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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/100 mL and temperature 283 K-308 K on the adsorption of GRL were investigated. The applicability of adsorption isotherms to study the adsorption behaviour has also been analyzed by Langmuir and Freundlich isotherm models. They were used to illustrate the experimental isotherms and isotherm's constants. It was found Freundlich isotherm model fitted well the adsorption data compare with Langmuir model. The equilibrium time at normal pH was found 60 min, the pH of the dye solution on the range of 3 was found favourable for the removal of GRL, also the extent of adsorption found to decrease as the temperature increased. The thermodynamic parameters (ΔG, ΔH and ΔS) were calculated, (ΔG) was calculated from equilibrium constant and were explained in the mean of the chemical structure of the adsorbate. The concentration of dye was measured before and after adsorption by using UV-Visible spectrophotometer at 590 nm.

Key Words: White marble, Maxilon blue GRL, Adsorption.

INTRODUCTION

Textile industries discharged a large quantity of highly coloured 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 colour removal and have certain disadvantages. Thus the removal of colour from effluents is one of the major environmental solutions.

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 coloured 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 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.

EXPERIMENTAL

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 ºC) for 1 h to a constant weight. Dry white marble was crashed in to powder and sieved to (75 µ) 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.

UV spectrophotometer was used for dye analysis. The pH measurements were obtained using a digital pH meter

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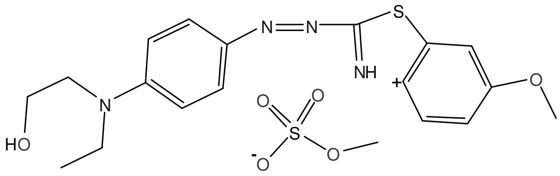
consort C 830. An IKA HS 501 shaker was used for all adsorption experiments.

TABLE-1
MAIN COMPOSITION OF WHITE MARBLE BY WEIGHT (%)[5]

Chemical composite	Weight (%)
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 dye

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 colour removal capacities of various adsorbents Fig. 2 showing the graphical representation of calibration curves of Maxilon Blue GRL dye at different pHs.

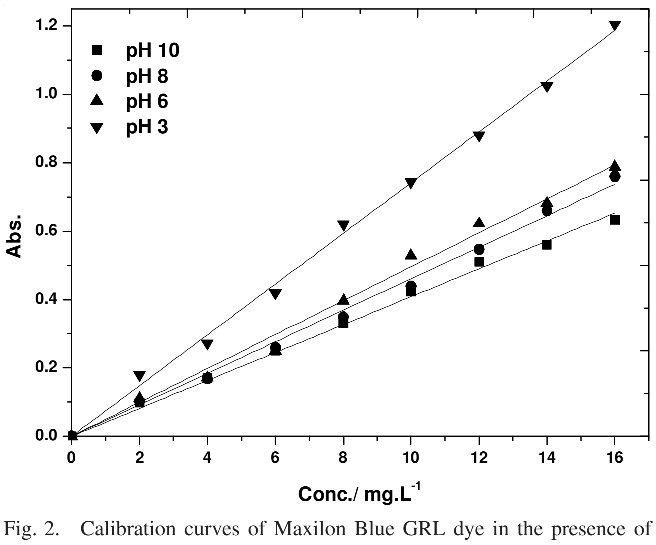


Fig. 2. Calibration curves of Maxilon Blue GRL dye in the presence of different pH

Dye adsorption experiment was performed by taking (100 mL) stock solution of dye (2-16) mg L^{-1} and treated with (0.5 g) 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 (100 mL) samples of dye concentration (10) mg L^{-1} in separate flasks and treated with (0.5 g) 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 h at fix temperature (room temperature). Also for all pH understudying the maximum wavelength region of the dye absorption not shifted.

Effect of temperature [10-35 ºC]: The effect of temperature was investigated with (0.5 g) 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 h at pH 6.

Effect of adsorbent dose [0.25-2 g]: The study was carried out with different dose of adsorbent of (75 µ) average particle size. The concentrations of samples were (2-16) mg L^{-1} treated fix temperature for 1 h 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). The dye adsorption an uptake was increased with time increased and reaches the contact equilibrium at 60 min (Fig. 3). 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]. 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[7].

Effect of solution temperature Maxilon Blue GRL adsorption: Fig. 4 represents the adsorption capacity of Maxilon Blue GRL dye onto white marble at 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 *i.e.*, 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. The uptake capacity of white marble material decreases with increasing temperature, due to the enhanced magnitude of the reverse (desorption) step in the mechanism (Fig. 4). This is possibly due to the exothermic effect of the surroundings during the adsorption process[8,9].

