Removal of Malachite green dye (MG) from water by using Residual Tea Leaves (RTL) as adsorbent

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Abstract

The present study is related to the removal of colorants. Adsorption of Malachite green dye on residual tea leaves was studied as a function of temperature, amount of adsorbent and pH.

A spectrophotometer technique was used for measuring the extent of adsorption. The data were fitted with Langmuir and Freundlich, isotherm equations and their corresponding constants were calculated from the slopes and intercepts of their respective lines.

The measured adsorption isotherms at the different temperatures 298 K, 308 K and 318 K were found that adsorption increase as the temperature increase within this range. from the measured adsorption isotherms at different pHs 3, 5 and 7it was found that the adsorbed amount of MG dye increases with increased acidity.

Thermodynamic parameters such as standard enthalpy change (ΔH^{o}), standard Gibbs energy change (ΔG^{o}), and standard entropy change (ΔS^{o}) of adsorption were calculated, and were explained in the mean of the chemical structure of the adsorbate. Results are showed that the adsorption process is endothermic.

Key word: Adsorption, Malachite green dye , residual tea leaves "RTL".

الخلاصة

يعني هذا البحث في ازالة الملونات. وقد تم في هذه الدراسة امتزاز صبغة المليخايـت الخـضراء (MG) على سطح الياف الشاي وذلك كدالة مع درجة الحرارة، وكمية الصبغة، والدالة الحامضية.

كمية الامتزاز حددت باستخدام المطيافية المرئية، ومن ثم تم مواءمة النتائج مع معادلات كـل مـن لانكماير ، و فرندلج، وثوابت كلتا المعادلتين تم احتسابها من خلال الميل ونقطة التقـاطع مـع الاحـداثيات المقابلة لكل حالة.

ايسوثرمات الامتزاز تم حسابها عند درجات حرارية مطلق مختلفة (298-318)، ووجد ان كمية الامتزاز تزداد مع زيادة درجات الحرارة ضمن هذا المدى.

كذلك تم حساب ايسوثرمات الامتزاز عند دوال حامضية مختلفة (7,5,3) ووجد ان كمية الامتزاز تقل مع زيادة الدالة الحامضية .

تم حساب الدوال الثرموديناميكية ΔG^{o} ، ΔH^{o} ، ΔS^{o} ومن خلالها تم دراسة سلوكية التركيب الكيميائي للمادة الممتزة، بينت النتائج ان عملية الامتزاز هي ماصة للحرارة.

Introduction

Dyes are widely use in textile, paper, plastic, food and cosmetic industries. The wastes coming from these industries can effect on our atmosphere causing pollution. Many dyes are difficult to degrade(1). Dye contaminated wastewater originates from a number of industries, such as textile, metal plating, packaging, and paper industry. The need for the treatment of dye contaminated wastewater arose from the environmental impact. They impart objectionable color on water bodies and retard photosynthesis hence lead the aquatic life on the path of dye contaminated wastewater originates from a number of industries, such as textile, metal plating, packaging, and paper industry(2-3).

Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather, food and cosmetic industry to color products. Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Most commercial dyes are chemically stable and are difficult to be removed from wastewater(4,5).

They have studied the feasibility of using low cost materials, such as waste orange peel(6), banana pith(7), rice husk(8), betonite clay(9), neem leaf powder(10), powdered activated sludge, perlite (11), and sewage sludge(12), as adsorbents for removal of various dyes from wastewaters.

The purpose of this work is study of the possibility of removal of Malachite green dye from water by low coast adsorbent surface *residual tea leaves (RTL).*

Materials

Adsorbent surface was prepared by taken 25 gm of residual tea leaves [Ceylon company 'Seri Lanka'] in beaker containing 250 ml of water, and heated for 6 hours at 60 ^{o}C, the mixture was allowed to stand for 10 minutes then filtered, aliquot solution neglected, this process is repeated about five to six times to remove all the color which result from commercial tea, until the aliquot of precipitate gave base line in uv-visible with no absorbance.

