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Screening Factors Influencing Adsorption of Methylene Blue Aqueous Solution Onto Immobilized Glycerine Pitch/Sodium Alginate Beads

Amir Asyraf Nasarudin[1], Norzita Ngadi*, Noorhalieza Ali[1], Roshanida A. Rahman[1], Aziatul Niza Sadikin[1], Nor Adha Omar[2]

[1]School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia
[2]Natural Oleochemicals Sdn Bhd, PLO 428, Jalan Besi 1, Kawasan Perindustrian Pasir Gudang, 81700 Pasir Gudang, Johor
[*]Corresponding author. Email: norzita@cheme.utm.my

ABSTRACT
Methylene blue (MB) as a basic dye usually found in coloring usage industries can cause several injuries to human health and body. The current trend of treating MB is by using several wastewater treating techniques and adsorption technology. However, adsorption technology was considered to be efficient in removing MB. The adsorption technology production considering many factors that can influence the efficiency of the adsorbent performance. Identification of significant factors that has substantial contributions to the response for methylene blue (MB) removal in aqueous solution had been investigated using the fractional factorial design. This identification is crucial in minimizing the experimental runs for preparing the glycerin pitch-alginate adsorbent. Five factors involved were glycerin pitch concentration, impregnation time, impregnation temperature, glutaraldehyde volume, and cross-linking time were screened using fractional factorial designs. Based on the results, three factors have contributing effects which were glycerin pitch (0.3%), impregnation time (24 hours) and impregnation temperature ($37^{o}C$) on the removal of MB (89.13%), where the results analyzed statistically using mathematical analysis of fractional factorial designs and analysis of variance (ANOVA). Results obtained indicate that fractional factorial design was a reliable method in screening the preparation method by eliminating the noise in range and factors to produce the adsorbent with the minimal experiment run and steps.

Keywords: *Glycerin pitch, sodium alginate, fractional factorial designs, methylene blue*

1. INTRODUCTION

Water contamination resulting from industrial activities has become severe over the years that threaten human and aquatic life. The rapid and demanding production from textile industries has contributed to the discharge of chemical dyes and pigments without proper treatment [1, 2]. Methylene Blue (MB) is the major contributor to the coloured effluents used in the textile and dye industry. It was categorized as cationic dyes, which are positively charged ions in aqueous solution [3, 4]. MB toxicity is harmful that it can lead to permanent injury to fish and humans such eyes soreness, nausea, diarrhoea, skin irritation and cancer [5-7]. The security of water supply has become serious issues in recent years. Adsorption technologies have emerged as the prevention of water pollution that has been discharged by the industries as effluent. Adsorption technologies have several advantages compared to the other techniques that can overcome the problem of contaminated water. It comprises low cost, simplicity, and high-efficiency adsorbent [8, 9]. Adsorbents have been successfully synthesized with different adsorption capacities and different precursors that are environmentally friendly [10-12].

The synthesis of new adsorbent using glycerol as a sustainable precursor to being impregnated on various polymer materials have been widely studied [13]. Its carbon properties, produced as Activated Carbon (AC) has been trending in treating water contamination. It has several advantages due to its high specific surface area and micropore volume [14]. AC is well known for treating various types of dyes. However, the cost for its synthesis is expensive. The cost was defined by its production process that requires high energy consumption, long activation time, and low adsorption capacity [15, 16]. The production of AC, based on the glycerol synthesis process, has involved chemical activation and high temperature. This process is not environmentally friendly and cost-effective for producing glycerol AC. Another alternative in adsorption technology that can overcome the drawbacks of AC is of high interest to treat water pollution [13].

In adsorption techniques, it involves several surface modification such as grafting, impregnation and cross-linking method [17]. These methods considering several parameters that can enhance the efficiency of adsorbent performance, such as impregnation ratio, pH, temperature, and time [18]. The screening of these factors may increase the adsorption efficiency. Fractional factorial designs can identify the important factors and interaction between the factors [19]. The use of fractional factorial designs may screen the factors that enhancing the adsorption efficiency with the minimum run of the experiment. The impregnation method and cross-linking method has been adopted in this study to enhance the adsorbent performance.

The usage of crosslinker in the chemical surface modifications can enhance the adsorbent performance in certain dye charge [20]. Glycerol cross-link with other biopolymer materials can be done when the polymer materials have a smaller weight ratio compared to the glycerol. The common crosslinker used in cross-linking the biopolymer material and glycerol is the glutaraldehyde [21]. To further enhance the adsorption capability, the implementation of the impregnation method can be used.

