OPEN ACCESS

Scholars International Journal of Chemistry and Material Sciences

Abbreviated Key Title: Sch Int J Chem Mater Sci
ISSN 2616-8669 (Print) |ISSN 2617-6556 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: http://saudijournals.com

Original Research Article

Box-Behnken Optimization of Methylene Blue Adsorption Using *Pterocarpus santalinoides* Fruit Activated Carbon

Nleonu Emmanuel C[1,2]*, Ojiabo Kenechukwu T[3], Chibuike Success T[1], Ihemadu Promise[1]

[1]Chemistry/Biochemistry Department, Federal Polytechnic Nekede, Owerri, Imo State, Nigeria
[2]Material and Electrochemical Research Unit, Federal Polytechnic Nekede, Owerri, Imo State-Nigeria
[3]Chemical Engineering Department, Federal Polytechnic Nekede, Owerri, Owerri, Imo State, Nigeria

DOI: https://doi.org/10.36348/sijcms.2026.v09i05.001 | **Received:** 17.07.2026 | **Accepted:** 10.09.2026 | **Published:** 14.09.2026

***Corresponding author:** Nleonu Emmanuel C
Chemistry/Biochemistry Department, Federal Polytechnic Nekede, Owerri, Imo State, Nigeria

Abstract

The removal of synthetic dyes such as Methylene Blue from aqueous effluents is a critical environmental challenge. This study investigates the efficacy of activated Carbon derived from *Pterocarpus santalinoides* Fruit as a low-cost and renewable adsorbent of Methylene Blue dye. The *Pterocarpus santalinoides* activated carbon was analyzed using scanning electron microscopy and Fourier transform infra-red spectroscopy. The Box-Behnken design of response surface methodology (RSM) method was adopted to optimize the adsorption process variables such as contact time (20 – 100 min), adsorbent dose (0.1 – 0.5 g), initial dye concentration (10 – 50 mg/l), and temperature (30 – 60 ℃). The characterization result revealed the good adsorptive properties of the *Pterocarpus santalinoides* activated carbon. The ANOVA result indicates that quadratic model was reliable for predicting methylene blue removal with R^2 of 0.9267 and 0.9618 for adsorption capacity. The optimum condition for the maximum removal efficiency of 95.90 % and adsorption capacity of 5.70 mg/g were achieved at contact time (56.33 min), adsorbent dose (0.43 g), MB concentration (36.26 mg/l) and temperature (55.91 ℃). Both Henry and Langmuir isotherms were well fitted to the adsorption data. The adsorption kinetics was best described by the Psuedo–second order model indicating a chemisorption-dominated process. Equilibrium Isotherm data showed a high correlation with the Langmuir model suggesting a monolayer adsorption on a homogeneous surface. This study successfully demonstrated the efficiency of Box Behnken Design of Response Surface Methodology (BBD – RSM) as a powerful tool for modeling and optimizing the adsorption process, providing a clear path-way for maximizing the efficiency of *Pterocarpus santalinoides* based activated Carbon for dye wastewater treatment and environmental remediation.

Keywords: *Pterocarpus Santalinoides*, activated carbon, adsorption, box behnken design, isotherm model.

1.0 INTRODUCTION

The textile, pharmaceutical, and leather industries extensively utilize synthetic dyes to color their products; with methylene blue (MB) being one of the most widely applied cationic dyes owing to its intense color and chemical stability. MB finds applications in dyeing natural fibers such as cotton, wool, and silk, as well as in biological staining procedures and as a redox indicator in chemical analysis (Berradi *et al.,* 2019). However, the discharge of untreated effluents containing such dyes into aquatic environments poses serious ecological concerns. These effluents elevate biochemical oxygen demand (BOD) and chemical oxygen demand (COD), thereby disturbing the balance of receiving water bodies (Hossain *et al.,* 2022). Synthetic dyes like MB are highly persistent and resistant to natural degradation processes, leading to bioaccumulation along food chains and potential long-term risks to aquatic life and human health (Rawat *et al.,* 2018).

A major contributor to dye pollution is the low fixation efficiency of dyeing processes, where up to 15% of applied dyes can remain unbound and enter wastewater streams as colored effluents (Khan *et al.,* 2014). This coloration reduces light penetration in water bodies, inhibiting photosynthesis in aquatic plants and creating oxygen-depleted (anoxic) conditions that harm fish and other organisms (Berradi *et al.,* 2019). Traditional wastewater treatment approaches, including biological degradation and chemical oxidation, frequently prove inadequate for removing recalcitrant dyes such as MB, owing to their resistance to

biodegradation and the risk of forming harmful secondary byproducts (Hossain *et al.,* 2022). Moreover, advanced methods such as membrane filtration and photocatalysis are often prohibitively expensive and energy-intensive, restricting their adoption in resource-limited settings and perpetuating the widespread problem of industrial dye contamination in developing regions (Ismail *et al.,* 2022).

Addressing dye pollution through sustainable, cost-effective adsorbents is therefore of critical importance. The development of biomass-derived activated carbons has received considerable attention because agricultural residues provide renewable carbon sources for wastewater treatment applications. Biomass-based adsorbents offer advantages including low precursor cost, availability, waste valorization potential, and tunable surface chemistry after activation. Recent studies have demonstrated that fruit wastes, agricultural residues, and plant-derived materials have been successfully converted into activated carbons for methylene blue removal, with adsorption performance strongly influenced by activation conditions, pore structure, surface functional groups, and experimental parameters (Shelke *et al.,* 2022; Tan *et al.,* 2016). Although numerous biomass-derived activated carbons have been reported, adsorption performance varies significantly depending on precursor composition and preparation conditions. Parameters such as BET surface area, pore volume, surface functional groups, pH, adsorbent dosage, initial dye concentration, and temperature strongly influence adsorption behaviour (Shelke *et al.,* 2022; Al-Ghouti & Da'ana, 2020). Therefore, investigation of locally available and underutilized biomass resources remains important for developing sustainable adsorption materials.

In the present study, *Pterocarpus santalinoides* fruit was investigated as a precursor material for activated carbon production. The study contributes to the existing literature by combining biomass conversion with statistical optimization using Box–Behnken Response Surface Methodology. RSM provides an efficient approach for evaluating the individual and interactive effects of multiple adsorption parameters while reducing the number of experimental runs compared with conventional one-factor-at-a-time approaches. The application of optimization techniques has been widely recognized as an effective strategy for improving adsorption process performance and understanding variable interactions (Myers *et al.,* 2016).

2.0 METHODOLOGY

2.1 Sample Collection and Pretreatment

Pterocarpus santalinoides fruits were collected from Federal Polytechnic Nekede, Owerri, Imo State, Nigeria. The collected material was thoroughly washed with tap water to remove dirt, dust, and surface impurities, followed by rinsing with distilled water. The cleaned biomass was sun-dried for 14 days and then oven-dried at 105 °C for 24 h to achieve constant weight and remove residual moisture. The dried material was pulverized using a mechanical grinder and stored in an air tight container.

2.2 Preparation of Activated Carbon

Activated carbon was prepared from *Pterocarpus santalinoides* fruit through a simple physical activation process. The dried and ground fruit was placed in a muffle furnace and heated at 500 °C for 3 hours. After activation, the furnace was allowed to cool to ambient temperature under vacuum conditions. The resulting activated carbon was dried at room temperature, ground further, and sieved to obtain a fine powder with a particle size of 250 mesh. The final powdered adsorbent was labeled, stored in airtight plastic bottles, and kept in a desiccator until required for characterization and adsorption experiments.

