



## Optimisation of Methylene Blue Adsorption onto Biosorbent from Palm Kernel Shell: A Design of Experiments (DOE) Approach

<sup>1</sup>Uwana Williams Peter, <sup>2\*</sup>Pereware Famous Tarbuka, <sup>3</sup>Kigho Moses Oghenejoboh, <sup>4</sup>Bamidele Honesty Akpeji, and <sup>5</sup>Ayomide Rhoda Odika

<sup>1,2,5</sup>Department of Chemical Engineering, Federal University of Petroleum Resources, P.M.B. 1221, Effurun, Nigeria

<sup>3</sup>Department of Chemical Engineering, Faculty of Engineering, Delta State University, Nigeria

<sup>4</sup>Department of Science Laboratory Technology, Federal University of Petroleum Resources, P.M.B. 1221, Effurun, Nigeria

Corresponding author: [tarbuka.f.pereware@gmail.com](mailto:tarbuka.f.pereware@gmail.com)

<https://orcid.org/0000-0002-6989-2962>

Article history: Received: 10-01-25, Revised: 12-03-25, Accepted: 27-03-25, Published: 30-03-25

### Abstract

The treatment of effluents produced by the textile industries in Nigeria leaves much to be desired because there has always been the complex problem of eliminating the synthetic dyes in the effluents such as methylene blue (MB) that do not respond well to the traditional cleaning mechanisms; the situation has led to the need to explore yet another cheap alternative biosorbent (in this case palm kernel shell) to increase the potential of the adsorption of the dyes. This study explores the potential of using activated carbon derived from palm kernel shells, a locally available agricultural waste, to remove MB from water solutions. The palm kernel shells were carbonised in a muffle furnace, and adsorption experiments were optimised using the Box–Behnken design within the response surface methodology framework. Key variables, including dye concentration, adsorbent dose, and contact time, were examined to assess their effect on dye removal efficiency. Statistical analysis identified a significant model with an *F*-value of 53.83 and *p*-values less than 0.05 for all factors. Optimal conditions achieved approximately 77% dye removal at an adsorbent dose of 0.75 g/100 mL, a contact time of 35 minutes, and a dye concentration of 133 mg/L. The regression model showed a predicted  $R^2$  of 0.8990 and an adjusted  $R^2$  of 0.9674, indicating high model accuracy. Adsorption isotherms were also analysed, with the Freundlich model fitting better ( $R^2 = 0.845$ ) than the Langmuir model ( $R^2 = 0.754$ ), suggesting adsorption occurs on a heterogeneous surface. Fourier Transform Infrared Spectroscopy (FTIR) analysis confirmed the presence of active functional groups before and after adsorption. The study demonstrates that activated carbon from palm kernel shells is a practical, low-cost adsorbent for treating textile effluent containing methylene blue.

**Keywords:** Methylene blue; Palm kernel shells; Adsorption; Box–Behnken design (BBD); Activated carbon; Isotherm.

### 1. Introduction

Water pollution poses a significant threat to both human health and the environment worldwide. Approximately 80% of untreated sewage is discharged into water bodies, contributing to the spread of over 50 diseases. The most common waterborne illness is diarrhoea, primarily transmitted by aquatic enteroviruses (Krishan *et al.*, 2023). Poor water quality is responsible for 80% of diseases and 50% of child deaths worldwide (Lin *et al.*, 2022). Pollution is estimated to cause 9 million premature deaths annually, with water pollution being a major contributor (Fuller *et al.*, 2022). Unsafe water, poor sanitation, and hygiene account for about 8–9% of the total disease burden globally. Industrial effluents, agricultural discharges, and urban waste are primary sources of water pollution (Haseena *et al.*, 2017). Water pollution, primarily resulting from agricultural, urban, and industrial activities, introduces excess nutrients, such as nitrogen and phosphorus, into aquatic ecosystems, leading to eutrophication (Wurtsbaugh *et al.*, 2019). This process causes harmful algal blooms, hypoxic zones, and degradation of water quality. Pollutants, including heavy metals, pesticides, and microplastics, can bioaccumulate in aquatic organisms and biomagnify through the food chain (Aliko *et al.*, 2022). These contaminants disrupt marine biodiversity, compromise ecosystem functions, and pose health risks to humans through the consumption of seafood (Muhammed *et al.*, 2025).

In Nigeria, industrial activities have gradually increased the problem of waste disposal. Rivers become more vulnerable because they play a key role in transporting industrial wastewater, often receiving pollutants either directly or indirectly (Eteng *et al.*, 2021). The heavy contamination of waterways with various pollutants has caused severe damage, making the water unsuitable for essential uses such as domestic consumption, agricultural irrigation, recreational activities, drinking water supply, wildlife sustenance, and industrial food processing. Industries like textiles, paper and pulp, paint, printing, and cosmetics contribute to this pollution through their use of dyes. (Rehman & manzoor, 2018). The use of synthetic dyes in aquatic environments is a significant environmental issue. In nearly every industry, artificial dyes are essential and frequently appear in industrial wastewater. The coloured aromatic organic compounds known as dyes provide visible colour and absorb light. More than 100,000 commercial dyes have been reported worldwide, and various dyes are used across different sectors for multiple purposes, including textiles, food, rubber, printing, cosmetics, medicine, plastics, concrete, and paper. These industries produce large volumes of wastewater that pollute water with toxic and carcinogenic dyes, rendering it unsuitable for human consumption. Human consumption (Khan *et al.*, 2022).

Methylene blue (3,7-bis(dimethylamino)phenothiazine chloride tetramethylthionine chloride) is an organic chloride salt used primarily as a dye

and medication. Methylene blue serves as a colourant for papers, wool, silk, food, cosmetics, and the pharmaceutical industry. As a medication, it exhibits antioxidant, antimalarial, antidepressant, and cardioprotective properties. Prolonged exposure to MB can adversely affect a person's health, although it has been shown to have positive medical effects when used carefully and as prescribed by a medical professional. However, a large amount of MB dye released as effluent from industries can be harmful to humans and aquatic life (Kayabaşı & Erbaş, 2020). Conventional advanced wastewater treatment technologies, such as ion exchange, membrane separation, and electrolysis, are expensive, which encourages the search for innovative, low-cost, and environmentally friendly methods of wastewater treatment as environmental regulations become stricter. Most traditional methods require high capital expenditure, substantial operational costs, and generate issues with sludge disposal. Although the adsorption technique is relatively inexpensive, there is an urgent need to replace commercial adsorbents, such as zeolite, activated alumina, and silica gel, with more affordable alternatives. The use of commercial activated carbon for adsorption is costly, particularly for developing countries such as Nigeria (Neolaka *et al.*, 2022).

