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Statistical Analysis and Optimization Studies of Adsorption of Malachite Green Using Bean Husk

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Abstract

As a dye, the main constituent of textile industrial wastewater is carcinogenic this research focuses on the treatment of wastewater containing malachite green dye using bean husk. Using central composite design of design of experiment (DOE), the optimized effect of adsorbent dosage, contact time, speed, initial concentration of dye and temperature were studied. The FTIR of bean husk shows that the adsorbent has potential adsorption sites which are being represented by their functional groups: C-O (1050.21), O-H of alcohol (3432.0), S-H (2357.0), and C=C of alkene or aromatic ring (1633.3) to form bonds with the dye molecules. The surface image reveals that the adsorbent is highly porous and has readily available pores for the adsorption of dyes. With the study of the elemental composition of bean husk, it is revealed that it has a high percentage of carbon and carbon compounds (100%). The optimum points predicted for Malachite green onto bean husk are dosage of 3g, contact time of 105 minutes, temperature of 45°C, agitation speed of 125rpm and concentration of 75ppm. The linear model suggested shows a good fit and a high coefficient of determination, with R-Squared value of approximately 76.5% while the adjusted R-squared is 64.7%. The probability of F-statistics is 0.132 which is greater than 0.005, this further confirms the reason why the design expert software selected the linear model because it has an insignificant lack of fit.

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Introduction

Industrialization and day-to-day use of chemicals for various purposes had led to contamination of our natural resources by release of diverse harmful organic and inorganic substances into our various water systems (Giwa *et al.*, 2015) In quest of making our world colorful, there is also an increase in the use of numerous dyes in the production of our clothes, our food our cosmetics, and even pharmaceuticals (Pokhrel and Viraraghavan, 2004). Recent studies have revealed that certain dyes can cause cancer growth and neurological disorders and even human genetic mutations (Ahmed and Dhedan, 2012). It is therefore of imperative importance to find a satisfactory treatment of waste water containing dyes, and recent research dwells on including chemical oxidation (Das and Bhattacharyya 2014), electrochemical treatment advanced oxidation (Gao *et al.*, 2013) photocatalytic decomposition (Chiu *et al.*, 2019; Balati *et al.*, 2019), biodegradation (Telke *et al.*, 2010), and adsorption method (Balati *et al.*, 2017; Hashemi *et al.*, 2015; Balati *et al.*, 2014).

Characterization of Adsorbent

The bean husk was thoroughly washed with water of temperature of 50°C and was then later washed with distilled water. The washed bean husk was placed in an oven at 110°C for 20 hours, grinded. It was then sieved using 10-20 µm mesh sieve. The bean husk is then placed in an air-tight container as the adsorbent. This preparation was described by (Abdulsalam *et al.*, 2022). The surface characteristics of the Bean husk was studied to elucidate the surface morphology, surface functional groups and elemental composition of the potential adsorbent as discussed by (Abdulsalam *et al.*, 2022). Scanning electron microscope (SEM),

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Fourier Transform Infrared Spectroscopy (FTIR), and Elemental Diffraction X – ray Spectroscopy (EDS) were the tools employed. The FTIR of bean husk as represented in Figure 1a shows that the adsorbent has potential adsorption sites which are being represented by their functional groups: C-O (1050.21), O-H of alcohol (3432.0), S-H (2357.0), and C=C of alkene or aromatic ring (1633.3) to form bonds with the dye molecules. The Scanning Electron Spectra that was used to study the surface morphology of the adsorbent is presented at ^{X} 100 magnification as depicted in Figure 1b. The surface image reveals that the adsorbent is highly porous and have readily available pores for adsorption of dyes. The elemental composition of bean husk (Figure 1c) shows that bean husk has a high percentage of carbon and carbon compounds (100%). It indicates that all elements present is either carbon or exist as a compound of carbon. Given that the efficiency of an adsorbent is also a function of it carbon content (Bello *et al.*, 2017), bean husk hence is very promising as a potential adsorbent.

