ADSORPTION OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION ONTO IRAQI RAW AL-HUSSAINIYAT CLAY

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The adsorption of Malachite Green (MG) cationic dye on Al-Hussainiyat clay was first studied in a batch system for various dye concentrations. The adsorption was studied as a function of contact time, adsorbent dose, pH, and temperature under batch adsorption technique. The concentration of the solution before and after adsorption was measured spectrophotometrically .The equilibrium data fit with Langmuir and Freundlich models of adsorption and the linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Different thermodynamic parameters such as Gibb's free energy, enthalpy and entropy of the on-going adsorption process have also been evaluated. The thermodynamic analyses of the dye adsorption on Al-Hussainiyat clay indicated that the system was endothermic in nature .

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INTRODUCTION

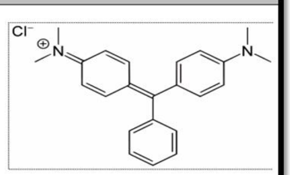
Wastewater pollution gives adverse effects on public water supplies which may cause health problems such as diarrhea.[1,2] It may also cause property damage such as the discharge of sewage that affects industrial water supplies by changing the character of the water. Apart from that, it may affect the buildings, monuments and boats by fading paints and colours.[3] Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Effluents discharged from these industries poses certain hazards and environmental problems. Wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect human beings.[4] There are various conventional methods of removing dyes from wastewaters. Among these methods, adsorption is the most versatile and widely used method because of its low cost and ease of operation.[5-6] A number of agricultural waste and by-products of cellulose origin have been studied for their abilities to remove dyes from aqueous solutions,[7] such as peanut hulls,[8] maize bran,[9] sawdust,[10] clay sugar beet pulp,[11] crab peel,[12] granular kohlrabi peel,[13] raw barley straw,[14] eggshell,[15] aquaculture shell powders etc.[16] Activated carbon is regarded as one of the most effective materials for the removal of dyes,[17] but due to its high cost and 10–15 % loss during regeneration , unconventional adsorbents like , wood,[18] silica,[19] clay and activated clay,[20-21] agricultural residues,[22] etc. have attracted the attention of several investigations for the removal of dyes. In the present work, the ability of Al-Hussainiyat clay to remove cationic dye, by adsorption, has been considered. The effects of contact time, initial dye concentration and pH on the amount of colour removal were investigated. The equilibrium experimental data were fitted into Langmuir and Freundlich equations to determine the best isotherm correlation.

MATERIALS AND METHODS

The adsorbate

The cationic dye (MG), in commercial purity, was used without further purification, λ_{max} = 617 nm.[23] The MG stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 20 mg L^{-1}. The experimental solutions were prepared by diluting the dye stock solution in accurate proportions to different initial concentrations from 2 to 16 ppm. The chemical name and their properties of this dye listed in Table 1

Table 1. The physical and chemical properties of MG

Specification		Structure of dye
Emprical formula	$C_{23}H_{25}ClN_2$	
Molar ass	364.9179	
Melting point	210 C₀	
Class	T.A.M	
Solubility	Water	• 4-{[4-(Dimethylamino)phenyl](phenyl)methylene}-N,N-dimethyl-2,5-cyclohexadien-1-iminium chloride

The adsorbent

Al-Hussainiyat clay was used as adsorbent throughout this study, it was obtained from the general company of Geological Survey and Mining, Ministry of Industry and Minerals Baghdad, Iraq. It was sieved to the required particle size between 150 and 212 μm. This clay was used in all experiments.[24] Surface information and analytical data for the clay under study were also supplied by the same company and are given below in Table 2.

Table 2. Chemical specifications of Al-Hussainiyat clay.

