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Optimization of Removal Conditions for Basic Red 46 from Aqueous Solutions on Pinecone as an Eco-Friendly Adsorbent

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Abstract: Pinecone removal performance was investigated for Basic Red 46 (BR 46) adsorption and optimal removal conditions were determined with the response surface methodology (RSM). Initial BR 46 concentration (20-60 mg L^{-1}), temperature (298 K-318 K) and contact time (10-180 min) were selected as independent variables and removal percentage of BR 46 values were used as dependent variables. The quadratic model of the response to the independent variables was developed and 3D plots were interpreted as per selected variables. The selected model and terms presenting the $p<0.05$ are significant and they are considered to be statistically significant with the interaction of the initial BR 46 concentration and contact time. Analysis of variance was used to examine the interaction of response with independent variables and the results evidencing that the model regression was acceptable. The reliability of optimization studies was evaluated with R^2, adjusted R^2 and predicted R^2 values which were obtained the 0.9792, 0.9604 and 0.8281, respectively. These determined R^2 values were showed that high relationship between the predicted and calculated removal percentages. The removal percentage of BR 46 was obtained 64.43%, 70.78%, and 74.52% for 60 mg L^{-1} dye concentration at 298 K, 308 K and 318 K, respectively. The optimized conditions with DE program was obtained 55.20 mg L^{-1} initial BR 46 concentration, 151 min contact time and 314 K temperature for 74.15% removal percentage of BR 46.

Keywords: Adsorption, Basic Red 46, pinecone, response surface methodology, optimization, removal percentage

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1. INTRODUCTION

Dyes are used in the many industries such as, chemical, food, automotive, cosmetics, textiles, plastics, rubber, paper and newspapers (Shi et al., 2022; Regti et al., 2017). Over 10,000 types of dyes are used in various productions and applications and they are cause different problems such as environmental pollution and health of people when waters are contaminated with them (Dutta et al., 2021; Mtshatsheni et al., 2019). These problems include the carcinogenic or toxicological diseases with the degradation products of wastewater containing dyes (Bhowmik et al., 2021; Katheresan et al., 2018). It is important to observe the hazard in receiving environments for pollution which are sourced by dye-based wastes. Different methods such as adsorption, oxidation, coagulation, flotation, ion exchange, membrane separation are developed for the removal of dyes from wastewater (Bayram et al., 2021; Ergüt & Özer, 2019; Bouatay et al., 2016). Adsorption is easily applicable with simple design, and cost-effectiveness for wastewater treatment under different conditions (Alipanahpour et al., 2019; De Gisi et al., 2016). Different adsorbents including clays, polymeric and siliceous materials, pumice, biosorbents, plant seeds and shavings are tested and proposed for removal of pollutions (Bensalah et al., 2021; Paredes-Quevedo et al., 2021; Almendros et al., 2015). Researchers are used various natural and low cost adsorbents which are include agricultural wastes for removal of pollutions from wastewater (Kopaç & Sulu, 2019; Yagub et al., 2014; Kul et al., 2023).

Basic dyes have the most harmful and toxic structures (Kopaç & Sulu, 2019; Salleh et al., 2011). Therefore, optimization of removal conditions for a basic dye (BR 46) on pinecone adsorbent was investigated in this study. The results of some studies were reported for the adsorption of BR 46 from wastewater (Alipanahpour et al., 2019; Deniz & Karaman, 2011; Deniz & Saygideger, 2010; Kopaç & Sulu, 2019; Shoushtarian et al., 2020; Paredes-Quevedo et al., 2021; Sarioglu & Bisgin, 2010; Yang et al., 2021). This study was focused on the applied RSM for optimization of the removal conditions of BR 46 adsorption on PCS adsorbent. Central composite design (CCD) which is a part of RSM was used to prediction of the interactions of the independent parameters and the response. Initial BR 46 concentration, contact time and temperature are selected as the independent variables because of they are the most significant parameters in adsorption process and their effects are investigated on the removal percentage which is selected as response (Aldemir et al., 2023; Aldemir et al., 2019).

2. MATERIALS AND METHODS

2.1. Materials

Basic Red 46 (BR 46) was used in the batch adsorption experiments. Chemical formula and molecular weight of BR 46 are $C_{18}H_{21}BrN_6$ and 401.3 g mol^{-1}, respectively. A stock solution was prepared by 1 g of BR 46 dissolved in 1000 mL of distilled water and 20, 30, 40, 50, 60 mg L^{-1} dye solutions were prepared with dilution of stock solution. All chemicals were used without further purification in the experiments.

2.2. Preparation of Pinecone Adsorbent (PCA)

The pinecone adsorbent (PCA) was prepared and used in batch adsorption experiments. Pinecones were collected from *Pinus sylvestris* species which were grown the Van Yüzüncü Yıl University campus. Pinecones were washed and dried at 65 ˚C in an oven for 48 h. After pinecones were crushed, it was ground into powder form and it was separated to dimensions with 230 mesh sieve. Surface morphologies, elemental compositions and characterization analyses of PCA for BR 46 adsorption were reported in the authors' previous paper (Aldemir et al., 2023).

