

Adsorption of Methylene Blue using Bottom Ash: Experimental Design, Isotherm Analysis, and Optimum Conditions

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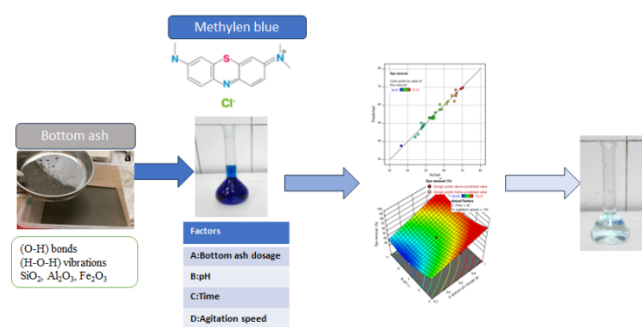
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Received: 04/03/2024, Accepted: 10/07/2024, Available online: 12/07/2024

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<https://doi.org/10.55555/gnj.005879>

Graphical abstract



Abstract

This study investigated the removal of methylene blue (MB) via adsorption using waste bottom ash. The bottom ash, sourced from a waste storage site in the Çorlu district of Tekirdağ province, Thrace Region, was utilized as the adsorbent. The research examined the impact of several variables on MB removal, including bottom ash dosage, pH, contact time, and agitation speed. It was found that all parameters had a single-variable effect, while pH exhibited a quadratic effect on MB removal in a model-based analysis. The optimization of the model for maximum MB removal identified the optimal conditions as 0.978 g bottom ash dosage, pH 3, 15 minutes of adsorption time, and 50 rpm agitation speed. Under these conditions, the model predicted an MB removal efficiency of 71%, which was experimentally confirmed to be 72.5%. The adsorption process was found to fit with the Freundlich isotherm, indicating a multilayer adsorption mechanism on the heterogeneous surface of the adsorbent. This research not only highlights the feasibility of using bottom ash from coal combustion as an economical adsorbent for dye-contaminated wastewater but also underscores its potential to inform and inspire future studies on waste recycling and wastewater treatment.

Keywords: Adsorption, bottom ash, methylene blue, dye removal optimization

1. Introduction

Energy is crucial for world economies, and coal reserves have the largest share in energy production (Mandal and Sinha 2014). Coal combustion produces two wastes, fly ash and bottom ash, which contain heavy metals and inorganics. Bottom ash constitutes 10-20% of the total coal residue (Hashim *et al.* 2021, Rashidi and Yusup 2016). Bottom ash is generally disposed of in landfills. However, in recent years, reusing studies of bottom ash have been carried out in civil engineering applications such as cement production and road/building construction or in environmental engineering applications such as an adsorbent material for dye and metal removal from wastewater (Sukpreabprom *et al.* 2015, Vu *et al.* 2020). Bottom ash is mainly composed of silicium dioxide (SiO₂), aluminum oxide (Al₂O₃), and iron oxide (Fe₂O₃) compounds. It has a specific gravity of 2.10-2.81 g/cm³ and a specific surface area of 1.0-9.44 m²/g (Jayaranjan, Van Hullebusch and Annachhatre 2014, Rashidi and Yusup 2016).

Many wastes such as bottom ash and fly ash have been used in recent years to remove pollutants in water and wastewater, especially dyes used in various industries. One of these dyes is methylene blue (MB). Many industries (textile, plastic, paper, pharmaceuticals, etc.) use MB extensively to color paper, cotton, silk and wool (Mussa *et al.* 2023, Ranote *et al.* 2023). MB, a cationic dye, is widely used, especially in the textile industry and is one of the most abundant pollutants in the aquatic environment (El-Habacha *et al.* 2023). Among many dyes, MB, an aromatic thiazine heterocyclic basic dye, is considered harmful to human health when it exceeds a certain threshold due to its high toxicity. It can pose serious dangers to human health and the environment due to its toxicological effects (Ranote *et al.* 2023).

