# Response Surface Methodology Optimization of Methylene Blue and Congo Red Dyes Adsorption on Sorghum Husk

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***Abstract:*** *The application of dyes by many industries to colour their products generates a considerable amount of coloured wastewater that is toxic to life. The aim of this study is to develop low-cost adsorbent from sorghum husk at optimum conditions for the removal of Methylene Blue (MB) and Congo Red (CR) dyes from aqueous solutions. The biosorbent characterization was carried out using Fourier Transform Infrared (FTIR) Spectroscopy, Brunauer Emmett Teller (BET) Surface Analyzer, and Scanning Electron Microscopy (SEM). Response Surface Methodology (RSM) optimization was carried out using Box-Behnken design of Design Expert software; it was also used to generate the experimental design used to carry out adsorption experiments. Effects of contact time, pH and adsorbent dosage on the biosorbent performance on the dyes removal were investigated. Optimization of the process variables gave optimum contact time of 138.05 min, pH of 3.00 and adsorbent dosage of 4.00 g with percentage removal of 94.22 % for MB and 88.63 % for CR. Therefore, the use of Box–Behnken design of RSM gives a reliable methodology for optimization of process variables for adsorption of MB and CR from aqueous solution.*

***Keywords:*** *Dyes, Response Surface Methodology, Adsorption, Sorghum Husk, Optimization*

## 1. INTRODUCTION

Dyes are coloured substances that can be applied to various substrates from a liquid in which they are completely, or at least partly, soluble. They are widely used by paint, textile, leather, paper, plastics and other industries in order to colour their products. As a result of this, a considerable amount of coloured wastewater is generated. The presence of little amounts of dyes in water is highly visible and undesirable [1]. Many dyes are difficult to degenerate, some are stable to light and others are non-biodegradable, toxic and even carcinogenic. They affect public health and cause many serious environmental problems and hazards to aquatic living organisms [1, 2]. Therefore, it is necessary to remove or reduce dyes from wastewater before it is discharged.

The methods used for removal of dyes from wastewater are divided into three types, namely; biological, chemical and physical methods. Anaerobic biodegradation or biological method has low removal efficiency [2]. Chemical method requires large amount of chemicals and produces large volume of sludge which itself requires treatment. These methods are costly and cannot be used effectively for removal of dyes. Therefore different physical methods such as membrane filtration processes and adsorption techniques are widely used [2, 3].

Adsorption is the process in which a solid is used for removing a soluble substance from water. Adsorption process involves the transfer of a mass of a fluid (adsorbate) to the surface of an adsorbing solid (adsorbent). Adsorption of dyes depend on the properties of the adsorbent the type of dyes and also on various parameters like, contact time, pH of the solution, adsorbent dosage, etc. In most cases, activated carbon is the most widely used adsorbent because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [3]. There is now increase in researches directed towards investigating the adsorption potentials of cheaper and effective adsorbents from agricultural waste materials, due to high cost of activated carbon [3].

Sorghum husk is a renewable and abundant natural resource. Its utilization as low cost adsorbent for dyes removal from aqueous solution will add value to it. Optimizing the process variables for adsorption of dyes is an excellent methodology for achieving the optimum conditions that enhances maximum dye removal on the adsorbent. Response Surface Methodology (RSM) is used to create an experimental model and also analyze the models that are built. It is based on a polynomial equation fitting to the experimental data, in order to describe the relationship between the response of interest and several variables, and also obtaining optimum conditions for the desirable responses [4].

RSM is a multivariable technique that simultaneously optimizes process parameters to get the best response within the experimental region under study. It is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes [5]. Box-Behnken design (BBD) diminishes the number of experiments for the particular optimization process [4]. RSM was used in this research work to optimize; contact time, pH and adsorbent dosage with percentage MB and CR removal as responses.

Available literature shows that much work has been carried out on the use of agro-waste materials as adsorbents for the removal of dyes from aqueous solution. However, optimization of adsorption process variables using response surface methodology with both cationic dye, MB, removal and anionic dye, CR, removal as responses on the same biosorbent has not been given attention. Therefore, in this study, sorghum husk was used to prepare low-cost biosorbent at optimum conditions for maximum removal of MB and CR dyes from aqueous solution.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The various materials/reagents and equipment used in this research are: Sorghum husk, collected from local mills and farmers within Quaan-Pan Local Government Area of Plateau State, Methylene Blue (MB), a cationic dye and Congo Red (CR), an anionic dye. Methylene blue, with molecular formula $C_{16}H_{18}N_3SCl$ and molecular weight of 319.85gmol$^{-1}$ was purchased from Merck, while Congo red with molecular formular $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66gmol$^{-1}$ was purchased from Sigma–Aldrich.

### 2.2 Preparation of Adsorbent

The sorghum husk was washed repeatedly with water to remove dirt that adhered on the surface of the adsorbent materials till colourless wash water was obtained. The material was then dried in an oven at between 60°C to 80°C till a constant weight was obtained. The dried adsorbent material was ground, sieved in a sieve of 425 µm mesh size and then used as adsorbent.