2.3. Adsorption Experiments

The 1000 mL aquoeus solutions of BR 46 were treated with the PCA adsorbent which were realized in a water bath. All experiments were carried out with 1.0 g of adsorbent mass (PCA) and solution pH equal to 5.0 which was determined with the preliminary experiments. BR 46 concentrations in the aqueous solutions were measured for 180 min. The suspensions were centrifuged at 5000 rpm and supernatants were analyzed using a spectrophotometer at 530 nm wavelength. Experiments were carried out in duplicate and averages of the obtained data were used for calculations. Concentrations of BR 46 in solutions were obtained with a calibration curve and the removal percentages of BR 46 were calculated with Eq. (1):

$$Removal\ percentage(\%)=\frac{(C_0-C_e)}{C_0}*100 \quad \text{(Eq. 1)}$$

where C_o, and C_e (mg L^{-1}) represents the initial, and equilibrium concentrations of BR 46. The experimental design of BR 46 adsorption on PCA adsorbent was realized in the selected ranges of initial BR 46 concentrations, process temperature, and contact time for optimization of these parameters with CCD which is a part of RSM.

2.4. Experimental Design Using Response Surface Methodology

In this study CCD which is a part of RSM were designed to trace the impact of experimental factors on the batch adsorption of BR 46 on PCA adsorbent. In RSM effects of the parameters with their interactions on the response as a removal percentage were evaluated. Experimental design was realized with the Design Expert 13 program and it was exhibited the correlation between dependent and independent parameters. The removal percentage of dye expresses as a domain of independent parameters of varying initial BR 46 concentration, contact time, and temperature (Table 1) according to the as mentioned model equation. The effect of these parameters on each other cannot be established with batch mode adsorption studies. Therefore, the optimum conditions as predicted by the batch mode studies might not be the actual optimum conditions. Initial dye concentration, temperature and contact time were identified as the significant parameters from the batch experiments, and a CCD of RSM was used to find the response (removal percentage) considering the effects of each of these parameters along with their mutual effects on each other (Umpuch and Fakthaisongdechakul, 2024). The aim of optimization studies is to supply the optimum adsorption conditions used in the process for desired removal percentages. The application steps of RSM on this removal process are listed as follows;

a) Determine the working limits for adsorption of BR 46 on PCA adsorbent in the aquoeus solutions according to the removal conditions,
b) Prepare the aqueous solutions of BR 46 with the applying values of independent variables which were proposed with experimental design to obtain the response values (%) after experiments,
c) Develop a model for represent the obtained response (removal percentage,%) on the adsorption conditions according to the experimental results,
d) Determine the highest removal values (response) which is a function and to be effected with the experimental conditions of BR 46 adsorption on PCA adsorbent (independent variables).

$$y = f(x_1, x_2, x_3 ....)$$ (Eq. 2)

Experiments were performed with the adsorption conditions (independent variables) for determination of the highest removal values (response) by the Design Expert (DE) program and the optimization results were applied with these parameters to the adsorption process for comparison of the obtained experimental removal percentages. Optimization of the selected operating intervals for the adsorption experiments were realized with CCD, the model equation which represents of relationship the response and the independent parameters was obtained and statistical analyses of outputs were carried out with the DE program. CCD is divided into two important sections which are lower and higher (factorial) values, and central values (middle point of the factorial values). The factorial values represented by +1 and -1, and the central values which are repeated points for predict the error represented by 0 for all parameters. CCD was used DE program to obtain optimum adsorption conditions of BR 46 on PCS adsorbent. The number of experiments were calculated with the formula; $N = 2k + 2^k + 6$ (k, number of variables). Six experiments were carried out at the center points for obtained error and quadratic model is developed which is represented the interaction between the response and independent variables. The quadratic model is shown with Eq. (3);

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{\substack{i=1 \\ j=1}}^{k} \beta_{ij} x_i x_j + err$$ (Eq. 3)

ŷ is the response (removal percentages of BR 46,%), X_i is the variables, k is the number of parameters and β_0, β_i, β_{ii}, β_{ij} are symbolized the fixed, linear, quadratic and interaction coefficients, respectively. The fit of model was determined with R^2 values and statistical importance was investigated with F test which were given by the Design Expert (DE) program after responses implemented. The importance of model using statistical outputs such as coefficient of variation, standard deviation was evaluated by the program (Umpuch and Fakthaisongdechakul, 2024; Ayhan et al., 2024; Ersingün, Aldemir, 2024; Langeroodi et al., 2018; Özbay et al., 2013).

2.5. Optimization Criteria of Removal Percentage for BR 46 on PCA Adsorbent

In this section, the desired removal percentage values of BR 46 adsorption on PCA adsorbent were determined for the selected experimental parameters, initial BR 46 concentration (20-60 mg L^{-1}, X_1), contact time (10-180 min, X_2), and temperature (298 K-318 K, X_3) on the response. The quadratic model which was obtained with CCD results and 3D figures which were showed changes of parameters were obtained with the results and they can characterize the interactions between parameters and estimate the optimum points of processes (Heydari et al., 2023). Statistical outputs of the data were obtained by the DE program, ‘sum of squares’ with ‘lack of fit’ tests were performed and standard deviation, R^2 values were calculated. The model best represent the operated process was determined with ANOVA results (Raj and Krishnan, 2024). The criteria of the selection of model representing the process are given as; model; ‘significant’, lack of fit; ‘insignificant’, model terms; ‘values of ($p<0.05$), regression coefficient (R^2); ‘highest value (~1.0).

