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ORIGINAL ARTICLE

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

Dounia Azzouni [a,*], Fida Baragh [b,c], Ayman M. Mahmoud [d], Mohammed M. Alanazi [e], Zakia Rais [a], Mustapha Taleb [a]

[a] *Laboratory of Engineering Electrochemistry, Modeling and Environment, Department of Chemistry, Faculty of Sciences Dhar El Mahraz, Sidi Mohamed Ben Abdellah University, Fez, Morocco*
[b] *Laboratory of Coordination and Analytical Chemistry, Faculty of Sciences, Chouaib Doukkali University, El Jadida, Morocco*
[c] *Laboratory of Catalysis, Materials and Environment, Higher School of Technology, Sidi Mohamed Ben Abdellah University, Fez, Morocco*
[d] *Department of Life Sciences, Faculty of Science and Engineering, Manchester Metropolitan University, Manchester, UK*
[e] *Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, P. O. Box 2457, Riyadh 11451, Saudi Arabia*

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Box-Behnken;
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Abstract This study aimed to examine the impact of operational factors on the adsorption capacity of methylene blue (MB) using a natural and cost-effective adsorbent, activated carbon from coffee grounds (CAP). The three-factor Box-Behnken design of the response surface methodology (RSM) was employed to optimize this economically viable process with maximum efficiency. Through extensive experiments, the factors influencing the adsorption process were identified, their interactions were measured, and a mathematical model was developed. The experiment evaluated the quantity of MB adsorbed by CAP based on pH (2.5–10), initial MB concentration (10–100 mg/L), and CAP adsorbent amount (0.05–0.1 g/L). The results revealed that both concentration and mass significantly influenced the decoloration enhancement. Optimal conditions for achieving a 91 % degradation efficiency were determined as 0.05 g/L adsorbent weight, 100 mg/L dye concen-

* Corresponding author.
E-mail address: azzouni.dounia@gmail.com (D. Azzouni).
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tration, and pH 2.5, with a desirability score of approximately 0.986, aligning closely with the predictions of the BBD model. In conclusion, this research addresses a research gap by demonstrating the high effectiveness of the CAP adsorbent in removing dyes from textiles.

1. Introduction

Water, being an essential and dynamic asset, undergoes damage due to the release of waste materials containing biologically resilient and unclean components into the natural environment [1]. According to the "United Nations World Water Development Report" published in March 2012, approximately 80 % of wastewater is directly discharged into the environment without undergoing any treatment, leading to the pollution of both surface and groundwater [2].

The majority of researchers in various fields such as chemistry, geology, agronomy, plant physiology, and medicine within the environmental sciences are focused on developing innovative methods to decrease the presence of persistent pollutants in wastewater [3]. It is worth noting that wastewater treatment is not only crucial for maintaining good health but also for preserving the environment [4]. Moreover, a healthy population can contribute to enhancing the socio-economic development of their country [5]. Additionally, treating wastewater can help mitigate the impact of various disturbances caused by human activities and improve water resource availability. Therefore, considering the fundamental significance of water, its purification should be accomplished through a suitable and cost-effective treatment process [6].

Within their environmental action program, the European Commission is currently implementing a water quality management system [7]. This is in response to the presence of contaminants in the natural environment, which originate from various sources, including organic substances such as detergents [8], as well as dyes that are highly concentrated in wastewater generated by the textile industry [9]. Additionally, metals such as copper, zinc, cobalt, and iron, which are essential for biological systems, are present in trace amounts but can have adverse effects [10], whereas elements like mercury, lead, and chromium have detrimental impacts [11].

In reality, textile dyes are non-biodegradable and necessitate the use of physical–chemical techniques for degradation, such as coagulation-flocculation [12], oxidation [13], ultrafiltration [14], ion exchange resins [15], and adsorption on activated carbon [16]. However, the application of these technologies is currently limited due to their high treatment costs. Among these techniques, adsorption methods have proven to be effective in eliminating organic substances [17]. Presently, activated carbon is the predominant adsorbent employed, thanks to its exceptional adsorption capacity, particularly for dyes. In fact, the adsorption process using activated carbon is widely recognized as the most commonly employed method for removing dyes from wastewater [18].

To further explore the impact of specific experimental factors such as initial dye concentration, adsorbent quantity, and solution pH on the adsorption capacity of MB (methylene blue), a response surface method (RSM) was employed [19]. RSM is a statistical and mathematical approach that has been adopted to precisely assess the efficiency of an experimental system [20,21]. By utilizing RSM, multiple parameters can be evaluated simultaneously with a minimal number of experiments. Consequently, conducting an investigation using RSM can help reduce costs, minimize process variability, and save time compared to the traditional approach of examining one factor at a time [22 –26].

Additionally, RSM provides a systematic and efficient approach to optimize experimental conditions by identifying the optimal values of the factors being studied. By exploring the response surface, researchers can understand the interactions and relationships among various factors and their impact on the response variable. RSM also enables the determination of the most influential factors and their optimal levels, leading to improved process efficiency and effectiveness [26–31]. In other words, Response surface methodology (RSM) is a powerful statistical technique and a valuable tool for modeling and studying the impacts of multiple parameters on a process. It offers several advantages, including minimizing the number of required experiments, assessing intricate interactions between independent variables, facilitating analysis and optimization, and enhancing the efficiency of existing designs.