2.3 Characterization of Activated Carbon

The surface functional groups of the activated carbon before and after methylene blue adsorption were characterized by Fourier Transform Infrared (FTIR) spectroscopy (Happ-Genzel). The surface morphology of the activated carbon before and after adsorption was investigated using Scanning Electron Microscopy (Phenom Prox).

Batch Adsorption experiments

The adsorption experiment were studied based on the influence of contact time (20, 40, 60, 80, 100 mins), adsorbent dose (0.1, 0.2, 0.3, 0.4, 0.5 g), MB concentration (10, 20, 30, 40, 50 mg), and temperature (30, 40, 50, 60 ℃) respectively. The removal of MB dye in solution was determined by measuring MB's absorbance before and after treatment with *Pterocarpus santalinoides* activated using UV-Vis spectrophotometer (D-8 Drawell) at maximum wavelength of 664 nm. The MB dye removal percentage and adsorption capacity (q_e) was calculated according to equation 1 and 2, respectively:

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

$$q_e = \frac{(Co - Ce)V}{m} \times 100 \quad (2)$$

Where C_O and Ce are the initial and the equilibrium methylene blue concentration (mg/l), respectively, V is the volume of solution (L) and m is the mass (g) of the adsorbent.

Design of Experiments Using BBD

Optimization of variables in removal of methylene blue dye was studied using Box-behnken design (BBD) of research surface methodology (RSM) provided by the Design Expert 13 software (start- Ease Inc., USA). Four experimental factors with three levels were selected as displayed in Table 1. The contact time, adsorbent dose, initial MB concentration, and temperature were set as parameters. Percentage removal efficiency was set as a responsive parameter. Based on

factorial experimental design, four factors with three levels, 29 runs were obtained by the Design Expert software version 13.

Table 1: Experimental range and coded levels of the selected process parameters

Parameters	Coding	Units	Design range and coded levels		
			-1	0	+1
Contact time (min)	A	min	20	60	100
Adsorbent dose	B	g	0.1	0.3	0.5
Dye concentration	C	ppm	10	30	50
Temperature	D	℃	30	45	60

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

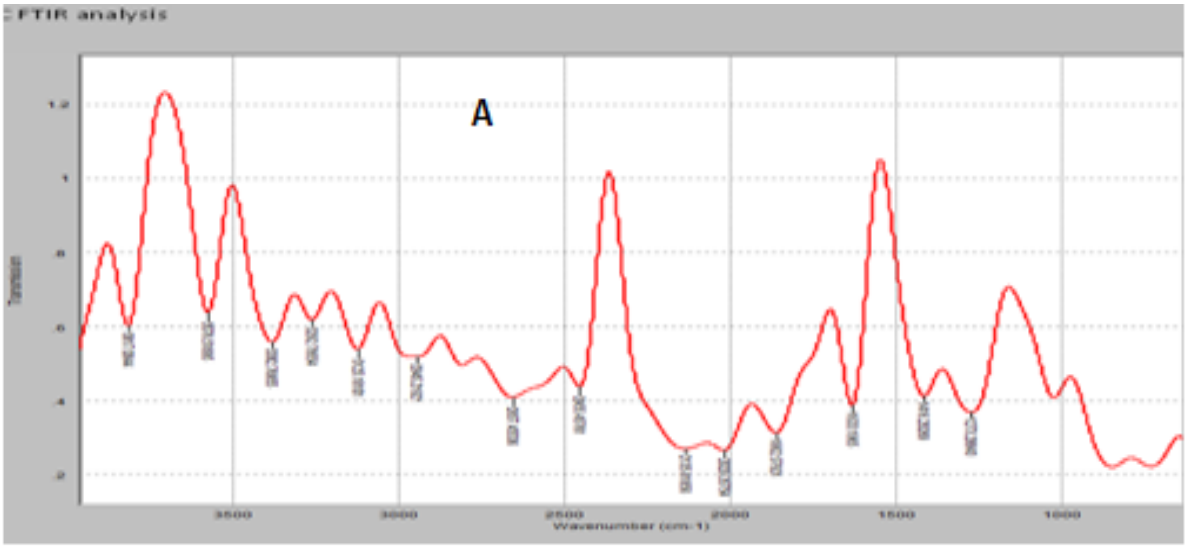
3.1.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was used to identify the surface functional groups on *Pterocarpus santalinoides* activated carbon (PSAC) before and after methylene blue (MB) adsorption and to explore the dominant adsorption mechanisms.

Before adsorption (Figure 1A), the FTIR spectrum revealed several characteristic bands, including a broad O–H stretch at 3382 cm^{-1} and sharper peaks at 3576–3817 cm^{-1}, indicating phenolic and alcoholic hydroxyl groups. Aromatic C–H stretching appeared at 3125 cm^{-1}, and the C=C stretch at 1633 cm^{-1} suggested π-electron-rich domains from lignin structures. Aliphatic C–H stretching occurred at 2945 cm^{-1}, with a C=O stretch at 1862 cm^{-1} from lactones or carbonyl groups. Additional C–O stretching at 1273 cm^{-1} and minor bands at 2020, 2135, 2455, and 2657 cm^{-1} pointed to activation-related impurities.

After MB adsorption (Figure 1B), several FTIR bands shifted or changed intensity, indicating the involvement of specific functional groups in binding. The O–H stretch shifted to 3201 cm^{-1}, and the free O–H region at 3578–3819 cm^{-1} remained, suggesting hydrogen bonding with the cationic nitrogen of MB. The aromatic C–H stretch shifted to 3014 cm^{-1}, and the C=C aromatic band at 1633 cm^{-1} remained, indicating π–π stacking interactions with the dye. The C=O stretch slightly shifted to 1880 cm^{-1}, suggesting coordination or ion-exchange interactions. Additional C–O stretching at 1309 and 1097 cm^{-1} highlighted the role of oxygen-containing groups in polar and electrostatic interactions. An out-of-plane aromatic C–H bending appeared at 934 cm^{-1}.

The observed changes in FTIR bands after methylene blue adsorption indicate possible involvement of surface functional groups during dye uptake. However, FTIR peak shifts alone cannot independently confirm specific adsorption mechanisms. Therefore, the adsorption process should be interpreted using combined evidence from FTIR analysis, equilibrium modelling, kinetic behaviour, and thermodynamic parameters. The interaction between methylene blue and activated carbon surfaces may involve several contributions, including electrostatic attraction between charged surface sites and dye molecules, π–π interactions involving aromatic structures, hydrogen bonding, and pore filling. Similar multi-mechanistic adsorption behaviour has been reported for biomass-derived activated carbons used for methylene blue removal (Hameed *et al.,* 2007; Shelke *et al.,* 2022).



