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STUDIES ON REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION USING *ANTIGONON LEPTOPUS* LEAVES POWDER

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Abstract — *The present experiment is aimed for removal of malachite green using Antigonon leptopus* leaves powder *from synthetic waste water. Water pollution is a major threat to humans and living organisms causing imbalance to the ecosystem. Several methods have been developed earlier but proven expensive. Here, Adsorption is a promising technology for removal of dyes using freely available materials at a low cost. The variables studied in the present study are agitation time, pH, adsorbent size, initial concentration, dosage of adsorbent and temperature. The study also incorporated isotherms like Langmuir, Freundlich and Temkin, Kinetics like first order and second order. This study revealed that the optimum concentration was 20 mg/L and temperature at 303 K .This study also stated that the optimum adsorbent size was 53µm. The adsorbent is analyzed using RSM and ANOVA analysis.*

Keywords- *Adsorption, Malachite green dye, Kinetics, Isotherms, Thermodynamics*

I. INTRODUCTION

A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics. It appears to be colored because they absorb some wavelengths of light in particular than other. Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants .These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non-biodegradable due to their complex molecular structures making them more stable and hard to biodegrade **[1].** They cause water pollution and also pose a serious threat to environment. These colored stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem **[2]**. Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms. The main source of discharge of dyes is textile industries where they are used to color products. Today there are over 1, 00,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually. The types of dyes are mainly basic dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes **[3].** Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. They don’t fade by water or sunlight and owing to their complexity in structures; they can’t be adequately treated in conventional treatment plants for waste waters. There are numerous harmful effects of dyes on ecosystem such as: (1) they pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes. (2) They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities. (3) They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes. (4) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations. (5) Consume dissolved oxygen and affect aquatic ecosystem. There are various ways to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. Many of these processes are not so popular due to their economic disadvantages and inefficiency. Coagulations and chemical and electrochemical oxidations have low feasibility on large scale plants. Adsorption is preferred over these processes and is widely used due to low cost and high performance. Common adsorbents are activated carbon, alumina silica and metal hydroxides. Economic advantages, performance efficiencies and environment are the main concerns when selecting an adsorbent, thus researchers generally go for using low-cost adsorbents like char from agricultural wastes and others **[4, 5].**

II. EXPERIMENTAL PROCEDURE

1. **Reagents and Materials**
2. **Preparation of adsorbent**
3. **Preparation of 1000 mg/L dye stock solutions**
4. **Equilibrium Studies**
5. **Isotherms**
6. **Kinetics models**
7. **Thermodynamics**
8. **RSM**

1.Reagents and Materials

ADSORBATE:
Malachite green dye is the adsorbate, its colour is green. It gives green colored solution in aqueous phase. It is a basic cationic dye. Its chemical formula is $C_{52}H_{54}N_4O_{12}$, molecular weight is 927, λmax=619 nm (Fig 1 (a) & (b)).

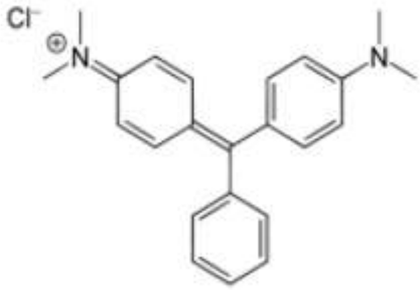

Fig. 1 (a) Structure of malachite green dye

Fig. 1 (b) Malachite Green Dye Sample

2. Preparation of adsorbent:

Preparation of adsorbent (Antigononleptopus leaves):
Antigononleptopus leaves were collected from Andhra university campus and the collected leaves were washed thoroughly with water, and completely dried in sun light .The dry mass was grinded and the resulting powder was separated into different sizes 53, 75, 103, 125 and 152 µm using BSS sieves (Fig. 2).

Fig. 2. Antigonon leptopus leaves

3. Preparation of adsorbate (Malachite green dye stock solution):

Malachite green dye stock solution (Fig. 3) of 1000mg/L was prepared by dissolving 1.0 g of Malachite green dye in 1000 ml of distilled water which was later diluted to required concentrations. All the solutions were prepared using distilled water. The pH of solution for pH studies is adjusted by adding HCl and NaOH, as required for concentration of the dye solution. The pH is determined from the absorbance of the solution at the characteristic wave length of dye using UV-Visible spectrometer. Wave length of Malachite green dye (λ_{max}=619 nm).

Fig. 3. Malachite green dye stock solution

III. RESULTS AND DISCUSSION

In the present investigation, the potential of dry *Antigonon leptopus* leaf powder as a adsorbent for removal of malachite green present in an aqueous solution is investigated. The effects of various parameters on adsorption of malachite green are studied. The measured data consists of initial and final concentration of malachite green, agitation time, adsorbent size, adsorbent dosage, pH of the aqueous solution and temperature of the aqueous solution. The experimental data are obtained by conducting batch experiments.

4. Equilibrium studies on adsorption:

From the experimentations on adsorption of malachite green, the percentage adsorption of malachite green is found from the relation $= \frac{C_0 - C_e}{C_0} \, x\, 100$

The amount of malachite green adsorbed per unit mass of the adsorbent, q_t in mg/g is computed by using the expression:

$$q_t = \frac{C_0 - C_e}{w}$$

The effects of various parameters on adsorption of malachite green are discussed below.

