Kinetic, Thermodynamic and Equilibrium Studies On the Removal of Malachite Green (Mg) Dyes by Adsorption On to Low Cost ACQNC Adsorbent

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Abstract:- The present work deals with adsorption of Malachite Green (MG) dyes carried out in the presence of Activated Cissus Quadrangularis Stem Nano Carbon (ACQNC). Various parameters like the effect of initial concentration, contact time, dose of adsorbent, temperature and pH were also studied. The result shows that when the amount of adsorbent increases, the percentage removal of dye increases. The applicability of Freundlich adsorption and Langmuir adsorption isotherm had also been tested. Adsorption kinetic data have been tested using pseudo second order, intra-particles models and the Elovich model. The thermodynamics parameter such as $\Delta G0$ $\Delta H0$ and $\Delta S0$ were calculated. The adsorption capacities of Activated Cissus Quadrangularis Stem Nano Carbon (ACQNC) were calculated using batch process.

Key Terms- Adsorption, Kinetics, Thermodynamics, Malachite Green, Activated Cissus Quadrangularis Stem Nano Carbon (ACQNC)

I. INTRODUCTION

Dyes are commonly used in many industries, like textile, food, paper, plastic, cosmetics and coloring industries. These industries commonly use synthetic dyestuff as a colorant. Discharge of dye containing waste water into the environment contaminates surface water and ground water however 7×10^5 tones of dye stuff are produced annually [1,2]. The dyes in the waste water even at very low concentration affect the aquatic life and human health by polluting the environment. The toxicity and carcinogenicity have lead to exploration of possible detoxicants [3, 4]. Dyes can causes allergic, dermatitis, skin irritation, cancer, mutation, etc. In general dyes are poorly biodegradable and some of the dyes produce aromatic amine which is highly carcinogenic in nature [5, 6]. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industries, coir pith, crude oil, residue, tropical grass, olive stone almond shell, pine bark, wool waste, coconut shell etc [7, 8]. The present study seeks to evaluate the efficiency of Activated Cissus Quadrangularis Stem Nano Carbon (ACQNC) adsorbent in the removal of malachite green dyes from dye solution.

II. EXPERIMENTAL METHODS

2.1 Adsorbent
The Cissus Quadrangularis Stem was obtained from Agriculture area was carbonized with con sulphuric acid and activated around 900°C in a muffle furnace for 5 hrs the it was taken out, ground well to fine powder and stored in a vacuum desiccators.

2.2 Adsorbate
The stock solution of malachite green concentration 1000 mg/L was prepared by dissolving 1 g of malachite green in 1000 ml of double distilled water. Different concentration of dyes solution range from (50 to 250 mg/L) were prepared from the stock solution by appropriate dilution

2.3 Batch adsorption experiments
Batch adsorption was tested by adding 25 mg of ACQNC to 50 ml of the dye solution of different initial concentration (50 to 250 mg/L) at a particular pH. The experiment was carried out using a wrist action shaker for the period of 180 min and 120 rpm using 250 ml stopper glass flasks at (300C to 600C). The residual concentrations of dyes in each sample after adsorption at different time intervals were determined by UV-Visible spectrophotometer. The equilibrium q_e (mg/g) was calculated by the following mass balance principle.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of dyes, V is the volume (L), M is the weight (g) of the adsorbent. The removal efficiency of the

adsorbents on dyes was calculated by using the following expression.

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \quad \text{.......................} (2)$$

2.4 Kinetic Experiments

The batch kinetic [9] experiments were basically similar to those used testing the adsorption equilibrium method. The dyes samples were taken at specific time intervals and the concentration of dyes was similarly measured. The all kinetic experiments were carried out at 30, 40, 50 and 60oC with initial dye concentration (50, 100, 150 200 and 250 mg/ L) the amount of adsorption at time t . The q_t (mg/g) was calculated by.

$$q_t = \frac{(C_0 - C_t)V}{M} \quad \text{..........................} (3)$$

Where C_0 (mg/L) is the liquid phase concentration of dye at any time.