### 2.3 Modification of Adsorbent

The dried sorghum husk was modified cationically and anionically according to the previous works [6, 7]. The cationic modification was carried out by mixing 100 g of the ground adsorbent (sorghum husk) with 800 ml of 0.05 M hydrochloric acid solution and kept at room temperature with occasional stirring for 5 hours. The mixture was then filtered to remove the unused hydrochloric acid. The modified adsorbent was washed several times with distilled water, oven-dried at 80°C for 12 hours and stored in a desiccator. The anionic modification was carried out by mixing 100 g of the ground adsorbent (sorghum husk) with 900 ml of 0.05 M sodium hydroxide solution and kept at room temperature with occasional stirring for 5 hours. The mixture was then filtered and washed several times with distilled water, oven-dried at 80°C for 12 hours and stored in a desiccator.

### 2.4 Characterization of Adsorbent

The unmodified and modified adsorbents were characterized using BET Surface Analyzer (NOVA 4200e), FTIR-Spectroscopy (FTIR, Nicolet 5700) and Scanning Electron Microscopy (SEM; FEI Sirion200, NLD).

### 2.5 Preparation of Dye Wastewater

500 ppm dye wastewater was prepared by dissolving 0.5 g each of MB and CR in 500 ml distilled water. The resulting solution was transferred into a 1 liter volumetric flask and diluted to the required volume with distilled water.

### 2.6 Experimental Design

In this study, Box-Behnken design was used to generate the experimental design. Three process parameters; contact time, solution pH and adsorbent dosage were chosen as the independent variables while the percentage of dyes (MB and CR) removed were the dependent response variables. The independent variables, the experimental range and levels for both MB and CR removal are presented in Table 1.

**Table 1: Experimental Factors and Levels of Variables**

| Independent Variables | Symbols | Levels | | |
|---|---|---|---|---|
| | | -1 0 | 0 | +1 |
| Time (min) | A | 0 | 90 | 180 |
| pH | B | 3.0 | 6.5 | 10 |
| Adsorbent Dosage (g) | C | 0.50 | 2.25 | 4.00 |

### 2.7 Batch Adsorption Experiments

Adsorption experiments were carried out according to the design developed with the response surface Box-Behnken design methodology. The experiments were carried out in 250 ml Erlen-meyer flasks with a working volume of 50 ml of aqueous solution.

The pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or 0.1 M HCl. A pH meter was used for all pH measurements. The required amount of adsorbent dosage was taken in the flasks. The flasks were then shaken for the specified time period in an orbital shaker (SO1; Stuart Scientific) at 150 rpm. Then the flasks were withdrawn from the shaker after the desired time of operation. The supernatant and the spent adsorbents were then separated by using a centrifuge at 5000 rpm. All colour measurements were carried out with a UV Spectrophotometer (752N; Heb Biotech) operating in the visible range in absorbance mode. Absorbance values were recorded at the wave length for maximum absorbance corresponding to each dye, which was 500 nm for MB and 480 nm for CR respectively. Dye concentrations in the supernatant were calculated from the calibration curve generated. The percentage of dye (MB and CR) removal (Y) was calculated using Equation 1.

$$Y\ (\%) = \frac{(C_0 - C_e)}{C_0}\ X\ 100\ \% \qquad \ldots\ldots\ldots\ldots (1)$$

Where, $C_0$ and $C_e$ are the initial concentration and equilibrium concentration.