The precipitate was suspended in HCl solution of 0.02 M to remove all undesired compounds, then it was washed with an excess amount of distilled water to remove the soluble material. Then it was dried in the room temperature for seven days, then kept in airtight containers. The dried material was ground well to a fine powder and sieved well for maximum particle size (150 μm).

Malachite green dye is obtained by (B. D. H. chemical Ltd. Pool, England) with purity 97 %. The structural form is given in Figure (1)(13).

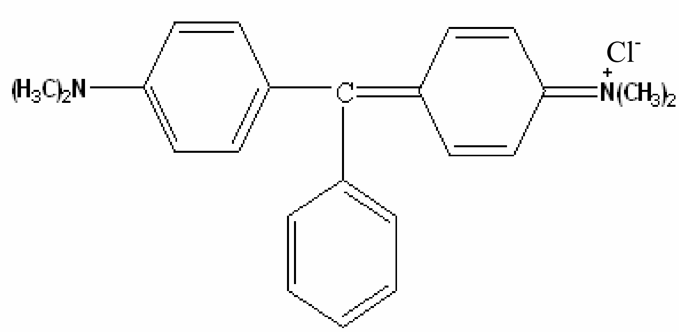

Figure 1: structure of Malachite green dye.

Spectronic (Apel pD-303 Japan spectrophotometer) single beam with 1 cm cells Bausch, was used for all absorbance measurements, pH measurements were made with Knick digital pH meter (Romania). Digital balance, Sartorius, (BP 3015 - Germany) and shaker water bath, SB. 4, Tecam were used.

Method

Adsorption experiments were carried out by shaking 50 mg RTL samples with 50 mL aqueous solution of MG dye of desired concentration at various pHs (3, 5 and 7) and temperatures (298, 308 and 318 K) for 1 h.

A thermostated shaker bath was used to keep the temperature constant. The initial concentrations of dyes solutes, C_0, were in the range of 10-50 ppm. All adsorption experiments were performed at 298 K and pH 7 except those in which the effects of temperature and pH of the solution were investigated. The pH of the solution was adjusted with HCl solution by using pH meter equipped with a combined electrode.

At the end of the adsorption period, the solution was centrifuged for 5 min at 1500 rpm and then the concentration of the residual [C_e] of MG, was determined with the aid of visible Spectrophotometer at a maximum absorbance λ_{max} for MG 620 nm.

The adsorbed amounts of MG was calculated from the concentrations in solutions before and after adsorption according to the equation (1)

$$Q_e = (C_o - C_e)\frac{V}{W} \quad \text{.....................(1)}$$

where C_0 and C_e are the initial and equilibrium liquid phase concentrations of dye solution (mg/L), respectively; Q_e is equilibrium dye concentration on adsorbent ($mg.gm^{-1}$), V is the volume of dye solution (L), and W is the mass of RTL sample used (g). All solutions were prepared using distilled water.

Results and Discussion

Adsorption isotherms

The obtained experimental equilibrium data for the adsorption of Malachite green (MG) on residual tea paper (RTL) at the different temperature 298, 308 and 318 K are presented in Figure (2). The adsorption isotherms were measured at neutral pH of 7.

The adjustment of adsorption isotherms at different temperatures are shown in Figure (2). It was found that the adsorption capacity of malachite green increases with increasing temperature.

This result may be explained as follow; in the range 298-318K an increase in the temperature doesn’t affect significantly sorption of MG dye on RTL.

The lower value of adsorbed amount Q_e at 298 K may be attributed to the large molecules size of dye which inhibits sorption; the temperature increase may enhances the molecules dye diffusion in the complex porous structure of RTL[14].