Agricultural waste materials are affordable, widely available, and can reduce waste disposal problems, making them promising precursors for activated carbon (AC). Several adsorbents have been reported in the literature for the removal of MB, such as pineapple peel waste. (Shehu *et al.*, 2023), chestnut shell (Zhang *et al.*, 2021), Rumex abyssinicus plant (Fito *et al.*, 2023) tunic, corn saffron (Dbik & Khomri, 2022), apple waste (Hesas *et al.*, 2013), fig leaf (Al-asadi, 2023), rice husk (Matsumoto *et al.*, 2021) and peanut shells (Kutluay & Baytar, 2020) from aqueous solution. This study aimed to optimise the adsorption of methylene blue (MB) dye onto modified palm kernel shell biosorbents. The Box–Behnken design (BBD) within response surface methodology (RSM) was utilised to explore the influence of adsorbent dosage, contact time, and dye concentration on MB removal, leading to the determination of the optimal preparation parameters. The properties of the precursor were assessed and characterised using Fourier-transform infrared spectroscopy (FTIR).

### 2. Materials and Methods

#### 2.1 Materials

The primary material used in this study was analytical-grade methylene blue dye pigment obtained from a local chemical store. It was used to simulate textile industry effluent containing methylene blue dye pigment with distilled water. The biosorbent was prepared from palm kernel shells (PKS), a waste product generated during palm oil production. The sulfuric acid ( $H_2SO_4$ ) used for

chemical activation was also purchased from a chemical store. Essential equipment and apparatus included A UV-spectrophotometer (Agilent B-TY-76551), which was used to monitor the adsorption of MB and to measure the concentration of MB in solution. An orbital shaker (ELMI S-3.022L) was used to agitate the adsorption mixtures. A magnetic stirrer heater (VEVO-SH-2) ensured uniform contact between dye molecules and biosorbent particles by preventing sedimentation and enhancing mass transfer. An oven (model no 99200-3) was employed to remove moisture from treated or untreated biosorbent. A muffle furnace (LPPL 114- Technico) was used for thermal treatment or carbonisation of PKS. PET bottles are used for storage. A mortar and pestle were used to reduce particle size to increase surface area. A 300 µm sieve was used for uniform size. Whatman filter paper was used to separate the solid biosorbent from the liquid after adsorption. Masking tape was used for labelling glassware, containers, or sample batches. Meanwhile, an Erlenmeyer flask, a measuring cylinder, and a beaker were employed in the preparation and mixing of solutions.

## 2.2 Methods

### 2.2.1 Preparation of activated carbon

Palm kernel shells were washed with water to remove unwanted particles and then dried in an oven at approximately 105 °C for 3 hours to remove the moisture content. After drying, the shells are crushed and charged into a muffle furnace to carbonise at 600 °C for 1.5 hours. Samples were crushed with a mortar to reduce their particle size and then sieved through a 300 µm sieve. Chemical activation was performed using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The reaction involving the precursor in the activated carbon production process is shown in Equation 1. After activation, the solution was filtered using filter paper, and the residue was washed with distilled water to remove excess H<sub>2</sub>SO<sub>4</sub>. The activated carbon was then dried in an oven at 110 °C for 3 hours and kept in an airtight container until use. This provided the activated carbon with a larger surface area required for adsorption, as activated carbon with a smaller particle size adsorbs more effectively than larger particles (Olafadehan et al., 2012).

Palm kernel shells → Carbon + Ash + Volatile gasses (1)

### 2.2.2 Preparation of the Adsorbate

A stock solution was prepared by dissolving 1 g of methylene blue in 1,000 mL of distilled water to obtain a concentration of 1,000 ppm. A standard solution of 100 ppm was prepared by diluting 100 mL of the stock solution to 1,000 mL of distilled water.

### 2.2.3 Characterisation of palm kernel shell carbon

The following tests were conducted on the palm kernel seed shell and its derived carbon. The iodine number was measured to characterise the activated carbon for liquid-phase adsorption; other characterisations included ash content and bulk density.

#### 2.2.3.1 Determination of the Ash Content

The ash content was determined by weighing approximately 1 g of powdered carbon in a porcelain crucible and heating the carbon to 700 °C for 3 hours in a muffle furnace. The crucible was then removed, placed in a desiccator, and weighed after cooling. (Jacob, 2009). The ash content was determined using Equation 2:

$$\text{Ash (\%)} = \frac{\text{Final solid weight (g)} \times 100}{\text{Initial carbon weight (g)}} \quad (2)$$

#### 2.2.3.2 Determination of Porosity

To determine the porosity, 10 mL of methylene blue solution was placed into a measuring cylinder, and 10 mL of water was added to each. Each sample was then filtered to collect the volume of water that could pass through it (Hammood et al., 2021).

Porosity was calculated using Equation 3:

$$\text{Porosity} = \frac{V_L}{V_s} \quad (3)$$

V<sub>L</sub> is the volume of liquid that penetrates the sample, and V<sub>s</sub> is = volume of the sample

#### 2.2.3.3 Determination of pH

The pH was measured by suspending 1.0 g of carbon in 100 ml of distilled water at pH 7.0 and heating at 90 °C for 20 min. The solution was then cooled, and the pH was measured using a pH meter. The pH meter was calibrated before analysis using a standard buffer within the range of the pH to be measured (Hammood et al., 2021).

### 2.2.4 Design of the Experiment

A statistical model for the adsorption of dye pigment was designed using the Box–Behnken design (BBD) for response surface methodology. Three independent variables were studied: A - dye concentration, B - adsorbent dosage, and C - contact time. There would be seven factorial points, seven axial points, and six replicates at the centre points, indicating 20 experimental runs to be obtained, as illustrated by Equation 4 (Hoo et al., 2022).

$$\text{Total number of experiments (N)} = 2^n + 2n + nc = 2^3 + 2 \times 3 + 6 = 20 \quad (4)$$

where *n* is the number of factors and *nc* is the number of centre points (six replicates).