The objective of this study was to investigate the impact of three independent parameters (pH, concentration, and adsorbent quantity) on the adsorption capacity of MB onto a CAP biomaterial. Initially, a statistical analysis was performed on the experimental parameters collected in a previous paper [31] to determine their significance. Subsequently, the response surface methodology (RSM) was employed to optimize the factors influencing the adsorption process. The study focused on examining the interactions between the independent variables to gain a deeper understanding of their combined effects. By analyzing these experimental findings, a mathematical model will be developed to better understand the dynamics of methylene blue (MB) adsorption onto the CAP biomaterial.

2. Materials and methods

2.1. Collection of raw material

Spent coffee grounds were recovered and collected from local coffee shops using the composite method. The grounds were sieved to remove any impurities, blended until homogeneous, and then placed in an oven. Subsequently, they were dried in an oven at 110 °C for 24 h and preserved in a vacuum to avoid mold formation.

2.2. CAP activated carbon preparation

A 10 g mass of raw coffee grounds was rinsed with water and then combined with 10 g of KOH in a 1:1 wt ratio. This mixture was evenly distributed in a crucible and placed inside an alumina tube within a pyrolyzer. The pyrolyzer was sealed,

and the following parameters were set: temperature increased gradually at a rate of 10 °C per minute until reaching 800 °C, where it was held for 2 h. Nitrogen gas was continuously injected into the reactor at a flow rate of 100 cc/min throughout the pyrolysis process. Subsequently, the resulting activated carbon (CAP) was collected and weighed using a precision balance. The CAP was then washed with warm deionized water using a filter to eliminate chemical compounds generated during pyrolysis and achieve a neutral pH. Lastly, the carbon material was dried in an electric oven at 110 °C for 24 h.

Characterization of the CAP involved scanning electron microscopy (SEM) using a Hitachi SU3500 SEM instrument, while the FTIR spectrum was obtained using a PerkinElmer Frontier FTIR spectrometer equipped with an ATR sampling accessory (diamond crystal). The FTIR measurements were conducted in transmittance mode across the entire range of 4000 to 400 cm-1. Additionally, solid-state nuclear magnetic resonance (SSNMR) analysis was performed using the Bruker AVANCE III solid-state NMR to examine the structure of the activated carbon.

2.3. Adsorption test

Adsorption kinetics refers to the variation in the quantity of adsorbed material as a function of the contact time between the adsorbent and adsorbate [32]. Understanding adsorption kinetics is crucial for optimizing the industrial application of an adsorbent in adsorption-based processes and identifying the factors that contribute to achieving rapid kinetics [33]. This knowledge enables the efficient utilization of adsorbents and facilitates the design of effective and time-efficient adsorption processes in practical industrial operations.

In order to conduct the adsorption tests, a 100 mL flask was utilized, and the activated carbon from coffee grounds (CAP) was added at a concentration of 0.05 g/L in aqueous solutions containing methylene blue (MB) dye at an initial concentration of approximately 50 mg/L. The samples were continuously stirred at 500 rpm and maintained at room temperature (20 ± 2) °C with a normal pH value. To determine the adsorption capacity, samples were collected at specified time intervals, filtered using a 0.22 mm PTFE syringe filter, and subsequently analyzed based on Equation (Eq.1) [31,34].

$$C_p = \frac{(C_i - C_t) \times V}{m} \tag{1}$$

The adsorption capacity (C_p) in mg/g is determined using the equation where C_i and C_t in mg/L represent the initial and equilibrium dye concentrations in the liquid phase, respectively.

V in liters denotes the volume of the dye solution, and m in grams corresponds to the quantity of activated carbon from coffee grounds (CAP) used

2.4. Optimization of MB removal by CAP adsorption

Building upon our previous research [31], a parametric study was conducted to investigate the impact of individual parameters on the removal rate of Methylene Blue. This study involved systematically varying a single parameter while keeping other parameters constant. By analyzing the adsorbent mass, initial dye concentration, and pH of the solution, we were able to determine their effects on the removal rate of Methylene Blue.

To optimize the adsorption process of the studied dye, we will utilize the experimental design methodology. Our focus will be on implementing this methodology using the natural adsorbent CAP as the model adsorbent. Through careful experimentation and analysis, we aim to enhance the efficiency and effectiveness of the dye adsorption process using CAP.

In order to achieve our objective, we conducted an experimental design of the adsorption process specifically targeting the removal of MB. This design incorporated a customized approach along with the utilization of response surface methodology (RSM). The factors investigated in this design included the concentration of the pollutant, the mass of the adsorbent, and the pH of the system. Each of these factors was studied at three different levels, allowing us to comprehensively analyze their influence on the adsorption process and optimize the removal of MB.

The required number of experiments (N) can be calculated using the following equation:

$$N = 2K(K-1) + N_0 \tag{2}$$

The equation to calculate the required number of experiments (N) takes into account the number of variables (K) and the number of center points (N_0) [35]. For this research, the total number of runs (N) was calculated to be 13, which included 12 factorial points along with 1 center point. The software JMP (Ver. 16.2.0) was employed for designing the experiments accordingly.

