicates a prediction issue assessment. The branch node displays the results of this evaluation, while the leaf node displays the regression's class label. The meaning of the data points and the mean squared error between them were calculated at the branch node. This procedure keeps on until the regression tree's mean squared error reaches the ideal value, at which point the decision tree halts the expansion.

The following steps are included in the RF model creation process: The training data set was first split into two data sets. Two thirds of the training sample is represented by the first section, while one third of the original data set is represented by the second, known as the bootstrap sample. Building a regression tree for every bootstrap sample generated during the training phase is part of the second step, which involves modeling the RF method. In accordance with this stage, many regression trees were produced, and each branch node's maximum depth attributes were randomly chosen to determine the best attributes. The sequence of the generated regression tree, which is taken into consideration during the RF model development process, is attained after a certain number of training cycles.

The last stage of RF modeling involves gathering the decision tree prediction results and calculating the new predictor's result using the average formula. The RF model's mathematical formulation is shown below:

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

N is the number of regression algorithms, $t_i(x)$ is the individual algorithm for the regression tree, and $\hat{f}_{rf}^N(x)$ is the included tree. The visual representation of the RF technique is shown in **Figure 6 C**.

3.8.4. Gaussian process regressor

A Gaussian Process (GP) is a non-parametric probabilistic model commonly used in statistics and machine learning for tasks such as regression, classification, and uncertainty quantification. It represents a collection of random variables, each characterized by a joint Gaussian distribution over a finite set. GPs offer a flexible and powerful approach for capturing complex relationships in data while providing predictions accompanied by associated uncertainty. Characteristics of GP are as adjust the non-parametric data, probabilistic prediction, interpolation and smoothing and marginalization of hyperparameter [301] . **Figure 6D** shows the visual representation of the GPR.

The Waikato Environment for Knowledge and Analysis (WEKA) software version 3.8.6 was used to create the prediction models mentioned above. N-fold cross-validation was used to train and validate the models, and the correlation coefficient (R), coefficient of determination (R²), and RMSE were used to assess accuracy and performance.

CHAPTER 4

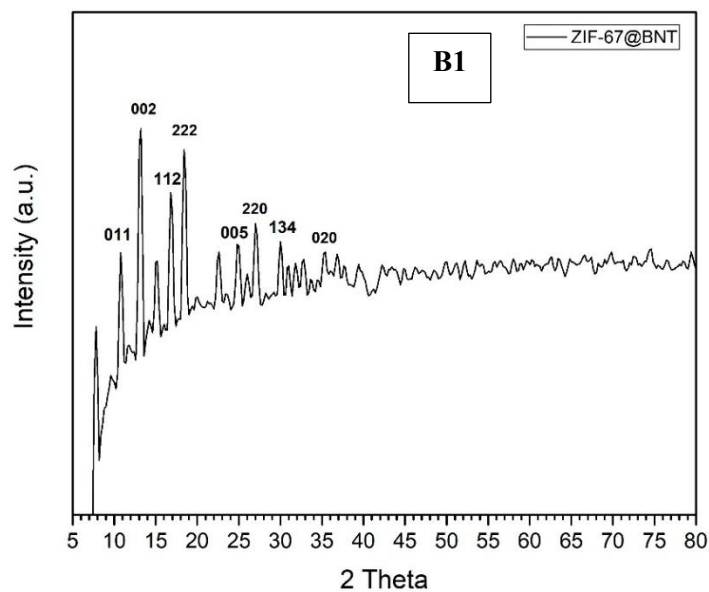
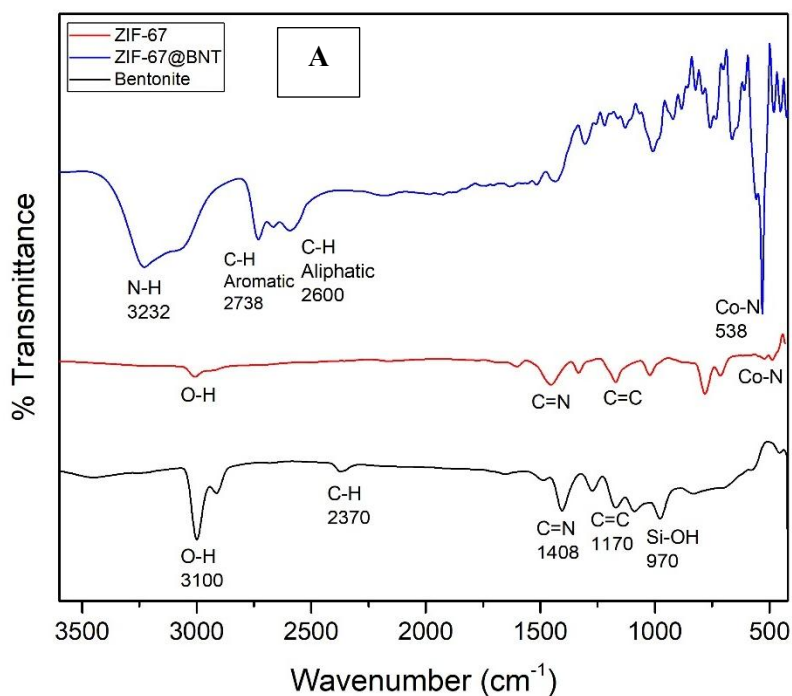
RESULTS AND DISCUSSION

4.1. Material Characterization

The XRD pattern of the ZIF67@BNT nanocomposite, shown in **Figure 7B1 and 7B2**, reveals distinct peaks, indicating a highly crystalline structure. The sharp peaks observed, particularly in the 2θ range of 5° to 30° , are characteristic diffraction of ZIF-67 as shown in **Figure 7B2**, suggesting that the crystallinity of ZIF-67 remains intact within the ZIF-67@BNT nanocomposite matrix. Furthermore, the phase consistency observed in the XRD pattern suggests that the integration of bentonite does not interfere with the crystalline framework of ZIF-67, which aligns with previous studies on ZIF-clay composites as shown in **Figure 7B1** [302]. The ZIF-67@BNT nanocomposite's ability to retain its crystalline structure shows that it may be a suitable adsorbent material, especially for the removal of contaminants like methyl orange, where strong structural characteristics are necessary for long-term performance.

Besides crystallinity, FTIR spectrum of the ZIF67@BNT composite (**Figure 7A**) shows key functional groups that confirm the structural composition of the material such as O–H stretching vibrations, C=N and C–N stretching vibrations, Si–O and Al–O bonds which is represented by the peaks at 3400 cm^{-1} , between 1400 cm^{-1} and 1600 cm^{-1} and the fingerprint region between 500 and 1000 cm^{-1} respectively. This indicates the presence of the imidazole ring in ZIF-67 and the bentonite, which gives the composite its hydrophilic properties and also confirms the clay mineral present in the composite. These functional group assignments indicate that the ZIF67@BNT nanocomposite retains the distinctive features of both ZIF-67 and bentonite, making it a suitable candidate for adsorption applications. The nanocomposite's structural integrity, evidenced by the

FTIR spectrum, is essential for its intended use in the removal of organic contaminants, where specific functional groups play a critical role in interaction and adsorption efficiency [303] Further details of the XRD and FTIR analysis are shown in the upcoming [section 3.6](#).



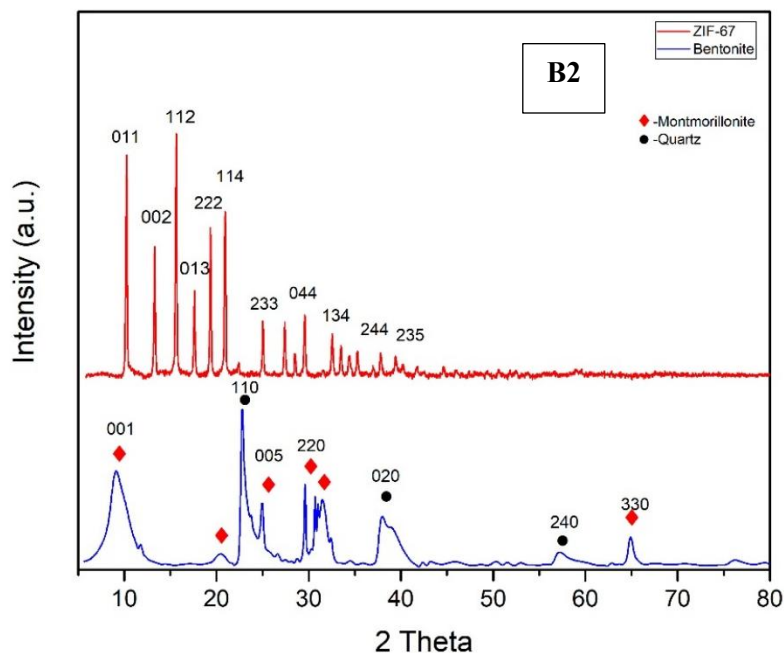


Figure 7: FTIR (A) and XRD (B1 and B2) analysis of ZIF67@BNT nanocomposite, ZIF67 and BNT

The thermal stability profile and breakdown behavior of the ZIF67@BNT composite are illustrated in **Figure 8**, which is a thermogravimetric analysis (TGA). The initial segment of the TGA curve, up to approximately 150°C, shows minimal weight loss, indicating stability in this temperature range, likely due to the evaporation of surface-adsorbed moisture or other volatile components. However, pronounced weight loss occurs between 150 and 600°C, with the primary decomposition phase observed from around 300 to 500°C. This substantial weight reduction is attributed to the degradation of the organic framework within ZIF67 and possibly the release of structurally bound water associated with the bentonite (BNT) component. Beyond 600°C, a slower rate of weight loss is noted, indicating the breakdown of more thermally resilient components within the composite, with stabilization occurring around 800°C [304] [305]. According to this thermal investigation, the ZIF67@BNT nanocomposite is quite stable when subjected to high temperatures, which means it might be useful in adsorptive removal operations.