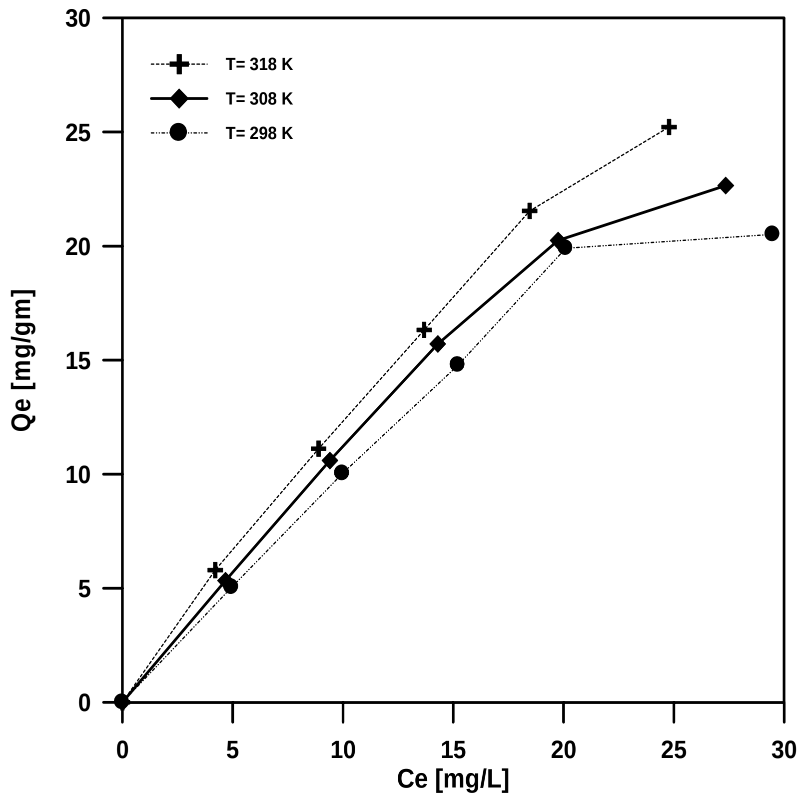

Figure 2. Adsorption isotherms of MG on RTL at different temperatures and (pH=7).

Thermodynamic parameters

The thermodynamic parameters for the adsorption of MG by RTL such as the standard enthalpy change (ΔH^o), the standard Gibbs energy change (ΔG^o) and the standard entropy change (ΔS^o) can be calculated from the variation of maximum adsorption with temperature (T) using the following basic thermodynamic relations [15]:

$$\ln Q_m = A - \frac{\Delta H^o}{RT} \quad \text{.......... .(2)}$$

$$\ln Q_m = -\frac{\Delta G^o}{RT} \quad \text{.......... .....(3)}$$

$$\Delta S^o = \left(\frac{\Delta H^o - \Delta G^o}{T} \right) \quad \text{.......(4)}$$

According to equation 2, the mean of the enthalpy change due do the adsorption of MG by RTL over the temperature range studied can be determined graphically Fig. 3 by the linear plotting of ln $\mathbf{Q_m}$ against 1/T using the least squares analysis.

The negative value of ΔG^o show that the adsorption is favorable for MG dye. However, it indicates that the dye adsorption is spontaneous, during the adsorption, some structural changes in the dye and the adsorbent occur the data are indicating the favorability of physisorption, the value of ΔH^o shows that the adsorption is endothermic [15]. The value of thermodynamic functions are listed in Table (1).

