Box-Behnken Response Surface Design for Acid Red - 87Adsorption on Chemically Activated Syzygium Cumini Seeds

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***Abstract*:- The present research analyzes the removal of Acid Red-87 dye using adsorption technique. The chemically modified *Syzygium cumini* seeds are used as adsorbent. The process variables such as adsorbent dose, dye concentration and time were chosen as independent variables in Box-Behnken design while percentage of acid red dye removal was considered as the response function. Three factors with three levels Box-Behnken response surface design was employed to optimize and, investigate the effect of process variables on the response. The Langmuir and Freundlich adsorption isotherm models were tested for their fitness of experimental data. Langmuir isotherm model was found to be an appropriate model compared to the Freundlich isotherm model. The optimal values of process variables for adsorption as suggested by response surface methodology was found to be the adsorbent dose of 5g, dye concentration of 20mg/l and time of 8 hrs. This study showed that statistical design methodology was an efficient and feasible approach in determining the optimum conditions for acid red dye removal by adsorption.**

Key Words: Syzygium cumini, adsorbent, Box-Behnken design, AcidRed-87, Langmuir, Freundlich.

1. INTRODUCTION

Syzygium cumini is an evergreen tropical tree in the flowering plant series that belongs to the plant family Myrtaceae, with surplus medicinal values. It is also known as black plum. It is native to India and Indonesia. It is also grown in other areas of Southeast Asia including Malaysia, Myanmar, Pakistan and Afghanistan. *Syzygium cumini*, a fairly fast growing species, can reach heights of up to 30 m and can live for more than 100 years. *Syzygium cumini* is always appreciated for the color, flavor and taste of its fruit. The extracts of the bark, seeds and leaves are used for the treatment of diabetes. A decoction of the bark and powdered seeds is believed to be very useful in the treatment of diarrhea, dysentery and dyspepsia. Recently, the plant extract of *Syzygium cumini* used for the prevention of diabetes [1]. *Syzygium cumini* have very short shelf-life since they are highly perishable. Drying can be suggested as one of the option to extend their shelf life [2]. It has been suggested that *Syzygium cumini* seed if activated can be used as an adsorbent and can be a suitable substitute for commercial activated carbon [3,4]. The study utilizes the Response Surface Methodology (RSM) to optimize the decolourisation of synthetic dye using activated *Syzygium cumini* seed. The synthetic dye used in this study is Acid Red-87 and the process variables are time, adsorbent dose and dye concentration. In the present study, the BBD (Box-Behnken Design) method was selected to optimize the variables of the decolorization process. The BBD is a RSM method used for analysis of the experimental design data [5]. The RSM is essentially a set of mathematical and statistical methods of designing experiments, building models, evaluating the effects of variables and searching for optimum conditions of variables to predict targeted responses. The RSM does not require a large number of runs and also does not require too many levels of the independent variables [6, 7].
The major objective of this study is to investigate removal efficiency of Acid Red-87 dye by adsorption using chemically activated *Syzygium cumini* seeds. The BBD method was used to investigate the effect of process parameters such as time, dye concentration, adsorbent dose on decolorization and to find the most suitable combination of variables resulting in maximum dye removal efficiency. A mathematical model has been developed correlating the percentage of decolorization and the process variables.

2. MATERIALS AND METHODS

2.1Preparation of Adsorbent Samples

The dye solution has been prepared synthetically. The *Syzygium cumini* seeds were purchased from local markets of Erode and washed with water for removing dust and foreign impurities. They were sun dried and crushed into fine powder. For chemical modification of adsorbent, 50 g of this powder was dipped into 500 ml of 10 % tartaric acid solution for 3- 4 hours after wrapping the beaker with aluminum foil. After that, it was filtered and first air dried followed by drying in oven at 80°C for one hour [3]. Thus produced, chemically modified adsorbent samples are stored in airtight flasks until further use. The SEM (Scanning Electron Microscope) analysis of the adsorbent has been carried out to confirm that it has been activated [10]

2.2 Adsorption Experiments

For optimizing the operational conditions of adsorption, various experiments are conducted by varying at a time one factor, keeping other variables constant in the