Environmentally friendly technologies are required to remove MB from wastewater effectively. Among these, the most effective method is adsorption due to its high efficiency and accessibility (Al-Asadi *et al.* 2023). The adsorption process, one of the treatment methods for dye removal from wastewater, is preferred more than other methods due to its ease and economic benefits (Gupta *et*

al. 2012). Although activated carbon is an excellent adsorbent, in recent years, various materials such as clay, fly ash, red mud, nanoparticles, industrial wastes and agricultural wastes have been frequently used for the removal of dyes because of low cost (Mussa *et al.* 2023). Operating costs can be reduced using low-cost adsorbent materials, and waste recycling can be achieved using waste materials as adsorbent. Many studies have stated that effective dye removal is achieved by using bottom ash as a low-cost adsorbent to remove various dyes through an adsorption process (Mittal *et al.* 2007, Mittal and Gupta 2010).

In adsorption experiments, numerous variables affect removal efficiency, including adsorbent dosage, temperature, pH, time, and agitation speed. In such studies, finding optimum conditions for both the adsorbent and the pollutant to be removed is crucial. This approach aims to minimize the costs and workload involved in experimental processes. In processes with many controllable effect variables, it is important in terms of cost and time to create a model that achieves optimal prediction accuracy with the minimum number of experiments. Therefore, it is necessary to map the variability in the response based on different effect variables using response surfaces. In the initial stage of experimental design, the controllable effect variables and their ranges are determined by experts or experienced individuals. Additionally, preliminary experiments are conducted to determine whether the variability of the response variable is adequately represented within the design space formed by the selected ranges of the controllable effect variables.

This study aims to investigate the removal of MB dye by the adsorption process using waste bottom ash as an adsorbent and to investigate the effects of operating parameters such as bottom ash dose, pH, adsorption time, and agitation speed. Within the scope of this purpose, the effect and optimization of operating parameters have been evaluated using experimental design. The objective of this study was to examine the removal of MB dye by adsorption process utilizing bottom ash as the adsorbent. The study evaluates the effects of operational parameters and their optimization using experimental design methodologies to achieve this objective.



Figure 1. 75 µm under-sieve bottom ash

2. Experimental

2.1. Materials

In this study, bottom ash was used as an adsorbent. The bottom ash used in the study was obtained from a waste disposal site in the Çorlu district of Tekirdağ province in the Thrace region of Turkey. After being taken from the facility, the bottom ash samples were allowed to air-dry for approximately 48 hours under laboratory conditions. The waste bottom ash, which was sieved using a sieve with a mesh opening of 75 µm, was used in the absorption experiment (Figure 1). The chemical composition of bottom ash is given in Table 1. As seen in Table 1, bottom ash oxide compounds contain higher concentrations of SiO₂, Al₂O₃, and Fe₂O₃.

Table 1. Chemical compositions of bottom ash

Parameter	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
Value (%)	41.05	8.8	5.32	17.21	12.48

The properties of the bottom ash were revealed by SEM images (FEI, Quanta FEG 250) and FTIR (Bruker, Vertex 70 ATR) analyses. SEM images with resolutions of 1000x, 2000x, 4000x, and 8000x of the 75-µm under-sieve bottom ash is shown in Figure 2. The 75-µm under-sieve waste bottom ash exhibits an angular particle shape, and the surface texture appears to be highly rough and porous.

