Adsorption Removal of Rhodamine-B Dye From Aqueous Solution Using Rhamnus Stone as Low Cost Adsorbent

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Abstract

In this study, low-cost Rhamnus stone was used as adsorbents for the adsorption of Rhodamine-B (RhB) dye from aqueous solution by batch experiments under different condition of adsorbent weight, contact time, pH and initial dye concentration. Kinetic data obeyed to Ho-Mckay pseudo second order equation. Freundlich and Langmuir isotherms were used to test the equilibrium data and the results shows better fit with Langmuir isotherm with maximum adsorption capacity 39mg/g. Thermodynamic parameters show the adsorption of RhB onto Rhamnus stone was spontaneous and endothermic. [DOI: 10.22401/JNUS.20.1.05]

Keywords: Rhodamine-B, Rhamnus stone, Adsorption, kinetic, Thermodynamic.

Introduction

One of the most important environmental problems faced the human in last century and current century are the treatment of waste water due to increasing in industrials chemical effluents such as heavy metals, dyes, pigments, and other organic and inorganic chemical compounds discharge to water resources [1]. Among these effluents, dyes get special concern from researchers because carcinogenic, toxic, and mutagenic effects to human and animals as well as it is reduce the light penetration and that affect the photosynthetic in plants [2]. To reduce the dyes in industrials water effluents chemical, physical-chemical, and biological methods such as photocatalytic degradation, extraction, chemical oxidation, microbiological decomposition, ion exchange, adsorption on activated carbon, combined of adsorption and degradation and ultrasonic decomposition were applied with highly cost [3]. The adsorption on agriculture waste has advantage of low cost and high efficiency as compared to other methods. RHB is synthesized organic dye used in paper, paint, food, leather, pharmaceutical, cosmetic, laboratories as biological stain and so on, this dye has carcinogenic and toxic affect hence the application in food and cosmetic currently restricted[4]. The degradation of RHB on heterogeneous photocatalyst by irradiation with solar [5], ultraviolet[1], and microwave radiation [6] have some interest recently due to high removal percentage but that limit by slow reaction and carcinogenic intermediate

compounds [7]. The activated carbon derived from agriculture waste such as Jackfruit peel [8]walnut shell [9], palm shell [10] also used to removal the RhB with well percentage removal but the activation process and carbonization process additional cost make the activated carbon not economic as compared to direct use of low cost agriculture waste.

The aim of currently article is to introduce the novel low cost adsorbent for removal of RHB from aqueous solution and get the optimum condition of adsorption such as initial concentration, pH, contact time and adsorbent dose. The adsorption isotherm includes Langmuir and Freundlich were used to test the adsorption data. The kinetic data analysis by rate equation to obtain the order of adsorption reaction.

Experimental work
RHB

The RHB dye purchased from sinopharma chemical reagent, china. Was used to prepare the 1000mg/L stock solution by dissolving 1g of dye in 1L of distilled water and then dilution to required concentration. The wavelength at maximum absorbance λ_{max} determined by scanning the wavelength and found to be 550nm. The chemical structure of RHB is shown in Fig.(1).
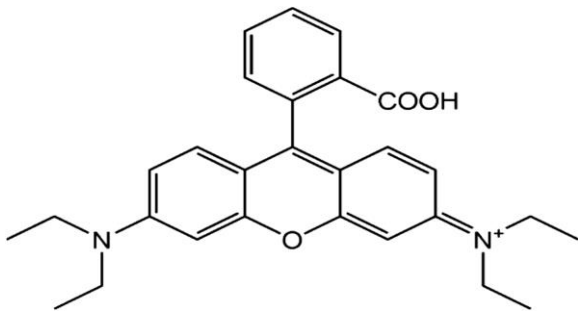
Fig.(1): structural formula of Rhodamine-B Adsorbent.

The Rhamnus stone was collected from Bismayah, Baghdad, Iraq. The stone was washed with distilled water and then dried at room temperature for 3 days, finally crushed, grinded and sieved. The surface of adsorbent was characterized by FTIR spectra to found the characterized groups affect the adsorption. FTIR spectra were measured by (Shimadzu 8400S, Japan) spectrophotometer in the range 4000 to $400 cm^{-1}$.

