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Optimization of Conditions for the Removal of Malachite Green from Synthetic Wastes Using Corn Cob Coke by Central Composite Design

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ABSTRACT:

In the present investigation Malachite green adsorption from synthetic waste solutions on to the coke of Corn cob was investigated. The critical parameters optimized by Central composite design were Malachite green concentration, Coke Percentage, pH and temperature. CCD design having 26 experiments and 2 central points was run and the critical parameters were identified. Optimal malachite green adsorption of 98% was observed when final run was carried out with variables levels when maintained as follows: Malachite green concentration – 0.018gm/L, Corn Cob coke- 2.3%, pH 5.5 and temperature 321.53 K. An R^2 value of 0.98 indicates best fit of model.

Key words: Corn Cob Coke, Adsorption, Malachite green, Central composite design.

I. INTRODUCTION:

Malachite green which is a cationic dye is used extensively for coloring in textile industries [1], fish farming [2] and medicine [3]. This dye when released into water is reported to be toxic to flora and fauna. Malachite green can induce cancer thereby acting as a tumor-enhancing agent [4]. Upon ingestion is also causes irritation to the gastrointestinal tract [5]. Many investigators have studied methods for removing malachite green from synthetic effluents by physical, chemical as well as biological treatment procedures. Few of the physical and chemical methods include adsorption, nanofiltration, electro kinetic coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, ozonation, supported liquid membrane, as well as liquid-liquid extraction [6]. Apart from adsorption the rest of the conventional methods are not cost effective regarding Indian context [7]. Adsorption is considered as the cheapest method chosen for the dye removal and several agricultural residues [8] and inexpensive materials [9-16] were used. Corn cob waste was identified as an inexpensive adsorbent [17] which has exhibited a good adsorption percentage of above 90% under systematically optimized conditions for the removal of malachite green from synthetic waste waters. This method of single factorial method of optimization does not completely reveal the combined interactions among various parameters. In order to reveal the fill response estimation of dependent parameters and optimize the conditions response surface methodology was adopted [1,7,18]. The Central composite design was used for malachite green removal from synthetic wastes by using materials like biomass of *Hydrilla verticillata* [7], Bark of *Arau* Cariocookii [1] and biomass of *Phormidiu* [19]. The critical parameters chosen in the present investigation were Dye concentration, Percentage of coke, pH and temperature. Corn cob coke was used as the adsorbent and the studies carried out during the preliminary studies [17] were considered to increase the efficiency of adsorption by Central composite design.

II.MATERIALS AND METHODS

2.1 Preparation of Activated carbon:

Corn cob was used as the adsorbent. Owing to its high degree of porosity the material was chosen and subjected to pretreatment. The corn cob pieces were treated with concentrated sulphuric acid in the ratio 1:1 for one hour to remove phenols and then used for the preparation of activated carbon [17].

2.2 Optimal conditions from batch studies: Batch studies have revealed that dye concentration, coke dosage, pH and temperature were critical of adsorption of malachite green. High temperatures were found to be favorable, while studies on pH indicated a variance in adsorption percentage. pH of 6 may be considered ideal for effective adsorption. The parameter Coke concentration which has a linear effect on adsorption of dye was kept constant while an increase in Malachite green under controlled conditions of coke dosage lead to an optimal adsorption.

2.3 Experimental Design and Data Analysis: From the batch studies condition chosen for optimization using CCD design were represented in table 1. The centre values of the variables are Malachite green (MG) concentration – 0.030gm/L, Corn cob coke (% W/V)- 2, pH 5 and temperature chosen was 323.15K. Keeping these as the centre values using Statistical package (Stat-Ease Inc, Minneapolis, MN, USA) Central Composite Design was generated.

The Effect of the process variables Malachite Green concentration (X_1), Corn Cob Coke percentage (X_2), pH (X_3) and Temperature (X_4).