The centre points were used to verify the reproducibility of the data and the experimental error. The variables were coded to the (-1, 0, +1) interval, where the low and high levels are coded as -1 and +1, respectively (Kumari et al., 2023). The axial points are located at (±α, 0, 0), (0, ±α, 0), and (0, 0, ±α), where α is fixed at 1.414. Table 1 shows the coded and actual values for the Box–Behnken design.

Table 1 Coded and Actual Values for the Factors of Box Behnken Design

Independent Variables	Symbols	Coded and Actual Levels				
		-α	-1	0	+1	+α
Dye concentration (ppm)	A	50	77.5	125	152.5	200
Adsorbent dosage (g)	B	1	2.5	5	7.5	10
Contact time (minutes)	C	5	16.5	30	45	60

### 2.2.5 Textile Wastewater Treatment Procedure

Batch adsorption was conducted using the box–Behnken design of the experiment in response surface methodology with 100 ml of sample, and the required variables would be used with adsorption time (5 to 60 minutes), adsorbent dosage (1 to 10g w/V %) and initial dye concentration (50 to 200mg/l) as factors. A 250-ml conical flask was placed on an orbital shaker with mixing speed set at a constant 200 rpm at ambient temperature according to Jacob (2009). The effects of adsorbent dose, contact time, and dye concentration on the percentage dye removal were also studied. Samples were withdrawn and filtered with Whatman's 11-cm filter paper, and the filtrate was subjected to dye concentration measurement with the aid of a UV-Vis spectrophotometer. From Equation 5, the percentage removal, *Pr*, was estimated.

$$P_r = \frac{C_o - C_i}{C_o} \times 100 \quad (5)$$

where C<sub>o</sub> is the initial dye concentration and C<sub>i</sub> is the final dye concentration.

## 3. Results and Discussion

### 3.1 Properties of palm kernel shell activated carbon

The experimental results for the physical properties of palm kernel shell-activated carbon are presented in Table 2. The adsorption efficiency of activated carbon is directly related to its total surface area. A larger surface area enhances the adsorption efficiency of activated carbon, making it a critical attribute in the selection of adsorbents for separation processes (Rasilingwani, 2018). According to the data presented in Table 2, the synthesised palm kernel shell activated carbon had a total surface area of 1038 m<sup>2</sup>/g. Ash content indicates the presence of mineral impurities in the carbon, primarily originating from the carbon precursor (Iwar et al., 2018).

Table 2 Characteristics of palm kernel shell activated carbon

Property	Value
Ash Content	0.1%
Total surface area	1038 m <sup>2</sup> /g
Specific gravity	1.51
Porosity	75.61%
Particle size	<300µm
pH	7.3

### 3.2 Adsorbent Characterisation using Fourier Transform Infrared Spectrophotometer (FTIR)

The activated carbon, both before and after treatment, was characterised using Fourier transform infrared (FTIR) spectroscopy. Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of the absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a broad spectrum. (Ghogomu et al., 2016). Table 3 shows the active functional groups present in the activated carbon before and after adsorption.

Table 3 FTIR spectrum data obtained from Figures 1 and 2

IR peak	Before Adsorption	After Adsorption
1	3574.5	3857.8
2	2318.4	3336.0
3	2105.9	2322.1
4	1982.9	1986.7
5	1561.8	1420.1

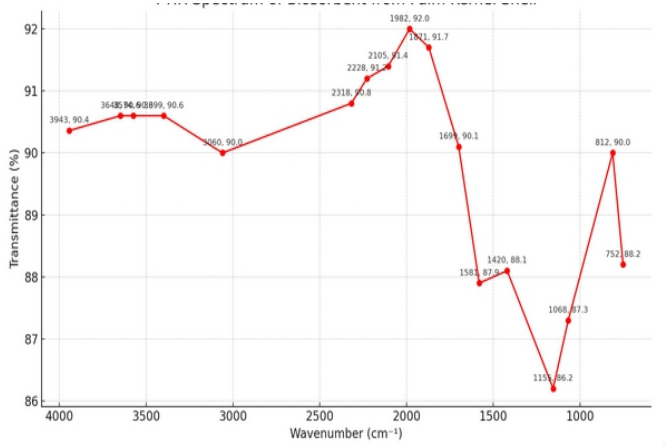


Figure 1 FTIR spectrum of palm kernel shell activated carbon (H<sub>2</sub>SO<sub>4</sub>) before adsorption, 300µm, 600°C.

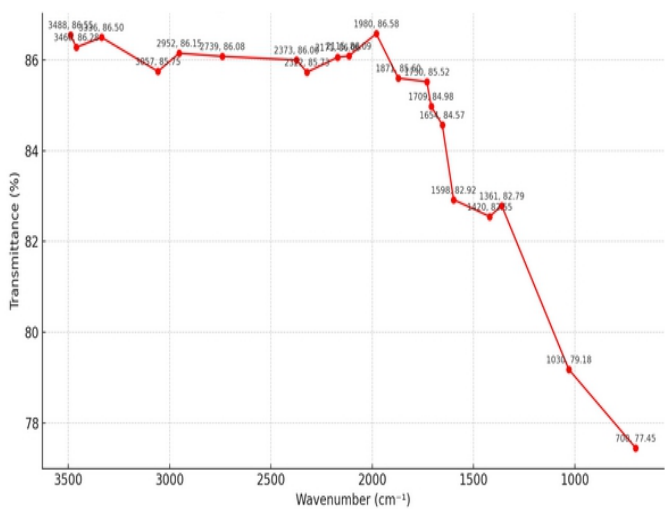


Figure 2 FTIR spectrum of palm kernel shell activated carbon (H<sub>2</sub>SO<sub>4</sub>) after adsorption at 300µm, 600°C.