The impregnation method involves the surface modification of polymer materials so that the chemical species can be blended inside the pores physically. This method can be categorized wet and dry impregnation. Dry impregnation allows the solvent to be added in a fixed amount to fill in the adsorbent pores. Wet impregnation method involves excess addition of solvent into material pores and then further dried. This method allows for the loading of chemical species can be fixed [17]. Encapsulation of glycerol that contains functional groups into a robust matrix such as sodium alginate beads or hydrogel by wet impregnation method is the current methodology that has been applied in pharmaceutical drugs. Glycerol hypothetically has a large and abundant pore after activation of glycerol in the matrix [23]. The adsorbent has enlarged the pore size and distributions across the adsorbent surface after chemical activation [13, 23]. A molecule of glycerol that consisted of three hydroxyl (-OH) groups and three carbon affect the glycerol adsorption caused by its hydrophobic or hydrophilic properties on its carbon surface [24]. Glycerol is commercially suitable to be used as AC adsorbent for treating multiverse species of the contaminant in the water treatment. Glycerin waste can be converted into AC and surface modified adsorbent to reduce the waste generated by the glycerin refinery plant. The transformation of the glycerin waste into adsorbent would generate economic and environmental benefits [25]. Considering the favourable choice of using organic waste compared to the commercial carbon derived from the wood, glycerin waste can be used in producing AC [26]. Glycerol as adsorbent has been thoroughly studied in recent years, especially on its impregnation or immobilization on different polymer and metal matrix [27]. The removal of specific water contaminants such as MB through adsorption by glycerol in glycerin waste adsorbents can be considered as a high potential and promising low cost adsorbent [25].

The focus of this study is to find the best way of producing glycerin waste adsorbent and find factors that improve the removal of MB. The screening method of this study is to get the best range using fractional factorial designs before proceeding into the optimization process in producing the glycerin waste adsorbent. The adequacy based on regression model can determined the significant factors in this study.

2. EXPERIMENTAL METHODS

2.1. Material and glycerine pitch preparation

The basic dye, MB (chemical formula = C16H18ClN3S.2H2O) was purchased from Qrec (Asia) Sdn. Bhd. The Glycerin Pitch (GP) sampled retrieved from Natural Oleochemical Sdn. Bhd., Malaysia. The samples were conserved under a frozen environment at 4°C to evade biodegradation. For usage, GP was diluted in distilled water with the dilution of 100g GP and 150mL distilled water.

2.2. Sodium alginate beads preparation

Alginate beads were prepared by using sodium alginate (2.78 g) and calcium chloride (1.1 g), sodium alginate was diluted in distilled water until fully dissolved at 50 ^{o}C and stirred at speed 6 using hotplate stirrer. Dissolved sodium alginate was cross-linked with calcium chloride using the titration method at a height of 10 cm using 10 mL pipette tips. Sodium alginate placed in pipette tips and calcium chloride in the beaker. Beads collected in the beaker were stirred slowly at 100 rpm at room temperature for 1 hour. The solution is filtered out and the beads were collected. For constant weight purposes, the beads were dried in the aired oven for 1 hour at 60^{o}C. After dried, the beads were kept in a desiccator to maintain the integrity of beads.

2.3. Batch experimental study

A preliminary study based on the univariate method was conducted to determine suitable ranges of each factor to be used in this screening study. These ranges were determined to be 0.3–0.7% for glycerin pitch concentration, 0.5–24 h for impregnation time, 37^{o}C–90^{o}C for impregnation temperature, 0.1–1 mL for glutaraldehyde volume, and 10– 80 minutes for cross-linking time. An MB stock solution of 100 mg/L was prepared. 100 mL of the MB solution with an initial dye concentration of 50 mg/L was introduced into a 250 mL beaker with a dilution of stock solution. The beaker was then shaken in the incubator shaker at a constant speed of 180 rpm and in certain specific temperature, as pre-determined by the preliminary experiment. The beaker was withdrawn from the incubator shaker after a pre-determined time set. The liquid filtrate after adsorption was measured using the Genesys 10S UV-Vis Spectrophotometer at wavelength 665 nm to determine the absorbance of the dye

(dye concentration). The decolourization of dye concentration is calculated by Equation 1 [19]:

$$q = (Ci-Cf)/Ci \times 100 \quad (1)$$

Where Ci and Cf are the initial and final concentrations of methylene blue solution (mg/l), q is denoted as the removal percentage (%).