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following range: particle size of adsorbent (20-40 to 80-100 microns mesh size), adsorbent dose (5-15 g), contact time, (8-24 hrs), initial dye (Acid Red-87) concentration (10-30 mg/l) and agitation speed (50-250 rpm). The solution volume (V) was 100 ml in all batch experiments. After adsorption experiment, dye solutions were filtered and remaining concentration of dye in filtrate was determined using UV-Visible spectrophotometer with at λ_{max} of 515,482 and 360 nm respectively for initial dye concentration of 10, 20 and 30mg/l respectively. All the experiments were conducted in triplicate fashion and average values were considered for calculations [8, 9]. The percent removal of dye from solution is calculated by the following equation;

$$\text{Percentage removal} = \frac{(\text{Initial Absorbance}) - (\text{Final Absorbance})}{(\text{Initial Absorbance})} \times 100$$

2.3 Design of Experiments

The various parameters that influence the process of adsorption and desorption kinetics were optimized using the design of experiments by Design Expert software 8.0.7.1 version. The number of runs was designed using BBD. The experiments were conducted accordingly and percentage of decolorization was determined. [11] The Box-Behnken design optimizes the number of experiments to be carried out to ascertain the possible interactions between the parameters studied and their effects on the removal of dye. Box-Behnken design is a spherical, revolving design; it consists of a central point and the middle points of the edges of the cube circumscribed on the sphere [12]. It is a three-level fractional factorial design consisting of a full 2^2 factorial seeded into a balanced incomplete block design. It consists of three interlocking 2^2 factorial designs having points, all lying on the surface of a sphere surrounding the center of the design [13]. In the present study, the three-level three-factorial Box-Behnken experimental design is applied to investigate and validate adsorption process parameters affecting the removal of dye. The ranges of variable are as follows: Adsorbent dose (5-15 g), dye concentration (10-30 mg/l) and time (8, 16, 24 h). The factors levels were coded as -1 (low), 0(central point middle) and 1 (high) [12].

Table 1: Experimental design levels of chosen variables

Variables	Levels in Box-Behnken design		
Coded level	Low(-1)	Middle (0)	High (+1)
Adsorbent Dose, (g)	5	10	15
Dye concentration,(mg/l)	10	20	30
Time, (hrs)	8	16	24

Table 1 shows the experimental parameters and the experimental Box-Behnken design levels used. RSM was applied to the experimental data using statistical software, Design-expert (trial version). Statistical terms and their definitions used in the Design-expert software are well defined [14]. Linear and second order polynomials were fitted to the experimental data to obtain the regression equations. The sequential F-test, lack–of–fit test and other adequacy measures were used in selecting the best model [15]. To analyze a process or system including a response Y, where Y depends on the input factors X_1, $X_2 \ldots X_k$, the relationship between the response and the input process parameters are described as:

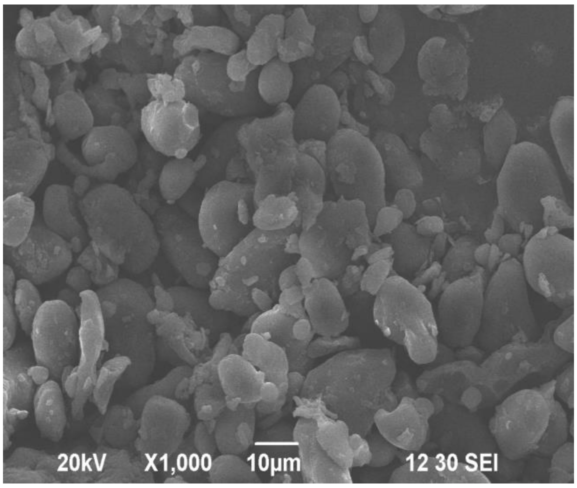
$$Y = f(X_1, X_2 \ldots\ldots X_k) + \varepsilon$$

Where, f is the real response function, its format being unknown and ε is the residual error which describes the differentiation that can be included by the function f. Because the relationship between the response and the input parameters can be described as a surface of the X_1, $X2 \ldots, X_k$ coordinates in the graphical sense, so the study of these relationships is named as the response surface study. The same statistical software was used to generate the statistical and response plots. A manual regression method was used to fit the second order polynomial equations to the experimental data and to identify the relevant model terms. Considering all the linear terms, square terms and linear by linear interaction terms, the quadratic response model can be described as:

$$Y = \beta_0 + \Sigma\, \beta_i x_i + \Sigma\, \beta_{ii} x^2_{ii} + \Sigma\, \beta_{ij} x_i x_j + \varepsilon$$

Where Y is the predicted response, β_0 is the constant, β_i the slope or linear effect of the input factor x_i, β_{ij} the linear by linear interaction effect between the input factor x_i and x_j, β_{ij} is the quadratic effect of input factor x_i [16].