Constituent	SO_3	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SiO_3	L.O.I
Wt %	<0.7	11-22 %	29-48%	0.80%	<2.0 %	0.2 %	20-28	10-14%

Batch mode adsorption studies

Batch experiments were carried out to determine the effects of pH, adsorbent dose, initial dye concentration and contact time by varying the parameter under study and keeping other parameters constant. The stoke solution was prepared by dissolving an accurately weighed quantity 0.25 g of solid dye in 1 L of deionized water to give 25 mg L^{-1}. The experimental solution of desired concentration was obtained by successive dilution of stock solution. The pH of all these solutions was maintained by adding 0.1 M HCl or 0.1 M NaOH. The experiments were carried out by taking 100 mL of MG solution and required amount of adsorbent into 250 mL conical flasks and stirred on water bath shaker at the speed of 200 rpm. The adsorption was monitored by determining the concentration of MG in solution using double beam UV-Visible spectrophotometer, at λ max 617 nm. Percentage of dye removal (φ, in %) and quantity of MG adsorbed on adsorbent at the time of equilibrium (Q_e) was calculated using Eq. 1 and 2 respectively.[25]

$$\varphi = 100 \times \frac{C_0 - C_e}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 and C_e are the initial and the equilibrium concentrations (mg L^{-1}) of MG in solution, respectively. Q_e is quantity of MG adsorbed on the adsorbent at the time of equilibrium (mg g^{-1}), V is volume (in L) of solution and W is the mass of adsorbent (g) taken for experiment.

Effect of variable parameters

Dosage of adsorbent

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

Initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 2 to 16 mg L^{-1}. All other factors are kept constant.

Contact time

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

pH

Adsorption experiments were carried out at pH 2, 3, 4, 5, 6, 7, 8, and 9. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute HCl and NaOH solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent and concentration of other ions were kept constant while carrying out the experiments.

Temperature

The adsorption experiments were performed at four different temperatures viz., 20, 25, 30, 35 and 40 °C in a thermostat attached with a shaker. The temperature made constant and was maintained with an accuracy of ±0.5 ºC.

RESULTS AND DISCUSSION

FT-IR study

Fourier Transform Infrared spectroscopy (FTIR) studies of Al-Hussiniyat clay the adsorbent were carried out and the spectra taken before and after adsorption were shown in Figs. 1 and 2. It is evident from the figures that there is no appreciable change in the spectra. This may be due to the fact that adsorption did not alter the chemical nature of the surface of the adsorbent, i.e the adsorption physical in nature.

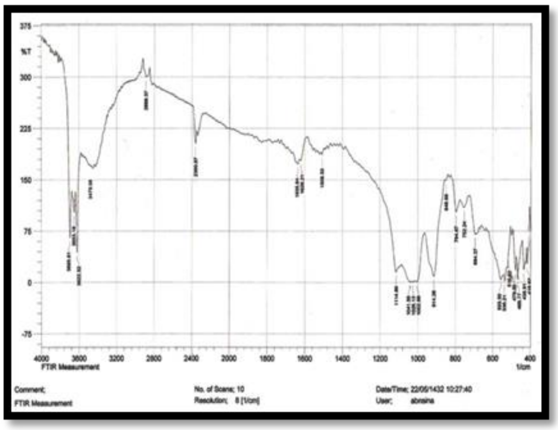


Figure 1. FTIR spectrum of al-hussiniyat clay before adsorption.

Effect of agitation time

Equilibrium Time

The effect of contact time on the amount of MG adsorbed per unit of adsorbent was investigated at 20 °C and constant pH and concentration. Figure 3 and Table 3 show the variation of Q_e and C_e with MG for 10 ppm at 20 ºC and pH =7 .

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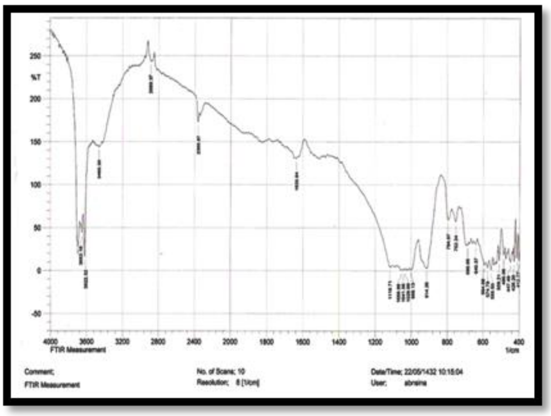

Figure 2. FTIR spectrum of al-hussiniyat clay after adsorption .