2.4. Design of experiment

The screening goal was to maximize the glycerin pitch-alginate beads adsorbent preparation conditions to yield the best sorption of MB from aqueous solution using a 2-level factorial design of Design Expert 7.1.5 software.

2.5. Fractional Factorial design

A fractional factorial design was used in screening the number of experiments. Fractional factorial design with resolution five reveals the importance of factors and lower order interaction which can be benefiting the on the response of the process. A 2-level fractional factorial design (2k-p) with resolution five was proposed to investigate five factors, where k is the number of factors and p is the fraction index. The number of experiments is varied over two-level (low and high) with six replicates at the centre point. The number of experiments needs to be run is 16 runs based on the provided fractional factorial design equations. All of the parameters with the provided levels are shown in Table 1. The experimental results of the design matrix that contained the response are tabulated in Table 2.

Table 1 Influential factors with respecting to a minimum and maximum level

Parameter	Factor	Level	
		Minimum (-)	*Maximum (+)*
GP concentration (%)	A	0.3	0.7
Impregnation time (h)	B	0.5	24.0
Impregnation temperature (^oC)	C	37.0	90.0
Glutaraldehyde volume (mL)	D	0.1	1.0
Crosslinking time (h)	E	10.0	80.0

Table 2 Design matrix for 24 fractional factorial designs with MB removal as a response.

Run	Factor A: GP concentration	Factor B: Impregnation time	Factor C: Impregnation temperature	Factor D: Glutaraldehyde volume	Factor E: Crosslinking time	Response: Removal MB
1	0.30	0.50	37	0.10	80.00	84.05
2	0.70	0.50	37	0.10	10.00	68.22
3	0.30	24.00	37	0.10	10.00	88.51
4	0.70	24.00	37	0.10	80.00	55.14
5	0.30	0.50	90	0.10	10.00	71.55
6	0.70	0.50	90	0.10	80.00	66.37
7	0.30	24.00	90	0.10	80.00	71.10
8	0.70	24.00	90	0.10	10.00	65.67
9	0.30	0.50	37	1.00	10.00	81.42
10	0.70	0.50	37	1.00	80.00	72.34
11	0.30	24.00	37	1.00	80.00	82.82
12	0.70	24.00	37	1.00	10.00	61.45
13	0.30	0.50	90	1.00	80.00	78.71
14	0.70	0.50	90	1.00	10.00	70.62
15	0.30	24.00	90	1.00	10.00	66.62
16	0.70	24.00	90	1.00	80.00	67.47
17	0.50	12.25	64	0.55	45.00	42.55
18	0.50	12.25	64	0.55	45.00	41.11
19	0.50	12.25	64	0.55	45.00	42.55
20	0.50	12.25	64	0.55	45.00	41.11
21	0.50	12.25	64	0.55	45.00	46.01
22	0.50	12.25	64	0.55	45.00	47.18

2.6 Regression Analysis and Model fitting

Fractional factorial designs have two levels for each factor as tabulate in Table 1, where the response is assumed to be quadratic within the factor levels chosen. The regression model response is explained by the regression equation shown in Equation 2, to express the behaviour of the design system from the experimental results.

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3+b_{11}X^2_1+b_{22}X^2_2+b_{33}X^2_3 \quad (2)$$

Y is the response, b_0 is the constant, b_i is the linear coefficient, b_{ii} represents the quadratic coefficient, bij is the interaction coefficient, Xi is the coded variable level, and i or j is the number of independent variables.

Analysis of variance (ANOVA) and the least-squares method was considered in examining the suitability of regression models for fitting the experimental data. The model fitting was calculated based on the of multiple coefficient determinations (R^2), and adjusted statistic coefficient (R^2_{adj}). ANOVA was generally used to evaluate the validity of the models with 95% significant level. The analysis was performed using the Design Expert 7.1.5 software.

3. RESULTS AND DISCUSSION

3.1. Half-normal plots and Pareto charts of MB removal

A 2^4 fractional factorial design run with six replicates at the centre points is to find the essential factors that can affect the removal of MB. The screening of the five factors is carried out to find the best preparation method or preparation formulae and to determine the main properties and their inter-relations.