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[9]. 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 298 K. As shown in Fig. 5, the dye uptake was found to decrease with an increase in pH. As the pH of the adsorption solution was lowered, the positive charges on the surface increased. This would attract the negatively charged functional groups located on the dyes. In subsequent studies, it was decided to maintain a pH of 3, at which the removal was maximized[10].

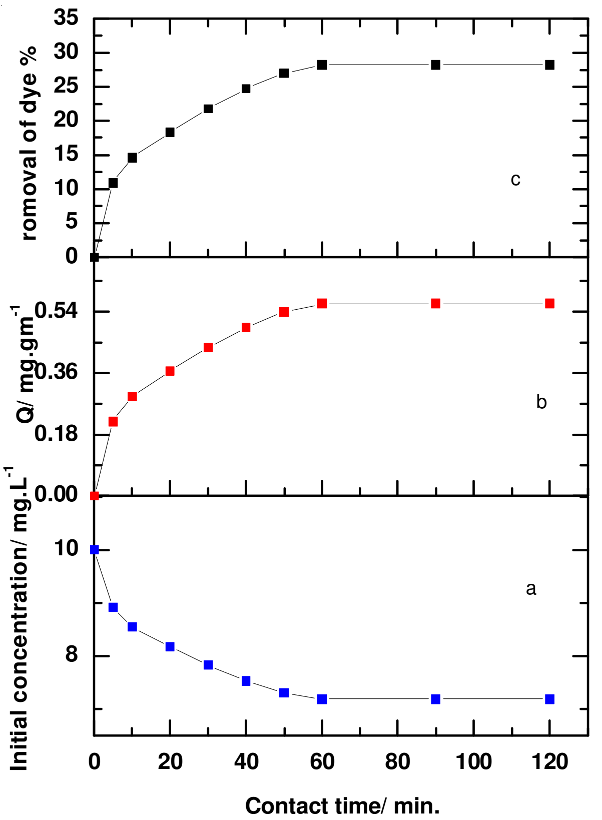


Fig. 3. Effect of contact time on a) initial concentration, b) adsorption capacity and c) removal of dye %, at pH 6, dye conc. 10 mg L^{-1}, Temp. 298 K and mass catalyst 0.5 g

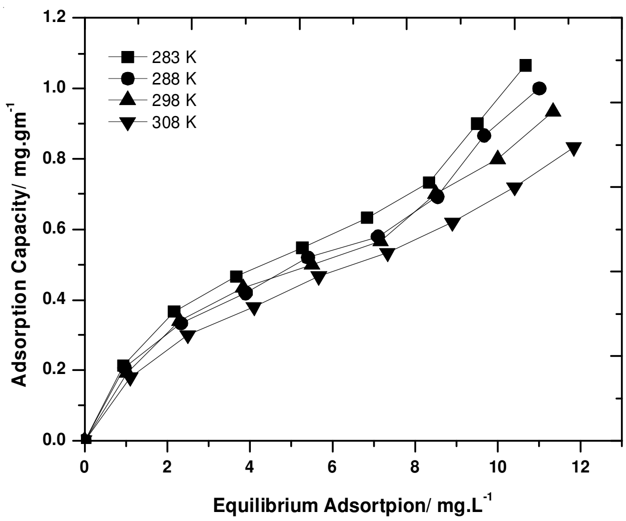


Fig. 4. Effect of temperature on the adsorption capacity of Maxilon Blue GRL dye, at pH 6 and mass catalyst 0.5 g

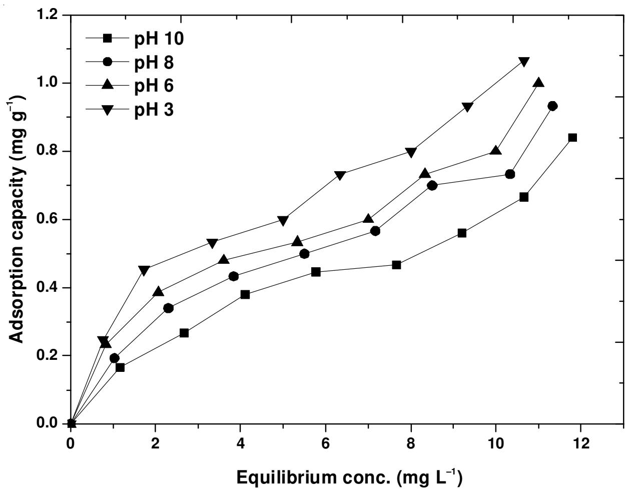


Fig. 5. Effect of pH on the adsorption capacity of Maxilon Blue GRL dye, at Temp. 298 K and mass catalyst 0.5 g

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[8]. 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[8]. 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 (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[11]. 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[12].