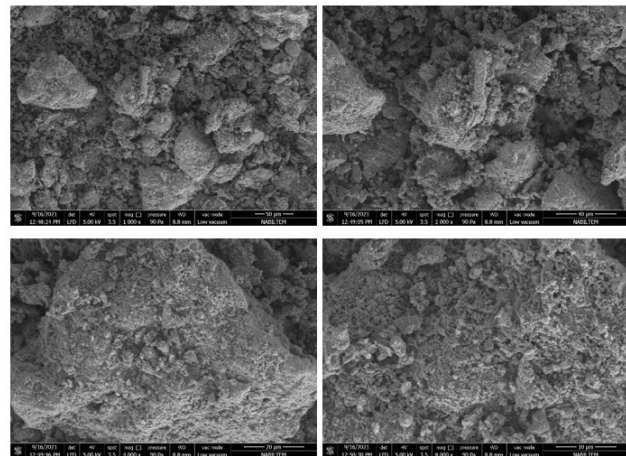


Figure 2. SEM analysis of bottom ash

FTIR analysis is used to determine the functional groups in the structures of solid, liquid, and solution organic compounds, the state of the bonds in the structure, the binding sites, and whether the structure is aromatic or aliphatic. FTIR analysis of bottom ash is given in Figure 3. As seen in Figure 3, the peaks of the bottom ash were as follows: 3362 cm⁻¹, 1400 cm⁻¹, 1017 cm⁻¹, 871 cm⁻¹, 566 cm⁻¹, and 448 cm⁻¹. It is caused by hydroxyl (O-H) bonds originating from the water molecule in the 3200 and 3700 cm⁻¹ (Park *et al.* 2020). In a study, it was stated that the peaks between 3500-1600 cm⁻¹ indicate the stretching of the (-OH) bond and the bending of the (H-O-H) vibrations (Fauzi *et al.* 2016). The bottom ash used in this study mainly consists of SiO₂, Al₂O₃, and Fe₂O₃ compounds (Rashidi and Yusup 2016). According to FTIR analysis, the peaks seen between 450 and 900 cm⁻¹ may be related to metal oxide bonds such as Al-O and Fe-O (Park *et al.* 2020). The presence of silica in the bottom ash can be attributed to the intense band at the absorption region near 1000 cm⁻¹, which corresponds to the asymmetric

stretching vibrations of the Si-O-Si or Si-O-Al (Drumm *et al.* 2019). Additionally, in another study, it was stated that peaks in the range of 1000–800 cm⁻¹ indicate CaCO₃ loss (Fauzi *et al.* 2016). According to Basri *et al.* (Mohd Basri *et al.* 2021), the peaks range of 1424 to 851 cm⁻¹ were attributed to the asymmetric stretching vibration of Si-O/Al-O and Si-O-Si stretching quartz, respectively. A band less than 500 cm⁻¹ indicates the bending of the Si-O-Si and O-Si-O bonds (Puligilla and Mondal 2015).

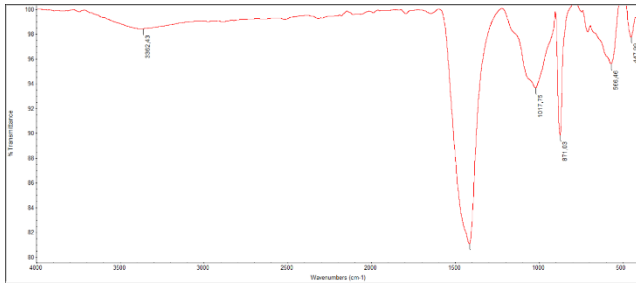


Figure 3. FTIR analysis of bottom ash

Methylene blue (MB, C.I.: 52015) with a molecular formula of C₁₆H₁₈ClN₃S and molecular weight of 319.86 g/mol was supplied from Merck. In the adsorption process, H₂SO₄ (CAS: 7664-93-9) and NaOH (CAS: 1310-73-2) were used to adjust the pH value and were obtained from Merck.

2.2. Experimental design and methodology of the model

Many variables affect the color removal efficiency in the adsorption process. For these processes where controllable effect variables are high, it is important in terms of cost and time to create an experimental design that achieves optimum prediction accuracy with the minimum number of experiments. Therefore, this study generates maps of response surfaces based on variables that affect the color removal efficiency in the adsorption process. In the preliminary experimental design phase, the

Table 2. Design summary of effect variables.

Factor: Name	Units	Type	Min.*	Max.*	Coded Low	Coded High	Mean	Std. Dev.*
A: Bottom ash dosage	g	Numeric	0.2	1.0	-1 ↔ 0.2	+1 ↔ 1.0	0.6	0.18
B: pH	-	Numeric	3.0	11.0	-1 ↔ 3.0	+1 ↔ 11.0	7.0	1.82
C: Time	min	Numeric	15.0	75.0	-1 ↔ 15.0	+1 ↔ 75.0	45.0	13.65
D: Agitation speed	rpm	Numeric	50.0	250.0	-1 ↔ 50.0	+1 ↔ 250.0	150.0	45.49

*Min.: Minimum. Max.: Maximum. Std. Dev.: Standard deviation

In experimental designs, a transformation is applied to response results to stabilize the response variance, making the response distribution closer to the normal distribution and improving the model fit (Myers *et al.* 2016). The Box-Cox procedure determines whether to apply a transformation to the response results (Box and Cox 1964). The theory on which the Box-Cox method is based is the maximum likelihood method (Myers *et al.* 2016).

Dye removal is optimized with the desirability function (Derringer and Suich 1980) in the ranges of variation of

the selected effect variables. In the first stage of the experimental design, a custom design was used in the study for the standard experimental design could not be applied due to the variability of the determined ranges of the variables.