Effect of agitation time:

Duration of equilibrium adsorption is defined as the time required for heavy metal concentration to reach a constant value during adsorption. The equilibrium agitation time is determined by plotting the % adsorption of malachite green against agitation time as shown fig. 4.1 for the interaction time intervals between 1 to 180 min. For 53 µm size of 10 g/L adsorbent dosage, 39 % of malachite green is adsorbed in the first 5 min. The % adsorption is increased briskly up to 40 min reaching 69%.Beyond 50 min, the % adsorption is constant indicating the attainment of equilibrium conditions **[1, 2].**

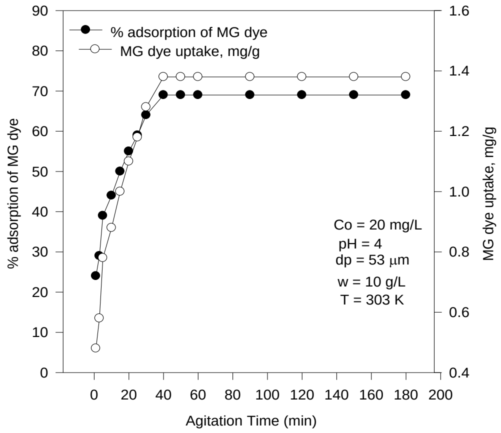

Fig. 4.1 Effect of agitation time on % adsorption of malachite green

The maximum adsorption of 69 % is attained for 40 min of agitation time with 10 g/L of 53 µm size adsorbent mixed in 50 mL of aqueous solution (C_0 = 20 mg/L). The rate of adsorption is fast in the initial stages because adequate surface area of the adsorbent is available for the adsorption of malachite green. As time increases, more amount of malachite green gets adsorbed onto the surface of the adsorbent due to vanderwaal forces of attraction and resulted in decrease of available surface area. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the adsorbent capacity is exhausted. The maximum percentage of adsorption is attained at 40 minutes. The percentage adsorption of malachite green becomes constant after 40 min. Therefore, all other experiments are conducted at this agitation time**.**

Effect of adsorbent size:

The variations in % adsorption of malachite green from the aqueous solution with adsorbent size are obtained. The results are drawn in fig. 4.2 with percentage adsorption of malachite green as a function of adsorbent size. The percentage adsorption is increased from 50% to 69 % as the adsorbent size decreases from 152 to 53 µm. This phenomenon is expected, as the size of the particle decreases, surface area of the adsorbent increases; thereby the number of active sites on the adsorbent also increases.

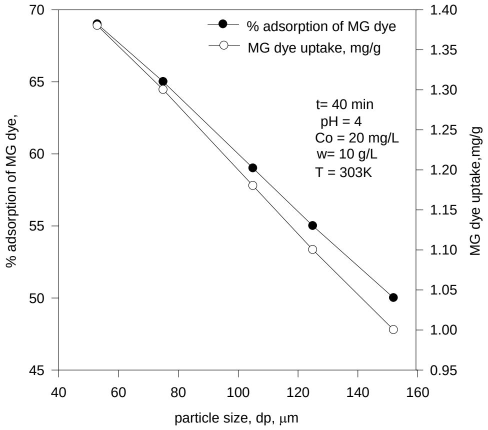

Fig. 4.2 % Adsorption of malachite green as a function of adsorbent size

Effect of pH:

pH controls adsorption by influencing the surface change of the adsorbent, the degree of ionization and the species of adsorbate. In the present investigation, malachite green adsorption data are obtained in the pH range of 2 to 8 of the aqueous solution (C_0 = 20 mg/L) using 10 g/L of 53 µm size adsorbent. The effect of pH of aqueous solution on % adsorption of malachite green is shown in fig. 4.3. The % adsorption of malachite green is increased from 65 % to 78% as pH is increased from 2 to 4 and decreased beyond the pH value of 4 **[3]**. % adsorption is decreased from pH 5 to 8 reaching 78% from 64%. Low pH depresses adsorption due to competition with H^+ ions for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and Malachite green ions replace H^+ ions bound to the adsorbent **[4, 5].**

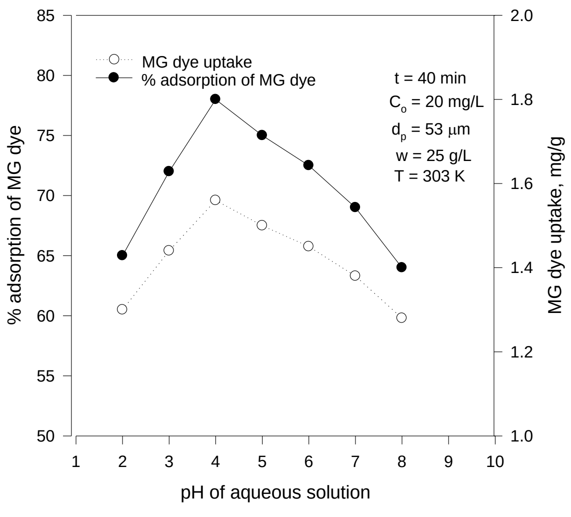

Fig. 4.3 Observation of pH along with % adsorption of malachite green

Effect of initial concentration of malachite green:

The effect of initial concentration of malachite green in the aqueous solution on the percentage adsorption of malachite green is shown in fig.4.4. The percentage adsorption of malachite green is decreased from 78% to 58.6% with an increase

[6] in C_0 from 20 mg/L to 200 mg/L. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent.

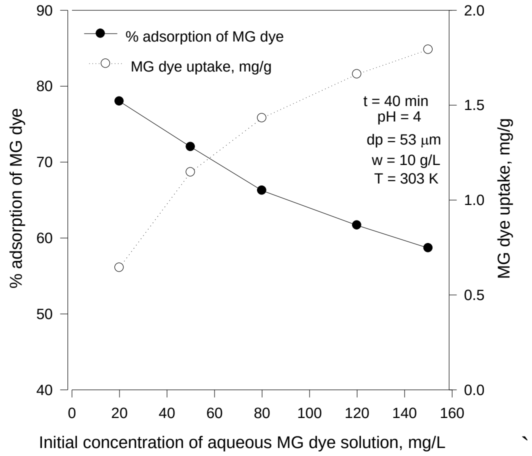

Fig. 4.4 Variation of initial concentration with % adsorption of malachite green

Effect of adsorbent dosage:

The percentage adsorption of malachite green is drawn against adsorbent dosage for 53 μm size adsorbent in fig.4.5. The adsorption of malachite green increased from 78% to 89.5% with an increase in adsorbent dosage from 10 to 30 g/L. Such behavior is obvious because with an increase in adsorbent dosage, the number of active sites available for malachite green adsorption would be more. The change in percentage adsorption of malachite green is marginal from 89.5 % to 91.5 % when 'w' is increased from 30 to 50 g/L. Hence all other experiments are conducted at 30 g/L dosage.