After selection the model which is the best represents of process, 3D plots were created with DE program. The optimization results were recommended by this program for selected working range of the independent parameters. In this study the optimization criteria were defined as initial BR 46 concentration (X_1), contact time (X_2), and temperature (X_3) were selected in range and the response (removal percentage of BR 46,%) was selected in range. The selection of the best solution for optimum points which were closed to the desired removal percentage of BR 46 with desirability values closest to 1.0 was chosen. Axial and center points for optimization of independent variables with CCD were given in Table 1. All experiments were realized respectively and obtained responses were implemented to DE program and outputs were evaluated with the ANOVA.

Table 1. Range and levels of the selected process parameters.

Independent parameters	Index	Range -1	and 0	Level +1
Initial dye conc. (mg L^{-1})	X_1	20	40	60
Contact time (min)	X_2	10	95	180
Temperature (K)	X_3	298	308	318

3. RESULTS AND DISCUSSION

The initial BR 46 concentration (20-60 mg L^{-1}, X_1), contact time (10-180 min, X_2), and temperature (298 K-318 K, X_3) were selected independent variables and CCD was applied to optimize these variables in order to removal percentage (RP,%) values of BR 46 adsorption on PCA adsorbent were determined for the response. CCD experiments with obtained removal percentage (RP,%) values as the response are given in Table 2. In order to evaluate the error, twenty experiments were performed for optimization, together with six replications conducted at the center values (zero level). Table 2 represents the experimental design of parameters in coded (-1, 0, +1) and uncoded form, with the obtained response values from experimental studies, calculated response values from model which was derived by the program and error values which were determined with the difference between responses. The removal percentages (%) of BR 46 were determined 61.23, 69.53 and 69.73 at 40 mg L^{-1} initial BR 46 concentration with 95 min adsorption for 298 K, 308 K, and 318 K, respectively. The removal percentages (%) of BR 46 were obtained 45.73, 64.48 and 72.05 at 40 mg L^{-1} initial BR 46 concentration with 308 K adsorption for 10, 95, and 180 min, respectively. The removal percentages (%) of BR 46 were realized 59.65, 69.53 and 69.95 at 308 K temperature with 95 min adsorption for 20, 40, and 60 mg L^{-1} initial BR 46 concentrations, respectively. The researchers were compared to the performance of reactive black 5 (RB 5) removal efficiencies on the gelatin bead, montmorillonite (MMT), surfactant-modified montmorillonite (OMMT), composite bead and they were obtained to 96.31%, 2.67%, 95.62%, and 94.39%, respectively (Umpuch and Fakthaisongdechakul, 2024).

3.1. The Results of ANOVA and 3D Figures of Variables with Response

The results of regression analysis were shown in Table 3. The suggested model performed to have $p < 0.05$ and F value of 52.19 which were showed that model was significant. In this case X_1 (initial dye conc. mg L^{-1}), X_2 (contact time, min), X_3 (process temperature, K), X_1X_2 and X_2^2 are significiant model terms. Values grater than 0.100 indicate the model terms which are X_1X_3, X_2X_3 and X_3^2 are not significiant. According to the results in Table 3, X_1 (initial dye conc. mg L^{-1}) and X_2 (contact time, min) had higher F values and lower p values which were showed that parameters the most effect the response (RP,%). Interactions between the independent variables were investigated and X_1X_2 were appeared to be significant. The F value of lack of fit test is 0.76 which was implied that lack of fit test not significant relative to error. A result of analysis in the change of parameters indicates that selected independent variables are significant and percentage of adsorption is a function of these variables.

Table 2. Experimental and calculated response values of CCD results.

	X1	X2	X3	Y1	Y1	Ɛ
Experiment Number	**X_1: Initial dye (BR 46) conc. (mg L^{-1})**	**X_2: Contact time (min)**	**X_3: Process temperature (K)**	**Obtained response, y_0 (RP,%)**	**Predicted response, y_P (RP,%)**	**Error, (y_0 - y_P)**
1	20(-1)	10(-1)	298(-1)	21.75	23.87	-2.12
2	20(-1)	10(-1)	318(+1)	37.45	36.23	1.22
3	20(-1)	180(+1)	298(-1)	58.44	57.69	0.75
4	60(+1)	10(-1)	318(+1)	54.45	55.45	-1.00
5	40(0)	180(+1)	308(0)	72.05	71.12	0.93
6	40(0)	95(0)	308(0)	64.45	67.32	-2.87
7	40(0)	95(0)	308(0)	64.35	67.32	-2.97
8	60(+1)	180(+1)	298(-1)	64.35	65.83	-1.48
9	40(0)	95(0)	308(0)	64.48	67.32	-2.84
10	40(0)	95(0)	298(-1)	61.23	60.18	1.05
11	20(-1)	180(+1)	318(+1)	64.75	66.81	-2.06
12	40(0)	95(0)	308(0)	69.53	67.32	2.21
13	20(-1)	95(0)	308(0)	59.65	57.45	2.20
14	60(+1)	95(0)	308(0)	69.95	71.13	-1.18
15	60(+1)	180(+1)	318(+1)	74.48	72.62	1.86
16	40(0)	10(-1)	308(0)	45.73	45.63	0.10
17	40(0)	95(0)	308(0)	69.53	67.32	2.21
18	60(+1)	10(-1)	298(-1)	47.22	45.42	1.80
19	40(0)	95(0)	318(+1)	69.73	69.75	-0.02
20	40(0)	95(0)	308(0)	69.53	67.32	2.21