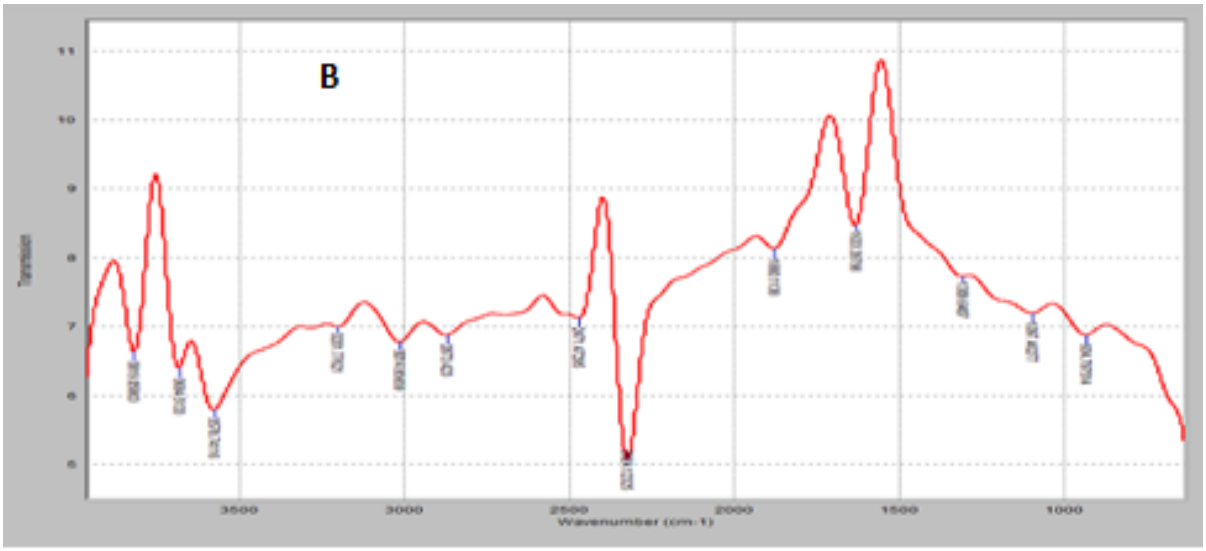


Figure 1: FT-IR Spectrum of *Pterocarpus santalinoides* activated carbon (A) before and (B) after adsorption of MB

3.1.2 Scanning Electron Microscopy

The surface morphology of *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC) before and after methylene blue (MB) adsorption was analyzed using Scanning Electron Microscopy (SEM). Before adsorption (Figure 2A), the SEM image shows a highly porous and heterogeneous surface with an interconnected network of pores and irregular cavities, typical of activated lignocellulosic materials. This structure provides abundant active sites, enhancing its potential as an adsorbent for cationic dyes like MB. After MB adsorption (Figure 2B), the surface morphology changes significantly, with many pores filled or reduced, resulting in a smoother surface. The reduced pore openings suggest that MB molecules have occupied the pores and adsorbed onto the surface. These observations confirm that MB is primarily adsorbed via pore-filling and surface attachment mechanisms, highlighting PSAC's strong binding affinity and high adsorption capacity for methylene blue, making it an effective, low-cost adsorbent for dye removal.

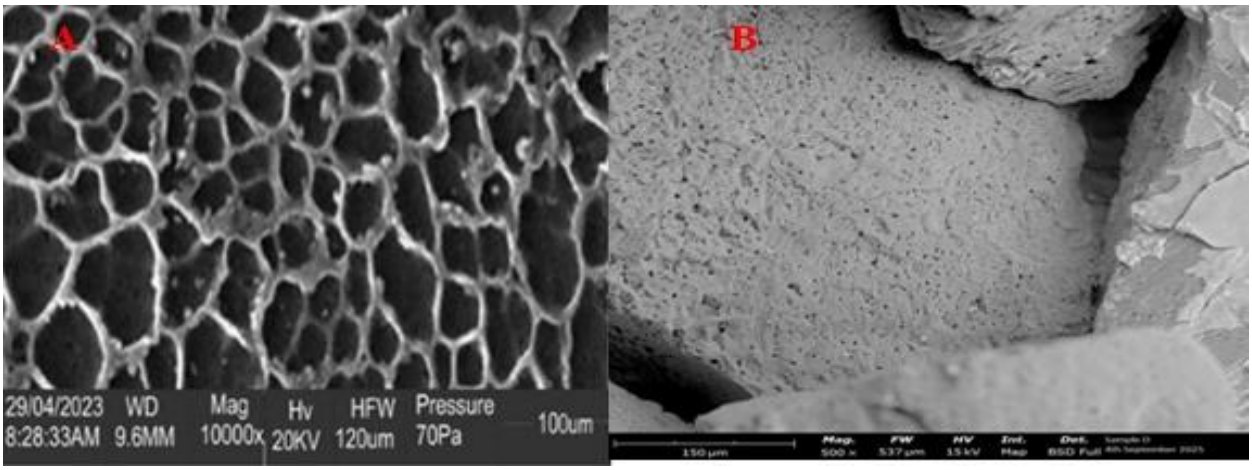


Figure 2: SEM image of *Pterocarpus santalinoides* activated carbon (A) before and (B) after adsorption of MB

3.2 Adsorption Study

3.2.1 Effect of Contact Time on Methylene Blue Adsorption

The effect of contact time on methylene blue (MB) adsorption onto *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC) was studied with an initial dye concentration of 40 mg/l, an adsorbent dose of 0.1 g per 100 ml, and room temperature. The results in Figure 3 show that MB removal increased rapidly from 76.43% at 20 min to 86.45% at 40 min (q_e = 34.58 mg/g), reflecting abundant surface sites. After 40 min, efficiency slightly decreased to 79.68% at 100 min due to site saturation, competition, and minor desorption. The rapid initial increase followed by a slower approach to equilibrium aligns with pseudo-second-order kinetics and chemisorption. Thus, 40 min is the optimal contact time, confirming PSAC as an effective, low-cost adsorbent for cationic dyes.

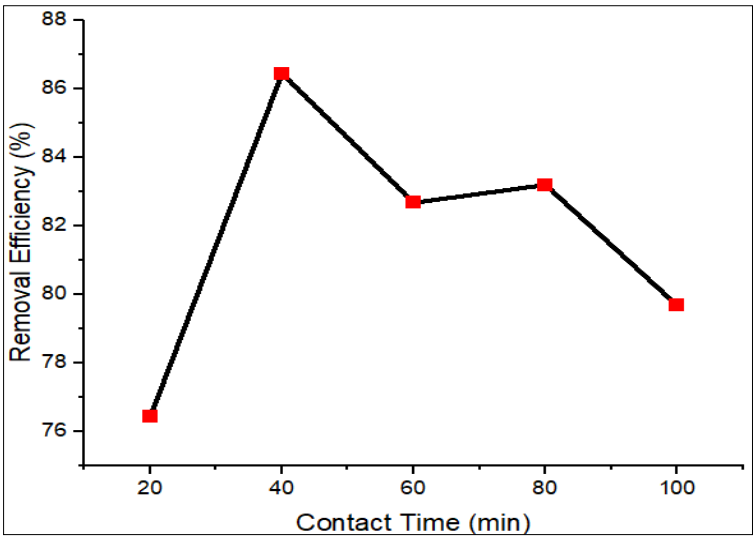


Figure 3: Effect of contact time on percentage removal of methylene blue by *Pterocarpus santalinoides* activated carbon

3.2.2 Effect of Initial Methylene Blue Concentration

The effect of initial methylene blue (MB) concentration on adsorption using *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC) was studied at concentrations from 10 to 50 mg/l, with a fixed adsorbent dose of 0.1 g per 100 ml and a 60-minute contact time at room temperature. The results in Figure 4 show that MB removal remained high (99.03–99.85%) across concentrations, peaking at 99.85% at 10 mg/l. Equilibrium adsorption capacity increased from 9.97 mg/g at 10 mg/l to 39.61 mg/g at 40 mg/l. The consistent high removal at lower concentrations indicates abundant active sites, while the slight decrease at 40–50 mg/l suggests site saturation. Optimal performance occurs around 30–40 mg/l, confirming PSAC as an effective adsorbent for cationic dyes.