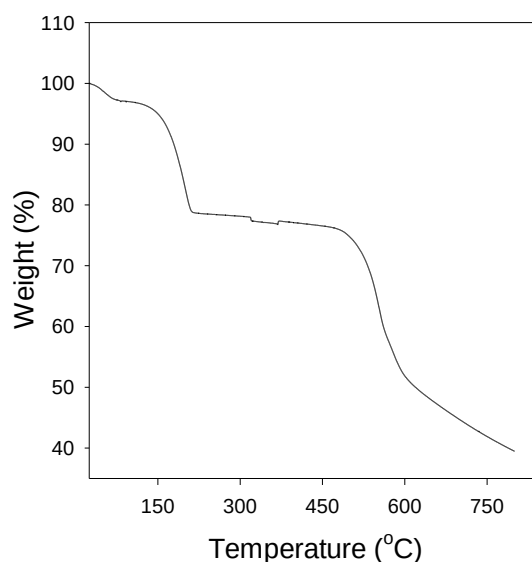


Figure 8: Thermogravimetric analysis of ZIF-67@BNT nanocomposite

4.2. Benchmarking the performance of the ZIF-67@BNT nanocomposite with its constituents

Figure 9 illustrates a comparative analysis of methyl orange (MO) adsorption capacities among ZIF-67, bentonite (BNT), and their composite form, ZIF-67@BNT. ZIF-67 alone demonstrated an adsorption capacity of 222.9 mg/g, which aligns with the known characteristics of metal-organic frameworks (MOFs), including their high surface area and porosity—features that make them suitable for diverse applications such as wastewater treatment [10, 15, 40, 41, 47–51], gas storage [52], catalytic processes [56, 57], and oilfield uses [53–55]. Interestingly, BNT exhibited an even higher adsorption capacity of 252.0 mg/g, likely due to its distinct structural and surface chemical properties that promote stronger interactions with the MO dye. The ZIF-67@BNT nanocomposite outperformed both parent materials, achieving the highest adsorption capacity of 275.3 mg/g. This enhanced performance is attributed to the synergistic integration of ZIF-67 and BNT, which likely results in improved structural integrity, an increased number of active adsorption sites, and

optimized pollutant–adsorbent interactions. Such results emphasize the effectiveness of material hybridization, where combining two functional components can lead to superior adsorption behavior compared to individual materials—a trend also supported by previous studies [11, 35, 58–61].

These findings highlight the promise of ZIF-67@BNT nanocomposites for water treatment applications, particularly for removing dyes like methyl orange. Based on this superior performance, further research will focus on optimizing the adsorption conditions using response surface methodology (RSM), investigating the adsorption kinetics and isotherms of MO onto the composite, and applying machine learning models to predict performance. Additionally, potential adsorption mechanisms will be explored and discussed in the following sections wherever relevant.

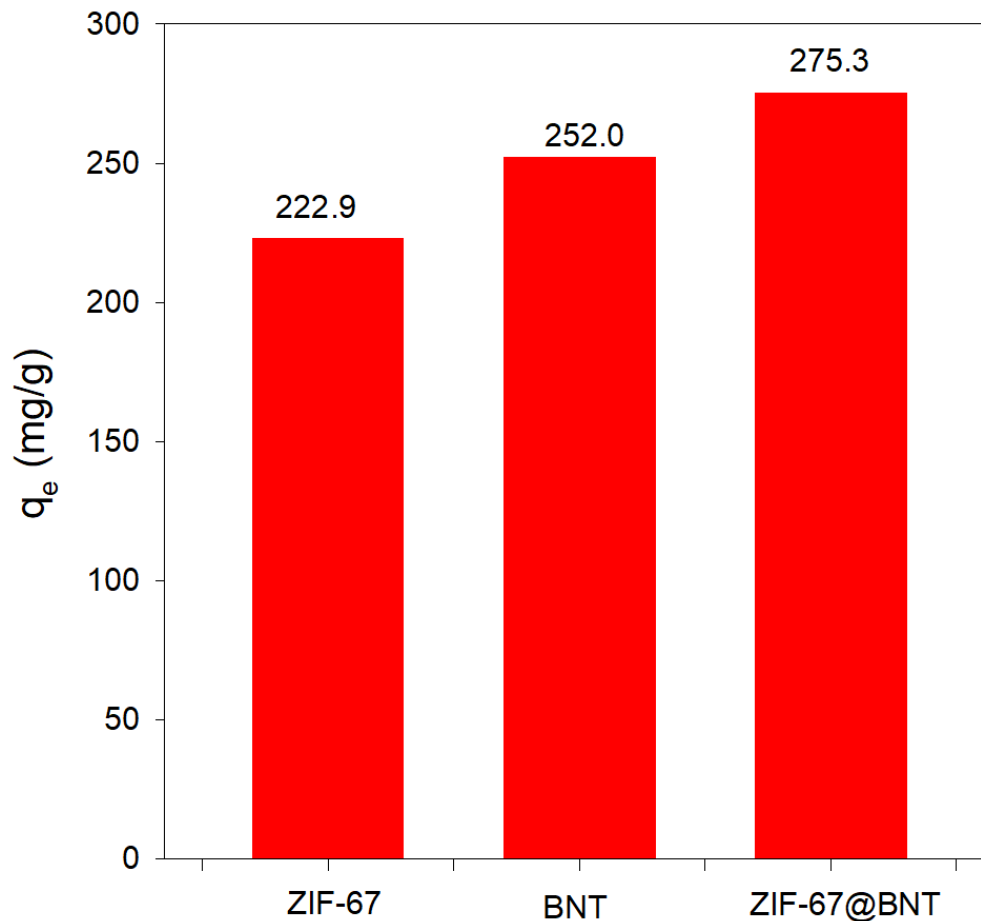


Figure 9: Benchmarking the adsorption of MO onto ZIF-67@BNT with its constituents (i.e., ZIF-67 and BNT). The adsorption took place from 100 ppm MO solution containing 50 mg/mL of each adsorbent.

4.3. Experimental design and analysis of variance

The batch experiments trials were developed by the design of experiments (DOE) using the response surface methodology (RSM), with the adsorption of the MO by ZIF67@BNT nanocomposite and result shown in **Table 9**. The outcomes clearly indicate that the uptake of MO by ZIF67@BNT is significantly impacted by changes in the experimental process parameters. The adsorption capacity ranged from 38 to 187 mg/g at its highest, underscoring the importance of carefully selecting process conditions for ZIF67@BNT to function effectively as an adsorbent. The upcoming sections offer a more thorough explanation of how process factors affect MO

adsorption. The RSM approach was used in a regression-based modeling exercise based on the findings of the adsorption experiment [306] [307]. Among the various RSM models generated, the quadratic model was chosen as it shows the strong correlation between the inputs and the output as well as its strong performance in accurately predicting the adsorption capacity of MO onto ZIF67@BNT nanocomposite.

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

Table 9: The RSM based DOE and the MO adsorption results using the ZIF-67@BNT nanocomposite adsorbent.

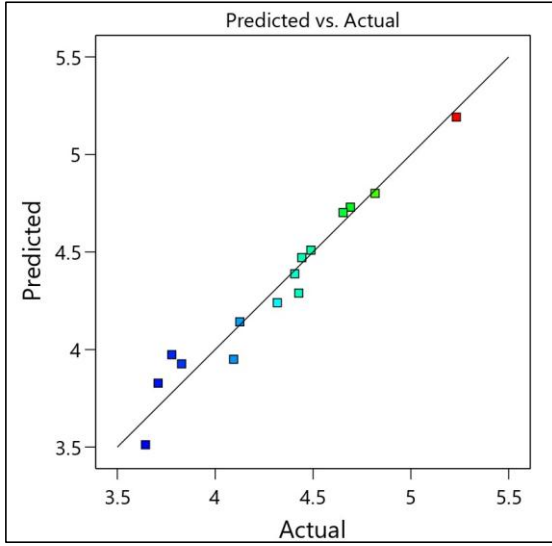
Run	A: Adsorbent Dose (mg)	B: Methyl Orange (mg/L)	C: Time (hour)	Adsorption capacity (mg/g)
1	15	30	5	82
2	5	20	3	89
3	15	30	1	46
4	10	20	5	105
5	10	10	3	62
6	5	10	5	84
7	10	20	3	85
8	5	30	1	109
9	10	20	1	75
10	5	30	5	187
11	15	10	5	44
12	5	10	1	41
13	10	30	3	124
14	15	10	1	38
15	15	20	3	60

Table 10: The respective statistical analysis of variance (ANOVA) for uptake of MO by ZIF67@BNT nanocomposite.