The important outputs of statistical analysis such as coefficient of variation, standard deviation, and R^2 values were given in Table 4. The CV was obtained 4.36%, with the R^2, adjusted R^2 and predicted R^2 values of analyses were determined as 0.9792, 0.9604 and 0.8281, respectively. Predicted R^2 value is in reasonable agreement with adjusted R^2 because of difference between these R^2 values is less than 0.2. The high R^2 values were explained with the regression model provides a good explanation of relationship between response and independent variables. ANOVA results were indicated that model correctness for BR 46 removal on PCS within the experimental range. The coded and real values for the quadratic model that is a function of the selected experimental conditions, initial BR 46 conc. (X_1), contact time (X_2), and temperature (X_3) on removal percentages of BR 46 (RP,%) are given in Eq. (4) and Eq. (5), respectively. It was observed that in these equations initial BR 46 conc. (X_1), contact time (X_2), and temperature (X_3) had positive coefficients which were supplied the increase of the removal percentages of BR 46.

Table 3. ANOVA results of the suggested model for BR 46 adsorption on PCA adsorbent.

Source	**Sum of squares**	**Degree of freedom**	**Mean of squares**	**F value**	**P value**	
Model (Quadratic)	3225.54	9	358.39	52.19	< 0.0001	significant
X_1-Initial dye conc. (mg L^{-1})	467.99	1	467.99	68.16	< 0.0001	
X_2-Contact time (min)	1624.86	1	1624.86	236.63	< 0.0001	
X_3-Process temperature (K)	229.15	1	229.15	33.37	0.0002	
X_1X_2	89.98	1	89.98	13.10	0.0047	
X_1X_3	2.70	1	2.70	0.3936	0.5445	
X_2X_3	5.27	1	5.27	0.7668	0.4018	
X_1^2	25.31	1	25.31	3.69	0.0838	
X_2^2	219.97	1	219.97	32.03	0.0002	
X_3^2	15.23	1	15.23	2.22	0.1672	
Residual	68.67	10	6.87			
Lack of Fit	29.59	5	5.92	0.7573	0.6161	not significant
Pure Error	39.08	5	7.82			
Cor Total	3294.21	19				

Table 4. Statistical values of suggested model for BR 46 adsorption on PCA adsorbent.

Standard deviation	2.62	R^2 value	0.9792
Mean value	60.15	Adjusted R^2 value	0.9604
Coefficient of variation	4.36	Predicted R^2 value	0.8281

Removal percentage (%) = $+67.32 + 6.84*[X_1] + 12.75*[X_2] + 4.79*[X_3] - 3.35*[X_1X_2] - 0.5812*[X_1X_3] - 0.8112*[X_2X_3] - 3.03*[X_1^2] - 8.94*[X_2^2] - 2.35*[X_3^2]$ (Eq. 4)

Removal percentage (%) = $-2435.33545 + 2.03132*[\text{initial concentration}] + 0.758031*[\text{contact time}] + 15.18402*[\text{temperature}] - 0.001973*[\text{initial concentration*contact time}] - 0.002906*[\text{initial concentration*temperature}] - 0.000954*[\text{contact time* temperature}] - 0.007584*[\text{initial concentration}^2] - 0.001238*[\text{contact time}^2] - 0.023536*[\text{temperature}^2]$ (Eq. 5)

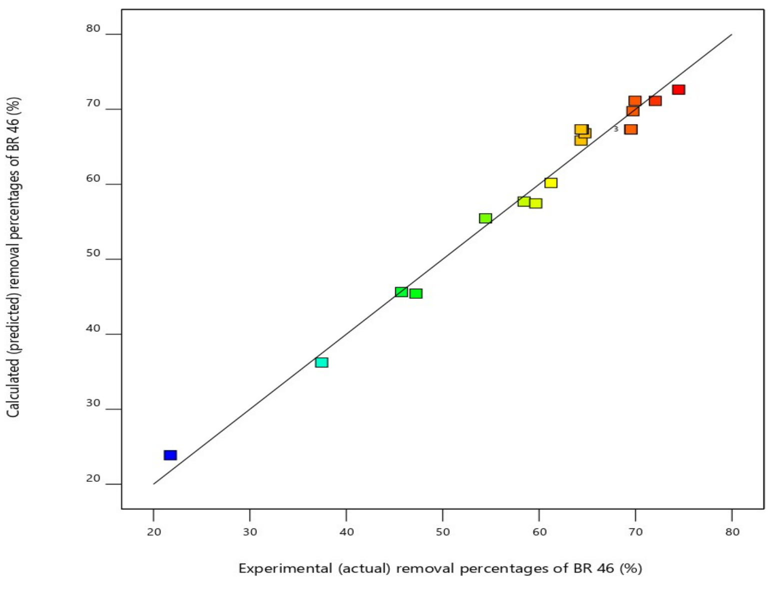

Figure 1. Distribution of calculated against observed removal percentages for BR 46 adsorption.