A standard polynomial regression equation was employed to represent the predicted response (Y):

$$Y = a_0 + \sum_{i=0}^{n} a_i x_i + \sum_{k=0}^{n} a_{ii} (x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} a_{ij} x_i x_j \tag{3}$$

where:

Y: represents the experimental response (the degradation efficiency (%));

a_0: the constant offset term;

a_i: the linear coefficients;

a_{ii}: the quadratic coefficients that are estimates of the main effect of factor i for the response Y;

a_{ij}: the interaction coefficients between factor i and factor j for the response Y;

x_i and x_j: the code values of the independent input variables calculated by the equation:

$$x_i = \frac{X_i - X_{i,0}}{\Delta X_i} (i = 1, 2, 3) \tag{4}$$

Xi and $Xi_{,0}$ respectively represent the real values of the independent variable and the center point of the design. While ΔXi is the value of the step change in the variable.

2.5. Methylene blue treatment

Table 1 presents the independent variables investigated in the methylene blue adsorption process, including both their real and coded values.

Table 1 Model variable values for the removal of the MB dye with CAP activated carbon.

Variables	Factor code	Coded and real value	
		−1	+1
Mass (g/l)	X_1	0.050	0.250
Concentration (mg/l)	X_2	10.000	100.000
pH	X_3	2.500	10.000

3. Results and discussion

3.1. Characterization of activated carbon (CAP)

After undergoing pyrolysis at 800 °C, the activated carbon (CAP) is characterized by a high surface area. In this case, a specific treatment was performed on this sample using water. Observation of the SEM image (Fig. 1) reveals that the CAP exhibits a macroporous structure with regular pores ranging in size from 10 to 20 µm. It appears to have a more complex carbonaceous structure.

The FTIR technique was used to analyze the functional groups present in the activated carbon. The spectrum corresponding to the CAP material is presented in Fig. 2.

In accordance with the data cited in the literature, particularly by Centrone et al. (2005) [36], the following absorptions can be observed:

- Around 3000 cm^{-1}, corresponding to the stretching vibrations of C—H bonds.
- Approximately at 1550 cm^{-1}, associated with the stretching vibrations of aromatic rings, with intensity depending on the degree of delocalization of the system.
- At around 700 cm^{-1} and 730 cm^{-1}, associated with out-of-plane deformations of C—H bonds, typical of monosubstituted benzene rings. Their intensity depends on the number of condensed benzene rings and is more pronounced in the presence of isolated benzene rings.

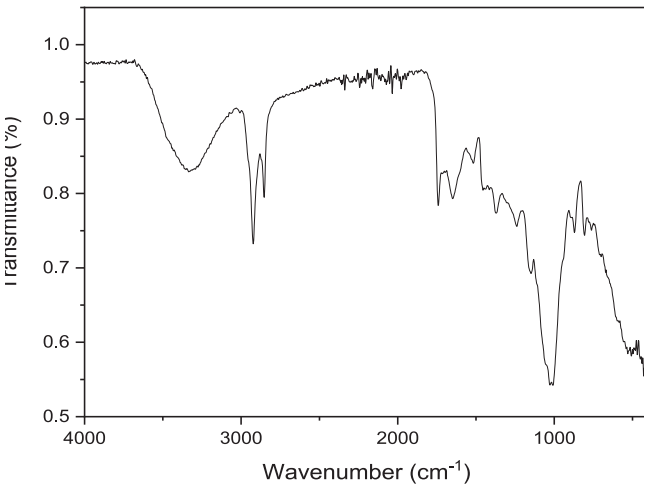

Fig. 2 FTIR spectrum of the CAP sample.

- Close to 550 cm^{-1}, associated with out-of-plane deformations of graphitic structures.
- Around 1570 cm^{-1}, a significant band attributed to the stretching vibrations of C=C bonds in aromatic rings can be observed.
- It is estimated that the IR spectra are not very informative due to low radiation emission and indistinct signals. Additionally, there is water vapor absorption during the preparation of KBr pellets and activated carbon; in particular, a clearly visible band appears at 3400 cm^{-1}.

The spectra of activated carbons reveal the disappearance of signals associated with the starting material, suggesting that the product consists of a predominantly polycyclic material composed of aromatic and heteroaromatic structures, as evidenced by the signals observed in the range of 105 to 150 ppm. Furthermore, the probable presence of signals around 180 ppm indicates the presence of carbonyl groups on the edges of the basic carbon planes (Fig. 3). Moreover, the literature mentions that alkaline treatment during the activation process can promote the formation of polycyclic pyrones [37].

