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Determination of the Optimum Composition of Chitosan-Grafted Cellulose/TiO_2 Films Using the Box Behnken Design Method

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Abstract. Determination of the optimum composition of chitosan-grafted cellulose/TiO_2 film was performed using the Box-Behnken Design method from Response Surface Methodology (RSM). Apart from being able to determine the best composition for a composite, this method can also determine the influencing factors of the composition on the performance of the composite. This method was conducted by combining factorial group design. This design used three factors and three levels. Adsorption capacity data from the adsorption process and percent removal from the photocatalyst process were used as responses in determining the optimum composition of chitosan-grafted cellulose/TiO_2 films. Based on the results, the counterplot of grafted cellulose vs TiO_2 shows that both variables have the same influence, where the more grafted cellulose and TiO_2 added to the composite, the more adsorption capacity of the chitosan-grafted cellulose/TiO_2 film. The results from determining the composition, obtained the best composition, namely chitosan; grafted cellulose; TiO_2 each of 0.85; 0.2; 0.2 g.

Introductions

In the fabrication of adsorbents, the applications of biopolymers for reducing water pollution were a fascinating issue [1]. According to Chen et al. (2019) and Rafiee & Rezaie Karder (2020), chitosan is a very common biopolymer used in coagulation, precipitation, flocculation, filtering, adsorption, and membrane production processes [2, 3]. Chitosan is a useful biosorbent for resolving aquatic environmental contamination because of its advantages. In comparison to commercial activated carbon, chitosan has a stronger ability to bind or interact with contaminants, particularly dyes and heavy metal ions [4]. Due to its protolytic nature, chitosan still performs poorly as an adsorbent for cationic contaminants at acidic pH levels below pKa (6.2) [5]. In addition, chitosan's mechanical characteristics still need to be improved in order for it to be used more effectively.

According to Chen et al. (2019), chitosan modification increased tensile strength by 230% [6]. Additionally, it was noted that modifying chitosan with TiO_2 efficiently decreased the dye concentration by 34% after 30 hours [7]. Excellent photocatalytic abilities can be found in TiO_2. TiO_2 has been extensively developed as a photocatalyst with a large surface area and high porosity for the treatment of wastewater [8]. Through the adsorption-photodegradation process, the features of chitosan and the properties of TiO_2 can be combined to produce multifunctional composites with high photocatalytic capabilities and biocompatibility that exhibit good multifunctional activity [9].

To produce composites with optimum composition and to know the factors influencing of the composition, we use the Box-Behnken design method to determine the composition of the the chitosan-grafted cellulose/TiO_2 composite. The software Minitab 18 was utilized to perform this composition optimization.

Materials and Methods

Materials

In this study, grafted cellulose (obtained from previous study [10]), chitosan (obtained from Tokyo Chemical Industry Co., Ltd., Japan, deacetylated to a level of 75.0-85.0%, 200-600 mPas and 1526.464 g/mol molecular weight), distilled water, methylene blue, TiO_2 and glacial acetic acid were purchased from Merck in Germany.

Methods

Design to formulate chitosan-grafted cellulose/TiO_2 films

Chitosan was dissolved in 100 mL of 2% acetic acid and stirred at a speed of 250 rpm for two hours using a magnetic stirrer. Grafted cellulose was added and mixed again for two hours after the mixture was homogenous. The mixture was eventually added with distilled water-dispersed TiO_2 and mixed for another two hours. It was then put onto a 17 x 12 cm film printer and dried for 48 hours in a 40°C oven. RSM technique along with Box-Behnken creation is used in the production of the chitosan-grafted cellulose film. This design makes use of the Minitab 18 program, which has three levels: low, medium, and high. Table 1**,** shows the components of chitosan, grafted cellulose, and TiO_2.

Table 1. Design variations in the composition of chitosan, grafted cellulose and TiO_2

Run	Chitosan	Grafted cellulose	TiO_2
1	0.8	0.05	0.1
2	0.9	0.05	0.1
3	0.8	0.2	0.1
4	0.9	0.2	0.1
5	0.8	0.1	0.05
6	0.9	0.1	0.05
7	0.8	0.1	0.2
8	0.9	0.1	0.2
9	0.85	0.05	0.05
10	0.85	0.2	0.05
11	0.85	0.05	0.2
12	0.85	0.2	0.2
13	0.85	0.1	0.1
14	0.85	0.1	0.1
15	0.85	0.1	0.1

Table 2. Design level for preparing chitosan-grafted cellulose/TiO_2 films

Factor(x)	Parameter	Level		
		low	medium	high
x_1	chitosan(g)	0.8	0.85	0.9
x_2	Grafted cellulose(g)	0.05	0.1	0.2
x_3	TiO_2 (g)	0.05	0.1	0.2

Determination of the optimum composition of chitosan-grafted cellulose/TiO_2 film.