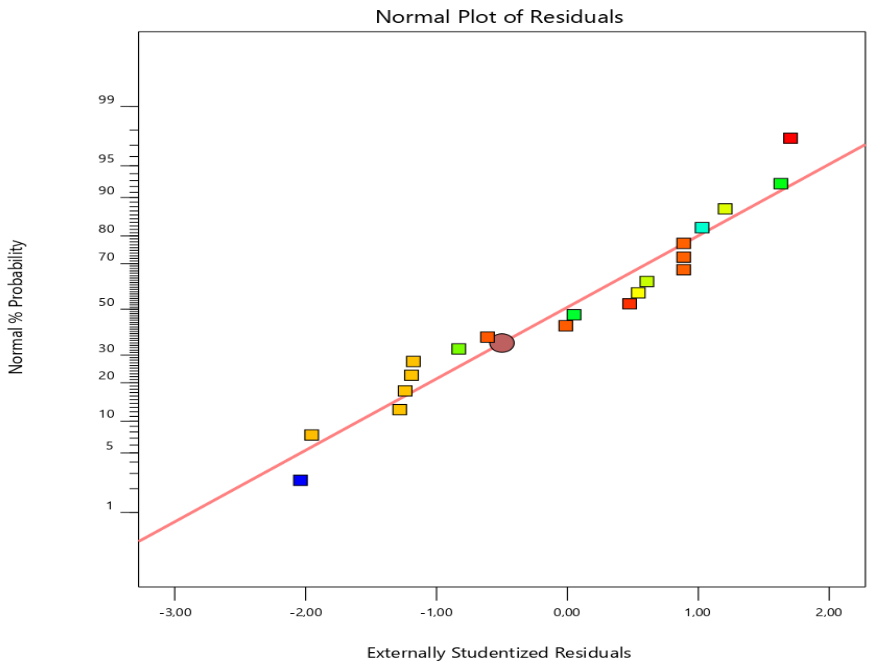

Figure 2. The normal probability plot of removal percentages for BR 46 adsorption.

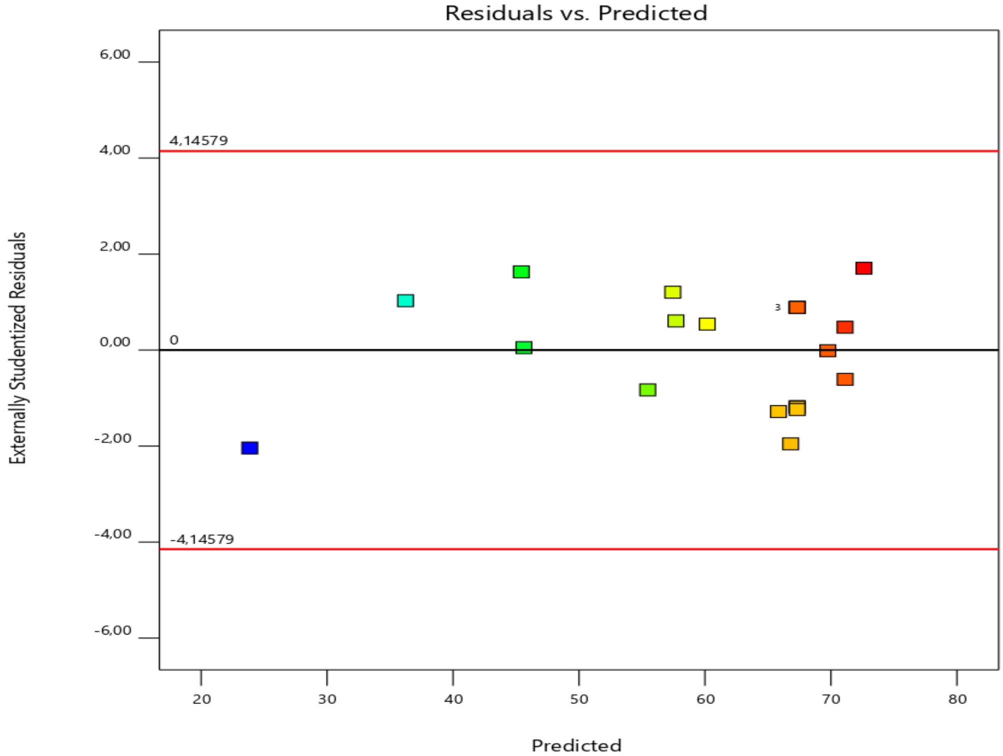

Figure 3. The plot of residuals versus predicted removal percentages for BR 46 adsorption.