The FTIR spectrum of the palm kernel shell activated carbon (H<sub>2</sub>SO<sub>4</sub>) before adsorption was characterized and shown in Figure 1, which showed a sharp peak at 3574.5 cm<sup>-1</sup> which indicated the presence of the O–H group, a sharp small peak at 2318.4 cm<sup>-1</sup> was assigned to the bending vibration of the C–N group, and a broad band at 2105.9 cm<sup>-1</sup> indicated the stretching due to group, a peak at 1982.9 cm<sup>-1</sup> was observed to have the presence of a =C–H, and a sharp peak at 1561.8 cm<sup>-1</sup> was assigned to the bending vibration of the C=C group. These groups act as binding sites for adsorption. The FTIR spectrum of palm kernel shell activated carbon (H<sub>2</sub>SO<sub>4</sub>) after adsorption indicated a change in wavenumber. It is observed from Figure 2 that some peaks disappeared and new peaks and band appeared after adsorption of methylene blue dye, which are 3857.8cm<sup>-1</sup> (O-H; sharp peak), 3336.0cm<sup>-1</sup> (O-H stretch, small band), 2322.1cm<sup>-1</sup> (very broad), 1986.7cm<sup>-1</sup> (N-H bend, broad) and 1420.1cm<sup>-1</sup> (=C-H bend, broad) (Ghogomu et al., 2016).

### 3.3 Experimental Results

In Table 4, the responses to the three factors show the sensitivities of the results to the random variables.

Table 4 Box-Behnken Design of the Experiment

Std	Run	Factor 1 A: Dye conc. (mg/l)	Factor 2 B: Adsorbent dosage (g/100ml)	Factor 3 C: Contact time (minutes)	Response Percentage dye removal (%)
6	1	200	0.55	10	20.0157
3	2	50	1	35	22.5947
13	3	125	0.55	35	72.1418
8	4	200	0.55	60	46.5214
16	5	125	0.55	35	73.6037
9	6	125	0.1	10	46.7721

7	7	50	0.55	60	23.1509
10	8	125	1	10	63.0237
14	9	125	0.55	35	72.1418
5	10	50	0.55	10	24.1061
15	11	125	0.55	35	72.1418
17	12	125	0.55	35	72.1418
11	13	125	0.1	60	67.1591
4	14	200	1	35	59.5916
1	15	50	0.1	35	30.7174
12	16	125	1	60	68.3611
2	17	200	0.1	35	14.6756

The best model recommended by the design expert was the quadratic model in Equation 6, which had an adjusted R<sup>2</sup> value of 0.9674 and a predicted R<sup>2</sup> of 0.8990. The equation in terms of coded factors can be used to predict the response for given levels of each factor. By default, the high levels of the factors are coded as +1, and the low levels are coded as -1. The coded equation helps identify the relative impact of the factors by comparing the factor coefficients. The quadratic equation is expressed in Equation 6:

$$\text{Percent Dye Removal} = +74.43 + 5.03A + 6.78B + 6.41C + 13.26AB + 6.87AC - 3.76BC - 37.71A^2 - 4.83B^2 - 8.28C^2 \quad (6)$$

Table 5 Experimental Analysis of Variance (ANOVA) on Percent Dye Removal

Source	Sum of Squares	Df	Mean Square	F-value	p-value
Model	8510.23	9	945.58	53.83	< 0.0001 significant
A-Dye Concentration	202.36	1	202.36	11.52	0.0115
B-Adsorbent Dosage	367.84	1	367.84	20.94	0.0026
C-Contact Time	328.64	1	328.64	18.71	0.0035
AB	703.28	1	703.28	40.03	0.0004
AC	188.52	1	188.52	10.73	0.0136
BC	56.62	1	56.62	3.22	0.1157
A <sup>2</sup>	5987.53	1	5987.53	340.84	< 0.0001
B <sup>2</sup>	98.20	1	98.20	5.59	0.0500
C <sup>2</sup>	288.37	1	288.37	16.42	0.0049
Residual	122.97	7	17.57		
Lack of Fit	47.11	3	15.70	0.8279	0.5435 not significant
Pure Error	75.86	4	18.97		
Cor Total	8633.20	16			

The analysis of variance (ANOVA) model was used to compare the mean response values at different factors (Ghorbani & Kamari, 2017). Each level of the factor was examined to determine whether the response differed significantly from the response at other levels of the factor.

According to Table 5, the Model F-value of 53.83 indicates that the model is statistically significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate that model terms are significant. In this case, A, B, C, AB, AC, A<sup>2</sup>, and C<sup>2</sup> are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (excluding those required to support the hierarchy), model reduction may improve your model. The lack of fit F-value of 0.83 implies that the lack of fit is not significant relative to the pure error. There is a 54.35 % chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good; we want the model to fit (Hoo et al., 2022).



### 3.5 Response Surface Plots

#### 3.5.1 Effect of contact time and adsorbent dosage

The interactive contribution of the adsorbent dose and contact time towards the percentage removal efficiency of methylene blue in aqueous solution is presented in Figure 3. The response surface appears to have experienced a marginal decrease in the effectiveness of dye removal as the adsorbent dosage increased at a contact time of 50 minutes, indicating the possible occurrence of either saturation or agglomeration effects at higher adsorbent concentrations. However, at the lower dosage, there was a gradual increase in contact time, which resulted in a steady improvement in the removal of methylene blue. This indicates that longer interaction time between the dye molecules and the active sites on the surface of the biosorbent enhances removal efficiency. In broader terms, removal efficiency was positively correlated with increased adsorbent dosage and contact time. However, it might be noted that the rate of increase slowed down as the system approached equilibrium. These two trends align with findings from other studies on adsorption, which have demonstrated that both contact time and adsorbent dose are crucial parameters affecting the kinetics of dye removal and maximum uptake (Sadaf & Bhatti, 2014).

