Synthesis of high-porosity hybrid geopolymer/alginate adsorbent for effective removal of methylene blue and optimization of parameters using RSM

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Abstract. In this work, high-porosity geopolymer/sodium alginate (GSA) adsorbent was successfully prepared by entrapping fly ash-based geopolymer into sodium alginate (SA) using a simple method. The geopolymer slurry was firstly prepared which involved the utilization of sodium hydroxide (NaOH) as the alkaline activator followed by the addition of SA and albumen into the slurry. Natural albumen was used as the foaming agent. The effect of mass ratio of geopolymer to SA, albumen content (wt%), NaOH concentration and curing temperature (°C) on the removal of methylene blue (MB) was investigated using one factor at time (OFAT) method and optimized by response surface methodology (RSM), which achieved by 30 run of experiments using central composite design (CCD). A quadratic model was employed to correlate all the independent variables for maximizing the MB removal through the analysis of variances (ANOVA). The model suggested that the optimum condition for the preparation of GSA adsorbent for the efficient MB removal of 84.94% was achieved with mass ratio of geopolymer to SA was 1:0.13, albumen content of 25 wt%, NaOH concentration of 7 M and curing temperature of 60 °C. The albumen content was the most effective factor in the preparation of GSA adsorbent that increased the MB removal, followed by the curing temperature and mass ratio of geopolymer to SA.

1. Introduction
Geopolymers are inorganic polymer green materials that contain amorphous to semi-crystalline structures [1–3], prepared by the chemical activation of aluminosilicate raw materials [4] such metakaolin [5], fly ash [3] and granulated blast furnace slag (GBFS) [6]. Currently, biomass fly ash [1], bottom ash [7], red mud [8], rice husk ash [5] and clays [9] are some of the new sources of aluminosilicate materials that have good characteristics to be used as geopolymer raw materials. They consist of polymeric silicon-oxygen-aluminium framework structures that are negatively charged, balanced by the exchanging of cations of the activators (sodium or potassium). The geopolymerization process involves the dissolution of amorphous aluminosilicates materials in alkaline solutions, i.e., NaOH, Na₂SiO₃, KOH, and K₂SiO₃ [10], followed by the concurrent reactions of gelation and condensation that results in the formation of geopolymer materials [3].

Among the significant factors that affecting the preparation of a geopolymer material are particle size of the raw materials, alkaline activator concentration and curing conditions (temperature and duration) [11]. As highlighted by previous work, the curing temperature and time normally occurred at
low temperature in the ranges of 40 to 120 °C and 3 to 24 h, respectively [1–3,12–14]. According to Bondar et al., application of higher temperature and longer time were required for a geopolymer system that involved the utilization of high concentration of alkaline activator beyond 7.5 M. Furthermore, the use of high concentration alkaline activator has resulted in unfavourable characteristics of the geopolymer materials such brittleness and efflorescence due to the excess of free alkali content of the binding system.

Porous geopolymer is a new class of eco-friendly alkali-bonded porous ceramics, have attracted more and more attention in the recent years because of their interesting combination of good mechanical and thermal properties [1–5], excellent chemical and high temperature stability [5–8], and large internal surface area [9,10]. They have been used as adsorbents and filters [13–15], membrane and catalyst supports [11,12], coatings [6,7], and catalysts [16,17]. Generally, aluminium [5,18,19] and silicon [20–23] powders have been used as pore foaming agent for the fabrication of geopolymer foams, but the pores generated by these foaming technique are typically closed pores.

Response surface method (RSM) is a mathematical and statistical tools which based on the fit of a polynomial equation to the experimental data and it can be well applied when a response or a set of responses of interest is influenced by several variables [16]. It is used extensively to determine the correlation between the reaction variables for optimization and this method is faster, practical and economical. This method can simultaneously optimize the levels of variables to achieve the best performance of the response [15–17]. Central composite design (CCD) is the most popular method among the RSM designs due to its simple structure and good efficiency, reduce number of experiments and high quality predictions in studying the interaction effects which cannot be achieved using the normal orthogonal design and single factor tests.

