# Effect of Different Parameters on the Adsorption of Textile Dye "Maxilon Blue GRL" From Aqueous Solution by Using White Marble.

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The adsorption of textile dye (Basic Maxilon Blue "GRL") from aqueous solution by white marble was studied. The effect of different experimental parameters such as shaking contact time, initial concentration of GRL "2-16 $mg.L^{-1}$", initial pH "3-10" of aqueous solution, adsorbent dose "0.25-2 g/100ml", and temperature "283 K-308 K" on the adsorption of (GRL) were investigated. The applicability of adsorption isotherms to study the adsorption behavior has also been analyzed by Langmuir and Freundlich isotherm models were used to illustrate the experimental isotherms and isotherm's constants, and it was found Freundlich isotherm model fitted well the adsorption data compare with Langmuir model. The equilibrium time at normal pH was found 60 minutes, the pH of dye solution on the range of "8-10" was found favorable for the removal of (B-GRL), also the extent of adsorption found to decrease as the temperature increased. The thermodynamic parameters ($\Delta G$, $\Delta H$, and $\Delta S$) were calculated, ($\Delta G$) was calculated from equilibrium constant, and were explained in the mean of the chemical structure of the adsorbate. The concentration of (GRL) was measured before and after adsorption by using UV-visible spectrophotometer at 590 nm.

## INTRODUCTION

Textile industries discharged a large quantity of highly colored wastewater effluent which is released in to nearby land or rivers without any treatment because the conventional testament methods are very expensive. On the other hand the low cost technologies don't allow a wishful color removal and have certain disadvantages. Thus the removal of colour from effluents is one of the major environmental problems.

Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade dyes [1], are widely used in textiles, paper, rubber, plastic, leather, cosmetics, pharmaceutical and food industries .the extensive use of dyes often caused pollution problems in the form of colored wastewater discharged in to environmental water bodies .it not only affects aesthetic merit but also reduces light penetration and photosynthesis. Many physical and chemical methods, such as coagulation, floatation, chemical, oxidation, solvent extraction, hyper filtration have been tried in order to remove colour from wastewater[2, 3]. The adsorption process is one of the effective method for removal dyes from the waste effluent, the process of adsorption has an edge over the other methods due to it is sludge free operation and completely removed dyes, even from the diluted solution[4]. Basic dye is the brightest class of soluble dye used by the textile industry[2].

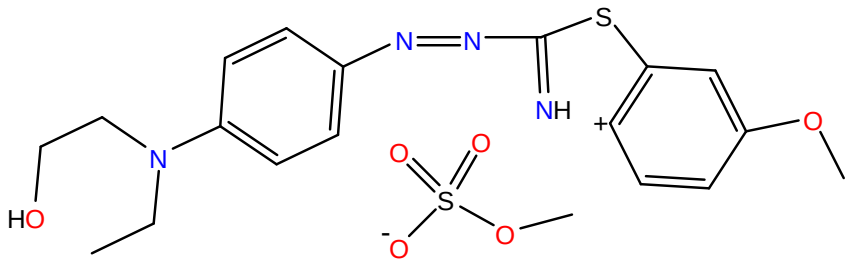
The present study the adsorption of basic dye on to (white marble) has been investigated. The effect of various parameters such as contact time, pH, temperature, adsorbent dose and concentration has been evaluated in the batch method experiments.

## MATERIALS AND METHODS

White marble used in this study was collected from Italia the extensively washed with (5% HCL) to remove bicarbonate washing with de-ionized water for several times, the main composite of white marble illustrated in Table 1. The dried in an oven at ($300^0$C) for 1 hour to a constant weight. Dry white marble was crashed in to powder and sieved to (75μ) particle size, then preserved in the desiccators for use. Commercial dye Maxilon Blue GRL (analytical reagent-grade), was purchased from Textile industry of Al-Hilla Factory. The chemical structure of Maxilon Blue GRL dye is shown in Fig. 1.

Table 1: Main composite of white marble by weight percent:[5]

| Chemical Composite | Percent % |
|---|---|
| $SiO_2$ | 72.04 |
| $Al_2O_3$ | 14.42 |
| $K_2O$ | 4.12 |
| $Na_2O$ | 3.69 |
| CaO | 1.82 |
| FeO | 1.68 |
| $Fe_2O_3$ | 1.22 |
| MgO | 0.71 |
| $TiO_2$ | 0.30 |
| $P_2O_5$ | 0.12 |
| MnO | 0.05 |




$C_{20}H_{26}N_4O_6S_2$

Fig.1: Chemical structure of Maxilon Blue GRL dye

**Equipment:** UV spectrophotometer was used for dye analysis. The pH measurements were obtained using a digital pH meter consort C830.An IKA HS 501 shaker was used for all adsorption experiments.

**Batch experiments:**

The Maxilon Blue GRL dye sample calibrated in order to find out various absorbance at various concentrations. The calibrated results are very effective to identify the respective color removal capacities of various adsorbents Fig. 2 showing the graphical representation of calibration curves of Maxilon Blue GRL dye at different pHs.