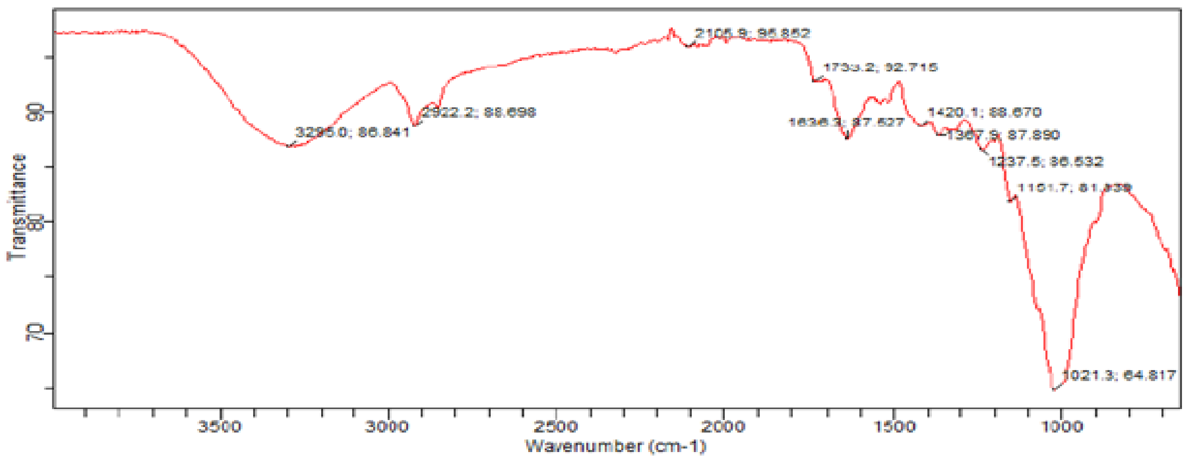
## 3. RESULTS AND DICUSSION

### 3.1 Characterization of Adsorbents

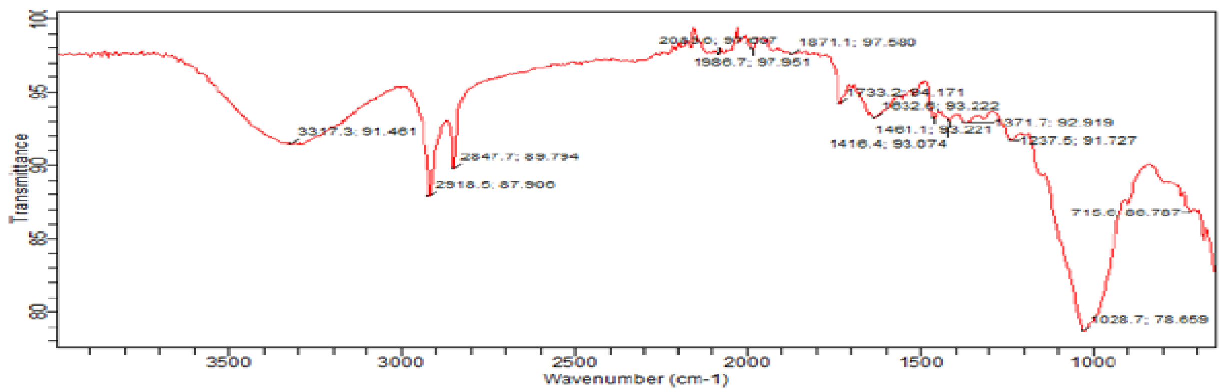
The results of the characterization carried out on the unmodified and modified samples of sorghum husk are presented in this section.

#### 3.1.1 FTIR analysis

The FTIR analysis was used to investigate the functional groups present on the adsorbents that could be responsible for the removal of dyes. The FTIR spectra of unmodified and modified sorghum husk were analyzed to determine the vibration frequency changes in their functional groups within the range of 4000–650 $cm^{-1}$ wave number (Figure 1).




**(a)**



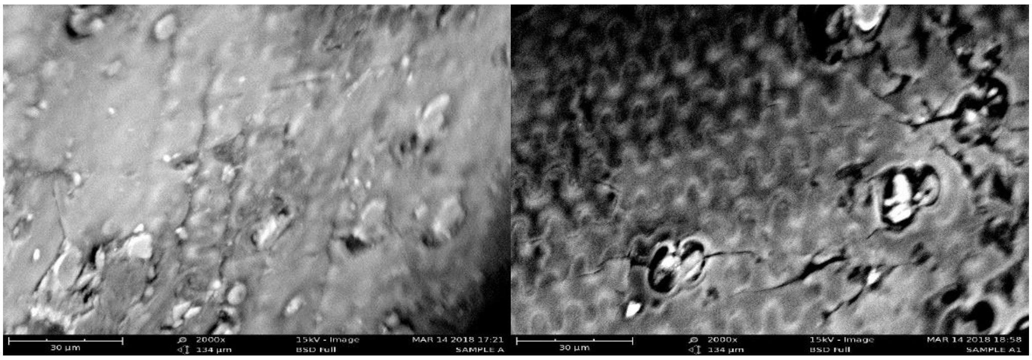

**(b)**

Figure 1: FTIR Spectra of a) Unmodified sorghum husk; b) NaOH modified sorghum husk

Various adsorption bands were observed for unmodified and modified sorghum husk, Figure 1 (a & b). The peaks at 3295.0 $cm^{-1}$ and 3317.3 $cm^{-1}$ presented by the unmodified and modified sorghum husk respectively showed the presence of O-H bond. It was noticed that the peak at 3317.3 $cm^{-1}$ shown by the modified sorghum husk was close to the broad peak at 3431.5 $cm^{-1}$ reported in other works [8]. The unmodified and modified sorghum husk presented peaks ranging from 2847.7 $cm^{-1}$ to 2922.2 $cm^{-1}$. These peaks show the presence of C-H bond. The peaks, located at 2105.9 $cm^{-1}$ in the unmodified sorghum husk and 2053.0 $cm^{-1}$, 1986.7 $cm^{-1}$ and 1871.1 $cm^{-1}$ in the modified sorghum husk showed the presence of N-H and –COO vibrations. The peak at 1733.2 $cm^{-1}$ maintained by both adsorbents and other peaks at 1636.3 $cm^{-1}$ and 1632.6 $cm^{-1}$ may be due to the C=O stretching vibration [9]. The peaks at 1420.1 $cm^{-1}$ and 1461.1 $cm^{-1}$ corresponded to the asymmetric C–H groups. Further peaks observed at 1021.3 $cm^{-1}$ and 1028.7 $cm^{-1}$ may be as a result of C-O bond [10]. These functional groups may act as adsorption sites for dyes molecules [11].

