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Adsorption of Methylene Blue Dye un der Box Behnken Design using Zeolite Synthesis from Bamboo Leave based Silica

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***Abstract**: Waste Bamboo Leaves (WBL) are mostly discharged through open burning which causes environmental pollution. As a result, these wastes should be valourised. The Waste Bamboo Leaves were calcinated and the selected calcination factors were optimised under I-optimal design using Response Surface Methodology. The obtained ash was used to produce zeolite. The experimental design was carried out using adsorbent dosage, agitation rate, and contact time as independent variables. Batch adsorption experiments were conducted using the experimental design result, then the experimental data obtained were optimized using Design-Expert software and the results were validated. Optimum values for adsorbent were 1 g of adsorbent dosage, 160 rpm agitation rate, and 45 min contact time. These resulted in 93.11% removal efficiencies and the adsorption capacity of 4.66 mg/g for the adsorption of methylene blue. Therefore, WBL is an efficient residue for zeolite synthesis for the removal of methylene blue dye from wastewater using Waste Bamboo.*

Keywords— Adsorption, Bamboo Leaves, Box Behnken, Methylene Blue, Zeolite

1.0 Introduction

Bamboo is a tribe of flowering perennial evergreen plants in the grass family of *Poace* and the subfamily of *Bambusoideae.* Bamboo is recognized as the fastest-growing plant in the world. It is an abundant, inexpensive and renewable resource (Supee *et al*., 2022). Bamboo is an outstanding renewable biomass resource due to its highly growing speed. The bamboo leaf itself has no commercial value and it is usually disposed of by open burning, thus causing environmental pollution and disposal problems. Bamboo leaves wastes have high silica content which makes it a precursor for zeolite production to remove methylene blue dye.

One of the most widely used dyes is methylene blue. Besides that, methylene blue is also used as a dye in the field of bacteriology and ink filler materials. Methylene blue (MB) dye is the most frequently used cationic dye which contains a phenothiazine functional group (Joshi *et al.*, 2022). Widespread use of methylene blue dye can lead to environmental pollution, especially water if handled inappropriately (Kutanri and Febi, 2022). The presence of a dye in the water can affect the water's characteristics. Organic dyes are harmful to humans, and the need to remove the colour from wastewater effluent becomes important to the environment (Mohammed et al., 2014). However, few researches have been done on bamboo leaves using an optimization approach. This study assessed the production of zeolite from bamboo leaves which is an agricultural residue to remove methylene blue dye using optimization (Box Behnken design).

2.0 Materials and Methods

2.1 Preparation of Bamboo Leaves Ash

Waste Bamboo Leaves (WBL) were sourced from the thickets in the suburb of Ogbomoso Township, Nigeria and transported to the Bioenvironmental, Water and Engineering Research Group (BWERG), Laboratory (Adsorption Section), LAUTECH, Ogbomoso. They were washed thoroughly, drained, and oven-dried for 48 h to constant moisture content. They were later pulverized and sieved to a uniform particle size (75 µm). The pulverized WBL samples were calcined in a muffle furnace, while the selected calcination factors such as temperature (600-750 °C) and time (3-6 h) were optimized under the I-Optimal Design of the Response Surface Methodology (Design Expert Software 12.0.1) (Table 1). The responses that were investigated were the ash yield and the silica content of the ash obtained.

2.2 Production of Zeolite from Bamboo Leaves Ash

The obtained bamboo ash was dissolved with 1 M NaOH while stirring and heated to 85 °C for 1 h. The mixture was filtered and 3 M H_2SO_4 solution was added drop wisely to the filtrate until the gel was formed (pH = 7). The formed gel was then allowed to stand for 24 h for the aging process. The gel was filtered and washed with hot distilled water. The washed gel was dried at 80 °C for 15 h. (Chow, 2017, Azman *et al.*, 2023). The dried solid was then crushed until smooth and mixed with 2 NaOH and distilled water (Azman *et al.*, 2023) and stirred to obtain homogeneous mixture. The mixture was allowed to age for 24 h. The mixture was crystallized with mechanical agitation and placed in water bath for 5 h at 60 °C. Then, the crystallized mixture was filtered and washed thoroughly with distilled water. Then, the obtained zeolite was dried at 60 °C for 5 h (Setiadji *et al.*, 2018).