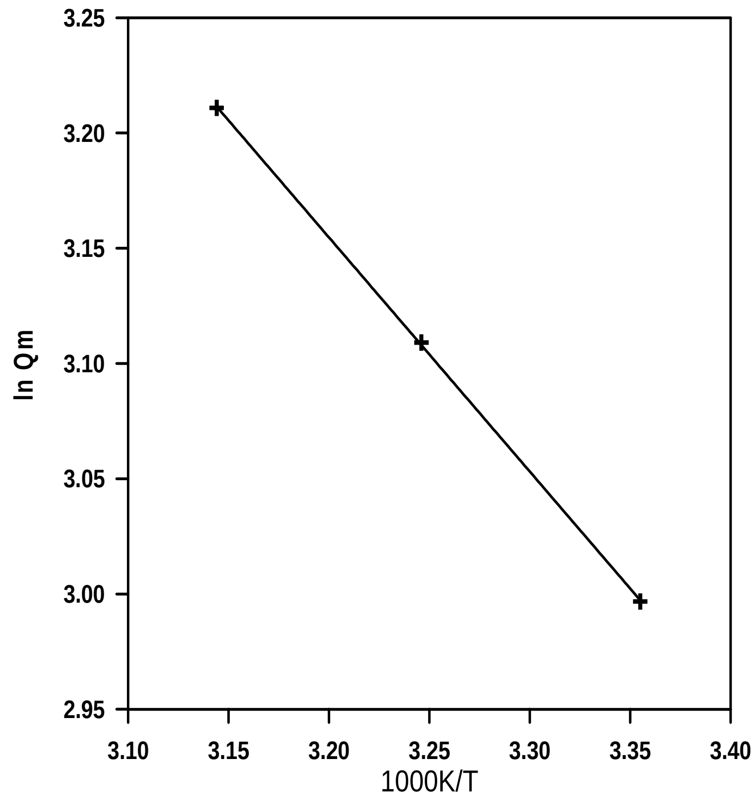

Figure 3: Van't Hoff equation for adsorption of MG dye on RTL surface.

Table 1. Thermodynamic functions ΔG^o, ΔS^o and, ΔH^o of MG on the adsorbent surface of RTL at 298K and pH 7.

Temperature/ K	ΔG^o / (kJ mole^{-1})	ΔS^o/ (J mole^{-1}K^{-1})	ΔH^o / (kJ mole^{-1})
298	- 16.215	82.728	8.438
308	- 17.205	83.256	
318	- 18.308	84.107	

Effect of pH

The effect of pH on adsorption process was investigated at three different pH values 3, 5 and 7 while keeping other parameters constant.

The result of variation of dye adsorption at these pH values is shown in Figure 4. The best results of adsorption have been given at high acidic medium, pH=3, this indicates presence of the strong force of interaction between dyes and RTL. In general the adsorption of dyes on the RTL involves ion exchange mechanism[16].

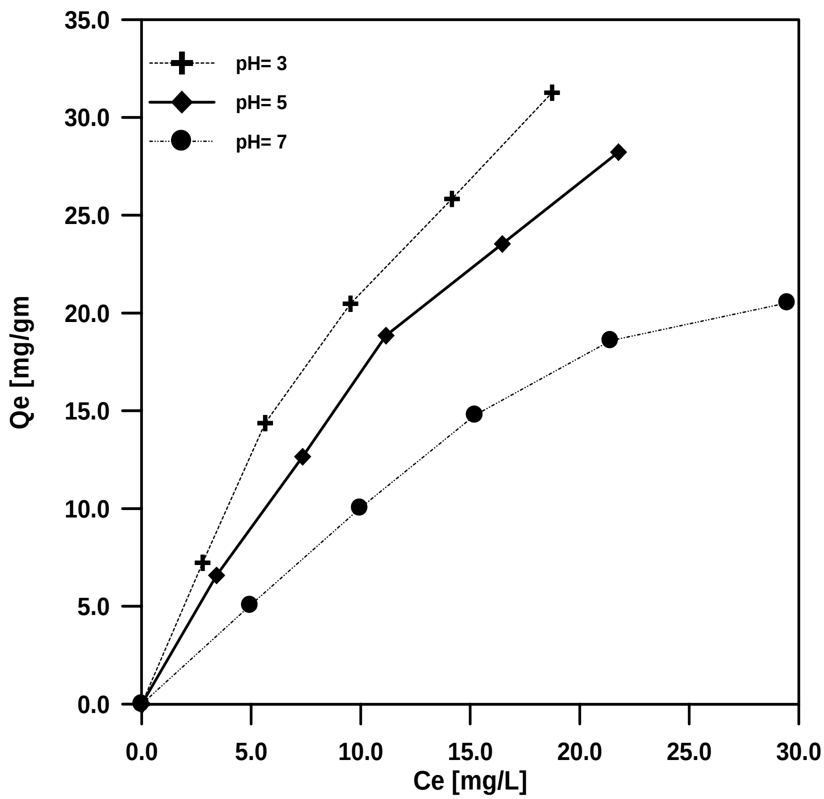

Figure 4. The effect of pH on the adsorption of MG dye on RTL surface at 298 K.