In this work, high porosity hybrid fly ash-based geopolymer/alginate adsorbent was developed by a simple method which involved the hybridization of geopolymer (inorganic) and sodium alginate (SA) (organic), and crosslinking between alginate and calcium ion (Ca²⁺) from calcium chloride solution. The effect of the mass ratio of geopolymer to SA, albumen content, NaOH concentration and curing temperature in the preparation of the GSA adsorbent for the removal of methylene blue (MB) were evaluated using one factor at a time (OFAT) method where the influence of each parameter to the removal of MB solution was investigated by keeping other parameters constant. The findings from OFAT method was employed as the initial range value for optimization process by RSM.

2. Experimental

2.1. Materials

The fly ash (FA) was supplied by a local power station and the fraction of particle size below 45 µm was chosen in the preparation of the adsorbent. The FA composition is given in Table 1 and the FA composed mainly of SiO₂ and Al₂O₃, and Fe₂O₃ as the minor component. The SiO₂/Al₂O₃ ratio ~ 2.10, suggesting that the FA is a good source for the preparation of geopolymer materials [18]. Sodium hydroxide (NaOH), sodium alginate (SA), methylene blue (MB) and calcium chloride (CaCl₂) were supplied by Sigma Aldrich, whereas natural albumen was purchased from Nutri-plus, Malaysia.

| Oxide (wt%) | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | SO₃ | Na₂O | TiO₂ | P₂O₅ |
|------------|------|-------|-------|-----|-----|-----|-----|------|------|------|
|            | 43.25 | 20.59 | 12.49 | 11.11 | 3.76 | 1.96 | 1.45 | 0.93 | 0.88 | 7.91 |

2.2. Synthesis of GSA adsorbent

In the preliminary stage, the influences of mass ratio of geopolymer to SA, content of albumen (wt%), NaOH concentration (M) and curing temperature (°C) on the MB removal were studied by using single-time factor experiment for each factor. The findings from the experiments served as the initial range value for the optimization process by RSM. Different concentrations of NaOH were mixed with the fly
ash of mass ratio of fly ash:NaOH was 3:1 and manually stirred for 10 min. Then, SA solution (2.0 wt%) was poured into the geopolymer slurry with different mass ratio of geopolymer to SA and stirred about 30 min at 500 rpm to obtain hybrid GSA slurry. Next, different amounts of albumen were added into the GSA slurry and stirred for another 10 min at 800 rpm. Finally, the slurry was added dropwise in a CaCl₂ solution (2 wt%) and the formed beads were remained in the solution for 24 h at room temperature. The beads with the diameter ~2-4 mm were drained, washed and cured at different temperatures for 24 h. Table 2 shows the summary of full experimental parameters for the GSA adsorbent preparation, and one parameter was varied at one time in each experiment. The ranges of parameters were chosen based on the literature studies and trials run in order to fit into our investigation [1,3,4,10,12,19,20].

| Experimental parameters          | Values                  |
|----------------------------------|-------------------------|
| Mass ratio of geopolymer to SA   | 1:0.11, 1:12, 1:13, 1:14, 1:15 |
| Content of albumen (wt%)         | 5, 10, 15, 20, 25, 30   |
| NaOH concentration (M)           | 4, 5, 6, 7, 8, 9, 10    |
| Curing temperature (°C)          | 40, 50, 60, 70, 80      |

2.3. Batch adsorption of MB by the GSA adsorbents for OFAT method and RSM experiments

A stock solution of MB was prepared by dissolving an accurate weight of 1 g of MB in 1 L of distilled water. The stock solution (1000 mg/L) was used to prepare MB at 350 mg/L, with a working volume of 100 mL for each conical flask and was made fresh for every experiment. Calibration curve for MB was prepared by the dilution method of 1000 mg/L stock solution. The adsorption of MB onto the GSA adsorbent was performed to determine the optimum parameters (mass ratio of geopolymer to SA, albumen content, NaOH concentration and curing temperature) for the preparation GSA adsorbents. The MB solution was mixed with 3.5 g/L of GSA adsorbent in a conical flask, agitated continuously at 200 rpm using an incubated orbital shaker (Lab Companion SIF6000R, Korea) at room temperature for 24 h. The remaining MB concentration in the solution was evaluated using UV spectroscopy (Shimadzu UV-1800, Japan) at 664 nm. The amount of MB removal was evaluated by calculating the removal efficiency (E), using Equation (1):

\[
E (\%) = \frac{C_i - C_f}{C_i} \times 100
\]

where, \( C_i \) and \( C_f \) represent the MB initial and final concentration (mg/L), respectively. The experimental data attained from this preliminary stage served as the initial data for the optimization study.