#### 3.5.2 Effect of the adsorbent dosage and dye concentration

The surface interaction between adsorbent dosage, initial dye concentration, and overall impact on the efficiency of methylene blue removal is illustrated in Figure 4. The response surface pattern showed that when adsorbent dosage increased, there was a significant rise in the percentage removal of the dye, which can be explained by the fact that more active binding sites were available to bind additional dye during the adsorption process. This trend aligns with known adsorption laws, according to which a greater amount of sorbent enhances the total surface area and reactive groups of absorption sites. Furthermore, the figure indicates that the percentage removal increased as the initial dye concentration rose up to about 140 ppm. This period of enhanced removal can be attributed to the greater driving force for mass transfer due to the concentration gradient. However, beyond 140 ppm, a decline in removal efficiency was observed despite continued increases in dye concentration. This decrease may be due to the saturation of active sites on the biosorbent, where the active sites could no longer accommodate all dye molecules, resulting in competition between molecules. These findings align with recent research evidence that, although higher initial dye concentrations may temporarily boost the rate of uptake, overall efficiency declines at elevated concentrations since the adsorbent eventually reaches its equilibrium loading capacity (Zhao *et al.*, 2023).

#### 3.5.3 Effect of contact time and dye concentration

Figure 5 illustrates how the percentage removal efficiency of methylene blue is dynamically influenced by both contact time and initial dye concentration in the solution. The three-dimensional response surface plot shows a significant increase in dye removal efficiency with longer contact times, particularly at lower to moderate dye concentrations. This trend reflects the general behaviour of adsorption kinetics, where increased contact time provides more opportunity for dye molecules to diffuse and adsorb onto the active sites available on the biosorbent surface. Furthermore, with increasing dye concentration, the percentage removal initially rose, assuming that the higher concentration gradient between the solution and adsorbent contributed to increased mass transfer and faster uptake. However, this rising trend was only observed up to 140 mg/l, after which the removal rate began to decline as the dye concentration continued to increase. This negative effect can be attributed to adsorption site saturation, where the abundance of dye molecules overwhelms the sorbent's capacity to hold them, leaving some molecules in solution. This behaviour indicates that the system was approaching its equilibrium limits under high loading conditions. These findings align with recent research, which suggests that although longer contact time generally enhances adsorption, excessively high dye concentrations can lead to overcrowding on the sorbent interface, hindering maximum absorption (Ahmed *et al.*, 2023).

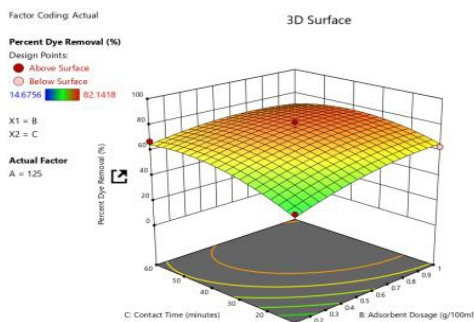


Figure 3 Surface interaction of contact time and adsorbent dosage on dye percent removal

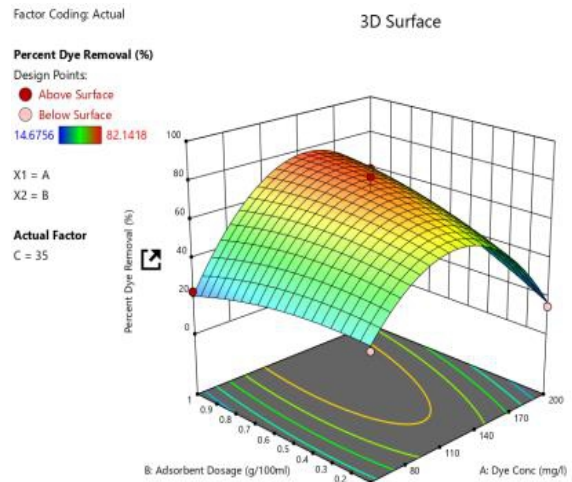


Figure 4 Surface interaction of adsorbent dosage and dye concentration on dye percentage removal

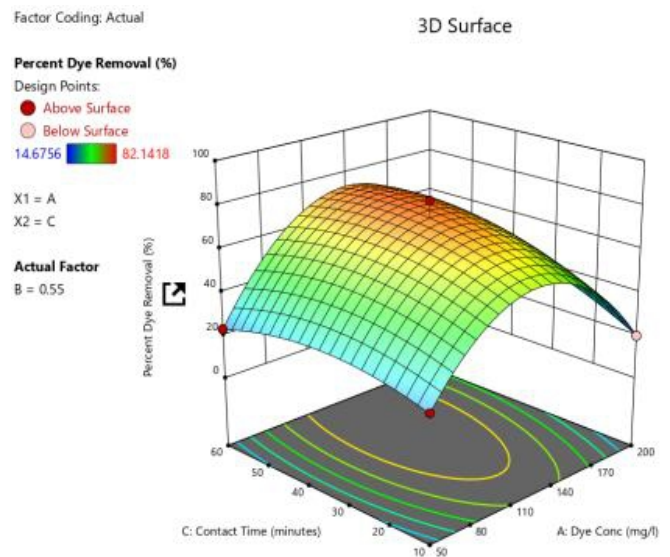


Figure 5 Surface interaction of contact time and dye concentration on dye percent removal

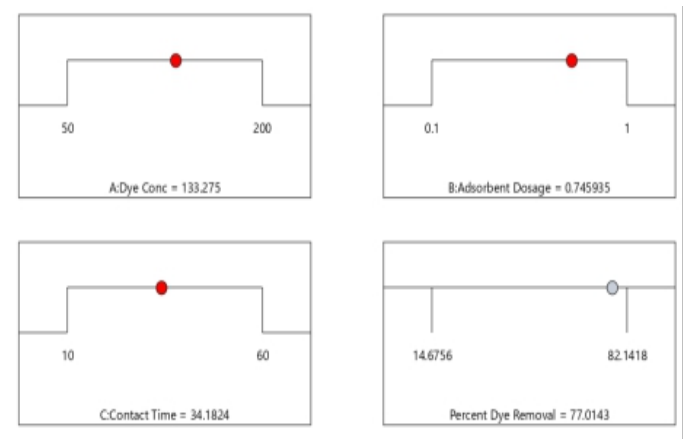


Figure 6 Numerical optimisation of the percent dye removal

As shown in Figure 6, the optimisation plot indicates the optimal set of operational parameters that led to the maximum recorded adsorption efficiency in removing methylene blue. The optimal dosage of adsorbent, 0.745 grams, and a contact time of 34 minutes were obtained, combined with an initial dye concentration of 133.275 mg/L according to the surface response model. Under these conditions, a maximum adsorption removal efficiency of 77.01 percent was achieved. This performance highlights the importance of the relationship between the variables under study, where careful adjustment of each value plays a significant role in the overall biosorption system's efficiency. The relatively moderate contact time suggests that the kinetics profile is favourable, allowing the system to reach equilibrium relatively quickly. Similarly, it can be observed that an optimised dosage of adsorbent provides an adequate concentration of active binding sites without causing issues related to particle aggregation or restricted diffusivity. The selected dye concentration remains below the saturation limit, as demonstrated in preliminary tests, allowing for high uptake without oversaturating the biosorbent surface. These findings support the robustness of the experimental design (DOE) approach used in the study and the potential for palm kernel shell-derived biosorbents to effectively remediate dyes under optimal conditions.

