# Microwaved Activated Carbon from Mahogany Fruit Husk for Methylene Blue Adsoption

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**Abstract**— The use of activated carbon from agricultural wastes has gained much research interest due to its great economic and environmental value. In this study, microwave energy was investigated as an alternative heat treatment in the activation of carbon from mahogany fruit husk toward methylene blue (MB) removal. Interactions between Mahogany fruit husk activated carbon (MFHAC) preparation variables were determined through optimization using response surface method (RSM) with central composite design (CCD). Analysis of the surface characteristics of the microwaved MFHAC revealed the presence of acidic functional groups. It also had well developed crystalline carbon structure with ordered pores. Overall, the process via microwave irradiation provides significantly lesser heating time and lower energy consumption as compared to conventional heating method to produce activated carbon of comparable quality. Hence, microwave-assisted activation of mahogany fruit husk can be used for the efficient removal of methylene blue in simulated wastewater.

**Index Terms**— Adsorption, Activated carbon, Mahogany fruit husk, Microwave-thermal treatment, Methylene blue dye removal, Response surface modeling; Simulated waste water

## 1 Introduction

AMONG all industrial sectors, textile industries are rated as high polluters, taking into consideration the volume of discharge and effluent composition [1]. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations while 10% is discharged from textile and associated industries [2]. The release of colored waste water from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain [3].

In general, several difficulties are encountered in removal of dyes from waste waters due to their high stability which make them resistant to degradation by light, chemical, biological and other exposures. Many treatment processes have been applied for the removal of dyes from waste water such as photocatalytic degradation [4], sonochemical degradation [5], ultrafiltration [6], membrane technology [7], and adsorption [8]. Amongst these techniques, adsorption seems to be one of the most effective methods because of its simple operation and easy handling.

Numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several workers. These materials could be used as adsorbents for the removal of dyes from aqueous solution [9].

To bridge the gap between commercially available and lignocellulosic-based ACs, different modifications on the surface of the latter have been explored to improve its pore size and characteristic. The application of microwave (MW) heating technology for regenerating industrial waste activated carbon has been investigated with very promising results [10].

This study has focused on the production, characterization, and modification through microwave energy treatment of activated carbon from mahogany fruit husk. It also explores the application of the modified Mahogany fruit husk activated carbon (MFHAC) on methylene blue adsorption.

## 2 Methods

### 2.1 Aqueous solution

A stock solution was prepared by dissolving 1g of methylene blue (MB) powder in 1L of distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations.

### 2.2 Preparation of activated carbon

Mahogany fruit husks were obtained from Batangas City, Philippines. They were rinsed thrice with distilled water and then dried in an oven at 105°C for 24 h to remove moisture. The samples were ground and sieved to a particle size between 2.0 mm and 4.75 mm. Carbonization was carried out by loading the dried precursor into a stainless steel vertical tube reactor placed in a tube furnace for 1h under purified nitrogen flow. Phosphoric acid ($H_3PO_4$) was used to activate the char via the chemical activation method. The carbonized MFH sample was soaked in $H_3PO_4$ at varying concentrations (30, 40 and 50%) with an impregnation ratio of 1:2 (weight of char: weight of $H_3PO_4$) for 2 hours at 80°C. Afterwards, the samples were filtered using a vacuum pump and oven dried overnight at 105°C. Activation of impregnated char was carried out using a modified commercial microwave with a frequency of 2.45 GHz at different power level ranging from 140 W to 420 W and various radiation time ranging from 2 min to 6 min under a nitrogen flow of 300 $cm^3$/min. The sample was then cooled to room temperature under nitrogen flow and washed with hot deionized water and 0.1 M HCl until the pH of the washed

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solution ranged from 6 to 7.

### 2.3 Design of experiment using RSM

The considered variables for this study were radiation power ($X_1$), radiation time ($X_2$) and chemical impregnation ratio ($X_3$). These three variables together with their respective ranges were chosen based on the researchers' preliminary studies. The ranges and the levels of the variables investigated are given in Table 1.

Performance of the process was evaluated by analyzing MB removal efficiency. Each independent variable was varied over three levels between -1 and +1 at the determined ranges based on some preliminary experiments. The total number of experiments obtained for the three factors was 20 (=2$k$ + 2$k$ + 6), where $k$ is the number of factors ($k$ = 3). Since each factor only had three levels, the appropriate model is the quadratic model, expressed as the following equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j + e_i \quad \text{eq. 1}$$

where $Y$ is the predicted response, $b_0$ is the constant coefficient, $b_i$ is the linear coefficient, $b_{ij}$ is the interaction coefficient, $b_{ii}$ is the quadratic coefficient, and $X_i$ and $X_j$ are the coded values of the AC preparation variables, and $e_i$ is the error.

