Using of Rsm on Removal of Methylene Blue from Aqueous Solutions by Grape Seed (Tunceli-Elazığ) as a Low-Cost and Eco Friendly Adsorbent

Ucuz ve Çevre Dostu Bir Adsorbent Olan Üzüm Çekirdeği ile Metilen Mavisinin Sulu Çözeltilerden Gideriminde RSM Kullanımı

Research Article

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ABSTRACT

Grape seeds are waste products of the wine and juice processes in big amounts. In this study, grape seeds were used in Methylene Blue (MB) removal in synthetic wastewater by transformation into active carbon. Optimization process was completed using RSM. Four different parameters could affect the removal in selected process were identified and maximum MB removal was achieved by optimization of these parameters. Central Composite Design (CCD) software was used to calculate the effects of each parameter on response/removal. Conducted empirical and statistical studies determined that the values for independent parameters that achieved the maximum response were; pH 3.7, contact time 55.5 minutes, absorbent dosage 1.4 g, and initial concentration of 160 mgL^{-1}. Using these parameters, MB removal from synthetic wastewater was conducted at an approximate yield of 99% with active carbon (*Vitis vinifera* seed) use. Furthermore, it was identified that the achieved model supported the conducted study by 82%.

Key Words
Active carbon, dye, metyhlene blue, RSM, *Vitis vinifera* L. seed.

ÖZ

Ucuz ve atık olarak değerlendirilen üzüm çekirdeği insanların gıda olarak kullandığı üzümden elde edilen ve bol miktarda bulunan bir atıktır. Bu atık aktif karbon haline getirilerek bir boyar madde olan Metilen Mavisinin (MM) sentetik atık sulardaki gideriminde kullanılmıştır. Optimizasyon süreci Response Surface Metodology (RSM) kullanılarak tamamlanmıştır. Çalışılan süreçte giderimi etkileyecek dört farklı parametre seçilmiş ve bu parametreler optimize edilerek maksimum Metilen mavisi giderimi bulunmuştur. Bu parametrelerin herbirinin (pH, zaman (dakika), adsorbent miktarı (g) ve başlangıç derişimi mgL^{-1}) cevap üzerindeki etkileri Central Compozite Design (CCD) programı kullanılarak hesaplanmıştır. Yapılan deneysel çalışmalar sonucunda quadratik bir model bulunmuş ve üç boyutlu grafikler elde edilerek Anova istatiksel verileri hesaplanmıştır. Gerçekleştirilen deneysel ve istatiksel çalışmalar sonucunda bağımsız parametrelerin maksimum değerleri pH 3.7, süre 55.5 dakika, adsorbent miktarı 1.4 gram ve başlangıç derişimi 160 mgL^{-1} olarak bulunmuştur. Bu veriler kullanılarak aktif karbon (*Vitis vinifera* L.) ile sentetik atık sulardan yaklaşık %99 verimle Metilen mavisi giderimi sağlanmıştır. Aynı zamanda bulunan modelin yapılan çalışmayı %82 desteklediği gözlenmiştir.

Anahtar Kelimeler
Aktif Karbon, boyar madde, metilen mavisi, RSM, *Vitis vinifera* L. çekirdekleri.

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INTRODUCTION

Activated carbon, like many other dye-removal treatments, is well suited for one particular waste system and ineffective in another. It is also expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation process results in 10-15% loss of the sorbent [1].

Response Surface Methodology (RSM) statistical software was used for adsorption tests in the present study. The effects of independent parameters on the response were identified using mathematical and statistical calculations. Optimization was finalized by CCD, which is a sub-program of RSM that provides results standardized by minimum number of tests and anchored by a quadratic model [2]. As a result of empirical processes, removal was explained with a quadratic equation and three dimensional graphics. In the present study, grape seed waste was calcined at 450°C and transformed into active carbon and the resulting adsorbent material was used in removal of synthetic MB solutions. CCD was used in this removal to analyze maximum MB removal percentage by optimizing the effects of independent variables such as pH, contact time, absorbent dosage and initial concentration. These optimum parameters were found as pH 3.7, contact time 55.5 minutes, absorbent dosage 1.4 g, and initial concentration of 160 mgL^{-1} using ANOVA and coded values equation. End of study 99% MB removal yield was obtained.