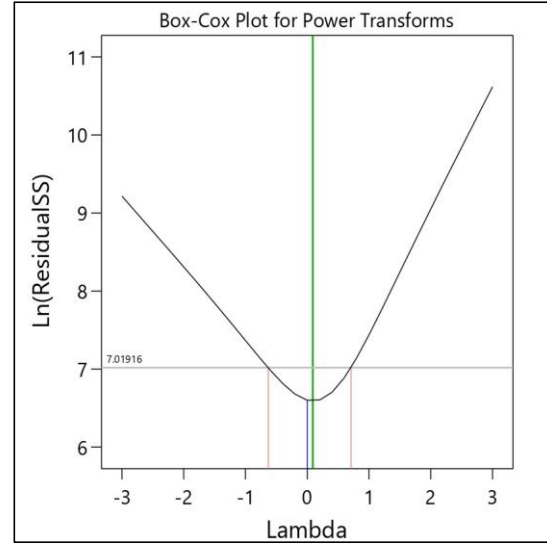
Source	Sum of squares	Degree of freedom (df)	Mean square	F-value	p-value	
Model	2.71	5	0.5424	36.79	<0.0001	significant
A-Adsorbent dose	0.7823	1	0.7823	53.06	<0.0001	
B-Methyl Orange	1.08	1	1.08	73.49	<0.0001	
C-Time	0.5330	1	0.5330	36.15	<0.000	
AB	0.1187	1	0.1187	8.05	0.0002	
A²	0.1942	1	0.1942	13.17	0.0195	
Residual	0.1327	9	0.0147		0.0055	
Core Total	2.84	14				

A strong model fit was demonstrated by the R^2 , adjusted R^2 , and predicted R^2 values, which were found to be 0.953, 0.927, and 0.822, respectively. A tight agreement between the actual and predicted MO removal levels is displayed in **Figure 10a**. The quadratic model's applicability was further demonstrated by the less than 20% difference between the adjusted and predicted R^2 values [306] [308]. The resulting quadratic model is presented in Equation 6 and it's important to mention that the natural log transformation used in Equation 6 follows the method established by Box and Cox plot, which provides a systematic approach to finding the appropriate power (Lambda) for transforming a dependent variable to enhance its normal distribution. A Lambda value of 0 indicates that a natural log transformation is most suitable. Total MO elimination was measured

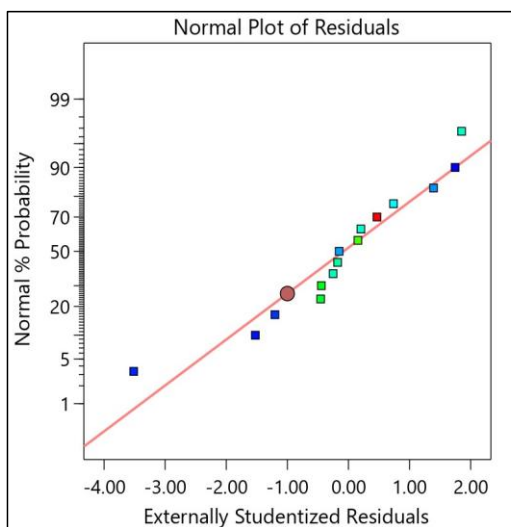
using Box-Cox plots (**Figure 10b**) [308]. In order to strengthen the model's validity, assumptions about the error term were thoroughly investigated. The normal distribution of the residuals is shown in **Figure 10c**, and the lack of correlation between the run sequence and the residuals is shown by the randomly distributed points in **Figure 10d**.



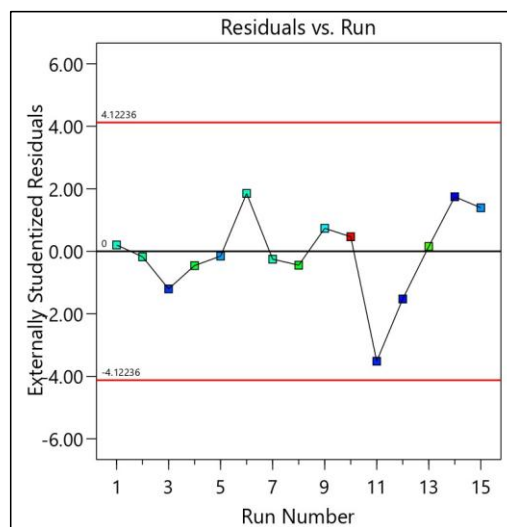
(a)



(b)



(c)



(d)

Figure 10: Model adequacies check plots (a) Plotting of actual against anticipated or predicted adsorption capacity (b) Box-Cox plot for MO removal model (c) normality distribution plot (d) plot of residuals Vs order of run

4.4. Examine the impact of process parameters using ANOVA

To determine how changes in the chosen process parameters—specifically, the initial MO content, ZIF67@BNT dose, and the time required for MO removal from contaminated water using the ZIF67@BNT adsorbent—would affect the results, the analysis of variance (ANOVA) approach was used. The full ANOVA findings are shown in **Table 10**, and a p-value of 0.05 or less indicates that the term or parameter being examined is statistically significant. The analysis was carried out at a 95% confidence level [309] [310]. MO adsorption by ZIF67@BNT was predicted using the quadratic model and the individual impacts of each component, including MO initial concentration, ZIF67@BNT dose, and duration, as indicated in **Table 10**.

Figure 11 illustrates the changes in the relevant factors that impact on the adsorption capacity trend. As the **Figure 11a** reveals that the adsorbent dose (ZIF67@BT) increases from 5 to 15 mg, the adsorption capacity decreases because the trend can be distinction to the process where at higher adsorbent doses there is greater accessible surface area, which lead to increase the interaction site between the ZIF67@BNT adsorbent and MO adsorbate. Additionally, in the adsorption process a decrease in concentration gradient leads to lowers the driving forces which outturn in lower adsorption capacity. In conclusion, the finding shows that above a certain amount of dose, adding ZIF67@BNT adsorbent does not significantly enhance the adsorption process, making it desirable to keep dose low in order to get the higher adsorption capacity [311].

Figure 11b demonstrate that increases in the MO concentration from 10 ppm to 30 ppm at lower dosage (5 mg) of ZIF67@BNT, increases the adsorption capacity. This behavior is commonly found in the adsorption studies [312], where higher initial concentration results in improving the adsorption capacity, which leads to more adsorption onto the adsorbent surface due to the gradient of concentration and acts as motivational factor that facilitates the movement of the molecules of adsorbate molecule which caused in increased the likelihood collisions with adsorbent surface and results in increase the chances of adsorption events and adsorbate molecule attached to the binding cite on the adsorbent. In contrast, ZIF67@BNT performs better at higher concentration of MO pollutant, achieving highest adsorption capacity values, which is useful in the applications with high contaminant loads.

Figure 11c demonstrates that the adsorption capacity rises with increasing time, this phenomenon also noted in plenty of studies [313], [314], [315], where extended contact time permits more adsorbate molecules adhered to the adsorbent surface which shows the improvement in the adsorption capacity. Increase in contact time shows the adsorption process remains effective, and

the adsorption process continues until equilibrium attained, which is very important to determining the time necessary for optimal effectiveness in practical applications.