2.3 Preparation of Methylene Blue Solutions

Methylene blue (empiric formula $C_{16}H_{18}ClN_3S$ and molar mass 319.85 g/mol) was dissolved in distilled water to prepare 100 mg/l MB solutions with the desired concentration. The methylene blue solution used in this research was the fresh solution.

2.4 Adsorption Studies

Batch experiments were carried out using a series of cups of 50 mL capacity. The effect of shaking time, weight of adsorbent, and initial concentration of MB was studied. The effect of shaking time was run by taking selected different contact times (30, 45 and 60 minutes). The dosage of the Bamboo leaves ash ranges from 1 to 2 grams and the agitation rate ranges from 120 to 160 rpm. 0.05g of MB was added to distilled water to obtain a concentration of 100 mg / L. After the required experiment, the solution was centrifuged and the concentration of MB was determined in filtrate using a UV-visible spectrometer (Thermo Scientific Genesys 20). The residual MB concentration in each solution was determined spectrophotometrically at the corresponding maximum wavelength (λmax) of MB (664 nm). The MB concentration was calculated from the equation obtained on the calibration curve**.** The adsorption capacity and removal efficiency were evaluated using Eqns. 1 and 2, respectively**.** Where q is the adsorption capacity of the zeolite, C_0 (g/L) is the initial concentration of adsorbent (g/L), C_t is the final concentration of adsorbate, V(L) is the volume of the solution treated and m (g) is the mass of the adsorbent.

$$\boldsymbol{Adsorption\ Capacity\ (q_e)} = \frac{(C_O - C_t)V}{m} \qquad (1)$$

$$\boldsymbol{Removal\ Efficiecy}\ (\%) = \frac{C_O - C_t}{C_o} \times 100 \qquad (2)$$

3.0 Results and Discussion

3.1 Optimisation of zeolite from calcined

The DOE (12.0.1) is represented in Table 1. The experimental design in the silica yield from the ash was I-optimal under response surface methodology. Calcination factors such as temperature (600-750 °C) and time (3-6 h) were optimized.

Table 1: I- optimal for calcination factors

Run	Factors		Responses	
	Temperature (ºC)	Time (h)	Ash yield (%)	Silica Content (%)
1	633.00	4.95	27.40	61.74
2	686.05	4.71	26.00	61.72
3	654.75	3.00	21.40	62.03
4	750.00	3.45	11.70	63.20
5	686.05	4.71	26.00	63.26
6	600.00	4.08	24.51	60.28
7	750.00	6.00	17.79	63.97
8	749.25	4.71	25.00	65.34
9	697.50	3.66	19.55	60.58
10	622.50	6.00	29.89	60.02
11	600.70	3.00	33.09	59.44
12	686.05	4.71	24.55	55.98
13	685.50	6.00	25.32	60.55

3.2 Analysis of variance for ash yield and silica content

The Model F-value and P- values are 18.51 and less than 0.0500 respectively which indicate model terms are significant (Table 3). The Lack of Fit F-value of 0.21 implies the Lack of Fit is not significant relative to the pure error. The standard deviation, mean, C.V%, R^2, $Adjusted\ R^2$, predicted R^2 are 1.75, 23.02, 7.59, 0.9766,0.9238,0.7912 respectively. Adequate precision is 14.6806. The Model F and P-value are 4.63 and 0.0415 respectively (Table 3). This implies that the model is significant. There is only a 4.15% chance that an F-value this large could occur due to noise. The model equation developed is significant with a F and P-value of 17.34 and 0.0012 respectively which implies the significance of the model. In this case, B, AB, A^2, B^2, and B^3 are significant model terms. The standard deviation, mean, C.V%, R^2, $Adjusted\ R^2$, predicted R^2 are 1.36, 61.97, 2.19, 0.5069,0.3974,0.1522 respectively. Adequate precision is 5. 4926.The predicted R^2, 0.1522 is in reasonable agreement with Adjusted R^2 of 0.3975.