III. RESULTS AND DISCUSSION

3.1 Effect of contact time and initial dye concentration

The experimental results of adsorption of various dye concentrations with contact time are shown in Fig.1. This figure shows that the % removal initially increases and reaches the limiting value. So, that the equilibrium was established at 50 minutes. Hence all the remaining

experiments were carried out at 50 minutes. The equilibrium data were given in Table.1 reveals that, the percentage removal was decreases with increase in initial dyes concentration. This was due to the number of available active sites was remains constant but the initial concentration of dyes increases, so that % removal decreases [10, 11].
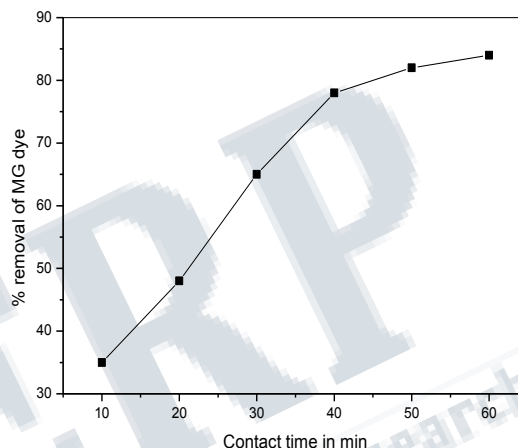
Fig.1-Effect contact time on the removal of malachite green by ACQNC

Table.1. Equilibrium parameter for the adsorption of MG dye onto ACQNC

MG (mg / L)	Ce (mg / L)				Qe (mg / g)				% Removal of MG dye			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
50	4.9720	4.5824	4.2496	4.0432	90.056	90.83	91.500	91.913	90.056	90.82	91.08	91.96
100	17.2696	15.6200	13.39	11.80	165.46	168.76	173.204	176.390	82.734	84.38	86.64	88.19
150	37.4792	33.8032	30.27	27.155	225.04	232.39	239.454	245.689	75.018	77.45	79.81	81.65
200	73.2368	68.5768	30.27	58.81	253.52	262.84	339.45	282.361	63.386	65.16	84.86	70.54
250	119.95	114.05	63.67	102.74	260.0	271.88	372.64	294.50	52.017	54.3769	74.5283	58.08

3.2 Effect of adsorbent dosages

The effect of the ACQNC doses was studied at 60oC by varying the amount of adsorbent dose 50-250 mg for the

initial concentration of 50 mg/L Fig. 2 reveals that increase in percentage removal of MG dye with increases in dose of adsorbent due to the increase in adsorbent surface area and the availability of more adsorption sites
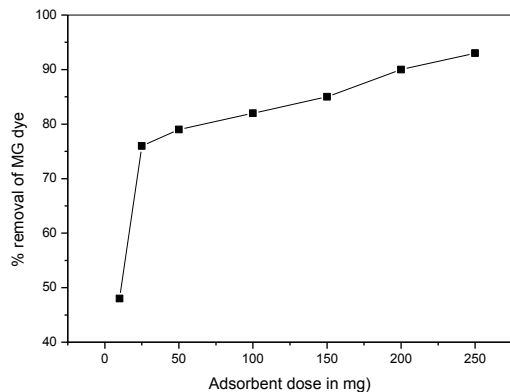
Fig.2-Effect of adsorbent dose on the removal of malachite green by ACQNC

3.3 Effect of pH

The solution pH is one of the most important factors that control the adsorption of MG dye. To examine the effect of pH on the % removal of MG dye the pH of initial solution were varied from 2.0 to 10.0 by adding NaOH or HCl in to them. The % removal increases as the pH increases up to 6.4. There after the % removal decreases. At pH 6.4 the optimum % removal takes place. So the remaining experiment was carried out at pH 6.4. The experimental result was shown in Fig. 3.
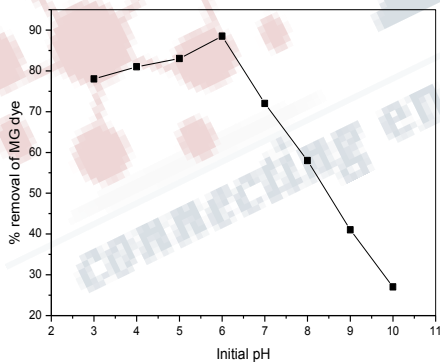
Fig.3-Effect of pH on the removal of malachite green by ACQNC

3.4 Adsorption isotherm studies
To quantify the sorption capacity of the absorbent for the removal of dyes, the most commonly used isotherms, are the Freundlich and Langmuir isotherms and hence these were used in this study.