The quality of the fit of polynomial model was expressed by the correlation coefficient ($R^2$). The model $F$-value (Fisher variation ratio), probability value (Prob > $F$), and adequate precision (AP) are the main indicators demonstrating the significance and adequacy of the used model [11].

TABLE 1
INDEPENDENT VARIABLES AND THEIR CODED LEVELS FOR CCD.

| Variables (Factors) | Code | Units | Coded variable levels | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | 1 |
| IR | $X_1$ | % | 30 | 40 | 50 |
| MW time | $X_2$ | Min | 2 | 4 | 6 |
| MW power | $X_3$ | Watt | 140 | 280 | 420 |

### 2.4 Batch equilibrium studies

Batch adsorption was performed in 20 flasks of 250 mL Erlenmeyer flasks. In each flask, we placed 100 mL of the aqueous solution with an initial MB concentration of 50 mg/L. Each of the prepared AC samples (0.30 g) was added to individual flasks, which were then kept in an isothermal shaker at 200 rpm and 30°C until equilibrium was reached at 4h. After agitation, the solid was removed by filtration through a Whatman #1 membrane filter paper. To correct any adsorption of dye on containers, control experiments were carried out in duplicate. The first part of the filtrate was discharged to avoid the effects of adsorption on to the filter paper and the remaining filtrate was analyzed for residual dye concentration. The filtrates were collected in clean, dried bottles, and were prepared for analysis using a UV-Vis spectrophotometer. The sorbed dye concentrations were obtained from the difference between the initial and final dye concentrations in solution. The percentage removal at equilibrium was calculated as following equation:

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad \text{eq. 2}$$

where $C_o$ and $C_e$ are the liquid-phase concentrations at initial state and at equilibrium (mg/L), respectively. The amount of dye adsorbed per unit mass of adsorbent at equilibrium conditions, $qe$ (mg/g), was calculated by equation:

$$q_e = \frac{(c_p - c_e)v}{w} \quad \text{eq. 3}$$

where $qe$ (mg/g) is the amount of solute adsorbed per unit weight of adsorbent; $C_o$ and $C_e$ (mg/L) are the liquid-phase concentrations of adsorbate at initial and equilibrium conditions, respectively; $V$ (L) is the volume of the solution; and $W$ (g) is the mass of adsorbent used.

### 2.5 Characterization of prepared activated carbon

The surface area, pore volume and average pore diameter of the samples were determined by using Quantachrome volumetric adsorption analyzer. The BET surface area was measured from the adsorption isotherm using Brunauer–Emmett–Teller equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the samples was examined using a scanning electron microscope. Surface functional groups of the activated carbon were analyzed with FTIR spectroscopy.

## 3 RESULTS AND DISCUSSIONS

Thirteen experiments were performed to obtain a response surface model for the methylene blue removal efficiency of activated carbon prepared from mahogany fruit husk at varying solution pH and Cr (VI) concentration. The experimental factors and corresponding response are shown in Table 1. The observed percent removal efficiencies varied between 53.93 and 96.69% for Cr (VI) removal.

### 3.1 Statistical analysis

Analysis of variance (ANOVA) was carried out to justify the adequacy of the model. The results of the second-order response surface model fitting in the form of ANOVA are given in table 3 for MB removal. The quality of the model developed was evaluated based on correlation coefficient, R-square, and standard deviation. Data given in Table 2 demonstrate that the model was significant at the 5% confidence level. The closer the R-square to unity and the smaller the standard deviation, the more accurate the response could be predicted by the model.

TABLE 2
EXPERIMENTAL FACTORS AND RESPONSE

| Std. No. | Point Type | Factors | | | % MB Removal* |
|---|---|---|---|---|---|
| | | A: Imp. Ratio (%) | B: Power (Watt) | C: Time (min) | |
| 1 | Fact | 30 | 140 | 2 | 73.58 |
| 2 | Fact | 50 | 140 | 2 | 75.54 |
| 3 | Fact | 30 | 420 | 2 | 65.29 |
| 4 | Fact | 50 | 420 | 2 | 55.80 |
| 5 | Fact | 30 | 140 | 6 | 94.20 |
| 6 | Fact | 50 | 140 | 6 | 64.86 |
| 7 | Fact | 30 | 420 | 6 | 80.78 |
| 8 | Fact | 50 | 420 | 6 | 46.56 |
| 9 | Axial | 30 | 280 | 4 | 81.07 |
| 10 | Axial | 50 | 280 | 4 | 65.68 |
| 11 | Axial | 40 | 140 | 4 | 75.83 |
| 12 | Axial | 40 | 420 | 4 | 63.07 |
| 13 | Axial | 40 | 280 | 2 | 57.82 |
| 14 | Axial | 40 | 280 | 6 | 64.55 |
| 15 | Center | 40 | 280 | 4 | 70.29 |
| 16 | Center | 40 | 280 | 4 | 69.48 |
| 17 | Center | 40 | 280 | 4 | 69.03 |
| 18 | Center | 40 | 280 | 4 | 70.04 |
| 19 | Center | 40 | 280 | 4 | 70.74 |
| 20 | Center | 40 | 280 | 4 | 70.12 |