2.4. Central composite design (CCD) for parameters optimization of adsorbent development

The optimization of parameters for the preparation of the GSA adsorbent was carried out using response surface method (RSM). Four parameters from the preliminary study (mass ratio of geopolymer to SA, albumen content (wt%), NaOH concentration (M) and curing temperature (°C)) were optimized using 2⁴ factorial CCD. Three levels, four variable concepts and 30 experimental points in a random order was adopted in this design. The four independent variables were prescribed into three levels (low, center and high). The RSM run was based on central composite rotatable design (CCD). CCD was chosen because it is the most common design used for optimization of similar processes and it used five level designs for the construction of second order response surface [16,21–23]. The designs include repetition of center points to calculate the experimental error, providing more reliable data. Thirty batch experiments were performed and the experimental result data were fitted to a second order polynomial regression model as shown in Equation 2 [24].

\[
\text{Experimental parameters for the preparation of GSA adsorbent.}
\]
\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_i X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \varepsilon \]  

(2)

where \( Y \) is predicted response, \( \beta_0, \beta_i, \beta_{ij} \) are constant and model coefficients, \( X_i \) and \( X_j \) are independent variables and \( \varepsilon \) is noise or error. In this study \( Y \) is the removal of MB (%).

Ranges of the operating variables for the RSM run were selected based on the results of the adsorption experiments in Section 2.2. (Table 3). The Design Expert 7.0 software was employed for the experimental design and data analysis of this optimization work.

**Table 3.** Central composite design of optimization of the adsorbent for three factors with their levels.

| Factors                          | Unit                  | –\( \alpha \) | Low (–1) | Central (0) | High (1) | +\( \alpha \) |
|----------------------------------|-----------------------|--------------|----------|-------------|----------|-------------|
| \( X_1 \): mass ratio of geopolymer to SA | -                     | 0.07         | 0.10     | 0.13        | 0.16     | 0.19        |
| \( X_2 \): albumen content      | %                     | 0            | 10       | 20.00       | 30.00    | 40.00       |
| \( X_3 \): NaOH concentration  | M                     | 1            | 4.00     | 7.00        | 10.00    | 13.00       |
| \( X_4 \): curing temperature  | °C                    | 25           | 40.00    | 55.00       | 70.00    | 85.00       |

3. Results and discussion

3.1 Synthesis of geopolymer/alginate adsorbent

The effects of mass ratio of geopolymer to SA on the removal efficiency of MB were investigated and the results are presented in Figure 1. The finding suggests that the MB removal efficiency by the GSA was gradually increased with the addition amount of SA from mass ratio of geopolymer to SA was 1:0.11 to 1:0.13, which explained that the presence of SA has enhanced the adsorption capability of the MB. The finding is consistent with findings of the past studies by other authors [12,25]. On the contrary, the MB removal efficiency slightly decreased as the mass of SA was further increased to the mass ratio geopolymer to SA was 1:0.14 to 1:0.16 resulted in the excessive of the \( \text{Ca}^{2+} \) and SA solidification which blocked the inner pores of the geopolymer matrix [12]. The GSA adsorbent of mass ratio of geopolymer to SA 1:0.13 was used to perform all further experiments as it indicated highest amount of MB removal.

![Figure 1. Effect of mass ratio of geopolymer to SA on the MB removal.](image)

The effect of addition of albumen on the MB removal is shown in Figure 2. With the increasing of albumen content up to 25 wt\%, the ability of pores formation was increased and some pores are easy to merge into connected pores resulted in the enhancing of porosity. Furthermore, the increasing of pores formation provides a large surface area for the adsorption and allowed the MB diffusion into the GSA adsorbent, thus, enhancing the adsorption ability of the GSA adsorbent and MB removal. Further addition of albumen (30 wt\%) contributed to the inhomogeneity of the size and distribution of the pores.
At this stage, large bubbles tended to form because the small bubbles were easy to burst as a result of the thinner pore wall [26]. In addition, this condition also led to the increasing of generation of connected pores and destroy the formation of capillary pores, which resulted in the decreasing of capillary MB adsorption onto the GSA adsorbent and MB removal.