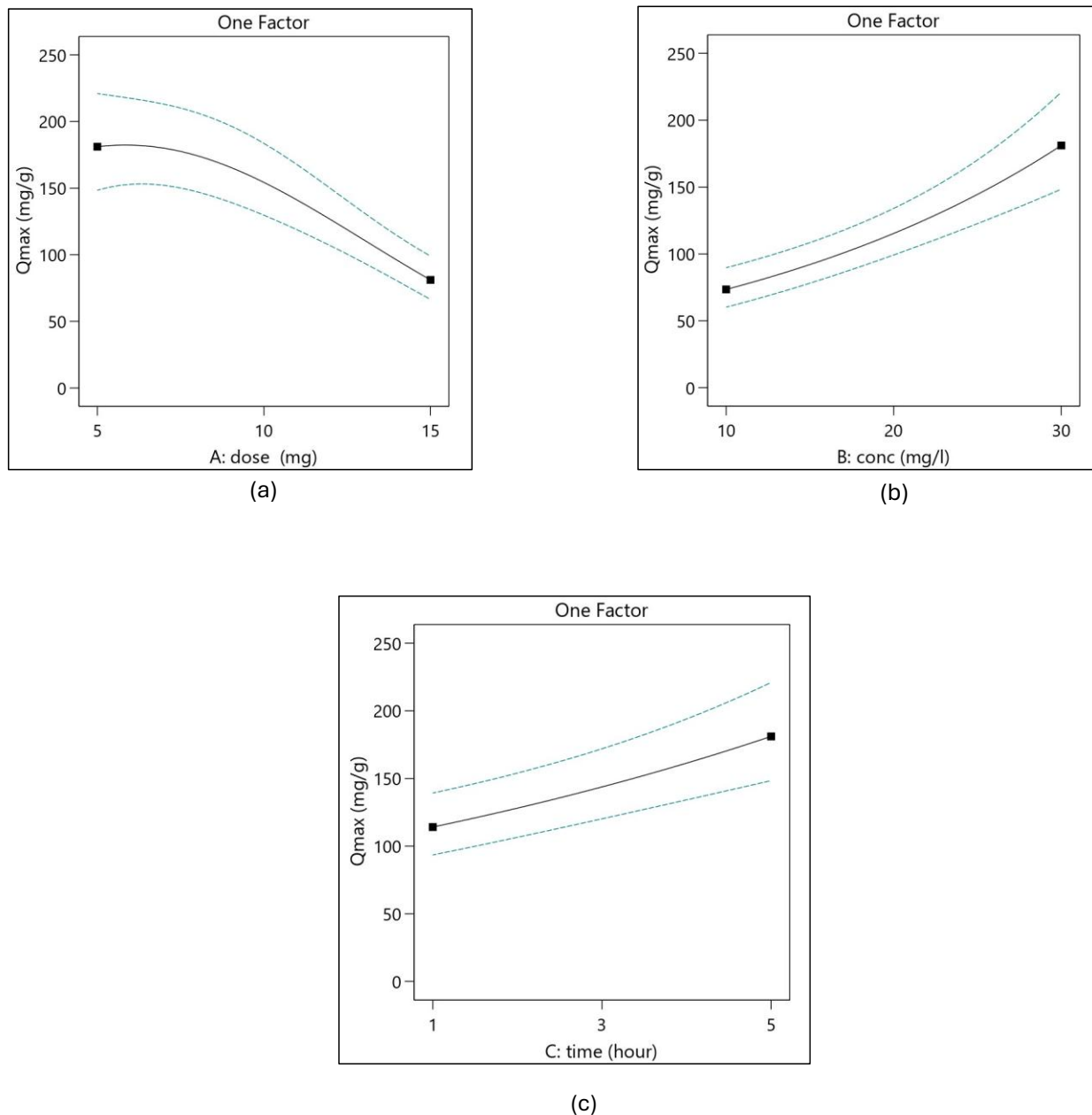


Figure 11: Effect of (a) ZIF67@BNT dose (b) MO concentrations (c) adsorption time (d) Interaction between the Concentration dose and adsorption capacity with Maximum time.

A significant benefit of the multivariate technique over the one-factor-at-a-time method is its capacity to investigate how interactions between independent variables impact the response of

interest—in this case, methyl orange elimination. **Figure 12** shows 3D surface plots that illustrate the interaction effects. These 3D surfaces show that the adsorption capacity may be optimized by adjusting the factors such as concentration, dose, and contact time and making the procedure efficient and feasible and for real world applications.

The 3D surface plot (as shown in **Figure 12c**) demonstrates the adsorption capacity ($Q_{\max}$) is affected by both the ZIF67@BNT adsorbent dose and the methyl orange (MO) initial concentration, with the maximum duration 5 hour. Regardless of the adsorbent dosage $Q_{\max}$ increases as the initial MO concentration increases. Although, at lower initial concentration the difference in the adsorption capacity ($Q_{\max}$) between the 5mg (low dose) and 15mg (high dose) adsorbent doses is minimum. This is probably because of the smaller number of MO molecules available which restrain the adsorption capacity even though more adsorbent (higher dose) is accessible. However, at higher MO concentrations (30 ppm) increasing in the ZIF67@BNT adsorbent dose became remarkable, allowing more molecules on the surface and significantly increase the $Q_{\max}$. The 3D plots (as shown in **Figure 12**) vividly illustrate the interaction impact as both the ZIF67@BNT dosage and MO initial concentration rises, so does $Q_{\max}$, as indicated by the surface upward slope. This explains the ZIF67@BNT adsorbent performs best in high contaminant conditions [316].