3.4.1 Freundlich isotherm
Linear form of Freundlich isotherm model [12] is represented by the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots\dots\dots\dots\dots(4)$$

Where q_e is the amount of dyes adsorbed per unit weight of the adsorbent (mg/L) K_f is (mg/g(L/mg)) the measure of adsorption capacity and 1/n is the adsorption intensity. The value of K_f and n are calculated from the intercept and slope of the plot of log q_e Vs log C_e respectively. The constant K_f and n values are given in Table.2. In general the K_f value increases for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n > 1 represents favorable adsorption condition [7] (or) the value of n are in the range of 1 to 10 confirms the favorable condition for adsorption. The adsorption co-efficient K_f of dyes on ACQNC was found from 5.8107to 6.1062 L/g. The K_f value indicates that the saturation time for adsorption of dyes is attained quickly due to the high affinity of Acid ACQNC towards the adsorbate. The values of n were in the range of 1.8611 to 2.9265 (mg/L) for MG dyes adsorption. So Freundlich isotherm is suitable for this adsorption. The K_f values also indicate the multilayer adsorption were possible. This reveals that the ACQNC was more efficient for the removal of MG dyes.

Table.2. Langmuir and Freundlich isotherm parameter for adsorption of MG dye onto ACQNC adsorbent

Temperature (°C)	Langmuir parameter		Freundlich parameter	
	Q_m	b	K_f	n
30	286.1309	0.0909	5.8107	2.9265
40	299.1008	0.0941	5.8979	2.8731
50	494.764	0.0452	5.1320	1.8611
60	323.577	0.1055	6.1062	2.7871

3.4.2 Langmuir isotherm
The Langmuir isotherm model [13] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$\frac{C_e}{q_e} = \frac{1}{Q_m\, b} + \frac{C_e}{Q_m} \quad \dots\dots\dots\dots\dots..(5)$$

Where C_e (mg/L) is the equilibrium concentration of the dye, q_e (mg/g) is the amount of dye per unit weight of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m

is the amount of dye at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption or rate of adsorption. The linear plot of C_e/q_e against the equilibrium concentration C_e shows the Langmuir model. The Langmuir constant Q_m and b were determined from the slope and intercept of the Langmuir plot and these values are given in Table.2. The feasibility of the Langmuir isotherm can also be expressed in terms of the dimensionless constant separation factor R_L [14, 15] by the equation

$$R_L = \frac{1}{1+bC_0} \quad \ldots\ldots\ldots\ldots\ldots(6)$$

Where C_0 (mg/L) is the initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of the isotherm.

$R_L > 1$ unfavorable

$R_L = 1$ Linear

$0 < R_L < 1$ Favorable

$R_L = 0$ Irreversible

The RL values lies between 0 and 1 indicate favorable adsorption for all initial concentration study. The calculated RL values were given in Table.3. The calculated RL values were within the range of 0.0365 to 0.1811. So the adsorption of MG follows the Langmuir isotherm.

Table.3. Dimensionless separation factor (RL)

C_0 (mg/L)	Temperature (°C)			
	30	40	50	60
50	0.1803	0.1753	0.3067	0.1593
100	0.0991	0.0960	0.1811	0.0866
150	0.0683	0.0661	0.1285	0.0594
200	0.0521	0.0504	0.0995	0.0452
250	0.0421	0.0407	0.0812	0.0365

3.5 Thermodynamic study

Thermodynamic parameter such as change in free energy (ΔG^0) (KJ/mol), Enthalpy (ΔH^0) (KJ/mol) and entropy (ΔS^0) (JK/mol) were calculated by using the following equation (7,8,9)

$$K_0 = C_{Solid}/C_{Liquid} \quad \ldots\ldots\ldots\ldots (7)$$

$$\Delta G^0 = -RTlnK_0 \quad \ldots\ldots\ldots\ldots (8)$$

$$\log K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad \ldots\ldots\ldots (9)$$

Where K_o is the equilibrium constant, C_{Solid} is the solid phase concentration at equilibrium (mg/L). C_{liquid} is the liquid phase concentration at equilibrium (mg/L). T is temperature in Kelvin and R is the gas constant (8.314 J mol^{-1}K^{-1}).A graph was drawn between log K_0 vs 1/T. The ΔH^0 and ΔS^0 values obtained from the slope and intercept of van't Hoff plots. These values were given in Table.4. The negative ΔG^0 were indicate the adsorption is spontaneous in nature and also the magnitude of ΔG^0 indicate the adsorption is physical adsorption (i.e., less than 70 KJ/mol). The value of ΔH^0 is positive, this indicates the adsorption is endothermic process. The positive ΔS^0 indicates increased randomness during the adsorption. This also support the adsorption was physical adsorption [16,17]