Table 2: ANOVA for Ash yield and Silica Content (%)

Source	**Ash yield (%)**					**Silica Content (%)**				
	Sum of Squares	**df**	**Mean Square**	**F-value**	**p-value**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	508.74	9	56.53	18.51	0.0064*	17.09	2	8.55	4.63	0.0415*
A-Calcination Temperature	2.93	1	2.93	0.9593	0.3828	16.00	1	16.00	8.66	0.0164*
B-Calcination Time	0.4146	1	0.4146	0.1358	0.7312	0.5859	1	0.5859	0.3172	0.5871
AB	8.64	1	8.64	2.83	0.1678	NA	NA	NA	NA	NA
A^2	3.89	1	3.89	1.27	0.3220	NA	NA	NA	NA	NA
B^2	7.60	1	7.60	2.49	0.1897	NA	NA	NA	NA	NA
A^2B	4.99	1	4.99	1.63	0.2703	NA	NA	NA	NA	NA
AB^2	23.70	1	23.70	7.76	0.0495*	NA	NA	NA	NA	NA
A^3	2.72	1	2.72	0.8909	0.3987	NA	NA	NA	NA	NA
B^3	1.66	1	1.66	0.5423	0.5023	NA	NA	NA	NA	NA
Residual	12.21	4	3.05			16.63	9	1.85		
Lack of Fit	0.7891	1	0.7891	0.2072	0.6799	11.38	8	1.42	0.2709	0.9090
Pure Error	11.42	3	3.81			5.25	1	5.25		
Cor Total	520.95	13				33.72	11			

3.3 Characterisation of raw, calcined WBL and zeolite

The elemental composition of the calcined ash for the 16 runs was investigated using X-ray fluorescence (XRF) and the sample with the highest silica content was calcined at 749 ℃ at 4.71 h for Zeolite production. The elemental composition of raw WBL was also determined using XRF. The result revealed the following elemental composition (Table 4). The silica content in calcined ash decreased from 67.42% to 65.34% this may be due to environmental factors. yield in % and silica yield in %.16 runs were generated and 3 runs were outliers. The cubic model showed the least standard deviation of 0.0070.

Table 3: XRD results

Oxide	Raw WBL	Calcined WBL	Zeolite
SiO_2	67.42	65.34	43.31
Al_2O_3	5.27	4.79	0.68
K_2O	2.58	3.36	0.73
CaO	4.97	9.36	0.07
MgO	3.29	2.03	0.14
Fe_2O_3	0.25	3.22	31.2
Na_2O	2.2	3.01	0.36
P_2O_5	0.98	0.01	0.18
TiO_2	0.08	0.4	0.09
MnO	0.05	0.03	0.03
ZnO	0.33	0.3	9.06
CuO	0.02	0.03	0.01
SO_3	0.15	0.14	0.03

Cr_2O_5	0.01	0.01	0.01
LOI	12.4	7.97	14.1

3.4 Model equation generated for ash yield and silica content

The model equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as + and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficient.

$$Ash\ yield = 28.93 - 20.54A - 12.33B + 14.01AB - 7.82A2 - 10.07B2 - 7.88A2B - 15.599AB2 + 26.48A2 + 22.41B3 \quad (1)$$

$$Silica\ yield = 62.03 + 1.58A + 0.2917B \quad (2)$$

The positive values indicate the favourability of the response while the negative signs show the opposition to the increased response. A is the calcination temperature and B is the calcination time.