![Figure 2](image1.png)

**Figure 2.** Effect of albumen content on the MB removal.

Figure 3 depicts the effect of NaOH concentration on the MB removal. In geopolymerization process, NaOH solution is used to activate and dissolve the silicon and aluminium ions of the source materials and form the geopolymer slurry. Figure shows that the MB removal slightly increased as the concentration of NaOH was increased up to 7 M. On the contrary, further increasing of NaOH concentration reduced the MB removal. Therefore, 7 M is the optimum NaOH concentration in the preparation of the GSA adsorbent. Generally, the increasing of NaOH concentration did not give significant effect on the MB removal. Previous studies have suggested that increasing the activator will increase the solubility silicon and aluminium ions in the source materials, but it has certain limitations because in the case of excess addition it will reduce the strength of a geopolymer system and 5 to 10 M is the possible ranges of activator molarities used for the activation of natural minerals [11,27,28].

![Figure 3](image2.png)

**Figure 3.** Effect of NaOH concentration on the MB removal.

The investigation on the effect of curing time on the adsorption of MB was conducted in the range of temperature from 40 to 80 °C [2,3,13,14,19,29] and the result is demonstrated in Figure 4. It is observed that as the curing temperature increased from 40 to 60 °C, the trend of MB removal also
gradually increased, but further increasing reduced MB removal. The finding is consistent with findings of the past studies that proposed 60°C as the optimum curing temperature [3,30,31] in the preparation of geopolymer. In this case, high curing temperature beyond 60 °C can cause excess of water evaporation that results in the loss of strength due to incomplete geopolymerization [10] and, reduce the homogeneity of pores formation and distribution [32] which affects the efficiency of MB removal. Furthermore, high curing temperature can lead to the decomposition of albumen that results in the formation of not stabilized cell structure and inhomogeneity of cellular morphology of the GSA adsorbent [26,32].

![Figure 4. Effect of curing time on the MB removal.](image)

### 3.2 Central composite design (CCD) for parameters optimization of adsorbent development

In Section 3.1, the studies only evaluated the changing of one parameter at a time and this method could not determine the optimum condition point for the preparation of the GSA adsorbent because there could be interaction between two or more parameters that could significantly affect the condition of GSA preparation. In order to find the optimum point in the preparation of the GSA adsorbent, the system was modelled and analysed using Design Expert software (Stat-Ease Inc., version 8.0.7.1). The optimization of the preparation parameters of adsorbent (mass ratio of geopolymer to SA, albumen content, NaOH concentration and curing temperature) was carried out using central composite design (CCD).

The outcome of the CCD analysis is tabulated in Table 4 and 30 run experiments were performed according to RSM. The interaction of independent variables and their response were also presented and shown as predicted and experimental values. The highest and lowest MB removal (%) were predicted 83.91 and 61.52, respectively. A quadratic polynomial equation (Equation 2) was employed in modelling the experimental data. It can be observed from Equation 3 that all coefficients have negative signs except $X_2$ and $X_4$ coefficients which have have positive signs. The negative and positive values indicate the antagonistic and synergistic effects, respectively. In this case, the negative signs of the coefficients of parameters indicate that the MB removal (%) decreases with the increase in the mass ratio of geopolymer to SA, albumen content (wt%), NaOH concentration (M) and curing temperature (°C) while the positive coefficients of the parameters explain that the MB removal increases with the increase of the parameters [33]. The model of MB removal (%) in terms of actual factors is presented in Equation 3.

\[
MB\text{ removal (\%)} = 83.91 - 034X_1 + 3.66X_2 + 0.73X_4 - 0.36X_1X_3 - 0.44X_1X_4 - 1.82X_1^2 - 3.76X_2^2 - 1.86X_3^2 - 1.19X_4^2
\]  