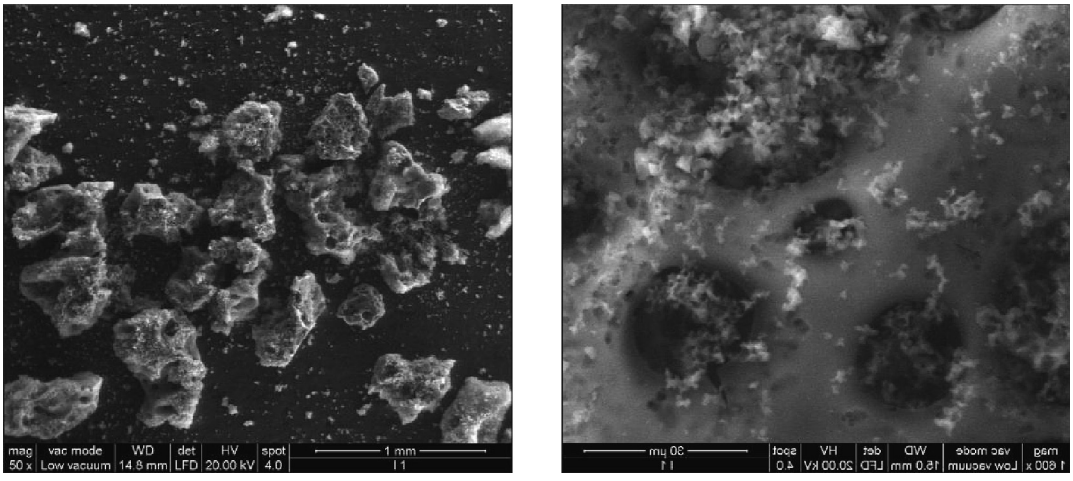

Fig. 1 SEM images of the CAP sample analyses.

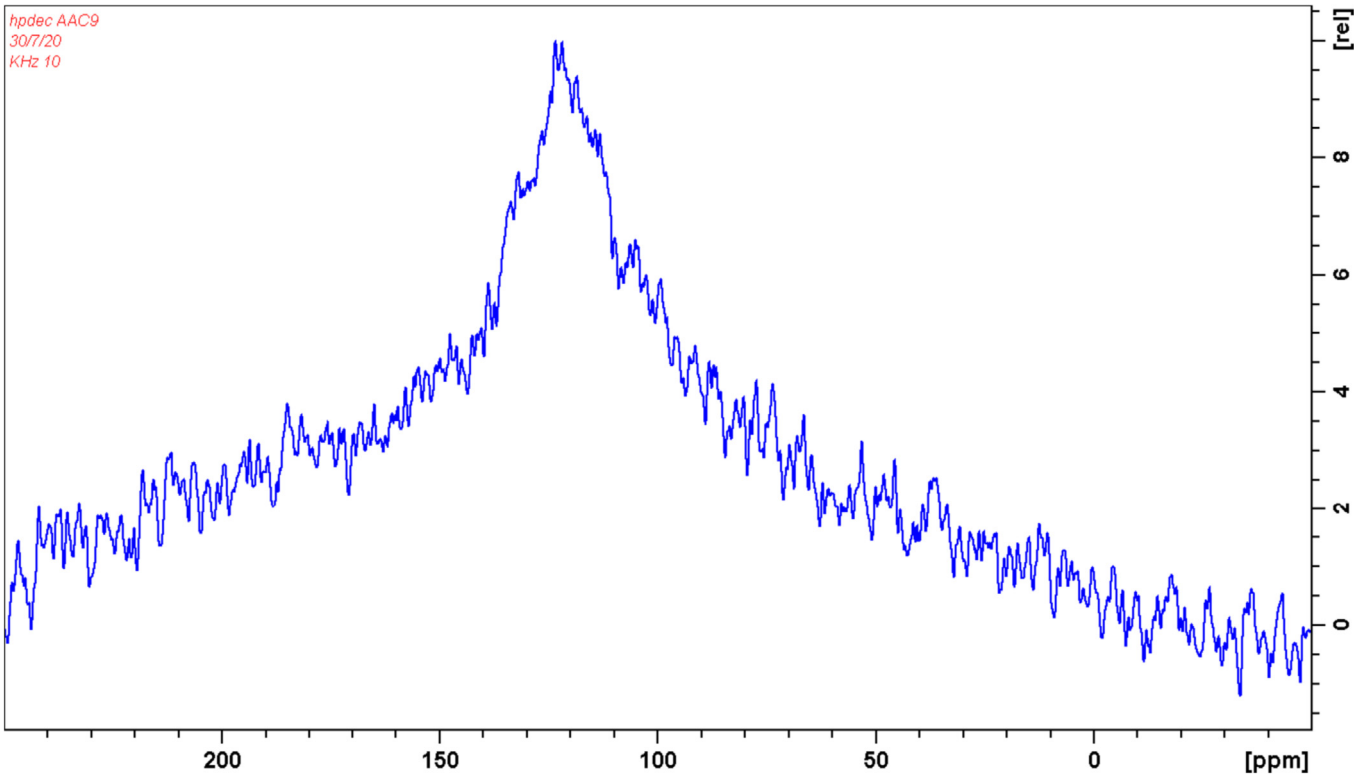

Fig. 3 NMR Spectrum of CAP (Activated Carbon from Coffee Grounds).

3.2. Experimental design and response surface plots of MB removal

3.2.1. Statistical analysis of the derived response surface model

The 13 experiments performed according to the custom design and the experimental and model-predicted responses are presented in Table 2 to summarize the matrix.