The interdependence of the variables was evaluated and optimal values were identified using half fraction factorial Central Composite Design (CCD). A CCD design with 26 experiments with 2 central points was used for the optimization of process parameters for the removal of malachite green from synthetic effluent. The 2^4 full factorial design having 28 experiments was conducted in triplicate and the mean values of the result were analyzed by second order polynomial model. This helps to predict the linear effect, their interactions and quadratic effects among the components by ANOVA analysis. The uncoded and coded variables used in the experimental design are represented in table 2. The model equation for analysis is given below:

$$Y=\beta_o+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_4X_4+\beta_{11}X_{11}+\beta_{22}X_{22}+\beta_{33}X_{33}+\beta_{44}X_{44}+\beta_{12}X_{12}+\beta_{13}X_1X_3+\beta_{14}X_1X_4+\beta_{23}X_2X_3+\beta_{24}X_2X_4+\beta_{34}X_3X_4 \quad \text{-- 1}$$

Where, Y is the measured response, β_o is the intercept term, $\beta_1, \beta_2, \beta_3, \beta_4$ are linear coefficients, $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are quadratic coefficient, $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are interaction coefficient and X_1, X_2, X_3, X_4 are encoded independent variables.

The amount of dye left unadsorbed was analyzed spectrophotometrically at 619nm[22]. The percentage of dye adsorbed was calculated from the following equation.

$$\%\ \text{MG adsorbed} = \frac{C_1 - C_2}{C_1} \times 293.150 \quad \text{-- (2)}$$

RESULTS AND DISCUSSION:

The experiments were conducted and the results were analyzed by statistical design. The percentage of dye removed was calculated, average of the triplicate was obtained and the results are tabulated in table 3 which also indicates the predicted values given by the software.

Figure 1 indicates the pereto chart for malachite green adsorption for the four variables which reveals the significance of the four adsorption parameter. The probability values of the variables the variables malachite green concentration, adsorbent dosage, pH and temperature and their linear (L) and quadratic effect (Q) were above 0.05 indicating their significance on the adsorption. Main effects plot shown in figure 2 indicates the variables contribute to dye adsorption.

The mathematical model relating to percentage of dye removed using the independent process variables and the second order polynomial coefficients for each term are represented in the equation 4.

$$Y = 97.95 - 24.71X_1 + 16.0\ X_2 + 4.0\ X_3 - 4.22\ X_4 - 9.22\ X_1^2 - 6.01\ X_2^2 - 19.43\ X_3^2 - 12.59\ X_4^2 + 10.27\ X_1X_2 - 4.71\ X_1X_3 - 0.38X_1X_4 + 3.81\ X_2X_3 - 4.05\ X_2X_4 \text{--Eq (4)}$$

The statistical significance of the polynomial equation was also verified by using ANOVA (Analysis of Variance) for the response surface quadratic model (Table 4). Larger T values and the *P* value of variables whose magnitude is lesser than 0.0001 indicates the variables significance. The coefficient estimates and the corresponding *P* values indicate that the linear effects of malachite green concentration and coke and quadratic effects of Malachite green concentration, Coke percentage as well as temperature have significant effect on the adsorption of malachite green. The mutual effect of malachite green and coke dosage were also found to be highly significant. The R^2 value will be usually between 0.00 to 1.00. A value close to 1.0 indicates that the model is accurate and it predicts better response. In the present investigation, an R^2 value of 0.98 indicates a good fit of the model with minimum deviation.

The central composite design was used to investigate interaction effects among variables. This was carried out by drawing three dimensional plots between any two variables keeping the rest constant at fixed levels. These 3D graphs (Figure 3 to 8) help to understand the optimal level of each variable that would contribute to optimal output, ie., malachite green adsorption. Figure 3 represents the response surface graph for the variables, malachite green concentration (gm/L) and coke dosage (%) keeping pH and temperature constant at 5 and 323.15 K respectively. The graph reveals that increase in coke increases the adsorption of malachite green. While an increase in dye concentration shows an increase in percentage of dye adsorbed up to certain extent beyond which, the percentage of dye adsorbed decreases, indicating the saturation of active sites. For 0.020gm/L dye concentration optimal adsorption would be seen at a coke dosage of 2.0 to 2.5%.