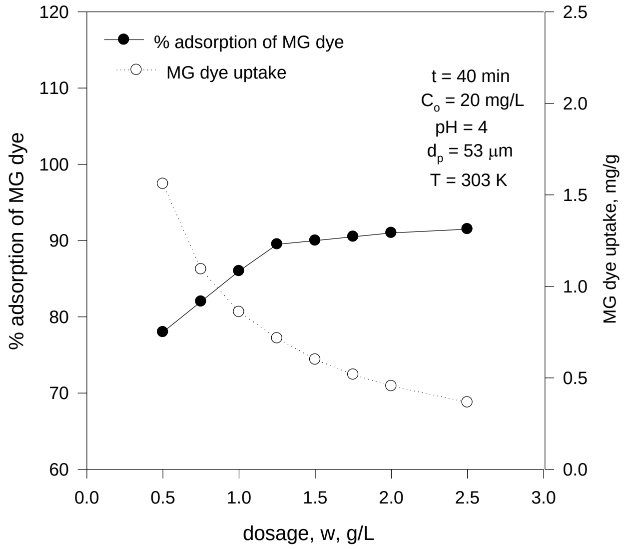

Fig. 4.5 Dependency of % adsorption of malachite green on adsorbent dosage

Effect of Temperature:

The effect of temperature on the equilibrium metal uptake was significant. The effect of changes in the temperature on the malachite green uptake is shown in Fig.4.6. When temperature was lower than 303 K, malachite green uptake increased with increasing temperature, but when temperature was over 303 K, the results were on the contrary. This response suggested a different interaction between the ligands on the cell wall and the metal. Below 303 K, chemical adsorption mechanisms played a dominant role in the whole adsorption process, adsorption was expected to increase by increase in the temperature **[7]** while at higher temperature, the plant powder were in a nonliving state, and physical adsorption became the main process. Physical adsorption reactions were normally exothermic, thus the extent of adsorption generally is constant with further increasing temperature.

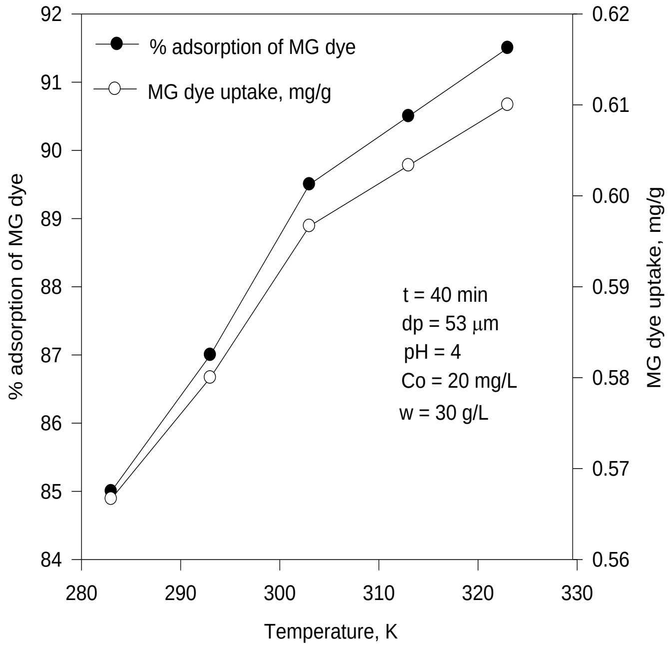

Fig. 4.6 Effect of temperature on % adsorption of malachite green

5. Isotherms:

Langmuir isotherm:

Irving Langmuir **[8]** developed an isotherm named Langmuir isotherm. It is the most widely used simple two-parameter equation. This simple isotherm is based on following assumptions:

Adsorbates are chemically adsorbed at a fixed number of well- defined sites

Each site can hold only one adsorbate specie

All sites are energetically equivalent

There are no interaction between the adsorbate species

The Langmuir relationship is hyperbolic and the equation is:

$q_e/q_m = bC_e / (1+bC_e)$

Equation (5.1) can be rearranged as

$(C_e/q_e) = 1/(bq_m) + C_e/q_m$

From the plots between (C_e/q_e) and C_e, the slope $\{1/ (bq_m)\}$ and the intercept (1/b) are calculated.Further analysis of Langmuir equation is made on the basis of separation factor, (R_L) defined as $R_L = 1/ (1+bC_e)$

$0< R_L<1$	indicates	favorable adsorption
$R_L>1$	indicates	unfavorable adsorption
$R_L = 1$	indicates	linear adsorption
$R_L = 0$	indicates	irrepressible adsorption

Langmuir isotherm is drawn for the present data and shown in Fig.5.1. The equation obtained 'n' $C_e/q_e = 0.07195C_e + 2.8055$ with a good linearity (correlation coefficient, R^2~0.9763) indicating strong binding of malachite green ions to the surface of "*Antigonon leptopus leaf*" powder.

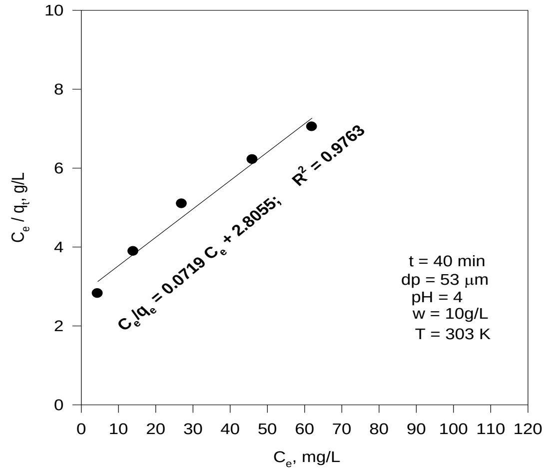

Fig. 5.1 Langmuir isotherm for % adsorption of malachite green

Freundlich isotherm:

Freundlich **[9]** presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations.