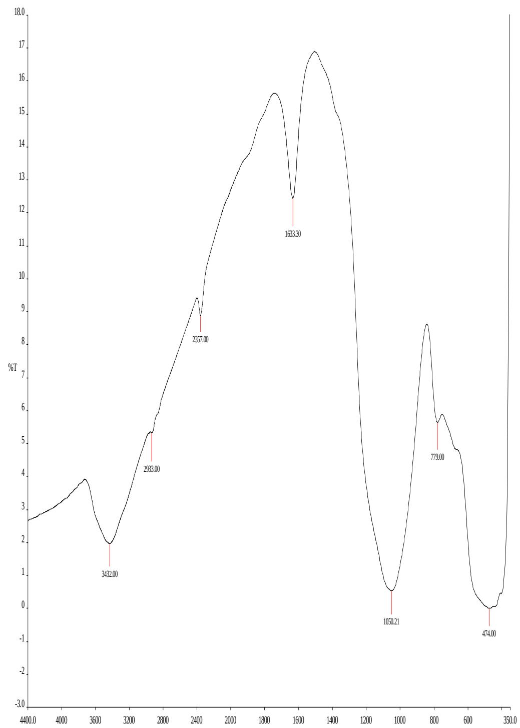

Figure 1a: Fourier Transform Infrared (FTIR) Spectroscopy Micrograph of bean husk