Pareto chart with standardized effects is capable of verifying the impact on the response of each factor. Pareto chart in Figure 2 used to confirm the experimental results obtained from the half-normal probability plot chart shown in Figure 1. Both charts' vertical line represents the minimum statistic significant effect scale at 5% significant level, while horizontal column lengths are relational to the degree of significance for each effect. Effects or interaction exceeding the vertical line in the Pareto chart considered significant. Results in both figures were in agreement with each other between the half-normal probability plot of standardized effects and Pareto charts.

Based on the results shown in the Pareto chart, glycerin pitch concentration is the most significant factor that has a maximum effect on the removal of MB. The least significant factors in the preparation methods were BC (Figure 2), which is the interaction between impregnation time and impregnation temperature. Based on Figures 1 and 2, the t-value limit was 2.26, where the significant factors passing this line, as shown in Figure 2 were A, AC, DE, C, B, AD, and AB. Impregnation temperature and time were the most significant factors since it was an essential part of preparing the glycerin pitch-alginate beads. Glutaraldehyde volume and cross-linking time is least signified factors due to its contributions to the high swelling of alginate beads and low pore size [28].

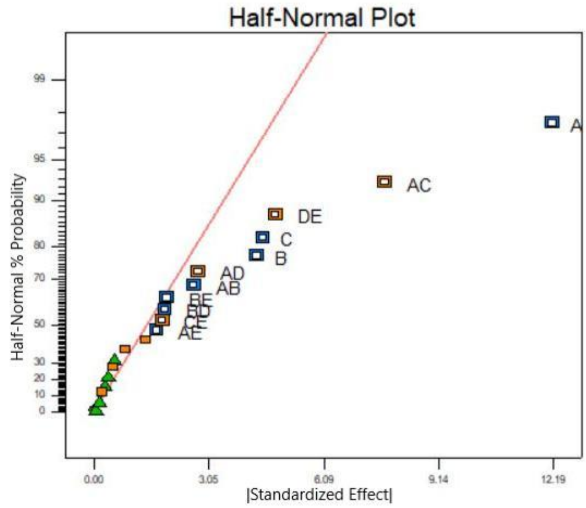

Figure 1 Half-normal plots of standardized effects for MB removal percentage. Error from replicates, positive effects, and negative effects are presented by (▲),(■), and (■). Shapiro- Wilk test with W-value (0.977) and p-value (0.882). Glycerin pitch concentration, impregnation time, impregnation temperature, glutaraldehyde volume, and cross-linking time are presented by A, B, C, D, and E.

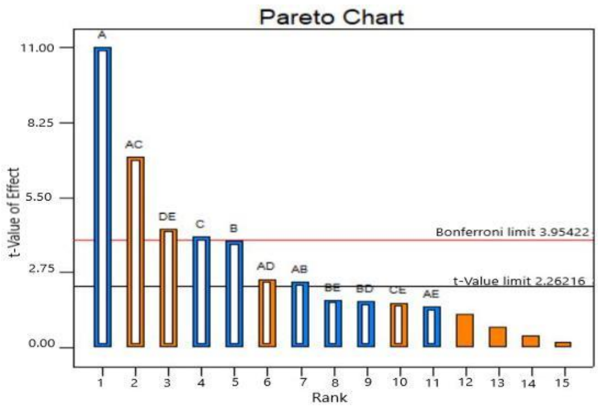

Figure 2 Pareto charts of standardized effects for MB removal. Positive effects and negative effects are presented by (■) and (■). Glycerin pitch concentration, impregnation time, Impregnation temperature, glutaraldehyde volume, and cross-linking time are presented by A, B, C, D, and E.

Glycerin pitch concentration, impregnation time and impregnation temperature have a significant effect on this analysis due to the facts that glycerol in the glycerin pitch can make a bond with the existed alginate OH bonds via inter or intra hydrogen bonding. The concentration of glycerin pitch is essential in increasing the concentration of glycerol existed. Impregnation condition and process is important in making the bond interaction happened between alginate beads and glycerin pitch [23].

3.2. Analysis of variance (ANOVA) for selected factorial model

Table 3 shows the ANOVA model for the removal of MB. The model F-value of 22.05 indicates the model is significant with p-value (Prob>F) less than 0.05, which is <0.0001. A value higher than 0.10 implies the model terms are not significant. The curvature F-value of 726.19 indicates there was substantial curvature in the design space. The lack of fit F-value of 0.42 implies the lack of fit is not substantial relative to the pure error.