Equilibrium experiments

The adsorption experiments performed by batch model in series of conical flask (250mL) where solution of RHB dye (50mL) with initial concentration vary from 20 to 120 mg/L. The pH adjusted by 0.1M of HCl and NaOH. 0.1g Rhamnus stone powder were added to RHB solution and maintained in constant stirring for 70 min to reach equilibrium. The mixture was then centrifuged and the supernatant concentration determines using spectrophotometer (APEL-303, Japan) at 550 nm. The removal efficiency and the equilibrium uptake of RHB dye q_e were calculated according to the equations [3]:

$$\%Removal= \frac{C_o-C_e}{C_o} 100 \quad .... (1)$$

$$q_e= \frac{C_o-C_e}{M} \times V \quad .... (2)$$

Where, C_o is concentration of dye before the adsorption (mg/L), C_e is equilibrium concentration (mg/L), M (g) adsorbent weight and V solution volume in liter.

Kinetic experiments

The 20mg/L of RhB dye solution under the ideal conditions were taken. The concentration of unadsorbed dye measured with time interval

5min and the quantity of RhB adsorbed at time t was calculated by [8]:

$$q_t= \frac{C_o-C_t}{M} \times V \quad .... (3)$$

Where, C_o is original concentration (mg/L), C_t is concentration at time t (mg/L), M (g) adsorbent weight and V (L) solution volume.