The influence of pH on dye adsorption is due to the alteration of surface charges of coke that would contribute to binding of dye [3]. Acidic pH would contribute to better adsorption of dye than basic environment which is reflected in figure 4. Optimal pH that would contribute to malachite green adsorption was observed to be between 5 to 6, when the variables coke dosage and temperature are kept constant at 2% and 323.15 K respectively.

Increase in temperature is known to increase the available surface area of the adsorbent material and also increase in dye concentration initially contributes to increase in the percentage of dye adsorbed (Figure 5). Further increase in dye concentration or temperature will have a negative effect which can be due to saturation of active sites due to the limited coke dosage taken (2%). Figure 6 illustrates the effect of pH and coke concentration on malachite green adsorption. From previous studies it is evident that pH of 6 is the optimal for malachite green adsorption on to corn cob coke and further increase has a negative effect [5]. While increase in coke always has a positive impact on adsorption percentage but due to variations in pH it has exhibited decreasing trend.

Figure 7 indicates the effect of temperature and corncob coke on malachite green adsorption. Increase in temperature contributes to increase in dye adsorption and increase in coke percentage also has a positive impact on dye adsorption. Maximum adsorption was observed when 2.5 to 3% coke is supplemented and temperature is maintained between 318.15 to 323.15 K. Interaction between temperature and pH studies indicate that the two are independent variables and an optimal adsorption is seen at a temperature of 323.15 K and pH between 5 to 6 (Figure 8).

A final run was carried out in triplicate keeping the variables at their predicted levels as given by the software. Optimal malachite green adsorption of 98% was observed with the values of variables as follows: Malachite green concentration – 0.018gm/L, Corn Cob coke- 2.3%, pH 5.5 and temperature 321.53 K. The optimal malachite green adsorption predicted was 107.26% which is nothing but 100%, and the obtained value is 98% which is indicates the effectiveness of the new substrate chosen for dye adsorption.

CONCLUSION:

Optimization of important variables that contribute to malachite green adsorption when optimized by Central composite design has revealed the interaction between variables. The optimal values of the critical parameters were revealed as follows: Malachite green concentration – 0.018gm/L, Corn Cob coke- 2.3%, pH 5.5 and temperature 321.55 K. Despite the expected 107.26% adsorption whose real working value is 100%, a 98% dye removal was observed by the synthetic effluent which is almost close to the previous studies. R^2 value of 0.98 indicates the best fit of model.

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Factor	Symbol	Level				
		-2	-1	0	+1	+2
MG Conc(g/L)	X_1	0.010	0.020	0.030	0.040	0.050
Coke(%)	X_2	0.50	1.25	2	2.75	3.5
pH	X_3	1	3	5	7	9
Temperature(K)	X_4	293.15	308.15	323.15	338.15	353.15

Table- 1: Levels of different process variables used in Central Composite design for removal of Malachite green dye

S.No	Uncoded variables indicating ranges				Coded Variables			
	MG Conc (gm/L)	Coke (%)	pH	Temperature (K)	MG Conc (gm/L)	Coke (%)	pH	Temperature (K)
1	-1	1	1	-1	0.020	2.75	7	308.15
2	1	1	1	-1	0.040	2.75	7	308.15
3	1	-1	-1	-1	0.040	1.25	3	308.15
4	2	0	0	0	0.050	2.00	5	323.15
5	-1	1	1	1	0.020	2.75	7	338.15
6	0	2	0	0	0.030	3.50	5	323.15