**Average of triplicate analysis*

The correlation coefficient for MB removal obtained in the present study was 0.9819, indicating that 1.81% of the total dissimilarity are not explained by the empirical model for MB removal. According to Bashir et al. [12], for a model to feature good fit, the correlation coefficient must be a minimum of 0.80. The R-squared obtained was higher than 0.80. An R-square value close to 1 demonstrates favorable agreement between the calculated and observed results within the experimental range.

ANOVA results for the quadratic response surface model for MB removal yielded a model F-value of 92.8018 and a probability > *F* less than 0.05. These values indicated that the model is significant. For the model terms, values of probability > *F* less than 0.05 indicated that the model terms are significant. In this study, A, B, C, AB, AC, $A^2$, and $C^2$ were significant model terms. Insignificant model terms BC and $B^2$, which has limited influence to the model were excluded from the study to improve the model. Based on the results, the response surface model constructed in this study for predicting MB removal efficiency was considered reasonable.

The Adequate Precision (AP) ratio of the model was 42.34. AP values higher than 4 are desirable and confirm that the predicted models can be used to navigate the space defined by the CCD. Hence, the AP ration for the model is desirable. The coefficient of variance (CV) value obtained was 2.47%. The obtained CV value from the model is below 10% which means that the model for MB removal will give reproducible results. Based on the statistical results obtained, the aforementioned model was adequate to predict MB removal within the range of variables studied. The final regression model, in terms of the factors used, is expressed by the second-order polynomial equation 4:

$$Y = 69.34 - 8.65*A - 7.25*B + 2.29*C - 2.04*A*B - 7.00*A*C + 5.97*A^2 - 6.22*C^2 \quad \text{eq. 4}$$

where, A is impregnation ratio (30 to 50% $H_3PO_4$), B is microwave radiation power (140 to 420 Watts), and C is microwave radiation time (2 to 6 min.).

Optimization of activated carbon production from mahogany fruit husk was performed using numerical method. The Design-Expert software used searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. Optimization requires that goals (i.e., none, maximum, minimum, target, or in range) are set for the variables and response where all goals then get combined into one desirability function. To find a good set of conditions that will meet all the goals, the three variables (i) impregnation ratio (30 to 50% $H_3PO_4$), (ii) microwave irradiation power (140 to 420 watt), and (iii) microwave irradiation time (2 to 6 min.) were set within range while methylene blue removal (%) was set at maximum. The "importance" of goals (option 1 to 5) for all variables was considered to be equally important in a setting of 3. For response, the "importance" was set at 5 in order to meet the objective of getting maximum MB removal. By applying the desirability function approach, the optimum level of various parameters was obtained as shown in Table 4.

TABLE 3
ANALYSIS OF VARIANCE AND ADEQUACY FOR THE QUADRATIC MODEL FOR MB REMOVAL

| Source of data | Sum of Squares | Degrees of freedom | Mean Square | F-Value | Prob. > F | Comment |
|---|---|---|---|---|---|---|
| Model | 1900.779 | 7 | 271.5399 | 92.8018 | < 0.0001 | Significant |
| A-IR | 747.879 | 1 | 747.879 | 255.5961 | < 0.0001 | |
| B-Power | 525.77 | 1 | 525.77 | 179.6878 | < 0.0001 | |
| C-Time | 52.53264 | 1 | 52.53264 | 17.95362 | 0.0012 | |
| AB | 33.33361 | 1 | 33.33361 | 11.39214 | 0.0055 | |
| AC | 392.4201 | 1 | 392.4201 | 134.114 | < 0.0001 | |
| $A^2$ | 114.0748 | 1 | 114.0748 | 38.98633 | < 0.0001 | |
| $C^2$ | 123.778 | 1 | 123.778 | 42.30252 | < 0.0001 | |
| Residual | 35.11223 | 12 | 2.926019 | | | |
| Pure Error | 1.844 | 5 | 0.3688 | | | |
| Std. Dev. = 1.71 | | $R^2$ = 0.9819 | | | | |
| CV = 2.47 | | Adjusted $R^2$ = 0.9713 | | | | |
| AP = 42.34 | | | | | | |