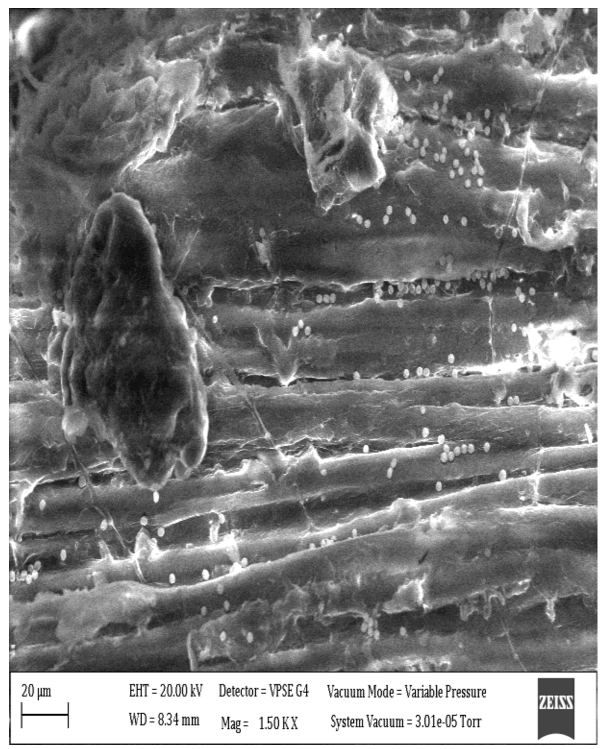

Figure 1b: Scanning Electron Microscopy (SEM) image of bean husk

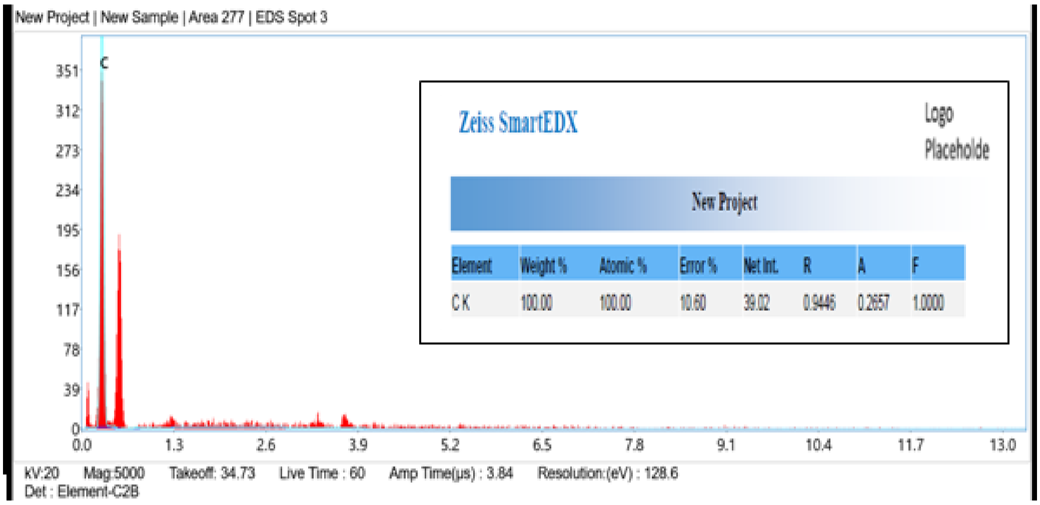

Figure 1c: Elemental Diffraction x ray Spectroscopy (EDS) of bean husk

Material and methods

Preparation of dye solution

A stock solution of Malachite green (MG), 1000 mg/L, was prepared by dissolving 1g of the Mg in some distilled water in a 1 L volumetric and made up to the mark using distilled water. The prepared stock solution was then wrapped with aluminium foil and stored in a dark to prevent exposure to direct light.

Optimization Studies of Sorption of Malachite Green

The Central Composite design (CCD) in the Design-Expert software 6.0.8 was used to evaluate the optimum values for adsorption parameters for dye removal from the real wastewater onto the adsorbent. The dependent variable (response) selected for this study is percentage removal which is expressed in percentage (%) while the independent variables are adsorbent dose, temperature, agitation speed and contact time. A total of sixteen runs were performed according to a matrix of central composite design.

Selected Factors for Adsorption of MG

The experiments for the adsorption malachite green onto mechanical shaker were performed at the selected temperature range of 30 - 60 °C, the contact time of 1 –3 h, the concentration of 50 – 100 ppm and an adsorbent dose of 1.0 – 5.0g. The response was expressed as percentage colour removal, %R, calculated as %R = $(C_o-C_e)/C_o$ x 100, Where C_o and C_e are the initial and equilibrium concentrations of the dye in mg/L respectively.

Results and Discussion

Sequential model sum of squares

Table 1: Table for sequential model sum of squares for Malachite green

Source	Sum of squares	DF	Mean square	F-value	Prob>F	Comments
Mean	9.16E+004	1	9.16E+004			
Linear	880	5	176	6.50	0.00612	Suggested
2FI	202	5	40.4	2.93	0.132	Aliased
Quadratic	0.000	0				Aliased
Cubic	0.000	0				Aliased
Quartic	0.000	0				Aliased
Fifth	0.000	0				Aliased
Residual	69.0	5	13.8			
Total	9.28E+004	16	5.80+003			

Using the sequential model sum of squares (Table 1), the design expert suggested the linear model because the probability of F-statistics is significant at 95% significant level i.e (Prob= 0.00612) compared to other models that did not produce F-statistics at all. It has the highest order polynomial and the additional terms are significant. Also, the model is not aliased (Abdulsalam *et al.*, 2020).

Lack of fit tests

Table 2: Table for lack of fit tests for Malachite green

Source	Sum of squares	DF	Mean squares	F-value	Prob>F	Comments
Linear	202	5	40.4	2.93	0.132	Suggested
2FI	0.000	0				Aliased
Quadratic	0.000	0				Aliased
Cubic	0.000	0				Aliased
Quartic	0.000	0				Aliased
Fifth	0.000	0				Aliased
Pure error	69.0	5	13.8			

Table 2 revealed the test of lack of fit. Since, the probability of F-statistics is 0.132 which is greater than 0.005, this confirms the reason why the design expert software selected the linear model because it has insignificant lack of fit. In other words, linear model is statistically fit (Giwa *et al.*, 2018).