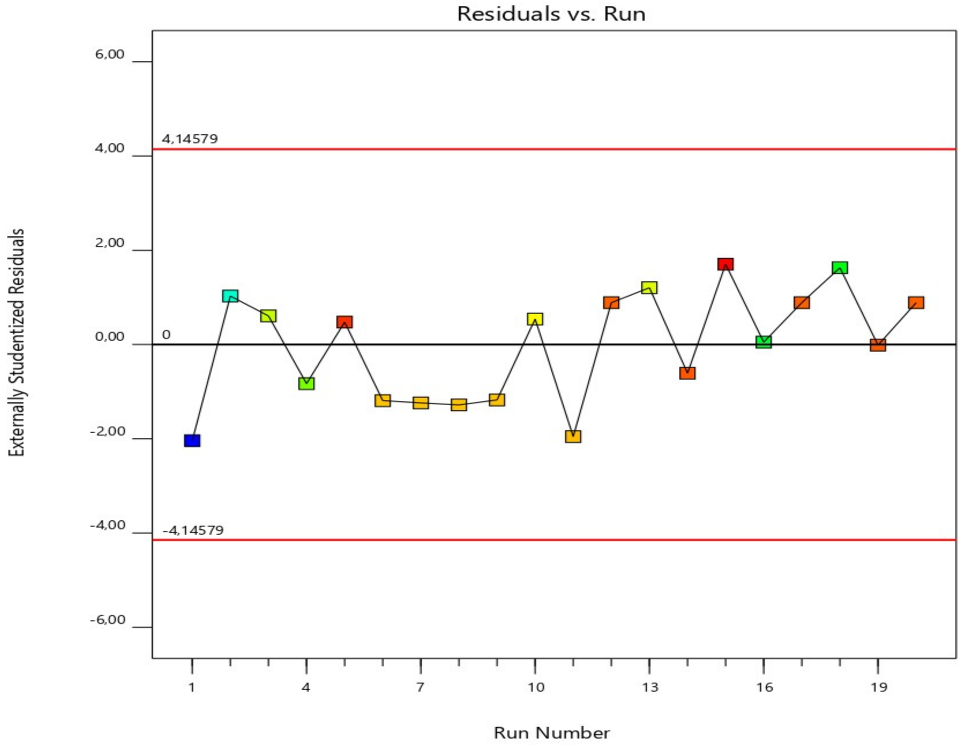

Figure 4. The plot of residuals versus experimental run for BR 46 adsorption.

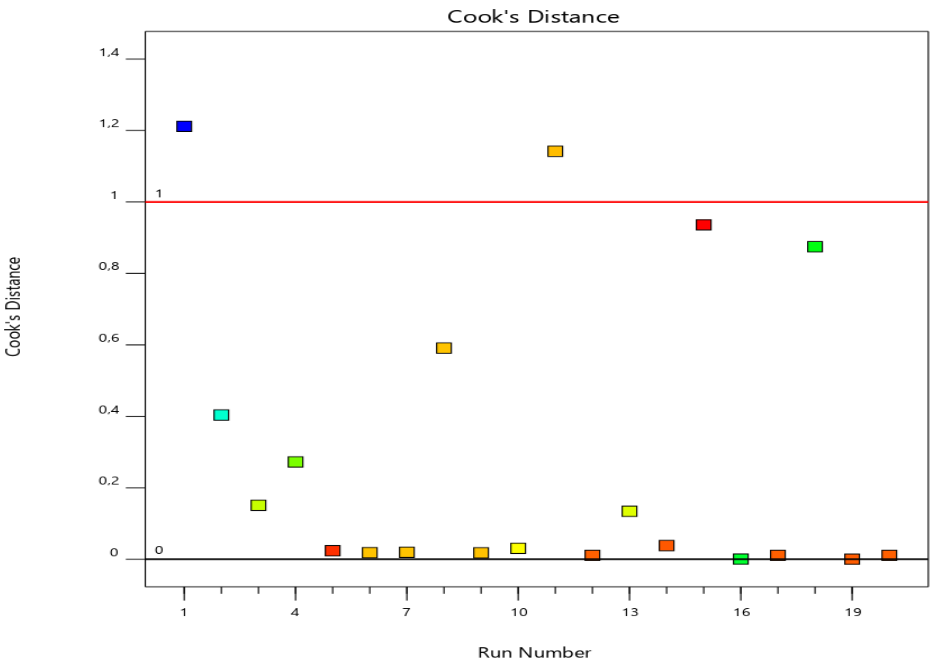

Figure 5. The plot of Cook's distance versus experimental run for BR 46 adsorption.

Plots of the predicted vs. the actual responses, normal probability values, residuals vs. predicted responses, residuals vs. experimental run and Cook's distance were given in Figure 1 – Figure 5, respectively. The correlation between the calculated RP of BR 46 (%) values from the model against the actual RP (%) values of BR 46 adsorption on PCA adsorbent are showed in Figure 1. The RP (%) values calculated from the model and the actual RP of BR 46 (%) values appear to be compatible and their distribution were showed homogeneously around the center line. The normal probability plots which show the expectation of the derived model, measured by the noise of residuals (Raj and Krishnan, 2024). The plot of normal probability versus residuals were shown in Figure 2. The all of points on residuals, the model reliability extends (Nguyen et al., 2022). The residual vs. predicted plot and the residual vs. experimental run plot of the BR 46 dye RP (%) on PCA are shown in Figure 3 and Figure 4, respectively. These plots were depicted a strong relationship between the predicted and the actual values of RP of BR 46 (%), suggesting that obtained data are extremely accurate. The distribution of response values were concentrated at a $p < 0.05$ which were indicated that PCA is an effective adsorbent for adsorption of BR 46, demonstrating good performance in its removal. Figure 5 was showed Cook's distance plot of the RP of BR 46 (%) adsorption by PCA. According to the figure, there were points due to their distribution which was concluded that the developed model by the program is highly represented of the process.

