

Optimization and Machine Learning-Based Modeling of MB Removal from Water via Hybrid Electrocoagulation–Adsorption

Abstract

This study investigates the performance of a hybrid electrocoagulation and adsorption process for removing Methylene Blue (MB) dye and reducing electrical conductivity (EC) in synthetic wastewater. The results show that solution pH is the main factor influencing treatment efficiency, with optimal performance within a narrow range of 6.0 to 7. pH above 7 led to a marked decrease in dye removal. Using an oak-based adsorbent further enhanced the process, with a higher dosage (0.08 g/L) improving removal due to increased surface area. The kinetics of EC reduction showed a rapid decrease with contact time, plateauing after 20 minutes. Although elevated temperatures (up to 30°C) improved both dye removal and EC reduction, their effect was secondary to pH. The system was optimized, yielding the following ideal operating conditions: pH = 7, adsorbent dosage = 0.08 g/L, contact time = 20 min, and temperature = 30°C. This work confirms the viability of the hybrid EC-Ads approach and establishes precise operational parameters for effective dye wastewater treatment.

- **Keywords:** Hybrid electrocoagulation-adsorption, Methylene Blue, Water conductivity reduction, Oak bio-adsorbent, Adsorption kinetics

1-Introduction

Industrial wastewater discharges into rivers and lakes adversely affect water resources worldwide [1]. Among these pollutants, water-soluble dyes are among the main causes of pollution [2]. The textile industry, which contributes significantly to global environmental pollution, consumes approximately 44.0 billion metric tons of freshwater annually [3]. Conventional textile processes—from pretreatment through printing and dyeing to final finishing—often release substantial amounts of pollutants [4]. Within this sector, the extensive use of complex dyes with diverse functional groups makes the textile industry the largest consumer of dyes [5]. One of the most commonly used dyes is MB, which is routinely used to dye silk, wool, cotton, and paper [6, 7]. Various physical, chemical, and biological processes are used to remove dyes from water, including coagulation, flocculation, ion exchange, membrane filtration, nanofiltration, chemical oxidation, photochemical degradation, photocatalytic degradation, reduction, precipitation, extraction, and adsorption [8]. However, some of these processes face limitations, such as high operating and maintenance costs, process complexity, and the formation of hazardous byproducts [9].

One such method for dye removal is EC, which uses soluble (sacrificial) electrodes. This method contrasts with advanced electrochemical oxidation processes (EAOPs), which use stable, insoluble electrodes [10]. In EC, chemical and physical processes occur, and sacrificial electrodes supply ions. The purification mechanism involves several stages: forming coagulants through the reaction of metal ions with hydroxyl ions generated at the cathode, adsorbing contaminants onto the

coagulants, and finally removing contaminants by sedimentation or flotation. The electrolytic reaction occurs at the electrode surface and leads to dissolution of the anode metal. Because of its ease of operation, high speed, and excellent treatment performance, electrolytic coagulation is currently one of the most widely used methods for wastewater treatment [10].

Despite its relative simplicity, EC also has several drawbacks. These include energy consumption, the formation of an oxide layer (passivation), sludge production [11], electrode consumption [10], the generation of secondary pollutants, and the low yield of coagulants from sacrificial anodes [12]. These limitations have redirected focus toward adsorption. The adsorption technique, which offers advantages such as lower cost, high efficiency, and ease of operation, is recognized as a promising and effective approach [13]. Recent studies have shown that certain physical treatment methods, particularly adsorption, perform better when bio-composite materials are used as adsorbents [14]. However, no single adsorbent has proven universally effective for removing all types of pollutants, as each type faces inherent limitations in its adsorption kinetics and capacity [13]. Among these configurations, continuous adsorption systems are widely used in industrial wastewater treatment due to their efficiency and scalability [15].

The search for efficient and cost-effective adsorbents continues. For example, wastewater from the shrimp industry and shrimp shell waste contain anionic pollutants. In one study, researchers produced adsorbents to remove methyl orange from shrimp shells via pyrolysis, with and without alkaline modification. The resulting adsorbents exhibited an exceptional adsorption capacity of up to 4,033 mg/g at 30 °C [16]. Additionally, palm leaf powder has been used as a bio-adsorbent to remove Malachite Green dye [17]. In another study, zinc oxide nanoparticles—synthesized via an environmentally friendly process using an extract from the brown alga *Padina pavonica*—were investigated for removing the dye MB; they exhibited an adsorption capacity of 192,308 mg/g and an efficiency of over 98% at low concentrations [18].

In this context, oak as an adsorbent for dye and metal removal has attracted significant attention as a suitable option. Given its availability and strong performance in contaminant removal, oak is a suitable choice for adsorption processes. Oak sawdust, alkaline-treated oak sawdust, and acid-treated oak sawdust have been successfully used for dye removal [19]. In addition, a one-step process was used to produce magnetic activated carbon (MAC) from oak shells. In adsorption experiments, the efficiency of MAC in removing the dyes rhodamine B and rose bengal was investigated, with the maximum adsorption capacity for rhodamine B reaching 198,0 mg/g [20]. Another study compared the adsorptive removal of cadmium ions from aqueous solutions under various conditions, using both raw oak waste and oak waste activated with sodium hydroxide. The results suggest that oak waste can serve as a promising, environmentally friendly adsorbent for remediating water contaminated with heavy metals.

Despite the proven effectiveness of electrocoagulation (EC) and adsorption as separate processes, a critical knowledge gap remains regarding their synergistic combination, particularly when using a characterized oak-based bioadsorbent for MB removal. Previous studies have lacked a systematic optimization of this hybrid system and, most importantly, a comprehensive analysis of the complex interactions among the parameters. To address this gap, our study makes three key contributions: First, we develop and optimize a novel hybrid electrochemistry-adsorption process using synthesized oak powder, while conducting a dual analysis of dye removal and conductivity reduction. Second, we apply response surface methodology using a Box-Behnken design (BBD)

for rigorous multivariate optimization. Third, and most importantly, we go beyond empirical modeling by employing machine learning techniques to predict performance and—crucially—to interpret the individual contribution and optimal range of each operating parameter (pH, temperature, time, dosage). This approach offers a novel, interpretable framework for understanding and scaling hybrid water treatment systems. Accordingly, this study aims to investigate the efficiency of a combined EC- and oak wood-based adsorption process for the removal of MB from aqueous solutions. To this end, synthesized oak wood powder was prepared and its structure was characterized using FTIR analysis. After the oak adsorbent was prepared, it was used in combination with EC to remove the MB dye. Subsequently, key operating parameters such as pH, temperature, time, and adsorbent concentration were optimized using the BBD experimental method. In addition, the kinetics of dye removal in the hybrid process were investigated. Finally, advanced machine learning models were employed for process modeling to predict and analyze the behavior of the developed hybrid system.