Based on the information provided in the table, it can be observed that the elimination percentage ranged from 0.4 % to 89 %. To determine the significance of the regression model and the polynomial coefficients, analysis of variance (ANOVA) was conducted, and the results are presented in Tables 3 and 4 [26,29,30].

The Fisher F-test for the model yields a P-value of 0.0007, which is less than the significance level of 0.05. This indicates that the model is highly significant, and there is only a 0.07 % chance that such a large F-value could occur due to random variation or noise [40–43]. Moreover, the calculated F-value for the model (F_{model} = 23.167) exceeds the critical F-value ($F_{0.05,\ 6,\ 6}$ = 4.28) obtained from the F-distribution table. This suggests that a substantial portion of the response variation can be explained by the regression equation [43–46].

The polynomial equation derived from the model for the removal efficiency of MB (Y) is given by:

$$\boldsymbol{Y(MB\%Removalrate) = 39.005 - 2.495x_1 + 39.658x_2 - 4.889x_3 - 2.677x_1x_2 - 2.216x_1x_3 - 4.110x_2x_3}$$

The "Prob > F" values less than 0.05 indicate that the most significant terms in the model are the mass (X_1), concentration (X_2), and the interaction between these two (X_1X_2). These terms have a substantial impact on the removal efficiency of MB. On the other hand, the remaining terms with a probability (P) greater than or equal to 0.05 are considered less significant and can be disregarded in the formulation of the polynomial equation as they do not significantly contribute to the removal efficiency of MB.

Thus, this can be simply written as follows:

$$\boldsymbol{Y(MB\%Removal\ rate) = 39.005 - 2.495x_1 + 39.658x_2 - 2.677x_1x_2}$$

The regression coefficient R^2 obtained in this study is 0.958622, indicating that the chosen custom model accounts for approximately 95.86 % of the variability observed in the experimental data. Additionally, the fitted regression coefficient R^2_{adj} is 0.917245, suggesting that around 91.72 % of the variability is explained by the model while taking into account the number of variables and degrees of freedom. These high regression coefficients provide strong evidence that the selected custom model accurately represents the experimental data [43–46].

To assess the agreement between the optimization model and the experimental data, two plots were analyzed: the correlation between the predicted response and the experimental data (Fig. 4a) and the residual probability plot (Fig. 4b). These plots were utilized to identify any potential discrepancies or divergences in the fit of the optimization model to the experimental data.

Table 2 Box–Behnken design and results of MB adsorption using CAP.

Test number	Factors			Response (% removal efficiency)		Residual
	X_1	X_2	X_3	**Experimental**	**Predicted**	
1	0.050	50.000	2.500	35.569	45.755	−3.443
2	0.250	100.000	5.500	43.888	60.010	−3.467
3	0.250	50.000	10.000	0.846	10.521	1.588
4	0.050	100.000	5.500	89.384	77.076	4.190
5	0.100	100.000	2.500	87.461	80.076	2.753
6	0.050	10.000	5.500	4.458	7.617	5.580
7	0.100	50.000	5.500	18.483	34.221	−15.247
8	0.100	10.000	2.500	5.692	10.617	3.168
9	0.250	10.000	5.500	−0.346	−9.448	−4.220
10	0.100	10.000	10.000	3.143	−7.549	6.611
11	0.050	50.000	10.000	26.212	27.587	−8.369
12	0.10	100.000	10.000	67.708	61.909	5.434
13	0.250	50.000	2.500	44.579	28.688	5.419

Table 3 ANOVA analysis of model Y response (MB removal efficiency).

Source	Total of squares	Degree of freedom	Mean squares	F-value	Prob > F
Model	11947.544	6	1991.260	23.167	0.0007
Error	515.698	6	85.950	–	–
Total	12463.243	12	–	–	–

R^2 = 0.958622, R^2 adjusted = 0.917245.

Table 4 Estimated polynomial coefficients for the response model Y (MB removal efficiency).

Coefficient	Coefficient estimate	Standard error	F value	Prob > F
a_0	39.005	3.126	23.167	0.0007
a_1	−2.495	0.792	9.929	0.019
a_2	39.658	3.946	100.991	< 0.0001
a_3	−4.889	3.914	1.559	0.258
a_{12}	−2.677	1.090	6.026	0.049
a_{13}	−2.216	1.082	4.193	0.086
a_{23}	−4.110	4.582	0.804	0.404

Fig. 4a displays a strong relationship between the experimental and predicted values of the response, indicating excellent agreement between the two. Furthermore, Fig. 4b reveals that the majority of the data points fall within the lower and upper limits of outlier detection (-10 and 10, respectively). This suggests that the statistical model utilized successfully captures the correlation among the three factors investigated in the removal of MB. Thus, it can be inferred that the chosen model is appropriate for accurately representing the relationship between the variables [21,46].

3.2.2. Three-dimensional response surface plots of the studied parameters

The 3D response surface plots, depicted in Fig. 5 and Fig. 6, offer a comprehensive visualization of the influence of the three parameters under investigation on the removal efficiency of MB when employing CAP-activated carbon. These plots provide a clear summary of how changes in each parameter individually, as well as their interactions, affect the overall removal efficiency. By examining these response surface plots, valuable insights can be gained regarding the optimal conditions for achieving maximum MB removal efficiency using CAP-activated carbon.