#### 3.1.2 Scanning electron microscopy (SEM) analysis

The SEM analysis was conducted for unmodified and modified sorghum husk. The SEM images for unmodified and modified sorghum husk are presented in Figure 2.




**(a)** **(b)**

Figure 2: SEM images of a) Unmodified sorghum husk; b) NaOH modified sorghum husk

Figure 2b showed that the modified sorghum husk adsorbent has more expanded pores than the unmodified adsorbent in Figure 2a. The expanded pores observed in the modified adsorbent enhanced the capacity of the adsorbent for the removal of CR dye molecules.

#### 3.1.3 BET surface analysis

The Brunauer Emmett Teller (BET) surface area measurement technique was used to find the adsorbent characteristics. The BET surface analysis gave the following characteristics about the adsorbents. The unmodified sorghum husk has surface area of 139.539 $m^2/g$, pore volume of 0.053 cc/g, micropore surface area of 180.937 $m^2/g$, etc, while the NaoH modified sorghum husk has surface area of 233.822 $m^2/g$, pore volume of 0.091 cc/g, micropore surface area of 225.365 $m^2/g$, etc. These characteristics are within the range of values obtained in previous research [12] for nitric acid treated rice husk.

### 3.2 Design Matrix Batch Adsorption Experiments

The Box-Behnken design used required 17 experimental runs for modeling a response surface. Detail of the experimental runs conducted with the set of input parameters and the responses obtained is given in Table 2. Contact time (A), pH (B) and adsorbent dosage (C) are three important factors affecting an adsorption process for a given adsorbent. Consequently, A, B and C were chosen to represent the independent variables while the removal of MB and CR at equilibrium (Y) was selected as the responses (dependent variables). The Box–Behnken model does not contain combinations of all the factors at their highest or lowest values at the same time and it can avoid extreme treatment combinations [13]. The design matrix used in table 2 above was generated based on the levels of factors in table 1. Factor C is the dosage of the unmodified as well as the modified adsorbent. The unmodified adsorbent was used to remove MB while the NaOH modified adsorbent was to remove CR. The experimental runs for the removal of MB and CR were carried out separately to obtain the responses. The unmodified adsorbent has more capacity for removal of MB, a cationic dye. However, it is modification enhanced the capacity of the adsorbent for the removal of CR, an anionic dye. Therefore, sorghum husk can either be used for the removal of cationic or anionic dyes as a result of modification.

Table 2: Experimental Design Matrix for Dyes Adsorption on Sorghum Husk with Responses

| | Factors | | | Responses | |
|---|---|---|---|---|---|
| Run | A:Time Min | B:pH | C:Adsorbent Dosage, g | MB Removal % | CR Removal % |
| 1 | 0 | 10 | 2.25 | 0.00 | 0.00 |
| 2 | 90 | 3.0 | 4.00 | 88.60 | 90.00 |
| 3 | 90 | 6.5 | 2.25 | 73.85 | 52.35 |
| 4 | 90 | 10.0 | 0.50 | 47.90 | 9.00 |
| 5 | 0 | 6.5 | 4.00 | 0.00 | 0.00 |
| 6 | 0 | 6.5 | 0.50 | 0.00 | 0.00 |
| 7 | 90 | 10.0 | 4.00 | 90.35 | 62.93 |
| 8 | 0 | 3.0 | 2.25 | 0.00 | 0.00 |
| 9 | 90 | 6.5 | 2.25 | 73.59 | 51.78 |
| 10 | 90 | 6.5 | 2.25 | 74.03 | 52.00 |
| 11 | 90 | 6.5 | 2.25 | 73.90 | 51.92 |
| 12 | 180 | 10.0 | 2.25 | 85.15 | 38.53 |
| 13 | 90 | 6.5 | 2.25 | 74.00 | 52.13 |
| 14 | 180 | 6.5 | 4.00 | 90.12 | 62.33 |
| 15 | 90 | 3.0 | 0.50 | 9.50 | 31.13 |
| 16 | 180 | 3.0 | 2.25 | 49.20 | 86.00 |
| 17 | 180 | 6.5 | 0.50 | 37.50 | 21.13 |

### 3.3 Analysis of Variance Study

Analysis of variance (ANOVA) was employed for the determination of significant variables. The ANOVA consists of statistical results tested by means of a specified classification difference which was carried out by Fisher's statistical test (F-test). The F-value represents the significance of each controlled variable on the tested model. The ANOVA was used to determine the main and interacting effects of the factors affecting the removal of MB and CR. The Sum of squares (SS) of each factor quantifies its importance in the process [14]. The correlation coefficients $R^2$ and adjusted $R^2$ have been calculated to check the adequacy of the model. A large value of $R^2$ does not imply that the regression model is a good one. However, adjusted $R^2$ is preferred to be used to determine the fit of a regression model as it does not always increase when variables are added [15]. Statistical analysis was carried out to check if the regression models complied with experimental data. All terms in the regression models are not equally of the same importance. A large *F*-value implies that the models are significant and values of "Prob>*F*" less than 0.05 indicate that models terms are significant. According to previous findings [16, 17], larger *F*-value with the associated *P*-value smaller than 0.05, means that the experimental systems can be modeled effectively with less error. The results of ANOVA studies for MB and CR adsorption on sorghum husk are presented in Tables 4 and 5.