2. Materials and Methods

2.1. Materials and Laboratory Equipment

MB was obtained from Merck. For the experimental procedure, dye solutions were prepared at 50 mg/L by diluting a 500 mg/L stock solution. Merck (Germany) supplied the other chemical compounds used in this study. We used double-distilled water to prepare all samples and solutions. The acorns used in the experiments were collected near the city of Kermanshah and then cut into small pieces. After an oil extraction process from the acorns, the resulting pomace was dried at 40 °C for 48 hours. The dried pomace was then ground into a fine powder using a household grinder for the adsorption experiments.

To identify the functional groups on the adsorbent surface, Fourier-transform infrared spectroscopy (FTIR) (Thermo AVATAR, USA) was used over the range 4000–400 cm⁻¹. In addition, UV-Vis absorption spectra were recorded using a Varian Cary 100 spectrophotometer at 25–20 °C.

2.2. Setup of the EC Apparatus

For the separation process, one iron electrode and one aluminum electrode, both 5 cm x 5 cm, were immersed in a beaker containing the solution, connected with two sets of alligator clips, and connected to a DC power supply via cables. The voltage was set at 12 V and the current at 0.1 A for the experiments.

2.3. Experimental Procedure

First, 50 mL of the solution for each pre-prepared adsorbent concentration (0 to 5 g/L) was adjusted to the desired pH values (3 to 11) using hydrochloric acid (HCl) and sodium hydroxide (NaOH). The beaker containing the test solution was placed on a hot plate along with a magnetic stir bar. The two electrodes connected to the power supply were secured in the beaker, and the separation process was studied at temperatures ranging from 20 to 50 °C and for time intervals

ranging from 0 to 60 minutes. The resulting samples, each evaluated with respect to the four parameters—adsorbent concentration, temperature, time, and pH—were centrifuged separately for 0 minutes at 4,000 rpm. Finally, the dye removal efficiency from the aqueous solution was measured at a wavelength of 660 nm using a UV-Vis spectrophotometer.

Based on the experimental design methodology, numerous experiments were conducted to investigate the factors influencing the combined EC and adsorption method (adsorbent concentration, temperature, time, and pH); these are discussed in the following sections. The percentage dye removal efficiency was calculated using the following equation:

$$\text{Removal efficiency (Y)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial dye concentration, and C_e is the final (or equilibrium) dye concentration.

2.4 Measurement of the Point of Zero Charge (PZC)

To measure the PZC of the magnetic oak adsorbent, the following procedure was performed: 100 mL of deionized water was added to an Erlenmeyer flask, and its mouth was sealed with a cotton plug. The deionized water was boiled for 10 minutes to remove dissolved CO_2 . After boiling, the water was rapidly cooled while the flask remained sealed. Separately, 0.5 g of the magnetic oak adsorbent was weighed into a 100 mL Erlenmeyer flask, and 10 mL of the CO_2 -free water was added. The flask was then sealed and agitated for 24 hours at 25°C. Finally, we measured the pH of the supernatant and reported this value as the PZC. This method has been reliably used by other researchers [21, 22].

2.5 Experimental Design and Machine Learning

Using the experimental design approach, we determined the effect of variations in time (0–60 minutes), adsorbent concentration (0, 1, 2 g/L), pH (0–11), and temperature (20–50 °C) on dye removal. The BBD design is a numerical and statistical method that is of fundamental importance for primary experimental design. Therefore, this useful and efficient numerical method was applied to optimize the dye removal process. Various variables can influence the results. Consequently, the BBD method can determine the relationship between independent and dependent (response) variables and optimize the desired treatment process. In practice, we optimized dye removal efficiency (the response variable) using the BBD method in Design-Expert software, version 11.1. The experimental design included three levels for each of the four independent parameters. We selected these four variables and their respective ranges based on the preliminary studies presented in Table 1.

Table 1. Ranges of actual and coded values for the independent variables used in the experimental design software.

Factor	Name	Units	Type	Min	Max	Coded Low	Coded High
A	pH	-	Numeric	3,00	11,00	-1 ↔ 3,00	+1 ↔ 11,00

B	Temperature	°C	Numeric	20,00	50,00	-1 ↔ 20,00	+1 ↔ 50,00
C	Adsorbent dosage	g/L	Numeric	0,00	2	-1 ↔ 0,00	+1 ↔ 2
D	Time	min	Numeric	0,00	50,00	-1 ↔ 0,00	+1 ↔ 50,00

The inherent complexity of adsorption processes requires advanced modeling approaches capable of analyzing nonlinear, complex interactions among effective parameters. Accordingly, this study adopts a comparative multi-model approach that combines classical statistical methods with advanced machine learning algorithms to provide a precise predictor of MB removal efficiency. Using a variety of algorithms enables a comprehensive evaluation and identification of the most reliable method for this application [22]. The analysis begins with classical regression models, with linear regression as a transparent, fundamental benchmark. To improve the model's generalizability and mitigate multicollinearity, the authors use variants of penalized regression—ridge regression and Lasso regression. The former limits coefficient magnitude, while the latter sets some coefficients exactly to zero, facilitating effective feature selection and yielding a more interpretable model [23]. In machine learning, ensemble methods model complex patterns. Random Forest combines the results of numerous uncorrelated decision trees, thereby preventing overfitting [24].

In contrast, Gradient Boosting (GB) demonstrates superior performance on engineering problems through sequential, step-by-step model construction, focusing on residual errors at each stage [25]. Furthermore, Support Vector Regression (SVR) models nonlinear relationships by mapping data into a higher-dimensional space and is characterized by its robustness to outliers. Ultimately, this parallel application of classical and modern methods pursues two main objectives: first, to achieve the highest possible accuracy in predicting the adsorption process, and second, to elucidate the effects and interactions of the operating parameters precisely. Consequently, a detailed comparative analysis at the end of this paper will identify the superior model, intended to guide process optimization.