TABLE 4
OPTIMUM OPERATING CONDITION FOR PRODUCTION OF MICROWAVE IRRADIATED MFHAC FOR MB REMOVAL

| IR (%$H_3PO_4$) | Power (Watt) | Time (Min) | %MB removal |
|---|---|---|---|
| 30 | 140 | 5.5 | 92.643 |

Confirming whether or not the selected model provides adequate approximation of the real system is important. A triplicate experiment was set up to validate the optimized condition. As shown in Table 5, the experimental data were in good agreement with the predicted value for MB removal of the microwave irradiated MFHAC produced under optimized condition. Relative error between predicted and experimental

values was at 2.930%, clearly showing that the model fitted the experimental data very well and therefore optimized.

TABLE 5
EXPERIMENTAL CONFIRMATION OF PREDICTED VALUE FOR MB REMOVAL OF MICROWAVE-IRRADIATED MFHAC PREPARED UNDER OPTIMUM CONDITION

| MB Removal (%) | | | | | |
|---|---|---|---|---|---|
| Predicted | Experimental | | | Mean | Rel. Error* (%) |
| | $T_1$ | $T_2$ | $T_3$ | | |
| 92.64 | 89.42 | 88.72 | 91.87 | 90.01 | 2.94 |

To assess the interactive relationships between independent variables and the responses of the model, three-dimensional (3D) surface response plots were used. In the plots shown in Figures 1a and b, one variable was kept constant at optimum level while the two others were varied within the experimental ranges.

Figure 1a shows the 3D response surface of the combined effects of impregnation ratio and radiation time when the radiation power was kept at optimum level (140 W). The improvement in removal efficiency in MB may be attributed to increases in both impregnation ratio and radiation time. A possible explanation for this effect is that the reaction between $H_3PO_4$ and the char is greater at higher radiation time, thereby facilitating the development of the pore structure and resulting in the formation of a larger number of active sites.

Figure 1b shows the 3D response surface of the combined effect of radiation power and impregnation ratio, while the radiation time was kept at optimum level (5.5 min). The contour plot demonstrates that the improvement in MB removal may be attributed to increases in impregnation ratio and radiation power. However, the improvement in MB removal caused by radiation power is seen only up 140 W. This may be explained by the fact that as radiation power increases above the optimum level, the active sites start to disintegrate which results to a decrease in MB removal.

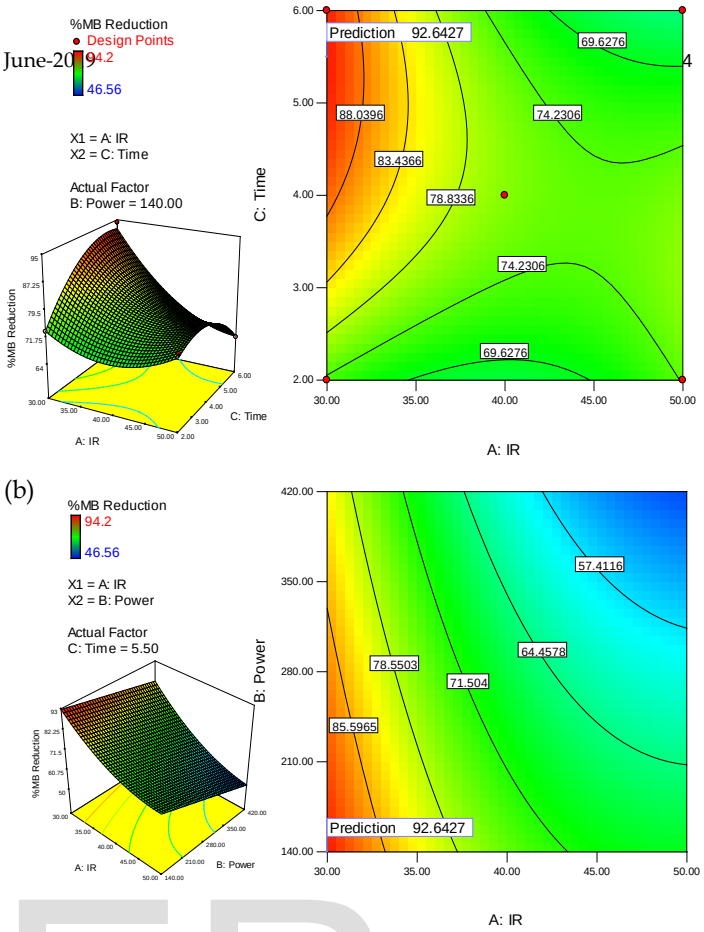


Fig. 1. Three dimensional response plot of MB removal with respect to (a) effect of impregnation ratio and radiation time, and (b) effect of impregnation ratio and radiation power

