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Adsorption of Malachite Green by Plaster Of Paris- Equilibrium and Thermodynamic Studies

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ABSTRACT

Adsorption of MG dyes by the plaster of Paris was studied through the batch equilibrium techniques. The influence of contact time, initial concentration of dyes, pH and other ions were experimentally verified. The Freundlich and Langmuir models tested to describe the equilibrium isotherm reaction. The kinetics process of dyes adsorption on plaster of paris were described by applying pseudo second order, Elovich model and intra- particle diffusion and the kinetics data indicate that the adsorption follows pseudo second order kinetic surface adsorption. The equilibrium and thermodynamic parameters of the adsorption process were determined from the sorption behavior of pop and it results indicate that the adsorption of MG dye by pop is follows spontaneous nature and endothermic process

Keywords; Adsorption, Kinetics, Malachite green, Plaster of paris (POP). Thermodynamics,

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INTRODUCTION

The effluent from the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important source of dye pollution [1]. Malachite green, a banned dye for human consumption, is a carcinogen. It is extensively used in Indian in the dyeing of cotton, wool, jute and leather as well as an antiseptic. Malachite green results in malignant transformation of Syrian hamster embryo cells, the chemical also used in coloring sweets, poses a serious threat to workers in printing and textile industries. A textile printing industry could cause both air as well as water pollution. The azo dye which are banned in our country, are often used by some traders. They cause radiation that is aggravated by ultraviolet rays and those working in industries using such a dye, yet such radiation are very mild, prolonged exposure is bound to create skin and eye ailment. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed. Recognizing the economic drawback of the commercial activated carbon [2]. Many investigators have studied the feasibility of using inexpensive alternative materials like Pearl milet husk, date pits, saw dust, and buffing dust of leather industry, coir pith, crude oil residue, tropical grass, olive stone, almond shells, pin bark, wool waste, wheat husk, de- oiled- soya, rice husk, jack fruit peel, coconut shell etc., as carbonaceous precursors for the removal of dye from waste water[3-5]. This paper focuses on the use of plaster of paris for the removal of malachite green dye from the aqueous solution.

MATERIAL AND METHODS

Absorbent

The Plaster of Paris obtained from commercial shop was activated at 400^0C in a muffle furnace for 5 hrs, then it was taken out ground well to fine powder and stored in a vacuum desiccators.

Adsorbate

The stock solution of malachite green concentration 1000mg/L have been prepared by dissolving 1 g of malachite green in 1000 ml of double distilled water. The different concentrations of dye solution ranging from 50 to 250 mg/L prepared from stock solution by appropriate dilution.

Batch sorption techniques

The batch experiments [6] were performed by fixed amount of 25 mg plaster of paris added to 50 ml of dye solution taken in 250 ml stopper glass flasks. The flasks were placed in an isothermal shaker with agitation speed 120 rpm for 180 min at constant temperature when the equilibrium was attained and the flasks were removed from the shaker. By centrifugation at 1500 rpm at 10 min the adsorbent was separated, the supernatant liquid was analyzed for the dyes concentrations with the help of UV-Visible spectrophotometer (perkin Elmer 2380) the

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amount of dyes ions adsorbed at equilibrium, q_e (mg,/g) can be calculated based on the balance principle