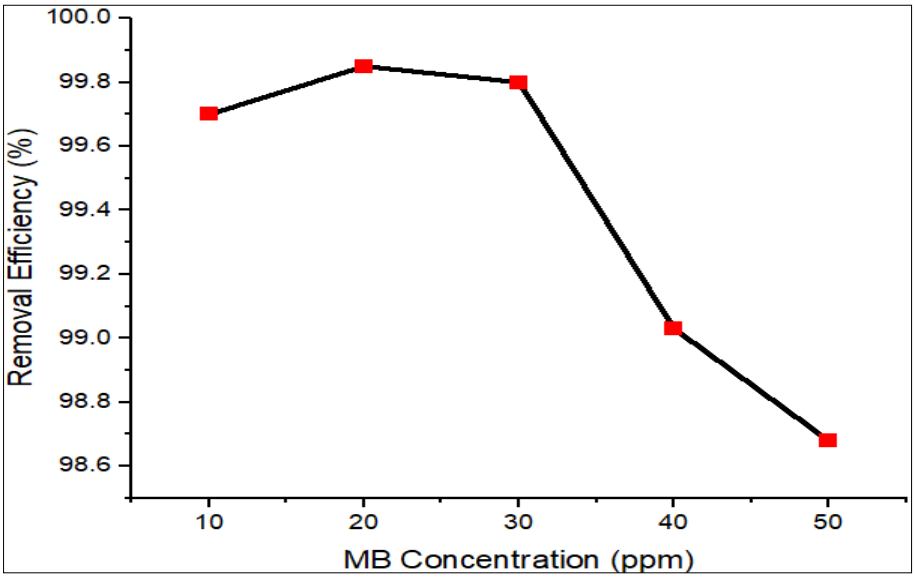


Figure 4: Effect of initial MB concentration on percentage removal of methylene blue by *Pterocarpus santalinoides* activated carbon

1.2.3 Effect of Adsorbent Dosage on Methylene Blue Adsorption

The effect of adsorbent dosage on methylene blue (MB) removal using *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC) was studied with dosages from 0.1 g to 0.5 g in 100 ml of 40 mg/l MB solution, at a fixed contact time of 60 minutes and room temperature. The results in Figure 5 show that MB removal increased significantly from 74.25% at 0.1 g to 99.93% at 0.4 g and 0.5 g, due to more available active sites and surface area. However, equilibrium adsorption capacity decreased from 29.70 mg/g at 0.1 g to 7.99 mg/g at 0.5 g as the dye was distributed across more sites. Removal efficiency rose sharply at low dosages and leveled off near 100% at 0.4 g, making it the optimal dosage for near-complete MB removal.

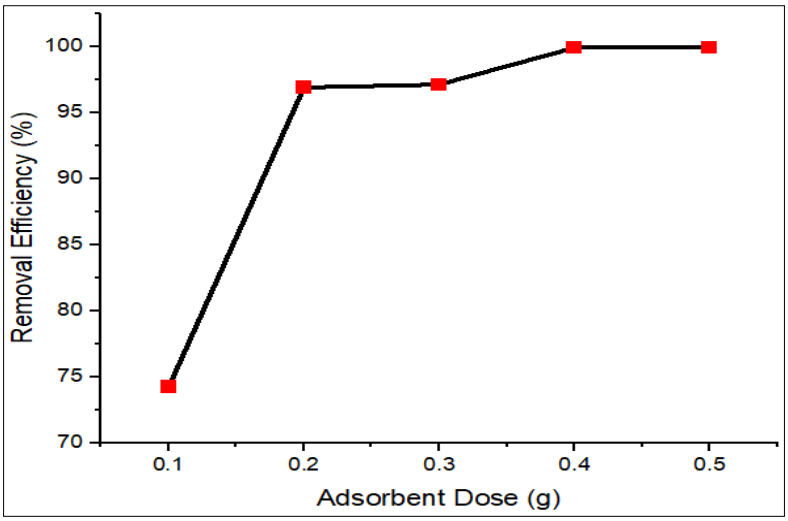


Figure 5: Effect of adsorbent dose on percentage removal of methylene blue by *Pterocarpus santalinoides* activated carbon

1.2.4 Effect of Temperature on Methylene Blue Adsorption

The effect of temperature on methylene blue (MB) adsorption onto *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC) was studied at 30–60°C using 100 ml of 40 mg/l MB solution, 0.1 g adsorbent, and a contact time of 60 minutes. The results in Figure 6 shows that MB removal increased from 82.68% at 30°C to 87.13% at 50°C (q_e = 34.85 mg/g), indicating an endothermic process. Higher temperatures improve dye mobility, intraparticle diffusion, and adsorbent-dye interactions. However, removal efficiency slightly decreased to 86.08% at 60°C, likely due to weakened interactions or increased thermal agitation. These findings confirm optimal performance at 50°C, demonstrating PSAC's effectiveness in MB removal at moderate temperatures.

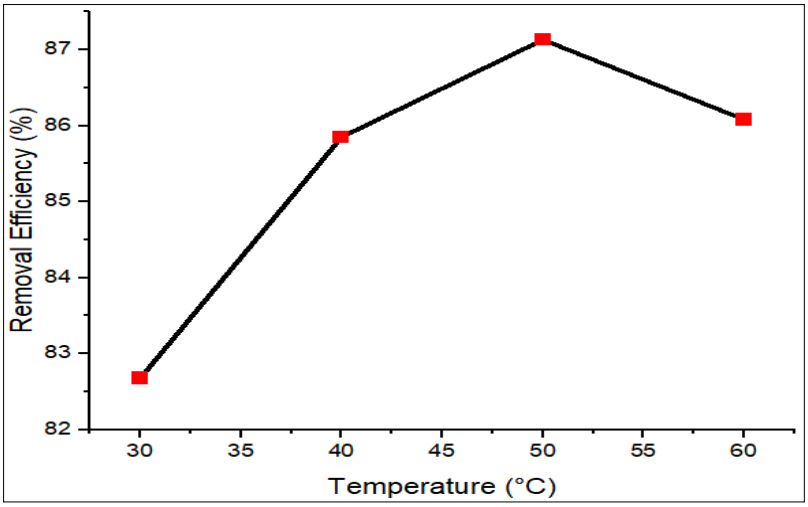


Figure 6: Effect of solution temperature on percentage removal of methylene blue by *Pterocarpus santalinoides* activated carbon

3.3 Box-Behnken Design (BBD) of Response Surface Methodology

The Box-Behnken Design (BBD) analysis results is tabulated in Table 2 and result, revealed that methylene blue (MB) adsorption onto activated carbon derived from *Pterocarpus santalinoides* fruit is strongly influenced by adsorbent dose, initial dye concentration, and their interactions. Increasing the adsorbent dose generally enhanced removal efficiency due to the availability of more active sites, while higher MB concentrations increased the driving force for adsorption, leading to higher adsorption capacities (Ren *et al.,* 2024). Contact time also played an important role, with longer times promoting greater dye uptake, although adsorption occurred relatively rapidly even at shorter durations. Temperature had a moderate effect, suggesting that the adsorption process is predominantly governed by physisorption mechanisms. The BBD model successfully predicted experimental outcomes, with minor deviations, confirming the suitability of the

quadratic model for optimizing adsorption conditions. The relationship between the independent parameters, and MB removal and adsorption capacity were expressed by the following quadratic model Equation 4 and 5.