The Freundlich isotherm is given by

$q_e = K_f C_e^n$

whereK_f(mg) represents the adsorption capacity when metal equilibrium concentration and n represents the degree of dependence of adsorption with equilibrium concentration Taking logarithms on both sides, we get

$$\log q_e = \log K_f + n \log C_e$$

Freundlich isotherm is drawn between ln C_e and ln q_e; ln q_e = 0.6517ln C_e - 0.4898; in Fig.5.2 for the present data. The resulting equation has a correlation coefficient of 0.9977.

The 'n' value in the above equations satisfies the condition of 0<n<1 indicating favorable adsorption.

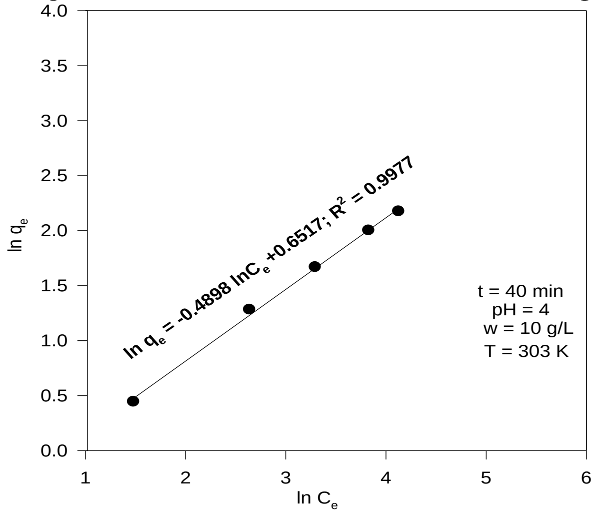

Fig.5.2 Freundlich isotherm for % adsorption malachite green

Temkin isotherm:

Temkin and Pyzhev **[10]** isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface and it is based on the following equation.

$q_e = RT \ln(A_T C_e)/b_T$

The linear form of Temkin isotherm can be expressed as

$q_e = (RT/ b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$

where $A_T = \exp [b(0) \times b(1) / RT]$

$b(1) = RT/ b_T$ is the slope

$b(0) = (RT/ b_T) \ln (A_T)$ is the intercept and

$b = RT/b(1)$

The present data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in Fig.5.3. The equation obtained for malachite green adsorption is: $q_e = 2.6872 \ln C_e - 2.9299$ with a correlation coefficient 0.9589. The best fit model is determined based on the linear regression correlation coefficient (R^2). From the Figs 5.1, 5.2 & 5.3, it is found that adsorption data are well represented by Freundlich isotherm with higher correlation coefficient of 0.9977, followed by Langmuir and Temkin isotherms with correlation coefficients of 0.9763 and 0.9589 respectively.

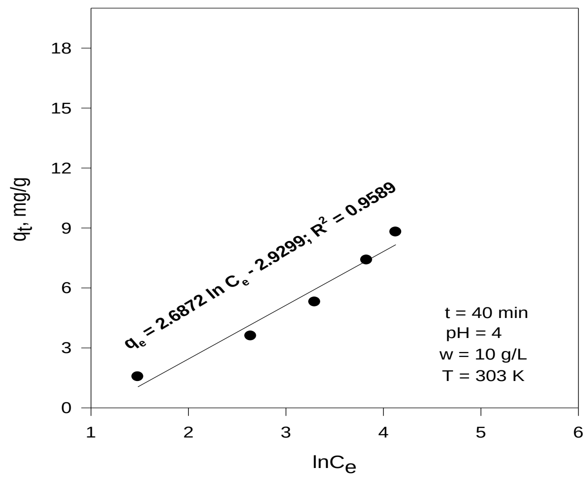

Fig. 5.3 Temkin isotherm for % adsorption of malachite green

6. Kinetics of adsorption:

The order of adsorbate – adsorbent interactions have been described using kinetic model. Traditionally, the first order model of Lagergren**[11]** finds wide application. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the first order rate equation of Lagrangen:

$(dq_t/dt) = K_{ad} (q_e - q_t)$

whereq_e and q_t are the amounts adsorbed at t, min and equilibrium time and K_{ad} is the rate constant of the pseudo first order adsorption **[12].**

The above equation can be presented as

$\int (dq_t/(q_e - q_t)) = \int K_{ad} dt$

Applying the initial condition $q_t = 0$ at t = 0, we get

$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303)\, t$

$\log (q_e - q_t) = -0.0115 - 0.0297t$

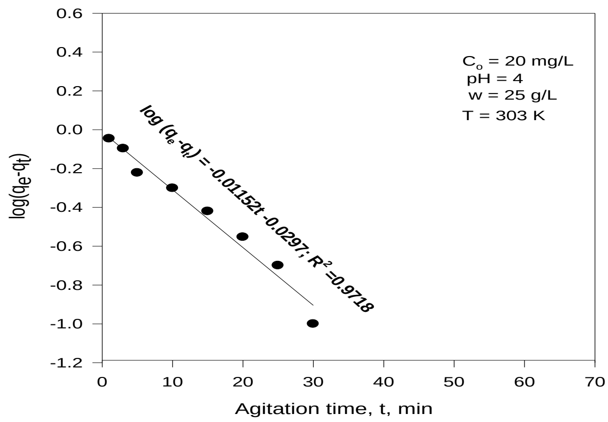

Fig. 6.1 first order kinetics for % adsorption of malachite green

Plot of $\log (q_e - q_t)$ versus 't' gives a straight line for first order kinetics, facilitating the computation of adsorption rate constant (K_{ad}). If the experimental results do not follow the above equation, they differ in two important aspects:

i) $K_{ad} (q_e - q_t)$ does not represent the number of available adsorption sites and

ii) $\log q_e$ is not equal to the intercept.

In such cases, pseudo second order kinetic equation: $(dq_t/dt) = K (q_e - q_t)^2$ is applicable, where

'K' is the second order rate constant.