In the study, bottom ash dosage, pH, time, and agitation speed were selected as the effect variables, and dye removal was the response variable. First of all, in the selected variation intervals of the effect variables (bottom ash dosage; 0.2, 0.4, 0.6, 0.8 and 1.0 g, pH; 3, 5, 7, 9 and 11, time; 15, 30, 45, 60 and 75 min, agitation speed; 50, 100, 150, 200 and 250 rpm) experimental design was carried out with the Design Expert V.13 trial program (Stat-Ease 2021). The effect levels of the variables on the response variable were determined with ANOVA, and the response surface graphs (interaction, contour, and 3D) of the terms with significant effect levels were created (Stat-Ease 2021). In statistical analysis, the variation ranges of the effect variables were performed based on coded values, which are dimensionless and defined concerning the mean of zero and the spread or standard deviation. The coded values allow for minimizing the levels of influence of response variables due to differences in the magnitude of the effect variables' variation ranges. The actual values are transformed into coded values using Equation 1 (Myers, Montgomery and Anderson-Cook 2016). The design summary of the effect variables is given in Table 2. Dye removal in the variation intervals of the selected effect variables is optimized with the desirability function (Derringer and Suich 1980).

$$\text{Coded value} = \frac{\text{Actual} - [(\text{maximum actual} + \text{minimum actual}) / 2]}{(\text{maximum actual} - \text{minimum actual}) / 2} \quad (1)$$

the selected effect variables. The general approach in the desirability function is to first convert each response variable (y_i) into an individual desirability function (d_i) ranging from 0 ≤ d_i ≤ 1. If the response (y_i) is the target value, then d_i = 1; if the response is outside the acceptable region of the target value, then d_i = 0. The individual desirability functions are shown in Figure 4. Desirability functions are defined by Equation 2, Equation 3, and Equation 4 if the target (T) is selected maximum value, minimum value, and lower (L) and upper (U) limit values for the response, respectively. In Equation 2, the desirability factor becomes linear if the weight value r = 1

is chosen. If $r > 1$, reaching the target value is of primary importance, and if r is $0 < r < 1$, the importance of obtaining the target value decreases.

$$d = \begin{cases} 0 & y < L \\ \left(\frac{y-L}{T-L}\right)^r & L \leq y \leq T \\ 1 & y > T \end{cases} \quad (2)$$

$$d = \begin{cases} 1 & y < T \\ \left(\frac{U-y}{U-T}\right)^r & T \leq y \leq U \\ 0 & y > U \end{cases} \quad (3)$$

$$d = \begin{cases} 0 & y < L \\ \left(\frac{y-L}{T-L}\right)^{r_1} & L \leq y \leq T \\ \left(\frac{U-y}{U-T}\right)^{r_2} & T \leq y \leq U \\ 0 & y > U \end{cases} \quad (4)$$

2.3. Adsorption process

The adsorption process was carried out in a shaker (Biosan PSU-10i) at room temperature. Necessary bottom ash was added to 100 mL of the solution with 25 mg/L MB concentration. The desired pH was adjusted with H_2SO_4 and NaOH using a pH meter (WTW 3210i). Afterwards, the adsorption process was performed in the shaker at the

desired agitation speed and time. At the end of the adsorption process, the sample was centrifuged at 4000 rpm for 5 minutes, and the MB concentration was determined in the spectrophotometer. The MB concentration was determined by calculating the absorbance value at a wavelength of 664 nm, utilizing a calibration curve.

3. Results and Discussion

3.1. Statistical analysis

The dye removal results of the run points are given in Table 3. The obtained model for dye removal is the reduced quadratic and polynomial analysis. As seen in Table 3, the experimental and predicted results obtained from the model are close to each other. In addition, experimental and predicted results are given in Figure 5a. The Box-Cox plot of response is shown in Figure 5b. Figure 5b is examined, and it is seen that there is no need to apply any transformation to the response results.

Effect levels of four different effect variables (bottom ash dosage, pH, time, and agitation speed) on dye removal were determined by ANOVA. For the response model, the reduced quadratic model was chosen considering the terms that have a significant effect level on the response. ANOVA performed for the reduced quadratic model is given in Table 4.

Table 3. Run points and the results of dye removal efficiency.