2. Results and Discussion

2.1. FTIR Results

Fig. 1 presents the FTIR spectrum of the oak sample, revealing numerous chemical compounds in its structure. A strong band at 3411 cm^{-1} corresponds to stretching vibrations of both -OH and -NH groups. Given its intensity and broad shape, this peak is likely predominantly attributable to hydroxyl (-OH) groups [26]. The peak at 2929 cm^{-1} is assigned to the C-H stretching vibration of aliphatic CH_2 groups [27]. The principal peaks in the region of 1016 to 1157 cm^{-1} are related to C-O-C stretching and glycosidic linkages, clearly confirming the predominant presence of cellulose and hemicellulose in the sample's cell wall [28]. The peak at 1702 cm^{-1} can be attributed to carbonyl (C=O) groups in lipids and proteins [29]. Furthermore, peaks at 1389 and 1454 cm^{-1} correspond to bending vibrations of methyl (- CH_3) and methylene (- CH_2 -) groups in fatty acids and lipid constituents [30]. Additionally, peaks observed in the region below 900 cm^{-1} suggest the presence of phenolic and aromatic compounds belonging to lignin within the oak tissue structure. Collectively, this spectrum confirms that the chemical structure of the oak adsorbent comprises structural polysaccharides (cellulose and hemicellulose) as the primary components, along with appreciable amounts of lipid, protein, and lignin.

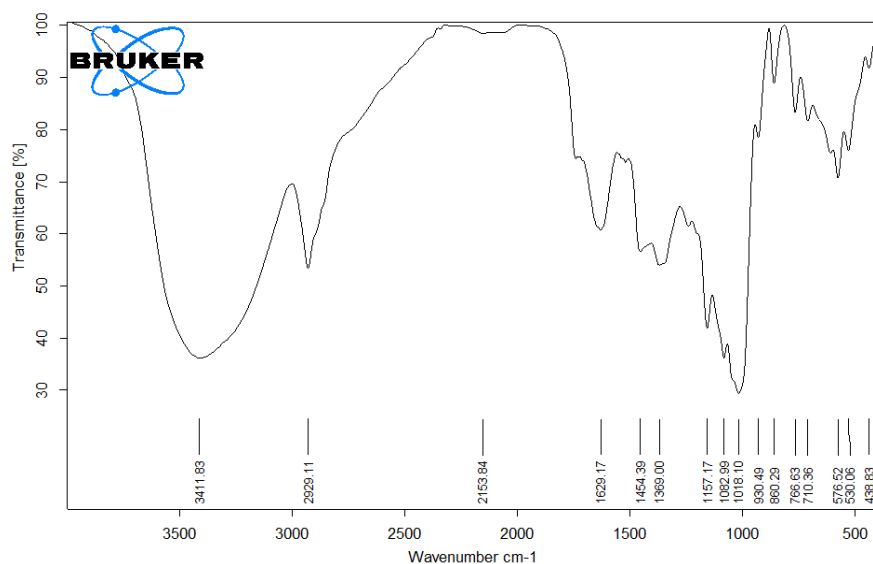


Fig. 1. FTIR spectrum of the oak sample.

2.2. Model Validation

A mathematical model fitted to the data may sometimes lack convincing power in explaining the experimental data of the independent variable. Analysis of Variance is a useful method for evaluating a model's adequacy. The values obtained for both responses, associated with a full design matrix, are summarized in Table 2

Table 2. BBD matrix and corresponding responses for the reduction of water electrical conductivity.

	Factor 1	Factor 2	Factor 3	Factor 4	Response	
Run	A: pH	B: Temperature °C	C: Adsorbent dosage g/L	D: Time min	%Yield	
					Actual	Predicted
1	7	30	0	30	70,3	77,47
2	7	30	1	30	71,8	73,77
3	7	30	1	00	73,8	74,99
4	3	20	2	0	40	47,93
5	11	00	2	00	02,7	02,07
6	3	20	0	00	03,7	03,40
7	3	00	2	00	74,7	70,00
8	11	20	2	00	47,7	49,22
9	7	30	1	30	72,8	73,77
10	7	20	1	30	78,8	78,48
11	7	00	1	30	71,8	71,07
12	3	20	0	0	39	38,92
13	11	30	1	30	07,4	07,07
14	3	00	2	0	49,3	49,42
15	3	00	0	00	00,3	06,09
16	11	00	0	00	00,2	49,03
17	3	00	0	0	43,1	42,23

18	11	20	2	0	38	36,09
19	3	20	2	00	64,4	63,14
20	3	30	1	30	66	60,27
21	7	30	1	30	74,4	73,66
22	11	20	0	00	46,1	40,36
23	7	30	2	30	73,7	71,98
24	11	00	2	0	39,1	40,06
25	11	20	0	0	34	34,46
26	7	30	1	0	63,0	61,70
27	11	00	0	0	38,1	38,70

Table 3 shows the ANOVA results for the color response function. The low p-value ($< 0,0001$) statistically confirms the model's accuracy. The correlation coefficient and adjusted R^2 indicate the proportion of variance in the response explained by the independent variables and their interactions. Specifically, R^2 represents the variance in the response explained by the model. For this function, the R^2 value is 0,9934, meaning the model explains 99,34% of the variance in the response. Furthermore, the adjusted coefficient of determination (adjusted R^2) is 0,9808.

Based on the ANOVA results, the proposed regression model is highly statistically significant (p-value $< 0,0001$) and effectively explains variation in the response variable. The main-effects analysis shows that all factors—pH, temperature, adsorbent dosage, and time—significantly influence the response variable. Among these, time, with the highest sum of squares (789,37), is identified as the most influential factor. Furthermore, the significance of all quadratic terms (A^2 , B^2 , C^2 , D^2) indicates the presence of nonlinear relationships and optimal points for each factor. Regarding interaction effects, only the interactions between pH and adsorbent dosage (AC) and between pH and time (AD) were significant. Finally, the non-significance of the Lack of Fit (p-value = 0,0421) indicates an adequate model fit and its sufficiency for prediction.