3.5 Model graph for optimization of ash yield and silica content

The 3D response surface plots for the ash and silica yield are shown in Figures 1 and 2 for the adsorption of methylene blue. The selected response surface model predictions were used to verify the models.

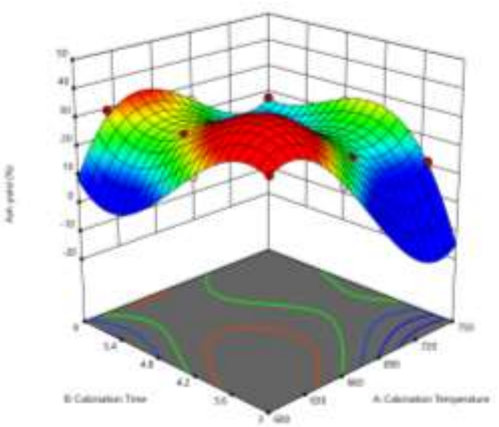

Figure 1: 3- D Graph for Ash yield

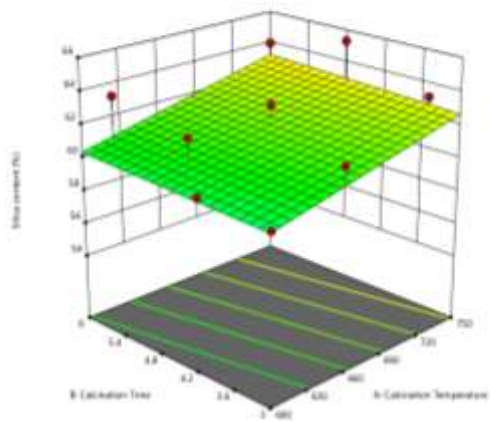

Figure 2:3-D Graph for Silica yield

3.6 Model summary of the experimental data for the batch adsorption

Box Behnken design was used for the experimental design in the batch adsorption using methylene blue. The factors considered are time, dosage, and agitation rate while the responses were adsorption capacity and adsorption efficiency in percentage. 17 experimental runs were generated and 3 were outliers (Table 4). The cubic model showed the least standard deviation of 0.0070 as well as the highest adjusted R^2 of 0.9999 and its predicted R^2 of 0.9997.

Table 4: Box Behnken design for removal efficiency

Run	Factors			Responses	
	A: Time (min)	B: dosage (g)	C: rate (rpm)	Adsorption capacity (mg/g)	Removal efficiency (%)
1	45	1.5	140	3.100	92.85
2	60	2	140	2.330	93.13
3	60	1	140	4.640	92.85
4	60	1.5	120	3.070	92.05
5	45	1	160	4.660	93.11
6	45	1.5	140	3.090	92.68

7	30	1	140	4.650	93.07
8	45	1.5	140	3.090	92.72
9	30	1.5	160	3.090	92.64
10	45	2	120	2.330	93.07
11	60	1.5	160	3.100	92.87
12	30	2	140	2.330	93.17
13	30	1.5	120	3.090	92.79
14	45	1	120	4.650	92.91

3.7 Analysis of Variance (ANOVA) for adsorption capacity

The model equation developed is significant with F and P values of 25823.65 and less than 0.0001 respectively which implies the significance of the model. In this case, B, and B² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The standard deviation, mean, C.V%, R^2, Ad$justed$ R^2, predicted R^2 are 0.0070, 3.28, 0.2141, 1.0000, 0.9999, 0.9997 respectively. Predicted R^2 and Adjusted R^2 are in agreement because the difference is 0.0002. Adequate precision is 433.4293 which indicates an adequate signal. This model can be used to navigate the design space (Table 5).

3.8 ANOVA for removal efficiency

The Model F-value of 16.60 implies the model is significant. There is only a 0.79% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, AC, and B² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant (Table 5). The lack of Fit F-value of 0.64 implies the Lack of Fit is not significant relative to the pure error. There is a 60.89% chance that a Lack of Fit F-value this large could occur due to noise. The standard deviation, mean, C.V%, R^2, Ad$justed$ R^2, predicted R^2 are 0.838, 92.85, 0.0903, 0.9739, 0.9153, and NA respectively. Adequate precision is 15.7491 which indicates an adequate signal. This model can be used to navigate the design space (Table 5).