MATERIALS and METHODS

Materials: Colorant (Methylene Blue) was procured from Scharlar (Spain). Chemical formula for the colorant is displayed in Figure 1. Grape seeds that were used as adsorbent were selected from "Öküzgözü" and "Boğazkere" variety grapes grown in Elazığ – Tunceli provinces in Turkey.

For pH adjustments, 0.1 M NaOH and 0.1 M HCl acid were used in adsorption experiments. Preparation of the adsorbent: Grape seeds were harvested in the month of September, which is the harvest season in Elazığ and Tunceli region. The seeds were separated from the grapes and washed with pure water a few times. After the physical dirt is removed from the seeds, they were placed in Muffule furnace for 40 minutes at 120°C to prevent the ingredients to burn completely. At the end of this period, the furnace temperature was increased to 500°C and kept at this temperature for 1 h for calcination. When the time was over, the seeds were removed from the furnace and milled. The seeds were grounded to small particle sizes and then sifted through a 230 (63 μm) mesh wide sieve to obtain maximum surface area and mesoporous character. Seeds prepared for adsorption process were stored in a desiccator until use.

Adsorption Experiments

Batch adsorption tests were conducted in 100 ml Erlenmeyer flasks. 50 ml synthetic MB solutions in different concentrations were placed in Thermo Orion (Singapore) equipment for pH measurements. Samples measured for pH were then taken into a JSR (Korea) brand shaker at 270 rpm and tests were commenced under adsorption conditions given in Table 1. Samples taken from the tests that completed adsorption processes were placed in the centrifuge device for supernatant separation. Sediments were obtained by 5 minutes long centrifuge at 6000 rpm from all tests. Supernatants separated from the sediment were transferred to UV-1800 spectrometer (Shimadzu, Japan) for MB analyses. All analyses were conducted at 630 nm wavelength. The equation shown below was used to identify MB removal on active carbon:

$$\%\,\mathrm{Re}moval = \frac{c_i - c_o}{c_i} 100 \quad (1)$$

where C_i is the baseline MB concentration (mg L^{-1}) and C_o is the final MB concentration in the solution (mg L^{-1}).

Statistical modeling and empirical design: Response surface methodology. RSM is both mathematical and statistical software that identifies optimum working conditions for an objective. It conducts empirical studies in an area where factors with systematic and processing conditions exist [2]. The system was modeled by calculating the effect values of these independent factors against the maximum response. Here, CCD, a sub-program, was used to determine maximum

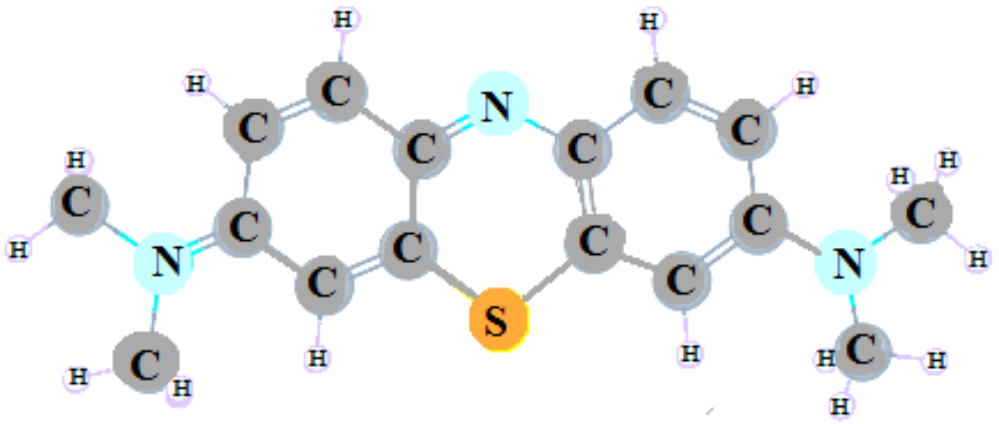

Figure 1. The chemical form of MB.

Table 1. The coded and actual values of influential parameters.

Variables	Symbols	Coded values				
		-2	-1	0	1	+2
pH	A	1.5	3.0	6.5	10	11.4
Contact time (min)	B	5.6	15	37.5	60	69.3
Adsorbent Dosage (g)	C	0.29	0.5	1.0	1.5	4.5
Initial concentration (mgL^{-1})	D	15.1	40	100	160	184.5

MB removal percentage. The tests were calculated using the effective factor on four removals. Total number of tests were determined as $30 = 2k + 2^k + 6$, where k is the number of factors present. Coded and real values for independent parameters are presented in Table 1.