$$q_e = (C_i - C_f)\, V / M \qquad (1)$$

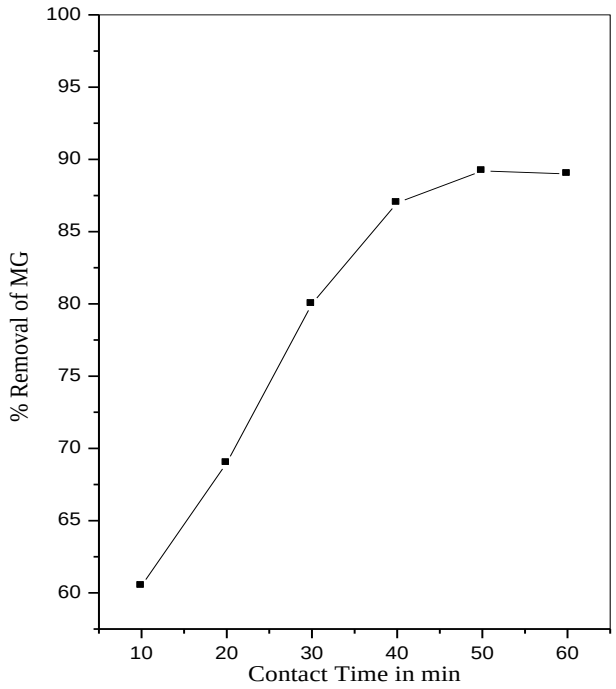
where the q_e is the amounts of dye uptake per unit mass of the sorbent (mg/g),C_i and C_f are the liquid phase concentration of dyes at initial and final (mg/L) respectively. V is the volume of the dye solution (L), and M is the mass of dry sorbent. Per cent removal of dye (R%) was calculated using the formula;

$$R\% = C_i - C_f / C_i \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on the percentage removal of dye was investigated at different dye concentrations (50 to 250 mg/ L) as shown Figure 1, The percentage removal of MG dye by plaster of paris was rapid in the beginning. The maximum percentage removal of 90% was achieved at 50 minutes observed that there is small increase in the amount of dye adsorbed over the time this is may be due to desorption.



Fig;1- Effect of Contact time on the removal of MG Dye onto POP
[MG]=50mg/L; Adsorbent dose=25mg/50ml;Temp=30^{0}C

Effect of initial concentration

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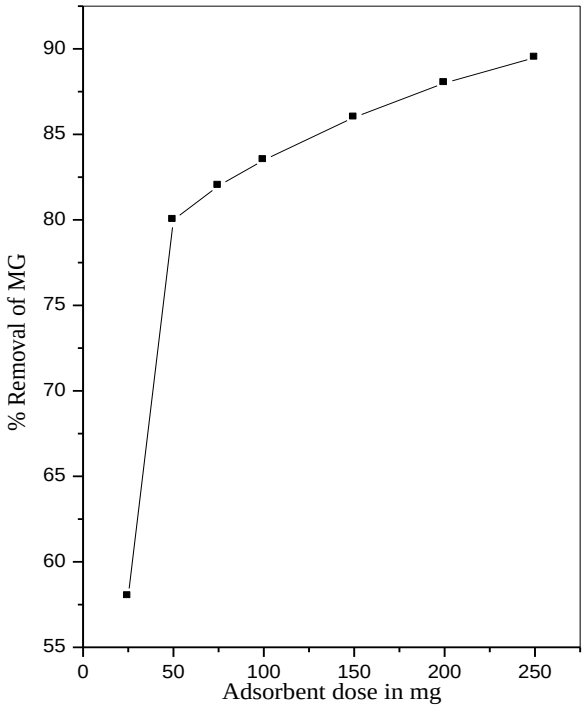
The effect of initial concentration of dye ranging from 50 to 250 mg/L on adsorption was investigated under the specified condition (initial pH 6.5 ,contact time 50 minutes, sorbent 25 mg/50 ml dye and Temperature 30-60 ^{0}C). The percentage removal of MG dye was found to decrease with increasing initial dye concentration. It was observed that the exits reduction immediate solute adsorption due to the lack of available active sorption sites required for the high initial concentration of MG dye.

Effect of dosage of POP

The Adsorption of MG dye on to plaster of paris was studied by varying dose of POP in the range of 50 to 250 mg/50 ml of dye solution The percentage of adsorption increased with increasing the dosage of the plaster of paris as shown in Figure 2 This is due to surface area and availability of more sorption sites [7, 8].