7	0	0	0	2	0.030	2.00	5	353.15
8	0	0	-2	0	0.030	2.00	1	323.15
9	1	1	-1	-1	0.040	2.75	3	308.15
10	0	0	0	0	0.030	2.00	5	323.15
11	0	0	0	0	0.030	2.00	5	323.15
12	0	0	0	0	0.030	2.00	5	323.15
13	-1	-1	1	-1	0.020	1.25	3	308.15
14	-2	0	0	0	0.010	2.00	5	323.15
15	-1	-1	1	-1	0.020	1.25	7	308.15
16	-1	1	-1	1	0.020	2.75	3	338.15
17	1	-1	1	-1	0.040	1.25	7	308.15
18	1	1	1	1	0.040	2.75	7	338.15
19	-1	-1	-1	1	0.020	1.25	3	338.15
20	0	0	0	-2	0.030	2.00	5	293.15
21	-1	1	-1	-1	0.020	2.75	3	308.15
22	1	1	-1	1	0.040	2.75	3	338.15
23	1	-1	1	1	0.040	1.25	7	338.15
24	0	0	2	0	0.030	2.00	9	323.15
25	1	-1	-1	1	0.040	1.25	3	338.15
26	-1	-1	1	1	0.020	1.25	7	338.15
27	0	0	0	0	0.030	2.00	5	323.15
28	0	-2	0	0	0.030	0.50	5	323.15

Table 2: Central Composite Design with coded and uncoded variables.

S.No	**MG Conc (gm/L)**	**Coke (%)**	**pH**	**Temperature (K)**	**Adsorption (%)**	**Predicted Value (%)**
1	0.020	2.75	7	308.15	95.48	95.73
2	0.040	2.75	7	308.15	77.51	76.97
3	0.040	1.25	3	308.15	56.74	55.30
4	0.050	2.00	5	323.15	52.39	54.80
5	0.020	2.75	7	338.15	98.47	95.78
6	0.030	3.5	5	323.15	100.00	101.76
7	0.030	2.00	5	353.15	62.40	68.55
8	0.030	2.00	1	323.15	52.40	55.11
9	0.040	2.75	3	308.15	77.68	77.93
10	0.030	2.00	5	323.15	98.20	97.95
11	0.030	2.00	5	323.15	97.60	97.95

12	0.030	2.00	5	323.15	98.00	97.95
13	0.020	1.25	3	308.15	85.00	85.20
14	0.010	2.00	5	323.15	100.00	104.22
15	0.020	1.25	7	308.15	88.97	86.02
16	0.020	2.75	3	338.15	80.56	79.22
17	0.040	1.25	7	308.15	47.87	46.72
18	0.040	2.75	7	338.15	78.94	76.25
19	0.020	1.25	3	338.15	81.06	77.48
20	0.030	2.00	5	293.15	76.51	76.99
21	0.020	2.75	3	308.15	89.48	87.28
22	0.040	2.75	3	338.15	70.29	69.11
23	0.040	1.25	7	338.15	48.27	46.34
24	0.030	2.00	9	323.15	59.17	63.08
25	0.040	1.25	3	338.15	49.57	46.82
26	0.020	1.25	7	338.15	89.16	86.41
27	0.030	2.00	5	323.15	98.00	97.95
28	0.030	0.50	5	323.15	64.90	69.77