(3)
Table 4. Experimental and predicted results of MB removal (%) by the GSA adsorbent.

| Run | Variables                  | MB removal (%) | Experimental | Predicted |
|-----|----------------------------|----------------|--------------|-----------|
|     | $X_1$: mass ratio of geopolymer to SA |                |              |           |
| 1   | 0.16                        | 30.00          | 4.00         | 70.00     | 79.11     | 79.01     |
| 2   | 0.13                        | 20.00          | 7.00         | 25.00     | 76.11     | 77.71     |
| 3   | 0.10                        | 10.00          | 10.00        | 40.00     | 71.34     | 71.20     |
| 4   | 0.10                        | 10.00          | 10.00        | 70.00     | 72.65     | 72.71     |
| 5   | 0.16                        | 10.00          | 10.00        | 40.00     | 72.11     | 71.28     |
| 6   | 0.13                        | 20.00          | 7.00         | 55.00     | 83.91     | 83.91     |
| 7   | 0.13                        | 20.00          | 7.00         | 85.00     | 81.73     | 80.61     |
| 8   | 0.13                        | 20.00          | 7.00         | 55.00     | 83.22     | 83.91     |
| 9   | 0.13                        | 40.00          | 7.00         | 55.00     | 75.93     | 76.18     |
| 10  | 0.19                        | 20.00          | 7.00         | 55.00     | 60.07     | 75.97     |
| 11  | 0.16                        | 10.00          | 10.00        | 70.00     | 70.44     | 71.01     |
| 12  | 0.16                        | 30.00          | 10.00        | 70.00     | 78.15     | 78.38     |
| 13  | 0.07                        | 20.00          | 7.00         | 55.00     | 77.42     | 77.31     |
| 14  | 0.10                        | 30.00          | 10.00        | 70.00     | 81.07     | 81.22     |
| 15  | 0.16                        | 10.00          | 4.00         | 70.00     | 72.66     | 72.49     |
| 16  | 0.16                        | 30.00          | 4.00         | 40.00     | 77.91     | 77.61     |
| 17  | 0.10                        | 10.00          | 4.00         | 70.00     | 72.33     | 72.76     |
| 18  | 0.10                        | 30.00          | 4.00         | 70.00     | 79.84     | 80.43     |
| 19  | 0.13                        | 0.00           | 7.00         | 55.00     | 61.29     | 61.52     |
| 20  | 0.10                        | 30.00          | 10.00        | 40.00     | 79.41     | 79.34     |
| 21  | 0.13                        | 20.00          | 1.00         | 55.00     | 75.77     | 76.14     |
| 22  | 0.13                        | 20.00          | 7.00         | 55.00     | 83.66     | 83.91     |
| 23  | 0.16                        | 30.00          | 10.00        | 40.00     | 78.94     | 78.72     |
| 24  | 0.10                        | 10.00          | 4.00         | 40.00     | 70.44     | 69.97     |
| 25  | 0.13                        | 20.00          | 13.00        | 55.00     | 76.64     | 76.75     |
| 26  | 0.13                        | 20.00          | 7.00         | 55.00     | 85.02     | 83.91     |
| 27  | 0.13                        | 20.00          | 7.00         | 55.00     | 83.55     | 83.75     |
| 28  | 0.13                        | 20.00          | 7.00         | 55.00     | 84.07     | 83.91     |
| 29  | 0.10                        | 30.00          | 4.00         | 40.00     | 78.06     | 77.25     |
| 30  | 0.16                        | 10.00          | 4.00         | 40.00     | 71.85     | 71.46     |

ANOVA was conducted to evaluate the validity and accuracy of the model. $P$-value was used to determine whether each coefficient was statistically significant at the 95% confidence interval. The results in Table 5 indicate that the MB removal within the experimental range can be adequately explained by the model and $P$-value less than 0.0001 was considered having significant impact on the system [34]. Whereas, the probability for lack of fit (LOF) that describes the variation of the data around the fitted model was insignificant which LOF of the model is 0.2063. This implies that the model is a good representation of the response. Furthermore, the determination coefficient, $R^2$ and adjusted $R^2$ which measures the fitness of the data to the model 98% and 97%, respectively. Both of $R^2$ values demonstrate that the correlation between the experimental and predicted data is very high which also
describes the model was significant. In addition, the predicted $R^2$ was 0.9470 which is in reasonable agreement with the actual adjusted $R^2$ of 0.9754 that also explained the model assured a good fitting of the data. Hence, the regression model provides an outstanding justification of the correlation between the independent variables and the response. The adequate precision value given by the analysis is 44.22, which is desirable and indicating an adequate signal because it is larger than 4. Adequate precision compares the range of the predicted values at the design points to the average prediction error and it determines the signal to noise ratio [23].

