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Optimization of Methylene Blue Adsorption onto *Swietenia Mahogani* Activated Carbon using Response Surface Methodology

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Abstract— Visible color is a sign of contamination in wastewater and much interest have been put into using lignocellulosic-based actvated carbons in removing colorants from the environment. In this work, activated carbon was prepared from *Swietenia mahogani* fruit husk using chemical impregrantion with phosphoric acid and heat treatment using a furnace. The resulting activated carbon was used to optimize the adsorption condition, specifically the solution pH and adsorbate concentration, for methylene blue (MB) removal in simulated waste water. Interactions between Mahogany fruit husk activated carbon (MFHAC) preparation variables were determined through optimization using response surface method (RSM) with central composite design (CCD). The surface morphology and functional groups were also analyzed. Overall, the AC produced from mahogany fruit husk can be used for the efficient removal of methylene blue in simulated wastewater.

Index Terms— Adsorption, Activated carbon, Central composite design, Mahogany fruit husk, Methylene blue dye removal, Response surface modeling; Simulated wastewater

1 Introduction

IN the field of wastewater treatment, the use of activated carbons (AC) for adsorption processes is highly acknowledged. AC has been long considered as the best adsorbent materials because of its large surface area, microporous structure, high degree of surface reactivity and high adsorption capacity [1-3].

The preparation of activated carbon can be completed by two methods, physical activation and chemical activation [4]. Physical activation involves pyrolysis of the resource materials at 800-1000˚C to produce the charcoal, followed by activation using either steam, carbon dioxide or oxygen [5]. This process leads to pore development, surface area increase and the ensuing mass loss. On the other hand, the chemical activation involves the impregnation of the char with a chemical reagent which act as dehydrating agent and oxidant usually Bronsted or Lewis acid or a strong alkali such as H_3PO_4, H_2SO_4, KOH or NaOH followed by heat treatment at room temperature of 450-900˚C [6].

Visible color is a sign of contamination in wastewater. A dye concentrations higher than 1 mg/L caused by discharges of textile effluent is highly visible and affect the aesthetic merit, water transparency and gas solubility in lakes, rivers, and other surface water [7]. Methylene blue affects the eyes which may be responsible for permanent injury to the eyes of human and animals. Once inhaled, it can cause to short periods of rapid or difficult breathing while oral ingestion produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [8]. There has been a remarkable interest in utilizing activated carbons to adsorb colorants.

The adsorption capacity of activated carbon is affected by certain factors such as pH, temperature, adsorbate concentration, adsorbent dosage and contact time. The adsorption capacity is greatly influenced by pH onto the surface charge of adsorbent, it acts as regulator of the adsorption process [9]. ACs prepared from a variety of agricultural wastes have been studied to develop new low cost and efficient activated carbon. For instance, different ACs have been produced by utilizing different agricultural biomass, such as rice husk [10], grape seed [11], rambutan peel [12], kenaf fiber [13], and date pit [14].

To date, there are limited studies on methylene blue removal from wastewater using activated carbon prepared from mahogany fruit husk and optimization of methylene blue adsorption conditions using response surface methodology (RSM). The optimization using RSM is particularly useful when all of the independent variables and their levels and responses are not clearly known [15]. A standard RSM technique called a central composite design (CCD) is appropriate for generating a quadratic surface and can help analyze interactions between parameters and optimize the effective parameters within a small number of experiments [16].

The main objective of this study was to optimize the methylene blue adsorption conditions using activated carbon prepared from *Swietenia mahogany* fruit husk. The adsorption parameters, specifically solution pH and adsorbate concentration, were investigated to istablish the optimum condition for the maximum removal of MB in simulated wastewater.

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.

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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 40% (v/v) H_3PO_4 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 muffle furnace at 400°C for 1 h. 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 solution ranged from 6 to 7.

2.3 Design of experiment using RSM

The considered variables for this study were solution pH (X_1) and adsorbate concentration (X_2). These two variables together with their respective ranges were chosen based on the researcher's 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 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 [17].