3. RESULTS AND DISCUSSION



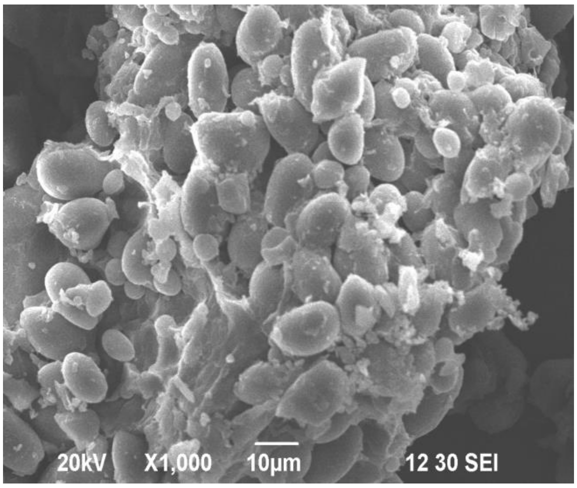


Figure 1 SEM of (a) Before Activation (b) After Activation

3.1Adsorbents Characterization

The SEM micrographs presented in Figure 1 shows the surface texture and porosity of the adsorbent. It is confirmed that the specific surface area of the adsorbent increases after activation of the sample.

3.2Isotherm Investigation

Chemical modification with tartaric acid has enhanced the adsorption efficiency of the *Syzygium cumini* seeds. The adsorption data were tested for their fitness into Langmuir and Freundlich isotherms (Figure 2 & 3). The correlation coefficient, R^2 value for Langmuir model is 0.891 and for Freundlich model is 0.717 that depicts Langmuir model is an appropriate model compared to that of the Freundlich model. It means that monolayer chemisorptions of Acid Red 87-dye occurred on the homogenously distributed active binding sites on the surface of *Syzygium cumini* seeds.