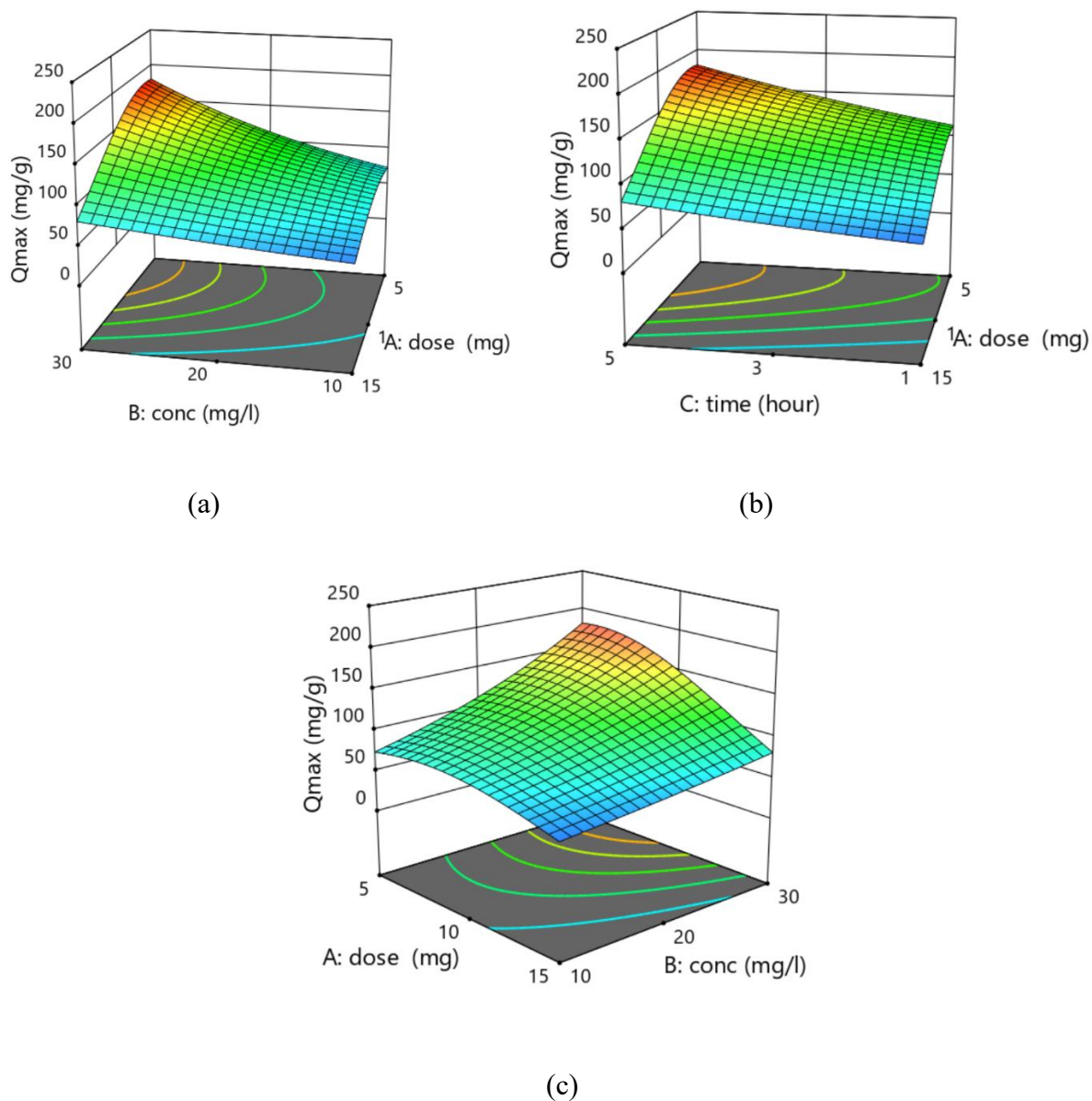


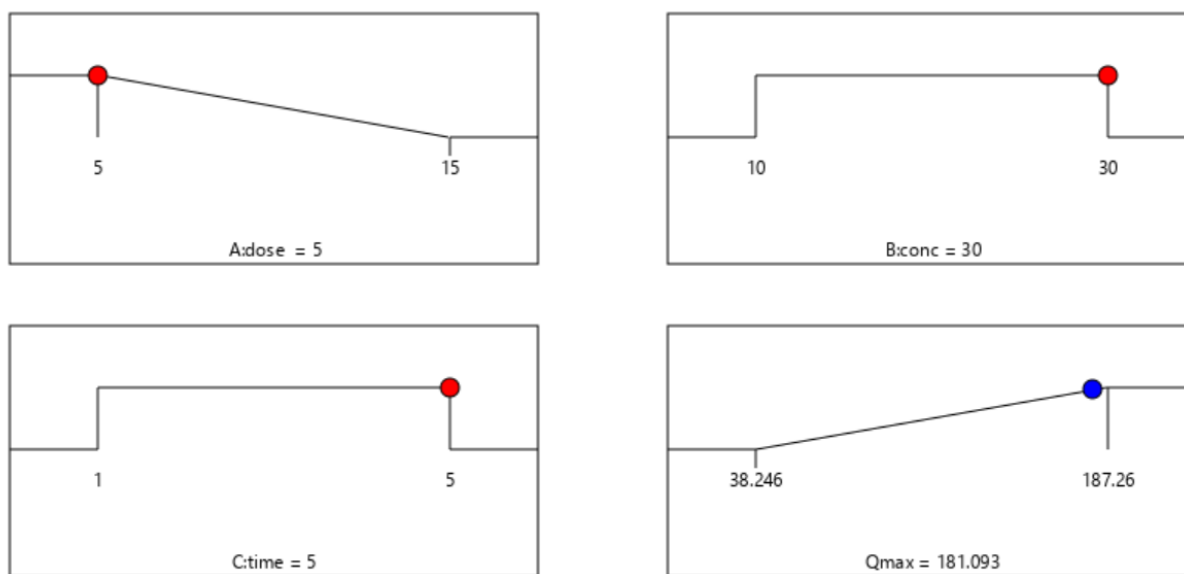
Figure 12: 3D Surface plots interaction between (a) MO Concentration vs ZIF67@BNT Dose vs adsorption capacity (b) Time vs ZIF67@BNT dose vs adsorption capacity (c) ZIF67@BNT Dose vs MO Concentration vs adsorption capacity

4.5. Optimization of results based on RSM model

The RSM experiments' findings and model were then used for response optimization to establish parameters that would enhance MO uptake capacity in the adsorption system. The results of this

optimization approach are shown in **Figure 13**. Based on the experimental results (**Table 9**) show that with a 5 mg adsorbent dosage, an initial CV concentration of 30 ppm, and a contact period of 5 hours, the MO adsorption capacity was 187.26 mg/g.

The RSM optimization tool was used to develop a variety of solutions, and the best result indicated by the desirability analysis shows that the best circumstances for optimizing the 181.093 mg/g adsorption capacity are achieved at 5 mg ZIF67@BNT adsorbent dosage, a low 30 ppm initial concentration, and a short contact time of 5 hour with the desirability 0.9870 which is very close to 1. The 3D surface plots also show that these settings provide the maximum desirability values, suggesting effective adsorption with minimum resources. When investigations are carried out with the identical beginning circumstances, this increases the confidence that the reported results can be reproduced [317].



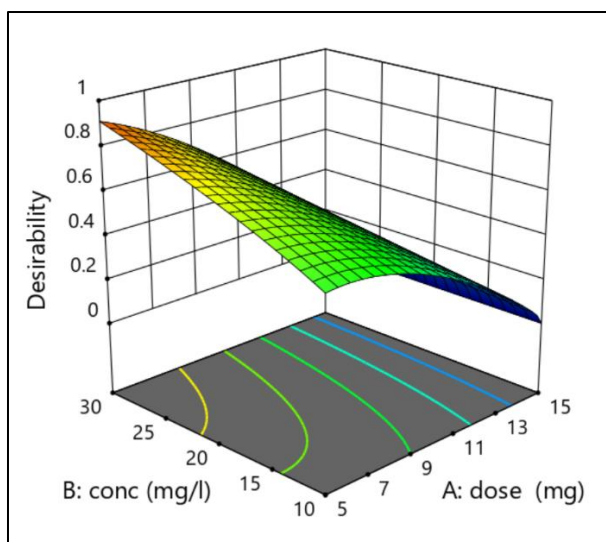


Figure 13: Result of response optimization plot and 3D surface using design expert

4.6. Adsorption kinetics and isotherm analysis

4.6.1. Adsorption Kinetics

Isotherm and kinetic models were used in the examination, and mathematical equations were looked at using techniques developed by earlier researchers. Kinetic studies illuminate the connection between the adsorption rate, the sorbent concentration in the polluted water sample, and the adsorption capacity of the investigated material [318], [319]. The adsorption kinetics data for MO uptake using ZIF67@BNT nanocomposite material was used to a variety of kinetic models, including pseudo-first order (PFO), pseudo-second order (PSO), and Avrami models. As shown in **Figure 14**, the experimental data that corresponds to each model is shown. The Avrami kinetic model, the pseudo-second order (PSO) model, and the pseudo-first order (PFO) model all fit the experimental data well, as is shown clearly in **Figure 14**. $R^2 = 0.9949$, the highest, is for the Avrami model. This alignment implies that there may be a change in the adsorption mechanism involved in MO adsorption by ZIF67@BNT. It suggests a slower approach to equilibrium compared to the PSO model, possibly due to more complex interactions or multiple stages in the

adsorption process. The Avarmi model may account for non-linear kinetics and better captures the tailing behavior observed at later points which jointly influence the adsorption rate [320]. However, because these kinetic models are empirical in nature, care must be taken when using them to understand the reaction process [321]. Furthermore, **Table 11** displays the R^2 values and coefficients for the fitted experimental data in respect to the kinetic models.

Table 11: Constants of Kinetic models for MO adsorption by ZIF67@BNT composite

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

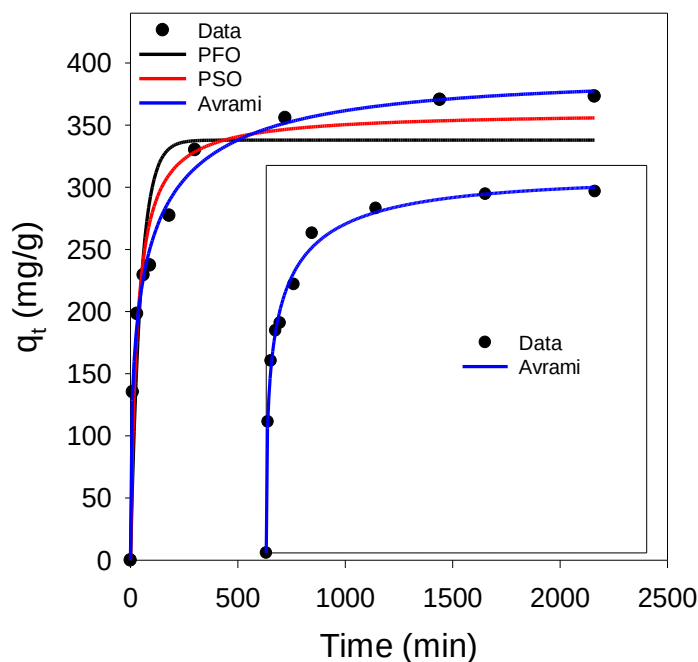


Figure 14: Adsorption kinetic model for MO adsorption by ZIF67@BNT composite

4.6.2. Adsorption Isotherm

The adsorption capacity was further evaluated by using isotherm experiments, and **Table 12** displays the maximum adsorption capacity ($q_{\max}$) values. As seen in **Figure 15**, the Langmuir, Freundlich, and Redlich–Peterson isotherm models were used to assess the experimental results. Understanding the interaction between the MO adsorbate and ZIF67@BNT adsorbent at equilibrium at a fixed temperature is made easier by these models. The R^2 value of 0.9746, which is significantly greater than the value obtained with the Freundlich model, indicates that the experimental data match the Langmuir model well. This suggests that rather than multilayer adsorption on a heterogeneous surface, MO adsorption onto ZIF67@BNT follows a homogenous monolayer adsorption pattern [55,56]. A three-parameter model called the Redlich–Peterson (R–P) isotherm was created to overcome the shortcomings of the Freundlich and Langmuir models. **Figure 15** illustrates how well the experimental results fit the Redlich–Peterson model.

Furthermore, the Redlich–Peterson isotherm behaves similarly to the Langmuir isotherm, and the adsorption conditions for MO dye on the ZIF67@BNT composite adsorbent surface are favorable, as confirmed by the "g" parameter value being larger than 1 [322]. With a maximum adsorption capacity ($q_{\max}$) of 528.7 mg/g predicted by the Langmuir isotherm, the ZIF67@BNT material demonstrated a high capacity for MO adsorption.

Table 12: Model parameters of isotherm model for MO adsorption by ZIF67@BNT composite.