The other form of the above equation is: $(dq_t/(q_e - q_t)^2) = Kdt$

let $q_e - q_t = x$

$dq_t = dx$

$1/x = Kx + C$

$C = 1/q_e$ at $t = 0$ and $x = q_e$

Substituting these values in above equation, we obtain:

$1/(q_e - q_t) = Kt + (1/q_e)$

Rearranging the terms, we get the linear form as:

$(t/q_t) = (1/Kq_e^2) + (1/q_e)t$.

$(t/q_t) = 0.7295t + 2.9138$.

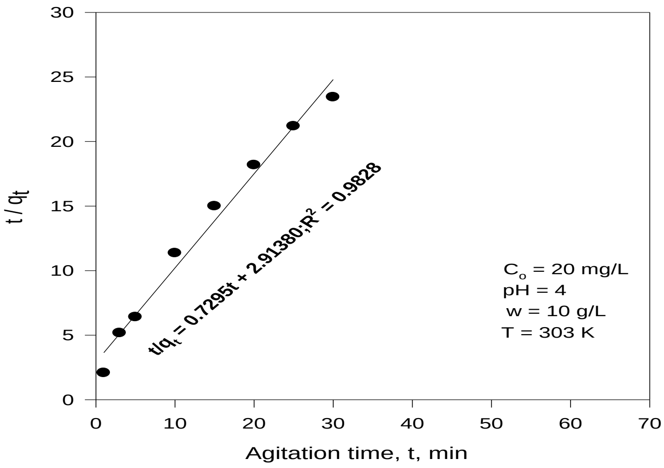

Fig. 6.2 second order kinetics for % adsorption of malachite green

The pseudo second order model **[11]** based on above equation, considers the rate -limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the adsorbate and adsorbent. If the pseudo second order kinetics is applicable, the plot of (t/q_t) versus't' gives a linear relationship that allows computation of q_e and K.

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagragen plots of log (q_e-q_t) versus agitation time (t) for adsorption of malachite green the adsorbent size (53 µm) of *Antigonon leptopus leaves* powder in the interaction time intervals of 1 to 180 min are drawn in figs.6.1 & 6.2.

7. Thermodynamics of adsorption:

Adsorption is temperature dependant. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of adsorption ((ΔH), change in entropy of adsorption (ΔS) and change in Gibbs free energy (ΔG) **[13].**

Enthalpy is the most commonly used thermodynamic function due to its practical significance. The negative value of ΔH will indicate the exothermic/endothermic nature of adsorption and the physical/chemical in nature of sorption. It can be easily reversed by supplying the heat equal to calculated ΔH.

The ΔH is related to ΔG and ΔS as

$\Delta G = \Delta H - T\,\Delta S$

$\Delta S < 1$ indicates that adsorption is impossible whereas $\Delta S > 1$ indicates that the adsorption is possible. $\Delta G < 1$ indicates the feasibility of sorption.

The Vant Hoff's equation is

$$\log (q_e/C_e) = \Delta H/(2.303\,RT) + (\Delta S/2.303\,R)$$

$$\log (q_e/C_e) = -0.6519\,(1/T) + 1.5831$$

Where (q_e/C_e) is called the adsorption affinity.

If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the reversibility of process. The negative value for ΔG indicates the spontaneity of adsorption. Whereas the positive value indicates is non spontaneity of sorption.

Experiments are conducted to understand the adsorption behavior varying the temperature from 283 to 323 K. the plots indicating the effect of temperature on adsorption of malachite green for different initial metal concentrations are shown in fig.7. The Vant Hoff's plots for the adsorption data obtained at various initial concentrations of the malachite green are shown in fig.7. The values are ΔG = -9171.43, ΔH = 12.48202 and ΔS = 30.30993.

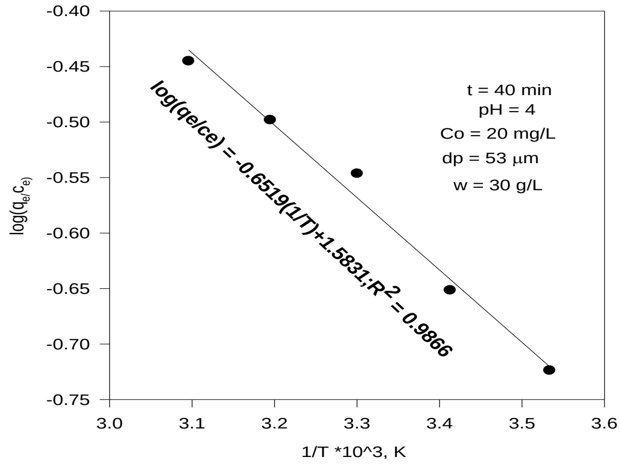

Fig 7. Vantoff's plot for % adsorption of Malachite green

Table –1

Isotherms constants

Langmuir	**Freundlich**	**Temkin**
q_m = 13.9082	k_f = 0.6127	A_T = 0.33611
b = 0.02562	n = 0.73863	b_T = 937.4598
R^2 =0.8966	R^2 =0.9977	R^2 =0.9589

8. Optimization using Response Surface Methodology (RSM):

8.1 Optimization using CCD

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the adsorption of Malachite green dye ions. The quadratic model is used in the present study, to relate four independent variables and percentage adsorption of Malachite green dye. The regression equation for is % adsorption of Malachite green dye (Y) is function of pH (X_1), C_o (X_2), w (X_3) and T (X_4).