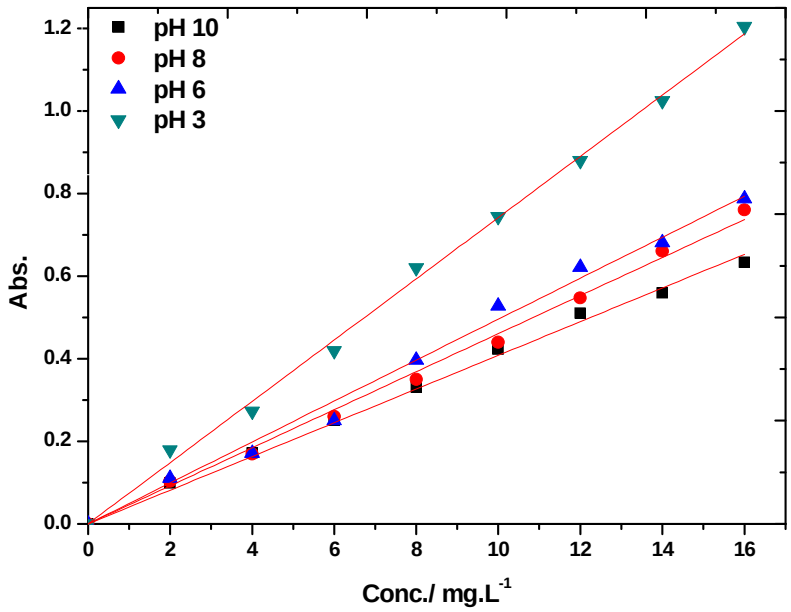



Fig. 2: Calibration curves of Maxilon Blue GRL dye in the presence of different pH.

Dye adsorption experiment were performed by taking (100 mL) stock solution of dye (2-16) $mg.L^{-1}$ and treated with (0.5gm) of dose adsorbent.

The variables studied were contact time, pH, temperature, adsorbent dose and concentration. After equilibrium time of treatment samples were super centrifuge sped to remove the adsorbent and measured at choose wavelength for maximum absorbance (λ max 590)

**Effect of period time (5- 120) min:** The experiment were carried out by taking (100mL) samples of dye concentration (10) $mg.L^{-1}$ in separate flasks and treated with (0.5 gm) of adsorbent dose at room temperature at pH (6).

**Effect of pH:** The effect of pH was studied in the treatment of (100 mL) aqueous solution of dye with (0.01 gm) dose of adsorbent and dye concentrations are [2-16 $mg.L^{-1}$]. Individually all the sample were treated for (1 hour) at fix temperature (room temperature).

**Effect of temperature (10- 35)$^0$C:** The effect of temperature was investigated with (0.5 gm)dose of adsorbent mixing with (100 ml)aqueous solution of dye concentration (2-16 ) $mg.L^{-1}$ and the sample were shaking a period for (1 hour) at pH (6).

**Effect of adsorbent dose (0.25- 2) gm:** The study was carried out with different dose of adsorbent of (75μ) average particle size. The concentrations of samples were (2-16) $mg.L^{-1}$ treated fix temperature for (1 hour) at pH (6).

## RESULTS AND DISCUSSION

**Effect of contact time and initial dye concentration:** The results of variation of adsorption of Maxilon Blue GRL dye with contact time are shown in Fig. 3. The adsorption of Maxilon Blue GRL dye that derived at initial concentration of 10 $mg.L^{-1}$ was studied at different contact time (0-120 min.).

It was observed from Fig.3; the dye adsorption an uptake was increased with time increased, and reaches the contact equilibrium at 60 minutes.

The result suggests that, adsorption takes place rapidly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate determining step[6, 7].

In addition, the fast adsorption at the initial stage also may be due to the fact that a large number of surface sites are available for adsorption but after a lapse of time, the remaining surface sites are difficult to be occupied. This is because of the repulsion between the solute molecules of the solid and bulk phases, thus, make it take long time to reach equilibrium[8].