Model Summary Statistics

Table 3: Table for model summary statistics for Malachite green

Source	Standard deviation	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	Comments
Linear	5.21	0.765	0.647	0.340	760	Suggested
2FI	3.71	0.940	0.820		+	Aliased
Quadratic					+	Aliased
Cubic					+	Aliased
Quartic					+	Aliased
Fifth					+	Aliased

The design expert based on the model summary statistics (Table 3) above shows that linear model has a high coefficient of determination, with R-Squared value of approximately 76.5% while the adjusted R-squared is 64.7%. Hence, linear model is suggested instead of the other models because it is good fit (Abdulsalam *et al.*, 2020).

ANOVA for response surface linear model.

Table 4: Analysis of variance table for Malachite green

Source	Sum of squares	DF	Mean square	F-value	Prob>F	Comments
Model	880	5	176	6.50	0.00612	Significant
Dose	608	1	608	22.5	0.000794	Significant
Contact time	7.52	1	7.52	0.277	0.610	Not significant
Temperature	33.3	1	33.3	1.23	0.293	
Concentration	77.7	1	77.7	2.87	0.121	
Agitation speed	1.42	1	1.42	0.0523	0.824	
Residual	271	10	27.1			
Lack of fit	202	5	40.4	2.93	0.132	Not significant
Pure error	69.0	5	13.8			
Cor total	1.15+003	15				

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ANOVA is used to determine the significance of model terms. Using the analysis of variance table (Table 4) the model and adsorbent dose are significant because they have the probability less than 0.05. Because for all terms which have probability less than 0.05, the software said it is an indication that the model terms are significant. The model F-value is 6.50 which is an indication that the model itself is significant and that even at a confident level of 0.61% such a high model F-value could have not have occurred due to noise. The lack of fit F-value of 2.93 is insignificant which indicates that the model has a good fit. Therefore, the model is significant.The R^2 predicted by the software is 0.340, this confirm a 34.0% accuracy when linear model is absorbed on a new set of data, this shows that there is slight variation between the predicted values and the actual values as the linear model predicted correctly. While the R^2 value gotten from the analysis of the result is 0.765. The software adjusted its R^2 to 0.647 which are still very high R^2 values, an indication that the model is significant, adequate precision of 7.37 was gotten. Whereas, the design expert has specified that any adequate precision greater than 4 is desirable. Since the adequate precision in this analysis indicate an adequate signal, the model can be used to navigate the design space (Abdulsalam *et al.*, 2019).

Effect of Adsorption Parameters

Effect of Adsorbent Dosage

It was observed that % removal of MG increased with an adsorbent dosage which shows the percentage colour removal (Fig 2). This may be due to the availability of more surface area and volume with increase in adsorbent dosage, which increases the presence of vacant sites that can be accessed by the dye molecules present in the wastewater and hence serve as binding sites (Abdulsalam *et al.*, 2020).