3.9 Model Equations Generated

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$Adsorption\ capacity = 3.10 - 0.0025A - 1.16B + 0.0037C + 0.0025AB + 0.0075AC - 0.0050BC - 0.0055A2 + 0.3970B2 - 0.0030C2 \quad (3)$$

$$\text{Removal efficiency} = 92.75 - 0.0954A + 0.1064B + 0.1529999C + 0.00440ABB + 0.2446AC + 0.0416BC - 0.1178A2 + 0.4228B2 - 0.0420C2 \quad (4)$$

Table 5: ANOVA for Adsorption capacity

Source	Sum of Squares	df	Mean Square	F-value	p-value	Sum of Squares	df	Mean Square	F-value	p-value
Model	11.45	9	1.27	25823.65	< 0.0001	1.05	9	0.1166	16.60	0.0079
A-Time	0.0000	1	0.0000	1.01	0.3474	0.0728	1	0.0728	10.37	0.0323
B-dosage	10.79	1	10.79	2.189E+05	< 0.0001	0.0604	1	0.0604	8.60	0.0427
C-rate	0.0001	1	0.0001	2.28	0.1746	0.1247	1	0.1247	17.75	0.0136
AB	0.0000	1	0.0000	0.5072	0.4994	0.0078	1	0.0078	1.10	0.3526
AC	0.0002	1	0.0002	4.57	0.0700	0.2394	1	0.2394	34.08	0.0043
BC	0.0001	1	0.0001	2.03	0.1973	0.0035	1	0.0035	0.4925	0.5215
A²	0.0001	1	0.0001	2.58	0.1520	0.0416	1	0.0416	5.93	0.0716
B²	0.6636	1	0.6636	13464.69	< 0.0001	0.5362	1	0.5362	76.35	0.0009
C²	0.0000	1	0.0000	0.7689	0.4096	0.0053	1	0.0053	0.7533	0.4344
Residual	0.0003	7	0.0000			0.0281	4	0.0070		
Lack of Fit	0.0002	3	0.0001	2.50	0.1985	0.0110	2	0.0055	0.6423	0.6089
Pure Error	0.0001	4	0.0000			0.0171	2	0.0086		
Cor Total	11.45	16				1.08	13			

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3.10 Model Graph for the Optimation of Adsorption Study

The plots of the predicted against the actual responses for the adsorbents (Figures 3 and 4). This indicates that there was a very strong agreement between the experimental and predicted values for the adsorption of the methylene blue (Adetoro and Ojoawo 2020) because virtually all the values fall on the line even as evident in actual and predicted R^2 (0.9997 and 0.9999 respectively). The 3D response surface (removal efficiencies and adsorption capacity) plots as functions of the adsorption factors (Figures 5 and 6) for the adsorption of methylene blue. The selected response surface model predictions were used to verify the models. All the predictions from the plots were within the main adsorption zone. The red zones in Figures 5 and 6 indicate the main adsorption zone, green in Figure 7 indicates the possibility of an adsorption zone (adsorption may occur at this zone, though it contains impurities), while blue indicates the cold adsorption zone i.e. adsorption is likely to occur at this zone, its probability is very low in Figure 6 and 7 (Adetoro and Ojoawo 2020). Two factors (time and dosage) at a time played prominent roles (Figure 5).