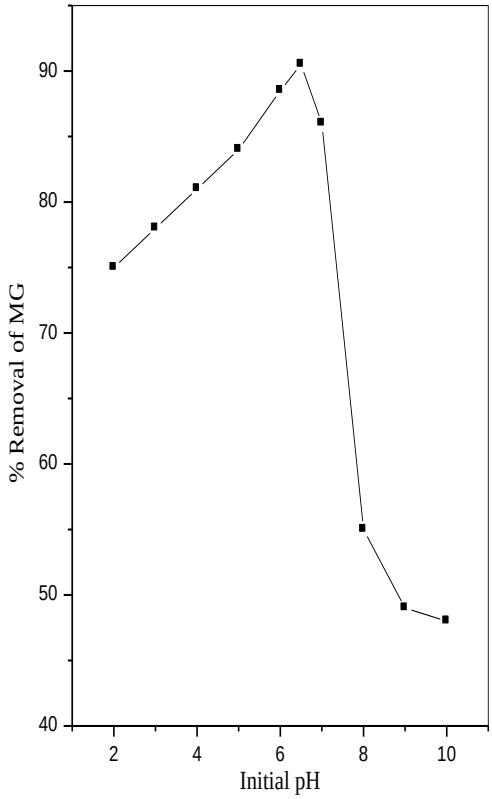


Fig;2- Effect of Adsorbent dose on the removal of MG Dye onto POP
[MG]=50mg/L; Conact time=50min; Temp=30^{0}C

Effect pH of solution

The pH value of the solution was an important controlling parameter in the adsorption process. The effect of pH MG dye adsorption onto plaster of paris was analysed over the pH range of 2.0-10.0 and the results are shown in Figure. 3. MG dye adsorption was found to increase with an increase in the initial solution pH .When pH > 6.5 decrease the removal of MG dye may be due to the occupation sites by anionic species which retards the approach of such

ions further towards the adsorbent surface .The experimental results the optimum pH range for the adsorption MG dye is 2.0 to 6.5 shown in Fig.3



Fig;3- Effect of Initial pH on the removal of MG Dye onto POP
[MG]=50mg/L; Conact time=50min; Adsorbent dose=25mg/50ml;Temp=30^0C

Effect of chloride ions

The effect of sodium chloride on the adsorption of malachite green on to POP is shown in Figure 4. The low concentrate NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is raised. At higher ionic strength, the adsorption of malachite green will be high owing to the partial neutralization of the positive charge on the POP surface and a consequent compression of the electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of malachite green ion by pairing their charges, and hence reducing the repulsion between the malachite green molecules adsorbed on the surface. This indicates that the POP to absorb more positive malachite green dye [9-13]

Adsorption isotherms
Langmuir model isotherm

The commonly used Langmuir isotherm equation[14] is given as

ISSN: 0975-8585

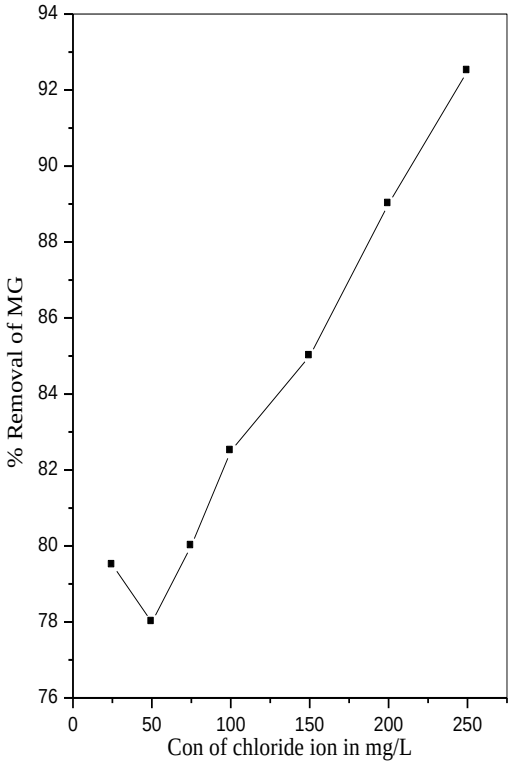
$$C_e/q_e = 1/ K_L q^0 + C_e/ q^0 \quad \text{.....(3)}$$