Table 3. Results of the ANOVA and predictor variables in the quadratic model

Source	Sum of Squares	Mean Square	F-value	p-value	
Model	4038,00	324,14	129,62	$< 0,0001$	Significant
A-Ph	340,60	340,60	136,20	$< 0,0001$	
B-Temperature	42,63	42,63	17,00	0,0014	
C-Adsorbent dosage	137,23	137,23	54,87	$< 0,0001$	
D-Time	789,37	789,37	310,60	$< 0,0001$	
AB	0,9006	0,9006	0,3801	0,0491	
AC	34,02	34,02	13,80	0,0030	
AD	12,78	12,78	0,11	0,0432	
BC	0,6806	0,6806	0,2722	0,6114	
BD	0,3906	0,3906	0,1062	0,7996	
CD	2,98	2,98	1,19	0,2968	
A^2	417,03	417,03	166,96	$< 0,0001$	
B^2	34,12	34,12	13,64	0,0031	
C^2	00,70	00,70	20,29	0,0007	
D^2	72,03	72,03	28,80	0,0002	
Residual	30,01	2,00			
Lack of Fit	20,67	2,07	1,18	0,0421	not significant
Pure Error	4,34	2,17			
Cor Total	4068,01				

R^2 : 0,9934; Adjusted R^2 : 0,9808; Predicted R^2 : 0,9613

The empirical second-order polynomial model proposed by the software is significant only for specific factor levels (the model was refitted accordingly) in terms of the coded variable values:

$$Yield = +73.62 - 4.35A + 1.54B + 2.76C + 6.62D - 1.47AC - 0.8938AD - 12.73A^2 - 3.63B^2 - 4.43C^2 - 5.28D^2$$

In addition, ANOVA calculations are performed using a specific design to identify outliers and evaluate the regression model's goodness of fit. This analysis shows an adequate correlation between the predicted values and the actual experimental data. This summary plot is well suited to illustrating the general relationship between the experimental data and the values derived from the fitted model. However, it may overlook important model details. Residual plots, by contrast, highlight these details and should be used to assess goodness of fit. Graphical analysis of the residuals is the most important method for determining whether the model needs to be refined or for verifying that the basic assumptions of the analysis are met.

3.3. Experimental Design Response Plots

Examining the normal probability plot of the residuals is an important way to assess model validity. Model-based analysis assumes that residuals follow a normal distribution with constant variance and a mean of zero, and that they are independent of one another. If the points in a normal probability plot of the residuals lie along a straight line, the residuals are normally distributed. Fig. 3 shows three plots of the response variable from the experimental design used to evaluate the model's validity. In plot (a), all data points lie exactly on a straight line, indicating that the predicted values are close to the actual values—a satisfactory result. Plot (b) shows the normal probability plot of the residuals and illustrates the extent to which the percentage of dye removal follows a normal distribution.

Regarding model validity, the points in the plot follow a diagonal line with minor deviations. Plot (c) examines the run number versus the internally studentized residuals. Based on the plot, the residual values are scattered randomly around the zero line without any discernible pattern (such as sinusoidal, expanding, or funnel shapes). This demonstrates that the model meets the independence-of-errors assumption, and no systematic relationship exists between the errors and the experimental run order.

3.4. Effect of Independent Variables on Dye Removal

3.4.1. Investigation of pH Effect on Dye Removal

To investigate the effect of wastewater pH on separation efficiency, experiments were conducted in which the pH was adjusted to values ranging from 3 to 11, and an electrolysis time of 30 minutes was selected. As shown in Fig. 3a, the degree of degradation increased from pH 3 to 9, with the highest degradation between pH 8 and 9. Specifically, at pH 9, decolorization reached approximately 90%, corresponding to the highest degree of dye degradation. Beyond pH 9, dye removal decreased as pH increased, reaching its lowest level at pH 11. This analysis shows that, for this dye removal process, the optimal pH is 9, and increasing pH beyond this point reduces removal efficiency. In this case, the dye removal mechanism is determined by two underlying mechanisms: one for adsorption and one for EC.

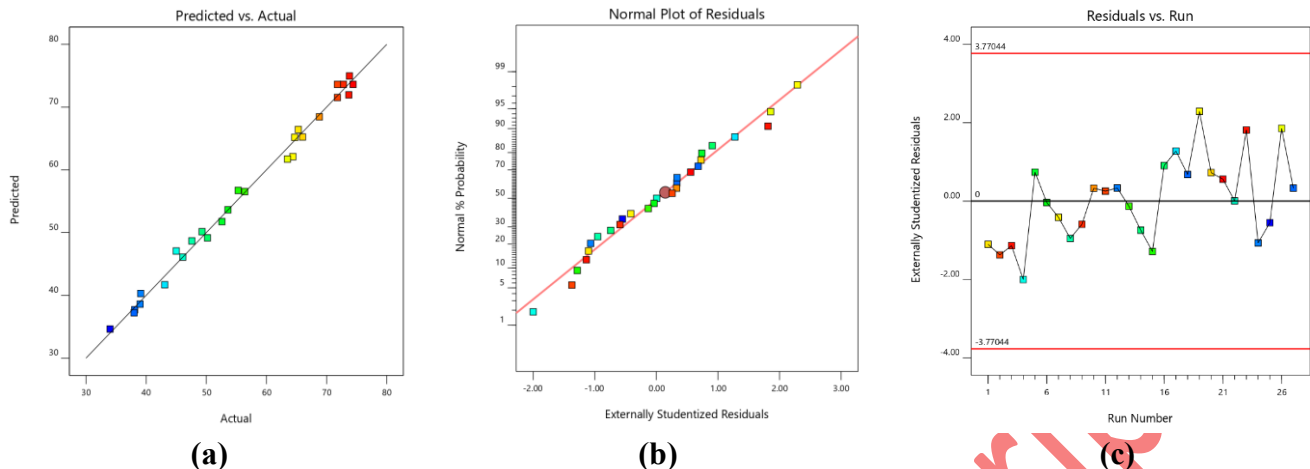


Fig. 9. Plots for evaluating model validity: (a) Predicted vs. actual values plot, (b) Normal probability plot of residuals, (c) Run number vs. internally studentized residuals plot.

Regarding the adsorption process, Borah et al. show that adsorption capacity increases as pH rises, reaches a maximum at pH 9, and then decreases again [31]. Solution pH can influence the adsorbent's surface charge, the degree of ionization of various pollutants, the dissociation of functional groups at active sites, and the dye's molecular structure [32]. At low pH values, hydrogen ions (H^+) surround the adsorbent surface, causing it to acquire a stronger positive charge. This reduces adsorption of cationic dyes onto the adsorbent. In other words, the excess H^+ ions compete with the cationic dye molecules for adsorption at the active sites. Consequently, the adsorbent's adsorption capacity is significantly reduced at low pH values. As the solution pH increases, the number of negatively charged sites increases. As a result, attraction and interaction between the adsorbent and cationic dye molecules strengthen, increasing adsorption capacity as pH rises [33].