Determination of the optimum composition of chitosan-grafted cellulose/TiO_2 film was carried out using the Box-Behnken Design method from RSM. This method is carried out by combining factorial group design [11]. This design uses three factors and three levels. Adsorption capacity data from the adsorption process and percent removal from the photocatalyst process are used as responses in determining the optimum composition of chitosan-grafted cellulose/TiO_2 films. To obtain this data, the following stages were carried out.

A total of 0.1 gram of chitosan-grafted cellulose/TiO_2 film with the composition as in Table 1 which had been cut into 1x1 cm pieces was put into 20 mL of 30 ppm methylene blue solution in a 250 mL

Erlenmeyer. Next, stir using a shaker for 60 minutes at a speed of 250 rpm. The resulting filtrate was then measured for absorbance using a UV-Vis spectrophotometer with a maximum wavelength. Next, the final concentration of the solution is calculated using a linear regression equation on the resulting calibration curve. The above procedure was repeated again with a different methylene blue removal process treatment, namely by using a UV lamp at a wavelength of 254 nm to calculate the percent removal of methylene blue.

Results and Discussions

Optimum Composition of Chitosan-Grafted Cellulose/TiO_2 Film on MB Adsorption Capacity

Determination of the optimum composition of chitosan-grafted cellulose/TiO_2 films using the Box Behnken Design method by entering data on the adsorption capacity (Qe) of each film that has been tested for its adsorption capacity of MB. The data can be seen in the Table 3. Adsorption capacity and percent removal were obtained using equation (1) and (2).

Table 3. Data on adsorption capacity and percent removal for each composite

Run	Qe (mg/g)	%R
1	6.5816	73.42%
2	5.6941	70.90%
3	6.3106	78.76%
4	6.5134	79.14%
5	6.0253	70.78%
6	5.9001	67.95%
7	6.5404	83.28%
8	5.8542	82.71%
9	6.1568	75.04%
10	6.3486	74.78%
11	5.6481	87.32%
12	6.7892	90.65%
13	6.2678	78.47%
14	6.2678	78.17%
15	6.2535	79.73%

$$Qe = \frac{(C_0 - C_t)}{W}\ x\ V \qquad \text{(e.q. 1)}$$

$$\%R = \frac{(C_0 - C_t)}{C_0}\ x\ 100\ \% \qquad \text{(e.q. 2)}$$

Where C_o, C_t, W, and V correspond for the initial adsorbate concentration (mg/mL). adsorbate concentration at t time (mg/L), adsorbate mass (g), and solution volume (L), respectively.

Response surface design analysis in this study used Minitab 18 software with 3 factors (x) in 3 levels to produce 15 runs as shown in Table 1. In this method, there are three statistical design models, namely linear, square, and 2-way interaction. The 2-way interaction and linear models have a P-Value value that is closer to zero than the square model, which is 0.021. Slight difference with the linear model which has a P-Value of 0.024. This value indicates that the model is significant [12].
Factors that are significant in the adsorption capacity of MB are the amount (w) of chitosan, grafted cellulose, chitosan-grafted cellulose and grafted cellulose-TiO_2, each of which has a P-Value of less than 0.050. Based on the lowest P-Value value for significant factors, grafted cellulose had a better contribution to MB adsorption capacity. Table 4 is an ANOVA analysis in this study.