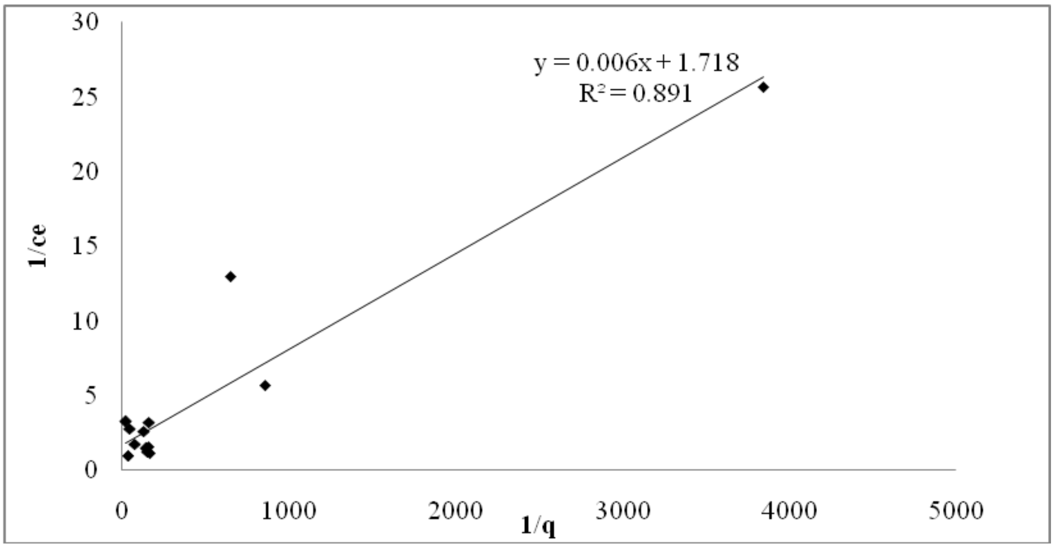


Figure 2 Langmuir isotherm plot

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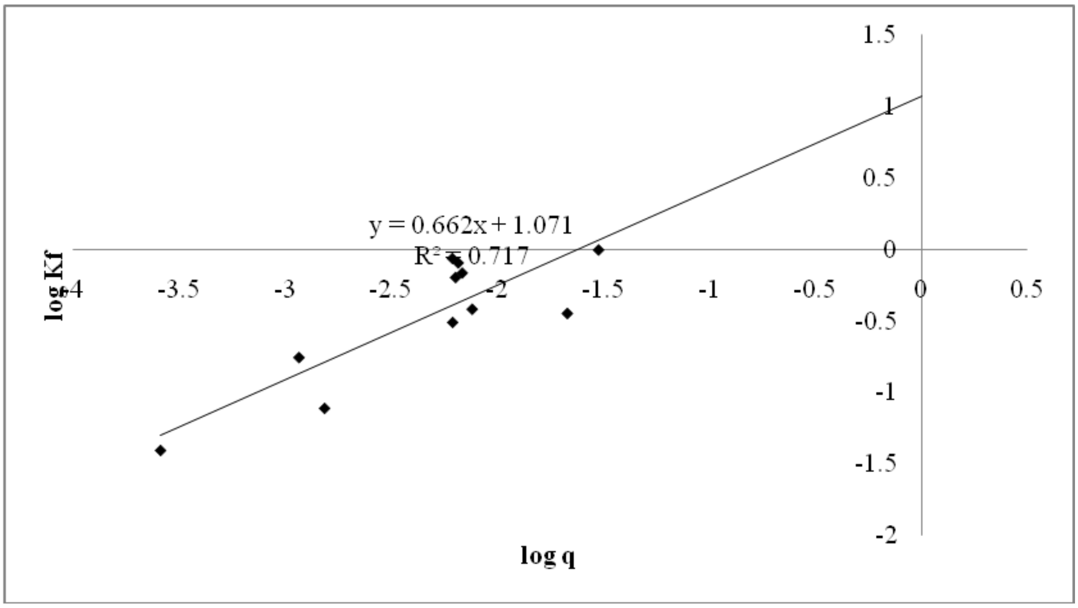

Figure 3 Freundlich isotherm plot

3.3Optimization of Parameters

The removal of Acid red-87 dye was investigated by adsorption method. The effects of process variables such as adsorbent dose, dye concentration and time on the dye removal efficiency were investigated using RSM. Different response functions such as linear, interactive, quadratic and cubic models were used to correlate the experimental data and to obtain the regression equation. To decide about the adequacy of the models to represent dye removal, three different tests namely sequential model sum of squares, lack of fit tests and model summary statistics were carried out in the present study and results are presented. Cubic model was not recommended for this system due to insufficient points to estimate the coefficients for this type of the model. Sequential model sum of squares and model summary statistics indicated that the quadratic model provided the best fit to experimental data with the lowest standard deviation, the highest correlation coefficient, adjusted R^2, predicted R^2 values and the lowest p value. Therefore, the quadratic model was chosen for further analysis.

Experimental data were used for determining of the response function equation coefficients for each independent variable. The response function with the determined coefficients for percent removal Y is presented by Equation

$Y=55.74-1.51X_1-0.39X_2-0.43X_3+5.60X_1X_2+1.29X_1X_3-0.98X_2X_3+10.71X_1^2+10.60X_2^2+25.72X_3^2$

The predicted values of percent removal were determined by the response function with the obtained coefficients. The high value of regression coefficient R^2=09962 indicates that the model predictions fit satisfactorily with the experimental observations.

Table 2: BBD Experimental Design with Coded/actual values for the three independent variables and Acid Red-87 dye removal efficiency.