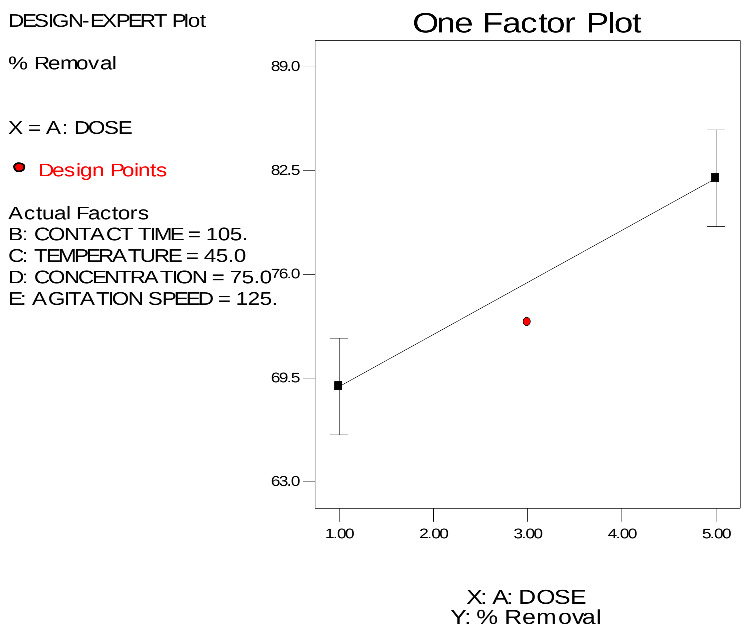

Figure 2: Effect of adsorbent dosage

Effect of Contact Time

The effects of contact time on percentage color removal of Malachite green is shown in Fig. 3. It was investigated by altering the contact time between the range of 1-3h, while keeping the doses, concentration and temperature constant. Percentage color removal increases with the contact time, it is because the surface is very large which enables adsorption to occur. When it reaches the state of equilibrium, the rate of adsorption is equal to the rate of desorption ((Abdulsalam *et al.*, 2020).

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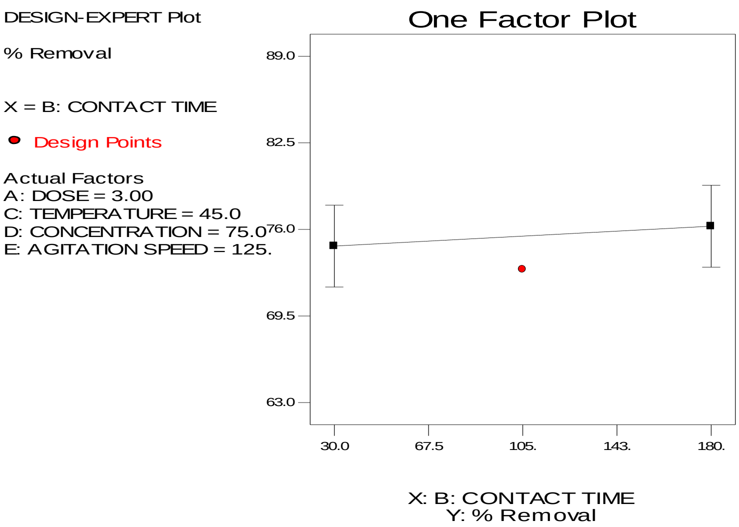

Figure 3: Effect of contact time

Effect of Temperature

The effect of temperature on percentage colour removal of malachite green is shown in Fig. 4. The percentage removal increases with increasing temperature, this may due to an increment of mobility of dye molecules or because an increase in temperature increased the size of adsorbent pores by swelling which allow the dyes molecules to pass through it more easily ((Abdulsalam *et al.*, 2020).

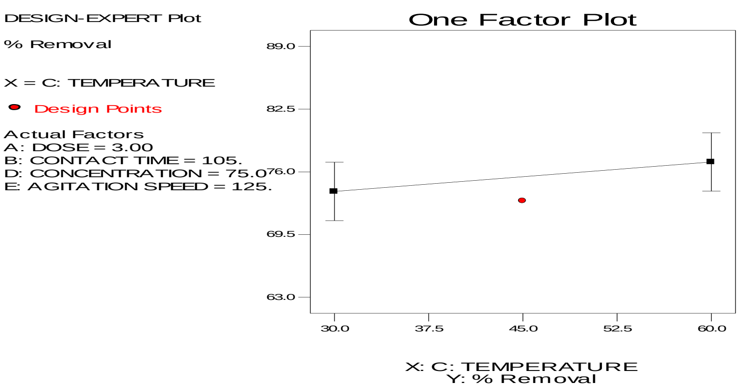

Figure 4: Effect of temperature

Effect of Concentration

The effect of concentration on percentage color removal of malachite green is illustrated in Fig. 5. It was observed that the initial concentration increases with the decrease in color removal; the higher adsorption
rate during the initial period may due to high number of available adsorption sites. If the concentration increases, the active sites needed for the adsorption of the dye molecules will be insufficient ((Abdulsalam *et al.*, 2022).