TABLE 1
INDEPENDENT VARIABLES AND THEIR CODED LEVELS FOR CCD.

Variables (Factors)	Code	Units	Coded variable levels		
			-1	*0*	*1*
Solution pH	X_1	-	6	9	12
Adsorbate Conc.	X_2	ppm	20	50	80

2.4 Batch equilibrium studies

Batch adsorption was performed in thirteen flasks of 250 mL Erlenmeyer flasks. In each flask, we placed 100 mL of the aqueous solution with varying initial MB concentration (20, 50, and 80 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 triplicate. 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:

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

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:

$$q_e = \frac{(C_p - C_e)v}{w} \qquad \text{eq. 3}$$

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 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 methylene blue concentration. The experimental factors and corresponding response are shown in Table 2. 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 3 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.

The correlation coefficient for MB removal obtained in the present study was 0.9569, indicating that 0.80% of the total dissimilarity are not explained by the empirical model for MB removal. For a model to feature good fit, the correlation coefficient must be a minimum of 0.80 [18].

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TABLE 2
EXPERIMENTAL FACTORS AND RESPONSE

Std. No.	Point type	Factors		MB Removal* (%)
		A: pH	B: MB Conc. (ppm)	
1	Fact	6	20	62.83
2	Fact	12	20	89.97
3	Fact	6	80	53.93
4	Fact	12	80	76.10
5	Axial	6	50	71.78
6	Axial	12	50	96.69
7	Axial	9	20	69.14
8	Axial	9	80	58.81
9	Center	9	50	90.06
10	Center	9	50	88.60
11	Center	9	50	89.82
12	Center	9	50	87.21
13	Center	9	50	88.36

**Average of triplicate analysis*

ANOVA results for the quadratic response surface model for MB removal yielded a model F-value of 66.62799 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, and B^2 were significant model terms. Insignificant model term A^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.

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

Source of data	Sum of Squares	Degrees of freedom	Mean Square	F-Value	Prob. > F	Comment
Model	2271.868	3	757.2894	66.62799	< 0.0001	significant
A	918.1014	1	918.1014	80.77659	< 0.0001	significant
B	182.6017	1	182.6017	16.0657	0.0031	significant
B^2	1171.165	1	1171.165	103.0417	< 0.0001	significant
Residual	102.2934	9	11.36593			
Pure Error	5.3892	4	1.3473			
Std. Dev. = 3.37	R^2 = 0.9569					
CV = 4.28	Adjusted R^2 = 0.9426					
AP = 26.36						

The Adequate Precision (AP) ratio of the model was 26.36. 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 ratio for the model is desirable. The coefficient of variance (CV) value obtained was 4.28%. 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.

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. By applying the desirability function approach, the optimum level of various parameters was obtained as shown in Table 4.

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

Solution pH	Adsorbate Concentration (ppm)	%MB removal
11.72	52.82	98.866

To assess the effect of solution pH and methylene blue concentration on the MB removal efficiency of the optimized MFHAC, contour plot was used.

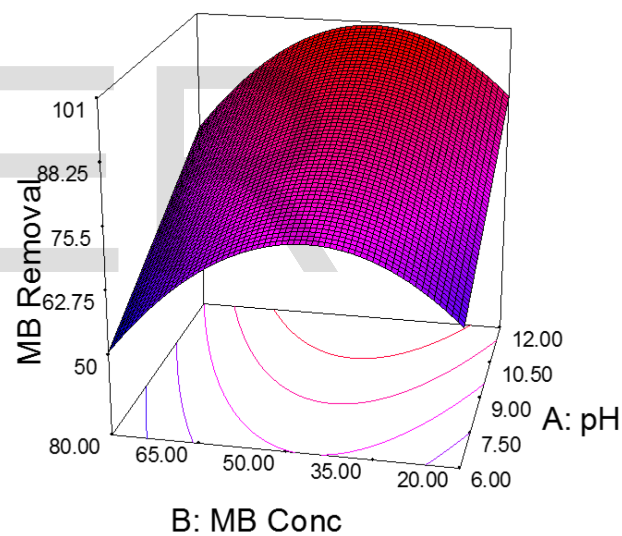

Fig. 1. Three dimensional response plot of MB removal with respect to methylene blue concentration and solution pH.