The ANOVA for response surface reduced quadratic model for MB removal on sorghum husk after discarding the insignificant model terms, excluding B, which was required to support hierarchy is presented in Table 4 below.

**Table 4: ANOVA for Response Surface Reduced Quadratic Model for MB Removal**

| Source | Sum of Squares | DFSquare | Mean Value | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 18843.98 | 5 | 3768.80 | 23.66 | < 0.0001 | significant |
| A | 8578.54 | 1 | 8578.54 | 53.85 | < 0.0001 | |
| B | 723.90 | 1 | 723.90 | 4.54 | 0.0564 | |
| C | 3791.90 | 1 | 3791.90 | 23.80 | 0.0005 | |
| $A^2$ | 5057.43 | 1 | 5057.43 | 31.75 | 0.0002 | |
| AC | 692.22 | 1 | 692.22 | 4.35 | 0.0612 | |
| Residual | 1752.34 | 11 | 159.30 | | | |
| Lack of Fit | 1752.22 | 7 | 250.32 | 8199.06 | <0.0001 | significant |
| Pure Error | 0.12 | 4 | 0.031 | | | |
| Cor Total | 20596.32 | 16 | | | | |

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From Table 4, the Model F-value of 23.66 implies that the model is significant. Values of "Prob> F" less than 0.0500 indicate that model terms are significant. The model gives a correlation coefficient (R-Square) value of 0.9149, a Predicted R-Square of 0.7337, an Adjusted R-Square of 0.8762 and an adequate Precision of 14.661. The predicted R-Square of 0.7337 is in reasonable agreement with the adjusted R Square of 0.8762. The adequate precision of 20.481 indicates that the signal is adequate. This model can therefore be used to navigate the design space. For the CR removal, the ANOVA for response surface quadratic model is given in Table 5.

**Table 5: ANOVA for Response Surface Reduced Quadratic Model for CR Removal**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 12053.64 | 4 | 3013.41 | 17.31 | < 0.0001 | significant |
| A | 5407.48 | 1 | 5407.48 | 31.07 | 0.0001 | |
| B | 1168.14 | 1 | 1168.14 | 6.71 | 0.0236 | |
| C | 2964.50 | 1 | 2964.50 | 17.03 | 0.0014 | |
| $A^2$ | 2513.52 | 1 | 2513.52 | 14.44 | 0.0025 | |
| Residual | 2088.48 | 12 | 174.04 | | | |
| Lack of Fit | 2088.29 | 8 | 261.04 | 5562.25 | < 0.0001 | significant |
| Pure Error | 0.19 | 4 | 0.047 | | | |
| Cor Total | 14142.12 | 16 | | | | |

The Model F-value of 17.31 in Table 5 above implies that the model is significant. Values of "Prob> F" less than 0.0500 indicate that model terms are significant. This model gives a correlation coefficient (R-Square) value of 0.8523, a predicted R-Square of 0.6259, an adjusted R-Square of 0.8031 and an adequate Precision of 14.109. The predicted R-Square of 0.6259 is in reasonable agreement with the adjusted R-Square of 0.8031. The adequate precision of 14.109 indicates that the signal is adequate. This model can be used to navigate the design space.

### 3.4 Development of Regression Model and Statistical Analysis

The design expert was subsequently used in statistical analysis and development of regression. The Box–Behnken design was adopted in this study for investigating the individual and mutual effects of the factors concerning the adsorption of MB and CR dyes from aqueous solution by sorghum husk adsorbents. A quadratic polynomial equation was developed to correlate and predict the dependent variables (i.e. percentage dye removal) as a function of independent variables (i.e. contact time, pH and adsorbent dosage) and their interactions, as given by Equation 2.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Where Y is the predicted response, $\beta_0$ is the constant term or intercept, $\beta_1$, $\beta_2$ and $\beta_3$ are the linear term coefficient, $\beta_{11}$, $\beta_{22}$ and $\beta_{33}$ are the quadratic term coefficient, $\beta_{12}$, $\beta_{13}$ and $\beta_{23}$ are the interaction term coefficient and A, B and C are the independent variables [18, 19].

The percentage removal (Y), of MB and CR dyes on sorghum husk were observed in the range of 0-90.35 % and 0-90 %. Regression between the dependent variables (MB and CR dyes removal) and the corresponding values of the three different independent variables; contact time, pH and adsorbent dosage, for adsorption on sorghum husk in terms of un-coded (actual) values yielded the different model equations below.

$$MB\ Removal\ (Y) = -28.74411 + 0.9438A + 2.71786B + 4.92357C - 4.26617E - 003\mathrm{A}^2 + 0.083524\mathrm{AC} \ldots . (3)$$

The coefficients in Equation 3 showed that the response function increases with contact time, pH and adsorbent dosage. In this case, adsorbent dosage has a more profound effect on the removal of MB than contact time and pH.

$$CR\ Removal\ (Y) = -2.30875 + 0.83024A - 3.45250B + 11.00000C - 3.00756E - 003A^2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

The coefficients in Equation 4 indicate that the response function for CR removal increases with contact time and adsorbent dosage, while it decreases with pH. In this case, adsorbent dosage has a more profound effect on the removal of CR than contact time and pH.