The variations in the corresponding coded values of four parameters and response are presented in table-2

Table-2

Levels of different process variables in coded and un-coded form for % adsorption of Malachite green dye using *Antigonon leptopus* powder

Variable	**Name**	**Range and levels**				
		-2	**-1**	**0**	**1**	**2**
X_1	pH of aqueous solution	2	3	4	5	6
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	adsorbent dosage, w, g/L	20	25	30	35	40
X_4	Temperature, T, K	283	293	303	313	323

The following equation represents multiple regression analysis of the experimental data for the adsorption of Malachite green dye:

$$\boldsymbol{Y = -1603.23+30.11X_1 + 2.75X_2 + 93.76X_3 +10.14\ X_4 - 3.90X_1^2 - 0.07X_2^2 - 36.47X_3^2}$$
$$\boldsymbol{-0.02X_4^2+ 0.07\ X_1X_2 -0.23X_1X_3 - 0.00X_1X_4+ 0.06X_2X_3- 0.00X_2X_4-0.01X_3X_4} \text{ ------ } \mathbf{(5.10)}$$

Table-3

Results from CCD for Malachite green dye adsorption by *Antigonon leptopus* powder

Run no.	X_1, pH	X_2, C_o	X_3, W	X_4, T	% adsorption of Malachite green dye	
					Experimental	Predicted
1	**3**	**15**	**25**	**293**	**82.22000**	**82.21208**
2	**3**	**15**	**25**	**313**	**83.98000**	**83.99458**
3	**3**	**15**	**35**	**293**	**83.42000**	**83.38958**
4	**3**	**15**	**35**	**313**	**85.08000**	**85.11208**
5	**3**	**25**	**25**	**293**	**80.62000**	**80.60958**
6	**3**	**25**	**25**	**313**	**82.18000**	**82.17208**
7	**3**	**25**	**35**	**293**	**81.98000**	**82.06208**
8	**3**	**25**	**35**	**313**	**83.62000**	**83.56458**
9	**5**	**15**	**25**	**293**	**81.38000**	**81.42958**
10	**5**	**15**	**25**	**313**	**83.18000**	**83.13708**
11	**5**	**15**	**35**	**293**	**82.79000**	**82.83708**
12	**5**	**15**	**35**	**313**	**84.48000**	**84.48458**
13	**5**	**25**	**25**	**293**	**81.21000**	**81.21708**
14	**5**	**25**	**25**	**313**	**82.68000**	**82.70458**
15	**5**	**25**	**35**	**293**	**82.92000**	**82.89958**
16	**5**	**25**	**35**	**313**	**84.28000**	**84.32708**
17	**2**	**20**	**30**	**303**	**76.89000**	**76.89833**
18	**6**	**20**	**30**	**303**	**76.92000**	**76.87833**
19	**4**	**10**	**30**	**303**	**86.28000**	**86.26333**
20	**4**	**30**	**30**	**303**	**84.52000**	**84.50333**
21	**4**	**20**	**20**	**303**	**81.98000**	**81.98333**
22	**4**	**20**	**40**	**303**	**84.82000**	**84.78333**
23	**4**	**20**	**30**	**283**	**84.32000**	**84.27833**
24	**4**	**20**	**30**	**323**	**87.48000**	**87.48833**
25	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**
26	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**
27	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**
28	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**
29	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**
30	**4**	**20**	**30**	**303**	**92.50000**	**92.50000**

Experimental conditions [Coded Values] and observed response values of central composite design with 2^4 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 20 min and adsorbent size at 53 μm

Table-5. Represents the results obtained in CCD. Response obtained from regression in eq.6.1 in the form of ANOVA is presented. From the Fisher's F-test (F_{model}= 22510) and a very low probability value ($P_{model}>F$=0.000000), it is known from table–5.6 that the model is highly significant. At 5% level, the computed F-value ($F_{0.05\ (14.15)}$ =MS_{model}/MS_{error} = 22510) is greater than that of the tabular F-value ($F_{0.05\ (14.15)\ tabulars}$= 2.42), indicating that the treatment differences are significant

Table-4
ANOVA of Malachite green dye adsorption for entire quadratic model

Model	580.6513	14	41.42	22510.0	
Error	0.0276	15	0.0018		
Total SS	580.6789	29			

Table-5
Estimated regression coefficients for the Malachite green dye adsorption onto *Antigonon leptopus* powder

	Regressn	**Std.Err.**	**t(15)**	**p**
Mean/Interc.	-1603.23	7.975728	-201.013	0.000000
(1)pH (L)	30.11	0.338367	88.983	0.000000
pH (Q)	-3.90	0.008184	-476.881	0.000000
(2)Initial Conc(L)	2.75	0.067673	40.566	0.000000
Initial Conc(Q)	-0.07	0.000327	-217.389	0.000000
(3)Dosage (L)	93.76	1.361588	68.864	0.000000
Dosage (Q)	-36.47	0.130948	-278.482	0.000000
(4)Temperature(L)	10.14	0.050260	201.782	0.000000
Temperature(Q)	-0.02	0.000082	-202.116	0.000000
1L by 2L	0.07	0.002143	32.429	0.000000
1L by 3L	0.23	0.042863	5.366	0.000079
1L by 4L	-0.00	0.001072	-1.750	0.100581
2L by 3L	0.06	0.008573	6.416	0.000012
2L by 4L	-0.00	0.000214	-5.133	0.000123
3L by 4L	-0.01	0.004286	-1.400	0.181911

[a]insignificant ($P \geq 0.05$)

The larger the value of t and smaller the value of P, the more significant is the corresponding coefficient term. The't' and 'P' values are analyzed from table-5. It is found that the X_1, X_2, X_3, X_4, X_1^2,X_2^2 , X_3^2 , X_4^2 X_1X_2, X_1X_3, X_2X_3 andX_2X_4 have high significance to explain the individual and interaction effect of independent variables on Malachite green dye adsorption. The other terms (X_1X_2, X_1X_4, X_2X_3, $X_2X_4$and X_3X_4) are insignificant and are not required to explain adsorption. The model is reduced to the following form by removing insignificant terms.

$$\boldsymbol{Y = -1603.23+30.11X_1 + 2.75X_2 + 93.76X_3 +10.14\ X_4 - 3.90X_1^2 - 0.07X_2^2 - 36.47X_3^2}$$
$$\boldsymbol{-0.02X_4^2+ 0.07\ X_1X_2 -0.23X_1X_3 - 0.00X_1X_4+ 0.06X_2X_3- 0.00X_2X_4 -0.01X_3X_4} \quad \text{------ } \mathbf{(5.10)}$$