Where q_e (mg/g) is the amount of MG dye adsorbed per unit mass of plaster of paris corresponding to complete coverage of the adsorptive site C_e (mg/L) is the equilibrium concentration of the MG dye in solution, q^0 (mg/g) is the monolayer adsorption capacity of adsorbent and K_L (L/mg) is the Langmuir constant related to the force to the free energy of the adsorption. The q^0 and K_L are calculated from the linear plot of C_e/q_e versus Ce and the values are tabulated in Table.2. In order to predict the adsorption efficiency of the sorption reaction in terms dimensionless separation factors R_L [15,16.] were determined by using the following relationship

$$R_L = 1/ (1+ bC_0) \text{ ..... (4)}$$

The values of R_L parameter given an idea about the shape of isotherm process

$R_L > 1$ unfavourable
$R_L = 1$ Linear
$0<R_L< 1$ Favourable
$R_L= 0$ Irreversible



Fig;4- Effect of the other ions on the removal of MG dye onto POP
[MG]=50mg/L; Contact time=50 min; Temp 30^0C; Adsorbent dose=25mg/50ml

ISSN: 0975-8585

TABLE 1: EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF MG DYE ON POP

MG	Ce (Mg / L)				Qe (Mg / g)				R (%)			
	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	5.3720	4.9824	4.6496	4.4432	89.256	90.0352	90.7008	91.1136	89.256	90.0352	90.7008	91.1136
100	18.0696	16.4200	14.1976	12.6048	163.8608	167.16	171.6048	174.7904	81.9304	83.5800	85.8024	87.3952
150	39.0792	35.4032	31.8728	28.7552	221.8416	229.1936	236.2544	242.4896	73.9472	76.3978	78.7514	80.8298
200	76.4368	71.7768	31.8728	62.0192	247.1264	256.4464	336.2544	275.9616	61.7816	64.1116	84.0636	68.9904
250	126.3560	120.4576	66.8792	109.1480	247.288	259.0848	366.2416	281.704	49.4576	51.81696	73.2483	56.3408

TABLE 2: LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR THE ADSORPTION OF MG ON POP

TEMPERATURE(^{0}C)	LANGUMUIR PARAMETER		FRUENDLICH PARAMETER	
	K_L	q0	K_f	n
30°	270.8751	0.0984	5.793287	3.0089
40°	283.9505	0.1001	5.867331	2.94413
50°	489.5315	0.0423	4.999310	1.8429
60°	308.7314	0.1087	6.050857	2.8416

TABLE 3: DIMENSIONLESS SEPERATION FACTOR (RL)

INITIAL CONCENTRATION (Ci)	TEMPERATURE °C			
	30°C	40°C	50°C	60°C
50	0.1687	0.1664	0.32058	0.1553
100	0.0921	0.0907	0.1908	0.0841
150	0.0633	0.0624	0.1359	0.0577
200	0.04831	0.0475	0.1055	0.0439
250	0.0390	0.0384	0.0862	0.03546

TABLE 4: THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF MG ON POP

Co	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
50	- 5333.43	- 5727.992	- 6116.419	- 6444.064	5.9516	37.2864
100	- 3808.034	- 4234.704	- 4831.004	- 5360.90	12.1097	52.4160
150	- 2628.035	- 3056.686	- 3517.927	- 3983.941	11.0903	45.2421
200	- 1209.915	- 1509.873	- 4465.77	- 2213.937	17.6039	62.7498
250	54.65745	- 189.213	- 2704.913	- 705.997	15.2284	50.67742