Table 3: Central Composite Design indicating dye adsorbed and predicted values

Figure 1: Pereto chart indicating significance of variables chosen for CCD

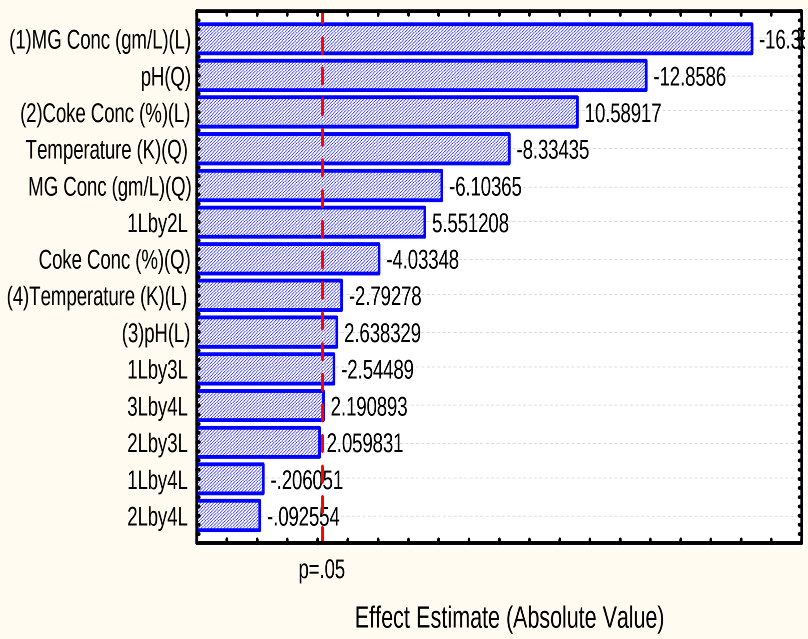
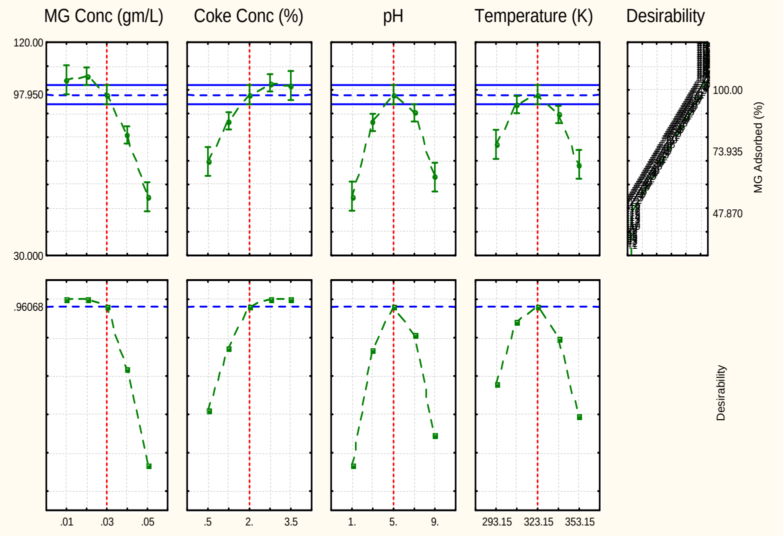


Figure 2: Main effects plot for the independent variables against percentage dye adsorbed by CCD



Model	Effect	Std.Err.	t- value	p
Mean/Interc.	97.9500	1.850273	52.9381	0.000000*
(1)MG Conc(gm/L)(L)	-24.7108	1.510741	-16.3568	0.000000*
MG Conc(gm/L)(Q)	-9.2210	1.510741	-6.1037	0.000038*
(2)Coke(%) (L)	15.9975	1.510741	10.5892	0.000000*
Coke(%) (Q)	-6.0935	1.510741	-4.0335	0.001420
(3)pH (L)	3.9858	1.510741	2.6383	0.020461
pH (Q)	-19.4260	1.510741	-12.8586	0.000000*
(4)Temperature(K)(L)	-4.2192	1.510741	-2.7928	0.015239
Temperature(K)(Q)	-12.5910	1.510741	-8.3343	0.000001*
1L by 2L	10.2713	1.850273	5.5512	0.000094*
1L by 3L	-4.7088	1.850273	-2.5449	0.024427
1L by 4L	-0.3813	1.850273	-0.2061	0.839943
2L by 3L	3.8113	1.850273	2.0598	0.060022
2L by 4L	-0.1712	1.850273	-0.0926	0.927669
3L by 4L	4.0538	1.850273	2.1909	0.047281