Run points	Factor 1	Factor 2	Factor 3	Factor 4	Response (Dye removal efficiency)		
	A: Bottom ash dosage	B: pH	C: Time	D: Agitation speed	Actual	Predicted	Residual
	g	-	Min	Rpm	%	%	%
1	0.8	9	60	200	66.79	66.60	0.19
2	0.6	7	45	250	55.20	55.97	-0.77
3	0.6	7	45	50	47.48	50.17	-2.69
4	0.6	7	45	150	52.99	53.07	-0.08
5	0.4	9	60	100	47.55	47.05	0.50
6	0.6	7	45	150	52.06	53.07	-1.01
7	0.6	3	45	150	69.19	69.02	0.17
8	0.4	5	30	200	49.02	49.53	-0.51
9	0.6	7	75	150	57.67	57.58	0.09
10	0.8	5	60	100	64.31	65.27	-0.96
11	0.4	5	30	100	47.99	48.09	-0.10
12	0.4	9	30	200	45.61	43.98	1.63
13	0.8	5	30	200	66.42	65.12	1.30
14	0.8	9	60	100	65.61	62.23	3.38
15	0.4	9	60	200	48.46	48.49	-0.03
16	0.4	5	60	200	54.17	54.04	0.13
17	0.2	7	45	150	36.45	37.68	-1.23
18	0.8	9	30	100	58.68	57.72	0.96
19	0.4	5	60	100	53.80	52.60	1.20
20	0.8	5	30	100	61.35	60.76	0.59
21	0.8	9	30	200	62.03	62.08	-0.05
22	0.6	7	15	150	48.46	48.55	-0.09
23	0.6	7	45	150	51.89	53.07	-1.18
24	0.8	5	60	200	70.25	69.63	0.62
25	0.6	11	45	150	57.67	60.44	-2.77
26	0.6	7	45	150	53.95	53.07	0.88

27	0.6	7	45	150	51.89	53.07	-1.18
28	1.0	7	45	150	66.40	68.45	-2.05
29	0.4	9	30	100	44.09	42.54	1.55
30	0.6	7	45	150	54.56	53.07	1.49

Table 4. ANOVA for the reduced quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	1963.80	7	280.54	121.52	< 0.0001	
A- Bottom ash dosage	1420.65	1	1420.65	615.35	< 0.0001	
B-pH	110.64	1	110.64	47.92	< 0.0001	
C-Time	122.27	1	122.27	52.96	< 0.0001	
D- Agitation speed	50.49	1	50.49	21.87	0.0001	significant
AB	6.31	1	6.31	2.73	0.1124	
AD	8.57	1	8.57	3.71	0.0670	
B ²	244.87	1	244.87	106.07	< 0.0001	
Residual	50.79	22	2.31			
Lack of Fit	44.18	17	2.60	1.97	0.2342	
Pure Error	6.61	5	1.32			not significant
Total	2014.59	29				

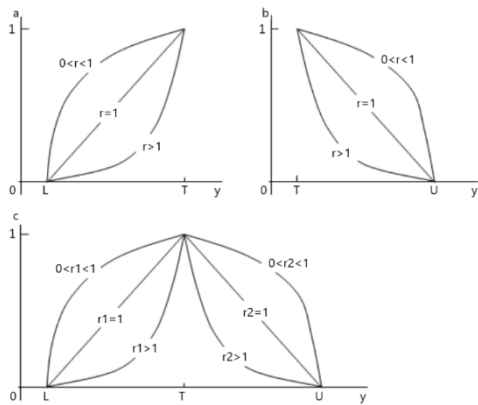


Figure 4. Individual desirability functions: (a) the target is to maximize response, (b) the target is to minimize the response, and (c) the target is as close as the possible target of the response.

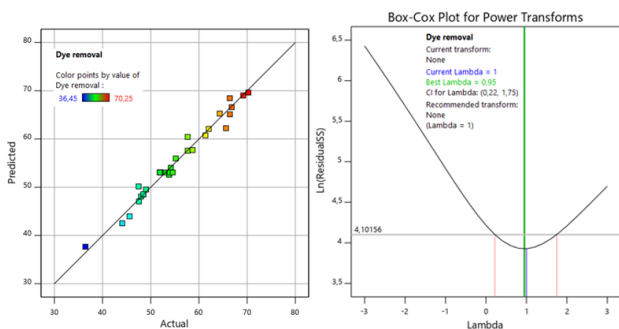


Figure 5. a) Predicted and actual values b) Box-Cox plot of dye removal.