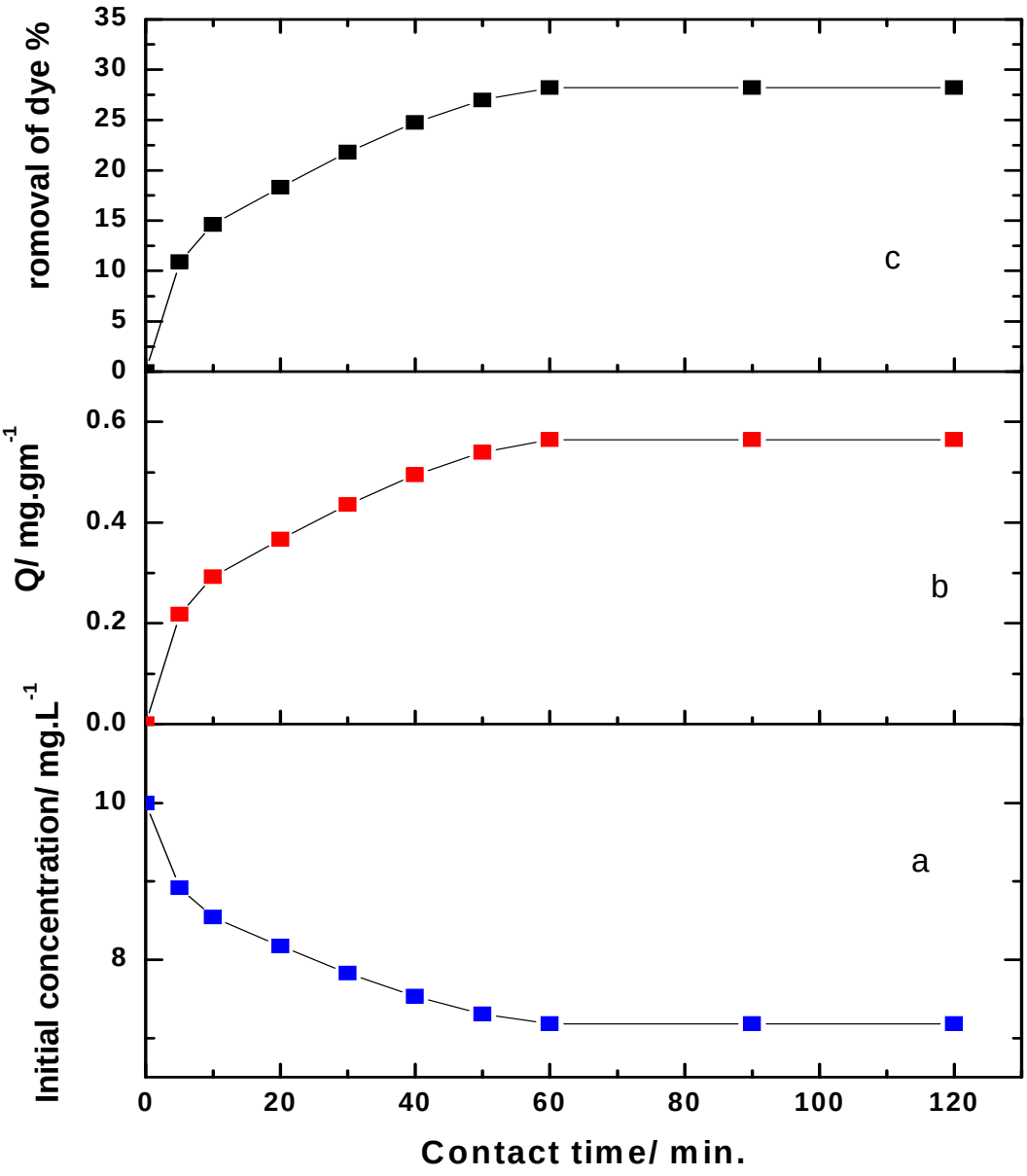



Fig. 3: Effect of contact time on a) initial concentration, b) adsorption capacity, and c) removal of dye %, at pH 6, dye conc. 10 $mg.L^{-1}$, Temp. 298 K and mass catalyst 0.5 gm.

**Effect of solution temperature Maxilon Blue GRL adsorption :** Fig. 4 represents the adsorption capacity of Maxilon Blue GRL dye onto White Marble at temperature of 283- 308 K at various initial dye concentrations (2-16 $mg.L^{-1}$). The result shows that the equilibrium

adsorption capacity of Maxilon Blue GRL dye was decreased while increasing the solution temperature from 303 to 343 K for all initial dye concentrations.

However, the adsorption phenomenon is usually affected by many parameters, particularly temperature. In fact, the temperature affects two major aspects of adsorption: the equilibrium position in relation with the exothermicity of the process and the swelling capacity of the adsorbent. Thus, adjustment of temperature may be required in the adsorption process. As generally observed from Fig. 4, the uptake capacity of white marble material decreases with increasing temperature, due to the enhanced magnitude of the reverse (desorption) step in the mechanism. This is possibly due to the exothermic effect of the surroundings during the adsorption process[9, 10].

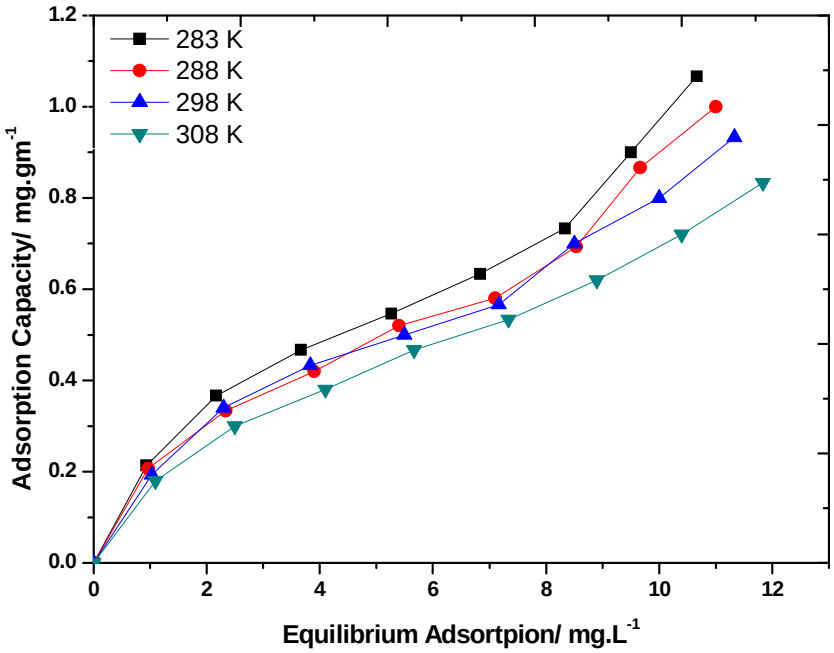



Fig. 4. Effect of temperature on the adsorption capacity of Maxilon Blue GRL dye, at pH 6, and mass catalyst 0.5 gm.