TABLE 5: THE KINETIC PARAMETER FOR THE ADSORPTION OF MG ON POP

Co	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
50	30	99.321	0.00127	0.9931	12.589	104.57	0.0691	0.9919	1.6152	0.9940	0.1851
	40	99.437	0.00134	0.9913	13.324	138.53	0.7243	0.9940	1.6373	0.9941	0.1741
	50	99.481	0.00144	0.9941	14.227	187.28	0.0758	0.9930	1.6582	0.9951	0.1641
	60	100.07	0.00141	0.9945	14.191	176.61	0.0746	0.9912	1.6568	0.9926	0.1663
100	30	182.70	0.00066	0.9947	22.304	167.44	0.0367	0.9915	1.5668	0.9936	0.1908
	40	185.79	0.00067	0.9951	23.206	197.71	0.0371	0.9951	1.5865	0.9925	0.1841
	50	189.38	0.00071	0.9958	25.623	264.35	0.0379	0.9900	1.6165	0.9923	0.1743

	60	193.13	0.00070	0.9965	26.342	263.64	0.0370	0.9913	1.6238	0.9933	0.1755
150	**30**	251.86	0.00041	0.9972	26.435	143.65	0.0246	0.9977	1.4819	0.9981	0.2131
	40	257.67	0.00044	0.9981	29.307	185.97	0.0250	0.9973	1.5172	0.9987	0.2015
	50	264.75	0.00046	0.9991	32.132	230.36	0.0251	0.9978	1.5474	0.9988	0.1933
	60	269.24	0.00038	0.9920	27.349	282.65	0.0268	0.9948	1.5643	0.9919	0.1777
200	**30**	292.34	0.00027	0.9919	23.060	76.174	0.0183	0.9951	1.3081	0.9918	0.2665
	40	299.66	0.00028	0.9916	25.368	94.069	0.0186	0.9933	1.3511	0.9920	0.2510
	50	308.30	0.00029	0.9911	27.817	113.47	0.0186	0.9935	1.3880	0.9930	0.2397
	60	315.71	0.00032	0.9900	31.958	151.82	0.0190	0.9939	1.4350	0.9931	0.2236
250	**30**	313.24	0.00017	0.9906	17.256	40.953	0.0150	0.9931	1.0758	0.9934	0.3420
	40	323.98	0.00017	0.9905	18.772	46.227	0.0148	0.9980	1.1168	0.9935	0.3298
	50	339.06	0.00016	0.9907	19.446	48.149	0.0141	0.9981	1.1359	0.9939	0.3294
	60	343.21	0.00019	0.99	22.672	61.048	0.0145	0.9982	1.1997	0.9979	0.3043

The values for MG – POP adsorption system was found to be 0 to 1. The calculated values of R_L were given in Table.3. Confirm that the plaster of paris is a desirable one for the adsorption of MG dye from the aqueous solution

Freundlich isotherm

The Freundlich isotherm is based on the multilayer adsorption on the heterogeneous surface [17] it is derived from the assumption that the sorption site are distributed exponentially with respect to the heat of adsorption The linear form of Freundlich isotherm has been represented

$$\log q_e = \log K_f + 1/n \log C_e \quad \text{.....(5)}$$

where q_e is the amount of dye adsorbed per gram weight of adsorbent (mg/g) C_e is the equilibrium concentration of dye solution (mg/L), K_f (L/g) and n are constant incorporating all factors affecting the adsorption capacity and adsorption intensity respectively. The values of K_f and1/n were obtained from the intercept and slope respectively and the values are given in Table. 2. The plot of log q_e against logC_e gives a straight line which indicates that the adsorption of MG dye follows the Freundlich isotherm model and the $0<1/n<1$ shown the MG dye is favourably adsorbed on to plaster of paris the results of k_f and n are strong evidence that the plaster of paris more efficient for removal of MG dye .