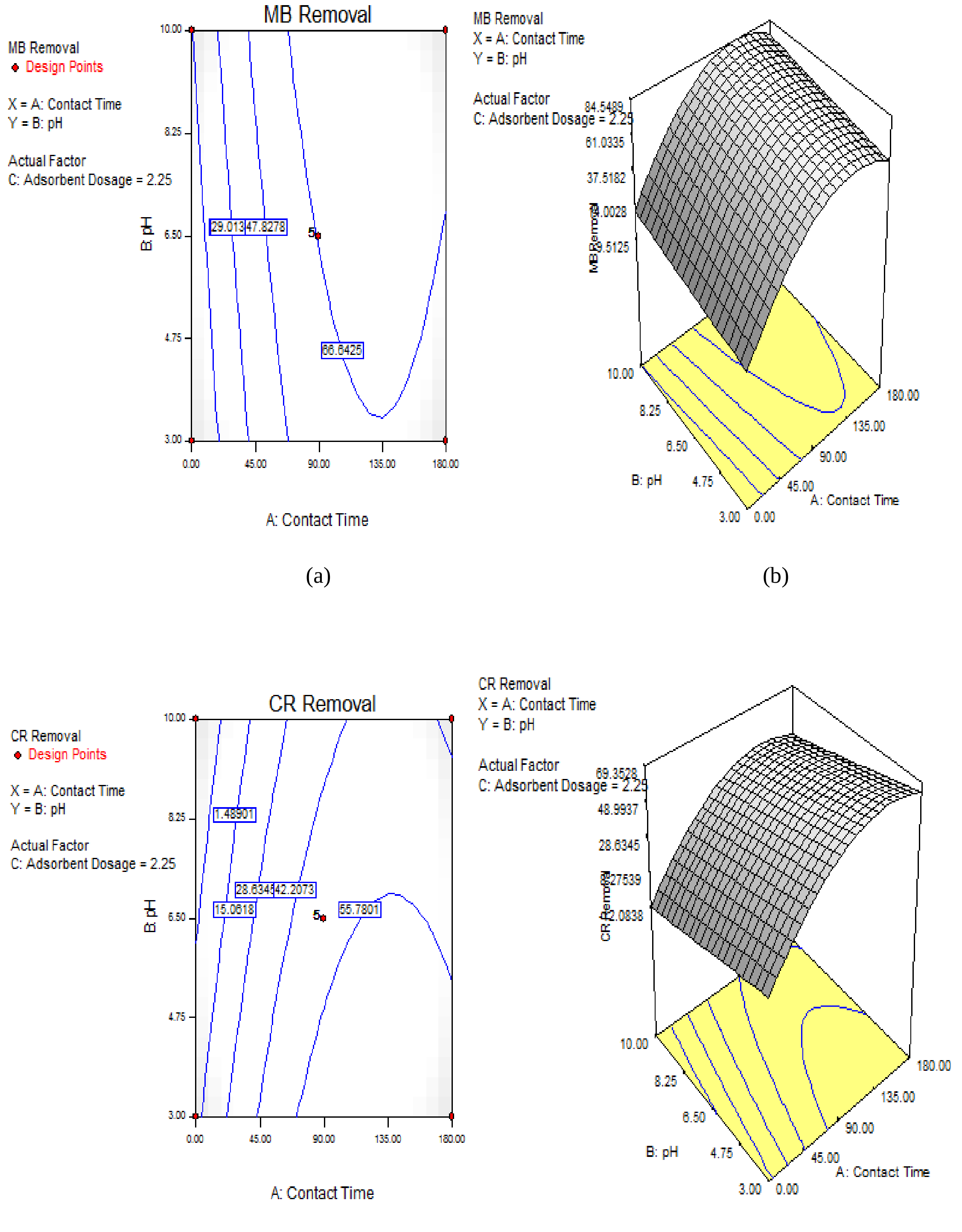
### 3.5 Effect of Process Variables on Adsorption of Dyes

The graphical representation of the adsorbed amount of MB and CR dyes on both sorghum husk relative to the three variables studied (contact time, pH, and adsorbent dosage) were used to achieve a better understanding of the interactions between the variables and determine the optimum level of each variable to a maximum amount of adsorption.

In order to explain the interaction effects of factors on adsorption of MB and CR dyes on sorghum husk, contour (2-Dimensional) plots and response surface (3-Dimensional) plots for the responses were analyzed.

### 3.5.1 Effect of contact time and pH on MB and CR removal

The interaction effect of contact time and pH at a constant adsorbent dosage of 2.25 g on the % removal of MB and CR is shown in Figure 3.