The findings from the analysis support the results obtained from the ANOVA and confirm that both concentration and mass significantly contribute to the enhancement of discoloration. These factors play a primary role in increasing the effectiveness of the discoloration process, as indicated by the experimental data and analysis [38,39].

3.2.3. Optimization and desirability function

Fig. 7 illustrates the optimal conditions that result in the maximum removal of BM (methylene blue).

The highest desirability ratio value, which was 0.986, led to the determination of the optimal conditions: an adsorbent mass of approximately 0.05 g/L, a dye concentration of 100 mg/L,

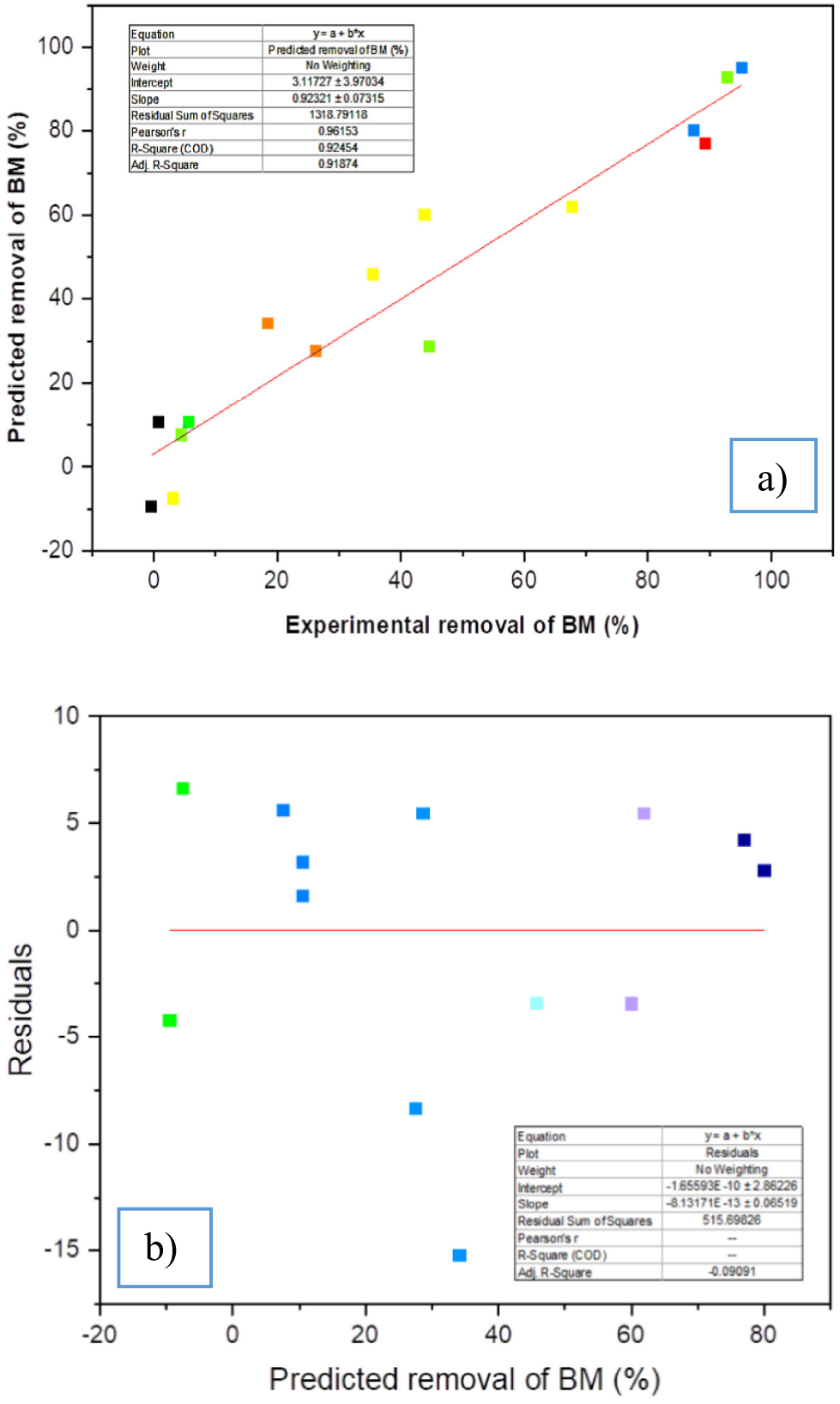

Fig. 4 Model Y parity plot: a) predicted vs. experimental response and b) residuals vs predicted response.