## 3.2 Characterization of optimized microwaved MFHAC

### 3.2.1 Surface functional groups

Surface chemistry is an important characteristic of activated carbons since it determines the surface properties of the carbon and has significant implications on their behaviors as ion exchangers, adsorbents, catalysts and catalyst supports. Intensity at around 3415 $cm^{-1}$ indicated H bonded to OH groups [13]. It also showed narrow bands at around 2918 and 2850 $cm^{-1}$ relating to C-H stretching of alkyl structures [14], specifically to methyl ($CH_3$) and methylene ($CH_2$) asymmetric stretching. The absorption energy around 2284 $cm^{-1}$ were characteristic of possible presence of nitriles or isocyanates.

The MFHAC also revealed bands at 1569 $cm^{-1}$, indicating the presence of aromatic and oleifinic C=C and C=O of bonded conjugated ketones, quinines, and aromatic group. The bands at 1078 $cm^{-1}$ microwaved MFHAC suggests stretching vibration of the C-O functional groups including alcohols, ethers, acids and esters [15]. The presence of hydroxyl group, carbonyl group, and ethers are evidences of the lignocellulosic structure of both microwaved MFHAC.

### 3.2.2 Surface morphology

Fig. 2 shows the SEM image of the derived microwaved MFHAC prepared under optimum conditions. It can be found that the microwave irradiated sample has well developed and uniform surface with an orderly pore structure. The presence of deep macropore hole structures on the microwave irradiated MFHAC samples suggests a well-developed pore structure, according to the study of Hameed et al. [16]. With this developed pore structure, there is a higher probability that methylene blue can be trapped and adsorbed onto the surface of the microwaved MFHAC. On the contrary, there are no pronounced macropore holes seen from the SEM image of the furnace-heated MFHAC sample, suggesting that the macropore did not form properly during heat treatment.

(a)

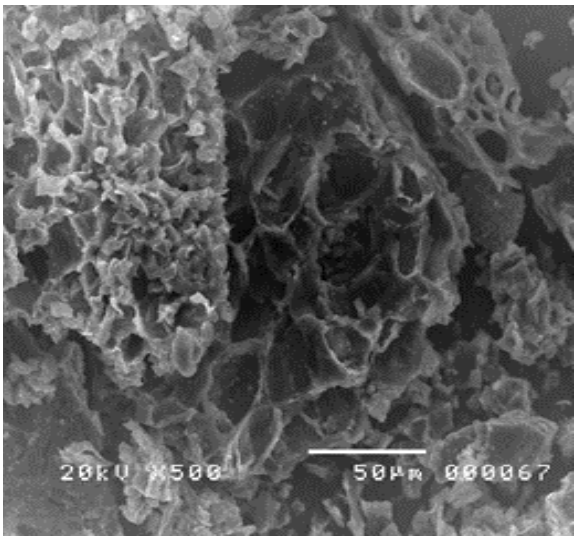


Fig. 2. SEM image of the optimized microwaved MFHAC at 500x magnification

The average pore diameters for the microwave irradiated MFHAC was found to be 3.4072 nm. This average pore diameter indicates that the AC prepared are in the mesopore region (2-50 nm diameter), according to the International Union of Pure and Applied Chemistry. The mesoporous characteristic of the produced ACs is suitable for methylene blue adsorption because the MB molecules have a minimum molecular cross-section of 0.8 nm, and the minimum pore diameter that the MB molecule can enter was estimated to be 1.3nm. Therefore, MB can enter most mesopores and the largest micropores [16].

## 4 Conclusions

Optimization of MB removal from solution using MFHAC prepared by microwave was investigated. Integration of microwave heating promotes porosity development. The interaction between MFHAC preparation variables, such as radiation power, radiation time, and impregnation ratio and responses were determined during optimization using RSM with CCD. Statistical analysis of the interaction between model responses and preparation parameters was significant at P value < 0.05. $R^2$ value of 0.9819 for MB removal was achieved. The optimum results attained from the model indicate that 5.5 min of microwave irradiation time is required to achieve 92.643% of MB removal when the radiation power and impregnation ratio are 140 W and 30%, respectively. Overall, the introduced process via microwave provides a faster and low energy consuming alternative to produce AC of comparable quality to conventionally prepared ACs.

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