(c) (d)

Figure 3: Plots of pH and Contact Time for MB and CR Removal: a) Contour Plot for MB Removal; b) 3-D Plot for MB Removal; c) Contour Plot for CR Removal; d) 3-D Plot CR Removal

It can be deduced from Figure 3 (a) and (b) that the % removal of MB dye on sorghum husk biosorbent increases to approximately 84.55 % with increase in the contact time to 135 min and then decreases with increasing contact time up to

180 min. This showed that contact time only influences MB removal up to equilibrium after which it begins to decrease, this in line with the previous findings [20]. The % removal of MB did not change with increasing pH. Figure 3 (c) and (d) showed that the % removal of CR dye increases with increase in the contact time between the sorghum husk biosorbent and the dye at lower pH values. However at higher pH values, the % removal of CR increases only slightly.

### 3.5.2 Effect of contact time and adsorbent dosage on MB and CR removal

The analysis of the relationship between the % removal, contact time and adsorbent dosage at a constant pH of 6.50 showed that the % removal of MB increases rapidly at higher adsorbent dosage and slowly at lower adsorbent dosage as the contact time also increases. The maximum % removal of 90.12 % was observed at a contact time of 135 min and adsorbent dosage of 4.00 g. This is in line with the findings of [21]. On the other hand, the % removal of CR increases slightly with increase in adsorbent dosage and contact time to a maximum of (62.33 %). These are presented in Figure 4.

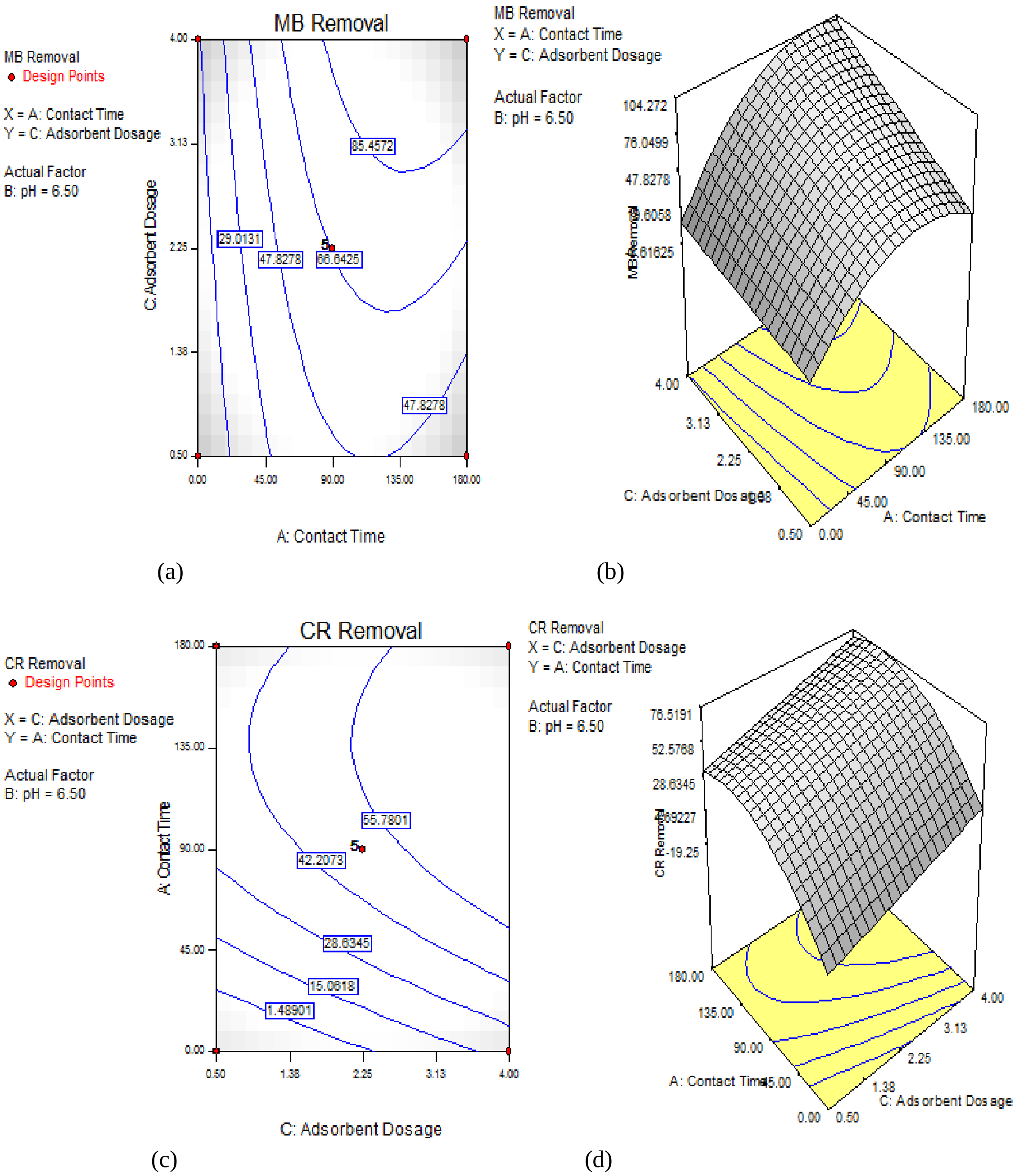



Figure 4: Plots of contact time and adsorbent dosage for MB and CR removal; a) contour plot for MB removal; b) 3-D plot for MB removal; c) Contour plot for CR removal; d) 3-D plot for CR removal