Table 4. ANOVA analysis of the adsorption capacity response to MB on chitosan-grafted cellulose/TiO_2 films

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1.43926	0.159917	6.79	0.024
Linear	3	0.74508	0.248361	10.54	0.013
Chitosan	1	0.28125	0.281250	11.94	0.018
grafted cellulose	1	0.44462	0.444625	18.88	0.007
TiO2	1	0.01921	0.019208	0.82	0.408
Square	3	0.09259	0.030864	1.31	0.368
Chitosan*Chitosan	1	0.01796	0.017963	0.76	0.422
*grafted cellulose*grafted cellulose*	1	0.02498	0.024979	1.06	0.350
TiO2*TiO2	1	0.04488	0.044880	1.91	0.226
2-Way Interaction	3	0.60158	0.200527	8.51	0.021
Chitosan**grafted cellulose*	1	0.29812	0.298116	12.66	0.016
Chitosan*TiO2	1	0.07784	0.077841	3.30	0.129
*grafted cellulose**TiO2	1	0.22562	0.225625	9.58	0.027
Error	5	0.11778	0.023556		
Lack-of-Fit	3	0.11770	0.039233	1005.99	0.001
Pure Error	2	0.00008	0.000039		
Total	14	1.55704			

Table 5. Statistical value of the adsorption capacity response to MB on chitosan-grafted cellulose/TiO_2 films

S	R-sq	R-sq(adj)	R-sq(pred)
0.153479	92.44%	78.82%	0.00%

Based on these results, a regression of 92.44% was obtained which can be seen in Table 5. A regression value above 70% is considered quite good. The higher the regression value, the higher the contribution and role of factor (x) to the response (y). The relationship between adsorption capacity and factor (x) based on the coefficient value can be seen in the 3D graph in Figure 1**.**

The Figure 1 on the counter plot of chitosan vs grafted cellulose shows the results that the more grafted cellulose added, the better the effect on the composite adsorption capacity of MB. Chitosan, which acts as a matrix in making this composite, actually has a poor adsorption capacity for MB if the weight is too excessive. This can also be seen from the surface graph of the relationship between chitosan and grafted cellulose. Where, the darker (dense) the green color on the plot indicates the better the response. Meanwhile, the darker (deeper) the blue color on the plot indicates the smaller the influence of the variable on the response.

The Figure 1 on the counter plot of grafted cellulose vs TiO_2 shows that the two variables have the same influence, where the more grafted cellulose and TiO_2 added to the composite, the more it will influence the composite's adsorption capacity on MB. This is because these two variables have active groups which play a role in the adsorption process of cationic dyes such as MB. It can be seen in the surface graph of the relationship between grafted cellulose and TiO_2 that the darker green the color, the better the response produced.

The figure 1 on the counter plot of chitosan vs TiO_2 shows that the more TiO_2 added, the better the effect on the adsorption capacity of the composite on MB. However, as above, the more chitosan added, the lower the effect on the composite absorption capacity on MB.