The p-values of the terms in the model are less than 0.05, indicating that it has significant effects, and greater than 0.1 has insignificant effects (Stat-Ease 2021). It can be seen in Table 4 that A, B, C, D, and B² are significant model terms. High F-values indicate the effect level of the terms on the response variable. When F-values are examined, it can be said that the A-bottom ash dosage with an F-value of 615.35 has the highest effect. Moreover, according to

the F-values, it can be said that the effects of pH and time on the removal efficiency are lower, but the square of the pH (B²) affects the removal efficiency more. In this case, it can be said that the removal efficiency will increase when the pH is very low and very high. As seen in Table 4, AB is not a significant model term. It has been added to the model to obtain a hierarchical model. Depending on the different results (replicate) at the run points, the fitting of the model is determined by the lack of fit test. A statistically significant lack of fit does not capture all the different results (replicate) obtained at run points. Therefore, the lack of fit should be non-significant. The significance of the lack of fit of the dye removal model within the scope of the study is not significant.

The equation in terms of actual factors is given in Equation 5. R² is the deviation between the estimated results from the model and the actual results (Myers *et al.* 2016). It is known that the value of R² varies in the range of 0-1. A high R² does not necessarily mean the regression model is good (Myers *et al.* 2016). Each variable or term added to the model, statistically significant or not, increases the R² value (Myers *et al.* 2016). Thus, the predictability of the mean response may be poor with models with large R². Therefore, it is preferred to use adjusted-R² instead of R². Because the adjusted R² value often decreases due to unnecessary (non-significant) terms added to the model (Myers *et al.* 2016). In terms of the fit statistic of the model, the difference between adjusted-R² and predicted-R² should be less than 0.2 (Stat-Ease 2021). The R², adjusted-R² and predicted-R² were found as 0.9748, 0.9668 and 0.9409 in this study, respectively. The difference between the adjusted-R² and predicted-R² of the model obtained for dye removal is 5. Adequate precision measures the signal-to-noise ratio, and it is desirable to have a value greater than 4 (Stat-Ease 2021). The adequate precision value of the model is 40.7266, which is considerably higher than 4. Therefore,

the obtained model can generate a suitable signal in the design space (at the selected variation intervals).

$$\begin{aligned} \text{Dye removal} = & 75.280 + 16.498 \text{ CA} - 12.221 \text{ CB} + 0.150 \text{ CC} \\ & - 0.015 \text{ CD} + 1.570 \text{ CAB} + 0.073 \text{ CAD} + 0.729 \text{ CB}^2 \end{aligned} \quad (1)$$

3.2. Effects of variables on MB removal

The solution pH is a crucial parameter in the adsorption processes. One of the primary factors affecting the effect of pH on removal efficiency in adsorption experiments is the pH at the point of zero charge (pHpzc). As established, when the pH exceeds the pHpzc, the surface of the adsorbent is negatively charged, resulting in a stronger attraction of dye cations to the adsorbent's surface. Conversely, at pH below the pHpzc, the adsorbent becomes positively charged, leading to the repulsion of dye cations and a decrease in adsorption efficiency. Adsorption based on pH is primarily governed by electrostatic forces. In this study, the pHpzc value of the adsorbent was determined to be 8.3.

Interaction, contour and 3D plots of AB and AD are shown in Figure 6. When analyzing the curves presented in Figure 6 based on the obtaining model, it is evident that removal efficiency decreases around pH 6.5-8.5. Notably, removal efficiencies at pH 3 and 11, representing low and high pH conditions, reached approximately 70% under specific reaction conditions. Consequently, because the adsorbent carries a negative charge above pHpzc, adsorption efficiency increased due to the electrostatic forces repelling dye cations, improving removal efficiency with increasing pH.