Table 5. ANOVA model for MB removal (%) responses.

| Model                      | Std. Dev. | $R^2$ | Adj $R^2$ | Pred $R^2$ | Predicted residual sum of square (PRESS) | Adeq Precision | $P$-value | $F$-value | Lack of fit (LOF) |
|---------------------------|-----------|-------|-----------|------------|------------------------------------------|----------------|-----------|-----------|------------------|
| MB removal (%)            |           | 0.84  | 0.9839    | 0.9754     | 0.9470                                   | 44.22          | <0.0001   | 115.94    | 0.2063           |
| Quadratic model           |           |       |           |            |                                          |                |           |           |                  |

Multiple coefficient of regression of second order polynomial quadratic model that explain the MB removal are tabulated in Table 6. Among the test variables in this study, the first order and second order effect of albumen content ($X_2$) are highly significant because the $P$-value is less than 0.0001, which is in agreement with perturbation plot as depicted in Figure 5. According to the curves of the perturbation plot, albumen content ($X_2$) that refers to C curve showed an apparent curvature, thus provided the most significant effect on the MB removal. The first order effect of mass ratio of geopolymer to SA ($X_1$) and curing temperature ($X_4$) are also significant because both $P$-values are less than 0.1000. Furthermore, the interaction effect between $X_1$ and $X_3$, and between $X_1$ and $X_4$ are significant at $P$ less than 0.1000, while the other terms are not significant ($P>0.1000$). The regression coefficient values of the model are $X_1 = 0.34$ (mass ratio of geopolymer to SA), $X_2 = 3.66$ (albumen content), $X_3 = 0.15$ and $X_4 = 0.73$ (curing temperature). It is inferred that the albumen content ($X_2$) gives the highest effect to the response of MB removal followed by then curing temperature ($X_4$) and mass ratio of geopolymer to SA ($X_1$), lastly is NaOH concentration ($X_2$).

Table 6. The quadratic model ANOVA for preparation of GSA adsorbent.

|                | Coefficient estimate | $F$-value | $P$-value |
|----------------|----------------------|-----------|-----------|
| Quadratic model| X_1                  | -0.34     | 4.22      | 0.0509    |
|                | X_2                  | 3.66      | 503.37    | <0.0001   |
|                | X_3                  | 0.15      | 0.87      | 0.3665    |
|                | X_4                  | 0.73      | 19.77     | 0.0005    |
|                | X_1X_2               | -0.29     | 2.04      | 0.1738    |
|                | X_1X_3               | -0.36     | 3.16      | 0.0957    |
|                | X_1X_4               | -0.44     | 4.91      | 0.0426    |
|                | X_2X_3               | 0.21      | 1.12      | 0.3063    |
|                | X_2X_4               | 0.094     | 0.22      | 0.6439    |
|                | X_3X_4               | -0.32     | 2.61      | 0.1271    |
|                | X_1^2                | -1.82     | 141.30    | <0.0001   |
|                | X_2^2                | -3.76     | 606.80    | <0.0001   |
|                | X_3^2                | -1.86     | 148.98    | <0.0001   |
|                | X_4^2                | -1.19     | 60.27     | <0.0001   |
Figure 5. Perturbation plot of the parameters that effect on the MB removal (%)