These values are significant in determination of the optimum response. Experimental design is detailed in Table 2. The same table reflects the response obtained with these values, in other words % MB removal. Test results demonstrated that our modeling was quadratic and it supported 82% of the scope of the present study. A quadratic model equation is presented below.

$$\gamma = \beta_o + \sum_{i=1}^{\partial} \beta_i x_i + \sum_{i=1}^{\partial} \beta_{ii} x_i^{\,2} + \sum_{i\le 1}^{\partial} \sum_{j=1}^{\partial} \beta_{ij} x_i x_j \qquad (2)$$

In this formula: Y is the response, β_0 is the constant factor, X_i (i = 1-3) are variables, β_i are the linear, β_{ii} are the quadratic, (i and j = 1-3) are the second-order interaction factor. All data were refined by the Design-Expert 10.0 program (trial version) and ANOVA test was determined to get the interaction between the independent parameters and the % Removal of MB. The standard of fit of this model was expressed by the factor of fixing R^2, F-test analyzed the statistical importance of this index [2,3]. Calculation of maximal points: Following the experimental studies, maximum points of effective parameters were determined based on the formula depicted in Equation 3 below. Matrices with different bases are formed

$$b = \begin{matrix} \beta_1 \\ \beta_2 \\ \beta_k \end{matrix} \qquad B = \begin{matrix} \beta_1 & \beta_{12} & \beta k \\ & \beta_{22}/2 & \beta_{2k}/2 \\ & & \beta_{kk} \end{matrix} \qquad (3)$$

using that equation and maximum points are found with the formula in Equation 4.

$$\gamma = \beta_o + x^1 b + x^1 B b$$

$$x_s \text{ (Stationary points)} = \begin{matrix} x_1 \\ x_2 \\ x_k \end{matrix} \qquad (4)$$

Table 2. Parameters, their intervals in the runs conducted in CCD and corresponding result.

Run	pH (A)	Contact Time (B) (minute)	Adsorbent Dosage (C) (g)	Initial Concentration (D) (mgL^{-1})	MB removal (%)
1	3	15	0.5	160	69
2	6.5	37.5	1.7	100	94
3	3	15	1.5	160	100
4	10	15	0.5	160	70
5	10	15	1.5	40	84
6	10	60	0.5	40	84
7	3	60	1.5	40	90
8	3	15	1.5	40	92
9	3	60	1.5	160	99
10	10	60	1.5	40	89
11	6.5	37.5	1	100	89
12	1.56	37.5	1	100	100
13	6.5	5.68	1	100	84
14	10	15	0.5	40	91
15	3	15	0.5	40	97
16	11.4	37.5	1	100	94
17	6.5	37.5	1	100	89
18	10	15	1.5	160	97
19	3	60	0.5	40	97
20	10	60	0.5	160	75
21	6.5	37.5	1	184.8	77
22	10	60	1.5	160	98
23	6.5	69.3	1	100	96
24	6.5	37.5	1	100	89
25	3	60	0.5	160	99
26	6.5	37.5	1	100	89
27	6.5	37.5	1	100	89
28	6.5	37.5	1	100	89
29	6.5	37.5	1	15.1	72
30	6.5	37.5	0.29	100	57