Removal Efficiency = +102.90 - 0.035A + 14.66B + 0.30C – 0.73D + 1.2AB – 0.00081AC – 0.001AD + 0.39BC – 0.092BD + 0.002CD + 0.0005A^2 – 36.65B^2 – 0.0052C^2 + 0.0078D^2. (4)

Adsorption Capacity = +29.08 – 0.08A – 124.19B + 0.826C – 0.459D + 0.04AB – 0.0047AC – 0.0010AD – 1.749BC + 0.0267BD – 0.0067CD + 0.0059A^2. (5)

Overall, the optimized conditions identified through BBD were a contact time of 60 minutes, adsorbent dose of 0.3 g, MB concentration of 30 ppm, and a temperature of 45 °C, achieving approximately 94–96% removal efficiency and 9.41 mg/g adsorption capacity. These results demonstrate that *Pterocarpus santalinoides* fruit-derived activated carbon is a highly effective, rapid, and reliable adsorbent for methylene blue removal. The study also highlights the importance of considering variable interactions, as adsorption performance depends not only on individual factors but also on their synergistic effects, providing a strong foundation for practical wastewater treatment applications.

Table 2: Batch adsorption process parameters used in BBD with the Experimental and predicted values for the response

Number of Run	Contact Time (min)	Adsorbent Dose (g)	Concentration (ppm)	Temperature (℃)	Removal Efficiency (%) Experimental	Removal Efficiency (%) Predicted	Adsorption (mg/g) Experimental	Adsorption (mg/g) Predicted
1	100	0.1	30	45	89.37	90.48	26.81	27.02
2	60	0.3	30	45	94.1	94.10	9.41	7.72
3	60	0.5	30	60	94.1	94.79	5.64	5.89
4	60	0.1	30	60	93.7	92.29	28.11	27.54
5	100	0.3	50	45	96.7	94.80	16.11	17.22
6	20	0.5	30	45	95.7	94.35	5.74	5.53
7	100	0.5	30	45	95.1	95.49	5.7	5.93
8	60	0.3	50	60	95.9	96.59	15.98	17.48
9	100	0.3	30	60	94.7	94.76	9.47	9.54
10	60	0.5	50	45	96.64	96.71	9.66	6.50
11	60	0.5	10	45	88	87.48	1.76	4.46
12	60	0.3	30	45	94.1	94.10	9.41	7.72
13	20	0.3	30	60	96.6	96.78	9.66	9.92
14	20	0.1	30	45	93.9	93.27	28.17	27.94
15	60	0.3	30	45	94.1	94.10	9.41	7.72
16	60	0.5	30	30	96.3	97.02	5.77	5.95
17	60	0.1	10	45	86.7	87.56	8.67	12.22
18	60	0.3	50	30	97.12	97.09	16.18	17.68
19	60	0.3	10	30	93.1	92.17	3.1	1.60
20	20	0.3	50	45	97.18	96.91	16.19	17.55
21	60	0.1	30	30	94.8	93.43	28.44	27.80
22	60	0.3	30	45	94.1	94.10	9.41	7.72
23	20	0.3	10	45	88.3	89.51	2.94	1.44
24	20	0.3	30	30	96.4	97.26	9.64	9.96
25	100	0.3	30	30	96.9	97.65	9.69	9.82
26	60	0.3	10	60	89.5	89.29	2.98	1.48
27	60	0.1	50	45	89.1	90.54	44.55	42.24
28	100	0.3	10	45	90.4	89.98	3.01	1.26
29	60	0.3	30	45	94.1	94.10	0.94	7.72

3.3.1 Model Validation and Analysis of Variance

Table 3, 4, and 5 displays the box-behnken design (BBD) validation and analysis of variance model for methylene blue adsorption onto *Pterocarpus santalinoides* fruit-derived activated carbon was validated through statistical analysis, showing its significance with an F-value of 12.64 and p-value < 0.0001. Initial methylene blue concentration was the most influential factor, followed by adsorbent dose and temperature, indicating that increasing carbon dose and optimizing temperature enhance dye removal. Several interaction and quadratic terms were significant, confirming nonlinear relationships. The model showed high reliability for predicting methylene blue removal, with an R^2 of 0.9267 for removal efficiency and 0.9618 for adsorption capacity, both indicating strong model fit. Adsorbent dose and MB concentration were found to have the most impact on adsorption capacity, while contact time and temperature had minimal effects. The results confirm that the quadratic model is statistically significant and effective for optimizing the process.

The relationship between the normal % probability against externally studentized residuals, residuals against run number, residual against predicted value, and predicted response against experimental data are depicted in Figure 3a-d in order to evaluate the correlation between the optimization model and the experimental data. The normal probability plot of residuals in Fig. 3a shows that the experimental data points are consistently distributed, confirming the assumptions of the empirical model. Figure 3b reveal that the data points are uniformly distributed over the range of −3.93041 to +3.93041 studentized residuals, falling between the lower and upper bounds of outlier detection. A homogeneous distribution around the basic lines is displayed by the residual against expected values plot in Figure 3c, with almost half of the residuals falling below and the other half above the basic line. This distribution reveals that the residual values were dispersed randomly with no discernible trend, and that the average residual values are very close to zero. The actual and predicted values of the response have a significant correlation as displayed in Fig. 3d, suggesting excellent agreement between the two values. This indicates that the statistical model applied effectively represents the relationship between the four variables investigated in the MB adsorption process (Bekele *et al.,* 2024; Chima *et al.,* 2023).

Table 3: ANOVA for methylene blue removal efficiency onto *Pterocarpus santalinoides*

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	247.98	14	17.71	12.64	< 0.0001	significant
A-Contact Time	2.01	1	2.01	1.43	0.2511	
B-Adsorbent Dose	27.82	1	27.82	19.85	0.0005	
C-MB Concentration	111.87	1	111.87	79.82	< 0.0001	
D-Temperature	8.53	1	8.53	6.09	0.0271	
AB	3.86	1	3.86	2.76	0.1192	
AC	1.66	1	1.66	1.19	0.2943	
AD	1.44	1	1.44	1.03	0.3280	
BC	9.73	1	9.73	6.95	0.0196	
BD	0.3025	1	0.3025	0.2158	0.6494	
CD	1.42	1	1.42	1.01	0.3319	
A^2	3.79	1	3.79	2.70	0.1224	
B^2	13.94	1	13.94	9.94	0.0070	
C^2	27.58	1	27.58	19.68	0.0006	
D^2	19.82	1	19.82	14.14	0.0021	
Residual	19.62	14	1.40			
Lack of Fit	19.62	10	1.96			
Pure Error	0.0000	4	0.0000			
Cor Total	267.60	28				

Table 4: ANOVA for methylene blue adsorption capacity onto *Pterocarpus santalinoides*

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2801.01	14	200.07	25.21	< 0.0001	significant
A-Contact Time	0.2002	1	0.2002	0.0252	0.8761	
B-Adsorbent Dose	1418.75	1	1418.75	178.74	< 0.0001	
C-MB Concentration	771.36	1	771.36	97.18	< 0.0001	
D-Temperature	0.0800	1	0.0800	0.0101	0.9214	
AB	0.4356	1	0.4356	0.0549	0.8182	
AC	0.0056	1	0.0056	0.0007	0.9791	
AD	0.0144	1	0.0144	0.0018	0.9666	
BC	195.72	1	195.72	24.66	0.0002	
BD	0.0100	1	0.0100	0.0013	0.9722	
CD	0.0016	1	0.0016	0.0002	0.9889	
A^2	5.87	1	5.87	0.7393	0.4044	
B^2	408.67	1	408.67	51.48	< 0.0001	
C^2	3.19	1	3.19	0.4018	0.5364	
D^2	8.47	1	8.47	1.07	0.3192	
Residual	111.13	14	7.94			
Lack of Fit	53.73	10	5.37	0.3745	0.9053	not significant
Pure Error	57.39	4	14.35			
Cor Total	2912.13	28				