MODELS									
Langmuir Adsorption Isotherm			Freundlich adsorption isotherm			Redlich–Peterson Adsorption Isotherm			
$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$			$q_e = K_F C_e^{1/n}$			$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$			
$q_{\max}$ (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	0.974 6	2.48	59.8	0.9024	14.06	0.0081	1.23	0.9823

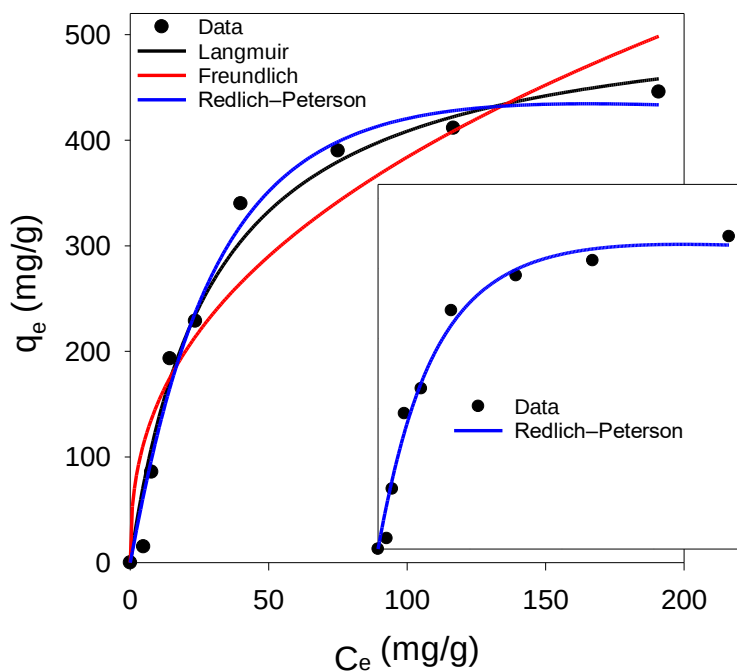


Figure 15: Adsorption Isotherm model for MO adsorption by ZIF67@BNT composite

4.7. Analysis after adsorption and hypothesized adsorption mechanism

XRD and FTIR measurements were conducted on ZIF67@BNT following MO adsorption in order to examine the behavior and the adsorption mechanism of MO on ZIF67@BNT-1 (Before adsorption) and ZIF67@BNT-2 (After adsorption) composite. The FTIR spectra and XRD patterns of the pristine and MO adsorbed ZIF67@BNT composite are shown in comparison in **Figure 16** and **Figure 17** respectively.

The XRD patterns of ZIF67@BNT-1 and ZIF67@BNT-2 illustrate the crystalline structure of the composite before and after its application in methyl orange adsorption. ZIF67@BNT-1 displays distinct, sharp peaks in the 5° – 30° 2θ range, characteristic of ZIF-67's highly ordered framework, indicating that the crystalline nature of ZIF-67 remains intact within the bentonite matrix. This ordered structure is essential for adsorption applications, as it suggests stability and robustness of

the composite material. After adsorption, the XRD pattern for ZIF67@BNT-2 shows noticeable differences. While the primary peaks remain visible, suggesting that the composite retains its crystalline structure which is crucial for reusability in adsorption applications., there is a reduction in overall peak intensity and slight broadening of certain peaks. These changes could indicate interactions between the ZIF67@BNT structure and the methyl orange molecules, which may cause minor distortions or modifications to the lattice structure of the composite. The lower intensity of peaks in ZIF67@BNT-2 could also result from the adsorption process, which potentially introduces some degree of amorphous content or slight structural disorder[316] [323].

The XRD analysis of ZIF67@BNT before and after methyl orange adsorption demonstrates that the composite retains its primary crystalline framework, suggesting good structural stability post-adsorption. The minor reductions in peak intensity and slight peak broadening observed in ZIF67@BNT-2 confirm that while the composite interacts with methyl orange, it maintains its structural integrity, which is crucial for reusability in adsorption applications. This stability, combined with effective dye adsorption, supports the potential of ZIF67@BNT as a viable material for environmental remediation applications, particularly for removing organic dyes from aqueous solutions.

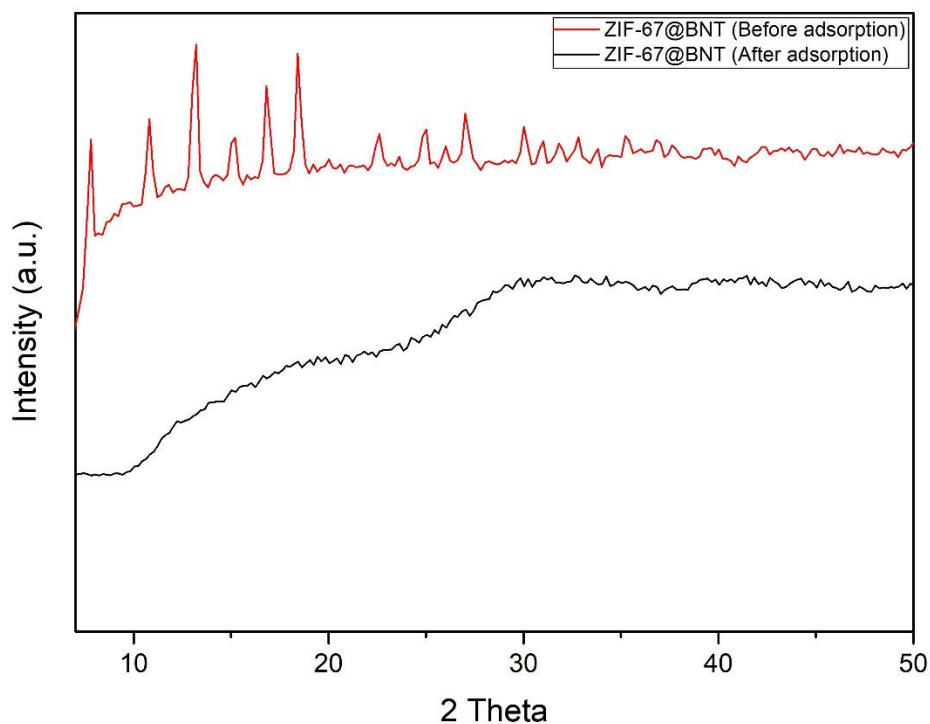


Figure 16: XRD Characterization of ZIF67@BNT Composite Before and After Adsorption of MO

The FTIR spectra of ZIF67@BNT-1 (Before adsorption) and ZIF67@BNT-2 (after adsorption) as shown in the **Figure 17** exhibit key changes that reveal the impact of methyl orange adsorption on the composite's functional groups. In the spectrum of ZIF67@BNT-1, a wide peak around 3400 cm^{-1} is visible, which corresponds to O–H stretching vibrations associated with hydroxyl groups in bentonite. This peak is also present in the spectrum of ZIF67@BNT-2, indicating that the composite retains its hydrophilic nature after adsorption.

Additionally, both spectra show peaks in the region of $1400\text{--}1600\text{ cm}^{-1}$, associated with C=N and C–N stretching vibrations from the imidazole ring in ZIF-67. In the spectrum of ZIF67@BNT-2, these peaks display slight shifts and changes in intensity, suggesting interactions between the

methyl orange molecules and the ZIF-67 structure. This indicates that methyl orange may have been adsorbed primarily through interactions with these nitrogen-containing functional groups.

In the fingerprint region ($500\text{--}1000\text{ cm}^{-1}$), several complex peaks attributed to Si–O and Al–O bending and stretching vibrations, characteristic of bentonite, are observed. In ZIF67@BNT-2, there are slight enhancements or changes in the peaks within this region, possibly due to the adsorption of methyl orange or residual organic fragments, which further supports successful adsorption onto the composite material.

The FTIR analysis demonstrates that the ZIF67@BNT composite retains its structural integrity after adsorption of methyl orange, as indicated by the persistence of characteristic peaks in both the unused and used samples. The subtle shifts and intensity variations in specific peaks, particularly in regions associated with nitrogen-containing groups and the clay matrix, suggest that methyl orange molecules interact with both ZIF-67 and bentonite components of the composite. These interactions reinforce ZIF67@BNT's efficacy as a methyl orange adsorbent and draw attention to its possible use in processes that purge polluted water of organic colors. Because of its durability, reusability, and high adsorption effectiveness, this composite is being seriously considered for use in real-world environmental cleanup projects [324].