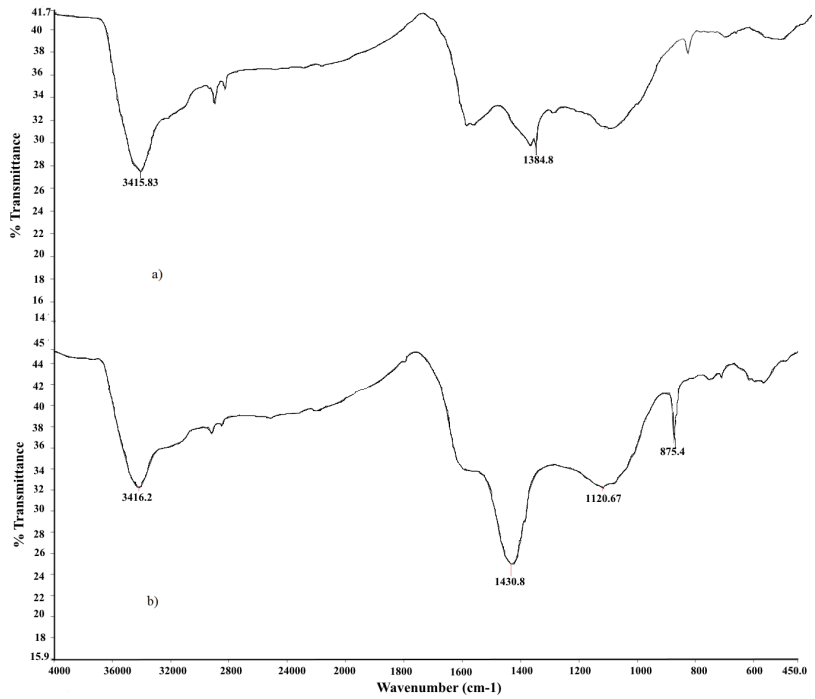

Figure 2. FT-IR spectra of active carbon. a) the spectrum of active carbon post adsorption b) the spectrum active carbon of pre-adsorption.

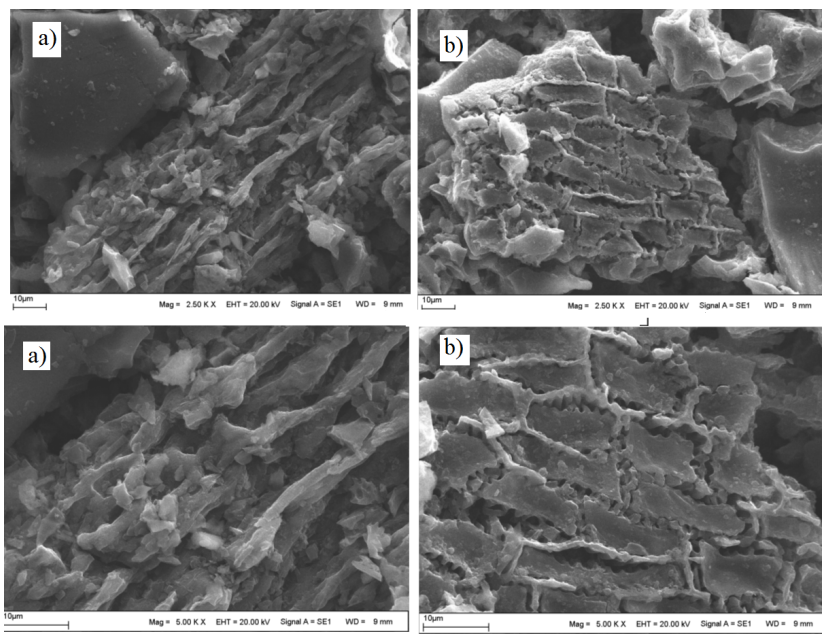

Figure 3. SEM image of activated carbon of *Vitis vinifera* seed (a) post-adsorption and (b) pre-adsorption of MB.

where b is a vector of the first order regression coefficient and β is a symbetric matrix whose main diagonal elements are the pure quadratic coefficients (β_{ij}) and whose off-diagonal elements are one half of the mixed quadratic coefficients (β_{ij}, i≠1) the stationary points (x_s) are the solution of Equation 4 [2].

$$x_s = -(-\frac{1}{2})B^{-1}b \quad (4)$$

RESULT and DISCUSSIONS

Infrared studies: FTIR peaks for the utilized adsorbent agent are given in Figure 2 (a) and (b) Wavelengths were examined before and after adsorption between 450 and 4000 cm^{-1}. Comparison of the spectra of active carbon before and after adsorption found in the figure demonstrated that certain oscillations disappeared and others varied as a result of adsorption. Oscillation peaks on 875 and 1120 cm^{-1} wavelengths that were present before adsorption could be C-O or C-O functional structures. These structures disappeared by reacting with certain present groups in MB parallel to the adsorption mechanism. In both cases, oscillation frequencies of certain functional groups were analyzed in specific wavelengths. Carboxyl and hydroxyl groups are important in MB suppression process [4]. C-O tension interval for cellulose/hemicellulose at 1430 cm^{-1} wavelength was observed at 1384 cm^{-1} wavelength and changed [5]. Also, O-H tension peak that existed at 3416 cm^{-1} wavelength before adsorption was transposed to the peak at 3415 cm^{-1} wavelength after the adsorption.