### 3.7 Adsorption isotherm

**3.7.1 Langmuir isotherm:** The Langmuir model describes monolayer adsorption. It assumes a uniform energy of adsorption and a single (homogenous) layer of adsorbed solute at a constant temperature. Based on the report of Ali et al. (2021) Equation 7 is a typical presentation of how the isotherm model is expressed.

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

**3.7.2 Freundlich isotherm:** This empirical model is used to describe biosorption onto a heterogeneous surface. The Freundlich isotherm, which is an empirical model, is expressed as presented in Equation 8 (Zhang et al., 2018). (2018).

$$\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e) \quad (8)$$

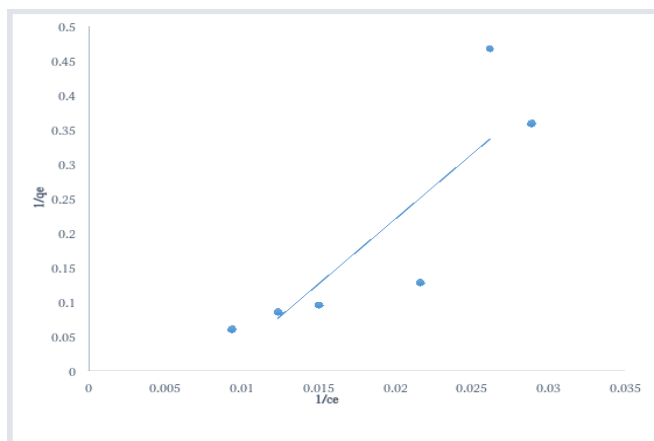


Figure 7 Langmuir isotherm plot for the removal of methylene blue dye from aqueous solution

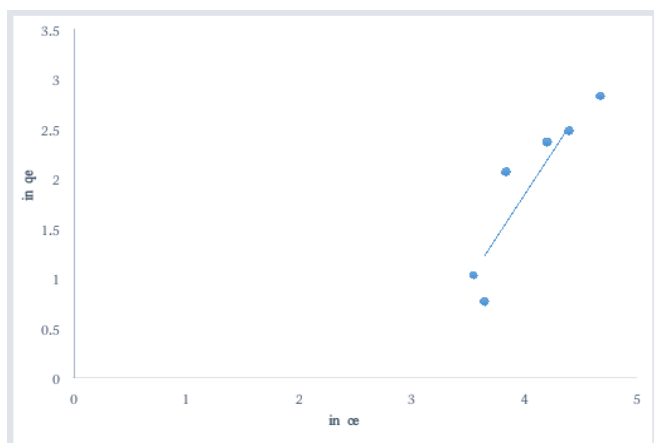


Figure 8 Freundlich isotherm plot for the removal of methylene blue dye from aqueous solution

Table 6 Isotherm parameters

Langmuir isotherm			Freundlich isotherm		
$K_a$	$q_m$	$R^2$	$K_f$	$1/n$	$R^2$
0.0247	6.297	0.754	1.619	0.581	0.845

Data of the adsorption isotherm shown in Table 6 has been fitted to the Freundlich and Langmuir models to determine which best reflects the equilibrium interaction between methylene blue and palm kernel shell biosorbent. Regression analysis indicates that the Freundlich isotherm has a better correlation with the experimental data, with a coefficient of determination of 0.845 (see Figure 8), compared to 0.754 for the Langmuir model (see Figure 7). This suggests that the Freundlich model, which assumes an uneven distribution of adsorption heat and affinities across the surface, is more suitable for describing the sorption process in this study. The closer fit with the Freundlich isotherm implies the possibility of multilayer adsorption on the biosorbent surface and the presence of various active sites with differing binding strengths, which are characteristic of biosorbents derived from agricultural waste products. Compared to the higher fit of the Freundlich model, the lower fit of the Langmuir model—which assumes that monolayers of methylene blue attach to a surface with finite and energetically identical sites—suggests that these assumptions may not fully capture the complexity of the interaction between the methylene blue solution and the prepared biosorbent. These findings are consistent with other literature, indicating that the Freundlich isotherm accurately reflects systems where developed bio-adsorbents are chemically activated and low-cost (Elgarahy et al., 2021).

### 3.8 Comparison with other adsorbents

To evaluate the performance of the activated carbon derived from palm kernel shells, a performance comparison between the activated carbon prepared in the present study and other adsorbents used for the adsorption of methylene blue was performed, and is presented in Table 7. The comparison was based on the removal efficacy of each adsorbent. The comparison helps to highlight how efficiently palm kernel shells adsorb MB. However, it is important to note that experimental conditions such as adsorbent dosages, optimisation parameters, and activation techniques can influence the adsorption performance and make direct comparison challenging.