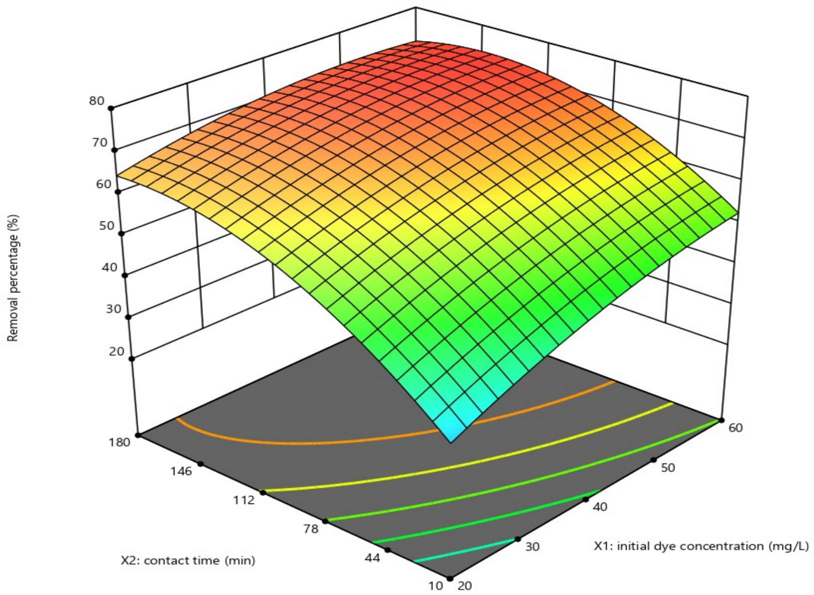

Figure 6. Effect of initial concentration and contact time changes on removal percentage.

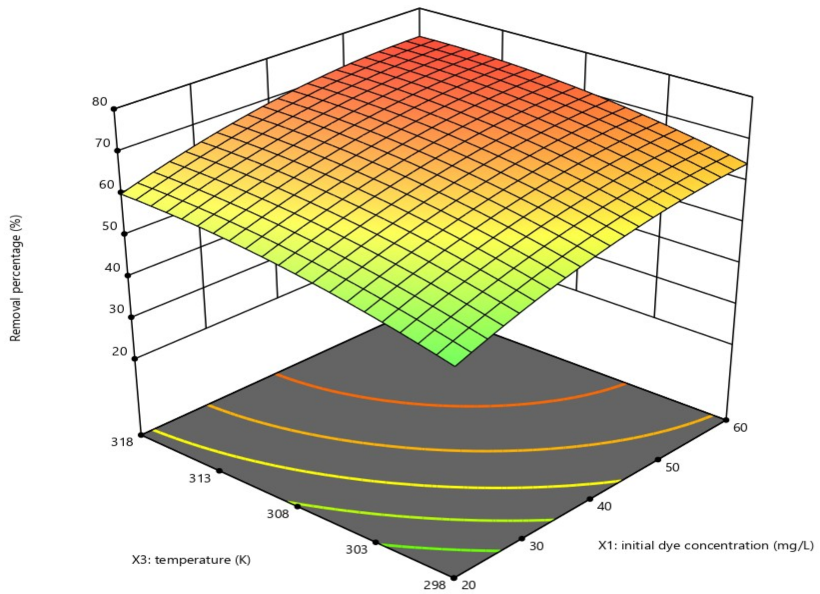

Figure 7. Effect of initial concentration and temperature changes on removal percentage.

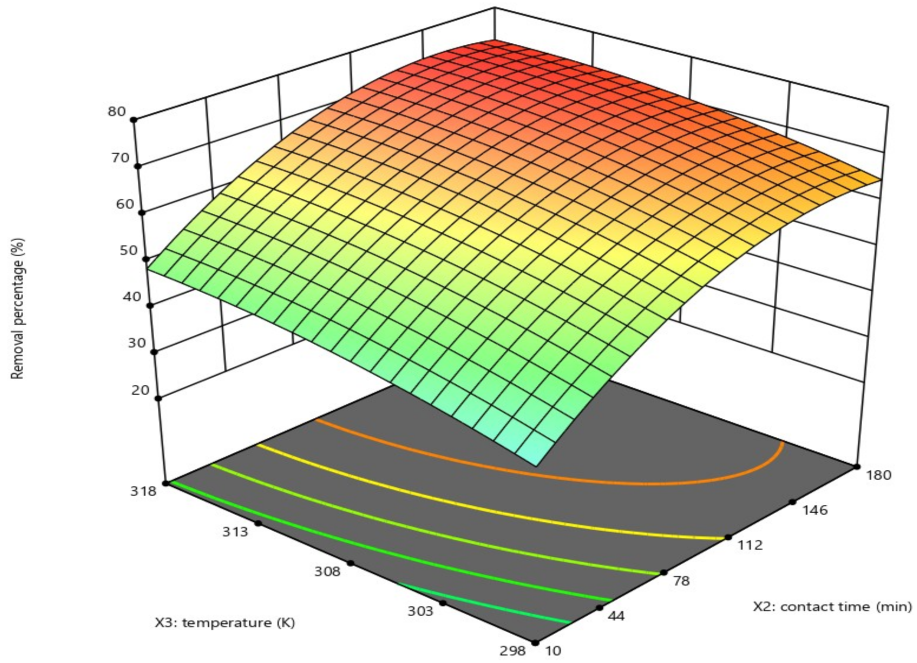

Figure 8. Effect of contact time and temperature changes on removal percentage.