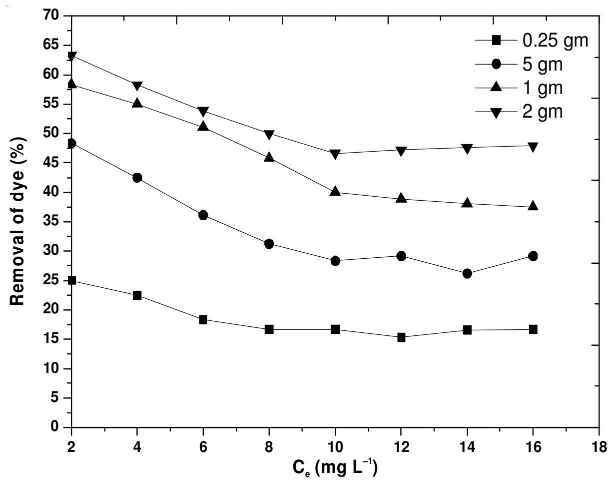


Fig. 6. Effect of mass catalyst concentration on the removal percent of Maxilon Blue GRL dye at pH 6 and Temp. 298 K

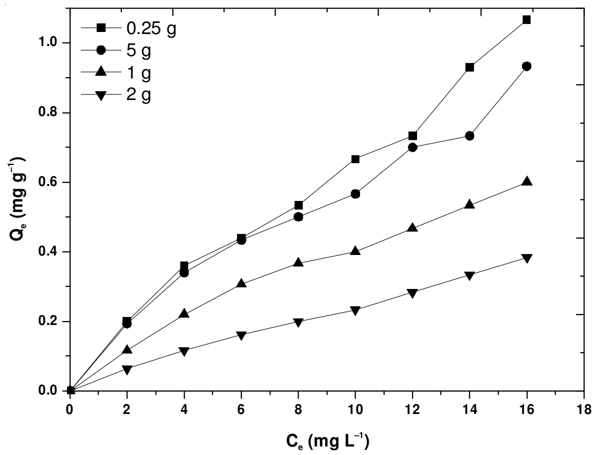


Fig. 7. Effect of mass catalyst concentration on the adsorption capacity of Maxilon Blue GRL dye pH 6 and Temp 298 K

Adsorption isotherms: 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[13]. The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution[4]. 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. (Langmuir isotherms graphs not shown).

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].

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

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

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where, Q_e is the adsorption capacity (mg gm^{-1}), C_e is the equilibrium concentration of dye (mg L^{-1}) and 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.

Thermodynamic studies: The thermodynamic parameters, ΔG°, ΔH° and ΔS° for the adsorption process were determined in temperature range of 302-322 K using the following relations[14].

$$K_c = \frac{C_{ads}}{C_e} \quad (3)$$

$$\Delta G^{\circ} = -RT \ln K_c \quad (4)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (5)$$

$$X_m = A_e \frac{-\Delta H^{\circ}}{RT} \quad (6)$$

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

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 K_c is the equilibrium constant and C_e (mg L^{-1}), the equilibrium concentration of the dye solution, results are illustrated in Table-2.

TABLE-2
THERMODYNAMIC DATA FOR THE REMOVAL OF GRL DYE WITH WHITE MARBLE ADSORBENT

Temp. (K)	-ΔG° (kJ mol^{-1})	-ΔH° (kJ mol^{-1})	-ΔS° (J K^{-1} mol^{-1})
283	9.0540	10.1231	3.7777
288	9.1388		3.4177
298	9.3820		2.4869
308	9.5860		1.7438

Conditions: Adsorbent dosage 0.5 g/100 mL; initial pH: 6.0

The adsorption capacity of the white marble decreased with increase in the temperature of the system from 302-322 K. 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[15].

Conclusion

The adsorption of GRL dye reaches equilibrium after 60 min. 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 3. All effective parameters give good fitting of Freundlich model better than Langmuir model.

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