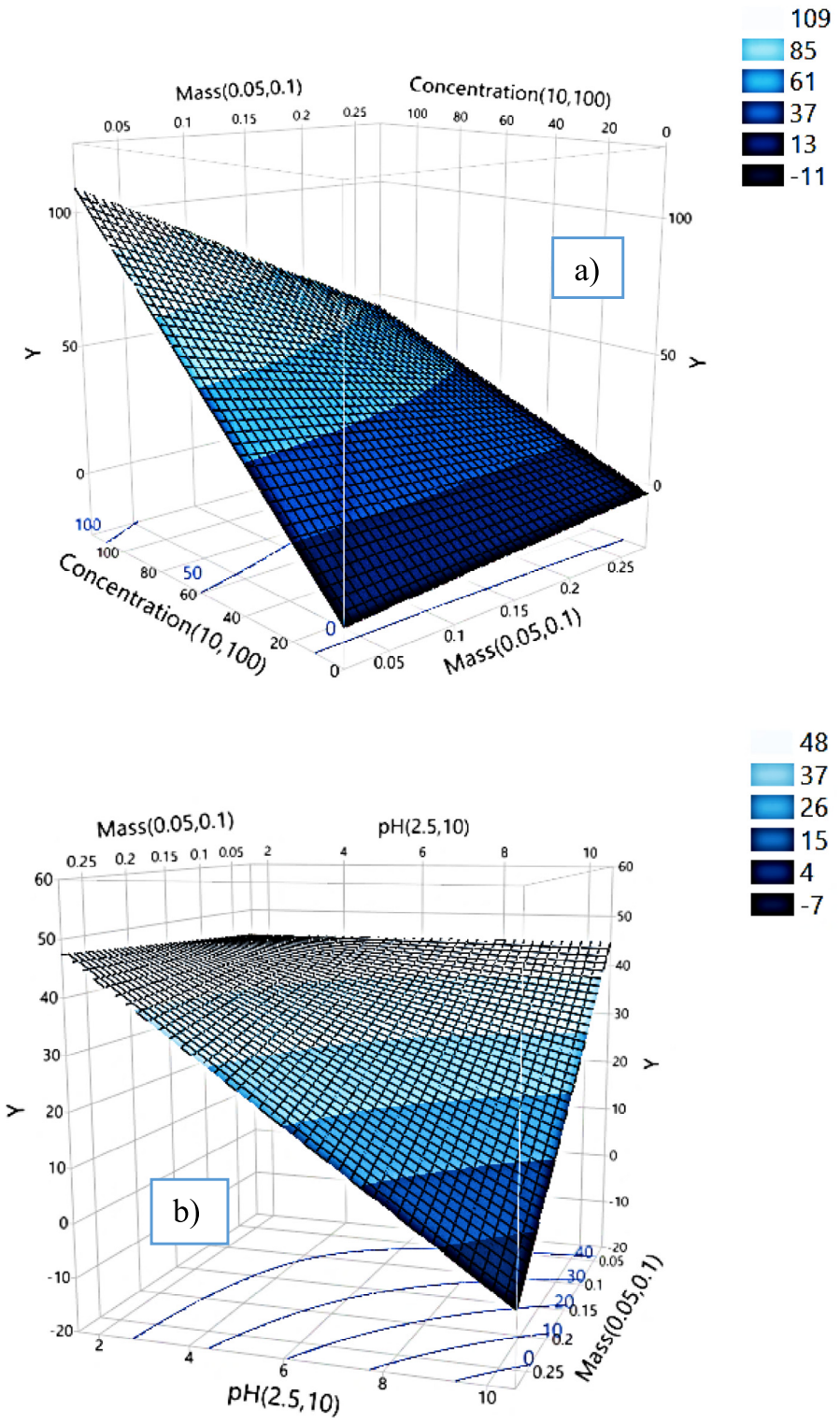

Fig. 5 Response surface plot for mass effect and the two parameters (a) dye concentration and (b) pH on the removal rate of MB % (Y).

and a pH of 2.5. These conditions yielded a degradation efficiency of 90.62 %, indicating the high effectiveness of the optimized parameters in achieving significant BM removal.

To assess the validity of the optimal model conditions, an experiment was conducted under the same specified conditions. The experimental result revealed a fading rate of 91 %, which aligns well with the value predicted by the model. This agreement between the experimental and predicted values further reinforces the accuracy and reliability of the customized model. Thus, the model can be deemed as a dependable tool for predicting and optimizing the removal efficiency of BM in practical applications.