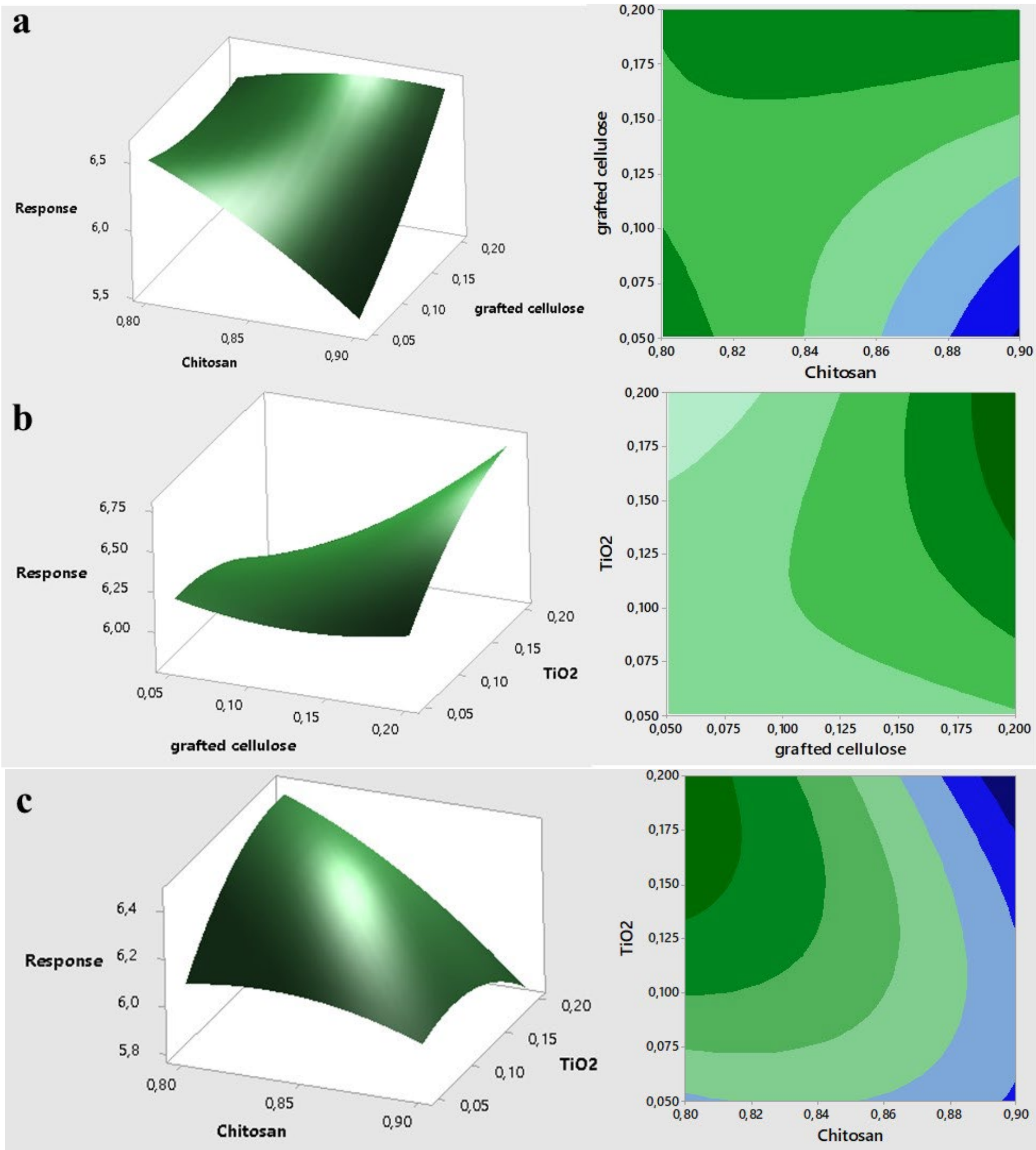

Fig. 1. 3D graphs and surface graphs of the relationship between (a) chitosan and grafted cellulose on adsorption capacity, (b) grafted cellulose and TiO_2 on adsorption capacity, (c) chitosan and TiO_2 on adsorption capacity.

The optimization results using this method provide 1 optimum composition solution for the chitosan-grafted cellulose/TiO_2 film based on its adsorption capacity for MB which is shown in Figure 2. Based on this result, it can be seen that the solution in the optimum composition of the composite is chitosan; grafted cellulose; TiO_2 of 0.83; 0.2; 0.2 g. These results can be used as a reference for preparing chitosan-grafted cellulose/TiO_2 films because they have a fairly good desirability value of 0.979

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Fig. 2. Solution for the optimum composition of chitosan-grafted cellulose/TiO_2 film on the MB adsorption capacity of the Behnken Design Box.

Optimum composition of chitosan-grafted cellulose/TiO_2 film for percent removal of MB

Determination of the optimum composition of chitosan-grafted cellulose/TiO_2 film on the percent removal of MB was also carried out to see whether the influence of the composition was different from the influence of the composition on the adsorption capacity of the composite. Based on the results obtained, it turns out that the influence factor of the optimum composition of chitosan-grafted cellulose/TiO_2 film on the percent removal of MB is different from that on the MB adsorption capacity. The percent removal value is obtained from the adsorption-photodegration process which is carried out by adding 254 nm UV light to the process. The data obtained can be seen in Table 5.

The linear and square models have P-Value values that are close to zero, namely 0.002 and 0.012. This value indicates that the model is significant [11]. Factors that are significant in the percent removal of MB are TiO_2, chitosan, and grafted cellulose, each of which has a P-Value of less than 0.050. Based on the lowest P-Value value on significant factors, TiO_2 has a much better contribution to percent MB removal. Based on these results, a regression of 97.16% was obtained which can be seen in Table 6. The relationship between percent removal and factor (x) based on the coefficient value can be seen in the 3D graph in Figure 3.