In the plot shown in Figure 1, adsorption at around pH 6 showed low MB removal efficiency while increasing the solution pH to around 11.72 increased the MB removal efficiency optimized MFHAC to its maximum. This is because of methylene blue's cationic nature. At basic pH, most of the acidic functional groups of the MFHAC have been deprotonated which lead to an overall negative charge. Ionic attraction between the negatively charged surface functional groups of the AC and the cationic MB increases the adsorption efficiency. On the other hand, the effect of MB concentration on MB removal efficiency showed the highest positive effect at around 52.82 ppm. Efficiency of MB removal was observed to decline beyond the optimum concentration. This may be because at

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around 52.80 ppm, all the active sites in the activated carbon have been completely filled with methylene blue and further agitation only leads to weakening of the interaction between the adsorbent and the adsorbate, leading to a decrease in adsorption efficiency.

3.2 Characterization of MFHAC

3.2.1 Surface functional groups

The intensity at around 3415 cm^{-1} indicated H bonded to OH groups [19]. It also showed narrow bands at around 2918 and 2850 cm^{-1} relating to C-H stretching of alkyl structures [20], 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} MFHAC suggests stretching vibration of the C-O functional groups including alcohols, ethers, acids and esters [21]. The presence of hydroxyl group, carbonyl group, and ethers are evidences of the lignocellulosic structure of MFHAC.

3.2.2 Surface morphology

Fig. 2 shows the SEM image of the optimized MFHAC. The sample has well developed and uniform surface with an orderly pore structure. The presence of deep macropore hole structures on the MFHAC samples suggests a well-developed pore structure [22]. With this developed pore structure, there is a higher probability that methylene blue can be trapped and adsorbed onto the surface of the MFHAC.

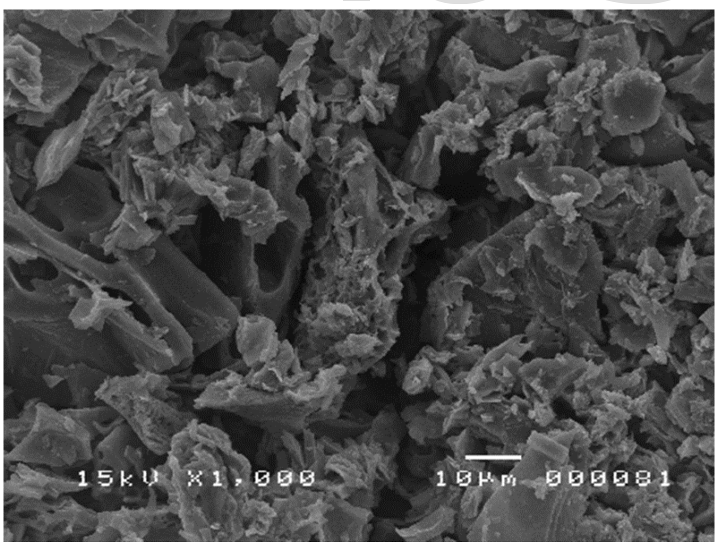

Fig. 2. SEM image of the MFHAC at 1000x magnification

4 Conclusions

Optimization of solution pH and adsorbate concentration for the adsorption of methylene blue onto MFHAC was investigated. The interaction between MFHAC the two variables and the methylene blue removal efficiencies 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 0.9569 for MB removal was achieved. The optimum results attained from the model indicate that pH of 11.72 will achieve 98.87% MB removal for a 52.82 ppm MB solution. The surface of the optimized MFHAC had a porous structure which contained rich acidic and basic functional groups. Overall, the produced AC from *S. mahogani* proves to be a cheap and effective alternative for removing MB in simulated wastewater.

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