Result and discussion
Characteristics of adsorbent surface

FTIR spectrum Fig.(2a) shows broad band from 3460.06 to $3176.54 cm^{-1}$, that refers to O-H alcohol and phenol groups as well as N-H stretch for amines [10] and C-O stretch at 1051.13 cm^{-1}. The intense band $2925.81 cm^{-1}$ and medium bands at 2858.13 cm^{-1} exhibit O-H carboxylic acid supported by C=O at 1741.60 and $1652.88 cm^{-1}$ and C-O at 1051.13 and $1242.07 cm^{-1}$[3]. Fig.(2b) shows shift the 3460.06 to 3494.99 and disappears 3176.54 cm^{-1}, that proved carboxylic groups affect the adsorption.
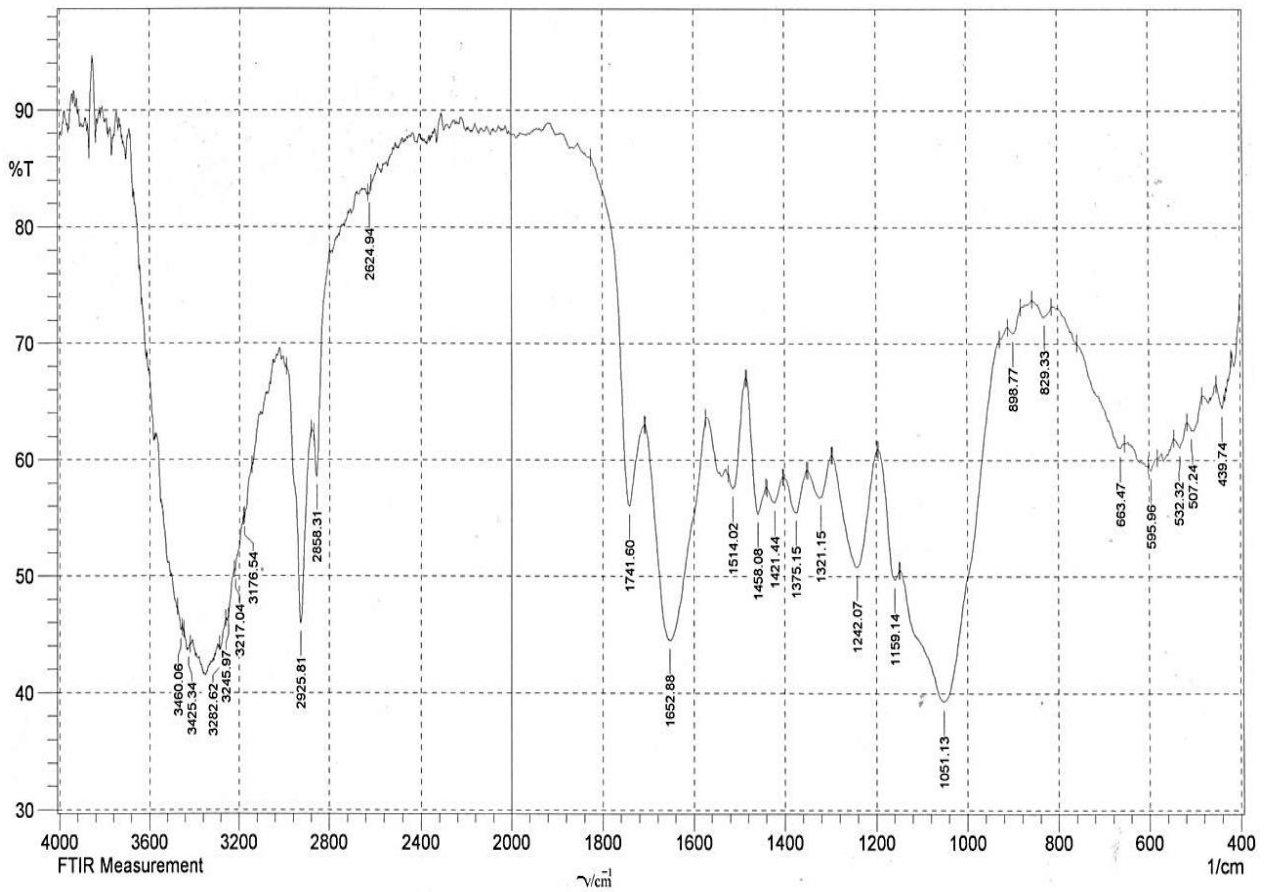
Fig.(2a): FTIR spectrum of Rhamnus stone surface before adsorption.
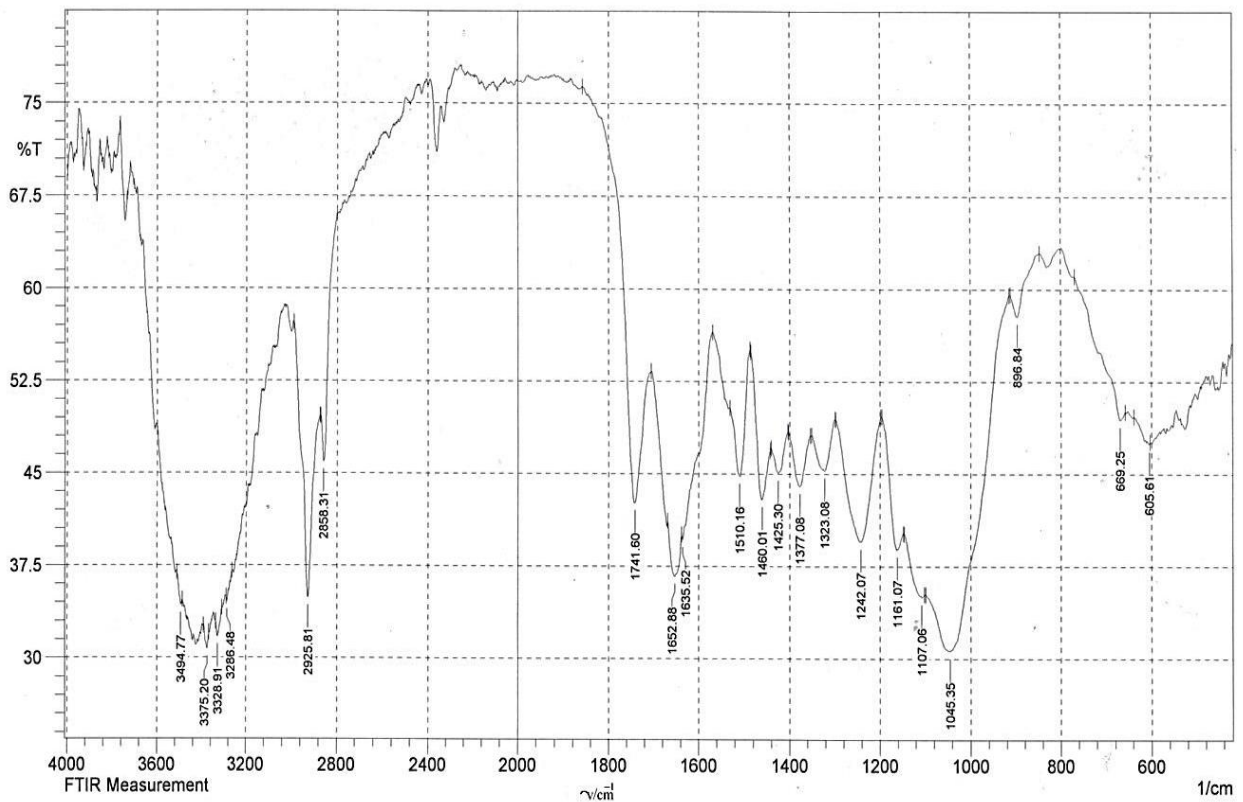
Fig.(2b): FTIR spectrum of Rhamnus stone surface after adsorption.