In the EC process, this phenomenon can be attributed to the formation of insoluble $Fe(OH)_2$, which precipitates at pH values above 9. Up to pH 9.0, these hydroxide ions are in equilibrium with ferrous ions (Fe^{2+}). In the presence of dissolved oxygen, Fe^{2+} is oxidized and converts to $Fe(OH)_3$, which is considered the most effective coagulating species among iron species, leading to efficient dye removal. At higher pH levels, soluble species such as $[Fe(OH)_3]^-$ and $[Fe(OH)_4]^-$ are formed, which reduces the efficiency of the dye removal process [34].

4.3.2. Investigation of Contact Time Effect on Dye Removal

Fig. 9b illustrates the variations in dye removal efficiency as a function of contact time. As shown in the figure, the percentage of dye removed increases sharply as contact time increases from 0 to 30 minutes. It then stabilizes around 40 minutes and reaches approximately 96%. Beyond this point, further prolongation of the contact time results in a nearly constant removal efficiency with no significant changes. Based on the results obtained, a contact time of 30 to 40 minutes was selected as the most effective duration for decolorization and dye removal.

This phenomenon can be explained by the fact that, at the beginning of the adsorption process, many surface sites are available for adsorption. Over time, as these surface sites are gradually

occupied, MB undergoes multilayer adsorption or diffuses into the adsorbent pores, leading to a decrease in the adsorption rate. This behavior may also be attributed to repulsive forces between adsorbed molecules on the adsorbent surface and those in the bulk solution. With longer contact times, adsorption capacity increases because more time is available for interaction between the adsorbent and the adsorbate, enabling better adsorption. Other researchers have also reported similar results in their studies [30].

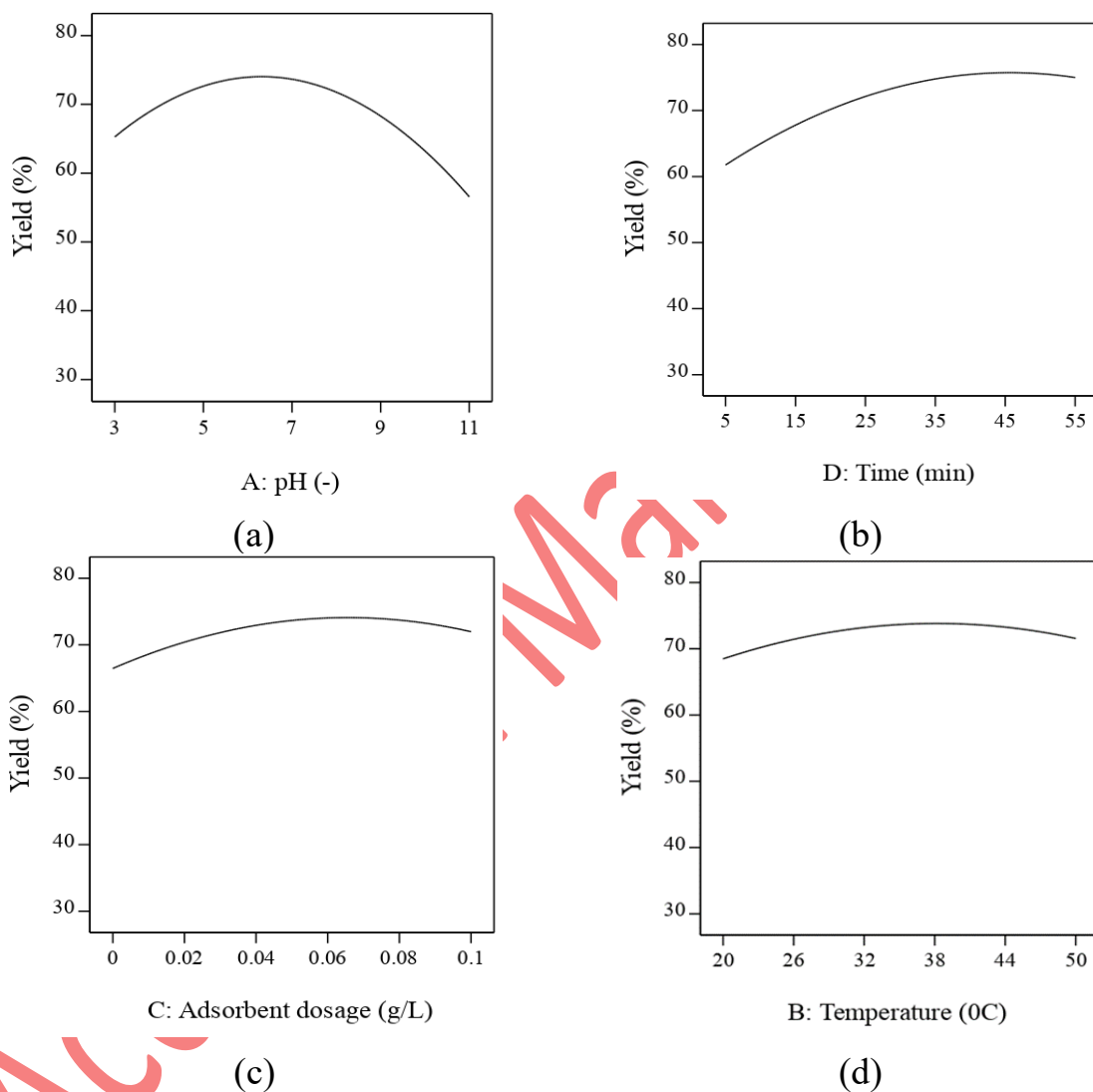


Fig. 4. (a) Effect of pH on dye removal, (b) Effect of contact time on dye removal, (c) Effect of adsorbent dosage on dye removal, (d) Effect of temperature on dye removal.

It can also be stated that as the electrolysis process continues, floc formation proceeds. As noted in previous research, metal hydroxide formation increases up to about 30 minutes, after which it stabilizes. This behavior can be attributed to a negative redox potential, which stabilizes ferrous ions (Fe^{2+}) in their reduced state [31, 32].

4.3. Investigation of the Effect of Adsorbent Dosage on Dye Removal

In this phase, the effect of adsorbent dosage on dye removal was investigated, with the results presented in Fig. 3c. As shown in the figure, increasing the adsorbent amount leads to a higher dye removal percentage, with maximum removal achieved at a dosage of 0.1 grams.