The optimum response and the relationship between significant model terms are depicted in Figure 6(a-f). The 3-D contour plots of mass ratio of geopolymer to SA with albumen content, mass ratio of geopolymer to SA with NaOH concentration, mass ratio of geopolymer to SA with curing temperature, albumen content with NaOH concentration, albumen content with curing temperature and NaOH concentration with curing temperature can be seen in Figure 6(a), (b), (c), (d), (e) and (f), respectively. In Figure 6(a), (d) and (e), increased in MB removal was observed when albumen content increased from 10.25% to 25.00% and this finding was confirmed by the significant P-value of less than 0.0001 as depicted in Table 6 and OFAT method in Figure 2. The MB removal was also increased as the curing temperature was increased from 47.5 to 70.00 °C. However, the change in NaOH concentration has small influence on the system’s efficiency as shown in Figure 6(a), (b) and (f). This observation agrees with the P-value (0.3665) for this variable (Table 6), which is higher than 0.1 indicating that the variable is not significant. Similar behaviour can be observed in Figure 7(a) and (b) when the mass ratio of geopolymer to SA was increased from 0.10 to 0.13, however beyond that ratio the MB removal started to decrease gradually. Furthermore, the interaction between the albumen content and NaOH concentration was insignificant as the P-value was 0.3063. The same result was also observed for the interaction between the curing temperature and alkaline activator concentration which P-value is 0.1271 Figure 6(f).

The optimum parameters for the preparation of the GSA adsorbent based on the analysis is summarized in Table 7. The optimum condition of MB removal was calculated using Equation 3. Three confirmation runs were conducted under the same experimental condition. The calculated and experimental MB removal were 84.94% and 86.13%, respectively. The difference between the calculated and experimental value was 1.19% which is within the acceptable range of deviation of 5%.

| Variable | Units | Level optimum condition |
|----------|-------|-------------------------|
| X₁: mass ratio of geopolymer to SA | - | 0.13 |
| X₂: content of albumen | % | 25.00 |
| X₃: NaOH concentration | M | 7.00 |
| X₄: curing temperature | °C | 60.00 |
| MB removal, calculated | % | 84.94 |
| MB removal, experimental | % | 86.13±1.19 |
Figure 6. MB removal (%) 3D surface plots as a function of (a) mass ratio of geopolymer to SA with albumen content (wt%), (b) mass ratio of geopolymer to SA with NaOH concentration (M), (c) mass ratio of geopolymer to SA with curing temperature (°C), (d) albumen content (wt%) with NaOH concentration (M), (e) albumen content (wt%) with curing temperature (°C), and (f) NaOH (M) with curing temperature (°C).
Figure 7 (a) and (b) shows the major diagnostic of the residuals analysis of the response surface design. The plots describe how well the model fits the statistical assumptions and provide adequate approximation to the true system. The normal probability plot in Figure 7(a) shows the normal probability of the residuals. The residual fitted well to the straight line indicating the normal distribution, which confirmed that there was no non-normality of the experimental results. On the other hand, the plot of predicted versus experimental data (Figure 7 (b)) shows the responses from the experimental results. It shows that the data points fitted well to the straight line within the acceptable variance range when compared to the calculated responses. This analysis is in good agreement with the data in Table 7 where the difference between experimental and calculated MB removal was only 1.91.

4. Conclusion
In this work, high-porosity hybrid GSA adsorbent was synthesized and utilized for the removal of MB. Four parameters namely, mass ratio of geopolymer to SA, albumen content, NaOH concentration and curing temperature that essentially affected the preparation of the GSA adsorbent were screened using OFAT method was conducted prior to the optimization using RSM-CCD methodology. The results propose that the statistical optimization approach is an efficient means to predict the optimum condition for the preparation of the GSA adsorbent for the effective removal of MB. The quadratic model was identified to be significant with the coefficient of determination, $R^2$ is 0.9839. The RSM results prove that the optimum condition of mass ratio of geopolymer to SA of 1:0.13, albumen content of 25 wt%, NaOH concentration of 7 M and curing temperature of 60°C can achieve the maximum MB removal of 84.94%. Furthermore, the values of regression coefficients model have evaluated that the albumen content (3.66) has the highest effect on the removal of MB followed by then curing temperature (0.73), mass ratio of geopolymer to SA (0.34) and lastly is NaOH concentration (0.15). It can be concluded that the optimum condition for the preparation of GSA adsorbent for effective MB removal was predicted through the application of RSM.

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