The binary influences of initial BR 46 concentration (X_1, mg L^{-1}), contact time (X_2, min), and process temperature (X_3, K) on removal percentage values (RP,%) of BR 46 are shown between Figure 6 and Figure 8, respectively. The effects of initial dye concentration and contact time on removal percentage of BR 46 (%) adsorption are shown in Figure 6. It can be showed that binary effects of the initial BR 46 concentrations and contact time positively affects the adsorption rate. With increase in initial dye concentration, removal percentages (%) were increased from 21.75 to 47.22, and 37.45 to 54.45 for 298 K and 318 K respectively. With increase in contact time, removal percentages (%) were increased from 21.75 to 58.44 and 47.22 to 64.35 for 20 mg L^{-1} and 60 mg L^{-1} initial BR 46 concentrations, respectively (Figure 6). The effects of initial dye concentration and temperature on the removal percentage of BR 46 (%) adsorption are shown in Figure 7. The removal percentages of BR 46 (%) were increased from 21.75 to 37.45 for 20 mg L^{-1} initial BR 46 concentrations with increased in 298 K and 318 K temperatures, respectively. The effects of contact time and temperature on removal percentage of BR 46 adsorption are shown in Figure 8. It can be observed that binary effects of the contact time and temperature positively affects BR 46 adsorption rate. The removal percentages (%) were increased from 47.22 to 54.45 at 10 min and the response were increased from 64.35 to 74.48 at 180 min for 60 mg L^{-1} initial BR 46 concentrations with increased in 298 K and 318 K temperatures, respectively (Figure 8).

3.2. The Optimization of Experimental Conditions of BR 46 Adsorption on PCA

In the optimization procedure, the operating cost of process is very important. Optimal process operating conditions are required for low cost, maximum outputs, and the desired quality of products. In this study, the optimum values of independent variables (initial dye concentration, contact time, temperature) which were selected parameters of BR 46 adsorption on PCA adsorbent. The lower and the upper limits of independent variables were determined with both the intervals specified in the standards and the preliminary experiments carried out. The lower and upper limit values for the initial dye concentration, contact time and process temperature were obtained as 20 to 60 mg L^{-1}, 10 to 180 min, and 298 K to 318 K, respectively. The calculated removal percentage (%) values of the BR 46 adsorption an PCA adsorbent were processed into the DE program and optimum values of independent variables which were selected as independent variables that would give the best response were determined by the DE program. The 3D figures which were created by DE program were showed that the most influential parameters on removal percentage (%) values were the initial BR 46 concentration and contact time. The optimization criteria explained in the Materials and Method section were processed in the DE program and suggested optimization solution was obtained. The range of independent variables used for the determination of removal percentage of BR 46 were given in Table 5. The suggested optimization conditions by DE program in Table 6 which the solution was arranged to the most appropriate removal percentage of BR 46 values selected as the response. The experiment was carried out at the optimized conditions by DE program and removal percentage (%) of BR 46 was obtained for these conditions which were given in the Table 6. The removal percentage (%) of experimental research for the optimized conditions which were given in the Table 6 was determined as 72.33%. The difference between the calculated and measured removal percentages (%) of BR 46 with DE program solution was obtained as the 2.45%. The difference between removal percentages (%) experimentally measured and recommended by program was less than 3.0%. This result showed that the proposed model sufficiently accurate for represent this removal process (Umpuch and Fakthaisongdechakul, 2024).

Table 5. Optimization criteria for independent variables and their intervals.

Parameters	Index	Variation	Lower Limit	Upper Limit
Initial dye conc. (mg L^{-1})	X_1	in range	20	60
Contact time (min)	X_2	in range	10	180
Temperature (K)	X_3	in range	298	318
Removal percentage (%)	R	maximize	21.75	74.48

Table 6. Optimization solution for variables and calculated response values.

Solution number	**Initial dye conc. (mg L^{-1})**	**Contact time (min)**	**Process temperature (K)**	**Removal percentage (%)**	**Desirability**
1	55.20	151.00	314.00	74.15	1.000

4. CONCLUSION

Pinecone adsorbent (PCA) performance was investigated for BR 46 removal from aqueous solutions. CCD which is a part of RSM was used to determine optimal removal conditions. Initial dye concentration (20-60 mg L^{-1}), temperature (298 K-318 K) and contact time (10-180 min) were selected as independent variables and removal percentage of BR 46 values were used as dependent variables. The quadratic model of the response to the independent variables was developed and 3D plots were interpreted as per selected variables. The both model and it terms presenting the $p < 0.05$ are significant and all model terms are considered to be statistically significant with the interaction of the selected independent variables and percentage of adsorption is a function of these variables. ANOVA was applied to examine the interaction of response with independent parameters and the results evidencing that the model regression was acceptable. The optimization results were analyzed statistically and evaluated with R^2, adjusted R^2 and predicted R^2 values which were found that 0.9792, 0.9604 and 0.8281, respectively. These values were indicated that high relationship between the predicted and calculated removal percentages. The removal percentage of BR 46 was obtained 64.43%, 70.78%, and 74.52% for 60 mg L^{-1} initial concentration at 298 K, 308 K and 318 K, respectively. The optimized conditions with the DE program was obtained 55.20 mg L^{-1} initial BR 46 concentration, 151 min contact time and 314 K temperature for 74.15% removal percentage of BR 46. The experiment was carried out at these optimized conditions by the DE program and removal percentage (%) of BR 46 was determined as 72.33%. The difference between the measured and calculated removal percentages (%) of BR 46 by program solution was obtained as the 2.45% which was less than 3.0%. The result of this study, PCA as a natural adsorbent can be used effectively for removal of pollutions from wastewater.

5 .CONFLICT OF INTEREST

There is no conflict of interest between the authors.

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