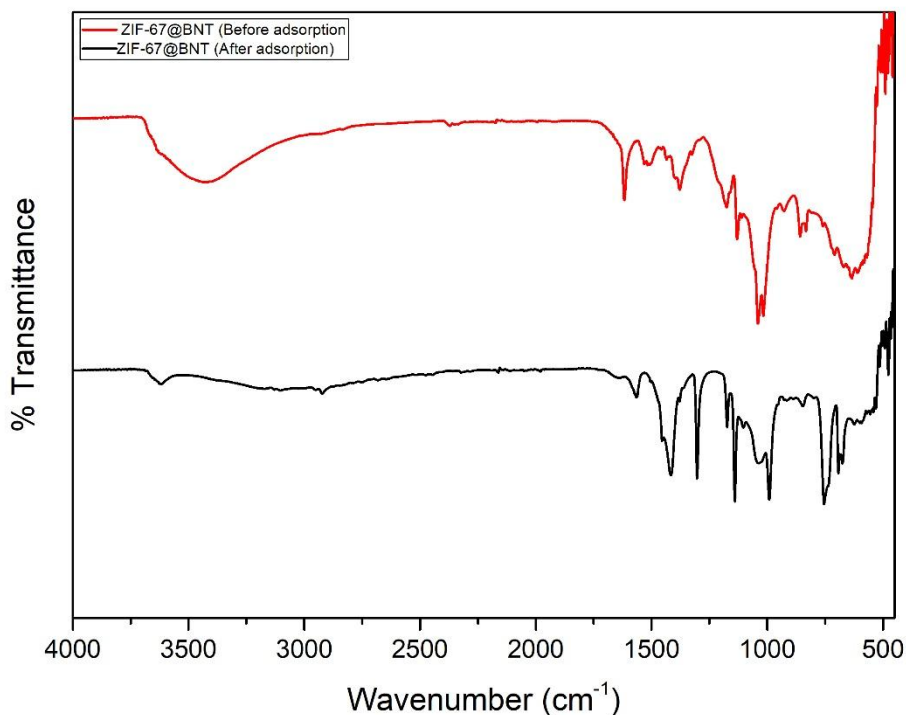


Figure 17: FTIR Characterization of ZIF67@BNT Composite Before and After Adsorption

4.7.1. Hypothesized adsorption mechanism

This hypothesized based on the FTIR and XRD results, adsorption of methyl orange onto the ZIF67@BNT composite is facilitated by a conjunction of mechanisms, including π - π stacking, electrostatic interaction, hydrogen bonding, and pore-filling. The ZIF-67 component, containing positively charged metal ions, interacts with the anionic methyl orange dye through electrostatic attraction. This interaction is particularly significant given the negatively charged nature of methyl orange, which is effectively drawn to the positive sites on ZIF-67's framework. Furthermore, ZIF-67's imidazole rings' aromatic structure permits π - π stacking interactions with methyl orange's aromatic rings, increasing the dye molecules' affinity for the composite. The bentonite component of ZIF67@BNT contributes hydroxyl (-OH) groups, which can form hydrogen bonds with

functional groups on methyl orange, further stabilizing the adsorbed dye molecules on the composite surface [319].

Beyond surface interactions, the porous structure of ZIF-67 facilitates a pore-filling mechanism, whereby methyl orange molecules can enter and be physically trapped within the internal channels of the composite. This pore-filling mechanism is supported by slight changes observed in the XRD patterns post-adsorption, indicating that dye molecules occupy some of the internal spaces. Together, these mechanisms π - π stacking, electrostatic attraction, hydrogen bonding, and pore-filling – provide a multi-faceted approach to effectively adsorb methyl orange onto ZIF67@BNT. This combination of interactions highlights the composite’s high adsorption capacity and stability, making it an excellent candidate for environmental applications in dye removal [316].

4.8. Predicting adsorption capacity with machine learning techniques

A powerful modeling technique with a wide range of uses is machine learning (ML). In light of this, the present MO adsorption data were also analyzed using a thorough ML-based modeling technique. Before developing the models, a hyperparameter tuning process was carried out to establish the optimal conditions for maximizing the performance of each algorithm tested.

This study employed four distinct regression models—Gaussian Process Regressor (GPR), Support Vector Regressor (SVR), Multi-Layer Perceptron Regressor (MLP), and Random Forest Regressor (RFR)—to optimize and evaluate the dataset, with a detailed summary presented in **Table 13**. The MLP model, based on an artificial neural network framework, was configured using a designated kernel, 20 optimization restarts, and a learning rate of 0.014. Additionally, both regularization and target value normalization were enabled to enhance model accuracy and stability. The RFR model was built using 100 decision trees, with a minimum of three samples

required to split nodes, a squared error criterion for performance evaluation, a maximum depth of six layers, and bootstrap sampling enabled to ensure model robustness. The SVR model employed a fifth-degree polynomial kernel, an automatically determined gamma value, and a regularization parameter (C) set to 1.0 to control model complexity. Similarly, the GPR model was designed with a specific kernel, 20 optimization restarts, and the same learning rate of 0.014, with regularization and normalization also activated. These carefully selected configurations aimed to optimize predictive performance while maintaining a balance between model complexity and generalization capability.

Table 13: Analysis of the response surface methodology data using descriptive statistics

Index	Dose (mg)	Initial Conc (mg/L)	Time (hour)	Final Conc. (mg/L)	Adsorption capacity (mg/g)
Count	22	22	22	22	22
Mean	8.409	26.818	9.681	22.530	112.492
Standard deviation	4.193	22.601	10.106	22.120	73.918
Minimum	5	5	1	4.746	15.183
Maximum	15	100	24	95.330	241.800
Range	10	95	23	90.583	226.617
Median	5	20	5	14.582	85.4135
Mode	5	10	24	23	-
Skewness	0.693	2.157	0.774	2.350	0.786
Sum	185	590	213	495.662	2474.832

Sample Variance	17.586	510.822	102.132	489.333	5463.985
Kurtosis	-1.208	5.043	-1.445	5.701	-0.7840

The performance of four machine learning models—Artificial Neural Network (ANN), Random Forest (RF), Support Vector Regression (SVR), and Gaussian Process Regression (GPR) were evaluated using both training and testing datasets, with results illustrated in **Figure 18** and summarized in **Table 14**. The ANN model achieved excellent predictive accuracy during training ($R^2 = 0.999$, RMSE = 0.833, MAE = 0.553), but its performance declined notably on the test set ($R^2 = 0.872$, RMSE = 25.582, MAE = 21.143), indicating potential overfitting. The RF model demonstrated a more balanced performance, with R^2 values of 0.955 for training and 0.927 for testing, though the testing errors were relatively high (RMSE = 38.835, MAE = 33.888), suggesting moderate generalization. In contrast, the SVR model, despite yielding strong results during training ($R^2 = 0.998$, RMSE = 3.997, MAE = 1.476), showed a significant drop in test performance ($R^2 = 0.907$, RMSE = 110.956, MAE = 96.385), reflecting severe overfitting. Among all models, GPR exhibited the most consistent and robust performance across both phases, achieving R^2 values of 0.996 and 0.962 for training and testing, respectively, along with the lowest test errors (RMSE = 21.687, MAE = 14.989). These results suggest that GPR offers superior

generalization and predictive reliability for the given dataset compared to the other models evaluated.

Table 14: Analysis of the response surface methodology data using descriptive statistics

	Testing			Training		
Algorithm	R ²	RMSE	MAE	R ²	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

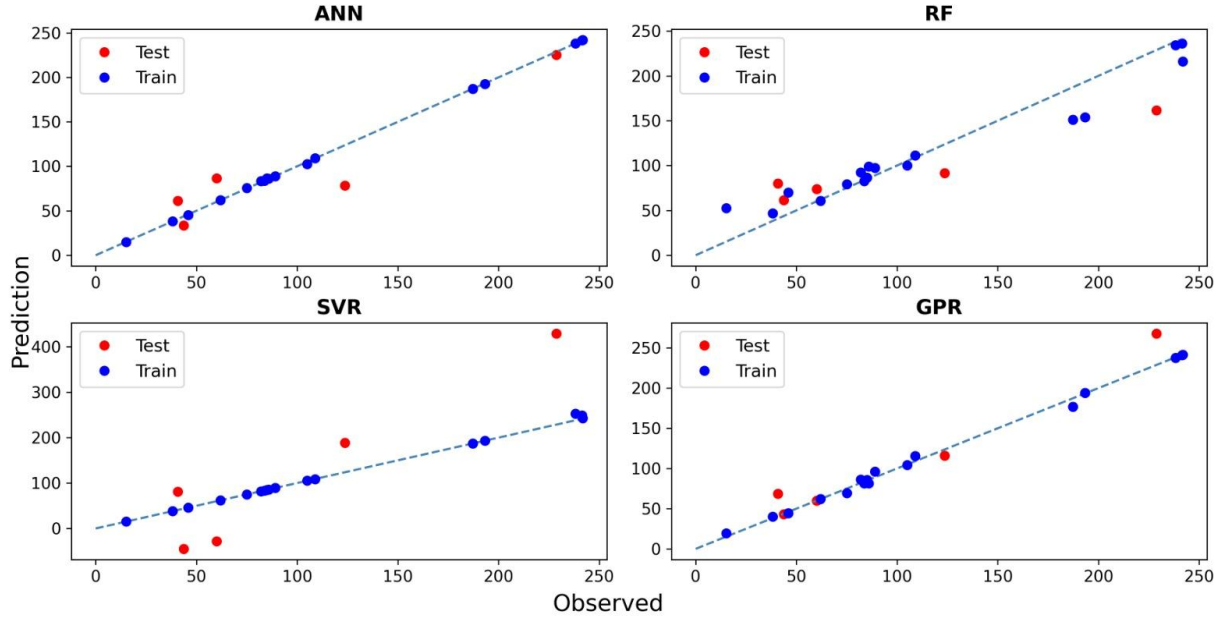


Figure 18: Actual vs predicted machine learning models

The Taylor diagrams in **Figure 19** provide a comparative visualization of model performance for both testing (left panel) and training (right panel) datasets by simultaneously representing the standard deviation, correlation coefficient, and centered root mean square error (RMSE). Each model is depicted as a distinct colored marker, with the star symbol denoting the reference dataset (observed values). In the testing phase, the **Gaussian Process Regression (GPR)** model (magenta) is located closest to the reference point, indicating superior performance with the highest correlation coefficient and a standard deviation closely matching the observed data. The **Artificial Neural Network (ANN)** and **Random Forest (RF)** models also show relatively good alignment, though further from the reference than GPR. In contrast, the **Support Vector Regression (SVR)** model (green) is located far from the reference, reflecting poor correlation and much higher deviation, confirming its overfitting and weak generalization noted earlier. In the training diagram, all models display high correlation coefficients; however, ANN, SVR, and GPR exhibit standard deviations tightly clustered near the reference, while RF shows a comparatively larger deviation. These