SEM Studies: Figure 3 includes the pre and post-adsorption SEM images of the active carbon. Figure 3 (a) demonstrates post-adsorption images of active carbon after bonding with MB at 5000x and 2500x magnification values, and these images are more dense and MB particles hold on to the surface when compared to the post-adsorption images shown in Figure 3 (b). The simplicity observed in pre-adsorption is apparent in post-adsorption images, proving the occurrence of adsorption in the current study.

Analysis of Variance: Optimization of parameters in the media in chemical and biological systems such as colorant removal is quite difficult. Because optimization of independent variables one by one is a complex and time consuming process. Optimization of the effects of independent parameters such as pH, contact time, absorbent dosage and initial concentration on % MB removal is difficult and causes several problems. RSM was preferred to eliminate and remove these problems. The software also analyzed % MB removal with the help of significant factors by finding an empirical model. Table 1 demonstrates real and coded values for selected parameters, while Table 2 displays empirical design and responses for batch-adsorption experiments. Calculated results are presented in Table 3. Multiple regression analysis applied to the experiments produced the second-order polynomial equation shown below. A quadratic model (Equation 5) for MB removal was derived in this equation using medium factors such as pH, contact time, absorbent dosage and initial concentration.

$$\text{MB Removal (\%)} = 82.849 - 3.108\,A + 2.387\,B + 5.880\,C - 0.573\,D - 1.452\,AB + 1.928\,AC + 0.152\,AD - 1.557\,BC + 2.440\,BD + 5.951\,CD + 8.016\,A^2 + 4.490\,B^2 - 2.860\,C^2 - 3.311\,D^2 \quad (5)$$

In this equation A is pH, B is contact time (minutes), C is adsorbent dosage (grams) and D is the initial concentration (mgL^{-1}). Analysis of variance creates a communication by testing the relationship between the empirical data and Equation 5, which is a second-degree polynomial equation. The interactions found are displayed in Table 3. The model F-value of 4.69 implies that the model is significant. The fit of model was checked by the coefficient of determination R^2, which was calculated to be 0.82, indicating that 82% of the variability in the response could be explained by the model. It indicates a good agreement between experimental and predicted values and implies that the mathematical model is reliable for MB removal. The value 0.0004 of "Prob > F", which is less than 0.05 indicates that the model terms are significant. According to the results of the statistical design and by application of Equations 3 and 4, the optimum values of tested factors were evaluated as pH, 55.5 contack time, 1.41 g amount adsorbent and 160 mg L^{-1} the initial concentration. Under the optimized conditions, maximum MB removal was predicted to be 99% respectively. Response surface plots: Effects of independent parameters on the response and interrelationships between these parameters are presented in Figures 4-7 Based on the found quadratic model, 2 and 3 dimensional graphs were given for each case. Percentage MB removal of variable time and pH parameters are demonstrated in Figure 4 in empirical constant baseline concentration (100 mgL^{-1}) and constant

Table 3. Analysis of variance test for MB removal on active carbon.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2735.459	14	195.390	4.687	0.003	Significant
A	193.242	1	193.242	4.636	0.048	
B	114.002	1	114.002	2.735	0.119	
C	691.663	1	691.663	16.592	0.001	
D	6.574	1	6.574	0.158	0.697	
AB	33.762	1	33.762	0.810	0.382	
AC	59.486	1	59.486	1.427	0.251	
AD	0.371	1	0.371	0.009	0.926	
BC	38.824	1	38.824	0.931	0.350	
BD	95.326	1	95.326	2.287	0.151	
CD	566.667	1	566.667	13.593	0.002	
A2	599.733	1	599.733	14.387	0.002	
B2	188.181	1	188.181	4.514	0.051	
C2	76.359	1	76.359	1.832	0.196	
D2	102.368	1	102.368	2.456	0.138	

$R^2 = 0.82$

absorbent dosage (1 g) values and in 3 – 10 pH and 15 – 60 minute time ranges.

While MB removal was at a maximum value at pH 3, it demonstrated a decrease between pH 3 and 6.5 and an increase between pH 6.5 and 10. In the next parameter of contact time, an increase was observed between the 15th minute to the 37th, followed by another period of increase between the 37th minute to the 60th minute. Response was directly affected by both parameters. Maximum 95-99% MB removal was obtained at approximately the 55th minute with pH value of 3. Other studies determined the maximum contact time as 60 and 79 minutes [6,7].