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### 3.6 Optimization of Process Variables

In this study, optimization of process parameters was carried out to determine the optimum values of the variables for maximum MB and CR removal. In optimizing the variables; contact time, pH and adsorbent dosage, the desired goal in terms of these variables was in range while the desired goal with respect to removal of MB and CR was set to maximum. This process was performed using the quadratic model within the studied experimental range of the process variables and the results obtained are presented in Tables 6 and 7.Table 7 showed that contact time of 138.05 min, pH of 3.00 and adsorbent dosage of 4.00 g were obtained as the optimum values of the process variables for MB and CR adsorption on sorghum husk. The model suggested a removal efficiency of 94.22 % for MB and 88.63 % for CR.

**Table 6: Constraints for Optimization of Process Variables for Adsorption of MB and CR**

| Lower<br>Name | Upper<br>Goal | Lower<br>Limit | Upper<br>Limit | Weight | WeightImportance | |
|---|---|---|---|---|---|---|
| Contact Time | is in range | 0.00 | 180.00 | 1 | 1 | 3 |
| pH | is in range | 3.00 | 10.00 | 1 | 1 | 3 |
| Adsorbent Dosa | is in range | 0.50 | 4.00 | 1 | 1 | 3 |
| MB Removal | maximize | 0.00 | 90.35 | 1 | 1 | 3 |
| CR Removal | maximize | 0.00 | 90.00 | 1 | 1 | 3 |

**Table 7: Solutions for Optimization of Process Variables for Adsorption of MB and CR**

| Number | Contact Time | pH | Adsorbent Dosage | MB Removal | CR Removal | Desirability | |
|---|---|---|---|---|---|---|---|
| 1 | 138.05 | 3.00 | 4.00 | 94.2173 | 88.6302 | 0.992 | Selected |
| 2 | 136.67 | 3.00 | 4.00 | 94.0708 | 88.6244 | 0.992 | |
| 3 | 132.88 | 3.00 | 4.00 | 93.5867 | 88.5503 | 0.992 | |
| 4 | 134.67 | 3.00 | 3.99 | 93.7074 | 88.5125 | 0.992 | |
| 5 | 124.62 | 3.00 | 3.94 | 91.1759 | 87.4234 | 0.986 | |

### 3.7 Validation of Model

The validation experimental run was carried out by combining the input variables; contact time, pH and adsorbent dosage set at optimum condition. The optimal contact time of 138.05 min, pH of 3.00 and adsorbent dosage of 4.00 g were used to obtain percentage removal of 93.10 % for MB and 87.96 % for CR, which were close to 94.22 % and 88.63 % removal predicted by the model for MB and CR respectively. The validation result is summarized in Table 8.

**Table 8: Validation of Model for MB and CR Removal**

| Sample | Experimental Value | | Model Value | | Error (%) | |
|---|---|---|---|---|---|---|
| | MB Removal | CR Removal | MB Removal | CR Removal | MB | CR |
| Sorghum Husk | 93.10 | 87.96 | 94.22 | 88.63 | 1.2 | 0.76 |

## 4. CONCLUSIONS

Bio-sorbents were prepared from sorghum husk for the removal of Methylene blue and Congo Red dyes from aqueous solutions. Effect of three independent variables i.e. contact time, pH and adsorbent dosage were investigated on the Methylene blue and Congo red dyes removal. The goal was to find best operating conditions that maximized the adsorbate removal. The BET analysis of the samples gave surface area of 139.539 $m^2/g$ and 233.822 $m^2/g$, micropore surface area of 180.93 $m^2/g$ and 225.365 $m^2/g$ for unmodified and modified sorghum husk. The SEM images revealed that the modified adsorbents have more expanded pores than the unmodified adsorbents, while the FTIR spectra revealed various functional groups on the adsorbents. The analysis of contour plots and response surface plots for the removal of MB and CR dyes on sorghum husk showed that adsorbent dosage has more profound effect on the percentage removal of MB and CR dyes than contact time and pH. The Box-Benkhen design using response surface methodology gave optimum contact time of 138.05 min, pH of 3.00 and adsorbent dosage of 4.00 g with percentage removal of 94.22 % for MB dye and 88.63 % for CR dye. The results indicated that adsorbents prepared from sorghum husk have the capacity for effective removal of both MB and CR dyes from aqueous solutions. This study has shown that the use of Box–Behnken design of RSM is a reliable methodology for optimization of process variables for adsorption of Methylene blue and Congo red from aqueous solution.

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