findings reinforce earlier conclusions, highlighting GPR's strong consistency and reliability, especially in capturing the true variance and trends in the data with minimal error.

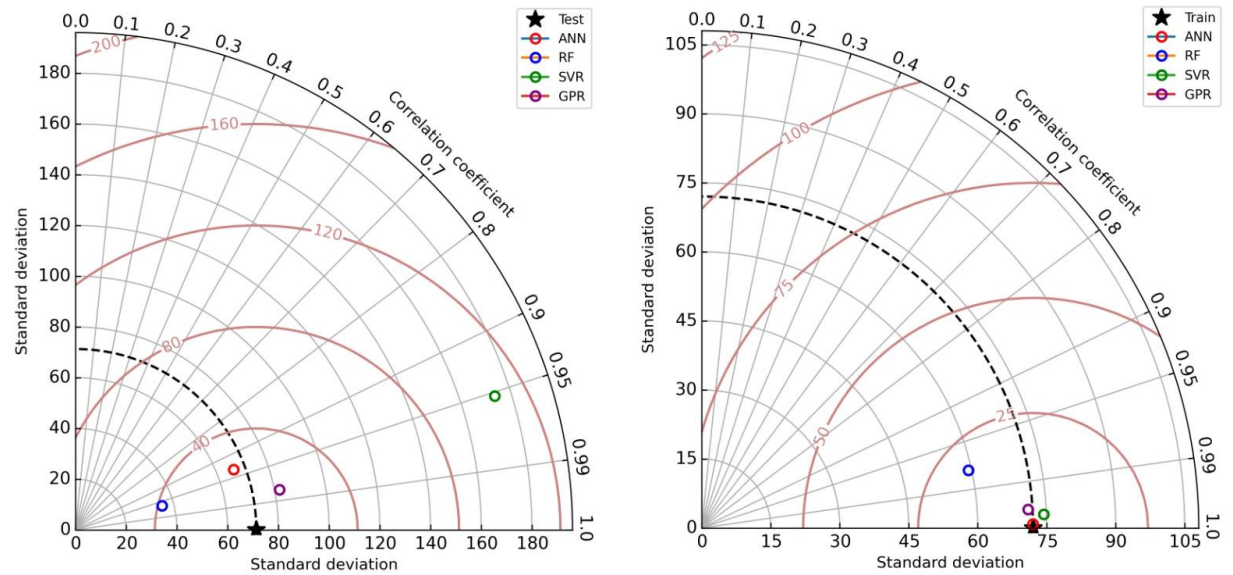


Figure 19: Taylor diagram for both testing and training

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

This study examined the adsorption of MO dye from polluted water through adsorption using the ZIF67@Bentonite composite adsorbent. For this study, a hydrothermal approach is used to synthesis ZIF67@Bentonite coomposite and a range of advanced analytical methods, including Fourier Transform Infrared Spectroscopy (FTIR), X-ray deffraction (XRD), and Thermogravametric analysis (TGA), were utilized to comprehensively evaluate the composite charactristics such as Crytatallin or structural, functional groups and thermal stability characteristics. The results from these characterizations highlighted that the ZIF67@Bentonite composite exhibited enhanced properties compared to ZIF67 alone, resulting in significantly improved adsorption performance.

The batch experimental sheet prepared for the intial Methyl orange (MO) adsorption trials with the help of Design of experiment (DOE) software and was employed to develop the statistically validated model using RSM and ANOVA. The RSM modeling results identified highest initial MO concentration as the most influential operational factor, followed by the lowest ZIF67@Bentonite dosage, and maximum time. Other research, including adsorption kinetics and the use of isotherm models, was conducted to investigate MO adsorption behavior in more depth. The adsorption kinetics were best fitted by the Avrami models, and the CV adsorption data were most closely aligned with the Redlich-Peterson (R-P) and Langmuir isotherms, which showed an outstanding adsorption capacity (528.7 mg/g). Moreover, post-adsorption research revealed that

the extraordinarily high adsorption of MO onto the ZIF67@Bentonite adsorbent is mostly due to electrostatic and π - π stacking interactions.

The non-linear dynamics of the adsorption process were not evaluated by RSM, despite the fact that it successfully adjusted configurations for optimum removal efficiency. To overcome these limitations, an advanced machine learning (ML) modeling approach was implemented to develop artificial intelligence (AI) models such as ANN, SVR, MLP and GPR, capable of accurately predicting MO removal from contaminated water using ZIF67@Bentonite.

These models provided insightful information on the non-linear relationships between affecting variables and MO dye's adsorption capability. Evaluation metrics and Taylor diagrams supported the validation results, which showed that the GPR technique performed better in terms of prediction accuracy than other models. This demonstrates how well the model captures the complexities of the adsorption process under various operating settings and how reliable it is at forecasting dye removal results. Furthermore, the machine learning approach proves effective in predicting MO adsorption onto the innovative ZIF67@Bentonite composite.

In conclusion, the new ZIF67@Bentonite adsorbent can effectively treat MO-contaminated water, and both traditional and sophisticated modeling approaches provide the best results for real-world uses.

5.2. Recommendations

- *Pilot and Large-scale Implementation:*

Future studies should focus on pilot-scale testing to assess the practical applicability and economic feasibility of the ZIF-67@Bentonite composite adsorbent in industrial-scale wastewater treatment.

- *Regeneration and Reusability Analysis:*

Investigating the regeneration and reusability of ZIF-67@Bentonite through multiple adsorption-desorption cycles would be beneficial to evaluate the composite's stability, longevity, and economic efficiency.

- *Adsorption Mechanism Studies:*

Conduct advanced spectroscopic and microscopic studies (such as SEM, TEM, XPS, or NMR) to gain deeper insights into the adsorption mechanisms, specifically focusing on the molecular interactions between MO molecules and active sites on the ZIF-67@Bentonite composite.

- *Comparative Analysis with Other Pollutants:*

Extend research efforts by evaluating the adsorption efficiency of the composite for other pollutants, including heavy metals, pharmaceuticals, organic dyes, and pesticides, to assess its broad-spectrum applicability.

- *Effect of Environmental Conditions:*

Evaluate the adsorption performance under different environmental conditions (varying temperature, pH, salinity, and presence of competing ions) to establish the robustness and applicability of ZIF-67@Bentonite in real wastewater environments.

- *Integration with Advanced Oxidation Processes (AOPs):*

Investigate the potential synergistic effects of integrating the adsorption method with advanced oxidation processes (e.g., photocatalysis, ozonation, Fenton-like reactions) to further enhance the removal efficiency and detoxification of persistent organic pollutants.

- *Life Cycle Assessment (LCA):*

Conduct a comprehensive life-cycle assessment (LCA) and techno-economic analysis to quantify the environmental impacts and economic sustainability associated with the synthesis and use of ZIF-67@Bentonite composites in practical applications.

- *Machine Learning and Optimization:*

Expand the use of machine learning methods by integrating hybrid ML approaches (e.g., ensemble learning, deep neural networks, optimization algorithms like Genetic Algorithms or Particle Swarm Optimization) to further improve prediction accuracy, optimize experimental conditions, and enhance overall removal efficiency.

- *Real Wastewater Application:*

Validate the performance of ZIF-67@Bentonite composites with actual industrial or municipal wastewater samples to assess its effectiveness and identify potential operational challenges or interferences in real-world scenarios.

- *Safety and Environmental Impact Evaluation:*

Future research should thoroughly investigate the environmental safety, ecotoxicological impacts, and potential secondary pollution risks associated with the use and disposal of spent ZIF-67@Bentonite composites.

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Publications

Book Chapter

1. Book: The Effect of Dust and Heat on Photovoltaic Modules: Impacts and Solutions
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