Table 3. The variation of values of Q_e and C_e with time the adsorption of MG

Time, min	C_e, mg L^{-1}	Q_e, mg g^{-1}
5	3.88	9.228
10	3.023	9.359
15	2.965	9.407
20	2.269	9.540
25	2.027	9.594
30	1.512	9.697
35	1.270	9.746
40	1.059	9.788
45	1.059	9.788
50	1.058	9.782

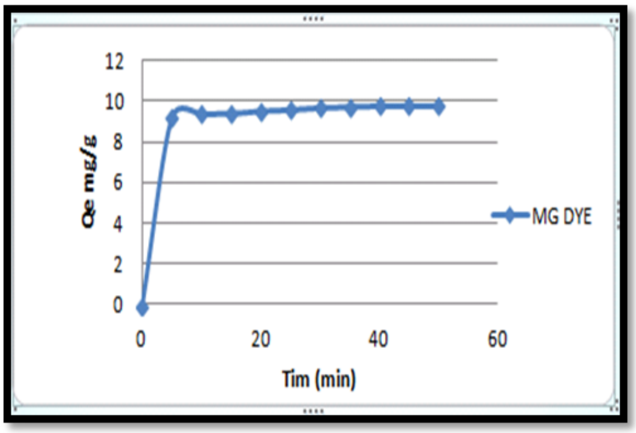

Figure 3. The effect of contact time on the adsorption of malachite green

A sharp change in adsorption is observed at 5 minutes and thereafter a gradual increase was observed in adsorption with increasing contact time up to 40 minutes, after which a maximum value of adsorption is attained. After this time, the amount of dye adsorbed was not significant, very small decreases in the amount of the dye adsorbed were observed, indicating to desorption process. Therefore, the time of 40minutes may be treated as the optimum contact time. Similar results have been reported for the adsorption.[25]

Adsorbent Dosage

The effect of adsorbent weight on the adsorption of MG dye was studied by changing the amount of adsorbent (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7g per 100 ml) in the test solution while keeping the initial dye concentration (10 ppm) and contact times (40 minutes) constant. The results are shown in Table 4 and Fig. 4.

Table 4. The values of Q_e (in %) and quantity of adsorbent for the MG concentration (10 ppm).

Quantity of adsorbent, W, g	C_{eq}, mg L^{-1}	Q, %
0.1	3.01	69
0.2	2.26	77
0.3	1.42	84
0.4	1.51	85
0.5	1.05	89
0.6	1.11	88
0.7	1.18	88

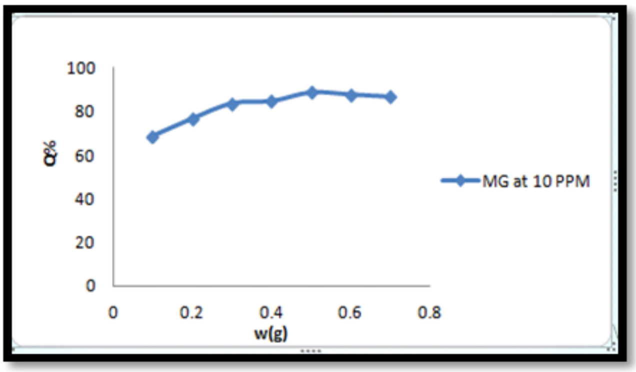

Figure 4. Effect of adsorbent dosage

It is apparent that the percentage removal (Q, %) of the dye increases with the increase in adsorbent dose but beyond a value of 0.5 g the percentage removal reaches almost to a maximum value. This is probably due to the greater availability of the exchangeable sites or the increased surface area where the adsorption takes place. As seen in Figure 4 optimum clay dosage that can be used in MG removal is 0.5 gm per 100 mL. Thus, all experiments were carried out by using 0.5 g of adsorbent.

Effect of pH

In the present work, the effect of pH on the MG adsorption onto Al-Hussainiyat clay was studied while the initial dye concentration, shaking time, amount of Al Hussainiyat clay at and temperature were fixed at 10 mg L^{-1}, 45 min, 0.5 g and 20 ◦C, respectively. The effect of pH on the adsorption of MG by the Al–Hussainiyat is presented in Figure5. The effect of pH on adsorption of dye was studied within pH range 3–10, the maximum adsorption takes place onto neutral medium (pH=7,[23,26,27] Fig. 5) due the high affinity of dye to connection with SiO_2 and Al_2O_3. The decrease in the removal of dye at pH 3, due to the similar electrostatic repulsion between the dye and Al-Hussaniyat surface only. Table 5 show the result obtained in the effect of pH on Malachite green removal.