Adsorption isotherm

The experimental data are analyzed according to the linear form of the Langmuir and Freundlich isotherms.

The Langmuir isotherm is represented by the following equation[17]:

$$\frac{C_e}{Q_e} = \frac{L}{X_m} + \frac{C_e}{X_m} \quad .... (5)$$

Here C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/gm) and X_m and L are Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively. The linear plots of $\frac{C_e}{Q_e}$ versus C_e suggest the applicability of the Langmuir isotherms as shown in Figures 5 and 6. The values of X_m and L are determined from the slope and intercept of the plots and the results are shown in Table (2), from the results, it is clear that the values of adsorption efficiency X_m is increasing with temperature.

From the values we can conclude that the maximum adsorption corresponds to a saturated mono layer of adsorbate molecules. on an adsorbent surface with constant energy. The trend shows that the adsorbent prefers to bind acidic ions and that specially predominates on sorbent characteristics, when ion exchange is the predominate mechanism[15, 18].

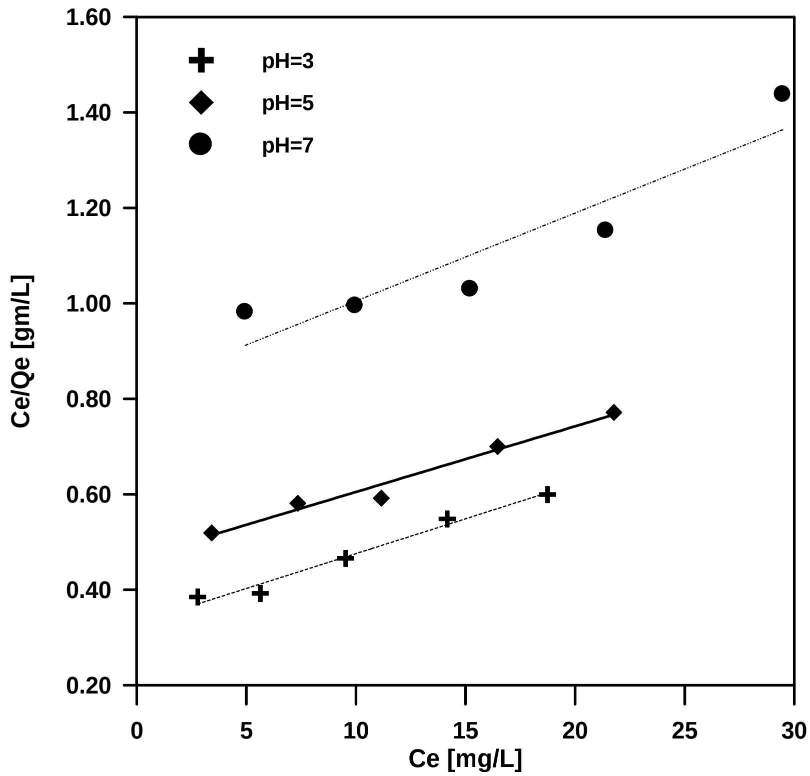

Figure 5: linearized Langmuir plot for MG on RTL surface at different pHs (T=298 K).