The Figure 3 on the counterplot of chitosan vs TiO_2 shows that the amount of chitosan in the area of 0.82-0.88 grams has a good influence on the percent removal of MB in chitosan-grafted cellulose/TiO_2 films. When the amount of chitosan added exceeds the dark green area, the effect on percent removal decreases. Meanwhile, with TiO_2, the more it is added, the more the effect on percent removal increases. This is because TiO_2 functions as a photocatalyst in chitosan-grafted cellulose/TiO_2 films, so in the photodegradation process with the help of UV light, the percentage of MB removal increases [13].

The Figure 3 on the counterplot of grafted cellulose vs TiO_2 shows that the two variables have the same influence, where the more grafted cellulose and TiO_2 added to the composite, the more it will influence the present MB removal. It can be seen in the surface graph of the relationship between grafted cellulose and TiO_2 that the darker green the color, the better the response produced.

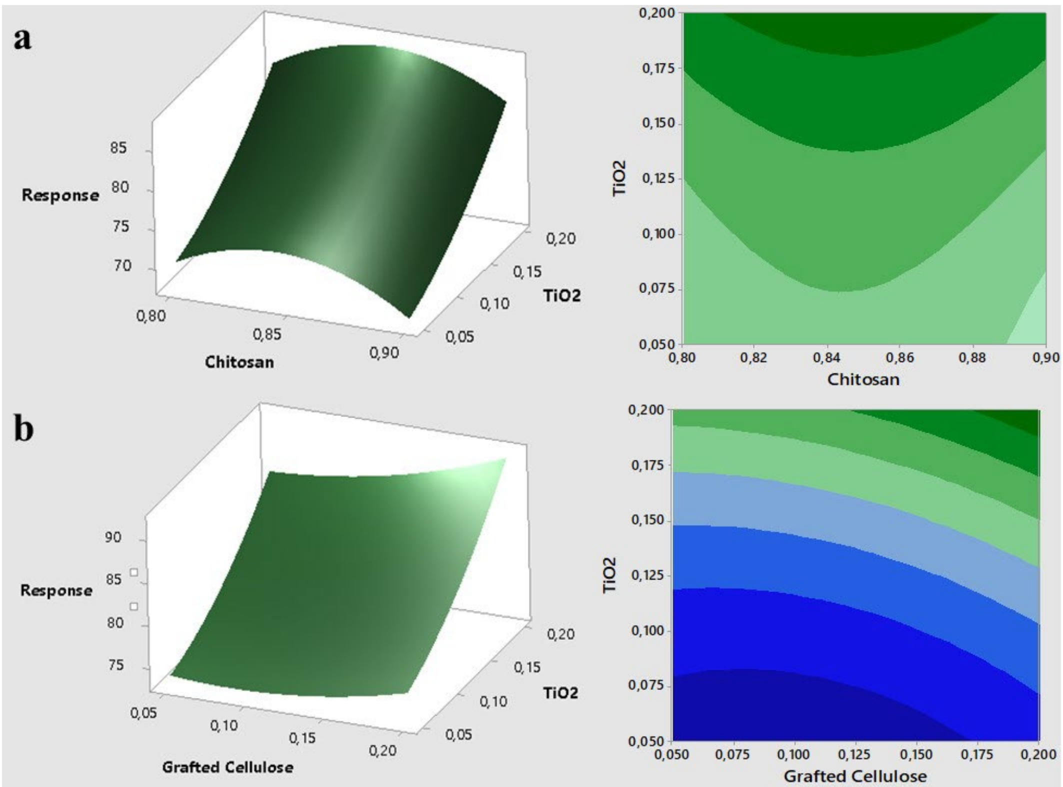
The Figure 3 on the counterplot of chitosan vs grafted cellulose shows that the greater the amount of grafted cellulose added, the better the effect on the present removal of MB in the adsorption-photodegradation process. However, as above, if the amount of chitosan added exceeds the limit in the dark green area, it will reduce the effect on the present removal.