**Effect of solution pH on dye adsorption:** The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity [10]. The effect of each individual solution pH (3-10) on the equilibrium uptake capacity of Maxilon Blue GRL dye was studied at different initial dye concentrations (2-16 $mg.L^{-1}$) at temperature 298 K.

As shown in Fig. 5, the dye uptake was found to increase with an increase in pH.

At lower pH, the surface charge may be positively, thus making (H+) ions compete effectively with cationic dyes causing a decrease in the amount of dye adsorbed[11], and at higher pH the surface of on white marble, may be negatively charged which enhance the positively charged on Maxilon Blue GRL dye through electrostatic force at attraction.[12] Similar observations were reported for adsorption of dyes indicating that the adsorbent has a net positive charge on its surface [12-14].

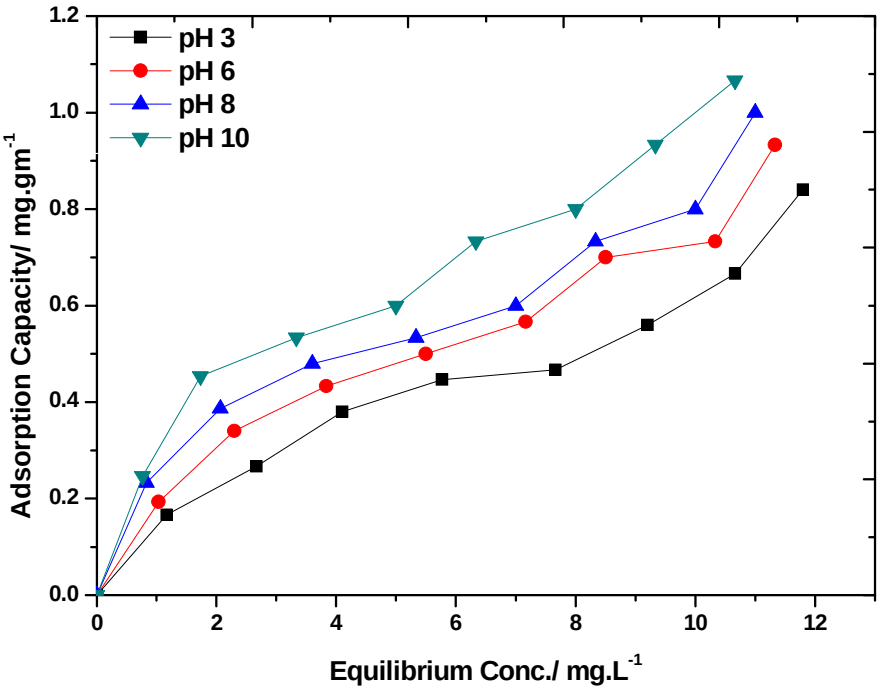



Fig. 5: Effect of pH on the adsorption capacity of Maxilon Blue GRL dye, at Temp. 298 K and mass catalyst 0.5 gm.

**Effect of adsorbent dose on efficiency of dye removal:** The solid/solution ratio is an important factor determining the capacity of a sorbent in a batch sorption was evaluated. The effect of sorbent dosages on the percentage removal of Maxilon Blue GRL dye has been shown in Fig. 6. It followed the predicted pattern of increasing percentage sorption as the dosage was increased[9].

This is probably because of the resistance to mass transfer of dye from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading in which the experiment was conducted[9].

It can be clearly seen that the removal of Maxilon Blue GRL dye increased with increasing the amount of white marble. However the amounts of adsorbed dye per unit weight (*Q*e) of the white marble decreased with increasing the solid/solution ratio as shown in Fig. 7.

The removal of the dye increased when the dosage was changed from 2.5 to 20 $g.L^{-1}$. at different dye concentrations (2-16 $mg.L^{-1}$). As expected, at constant initial concentration of dye, increasing the sample dose provides a greater surface area and larger number of sorption sites and hence enhancement of dye uptake[15].

The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose[16].