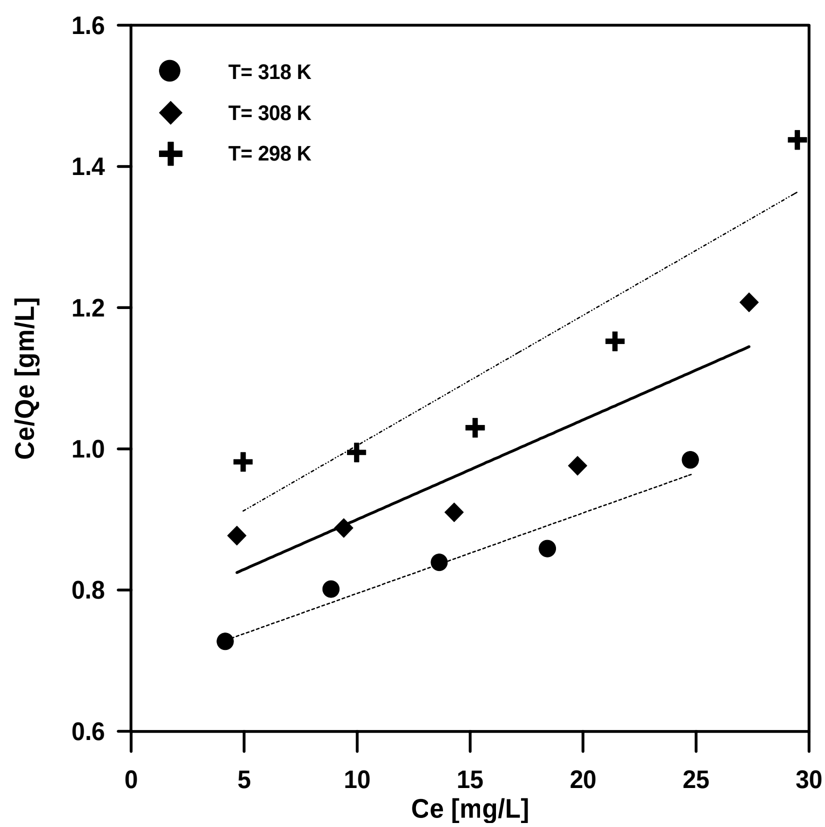

Figure 6: linearized Langmuir plot for MG on RTL surface (pH=7), at different temperatures.

The Freundlich equation is also applied to study the behavior of the adsorption of MG by RTL adsorbent surface. The Freundlich isotherm is represented as[19]:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \text{..........} (6)$$

Here Q_e is the amount of MG adsorbed (mg/gm), C_e is the equilibrium concentration of MG in the solution (mg/L), and K_f and 1/n are constants, incorporating all factors affecting the adsorption capacity.

Linear plot of ln Q_e versus ln C_e as shown in Figures 7 and 8. It shows that the adsorption of MG follows Freundlich isotherm. The values of K_f and n are given in Table (2).

The intensity of adsorption and energy involved in an interaction between MG dye and the adsorbent predict the possibility of physisorption and the possibility of mono-layer formation [19].