Table. 4. Thermodynamic parameter for the adsorption of MG onto ACQNC adsorbent

C_0 (mg/L)	ΔG^0				ΔH^0	ΔS^0
	30°C	40°C	50°C	60°C		
50	- 5550.835	- 5968.794	- 6381.572	- 6729.448	6.4266	39.5732
100	- 3946.587	- 4389.473	- 5011.674	- 5567.706	12.6685	54.7089
150	- 2769.424	- 3213.115	- 3692.364	- 4178.738	11.4882	47.0177
200	- 1382.059	- 1692.702	- 4629.514	- 2424.078	17.7098	63.6556
250	- 203.415	- 456.772	- 2883.101	- 996.3114	14.9639	50.6270

3.6 Adsorption kinetics
The kinetics studies were done by using pseudo second order [18] Elovich [19, 20] and intra-particle diffusion [21] models.

3.6.1 The pseudo-second-order kinetic model
The linear form of pseudo second order equation is expressed as

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where k_2(g/mg min) is the pseudo second order rate constant .For the boundary conditions t = 0 to t= t and q_t= 0 to $q_{t = }q_t$ integrated form of Eq. (10) becomes:

$$(q_e - q_t) = \frac{1}{q_e} + K_2 t \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

This is the integrated rate law for a pseudo second order reaction. Equation (11) can be rearranged to obtain Eqs (12) which has a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots\ldots\ldots (12)$$

If the initial adsorption rate (h)(g/mg min) is

$$h = K_2 \, q_e{}^2 \qquad \text{..................................(13)}$$

Then Eqs. (12) and (13) becomes:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad \text{.....................(14)}$$

where k_2(g/mg min) is the pseudo second order rate constant, q_e is the amount of dye adsorbed on the per unit mass of adsorbent (mg/g) at equilibrium, q_t is the amount of dye adsorbed at time "t". A Graph is drawn between t/q_t versus "t", the q_e and k_2 can be calculated from the slope and intercepts of the graph. The correlation coefficient value (γ) were also calculated. These values are given in Table.5. The correlation coefficient value (γ) for the pseudo second order was greater than 0.9900 (i.e., γ > 0.9900) and also q_e value calculated from the model was almost equal to the experimental value. So the adsorption of MG dye by ACQNC follows pseudo second order model.

Table.5. The kinetic Parameter for the adsorption of MG on to ACQNC

Co	Temp °C	pseudo second order				Elovich model			Intra-Particle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	Intercept
50	30	100.08	0.0012	0.991	12.845	110.52	0.0691	0.9918	1.622	0.994	0.1832
	40	100.20	0.0013	0.992	13.590	146.80	0.0724	0.9920	1.644	0.995	0.1724
	50	100.25	0.0014	0.993	14.507	198.99	0.0758	0.992	1.665	0.996	0.1625
	60	100.84	0.0014	0.993	14.469	187.46	0.0745	0.9927	1.663	0.997	0.1646
100	30	184.21	0.0006	0.994	22.799	177.59	0.0367	0.9926	1.574	0.997	0.1887
	40	187.31	0.0067	0.992	23.709	209.83	0.0371	0.9929	1.594	0.997	0.1821
	50	190.91	0.0007	0.992	26.160	280.91	0.0379	0.9935	1.623	0.994	0.1725
	60	194.66	0.0007	0.991	26.884	279.72	0.0370	0.9939	1.631	0.995	0.1737
150	30	254.83	0.0004	0.990	27.318	155.46	0.0246	0.9941	1.494	0.996	0.2095
	40	260.67	0.0004	0.991	30.247	201.50	0.0250	0.9948	1.529	0.996	0.1983
	50	267.77	0.0004	0.991	33.124	249.64	0.0251	0.9950	1.558	0.992	0.1903
	60	272.26	0.0003	0.992	28.184	307.97	0.0268	0.9991	1.575	0.991	0.1750
200	30	297.92	0.0002	0.992	24.505	85.686	0.0183	0.9994	1.333	0.993	0.2583
	40	305.36	0.0002	0.993	26.884	105.97	0.0186	0.9960	1.375	0.991	0.2436
	50	314.08	0.0002	0.995	29.404	127.84	0.0186	0.9985	1.410	0.992	0.2329
	60	321.60	0.0003	0.995	33.692	171.46	0.0190	0.9986	1.455	0.993	0.2176
250	30	322.79	0.0001	0.995	19.574	49.662	0.0150	0.9980	1.136	0.993	0.3205
	40	333.85	0.0001	0.998	21.157	55.877	0.0148	0.9983	1.173	0.995	0.3101
	50	348.89	0.0001	0.998	21.806	57.738	0.0148	0.9927	1.189	0.998	0.3105
	60	353.73	0.0002	0.998	25.266	73.520	0.0145	0.9929	1.248	0.998	0.2878