The increased removal efficiency at higher adsorbent dosages is due to more active sites available for adsorbing MB molecules in the solution. Consequently, the adsorbent and pollutant interact more effectively, increasing removal. However, beyond a specific threshold, further increases in adsorbent dosage do not significantly improve removal efficiency. Based on these results, adding an optimal amount of adsorbent (0.06 g L⁻¹) achieves maximum adsorption capacity, after which the residual pollutant concentration in the solution remains almost constant. Furthermore, as adsorbent dosage increases, the amount of MB adsorbed per unit mass decreases. This occurs because the pollutant amount remains constant while the adsorbent increases, ultimately decreasing unit adsorption capacity. It appears that increasing the adsorbent concentration causes particle aggregation and a reduction in the effective contact surface area with the pollutant. The findings of this section are consistent with results reported in other studies [38].

3.3. Investigation of the Effect of Temperature on Dye Removal

In this stage, we examined the effect of temperature on the dye removal process. According to Fig. 3d, as temperature increases from 20 to 50°C, dye removal also increases, resulting in greater dye removal.

As temperature increases up to 30°C, dye removal efficiency in the combined adsorption and EC process increases. This is primarily due to enhanced adsorption kinetics, a decrease in solution viscosity, and more efficient floc formation. However, beyond this optimal temperature, efficiency drops significantly, which can be attributed to several factors, including thermal instability of flocs, decreased adsorption capacity due to the exothermic nature of the adsorption process, and possibly increased pollutant solubility. This pattern aligns with similar studies investigating the effect of temperature on hybrid treatment processes [39-41].

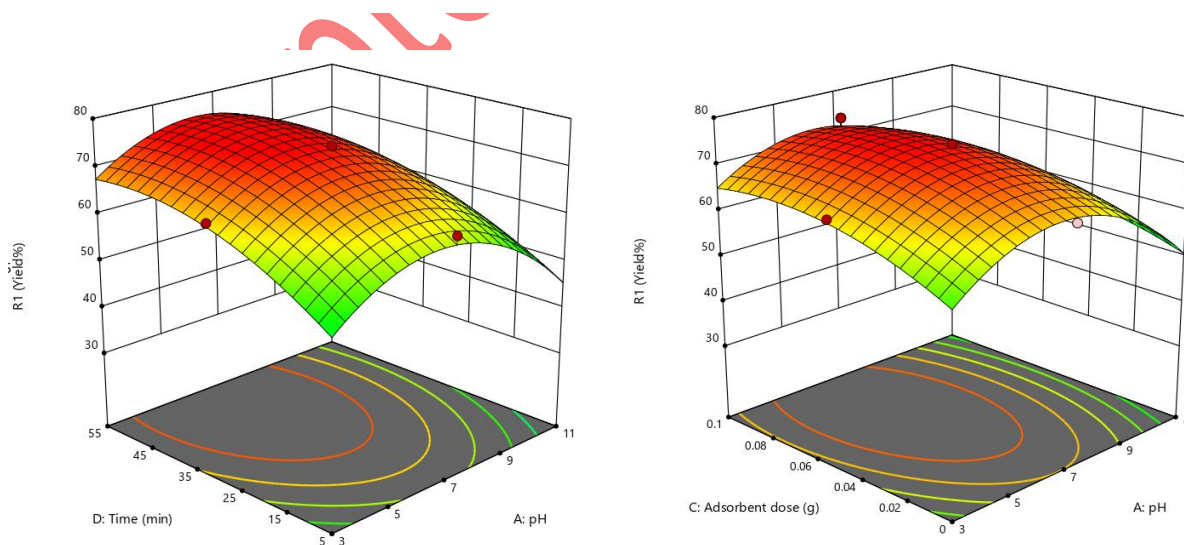
3.4. Influence of Binary Interactions on Dye Removal Efficiency

For a more precise visualization of the results, Fig. 4 presents two-dimensional contour plots and three-dimensional response surface plots. In these plots, regions of higher removal percentages are colored red, while the color shifts to green as the removal percentage decreases.

The contour plot in Fig. 4a illustrates the simultaneous influence of pH and contact time on MB removal efficiency. This pattern cannot be attributed to the adsorption mechanism alone; it is also governed by the chemistry of iron species and the kinetics of the electrochemical coagulation process. The highest removal efficiency (above 95%) was achieved in the near-neutral to mildly alkaline pH range (7-9) at 30-40 minutes. Within this optimal range, favorable conditions are established for both processes to occur simultaneously: the surface charge of the adsorbent in this pH range is suitable for the effective adsorption of cationic MB molecules, while the formation of metal hydroxide species (such as Fe(OH)₃) as coagulants reaches its maximum [34]. The gradual increase in efficiency over time within this pH range can be attributed to continued electrolysis and the continuous generation of flocs. As noted in previous studies, hydroxide formation increases up to about 30 minutes, after which it stabilizes [37]. The decrease in efficiency at acidic pH

(below 7) is primarily due to the high solubility of flocs and the protonation of adsorption sites, which disrupts the favorable electrostatic interaction with the dye cations. Furthermore, the reduced efficiency at highly alkaline pH (above 10) can be attributed to the formation of soluble anionic iron species (such as $[\text{Fe}(\text{OH})_4]^-$), which lose their coagulation capability [34]. Therefore, optimal system performance depends on a favorable overlap between the pH range and the effective time for both adsorption and coagulation.

Similarly, Fig. 4b shows the combined effect of pH and adsorbent dosage on MB removal efficiency. The pattern observed in this plot results from a complex interaction between surface adsorption and chemical coagulation mechanisms. The highest removal efficiency (above 95%) was again obtained in the near-neutral to mildly alkaline pH range (7–9) and at intermediate adsorbent dosages (0.04–0.06 g/L). In this optimal range, the two mechanisms act synergistically: on one hand, within this pH range, metal hydroxide species such as $\text{Fe}(\text{OH})_3$ are formed as the most efficient coagulants [34]; on the other hand, the surface charge of the adsorbent is favorable for optimal adsorption of cationic molecules. Intermediate adsorbent dosages are also optimal because they provide sufficient active sites for adsorption while preventing particle re-agglomeration at higher dosages, which reduces effective surface area. The decrease in efficiency at low adsorbent dosages (less than 0.02 g/L) is clearly due to insufficient surface adsorption sites to support the coagulation process. Conversely, the reduction in efficiency at high adsorbent dosages (above 0.08 g/L) can be attributed to adsorbent particle aggregation, reduced available surface area, and possibly the formation of physical barriers that hinder floc formation and sedimentation. This phenomenon indicates that excess adsorbent is not only non-beneficial but can also reduce the overall efficiency of the hybrid system by interfering with the coagulation process. Therefore, this plot shows that achieving maximum efficiency in a hybrid system requires a precise balance between the chemical conditions (pH) optimized for coagulation and the operational parameters (adsorbent dosage) optimized for adsorption, enabling both processes to act synergistically.