Table 5. The values of Q_e %and C_e for 10 ppm MG at different pH.

pH	C_{eq}, mg/l	Q, %
3	5.45	45%
4	5.55	44%
5	5.53	44.7%
6	5.56	45.4%
7	1.05	89%
8	2.77	72%
9	2.50	75%

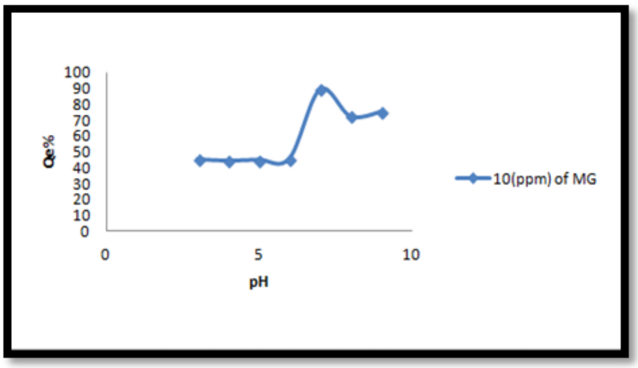

Figure 5. Effect of pH on removal of MG at 10 ppm

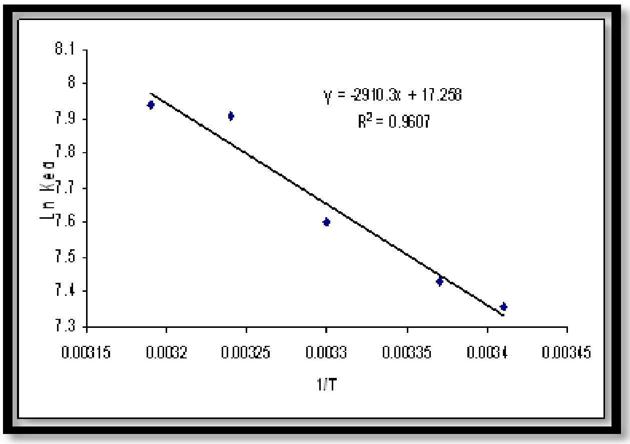

Figure 6. Van't Hoff plot of MG adsorption

Thermodynamic parameters

The thermodynamic studies play an important role in understanding the nature of adsorption. The thermodynamics parameters related to the adsorption of dye, such as, enthalpy change, ΔH^o entropy change ΔS^o and Gibbs free energy change ΔG^o. ΔH^o has been calculated for all adsorption processes, according to Van't Hoff equation (Eqn. 3) via plotting logarithmic value of the adsorption equilibrium constant (K_{eq}) as $\ln Q_e/C_e$ against the temperature as $(1/T)$[28] The results are listed in Table 6 and Figure 6.

$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (3)$$

$$\Delta G = -RT \ln K_{eq} \qquad (4)$$

where R is the gas constant, K_{eq} is adsorption equilibrium constant. The plot of ln K_{eq} against $1/T$ (in Kelvin) should be linear. The slope of the Van't Hoff plot is equal to $-\Delta H^{\circ}/R$, and its intercept is equal to $\Delta S^{\circ}/R$. ΔH^o and ΔS° obtained are given in Table 7. The positive values of ΔH° indicate that the adsorption is involved with weak forces of attraction. It was observed that the ΔH° values increased with decrease of particle size. The adsorption was found to be endothermic in nature. The positive values of ΔS° suggest the increased randomness. The negative ΔG° value indicated the spontaneous nature of the adsorption model.[29]

Table 6. Values of $1/T$ and ln K_{eq} for the MG

	T, K	1/T	C_e, mg.L^{-1}	Q_e, mg.g^{-1}	lnK_{eq}
C_0, 10 ppm	293	0.00341	1.134	1.778	7.357
	298	0.00337	1.059	1.791	7.43
	303	0.00330	0.907	1.818	7.603
	308	0.00324	0.763	1.847	7.791
	313	0.00319	0.665	1.867	7.940

Physisorption and chemisorptions can be classified, to a certain extent, by the magnitude of enthalpy change. Bonding strengths of 84 kJ mole^{-1} are typically considered as those of physisorption bonds. Chemisorption bond strengths can be 84–420 kJ mole^{-1}.[30] Generally, ΔG° for physisorption is less than that for chemisorption .