3.6.2 The Elovich equation
The Elovich model equation is generally expressed as

$$\frac{dq_t}{dt} = \alpha \, \exp (-\beta q_t) \qquad \text{.....................(15)}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) during any one experiment. To simplify, the Elovich equation. Chien and Clayton assumed αβt>>t and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(15) becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad \text{.........................(16)}$$

The MG dyes adsorption fits the Elovich model; a plot of q_t vs. ln (t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (αβ). The Elovich parameters α, β and correlation coefficient (γ) were given in Table.5. The initial adsorption rate (α) and desorption constant (β) increases with increase in initial concentration of MG dyes and also the correlation coefficient (γ) were greater than 0.9900 (i.e., γ > 0.9900). The Elovich model can also suitable for the MG adsorption onto ACQNC.

3.6.3 Intra–particle diffusion model

According to Weber and Morris suggested the intra-particle diffusion model is

$$q_t = K_{id}\, t^{1/2} + C \qquad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

Where k_{id} is the intra-particle diffusion constant (mg/g min), and q_t is the amount of the dye adsorbed at time "t". According to Weber and Morris model, a graph is drawn between q_t and $t^{1/2}$, the line was passing through the origin. But here the intercept value indicates the lines were not passing through origin. This was due to that the intra-particle diffusion takes place along with some other process. This may be boundary layer adsorption or instantaneous adsorption.

3.7. Effect of the ionic strength on the adsorption of Malachite Green

The effect of sodium chloride on the adsorption of malachite green on to ACQNC is shown in Fig.4. In a low solution concentration of NaCl had less influence on the adsorption capacity. The partial neutralization of the positive charge on the adsorbent surface and a consequent compression of the electrical double layer by the Cl- anion cause the increase in the adsorption of the malachite green at higher ionic strength. The chloride ions can also enhances adsorption of malachite green ion onto activated calcite by pairing of their charges and hence reducing the repulsion between the malachite green molecules adsorbed on the surface. The ACQNC to adsorb more of positive malachite green dye [16,17]
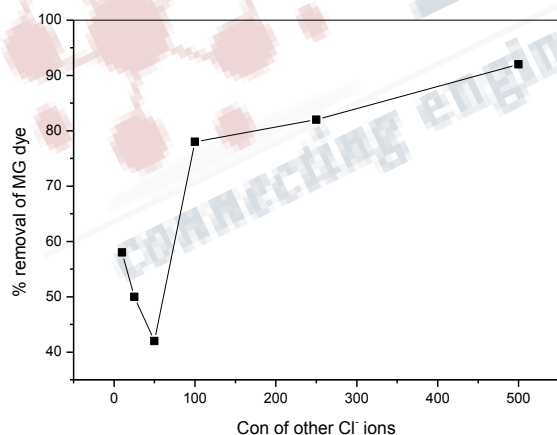
Fig.4-Effect of other ions on the removal of malachite green by ACQNC

IV. CONCLUSION

The adsorption characteristics of MG dye onto ACQNC are strongly affected by the initial dye concentration, initial pH and the adsorbent dose. The pH 6.4 was favorable for the optimum adsorption of MG dye by ACQNC. The RL values and other adsorption parameters indicate both Langmuir and Freundlich isotherms favorable for ACQNC adsorption. The pseudo second order, Elovich and intra-particle kinetic model were found to applicable for the adsorption of MG onto ACQNC reaction model. The thermodynamics parameters $\Delta G0$, $\Delta H0$ and $\Delta S0$ values indicate the adsorption is endothermic and physical adsorption.

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