Table 5: Analysis of variance (ANOVA) results for the response model of methylene blue degradation and adsorption

Parameter	Removal Efficiency	Adsorption Capacity
Model	Quadratic	
Standard deviation	1.18	2.82
Mean	93.68	12.16
Coefficient of variance (CV,%)	1.26	23.18
Coefficient of determination (R^2)	0.9267	0.9618
Adjusted R^2	0.8534	0.9237
Predicted R^2	0.5777	0.8629
Adequate precision	11.9388	20.2253
PRESS	113.02	399.12

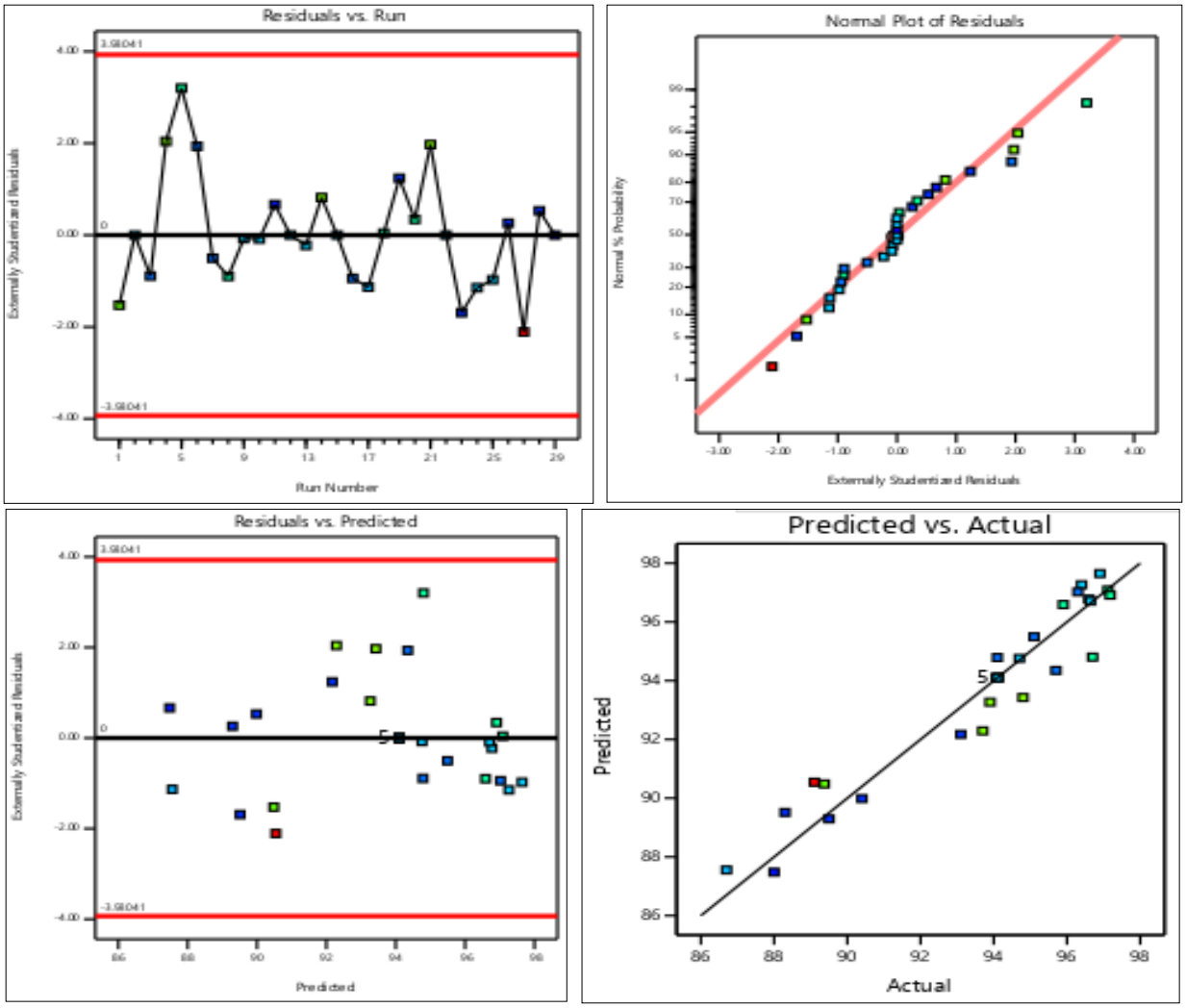


Figure 8: (a) Normal plot of residuals, (b) residuals vs run number, (c) predicted vs actual value (d) fitted models for MB adsorption

3.3.2 Interaction effect of studied variables on the removal of MB

The three dimensional (3D) response surface plots against any two independent process variables created from the Box-behnken design demonstrate that the removal of methylene blue was govern by the combined effects of the studied variables rather than the individual effects alone (Nayeri *et al.,* 2019; Elmoubarki *et al.,* 2017). Statistical significant terms in the ANOVA ($p<0.005$) of the combined effects of the investigated process variables confirm that out of the six interactions, only adsorbent dose and initial MB concentration shows a significant interaction.

3.3.2.1 Adsorbent dose and Initial MB concentration

Figure 8 displays the combined effect between adsorbent dose and initial MB concentration on the

adsorption performance of *Pterocarpus santalinoides* fruit activated carbon. The plot demonstrates that increasing the adsorbent dose directly increases MB removal because of availability of more adsorption sites and a larger total surface area. Also, increasing the initial MB concentration increases the number of dye molecules competing for available adsorption sites. The response plot shows that at low MB concentrations, higher amount of the dye molecules can be removed because the available adsorption sites are present in excess compared to the number of MB molecules. As the initial MB concentration increases, the adsorbent sites become progressively highly loaded, and the available sites diminishes (Nayeri *et al.,* 2019). This observation highlights the need for higher adsorbent dosage at higher MB concentrations to compensate saturation effects on the adsorbent sites. The interaction between adsorbent dosage and contaminant concentration provides valuable insight for optimizing adsorbent requirements, as higher pollutant loads generally require appropriate adjustment of dosage to achieve efficient removal (Ghaedi *et al.,* 2019; Sahu *et al.,* 2024).