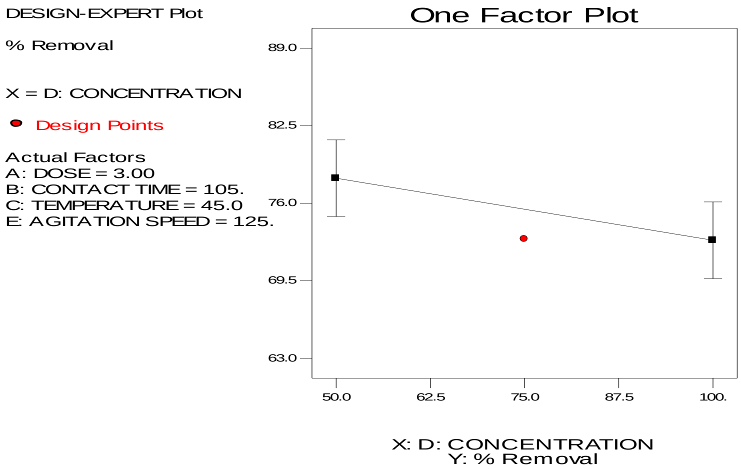

Figure 5: Effect of concentration

Effect of Agitation Speed

The effect of agitation speed on the percentage removal of Malachite green was carried out at different a stirring speed (Fig. 6) which shows that agitation speed does not have any pronounced effect on percentage dye removal. Increasing agitation speed decreases the boundary layer resistance of the transfer of dye molecules from the bulk solution to the surface ((Abdulsalam *et al.*, 2022).

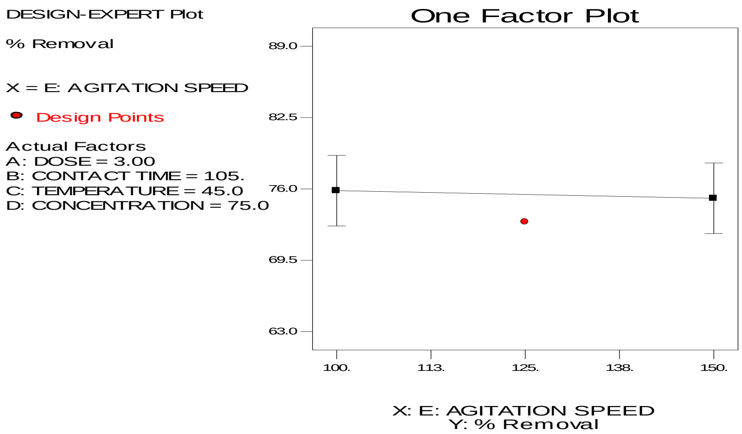

Figure 6: Effect of agitation speed

Optimum Point Prediction

The optimum points predicted by the software for Malachite green are dosage of 3 g, contact time of 105 minutes, temperature of 45 °C, agitation speed of 125 rpm; and concentration of 75 ppm. Similar result was reported by Abdulsalam *et al.*, 2022 for the optimized Sorption of Methylene Blue (Abdulsalam *et al.*, 2022).

Conclusion

Bean husk is efficient for the removal of Malachite green from solution. The adsorbent was characterized using FTIR (surface functional group), SEM (surface morphology of the adsorbent) and EDX (elemental composition of the adsorbent). The optimum parameters for MG were found to be adsorbent dosage of 3g, temperature of 45°C, contact time of 105 minutes, agitation speed of 125rpm and concentration of 75ppm Statistical analysis was done using Model Summary Statistics, Analysis of Variance (ANOVA) and Diagnostic Case Studies, the experimental value were in good accordance with the predicted value and the model established was significant.

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