Effect of initial pH

The pH of the solution affected on electrical charge of adsorbent surface and the ionic forms of adsorbate molecule. Therefore, the adsorption of RhB (cationic dye) increase with decrease the acidity that is because in acid medium the hydrogen ion competed with RhB dye molecule and as the number of hydrogen ion reduced more adsorption site will be free to adsorb RhB dye[2]. Figure.3 shows the optimum pH is 9.
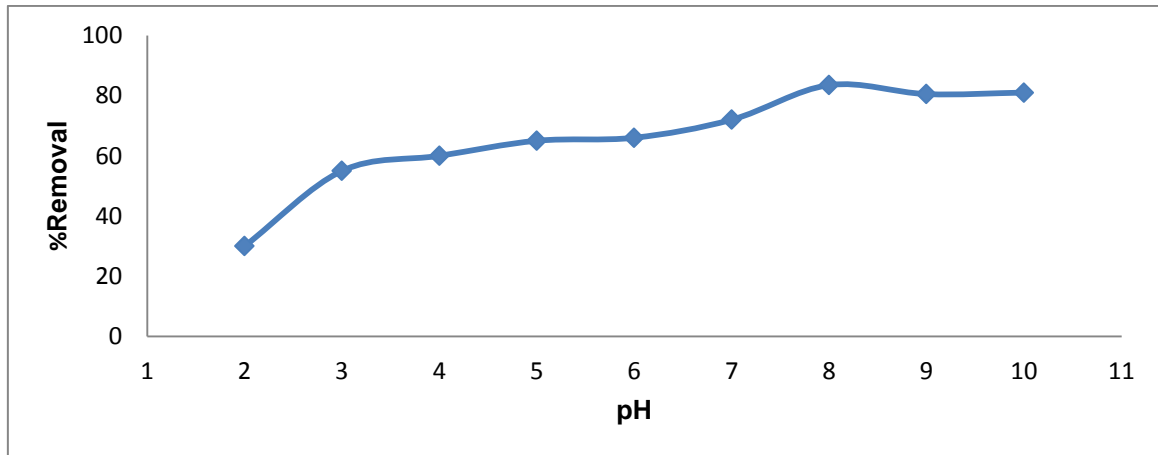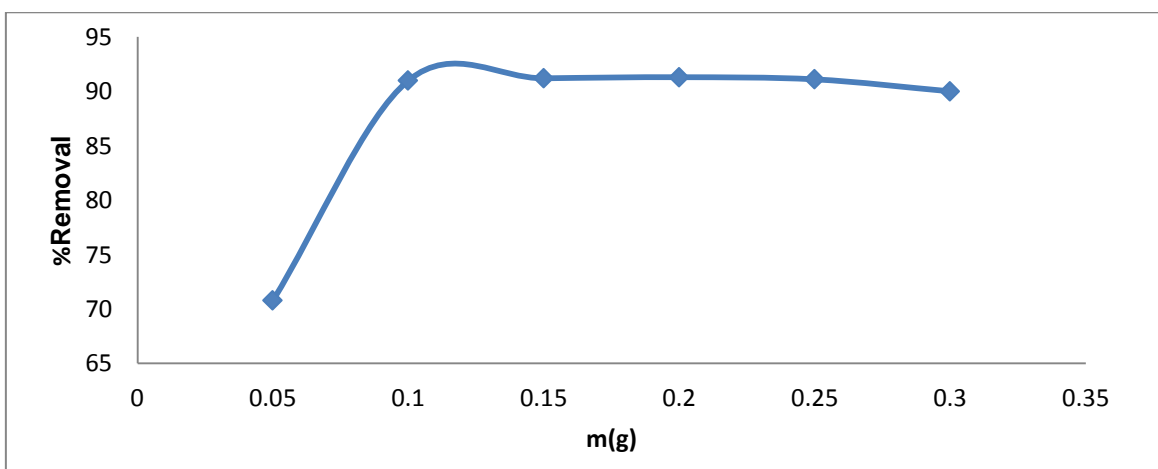