Run	Adsorbent Dose (g)	Dye concentration(mg/l)	Time(hrs)	Acid Red-87 dye removal efficiency (%)	Predicted Values
1	0(10)	-1(10)	-1(8)	84.654	91.9
2	0(10)	-1(10)	1(24)	70.316	93
3	0(10)	1(30)	-1(8)	72.595	93.08
4	0(10)	1(30)	1(24)	80.675	90.26
5	-1(5)	0(20)	-1(8)	96.764	95.4
6	-1(5)	0(20)	1(24)	91.283	91.96
7	1(15)	0(20)	-1(8)	90.495	89.8
8	1(15)	0(20)	1(24)	90.175	91.52
9	-1(5)	-1(10)	0(16)	90.444	84.55
10	-1(5)	1(30)	0(16)	91.718	72.57
11	1(15)	-1(10)	0(16)	94.387	70.33
12	1(15)	1(30)	0(16)	91.731	80.75
13	0(10)	0(20)	0(16)	55.741	55.74
14	0(10)	0(20)	0(16)	55.741	55.74
15	0(10)	0(20)	0(16)	55.741	55.74
16	0(10)	0(20)	0(16)	55.741	55.74
17	0(10)	0(20)	0(16)	55.741	55.74

Table 3: Sequential Model Sum of Squares [Type I]for Acid red-87 dye removal.

Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**p value Prob>F**	**Remark**
Mean vs Total	1.031E+005	1	1.031E+005			
Linear vs Mean	20.83	3	6.94	0.021	0.9956	
2FI vs Linear	136.16	3	45.39	0.11	0.9518	
Quadratic vs 2FI	4076.66	3	1358.89	591.06	< 0.0001	Suggested
Cubic vs Quadratic	16.09	3	5.36	6.366E+007	< 0.0001	
Residual	0.000	4	0.000			
Total	1.074E+005	17	6315.11			
Lack of Fit Tests						
Linear	4228.92	9	469.88	-	-	-
2FI	4092.76	6	682.13	-	-	-
Quadratic	16.09	3	5.36	-	-	-
Cubic	0.000	0		-	-	-
Pure Error	0.000	4	0.000	-	-	-

The statistical significance of the response function was checked by F-test and the ANOVA results for response surface quadratic model and model terms are summarized in Table 5. The F value and very low probability value 0.0001 indicated that the model was statistically significant and the model equation can adequately be used to describe the dye removal under a wide range of operating conditions. The p values are used to estimate whether F is large enough to indicate statistical significance and used to check the significance of each coefficient. P values lower than 0.05 indicate that the model and model terms are statistically significant [17]. In this case, the model equation and all regression coefficients are significant except for one linear coefficient (X_1) and two cross-product coefficients (X_1X_2 and X_1X_3). Although they are non significant, they are still considered in equation because it is a hierarchical model. Furthermore the study of contour plots and the regression equation highlight certain interactions between the selected parameters as well as their individual effects on dye removal. The analysis showed that the form of the model chosen to explain the relationship between the factors and the response is correct. [18].

Table 4: Model Summary Statistics for Acid dye removal.

Source	**Adjusted Dev.**	**Predicted R-Squared**	**R-Squared**	**R-Squared**	**PRESS**	**Remark**
Linear	18.04	0.0049	-0.2247	-0.5269	6489.13	
2FI	20.23	0.0369	-0.5409	-1.6364	11204.17	
Quadratic	1.52	0.9962	0.9913	0.9394	257.49	Suggested
Cubic	0.000	1.0000	1.0000	+		Aliased

Table 5: ANOVA results for Response Surface Quadratic Model

Source	Sum of Squares	df	Mean Square	F Value	p-Value	Remarks
Model	4233.65	9	470.41	204.61	<0.0001	Significant
A-Time	18.1	1	18.18	7.91	0.0261	
B-Dye Concentration	1.19	1	1.19	0.52	0.4956	
C-Adsorbent Dosage	1.46	1	1.46	0.64	0.4513	
AB	125.64	1	125.64	54.65	0.0002	
AC	6.66	1	6.66	2.90	0.1326	
BC	3.86	1	3.86	1.68	0.2361	
A^2	483.34	1	483.34	210.23	<0.0001	
B^2	473.53	1	473.53	205.97	<0.0001	
C^2	2786.23	1	2786.23	1211.91	<0.0001	
Residual	16.09	7	2.30			
Lack of Fit	16.09	3	5.36			
Pure Error	0.000	4	0.000			
Core Total	4249.7516	16				

The high value of R^2, 0.9962 indicated a high dependence and correlation between the observed and the predicted values of response. The value of adjusted R^2, 0.9913 suggested that the total variation of about 99% for dye removal was attributed to the independent variables and only about 1 % of the total variation cannot be explained by the model. The value of the adequate precision is a measure of the signal (response) to noise (deviation) ratio. A ratio greater than 4 is desirable. In the present study, the ratio was found to be 34.107, which indicates the adequate signal.Therefore the quadratic model can be used for the acid red dye removal by adsorption process [19, 20].