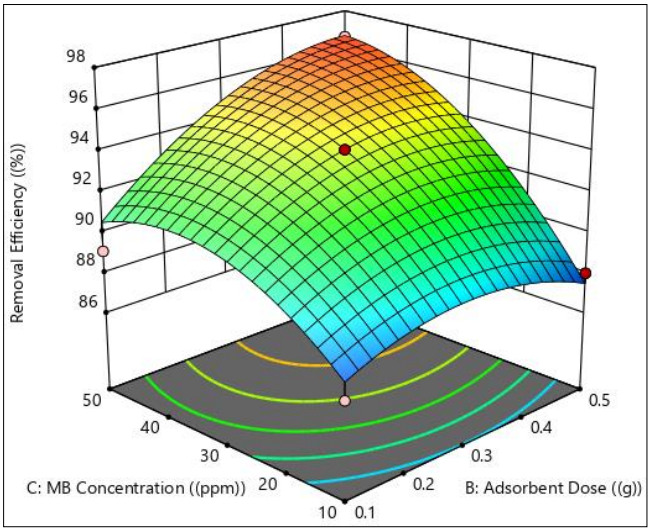


Figure 8: 3D surface plots of the effect of initial MB concentration and adsorbent dose on the percentage removal of MB

Numerical optimization

Numerical optimization of MB removal was analyzed using BBD-RSM method, the highest removal efficiency of MB was prioritized as desirable aim while optimizing the operational parameters. The optimal variables of contact time = 72.1237, adsorbent dose = 0.4778, MB concentration = 31.3279, temperature = 30.2448, removal efficiency = 97.6801 and adsorption capacity = 5.74285. The removal efficiency of MB achieved was 96.59 and 89.37 respectively.

Table 6: Optimal conditions of the selected factors for MB adsorption onto *Pterocarpus santalinoides*

Optimized process parameters						Desirability
Adsorbent dose (g)	**Contact time (min)**	**Initial concentration (ppm)**	**Temperature (°C)**	**Removal efficiency (%)**	**Adsorption capacity (mg/g)**	
0.478	72.12	31.33	30.24	97.68	5.743	1.000

3.3 Adsorption Isotherm Model Parameters

Adsorption isotherm studies investigate the effective removal of MB from aqueous solution using *Pterocarpus santalinoides*. The studies use Henry, Langmuir, Freundlich, Temkin, Flory-Huggins, Jovanovic, and Halsey models, to determine the adsorption capacity of *Pterocarpus santalinoides*. Adsorption models showed a relationship between the amounts of MB solution in *Pterocarpus santalinoides*. The adsorption isotherm model equations applied are presented in equations 6 to 17 (Table 7). Where qe (mg/l) is the amount of adsorbate adsorbed per gram of the adsorbent, Ce (Mg/l) is the concentration of adsorbate at equilibrium, q_{max} (mg/g) is the maximum monolayer coverage capacity K_L is Langmuir isothermal constant (L/mg), K_F is Freundlich isothermal constant (mg/g), K_{HE} is Henry's adsorption constant (mg/l), K_T is Temkin isotherm constant (L/g), K_J is Jovanovic adsorption rate, and K_H is Halsey isotherm constant (mg/l). The adsorption isotherm constants and correlation coefficients for various models are shown in Table 8. The Langmuir isotherm best fit the methylene blue (MB) adsorption data on *Pterocarpus santalinoides* fruit-derived activated carbon (PSAC), with R^2 = 0.9999, indicating monolayer adsorption on a homogeneous surface. The maximum monolayer capacity (q_m) was

37.037 mg/g. The suitability of the Langmuir model suggests that methylene blue adsorption may involve predominant occupation of available adsorption sites until saturation is approached (Nleonu *et al.,* 2026). However, the adsorption system may still involve heterogeneous interactions due to the complex surface chemistry of biomass-derived activated carbons. The Henry model (R^2 = 1.0000) described low-coverage behavior but couldn't account for site saturation. These findings confirm monolayer chemisorption and PSAC's effectiveness as a low-cost adsorbent for cationic dyes.

Table 7: Adsorption isotherm equations used in adsorption studies of MB on *Pterocarpus santalinoides*

Descriptions	Equations	Equation No
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	6
Freundlich isotherm	$Logq_{e=} = LogK_f + \frac{1}{n} LogC_e$	7
Henry isotherm	$q_{e=} = K_{HE} C_c$	8
Halsey isotherm	$q_e = \frac{1}{n_H} I_n K_H - \frac{1}{n_H} lnC_{qe}$	9
Temkin isotherm	$q_e = \frac{Rt}{b} I_n K_T + \frac{RT}{b} lnC_{qe}$	10
Flory-Huggins	$log\frac{C_0 - C_e}{C_0} = logK_{FH} + nlog(1-\theta)$	11
Jovanovic	$q_e = q_m(1 - e^{-KC_e})$	12
Pseudo-first order	$\text{In}\frac{A_o}{A_t} = K_1 t$	13
Pseudo-second order	$\frac{1}{A_t} - \frac{1}{A_o} = K_2 t$	14
Intraparticle diffusion models	$q_t = K_i t^{1/2} + C$	15
Gibbs free energy change	$\Delta G = -RTlnK_d$	16
Enthalpy and Entropy	$\Delta G = \Delta H° - T\Delta S°$	17

Table 8: Adsorption isotherm model parameters

Isotherm Model	k	q_m	n	b(KJ/mol)	R^2
Henry	40	-	-	-	1
Langmuir	37.0370	50	-	-	0.9999
Freudnlich	30.4579	-	7.1788	-	0.4173
Temkin	9.624×10^{9}	-	-	0.78	0.4879
Halsey	3.4866×10^{24}	-	7.1839	-	0.4173
Jovanovic	0.0360	1215.07	-	-	0.1615
Flory-Huggins	2.506×10^{-05}	-	-	-	0.5837

3.4 Adsorption Kinetics Study

The adsorption kinetics of methylene blue (MB) onto activated carbon from *Pterocarpus santalinoides* fruit were evaluated using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models (Table 9). The pseudo-second-order model best fit the data, with the highest correlation coefficient (R^2 = 0.9964) and equilibrium capacity (q_e = 32.22 mg/g), indicating chemisorption as the rate-limiting step. The pseudo-first-order model showed poor correlation (R^2 = 0.4152), suggesting minimal physisorption, while the intraparticle diffusion model fit well (R^2 = 0.9082) but was not the sole rate-controlling mechanism. These results align with prior studies on plant-derived activated carbons, where pseudo-second-order kinetics commonly describes dye adsorption (Francis & Jock, 2023). However, fitting adsorption data to the pseudo-second-order equation does not independently prove that chemisorption is the dominant mechanism. Previous studies have emphasized that kinetic models are mathematical representations of adsorption behaviour and should not be interpreted as direct mechanistic evidence without additional supporting analyses (Tran *et al.,* 2017). Therefore, the present adsorption mechanism was interpreted by integrating kinetic results with FTIR observations, equilibrium models, and thermodynamic analysis. The results suggest that surface interactions between methylene blue molecules and activated carbon functional groups contribute to adsorption, while diffusion and pore accessibility also influence the adsorption process.

Table 9: Kinetic model parameters

Kinetic Model	K	q_e	C	R^2
Pseudo-first order	0.0125	17.80		0.4152
Pseudo-second order	0.00096	32.22		0.9964
Intraparticle Diffusion Model	10.95		2.48	0.9082

3.5 Thermodynamic Parameters for the Adsorption of Methylene Blue

Thermodynamic parameters for methylene blue (MB) adsorption onto activated carbon from *Pterocarpus santalinoides* fruit are summarized in Table 10. Negative Gibbs free energy (ΔG°) values (–25.19 kJ/mol at 303 K to –27.69 kJ/mol at 333 K) confirm the adsorption is spontaneous and thermodynamically favorable. The positive enthalpy change (ΔH° = 69.70 kJ/mol) indicates an endothermic process, while the negative entropy change (ΔS° = –439.27 J/mol.K) suggests an ordered arrangement of MB molecules. A strong linear correlation (R^2 = 0.9992) validates the thermodynamic assessment. The increased spontaneity with temperature rise points to improved diffusion and chemisorptions (Nleonu *et al.,* 2023). These findings align with previous studies on plant-derived activated carbons, supporting the potential of *Pterocarpus santalinoides* fruit-derived activated carbon for methylene blue removal. The thermodynamic results obtained in this study suggest that methylene blue adsorption onto *Pterocarpus santalinoides* activated carbon is favourable under the investigated conditions.