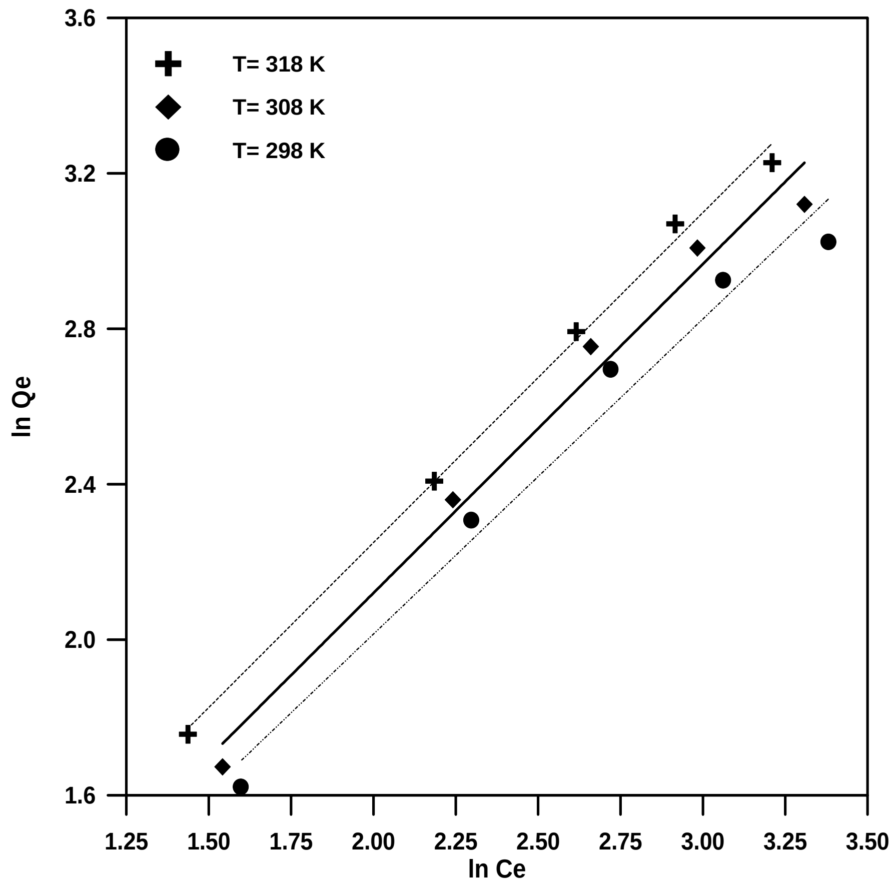

Figure 7:Linearized Freundlich plot of MG adsorption by RTP surface (pH=7)at different temperatures.

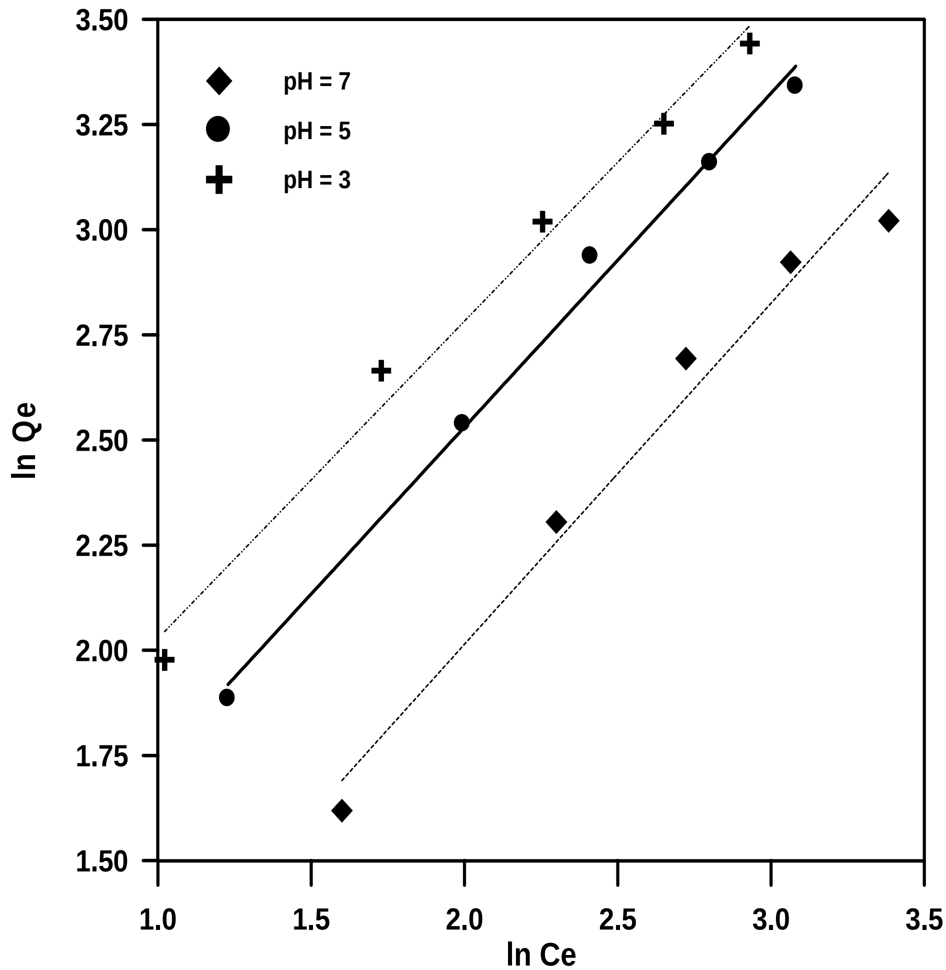

Figure 8: Linearized Freundlich plot of MG adsorption on RTL surface at different pHs, (T=298 K).