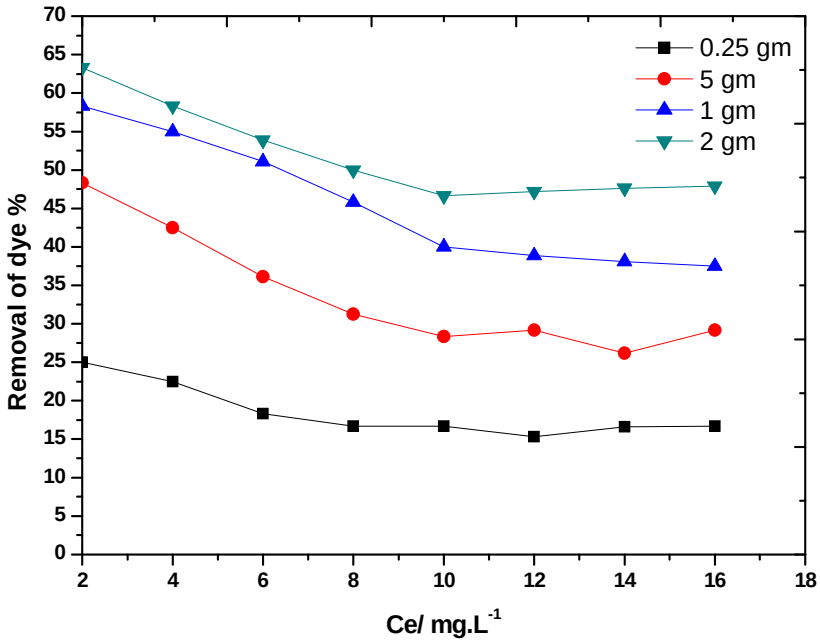



Fig. 7. Effect of mass catalyst concentration on the removal percent of Maxilon Blue GRL dye at pH 6, and Temp. 298 K

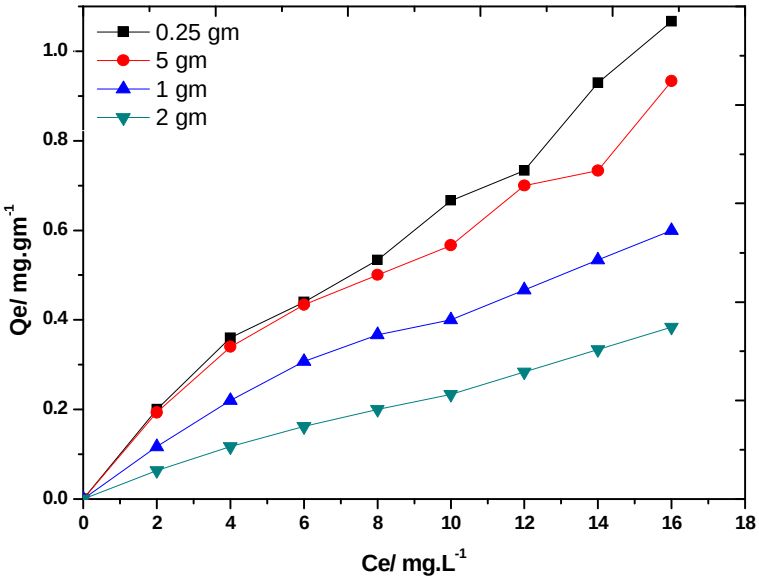



Fig. 7. Effect of mass catalyst concentration on the adsorption capacity of Maxilon Blue GRL dye pH 6, and Temp 298 K

**Effect of initial dye concentration on efficiency of dye removal:** The effect of the initial dye concentration on the dye adsorption capacity was investigated in the range (2–16 $mg.L^{-1}$) at room temperature without changing the initial pH of the medium. The results represented in Fig. 5 shows that the percentage of removal decreased with increasing initial dye concentration for white marble. Also from Fig. 3, 4, and 5 reveal that, percent adsorption decreased with increase of the initial dye concentration, but the actual amount of dye adsorbed per unit mass of the adsorbent increased with increase of the dye concentration showing due to that the adsorption is highly dependent on initial concentration of dye.

The lower uptake at higher concentration resulted from an increased ratio of initial adsorption number of moles of the dye to the available surface area; hence fractional becomes dependent on initial concentration. The initial dye concentration provides an important driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases. Therefore, at higher initial dye concentration, the number of ions competing for the available sites on the surface of white marble was high, hence, resulting in higher Maxilon Blue GRL adsorption capacity[8]. Similar results were also reported by other researchers.[17]

**Adsorption isotherm :** The adsorption are equilibrium equation and apply to condition resulting after the adsorbate –containing phase has seen in contact with the adsorbent of sufficient time to reach equilibrium[18].

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution[19]. The adsorption data for wide range of adsorbate concentrations and adsorbent doses were analyzed using Langmuir and Freundlich isotherms in order to find the adsorption capacity of GRL dye adsorbate.

***Freundlich model:*** Freundlich suggested that the ratios of the amount of solute adsorbed onto a gained mass of adsorbent to the concentration of the solute in the solution are not constant at different concentration of solution[4, 19].

The equilibrium data obtained with varying dose of adsorbent and fixed concentration of dye confirm to the Freundlich equation given as

$$Q_e = K_f C_e^{1/n} \quad (1)$$

$$lnQ_e = lnK_f + \frac{1}{n} lnC_e \quad (2)$$

$Q_e$ is the adsorption capacity ($mg.gm^{-1}$).
$C_e$ is the equilibrium concentration of dye ($mg.L^{-1}$).
$K_f$ and n are Freundlich constants.

The constant ($K_f$), is a partition coefficient in equilibrium is positively related to extend of degree of adsorption while then constant, n provides a rough estimation of the intensity of adsorption.

A linear from of the Freundlich expression will yield the constant K and n hence as shown in Fig. 8-10.