Figure 5 demonstrates the effects of independent parameters pH and initial concentration on MB removal at constant time and adsorbent dosage values. Similar to Figure 4, increase and decrease in pH values affected MB removal similarly, however, although there was no significant increase or decrease for baseline concentration, for maximum 150-160 mgL^{-1} baseline concentration values, a maximum of 85-86% MB removal was obtained.

In other studies, pH values as an effective parameter in colorant removal were selected between 2 and 12. Optimum alkali form pH was found to be 2.0, 4.5, and 5.23 in these studies [8-10]. In the present study, the optimum pH value

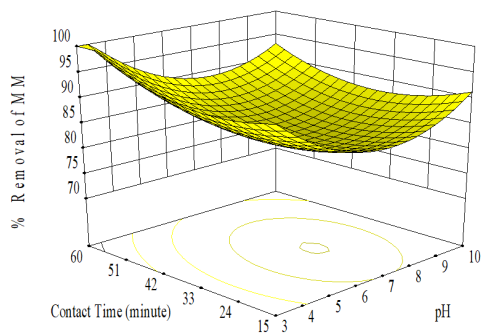

Figure 4. 3D response surface plots showing the effect of pH and the contact time on MB removal at fixed adsorbent dosage and initial concentration.

was given in alkali form and as 3.7, similar to other studies. Figure 6 demonstrates the effects of time and adsorbent dosage under constant pH and baseline concentrations on response. As is shown in the figure, increasing response that started at minute 15 is positively affected by time and the positive effect continued until minutes 55 – 57 and maximum response for MB removal was obtained on 55.5th minute. Adsorbent dosage increased concavely from 0.5 g to 1.5 g and the increase was directly proportional to the response. Maximum response for MB removal was obtained with maximum 1.4 g adsorbent dosage value and 84% MB removal.

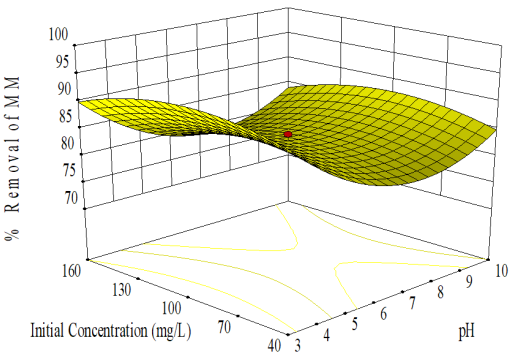

Figure 5. 3D response surface plots showing the effect of pH and initial concentration on MB Removal at fixed adsorbent dosage and contact time.

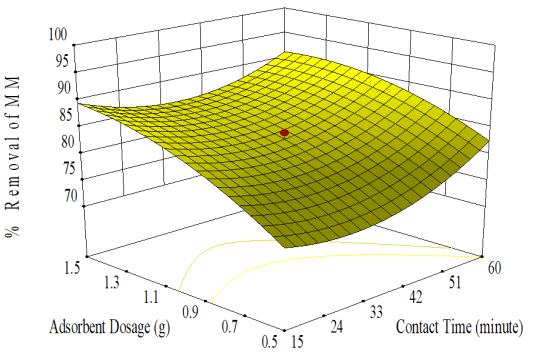

Figure 6. 3D response surface plots showing the effect of adsorbent dosage and contact time on MB Removal at fixed pH and initial concentration.

Figure 7 shows the effects of adsorbent dosage and initial concentration on response and it could be observed that the adsorbent dosage increased concavely from 0.5 g to 1.5 g, similar to the other figures, and reached the optimum MB removal at maximum 1.4 g value, and while initial concentration yielded the maximum response at 40 mgL^{-1} value, it decreased until 150 mgL^{-1} level. This finding was consistent with other studies conducted. In other words, it was reported that removal or adsorption values increased in reverse proportion with the decreasing colorant concentration. Similar results were obtained with adsorbents such as coal, algae, activated carbon and clay material [11-14].