Table 4 represents the model's overall statistics for the removal of MB. The "predicted R-Squared" of 0.8166 is in reasonable agreement with the "Adjusted R-Squared" of 0.9205. The coefficient of variation (C.V.) in this model is 3.45, which is low and can be identified as improved precision and reliability of the experiments performed. The signal to noise ratio (adequate precision) value that is higher than four significantly indicates the suitability of factorial models for future prediction.

Table 3 ANOVA for the selected factorial model (MB)

Source	Sum of squares	df	Mean square	F value	p-value (Prob > F)	
Model	1191.41	11	108.31	22.05	< 0.0001	significant
A-Glycerin Pitch concentration	594.00	1	594.00	120.95	< 0.0001	
B-Impregnation time	74.37	1	74.37	15.14	0.0037	
C-Impregnation temperature	80.29	1	80.29	16.35	0.0029	
AB	27.92	1	27.92	5.69	0.0409	
AC	238.84	1	238.84	48.63	< 0.0001	
AD	30.60	1	30.60	6.23	0.0341	
AE	10.93	1	10.93	2.23	0.1700	
BD	13.99	1	13.99	2.85	0.1257	
BE	14.77	1	14.77	3.01	0.1169	
CE	13.00	1	13.00	2.65	0.1382	
DE	92.70	1	92.70	18.88	0.0019	
Curvature	3566.31	1	3566.31	726.19	< 0.0001	significant
Residual	44.20	9	4.91			
Lack of Fit	11.19	4	2.80	0.42	0.7870	not significant
Pure Error	33.01	5	6.60			
Cor Total	4801.92	21				

Table 4 ANOVA for selected factorial model (methylene blue)

Std. Dev.	2.22	R-Squared	0.9642
Mean	64.21	Adj R-Squared	0.9205
C.V. %	3.45	Pred R-Squared	0.8166
PRESS	226.62	Adeq Precision	26.833

Quadratic models in the coding unit, which show a relationship with MB removal for each factor and their interaction is expressed and given in Equation 3. This equation was evaluated and calculated based on the least squared method.

$$\text{Removal of MB} = 72.00-6.09A-2.16B-2.24C-1.32AB+3.86AC+1.38AD-0.83AE-0.94BD-0.96BE+0.90CE+2.41DE \quad (3)$$

3.3 Diagnostics case statistics

Table 5 Case statistics of MB removal.

Std Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Value DFFITS	Cook's Distance
1	84.05	83.96	0.089	0.750	0.080	0.076	0.131	0.001
2	68.22	68.62	-0.40	0.750	-0.364	-0.345	-0.598	0.031
3	88.51	89.13	-0.62	0.750	-0.555	-0.533	-0.923	0.071
4	55.14	55.27	-0.12	0.750	-0.112	-0.105	-0.182	0.003
5	71.55	73.00	-1.44	0.750	-1.301	-1.361	* -2.36	0.391
6	66.37	67.32	-0.95	0.750	-0.857	-0.843	-1.460	0.169
7	71.10	71.84	-0.74	0.750	-0.665	-0.643	-1.114	0.102
8	65.67	66.90	-1.23	0.750	-1.109	-1.125	-1.949	0.284
9	81.42	81.30	0.12	0.750	0.112	0.105	0.182	0.003
10	72.34	71.72	0.62	0.750	0.555	0.533	0.923	0.071
11	82.82	82.42	0.40	0.750	0.364	0.345	0.598	0.031
12	61.45	61.54	-0.089	0.750	-0.080	-0.076	-0.131	0.001
13	78.71	77.48	1.23	0.750	1.109	1.125	1.949	0.284
14	70.62	69.89	0.74	0.750	0.665	0.643	1.114	0.102
15	66.62	65.67	0.95	0.750	0.857	0.843	1.460	0.169
16	67.47	66.03	1.44	0.750	1.301	1.361	* 2.36	0.391
17	42.55	43.42	-0.87	0.167	-0.430	-0.410	-0.183	0.003
18	41.11	43.42	-2.31	0.167	-1.140	-1.162	-0.519	0.020
19	42.55	43.42	-0.87	0.167	-0.430	-0.410	-0.183	0.003
20	41.11	43.42	-2.31	0.167	-1.140	-1.162	-0.519	0.020
21	46.01	43.42	2.59	0.167	1.280	1.334	0.597	0.025
22	47.18	43.42	3.76	0.167	1.860	2.235	1.000	0.053