Thermodynamic treatment of the adsorption reaction

The adsorption process connected with thermodynamic parameters viz standard free energy (ΔG^0) (kJ/mol), standard enthalpy (ΔH^0) (kJ/mol) and standard entropy (ΔS^0) (J/k /mol) were determined using the following relationship when the adsorption process reaches equilibrium level

$$\Delta G^0 = -RT \ln K_0 \quad \text{.....(7)}$$

where ΔG^0 is the sorption free energy, T is the absolute temperature in K. R is the universal gas constant (8.314 J mol. K)

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$$\ln K_0 = \Delta H^0/ RT + \Delta S^0/R \text{ .....(8)}$$

The standard enthalpy (ΔH^0) and (ΔS^0) entropy changes are respectively determined from the slope and intercept of the $\ln K_0$ against 1/T Thermodynamic parameters obtained from Eqs (7) and (8) for the sorption of MG dye onto POP. The values given in Table 4. The negative values of ΔG^0 confirm the feasibility of the process and the spontaneous nature of sorption The positive values of ΔS^0 reflect an increased degree of disorder ness at solid/ solution interface during the adsorption of MG on to POP The endothermic nature of the dye adsorption by plaster of paris was confirmed by the positive values of enthalpy(ΔH^0). The values of ΔH^0 to the sorption reaction can be used to distinguish between physical adsorption and chemical adsorptions. The ΔH^0 value for chemical adsorption is around 83 to 830 (kJ/ mol) while physical adsorption 8 to 25 kJ/mol the present investigation work shows low ΔH^0 values. It gives clear evidence for physical adsorption i.e weak interaction between MG dyes and POP.

The pseudo- second -order equation

The pseudo – second – order kinetic rate equation is expressed [18] as

$$t/q_t = 1/ k_2 q_e^{\ 2} + 1/ q_e (t) \text{ .....(9)}$$

where k_2 (g/mg/min) is the rate constant of second – order – kinetic adsorption, q_e is the equilibrium adsorption capacity (mg/g), q_t is the amount of dye adsorbed on the sorbent at time t, (mg/g) The equilibrium adsorption (q_e) and k_2 (g/mg/min) can be calculated from the slope and intercept of the plot of t/q_t versus t, the linear plot indicate good agreement between calculated values and experimental value in Table 5

Elovich model

The Elovich equation is another kinetic rate equation .It is often valid for systems in which the absorbing surface is heterogeneous the Elovich equation [19,20.] has been represented as

$$dq_t / dt = \alpha e^{-\beta q t} \text{ .....(9)}$$

where α is the initial adsorption rate (mg/g min) and β is the adsorption constant (g/mg) during any experiments. The Elovich equation can be simplified by assuming that αβt >>> 1 and integration of the kinetic rate equation with same boundary condition $q_t = 0$ at t=0 $q_t = q_t$ at t=t Eqs(9)

$$q_t = 1/ \beta \ \ln (\alpha\beta) + 1/ \beta \ln(t) \text{ .....(10)}$$

A plot of q_t versus ln t yield a linear curve with slope (1/ β) and an intercept (1/ β) ln (α β) the plot of linear with good correlation co efficient as the calculated α β and (γ) values given in Table 5

ISSN: 0975-8585

Intra –particle diffusion model

According to Weber and Morris suggested kinetic model [21] to identify in the sorption process is intra- particle diffusion mechanism or not. The intra- particle diffusion equation is given as

$$q_t = k_{id}\, t^{1/2} + C \quad \text{.....(11)}$$

The k_{id} values can be calculated from the slope of the plot of qt versus $t^{1/2}$ gives multilinear form for the adsorption of malachite green. The initial portion of curve is reflecting the boundary layer diffusion effect and final linear part of curve show the effect of intra-particle diffusion. The larger the intercept, greater the contribution of the surface sorption in the rate controlling step i.e values of C give an idea about the thickness of boundary layer. The constant C was increased with increasing the MG dye concentration which is shown increase of the boundary layer thickness and decrease of the chance of the external mass transfer. Hence increase of the chance of internal mass. The clear observation suggested that the mechanism of removal of Malachite green by plaster of paris controlled by some degree of boundary layer.

CONCLUSION

The present investigation reveals that plaster of paris can be effectively used as an adsorbent for the removal of malachite green dye from aqueous solution the data of kinetic study shows adsorption follows the pseudo – second- order rate. The intra –particle diffusion does not involved in the rate determining steps.

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