Table 2. Freundlich and Langmuir constants for different pH, and temperatures for MG on RTL surface.

Temp. (K)	pH	Freundlich parameters			Langmuir parameters		
		1/n	K_f	R^2	X_m	L	R^2
298	**7**	0.810	1.482	0.9758	21.720	26.480	0.8661
308	**7**	0.846	1.534	0.9817	25.368	37.380	0.8271
318	**7**	0.848	1.737	0.9964	29.0928	51.538	0.9473
298	**5**	0.793	2.568	0.9926	27.408	62.297	0.9739
298	**3**	0.754	3.573	0.9964	32.108	73.160	0.9787

Conclusions

Adsorption isotherms show that the quantity of adsorption for MG dye by RTL from their aqueous solutions increases by increasing their concentration. Adsorbed amount of MG dye decreases with increasing pH but when temperature increased adsorption capacity is increased within study range, this indicates that the adsorption process is endothermic.

A good result have been attained in acidic and neutral medium, but in basic medium MG dye give unsatisfactory results in adsorption process, therefore the study had been done in acidic and neutral medium.

References

1.T. Hajira, S. Muhammad and J. Qazi, ***Afri. Journal of Biotechnology*** 2008., **7 (15)**, 2649.

2. N. Oladoja, C. Aboluwoye, Y. Oladimegi, ***Turkish J. Eng. Env. Sci.*** 2008**, 32** , 303.

3. S. Netpradit, P. Thiavetyan, and S. Towprayoon, , ***Water Res.,*** 2004, **38**, 71.

4. S. Atef ALzaydien, ***American Journal of Applied Sciences***, 2009**, 6 (6),** 1047.

5. M .Mahejabeen, T. Hajira. ***Afr. J. Biotechnol.*** 2007, **6**, 2541.

6. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani and K. Ranganathan, ***Bioresour. Technol.***, 1996, **57,** 37.

7. C. Namasivayam, D. Prabha and M. Kumutha,. ***Bioresour. Technol.,*** 1998 **64,** 77.

8. G. McKay, G. Ramprasad and P.P. Mowli,. ***Water Air Soil Pollut.,*** 1986, **29,** 273.

9. K.Ramkrishna, and T. Viaraghavan,. ***Water Sci. Technol.,*** 1997 **36,** 189.

10. K. Bhattacharya, and A. Sharma, 2005. ***Dyes Pigm.,*** **65,** 51.

11. M. Dogan, M. Alkan, A. Turkyilmaz and Y. Ozdemir, ***J. Hazard. Mater.,*** 2004. **109**, 141.

12. M. Otero, F. Rozada, L. Calvo, A. Garcia and A. Moran, ***Biochem. Eng. J.,*** 2003. **15**, 59.

13. J. Cassar and R. Deanglis, **"Eassay with the support of culture"** 2000., 1, 2.

14.S. Daniela and B. Doina, ***Acta. Chim. Solv.,*** 2005, **52**, 73.

15. O. Yavus, Y. Altunkaynak, and F. Guzel ***water research,*** 2003. **37**, 948.

16. K. Selvarani, **2000.** "Studies on low cost adsorbents for the removal of organic and inorganic from water". Ph D., Thesis, Regional engineering College, Tiruchirapalli.

17. Langmuir 1: "adsorption of gases on plane surface of glass, mica and platinum", ***J. Am. Chem. Soc.*** 1918, **40,** 1361.

18. R. Viraji, C.Namasivayam and K. Kadirrelu, ***Waste Management,*** 2001, **21**, 105**.**

19**.** S. Senthikamur, P. R. varatharagan, K. porkodi and C. V. Subburraam, ***Colloid interface Sci.,*** 2005, **284 ,** 79.