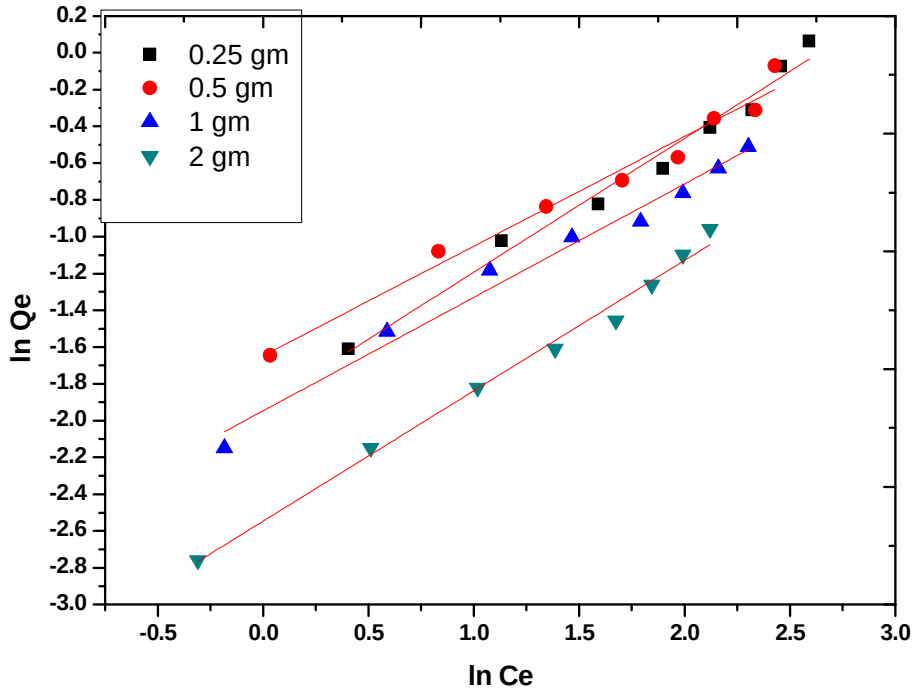



Fig. 8. Linearized form of Freundlich model shows of mass catalyst effect in pH equal to 6, and Temp 298 K.

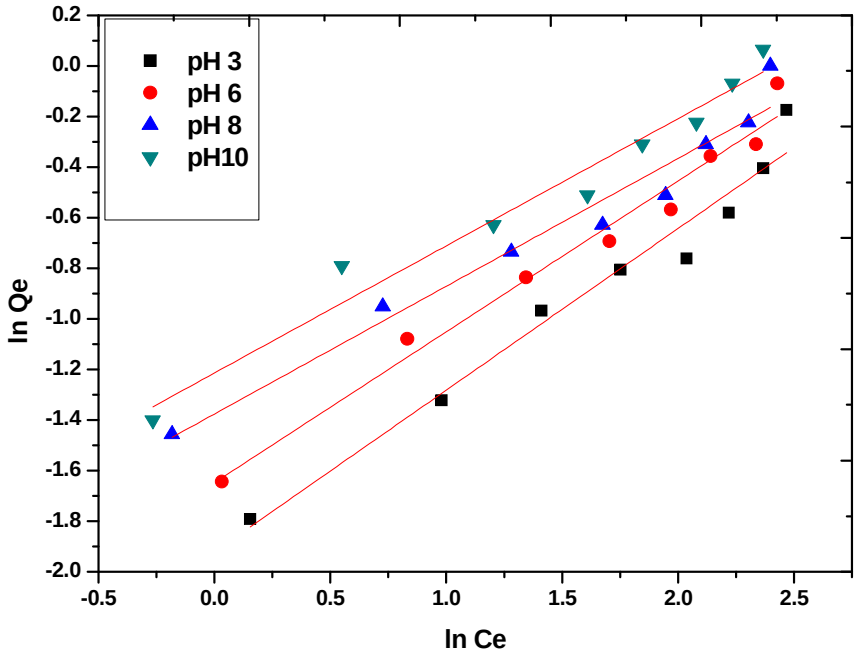



Fig. 9. Linearized form of Freundlich model shows effect in pH .

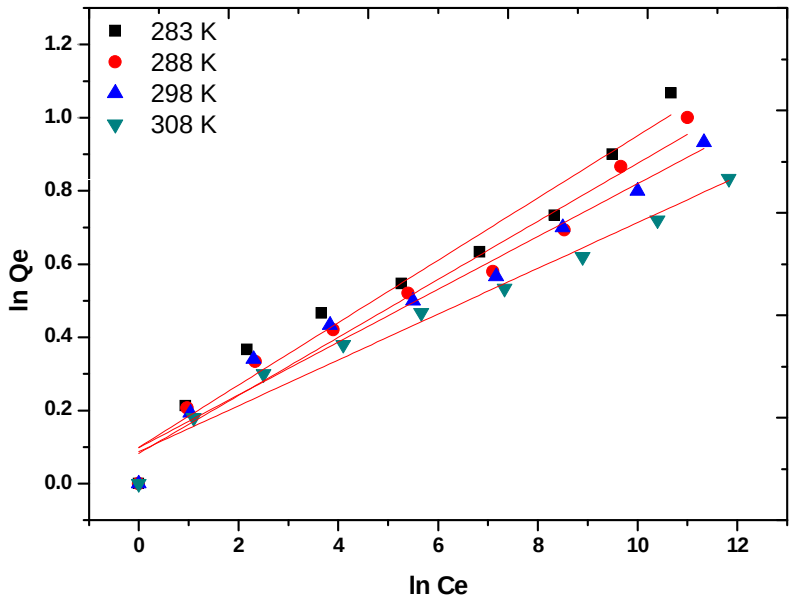



Fig. 10. Linearized form of Freundlich model shows effect of temperature.