As is well known, below the pHpzc, the adsorption efficiency is driven by electrostatic forces, typically resulting in a low removal rate of cationic dyes. However, in this study, we achieved high removal efficiency of MB, a cationic dye, at pH values below pHpzc. The elevated removal efficiency at pH 3 is thought to spring from alterations in the adsorbent structure under acidic conditions. Gürses *et al.* (2006) (Gürses *et al.* 2006) conducted a study involving clay and found that the removal efficiency of MB increased under acidic conditions. They suggested that this increase was due to access of protonated MB species (MBH₂⁺) to the interlayer regions after some oxides from the clay surface removal. The highest adsorption capacity was observed at low pH values, such as pH 1 (Gürses *et al.* 2006). It was noted that the tendency to remove oxides decreased as pH increased, while exchangeable alkali and other metal cations on the clay's surface and interlayer region underwent hydration, creating a hydrophilic environment. It was suggested that if the clay's surface charge approached zero under such conditions, MB uptake could be reduced. Similar results were obtained in this study and the high removal efficiency at pH 3 can be explained by a similar mechanism. It is obvious that the removal efficiency at pH 11 is due to electrostatic forces. In the study, MB removal rates of 69.19% at pH 3, 51.89% at pH 7 and 57.67% at pH 11 were achieved at pH 3, pH 7 and pH 11, respectively, using a base ash dose of 0.6 g, an agitation speed of 150 rpm and a duration of 45 minutes.

As seen in this study, the decrease in removal efficiency at neutral pH values (pH 6-8) is attributed to the fact that the adsorbent carries zero charge at these pH values (Gürses *et al.* 2006).

Figure 6 also shows the effect of bottom ash dosage on MB removal efficiency. The bottom ash dosage is one of the important parameters in MB removal by adsorption process, and as the bottom ash dose increases, MB removal increases. Increasing the dosage of bottom ash leads to a rise in MB removal due to the increased presence of active sites. MB removal enhanced from 36.45% to 52.89±1.15% when the bottom ash dosage increased from 0.2 g to 0.6 g, and it reached 66.40% at 1.0 g bottom ash dose (pH: 7, agitation speed: 150 rpm, time: 45 min.).

As seen in Figure 6, since the adsorption time has little effect on MB adsorption, the effects of AC, BC and CD are eliminated in the model. While 48.46% MB removal was obtained with 15 min adsorption at 150 rpm, 0.6 g bottom ash dose and pH 7 conditions, a slight increase was observed from 52.89±1.15% to 57.67% when the adsorption time enhanced from 45 min to 75 min.

The constraints selected for the desirability functions used to optimize dye removal efficiency according to the effect variables are given in Table 5. The selection of constraints considered scenarios with low energy costs. For this reason, priority was given to conditions where adsorption time and agitation speed were at minimum levels and high removal efficiency was achieved. It was also observed from the model that bottom ash dose and pH had a more significant effect on MB removal. As a result of the experimental study, the conditions that provide the best removal efficiency were determined at 0.978 g bottom ash dosage, pH 3, 15 minutes adsorption time, and 50 rpm mixing speed. Under these conditions, the model predicted an MB removal efficiency of 71%, while experimental results provided an actual MB removal rate of 72.5%.

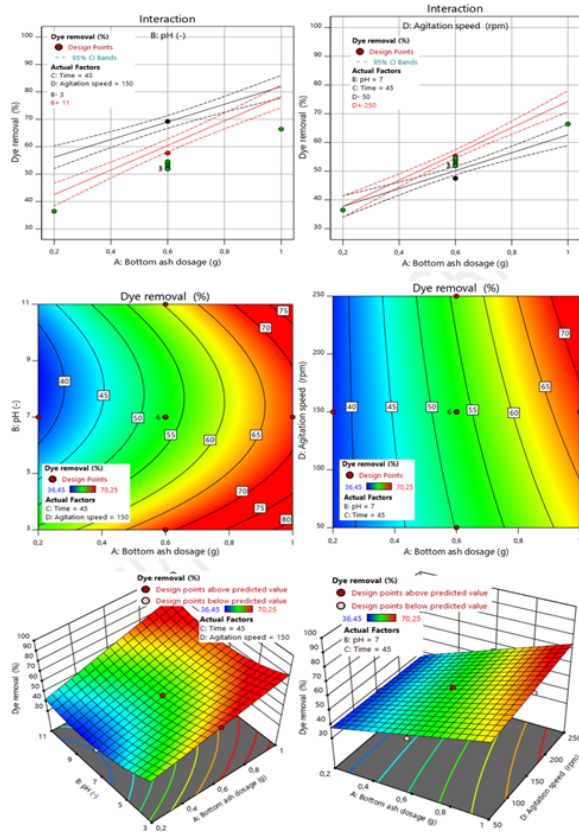


Figure 6. Interaction, contour and 3D plots of AB and AD terms.