A synergistic effect is indicated by positive sign of the coefficient which means response increases with an increase in effect, while an antagonistic effect is indicated by a negative sign which means response decreases with an increase in effect. In the observed response values, a measure of the models variability is provided by the correlation coefficient (R^2). In the present study, the value of the regression coefficient (R^2 = 0.9999) for eq.5.10 indicates that 0.001 % of the total variations are not satisfactorily explained by the model. It is proved from that table that $F_{statistics}$ value for entire model is higher. This large value means that % adsorption can be adequately explained by the model equation. Generally P values lower than 0.05 indicates that the model is considered to be statistically significant at 95% confidence level. The % adsorption prediction from the model is shown in table-5. It is implied from table-5 that all the squared terms of all the variables and the linear terms are significant (P < 0.05). Among the interaction terms, all the terms (P < 0.05) are insignificant on the adsorption capacity. Fig. 8 and Fig. 9 show Pareto chart and normal probability plot (NPP) of residual values. It could be seen that the experimental points are reasonably aligned suggesting normal distribution.

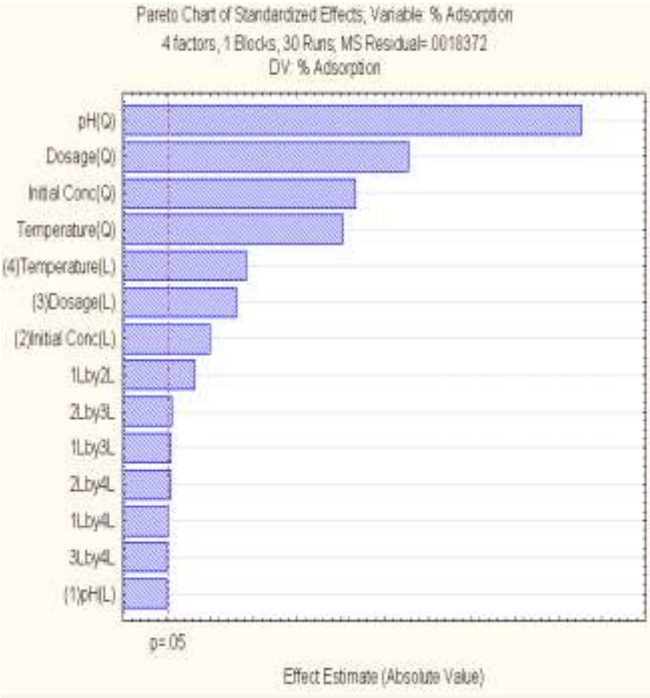

Fig. 8. Pareto Chart

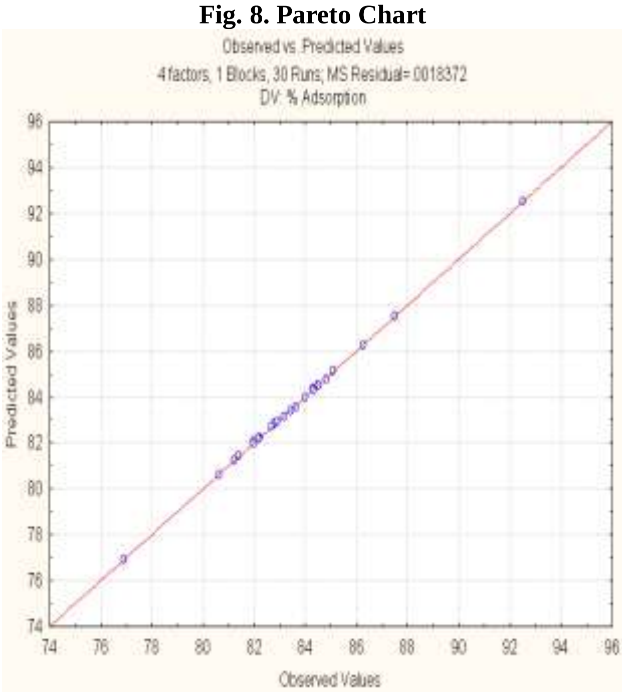

Fig. 9. Normal Probability Chart

8.2. Interaction effects of adsorption variables:

The three-dimensional view of response surface contour plots [Fig.10 (a) to (f)] show % adsorption as a function of for various combinations of independent variables. The plots are represented as a function of two factors at a timekeeping other factors fixed at zero level. It is found from the response surface plots that the % adsorption is maximal at low and high levels of the input variables. However, there exists a region where neither an increasing nor a decreasing trend in % adsorption is observed. The adsorption variables should be optimum to maximize the % adsorption. The % adsorption of Malachite green dye is strongly influenced by the pH as evident from figs. 10 (a) to (f).

The predicted optimal set of conditions for percentage adsorption of Malachite green dye is

pH of aqueous solution	= 4.0094
Initial Malachite green dye dye concentration	=18.6548 mg/L
Adsorbent dosage	=31.5332 g/L
Temperature	=305.5716K
%adsorption of Malachite green dye	= 92.50000

The optimal sets of conditions obtained with CCD are shown in table-6 along with experimental values.