***Langmuir adsorption isotherm:*** The Langmuir equation correlates the amount of adsorbent with adsorbed with the equilibrium aqueous concentration. The linear transformation of Langmuir adsorption isotherm[2] is given as

$$\frac{C_e}{Q_e}=\frac{1}{Q_{\max}K_L}+\frac{C_e}{Q_{\max}} \qquad (3)$$

Where Qe is the equilibrium adsorbate concentration on the adsorbent ($mg.g^{-1}$), Ce is the equilibrium adsorbate concentration in solution ($mg.L^{-1}$), Qmax is the monolayer capacity of adsorbent ($mg.g^{-1}$), and $K_L$ is the Langmuir adsorption constant ($L.mg^{-1}$).

The Langmuir constant $K_L$, is a measure of the affinity between adsorbate and adsorbent. The reciprocal value of $K_L$ gives the concentration at which half the maximum adsorption capacity of adsorbent is reached.

A plot of $C_e/Q_e$ vs. $C_e$ will give straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}K_L$ [20] results show in Fig. (11- 13).

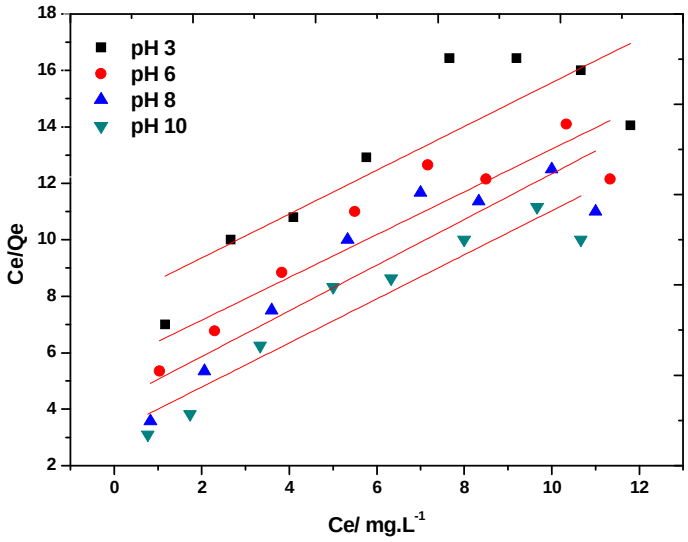



Fig. 11. Linearized form of Langmuir model shows effect of solution pH.

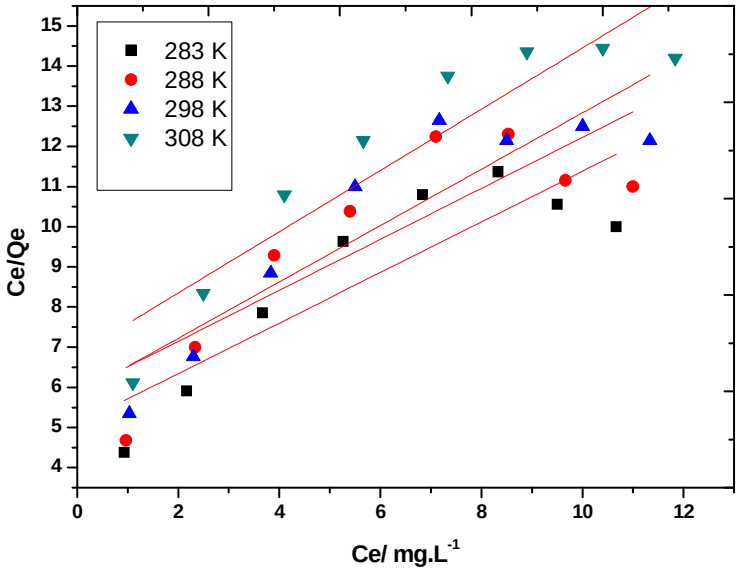



Fig. 12. Linearized form of Langmuir model shows effect of temperature.