Table 7 Removal efficiency comparison with other adsorbents

S/N	Adsorbents	Removal efficiency (%)	References
1	Palm kernel shells	77.01	Present study
2	Coffee ground pyrolysis	90.62	(Azzouni et al., 2023)
3	Pineapple peels waste	98.19	(Shehu et al., 2023)
4	Rumex abyssinicus plant	99.9	(Fito et al., 2023)
5	Tunics corm saffron	82.25	(Dbik & Khomri, 2022)

## 4. Conclusion

This study has established that palm kernel shells activated carbon is a promising low-cost biosorbent capable of completely removing methylene blue dye from aqueous textile effluents. Using the Box-Behnken design with response surface methodology (RSM), the most critical parameters of the process - namely, adsorbent dosage, contact time, and dye concentration—were systematically optimised to achieve maximum dye removal efficiency. The results show that the highest adsorption efficiency reached 77.01 percent under specific conditions, with a dye concentration of 133.275 mg/L, an adsorbent dose of 0.745 g, and a contact time of 34 minutes. This experiment highlights the suitability of palm kernel shell-derived adsorbents for real-life applications in treating dye-contaminated wastewater. Additionally, it demonstrates that, compared to the Langmuir model ( $R^2 = 0.754$ ), the experimental data fit better with the Freundlich isotherm model ( $R^2 = 0.845$ ), which suggests that the adsorption process involves multilayer coverage on a heterogeneous surface. This can be explained by the physicochemical characteristics of the prepared activated carbon and is further confirmed by Fourier Transform Infrared Spectroscopy (FTIR), where it was observed that the functional group binding dye molecules was present both before and after adsorption.

The adsorbent derived from palm kernel shells also possesses competitive properties compared to other biosorbents reported in the literature, particularly due to its availability, environmentally friendly chemical nature, and ease of preparation. These findings suggest its potential application in small-scale wastewater treatment facilities or decentralised systems, especially in resource-scarce environments. In conclusion, processing palm kernel shells to produce activated carbon will not only offer an environmentally conscious method of managing agricultural waste but will also serve as a suitable alternative to the conventional industrial activated carbon used commercially. Future research could focus on improving regeneration techniques, scaling up the process, and testing its effectiveness in real industrial wastewater streams.