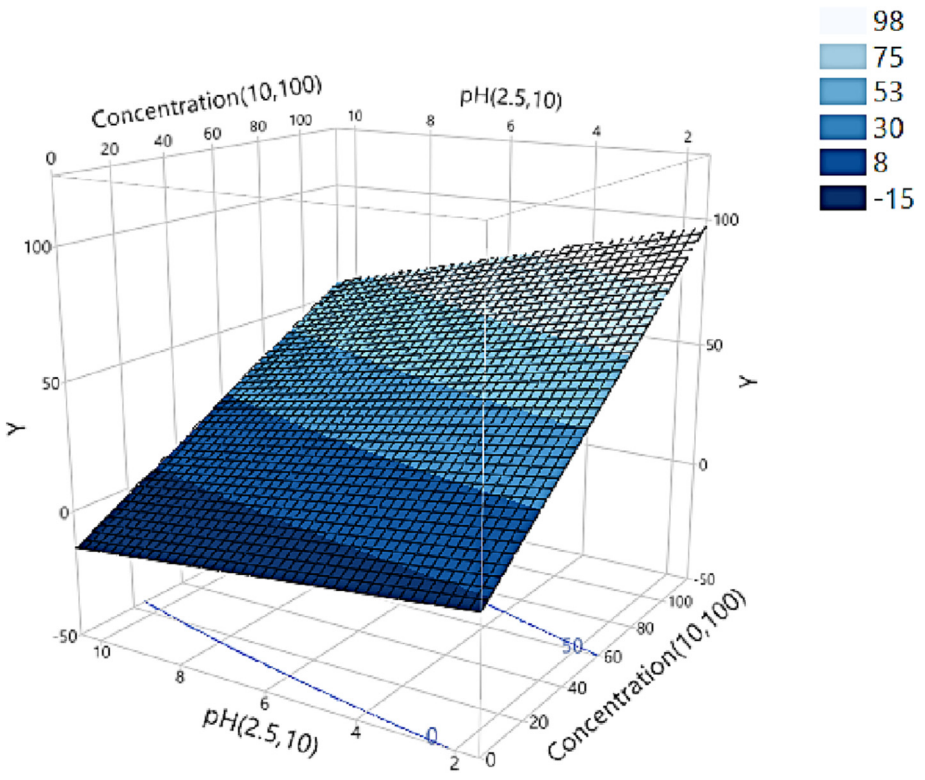

Fig. 6 Response surface plots for dye concentration and pH effects on the MB % removal rate (Y).

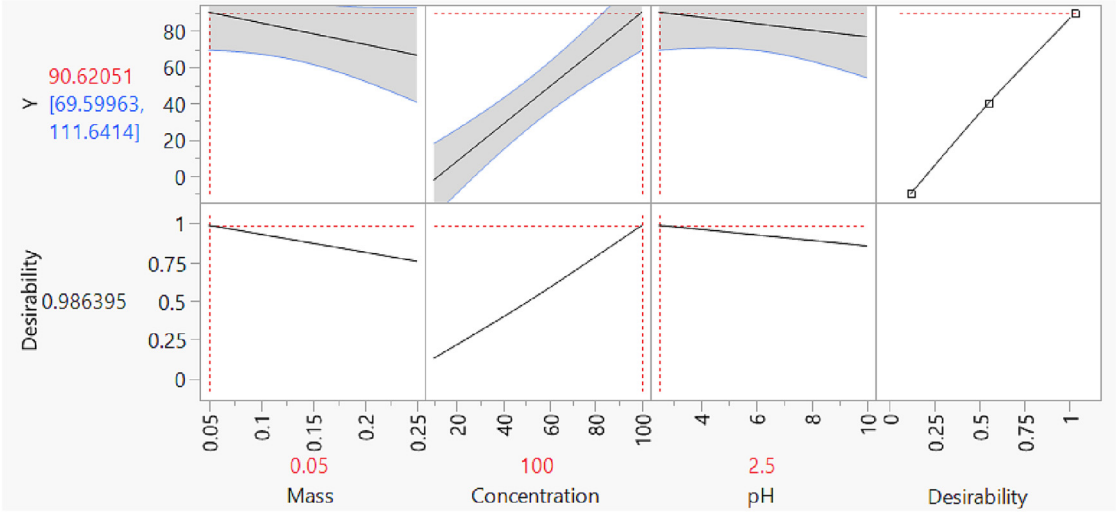

Fig. 7 Desirability plot for the removal efficiency of MB by activated carbon CAP: MB concentration (Concentration), adsorbent mass (Mass), pH and dye removal rate % (Y).

4. Conclusion

In this study, the methodology of experimental design was successfully applied to optimize the adsorption capacity of MB by CAP, while precisely determining the influence of specific parameters (pH, dye concentration, and adsorbent amount) on the adsorption process of methylene blue using activated carbon. The analysis of the data obtained revealed that the pH of the dye had an adverse impact on the adsorption capacity of methylene blue by CAP. Conversely, the remaining factors, including dye concentration and adsorbent amount, were found to significantly affect the treatment process of MB adsorption onto the biomaterial.

Furthermore, the fitted optimal design model exhibited a high coefficient of determination (R^2 = 0.958622) and an adjusted R^2 coefficient of 0.917245, indicating the strong goodness-of-fit between the model and the experimental data.

The p-value associated with the model was found to be smaller than 0.05, demonstrating its statistical significance. The response surface experimental design and methodology were employed to determine the optimal conditions for MB removal, which involved a solution pH of 2.5, a methylene blue concentration of 100 mg/L, and an adsorbent dosage of 0.05 g/L.

These quantitative findings highlight the effectiveness of the experimental design methodology in optimizing the adsorption capacity and understanding the impact of key parameters on the removal of methylene blue using CAP. The results provide valuable insights for further research and practical applications in the field of wastewater treatment.

CRediT authorship contribution statement

Dounia Azzouni: Investigation, Formal analysis, Conceptualization. **Fida Baragh:** Writing – review & editing. **Ayman M. Mahmoud:** Conceptualization. **Mohammed M. Alanazi:** Conceptualization, Supervision, Validation. **Zakia Rais:** . **Mustapha Taleb:** Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Mohammed M Alanazi reports financial support was provided by King Saud University College of Pharmacy. Mohammed M Alanazi reports a relationship with King Saud University College of Pharmacy that includes: funding grants.].

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