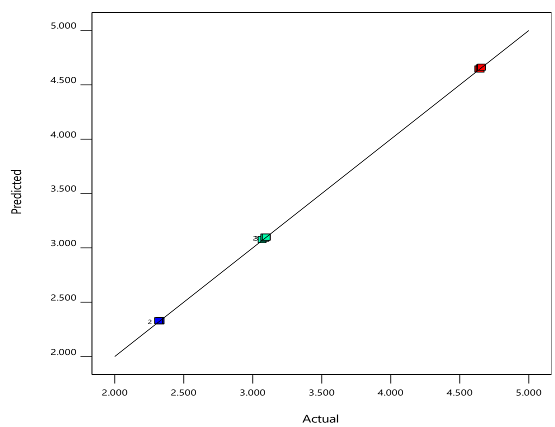

Figure 3: normal plot of predicted versus normal for Adsorption capacity

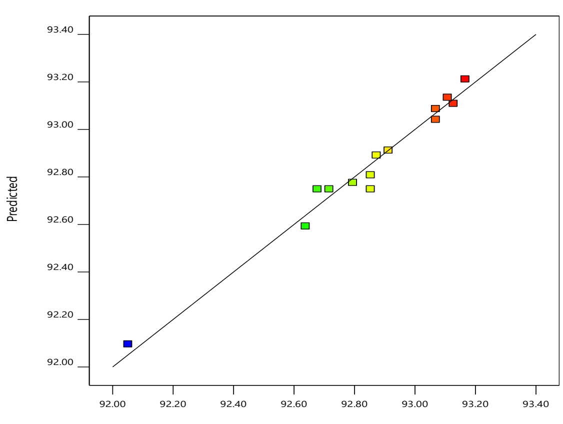

Figure 4: Plot of predicted versus normal for Removal efficiency

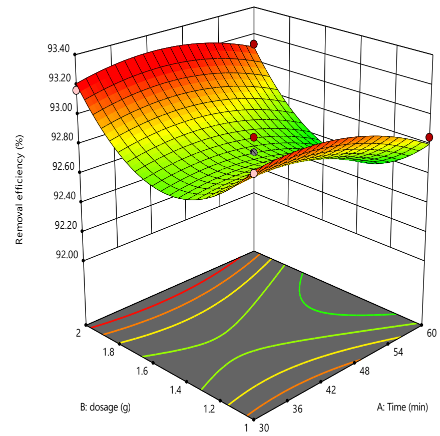

Figure 5: 3-D plot for Average removal efficiency

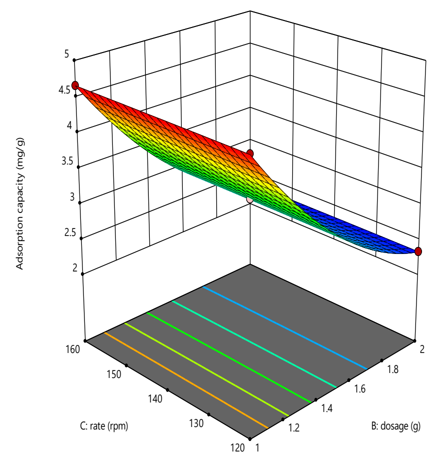

Figure 6: 3-D plot for Average adsorption Capacity

3.9 Comparison with various adsorbent

The data of different studies for the removal of MB by various composites along with the data of the present study are depicted in Table 6. On comparing the removal efficiency of bamboo leaves with various adsorbents, it exhibits that the adsorbent used in the present study was effective in the removal of MB from its aqueous solution and the prepared adsorbent. Its adsorption capacity with other adsorbents was relatively lower than 12.41 mg/g (de Oliveira *et al.*,2020) and 54.35 mg/g (Joshi *et al.*, 2022). This could be, due to their variation in surface area, surface chemistry, material preparation and experimental conditions.

Table 6: The comparison of studies using various adsorbents for the removal of methylene blue

Adsorbent	Removal Efficiency %	References
Waste Bamboo Leave	87.79	Kutanri and Febi, 2020
Waste Bamboo Leave	87.00	Zahari *et al.*, 2022
Grape wood waste	98.00	Mousavi *et al.*, 2022
Polymer and Protein nanoparticle	69.00	Fathi *et al.*,2024
Waste Bamboo Leave/Zeolite	93.17	This study

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