Fig.(3): Effect of pH on percentage removal of 20mg/L initial concentration of RhB dye at 303K.

Effect of adsorbent weight

The influence of different weight of Rhamnus stone on RhB percentage removal at a contact time 70min was investigated by ranged the Rhamnus stone weight from 0.05g to 0.35g in 20mg/L RhB solution. Fig.(4) shows increased percentage removal with increasing of Rhamnus stone weight and that is because more surface area implies greater number of adsorbent sites attained by increase the weight of Rhamnus stone[8].

Fig.(4): Effect of adsorbent weight on percentage removal of 20mg/L initial concentration of RhB dye at 303K.

Effect of contact time

The removal of RhB dye by adsorption on Rhamnus stone was studied as a function of contact time, and percentage removal plotted against time at 303K. Fig.(5) shows the adsorption rate of RhB onto Rhamnus stone is fast at the beginning and become constant after 70min.
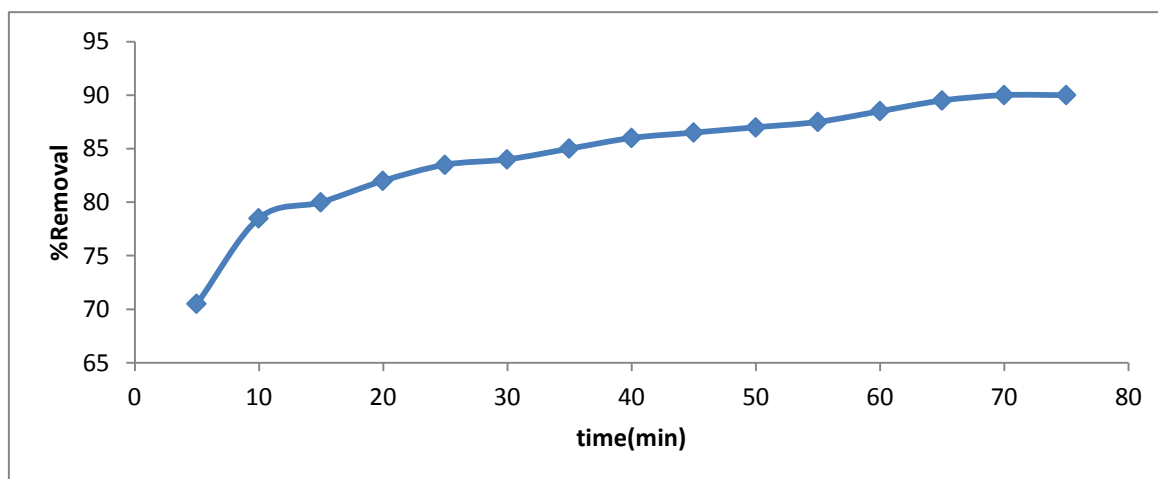
Fig.(5): Effect of contact time on percentage removal of 20mg/L RhB dye at 303K.