The former is between -20 and 0 kJ mol^{-1} and the later is between -80 and -400 kJ mol^{-1}.[31] Therefore , the values of ΔH° and ΔG° suggest that adsorption of MG onto Al-hussiyat deposit was driven by a physisorption.

Adsorption Isotherms

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents, and comprehensive understanding of the nature of interaction . Isotherms help to provide information about the optimum use of adsorbents.

Therefore, in order to optimize the design of an adsorption system to remove dye from solutions, it is necessary to establish the most appropriate correlation for the equilibrium curve. Out of several isotherm equation available for analyzing experimental sorption equilibrium parameters, the most common isotherms are the Langmuir and Freundlich models.

Table 7. Thermodynamic parameters of MG adsorption on AL-hussianyat clay at 10 ppm ,0.5g ,and pH 7

C_0, ppm	ΔH°, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	ΔG°, kJ mol^{-1}				
			20 °C	25°C	30°C	35°C	40°C
	15.17	35	-14.6	-18.40	-19.15	-19.6	-20.02

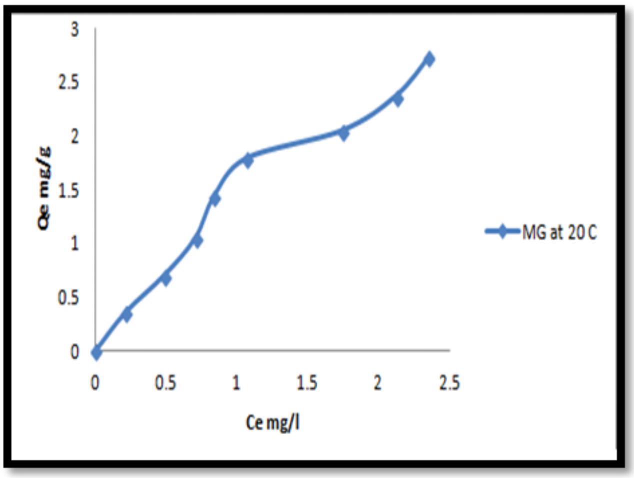

Figure 7. Adsorption isotherms of MG on Al-Hussiniyat clay at 20 °C.

Table 8 and Figure 7 shown the adsorption isotherm was of S-type ,indicating that the adsorbent is possibly mesoporous or is not porous and has a high energy of adsorption.[32] Also, this indicating a vertical or flat orientation of adsorbate , and the adsorbate is mono functional.[33]

Table 8. The values of C_{eq} mgL^{-1} and Q mg g^{-1} for adsorption of Malachite green

C_0 , ppm	C_{eq}, mg/L	Q_e, mg g^{-1}
2	0.211	0.357
4	0.484	0.703
6	0.748	1.050
8	0.832	1.433
10	1.059	1.791
12	1.739	2.052
14	2.118	2.375
16	2.344	2.731

The Freundlich equation was employed for the adsorption of MG dye on the adsorbent, which is represented by Eqn. 5.[34]

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \qquad (5)$$

where Q_e is the amount of MG dye adsorbed (mg g^{-1}), C_e is the equilibrium concentration of dye in solution (mg L^{-1}), and K_f and $1/n$ are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively.

Linear plots of log Q_e versus log C_e shows that the adsorption of malachite green dye obeys the Freundlich adsorption isotherm (Figure 8). The values of K_f and $1/n$ are given in Table 5. These data are analyzed according to the linear form of Langmuir equation (Eqn. 6).

$$\frac{Ce}{Qe} = \frac{1}{Q_m} k_L + \frac{C_e}{Q_m} \qquad (6)$$

where C_e is the equilibrium concentration (mg L^{-1}), Q_e is the amount adsorbed at equilibrium (mg g^{-1}), and Q_m and k_L are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively.[35] The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (Fig. 9). The values of Q_m and k_L were determined from slope and intercepts and are presented in Table 10. To confirm the favourability of the adsorption process, the separation factor (R_L) is calculated by using the (Eqn. 7) and presented in Table 10.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (7)$$