Table 10: Thermodynamic parameters for the adsorption of methylene blue

Temperature(K)	ΔG°(KJ/mol)	$\Delta H°$(KJ/mol)	$\Delta S°$(J/mol)	R^2
303	−25.19	69702.59	−439.27	0.9992
313	−26.02			
323	−26.85			
333	−27.69			

4.0 CONCLUSION

The study successfully optimized the adsorption of methylene blue using activated carbon derived from *Pterocarpus santalinoides* fruit through Box-Behnken Design (BBD) and Response Surface Methodology (RSM). The experimental results and model predictions showed good agreement, confirming the reliability of the quadratic models for both removal efficiency and adsorption capacity. Among the process variables, adsorbent dose, methylene blue and temperature concentration were identified as the most significant factors influencing adsorption, while adsorbent dose and temperature influenced adsorption capacity. The statistical analysis, including ANOVA and lack-of-fit tests, indicated that the models were significant and adequately fitted the experimental data. The coded and actual factor equations further highlighted the non-linear behavior and interaction effects among the variables, providing a robust predictive tool for optimizing adsorption conditions.

5.0 RECOMMENDATION

1. Future studies should focus on scaling up the adsorption process to pilot or industrial levels to assess its practical applicability in wastewater treatment.
2. Exploring the regeneration and reusability of activated carbon to enhance its economic feasibility and sustainability.
3. Investigating adsorption performance for other industrial dyes and contaminants to broaden the versatility of the adsorbent.
4. Optimizing operating parameters under continuous flow systems, combined with kinetic and isotherm modeling, to better understand adsorption mechanisms and facilitate real-world implementation in water treatment facilities.

ACKNOWLEDGEMENT

The authors acknowledge the Tertiary Education Trust Fund (TETFund) for their financial support. We appreciate the management of Federal Polytechnic Nekede, Owerri, for providing the research facilities for this work. We also appreciate the laboratory assistance of Onu Faustina and Eziefula Amarachi Cynthia, members of the Materials and Electrochemical Research Unit (MERU) of the Chemistry Department, Federal Polytechnic Nekede, Owerri, Nigeria.

Funding: This research was funded by the Institutional Based Research grant of the Tertiary Education Trust Fund (TETFund) with grant number TETF/ES/DR&D/CE/POLY/NEKEDE/IBR/2026/VOL.1.

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

REFERENCES

- Al-Ghouti, M. A., & Da'ana, D. A. (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review. *Journal of Hazardous Materials, 393*, 122383.
- Bekele, E. A., Korsa, H. A., & Desalegn, Y. M. (2024). Electrolytic synthesis of γ-Al_2O_3 nanoparticle from aluminum scrap for enhanced

methylene blue adsorption: Experimental and RSM modeling. *Scientific Reports, 14*, 16957.

- Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon, 5*(11), e02711.
- Chima, G. C., Nleonu, E. C., & Ben Amor, I. (2023). Comparative optimization of photocatalysis and adsorption of methylene blue using aluminum doped magnetic iron oxide by central composite design. *International Journal of Research Publication and Reviews, 4*(8), 3091–3097.
- Elmoubarki, R., Taoufik, M., Moufti, A., Tounsadi, H., Mahjoubi, F. Z., Bouabi, Y., Qourzal, S., Abdennouri, M., & Barka, N. (2017). Box–Behnken experimental design for the optimization of methylene blue adsorption onto Aleppo pine cones. *Journal of Materials and Environmental Sciences, 8*(6), 2184–2191.
- Francis, A. O., Otoikhian, S. K., & Zaini, M. A. A. (2023). *Vitex doniana* seed activated carbon for methylene blue adsorption: Equilibrium and kinetics. *International Journal of Phytoremediation, 25*(12), 1625–1635.
- Ghaedi, M., Hassanzadeh, A., & Nasiri Kokhdan, S. (2011). Batch and fixed-bed column studies for the removal of methylene blue using date stones activated carbon. *Journal of Chemical Engineering Data, 56*(6), 2515-2522.
- Hameed, B. H., Ahmad, A. L., & Aziz, N. (2007). Isotherm, kinetics and mechanism of methylene blue adsorption on activated carbon prepared from oil palm empty fruit bunch. *Journal of Hazardous Materials, 141*(3), 819-825.
- Hossain, M. M., Mottalib, M. A., Mukib, M. Z. B., Rahman, M. M., Islam, M. S., & Hasan, M. M. (2022). A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicology and Environmental Safety, 231*, 113160.
- Ismail, M., & Sakai, H. (2022). Review on effect of different type of dyes on advanced oxidation processes (AOPs) for textile color removal. *Chemosphere, 291*(Pt 3), 132906.
- Khan, S., & Malik, A. (2014). Environmental and health effects of textile industry wastewater. In A. Malik, E. Grohmann, & R. Akhtar (Eds.), *Environmental deterioration and human health* (pp. 55-71). Springer.
- Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. M. (2016). *Response surface methodology: Process and product optimization using designed experiments* (4th ed.). John Wiley & Sons.
- Nayeri, D., Mousavi, S. A., Fatahi, M., Almasi, A., & Khodadoost, F. (2019). Dataset on adsorption of methylene blue from aqueous solution onto activated carbon obtained from low cost wastes by chemical-thermal activation: Modelling using response surface methodology. *Data in Brief, 25*, 104036.
- Nleonu, E., Okeke, C., Okeke, P., & Chiemeka, O. (2026). Synthesis and characterization of C-Fe_3O_4 nanoparticles for efficient removal of methylene blue in aqueous solution. *Journal of Physical Chemistry and Functional Materials, 9*(1), 11–19.
- Nleonu, E. C., Onyemenonu, C. C., Okeke, P. I., & Opara, J. N. (2023). Adsorption characteristics of *Chrysophyllum albidum* (African star apple) peels towards heavy metal ions. *Chemical Review and Letters, 6*(1), 44–54.
- Rawat, D., Sharma, R. S., Karmakar, S., Arora, L. S., & Mishra, V. (2018). Ecotoxic potential of a presumably non-toxic azo dye. *Ecotoxicology and Environmental Safety, 148*, 617-627.
- Ren, J., Wang, Y., Zhang, Y., Li, X., & Chen, H. (2024). Adsorption properties and mechanisms of methylene blue on biomass-derived activated carbon: Experimental and theoretical investigations. *Materials, 17*(17), 4329.
- Sahu, D., Singh, S., & Kumar, P. S. (2024). Applications of different adsorbent materials for the removal of organic and inorganic contaminants from water and wastewater: A review. *Desalination and Water Treatment, 317*, 100–120.
- Shelke, B. N., Jopale, M. K., & Kategaonkar, A. H. (2022). Exploration of biomass waste as low cost adsorbents for removal of methylene blue dye: A review. *Journal of the Indian Chemical Society, 99*(7), 100530.
- Tan, I. A. W., Hameed, B. H., & Ahmad, A. L. (2016). Application of agricultural based activated carbons by microwave and conventional activations for basic dye adsorption: Review. *Journal of Environmental Chemical Engineering, 4*(1), 89–99.
- Tran, H. N., You, S. J., Hosseini-Bandegharaei, A., & Chao, H. P. (2017). Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Research, 120*, 88-116.