## Reference

- Al-asadi, S. T. (2023). Application of response surface methodology on efficiency of fig leaf activated carbon for removal of methylene blue dye. *Eurasian Chem. Commun.*, 5(May), 794–811. <https://doi.org/10.22034/ecc.2023.395655.1631>
- Ali, Y. A. E. H., N'diaye, A. D., Fahmi, D., Kankou, M. S., & Stitou, M. (2021). Adsorption of Congo red from Aqueous Solution using Typha australis Leaves as a Low Cost adsorbent. *Journal of Environmental Treatment Techniques*, 9(2), 534–539. <https://dormaj.org/index.php/jett/article/view/153>
- Aliko V., Multisanti C. R., Turani B., & Faggio C. (2022). Get Rid of Marine Pollution: Bioremediation an Innovative, Attractive, and Successful Cleaning Strategy. *Sustainability*. <https://doi.org/10.3390/su141811784>
- Azzouni, D., Baragh, F., Mahmoud, A. M., Alanazi, M. M., Rais, Z., & Taleb, M. (2023). Optimization of methylene blue removal from aqueous solutions using activated carbon derived from coffee ground pyrolysis : A response surface methodology ( RSM ) approach for natural and cost-effective adsorption. *Journal of Saudi Chemical Society*, 27(5), 101695. <https://doi.org/10.1016/j.jscs.2023.101695>
- Elgarahy, A. M., Elwakeel, K. Z., Mohammad, S. H., & Elshafie, A. E. (2021). A critical review of biosorption of dyes, heavy metals and pharmaceuticals from aqueous media. *Chemosphere*, 265, 129090. <https://doi.org/10.1016/j.chemosphere.2020.129090>
- Dbik, A., & Khomri, M. El. (2022). *Optimization of Methylene Blue Adsorption on Agricultural Solid Waste Using Box – Behnken Design ( BBD ) Combined with Response Surface Methodology ( RSM ) Modeling*. 12(4), 4567–4583.
- Fito, J., Abewaa, M., Mengistu, A., Angassa, K., Ambaye, A. D., Moyo, W., & Nkambule, T. (2023). Adsorption of methylene blue from textile industrial wastewater using activated carbon developed from Rumex abyssinicus plant. *Scientific Reports*, 1–17. <https://doi.org/10.1038/s41598-023-32341-w>
- Fuller, R., Landrigan, P. J., Balakrishnan, K., Bathan, G., Bose-O'Reilly, S., Brauer, M., Caravanos, J., Chiles, T., Cohen, A., Corra, L., Cropper, M., Ferraro, G., Hanna, J., Hanrahan, D., Hu, H., Hunter, D., Janata, G., Kupka, R., Lanphear, B., ... Yan, C. (2022). Pollution and health: a progress update. *The Lancet Planetary Health*, 6(6), e535–e547. [https://doi.org/10.1016/s2542-5196\(22\)00090-0](https://doi.org/10.1016/s2542-5196(22)00090-0)
- Ghogomu, Muluh, S. N., Ajifack, D. L., Alongamo, A. A. B., & Noufame, D. T. (2016). Adsorption of Lead (II) from Aqueous Solution using Activated Carbon Prepared from Raffia Palm (Raphia Hookeri) Fruit Epicarp. *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 9(7), 74–85. <https://doi.org/10.9790/5736-0907017485>
- Ghorbani, F., & Kamari, S. (2017). Application of response surface methodology for optimization of methyl orange adsorption by Fe-grafting sugar beet bagasse. *Adsorption Science and Technology*, 35(3–4), 317–338. <https://doi.org/10.1177/0263617416675625>
- Hammood, Z. A., Chyad, T. F., & Al-Saedi, R. (2021). Adsorption Performance of Dyes over Zeolite for Textile Wastewater Treatment. *Ecological Chemistry and Engineering S*, 28(3), 329–337. <https://doi.org/10.2478/eces-2021-0022>
- Haseena, M., Faheem Malik, M., Javed, A., Arshad, S., Asif, N., Zulfiqar, S., & Hanif, J. (2017). Water pollution and human health. *Environmental Risk Assessment and Remediation*, 01(03). <https://doi.org/10.4066/2529-8046.100020>
- Hesar, R. H., Arami-niya, A., Mohd, W., Wan, A., & Sahu, J. N. (2013). *Preparation and Characterization of Activated Carbon from Apple Waste by Microwave-Assisted Phosphoric Acid Activation: Application in Methylene Blue Adsorption* *Roosbeh*. 8, 2950–2966.
- Hoo, H. M., Mohamad, M., Wannahari, R., Masri, M. N., Teo, P. Ter, & Mohidem, N. A. (2022). Optimization Study of Malachite Green Dye Adsorption by Eggshell Using Response Surface Methodology. *Key Engineering Materials*, 908 KEM(June), 367–372. <https://doi.org/10.4028/p-66g2qs>
- Iwar, R. T., Ogedengbe, K., & Okwuchukwu, P. (2018). Column Studies on the Adsorption of Cadmium ( Cd ) in Aqueous Solution on Raffia Palm Seed ( Raphia Hookeri ) Activated Carbon. *American Journal of Environmental Engineering and Science*, 5(3), 38–45. <http://www.openscienceonline.com/journal/ajeas>
- Jacob, N. (2009). Adsorption and Treatment of Organic Contaminants using Activated Carbon from Waste Nigerian Bamboo . *J. Appl. Sci. Environ. Manage.*, 13(3), 39–47.
- Kayabaşı, Y., & Erbaş, O. (2020). Methylene blue and its importance in medicine. *Demiroglu Science University Florence Nightingale Journal of Medicine*, 6 (3), 302–308. <https://doi.org/10.5606/FNG.BTD.2020.25035>
- Khan, I., Saeed, K., Zekker, I., Zhang, B., Hendi, A. H., Ahmad, A., Ahmad, S., Zada, N., Ahmad, H., Shah, L. A., Shah, T., & Khan, I. (2022). *Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation*.
- Krishan Amit, Shweta Yadav, & Ankita Srivastava. (2023). Water Pollution's Global Threat to Public Health: A Mini-Review. *International Journal of Scientific Research in Science, Engineering and Technology*, 321–334. <https://doi.org/10.32628/ijrsrset2310643>
- Kumari, S., Verma, A., Sharma, P., Agarwal, S., Rajput, V. D., Minkina, T., Rajput, P., Singh, S. P., & Garg, M. C. (2023). Introducing machine learning model to response surface methodology for biosorption of methylene blue dye using Triticum aestivum biomass. *Scientific Reports*, 1–17. <https://doi.org/10.1038/s41598-023-35645-z>
- Kutluay, S., & Baytar, O. (2020). Optimization of Process Conditions For Adsorption Of Methylene Blue On Formaldehyde-Modified Peanut Shells Using Box- Behnken Experimental Design And Response Surface Method. *August 2022*. <https://doi.org/10.36222/ejt.649205>
- Lin, L., Yang, H., & Xu, X. (2022). Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review. *Frontiers in Environmental Science*, 10. <https://doi.org/10.3389/fenvs.2022.880246>
- Matsumoto, K., Kamiya, K., Webo, W., Masu, L. M., Nziu, P. K., Klunk, M. A., & Das, M. (2021). Response surface methodology approach for optimization of methylene blue adsorption using activated carbon from rice husk Response surface methodology approach for optimization of methylene blue adsorption using activated carbon from rice husk. *IOP Conference Series: Materials Science and Engineering PAPER*. <https://doi.org/10.1088/1757-899X/1091/1/012034>
- Moyo, P., Chapungu, L., & Mudzengi, B. (2013). *Effectiveness of water Hyacinth ( Eichhornia crassipes ) in remediating polluted water : The case of Shagashere river in Masvingo, Zimbabwe*. 4(4), 55–62.
- Muhammad, N. S., Abdul, K., Fariha, Muhammad, N. K., Muhammad, M. Q., Ashique, A. C., Mehak, N., & Sumaira, S. (2025). Contaminated Waters: Unveiling The Environmental and Health Impacts of Global Water Pollution. *Kashf Journal of Multidisciplinary Research*. <https://doi.org/10.71146/kjmr448>
- Neolaka, Y., Riwu, A. A. P., Aigbe, U. O., Ukhurebor, K. E., Onyancha, R. B., Darmokoesoemo, H., & Kusuma, H. S. (2022). Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes. *Results in Chemistry*, 4, 100273. <https://doi.org/10.1016/j.rechem.2022.100273>
- Olafadehan, O. A., Jinadu, O. W., Salami, L., & Popoola, O. T. (2012). Treatment Of Brewery Wastewater Effluent Using Activated Carbon. *International Journal of Applied Science and Technology*, 2(1), 165–178.
- Rasilingwani, T. E. (2018). *Removal of Congo red dye from aqueous solution using a clay based nanocomposite*, Supervisor : Prof JR Gumbo (Issue May).
- Rehman, R., & manzoor, iqra and mitu liviu. (2018). *Isothermal study of congo red dye biosorptive removal from water by*. 32(2), 213–223.
- Sadaf, S., & Bhatti, H. N. (2014). Batch adsorption of methylene blue by using Citrus reticulata peels: kinetic, equilibrium and thermodynamic studies. *Journal of Molecular Liquids*, 195, 165–173. <https://doi.org/10.1016/j.molliq.2014.02.021>
- Shehu, H., Magaji, L., Aliyu, S. A., Isyaku, S., Rabilu, A. S., & Ali, D. Z. (2023). *A periodical of the Faculty of Natural and Applied Sciences , UMYU , Katsina Optimization of Methylene Blue Adsorption onto Activated Carbon derived from Pineapple Peel Waste using Response Surface Methodology*. 2(4), 45–55.
- Wurtsbaugh W. A., Paerl H. W., Dodds W. K. (2019). Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. *WIREs Water*. <https://doi.org/10.1002/wat2.1373>
- Zhang, M., Liu, X., Li, W., Guo, L., Tan, Z., Wang, Q., & Zhang, L. (2021). *Application of response surface methodology for optimization of methylene blue adsorption onto activated carbons prepared from chestnut shell*. 226, 441–451. <https://doi.org/10.5004/dwt.2021.27282>
- Zhang, Z., Li, Y., Du, Q., & Li, Q. (2018). Adsorption of Congo Red from Aqueous Solutions by Porous Soybean Curd Xerogels. *Polish Journal of Chemical Technology*, 20(3), 95–102. <https://doi.org/10.2478/pjct-2018-0044>
- Zhao, L., Wu, S., Zhang, Y., & Chen, X. (2023). Adsorptive removal of methylene blue using biochar derived from agricultural waste: Effects of operational parameters and isotherm modeling. *Environmental Research*, 225, 115565. <https://doi.org/10.1016/j.envres.2023.115565>