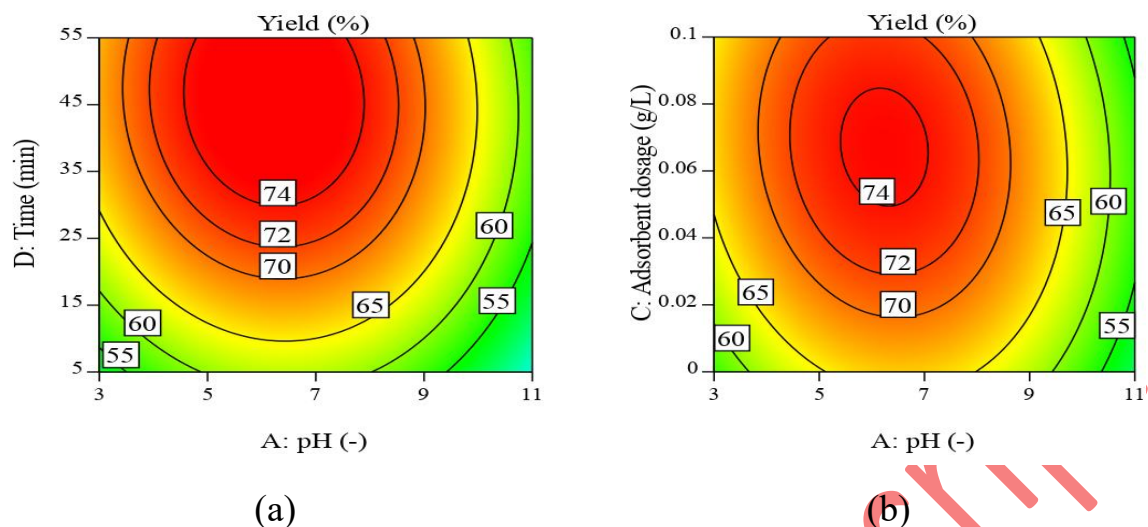


Fig. 1. Effect of binary interactions on dye removal.

1.3. Optimization of MB Dye Removal Process

A series of experiments was designed to optimize four numerical variables—adsorbent concentration, temperature, time, and pH—in the process of reducing water electrical conductivity via the combined EC and adsorption (EC) method. The polynomial model equations considered the interactions among these four factors for the response of MB dye removal from solution. In total, Design-Expert software proposed 16 solutions to identify the optimal conditions and results. The quality of the responses was evaluated using ANOVA, and the results indicate that the variables significantly affect the reduction of dye and impurities in the MB solution. Table 1 presents the upper and lower bounds of the variables and responses, as well as the desirable values of the variables and responses. The optimization results revealed that the best values for the four variables at a desirability of 1 are: a pH of 9, an adsorbent dosage of 0.083 g, a contact time of 50 minutes, and a temperature of 31°C.

Table 1. Constraints of the studied variables, response for optimization, and the optimization

Name	Goal	Lower Limit	Upper Limit	Best Results
A: pH	is in range	3	11	9.061
B: Temperature (°C)	is in range	20	50	31
C: Adsorbent dosage(g/L)	is in range	0	0.1	0.083
D: Time (min)	is in range	0	50	50.00
Yield (%Dye Removal)	maximize	34	74.7	70

1.4. Kinetic Studies

Adsorption kinetics describe the mechanism of pollutant ion adsorption, the time required to reach equilibrium, and potential rate-controlling steps such as mass transfer and chemical reaction

processes [41]. Kinetic studies of the treatment process play a crucial role in determining the hydraulic retention time in any reactor system to achieve desirable removal [42]. Therefore, the rate constant is paramount in designing wastewater treatment units. Understanding the type and rate of reactions is essential for designing a treatment unit. The rate of a reaction represents the change in reactant concentration per unit time. The results indicated that the dye removal followed first-order kinetics, showing good correlation coefficients (>0.90), as expressed by the following equation:

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

In this equation, the parameters are defined as follows: C_0 represents the initial dye concentration (in mg/L), C denotes the dye concentration at time t (in mg/L), t is the reaction time (in minutes), and k is the reaction rate constant (in min^{-1}). All experiments were conducted at room temperature.

The adsorption behavior showed that the adsorbent system fitted well with the pseudo-first-order model ($R^2 > 0.9$). The values of the rate constants for different oak adsorbent concentrations are presented in Table 6. The results demonstrate that the rate constant increases with increasing oak concentration. For the solution without oak, the rate constant was 0.007 min^{-1} , whereas for a concentration of 1.0 g/L , it reached the highest value of 0.0094 min^{-1} . The initial increase in the rate constant is attributed to the increased available adsorption surface area and the synergistic effect between the two processes. However, at higher concentrations (e.g., 2 g/L), the slight decrease in k likely results from biochar particle aggregation and reduced effective surface area, along with potential interference in the EC process. Consequently, approximately 1.0 g/L is identified as the optimal biochar concentration in this hybrid system.

Table 6. Kinetic parameters of EC/oak coupling for several amounts of oak

Oak concentration (g/L)	k (min^{-1})
0	0.007
0.4	0.008
1	0.009
1.5	0.0094
2	0.0088

4.3.8. Comparative Evaluation of Prediction Model Performance

According to the evaluation protocol adopted in this study, all evaluated models were assessed using an 80:20 training-to-test data split. Performance evaluation of various machine learning models for predicting MB dye removal efficiency on the test data (Table 7) showed that the Gradient Boosting (GB) model significantly outperformed the other evaluated models. This model, with the lowest Mean Squared Error ($\text{MSE} = 2.646$) and Mean Absolute Error ($\text{MAE} = 1.448$), along with the highest coefficient of determination ($R^2 = 0.9691$), demonstrated the highest predictive accuracy for MB adsorption efficiency. Among the linear regression models, Lasso Regression (LaR) ($\text{MSE} = 170.96$, $R^2 = 0.449$) performed worse than Simple Linear Regression (LR) ($\text{MSE} = 159.76$, $R^2 = 0.354$), highlighting the inherent limitation of these models in identifying and modeling the complex relationships between operational parameters and adsorption efficiency. The Support Vector Regression model ($\text{MSE} = 115.41$, $R^2 = 0.414$),

although yielding better results than traditional linear models, could not match the performance of the superior ensemble models. The Random Forest (RF) model ($MSE=30,047$, $R^2=0,903$) showed acceptable performance, indicating its ability to learn nonlinearities and variable interactions, though it performed considerably worse than GB.