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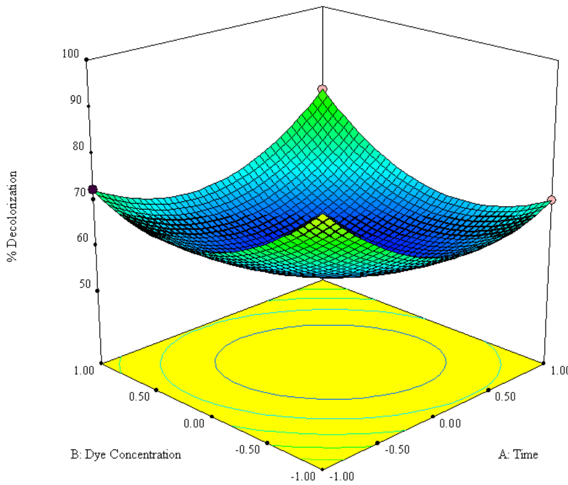

Figure 4 Effect of time and dye concentration on decolourisation of dyes

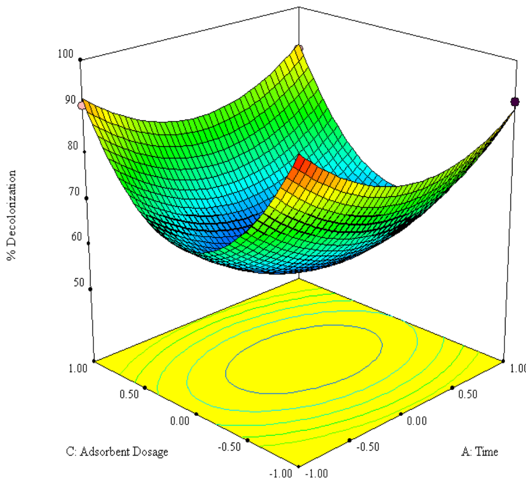

Figure 5 Effect of time and adsorbent dosage on decolourisation of dyes

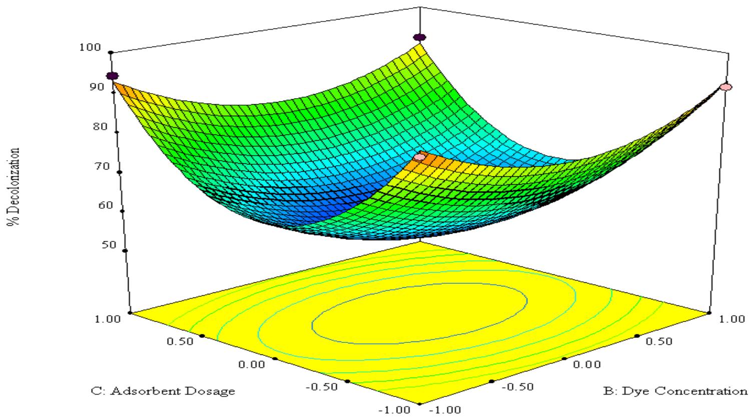

Figure 6 Effect of dye concentration and adsorbent dosage on decolourisation of dyes

3.3.1 Effect of Time, dye concentration and adsorbent dosage on decolourisation of dyes.

The percentage adsorption of Acid red-87 dye with activated adsorbent was studied by pre-selected range of dye concentation,time and adsorbent dosage. The results have been depicted in Figure4-6. The results indicated that maximum adsorption occurs in the ragnge of 16 hours,15g of adsorbent dosage with 10mg/l of dye concentration. The maximum percentage removal is about 94.387%.

CONCLUSION

The Box-Behnken design can be employed to develop mathematical models for predicting Acid Red – 87 removal. The desired removal of Acid Red - 87can be achieved by choosing the predicted conditions using the developed models. Parameters interacting together can be identified in such a typical process like adsorption. The removal is sensitive to the adsorbent concentration in the present study. The value of $R^2 > 0.99$ for the present mathematical model indicates the high correlation between observed and predicted values. The maximum percentage removal is about 94.387%. *Syzygium cumini* seeds can be used as an alternative adsorbent material.

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