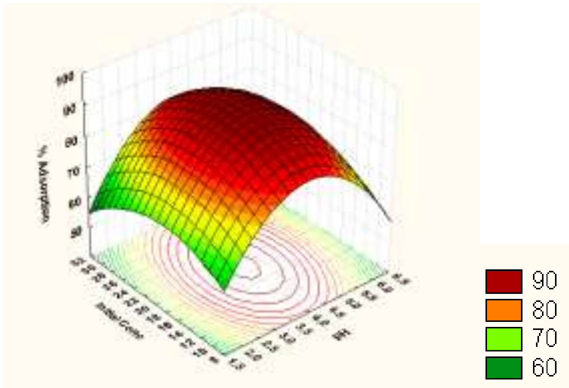

Fig. 10 (a) Surface contour plot for the effects of pH and initial Malachite green dye concentration on % adsorption

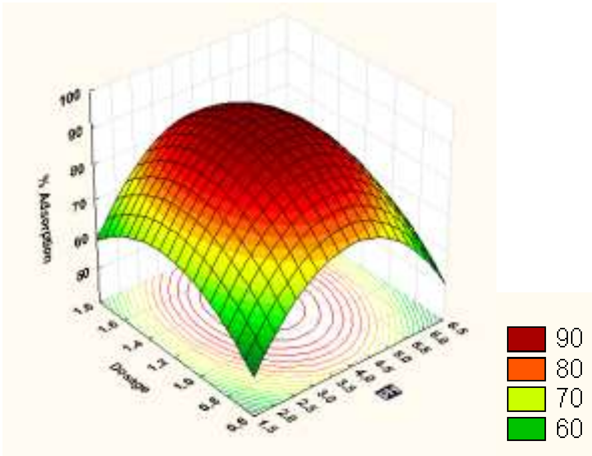

Fig. 10 (b) Surface contour plot for the effects of pH and dosage on % adsorption of Malachite green dye

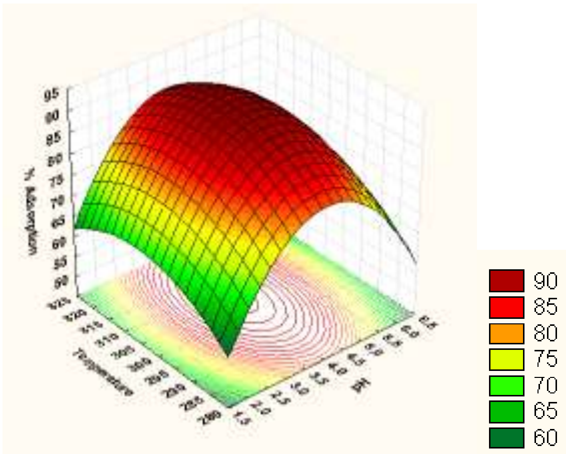

Fig. 10 (c) Surface contour plot for the effects of pH and Temperature on % adsorption of Malachite green dye

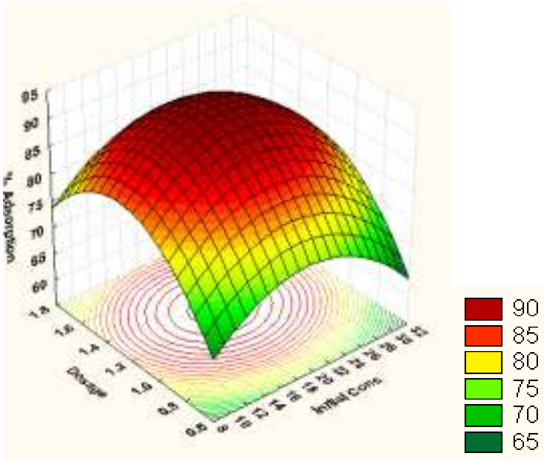

Fig. 10 (d) Surface contour plot for the effects of initial concentration and dosage on % adsorption of Malachite green dye

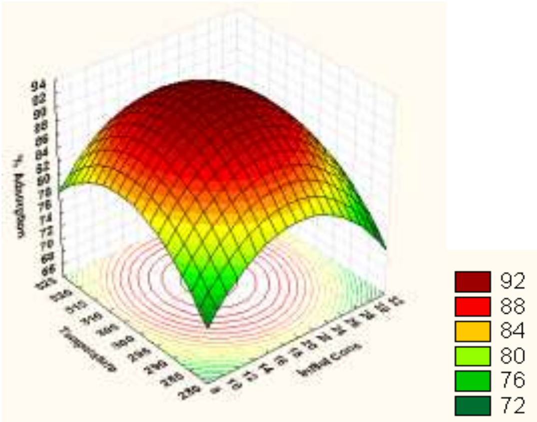

Fig. 10 (e) Surface contour plot for the effects of initial concentration and Temperature on % adsorption of Malachite green dye

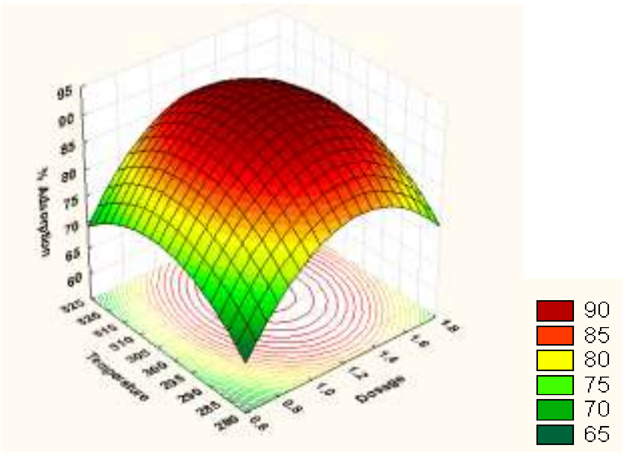

Fig. 10 (f) Surface contour plot for the effects of Dosage and Temperature on % adsorption of Malachite green dye

Table –6
Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental value
pH of aqueous solution	**4.0094**	**4**
Initial cobalt concentration, mg/L	**18.6548**	**20**
Adsorbent dosage, w, g/L	**31.5332**	**30**
Temperature, K	**305.5716**	**303**
% adsorption	**92.5926**	**89.5**

Table – 7

Malachite green uptake capacities for different adsorbents

Authors	Adsorbent	q_t, mg/g
P T Godbole et.al.,	Immobilized *Saccharomyces cervisiae*	17
Uma et.al.,	Timber waste	13.87
Georgiadis I.K. et.al.,	Diasporicgreek raw Bauxite	4.5
R.Rajeshkannan et.al.,	*Hydrillaverticillata*	91.97
SitiAminahZulkepli	Multi walled carbon nanotubes	112.36
Present investigation	***Antigonon leptopus* leaves powder**	**17.668**

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