Table 6. ANOVA analysis of the percent removal response of MB on chitosan-grafted cellulose/TiO_2 films.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	530.159	58.907	19.03	0.002
Linear	3	422.273	140.758	45.48	0.000
Chitosan	1	3.836	3.836	1.24	0.316
Grafted cellulose	1	34.653	34.653	11.20	0.020
TiO2	1	383.784	383.784	124.00	0.000
Square	3	101.284	33.761	10.91	0.012
Chitosan*Chitosan	1	74.811	74.811	24.17	0.004
*Grafted cellulose*Grafted cellulose*	1	5.920	5.920	1.91	0.225
TiO2*TiO2	1	13.207	13.207	4.27	0.094
2-Way Interaction	3	6.601	2.200	0.71	0.586
Chitosan**Grafted cellulose*	1	2.102	2.102	0.68	0.447
Chitosan*TiO2	1	1.277	1.277	0.41	0.549
*Grafted cellulose**TiO2	1	3.222	3.222	1.04	0.354
Error	5	15.475	3.095		
Lack-of-Fit	3	14.105	4.702	6.86	0.130
Pure Error	2	1.370	0.685		
Total	14	545.634			

Table 7. Statistical value of the percent removal response of MB on chitosan-grafted cellulose/TiO_2 films.

S	R-sq	R-sq(adj)	R-sq(pred)
1.75928	97.16%	92.06%	58.07%



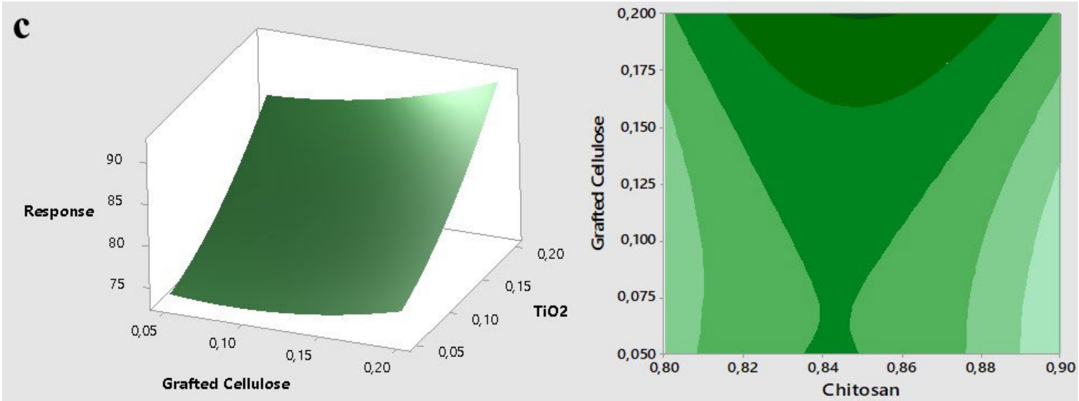


Fig. 3. 3D graph and surface graph of the relationship between (a) chitosan and TiO_2 to percent removal, (b) grafted cellulose and TiO_2 to percent removal, (c) chitosan and grafted cellulose to percent removal.

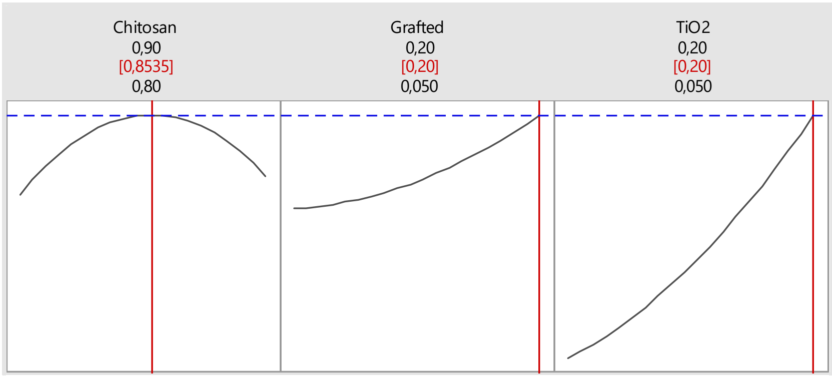


Fig. 4. Optimum composition solution for chitosan-grafted cellulose/TiO_2 film for percent MB removal from Box Behnken Design.

Conclusions

Based on the results obtained in this research, the best composite film composition design was obtained for films with Run 12, the composition of chitosan, grafted cellulose, and TiO_2 were 0.85; 0.2; 0.2 grams respectively. In determining the optimum composition for MB adsorption capacity, the most significant factor was grafted cellulose, while in determining the optimum composition for the percent removal of MB, it was TiO_2. It can be concluded that determining the optimum composition design for composite films can be done using the RSM method so that the best design is produced and what factors greatly influence the response or results to be obtained. In this research, laboratory validation of the RSM results has not been carried out. These stages will be carried out in future research.

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