Overall, the modeling results confirm that the relationship between operational parameters and MB dye removal efficiency is notably complex and can be best modeled using advanced techniques such as GB. This finding underscores the importance of advanced ensemble methods for complex adsorption processes and highlights the GB model's superior predictive performance in this domain.

In this study, we used the Gradient Boosting algorithm within a regression framework to predict dye removal efficiency. The model was implemented in MATLAB using the fitensemble function and the LSBoost method. The optimal GB model parameters included a learning rate of 0,100 and 200 trees, achieving the lowest cross-validation error (49,1072). Feature-importance analysis of the final model showed that contact time (weight = 1,2082) contributed most to predicting removal efficiency and was the most influential factor. This was followed by pH (weight = 0,0761), adsorbent dosage (weight = 0,1700), and temperature (weight = 0,0846), in descending order of importance. This weight distribution shows that contact time and pH conditions played a more decisive role in process efficiency.

In the plot comparing predicted and actual values (Fig. 9a), points cluster tightly along the 1:1 line (line of equality), indicating the model's strong ability to reproduce observed values across the entire data range. This favorable pattern clearly shows that the GB model maintains high predictive stability and accuracy across the examined concentration ranges and operational conditions. The absence of any funnel- or parabolic-shaped pattern in the data scatter suggests that substantial heteroscedasticity or systematic error is unlikely.

The residual plot for the GB model (Fig. 9b) provides valuable analytical insights. This plot shows an approximately random, unstructured distribution of residual points around the zero axis, indicating a satisfactory model fit. The uniform scatter of points along the predicted axis suggests adherence to the assumption of homoscedasticity, namely, approximately constant error variance. The tight clustering of residuals within ± 5 units indicates the model's strong predictive accuracy in estimating adsorption efficiency. Furthermore, the near-zero mean of the residuals suggests the absence of a substantial systematic bias in the model's predictions, confirming that the model is adequately trained and generally consistent with the fundamental assumptions of regression analysis.

Table 6. Performance evaluation of machine learning models in predicting MB dye adsorption efficiency for test data.

<i>Models</i>	<i>MSE</i>	<i>MAE</i>	<i>R-squared</i>
<i>Linear Regression</i>	109,76	11,70	0,304
<i>Lasso Regression</i>	170,96	11,63	0,449
<i>Random Forest</i>	30,047	5,286	0,903
SVR	110,41	8,082	0,0214
GB	3,646	1,448	0,9691

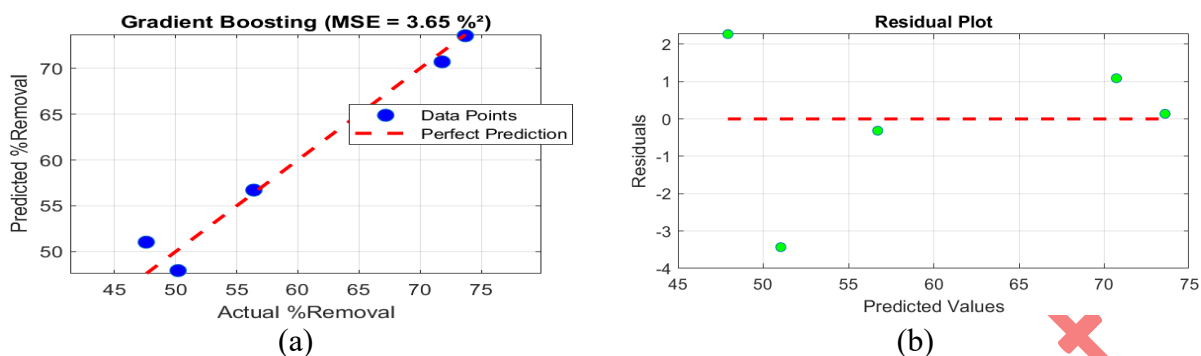


Fig. 9. Diagnostic plots of the final GB model: (a) Predicted vs. actual values plot; (b) Residual plot

4. Conclusion

This study investigated laboratory-scale water treatment and the reduction of water's electrical conductivity using a combined EC and adsorption method. The results showed that pH is a key factor in removing MB dye from the solution. At 31°C, with a pH of 9 and an oak adsorbent concentration of 0.083 g/L, the maximum percentage reduction in electrical conductivity was achieved. In fact, if the pH exceeds 9, the dye removal percentage decreases. The reduction in water electrical conductivity and dye removal can be attributed to physical removal, chemical adsorption, and the electrochemical nature of the process. The highest efficiency was observed within the pH range of 6.5 to 9. Furthermore, we examined changes in water electrical conductivity with increasing contact time. Electrical conductivity decreased sharply with longer contact time, reaching its minimum at 20 minutes. However, beyond 20 minutes, the reduction in electrical conductivity remained almost constant with no significant further change. Investigation of adsorbent dosage showed that water electrical conductivity decreased at higher adsorbent amounts due to increased specific surface area, leading to a higher removal percentage, which is desirable. The results confirmed that the amount of MB dye removed by the oak adsorbent depends strongly on the operating temperature of the system and the solution. To this end, the effect of temperature on the dye removal process and electrical conductivity reduction was tested. Higher temperatures resulted in greater reductions in both water electrical conductivity and dye concentration. The optimization results indicated that the best values for the four variables were pH 9, adsorbent dosage 0.083 g/L, contact time 20 minutes, and temperature 31°C.

Declaration of generative AI in scientific writing

During the preparation of this work, the authors used DeepSeek (DeepSeek AI) to improve the readability and language of the manuscript. Specifically, this tool was employed for linguistic editing, rephrasing sentences for greater clarity, and enhancing the overall flow of the text. Following the use of this tool, the author(s) reviewed and edited the content as necessary and assume full responsibility for the published material. No artificial intelligence or AI-based technology is listed as an author or co-author, and the tool was not used for data analysis or the extraction of insights as part of the research process.

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