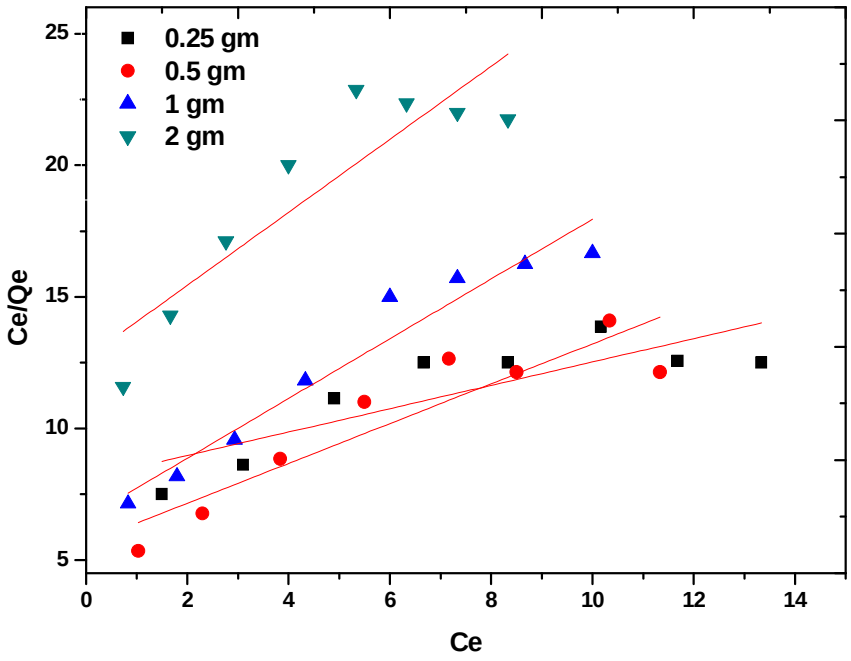



Fig. 13. Linearized form of Langmuir model shows effect of mass catalyst.

**Thermodynamic studies:** The thermodynamic parameters, ΔG°,ΔH°, and ΔS° for the adsorption process were determined in temperature range of [302K- 322K] using the following relations[21, 22]

$$K_c = {}^{C_{ads}}/_{C_e} \quad (4)$$

$$\Delta G^\circ = -RT\ln K_c \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$X_m = Ae^{\frac{-\Delta H^\circ}{RT}} \quad (7)$$

$$\ln X_m = \ln A - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where $X_m$ is the maximum value of adsorption at a certain value of equilibrium concentration $C_e$ Where R is the universal gas constant. T is the absolute solution temperature (Kelvin) and Kc is the equilibrium constant and Ce ($mg.L^{-1}$), the equilibrium concentration of the dye solution, results are indicated from Fig. 14, and illustrated in Table 2.

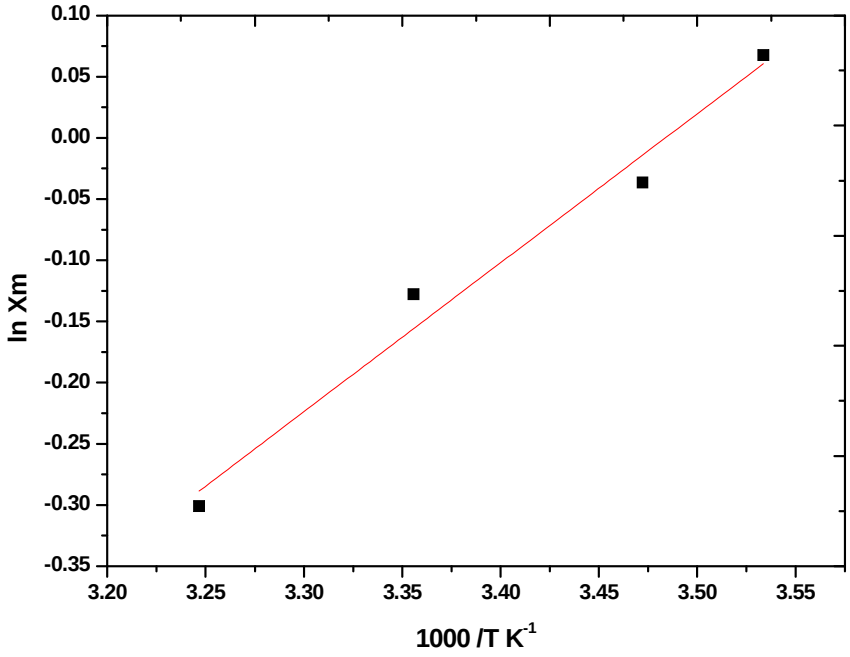



Fig. 14: Linearized form of VantHoff relation.

The adsorption capacity of the white marble decreased with increase in the temperature of the system from [302K- 322K]. In desorption of the dye, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system[23, 24].

Table 2: Thermodynamic data for the removal of GRL dye with white marble adsorbent.

| $\Delta S^{\circ}$ J.K$^{-1}$.mole$^{-1}$ | $-\Delta H^{\circ}$ kJ.mole$^{-1}$ | $-\Delta G^{\circ}$ kJ.mole$^{-1}$ | T/ K |
|---|---|---|---|
| 3.7777 | 10.1231 | 9.0540 | 283 K |
| 3.4177 | | 9.1388 | 288 K |
| 2.4869 | | 9.3820 | 298 K |
| 1.7438 | | 9.5860 | 308 K |

***Conditions: Adsorbent dosage 0.5gm/100mL; initial pH: 6.0.***

## CONCLUSIONS

The adsorption of GRL dye reaches equilibrium after 60 minutes. Adsorption capacity of GRL dye was decreased while increasing the solution temperature. From Gibbs free energy value, the adsorption process consider spontaneous. Highest value of adsorption capacity was found at pH 6. All effective parameters give good fitting of Freundlich model better than Langmuir model.

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