* Exceeds limits

The difference between predicted and actual value varies between 0.1% to 8.3%, showing that there was a small error of less than 10% on average compared to the model predictions. Based on Table 5, Cook's distance generally <1. Standard order 1, 4, 9, 12, 17, and 19 gives a strong influence on the model predictions efficiency. The externally studentized residuals were used to check the outlier's large values, to keep them within a small value. DFFITS is an idea that depicts how a point influences the regression or changes the anticipated incentive for a point that is out of the regression. As appeared in Table 5, all tests are inside the predefined run except standard orders 5 and 6. The model has a decent capacity to measure them, where the DFFITS limit was ± 2.

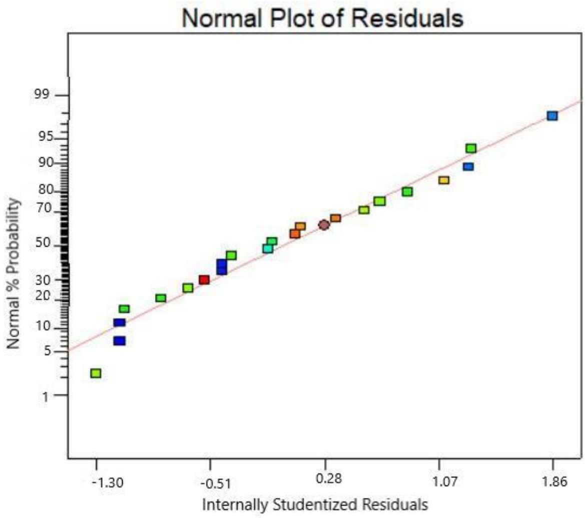

Figure 3 Normal plot of residuals for MB removal

Normal probability against internally studentized residuals variation has developed the model for removal of MB. Identifying outliers and variations of the data errors for different data points using studentification was one of the simple methods. These methods can assess the deviation of the data [29]. Datapoint that can fit the line as shown in Figure 3 shows that the model arguably has less noise and outliers in the model. A model's consistency was evaluated using internally studentized residuals versus normal likelihood. The outcome of this study may complement the experimental data because this is the first stage of the screening assessment [30]. Hence, it can be resolved that this model assumption is correct and reliable.

3.4 Point prediction of maximum MB removal

The point prediction for this model has concluded that the best settings for the experiment were at point 0.3% glycerin pitch, 24 hours impregnation time and 37^{O}C impregnation temperature with the removal of MB at 89.128% and desirability of 1. The result was obtained after the confirmation of the model and its reliability through R-squared. The point prediction from this result can be used as the range in the Box Behnken for Response Surface Method (RSM), where the point prediction would be the midpoint of the range. The range with 50% difference uses a range of glycerin pitch (0.1%-0.5%), impregnation temperature (18.5^{o}C-56^{o}C) and impregnation time (12-36 hour).

The standard error of the mean (SE Mean) is the standard deviation between the samples. It also shows the accuracy of the average estimate of a sample taken, where a smaller value of sample means it is good. The results in this table were considered good, with a small value of 1.9. The value was insignificant compared to the standard error prediction. The value of 95% confidence level (CI) was considered a true value with 84.84% and 93.42% and prediction intervals (PI) with 82.53% and 95.73% at the low and high response. The value was tabulated in Table 6.

Table 6 Response SE Mean, CI and PI.

Response	Prediction	SE Mean	95% CI low	95% CI high	SE Pred	95% PI low	95% PI high
Removal MB	89.1275	1.90	84.84	93.42	2.92	82.53	95.73

4. CONCLUSION

There were five factors considered in this study, which were glycerin pitch concentration, impregnation time, impregnation temperature, glutaraldehyde volume, and cross-linking time with the response of MB removal. The factors screened using 24 fractional factorial designs, and the results show that the main factors identified as (glycerin pitch concentration, impregnation time, and impregnation temperature) have significant contributions to the increase the MB removal. The development of the regression model for MB removal showed R-squared and prediction R-squared values of 0.9642 and 0.8166. The results of this study successfully proving that the fractional factorial design is a reliable method to evaluate the effect of factors that influence the glycerine pitch adsorbents process. The adequacy results from the regression models able to minimize the run to be used in the optimization process.

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