3.3. Adsorption Isotherms

The adsorption isotherms were determined at the optimum conditions obtained from the model. The initial MB concentrations were selected between 5 and 50 mg/L for the adsorption isotherms. While 97.2% MB removal was obtained at 5 mg/L MB concentration, a decrease was observed with increasing MB concentration. MB removal was reduced to 55.6% at 50 mg/L MB concentration. Langmuir and Freundlich models were used for isotherm studies. Langmuir and Freundlich Isotherm models are detailed in the literature (Cifci *et al.* 2022).

Table 5. The constraints of the optimization

Name	A: Bottom ash dosage	B: pH	C: Time	D: Agitation speed	Dye removal
Goal	is in range	is in range	minimize	minimize	maximize
Lower Limit	0.2	3	15	50	36.45
Upper Limit	1	11	75	250	70.25

As a result of the isotherm study, it was seen that the adsorption of MB to the bottom ash used was compatible with the Freundlich Isotherm model, as the R^2 value was found to be higher ($R^2:0.9868$ (Table 6)). To determine the suitability of isotherm models, error functions such as Average relative error (ARE), Chi-square (χ^2), and Error Sum of Squares (SSE) were calculated according to the formulas given in the literature, in addition to R^2 (Mallakpour and Tabesh 2019). The fact that ARE, χ^2 , and SSE error functions are lower in the Freundlich Isotherm model also shows that this model is more suitable. According to the Freundlich Isotherm model, it is assumed that multilayer adsorption takes place on the heterogeneous adsorbent surface (Al-Ghouti and Da'ana 2020).

According to the Langmuir Isotherm model, q_{max} was calculated as 2.93 mg/g. In the range of 5 and 50 mg/L MB concentration, the R_L value ranges between 0.02 and 0.353. The fact that the R_L , which defines the adsorption tendency, is between 0 and 1 indicates that the bottom ash and MB adsorption are favorable (Mallakpour and Tabesh 2019).

According to the Freundlich isotherm model, $1/n$ was obtained as 0.3248. Calculating the $1/n$ value between 0 and 1 shows that MB's adsorption of bottom ash is favorable (Al-Ghouti and Da'ana 2020).

Table 6. Langmuir and Freundlich Isotherm parameters for MB removal using bottom ash

	Langmuir Isotherm	Freundlich Isotherm	
q_{max} (mg/g)	2.93	n	3.08
K_L (L/mg)	0.367	$1/n$	0.3248
R_L	0.02-0.353	K_F	1.00
R^2	0.9655	R^2	0.9868
ARE	19.28	ARE	4.55
χ^2	0.61	χ^2	0.05
SSE	0.62	SSE	0.02

4. Conclusion

This study investigated methylene blue (MB) removal by adsorption process using bottom ash. The bottom ash was analyzed using SEM images and FTIR analysis, and it contained mainly silicon, aluminum, iron, and oxygen. To determine the effect of bottom ash on MB removal, bottom ash dose (0.2-1.0 g), pH (3-11), time (15-75 minutes), and stirring speed (50-250 rpm) variables were selected effect variables and experiments were carried out. According to the experimental results, R^2 , adjusted R^2 , and estimated R^2 values in the developed model were found to be 0.9748, 0.9668, and 0.9409, respectively. The optimum values for the MB removal using the desirability function were obtained as 0.976 g bottom ash dose, pH 3, 15 min time, and 50 rpm mixing speed. For these values,

the MB removal calculated by the model was 71.0%, while the experimental MB removal was 72.5%.

In the experimental results, it was found that the MB removal efficiency was highest at pH: 3 and pH: 11. The reason for the high removal efficiency at pH: 11 is that the surface charge of the bottom ash is minus at high pHs and the dye cations are electrostatically attracted. It has been stated that the high removal efficiency at pH 3 is due to the deterioration of the structure of the bottom ash at this pH and its consequent attraction of MB cations. It was concluded that MB adsorption with bottom ash is more suitable for the Freundlich isotherm model, and the adsorption occurs in multilayers on the heterogeneous adsorbent surface.

This research highlights the potential of using bottom ash, a byproduct of coal combustion, to decolorize wastewater containing dyes such as MB. This approach offers an economically viable wastewater treatment method and contributes to the sustainable reuse of waste materials. These studies are thought to improve our understanding of adsorption processes and their applications in environmental remediation.

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