*P value must be less than 0.0001

Table 4. Analysis of Variance

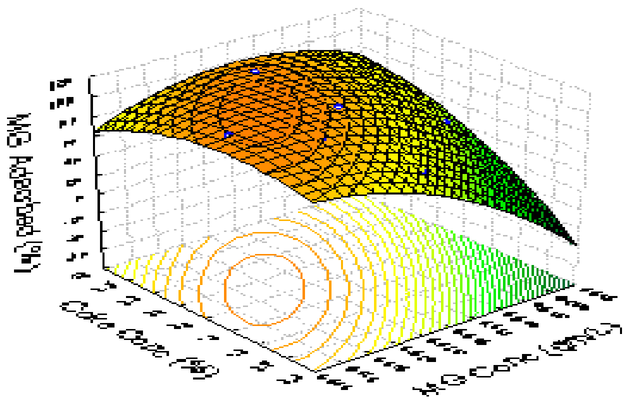


Figure 3: Effect of Malachite green and Coke dosage on dye adsorption

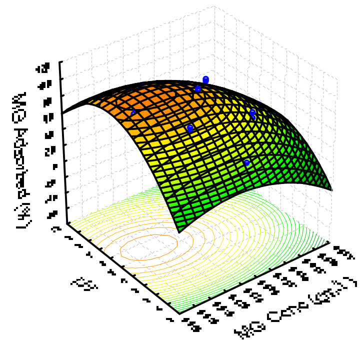


Figure 4: Effect of pH and Malachite green concentration on dye adsorption

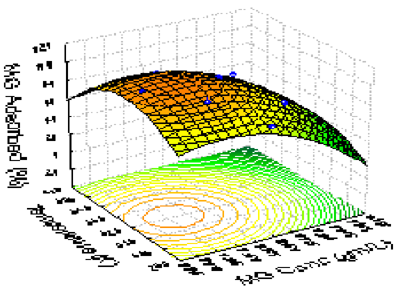


Figure 5: Effect of Temperature and malachite green concentration on dye adsorption

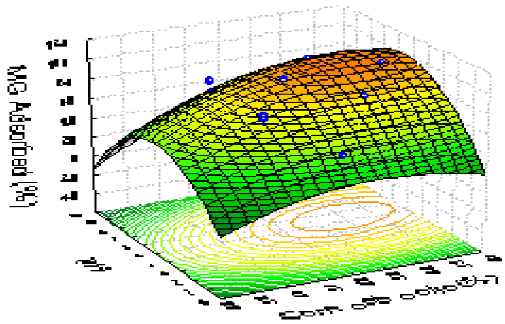


Figure 6: Effect of Corn cob coke dosage and pH on Malachite green adsorption

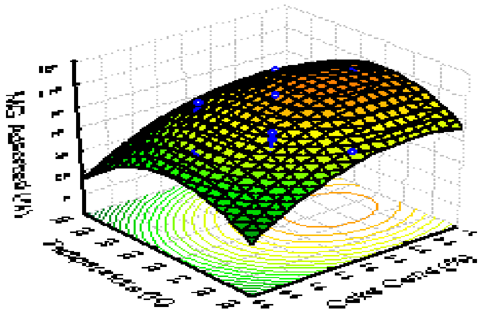


Figure 7: Effect of temperature and corn cob dosage on malachite green adsorption

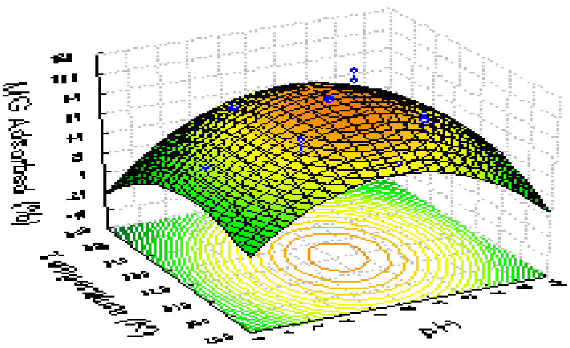


Figure 8: Effect of temperature and pH on malachite green adsorption