Adsorption Equations: Adsorption process was expounded by using some models. In this study Freundlich and Langmuir isotherms models were performed to calculated sorption data, because of isotherms' shape. The equation of Freundlich were shown Equation 6 [15].

$$q_e = K_F C_e^{1/n} \quad (6)$$

Where, q_e is the amount of MB concentration per unit weight active carbon ($mg\ g^{-1}$), C_e is the equilibrium concentration of MB concentration ($mg\ L^{-1}$) in Equation 6. K_F is an adsorption constant and it represents the general adsorption capacity of MB concentration on the adsorbent for an unit C_e. As shown in Equation 6, the slope 1/n, ranging between 0 and 1, it was used to measure the adsorption intensity.

$$\frac{1}{q_e} = \frac{1}{K_L Ce} + \frac{1}{Q_m} \quad (7)$$

In a adsorption process, K_L is the intensity of the adsorption system ($L\ mg^{-1}$), and Q_m is a constant reflecting the adsorption capacity ($mg\ g^{-1}$). K_F is a invariable value in the adsorption process and it is relevant to the bonding energy. These coefficients Q_m and K_L were obtained from the graphic of 1/qe versus $1/C_e$ in Equation 7.

$$R_L = \frac{1}{1 + bCo} \quad (8)$$

The nature of Langmuir isotherm dimesionless coefficient separation factor or equilibrium parameter, R_L is defined and C_o is initial dye concentration (mgL^{-1}) by the equaiton 8.

Table 4. Langmuir and Freundlich isohterm constant and regression coefficients of MB adsorption.

	Langmuir				Freundlich		
	qm (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mgg^{-1})	n^{-1}	R^2
Activated carbon of *Vitis vinifera* L. seed	17.0	0.024	0.69	0.89	0.65	138 .0	0.93

Table 5. Comparison of the MB adsorption capacities of the various adsorbent.

Adsorbent	Adsorption capacity, mg g^{-1}	Reference
Parthenium hystrophorous Weed	23.8	[22]
Orange peel	11.62	[23]
Green algae Scenedesmus	68	[24]
Red mud	27.8	[25]
Fly ash	15.0	[26]
Activated carbon of Water Hyacinth	2.15	[27]
Pseudomonas Putida	44.37	[28]
Vitis vinifera L.seed	17.0	This study

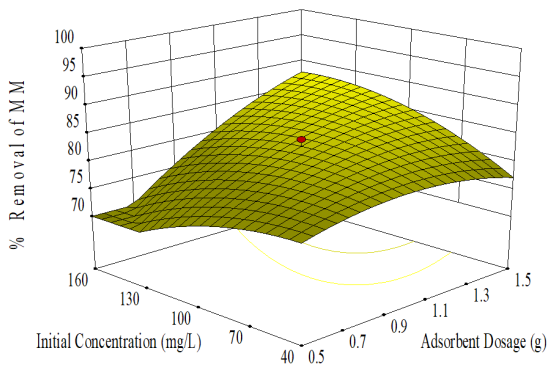

Figure 7. 3D response surface plots showing the effect of adsorbent dosage and initial concentration on MB Removal at fixed pH and contact time.

Table 4 shows the analysis coefficients obtained with the solution of Langmuir and Freundlich isotherm equations. The values of R_L indicates the type of isotherm to be irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L =1) or unfavorable (R_L > 1) [16-18]. Obtained Langmuir equation coefficient value R_L of 0.65 confirmed the adsorption process in the present study to be complete and significant. Various conducted studies found similar R_L values with the present study [14,19-22]. Concurrently, comparisons of the maximum adsorption capacity (qm) value found in this study to other studies are presented in Table 5.

CONCLUSIONS

As a result of the present study, MB colorant was removed from synthetic wastewater with 99% yield by adsorbing the colorant on active carbon obtained from grape seeds using an efficient and valid modeling. This is the first study using seed of *Vitis vinifera* on adsorption of MB colorant. The removal efficiency was optimized with experimentally changing independent parameters used in wastewater medium with CCD utilization. A quadratic model was also achieved as a result of empirical studies and ANOVA statistical data. The Langmuir equation coefficient value RL of 0.65 confirmed that the adsorption process in the present study is complete and significant. The obtained adsorbent material, the model and the optimum parameters for adsorption process will provide alternatives for MB removal in various media.

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Nomenclature

ANOVA : Analysis of variance
β0 : Constant coefficient of Equation 1
β_i : Linear coefficient of Equation 1
β_{ii} : Quadratic coefficient of Equation 1
β_{ij} : Interaction coefficient of Equation 1
CCD : Central Compozite Design
FTIR : Fourier transform infrared
RSM : Response Surface Methdology
R^2 : Coefficient of determination
MB : Metyhlene Blue

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