Table 9. The experimental data C_e/Q_e, C_e, log C_e, and log Q_e for the adsorption of MG

C_0	C_e, mg L^{-1}	C_e/Q_e	log Q_e	log C_e
2	0.211	0.591	-0.447	-0.675
4	0.484	0.688	-0.153	-0.315
6	0.748	0.712	-0.021	-0.126
8	0.832	0.65	0.156	-0.079
10	1.059	0.666	0.253	0.024
12	1.739	0.841	0.312	0.24
14	2.118	0.891	0375	0.325
16	2.344	0.898	0.436	0.369

The values of R_L are found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable . R_L values indicate that the type of isotherm is irreversible (R=0) , favorable ($0 < R_L < 1$) , liner (R_L=1) or unfavourable ($R_L > 1$).[28]

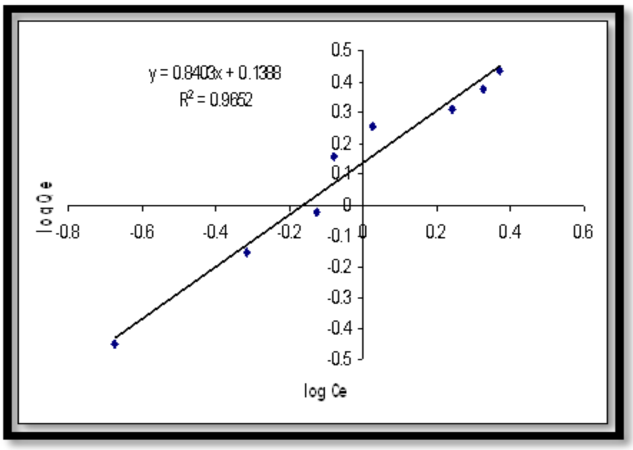

Figure 8. The linear plot of Freundlich isotherm

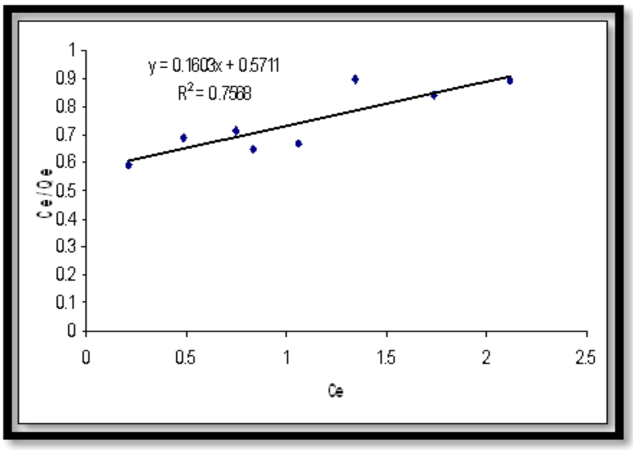

Figure 9. The linear plot of Langmuir isotherms

The values of n>1 indicate favourable adsorption conditions.[25] The values of linear R^2 coefficient were high (> 0.9) for Freundlich isotherm indicating the useful values of its constants .the adsorption isotherm for the present system is explained better by Freundlich isotherm model.[32]

Table 10. The parameters of Freundlich and Langmuir equation for the adsorption of MG dye .

Freundlich parameter				
***T*, ˚C**	**1/*n***	***K***		
20	0.816	0.717		0.9652
Langmuir parameter				
T, ˚C	***q*L**	***K*L**	***R*L**	***R*²**
20	0.816	0.717	0.260	0.765

CONCLUSIONS

The main conclusions that can be drawn from the above mentioned results and discussion are given below. The optimum pH for favourable adsorption were 7 for MG.

1) The adsorption system could be explained by the electrostatic attraction (physical adsorption). This confirmed by the values obtained of ΔH° and ΔG°.

2) The amount of dye adsorbed onto the adsorbent increases with an increase in the adsorption temperature of the dye solution from 20-40 ˚C . This trend is indication of the fact that the adsorption process is endothermic in nature.

3) Thermodynamic analysis indicated that the adsorption of the dye onto clay was endothermic and spontaneous .

4) For equilibrium adsorption, MG dye was best fitted to the Freundlich isotherm.

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