Effect of initial concentration

The availably of free adsorption sites reduced by increasing the initial concentration of dye therefore the removal percentage decreasing and the amount of dye removed increasing [11]. Fig.(6) reveal that 20mg/L is the ideal initial concentration of RhB.
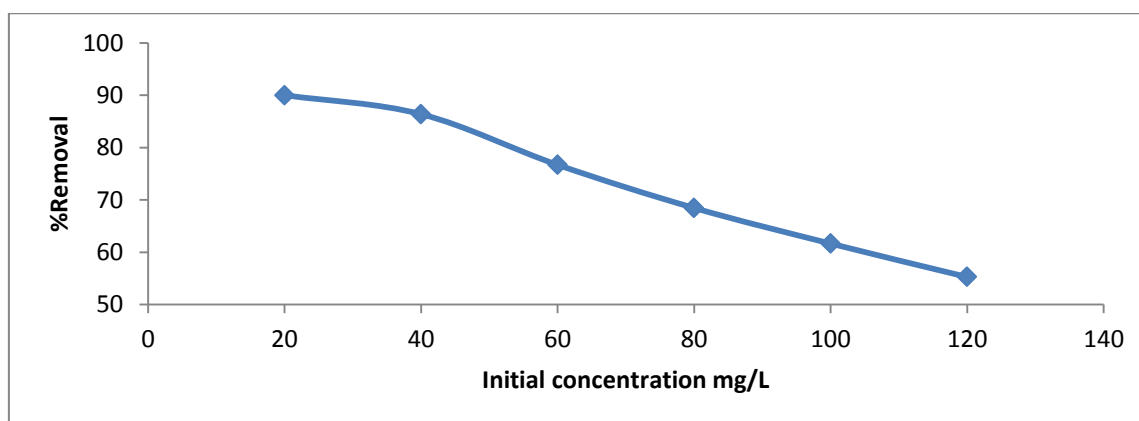
Fig.(6): Effect of initial concentration on percentage removal of RhB dye at 303K.

Equilibrium isotherm

The relationship between the quantity of dye molecules adsorbed per unit mass of adsorbent and its equilibrium concentration at constant temperature is called the adsorption isotherm. The adsorption isotherms are basic requirement for designing any adsorption system. The experimental data were fitted to Langmuir and Fruendlich isotherms. The Langmuir assumes the adsorbent surface is uniform with limit number of active site and no more adsorption take place after formation monolayer [2,12]. Freundlich assumes heterogeneous surface and the concentration of adsorbate affect the adsorption capacity [13]. The linear form of Langmuir equation and

separation factor defined by Weber and Chakkravorti are given by following equations [4]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$ .... (4)

$$R_L = \frac{1}{1 + K_L C_o}$$ .... (5)

Where C_e (mg/L) RhB dye concentration at equilibrium, q_e (mg/g) equilibrium uptake, q_m and K_L are Langmuir constants obtained from plot of $\frac{C_e}{q_e}$ versus C_e Fig.(7). The value of dimensionless separation factor R_L ranged from 0.2644 to 0.0565 this indicate favorable adsorption of RhB dye onto Rhamnus stone [10].

The Freundlich isotherm in the logarithmic form written as follows [9]:

$$Log \ q_e = \log K_F + \frac{1}{n} \log C_e$$ .... (6)

Where C_e (mg/L) RhB dye concentration at equilibrium, q_e (mg/g) equilibrium uptake. From slope and intercept of figure.8.(plot of log q_e verses log C_e) the Freundlich constants K_F and $\frac{1}{n}$ calculated and the result summarized in Table (1). The heterogeneity factor $\frac{1}{n}$ value near to zero that conform heterogeneous distribution of adsorption sites on the adsorbent surface [2,14]. The adsorption of RhB dye on to Rhamnus stone follows Langmuir as well as Freundlich model and the Langmuir adsorption model appears better fit (R^2=0.996) than the Freundlich model (R^2=0.959) and the maximum adsorption capacity increased with increased temperature exhibit endothermic process[15] .
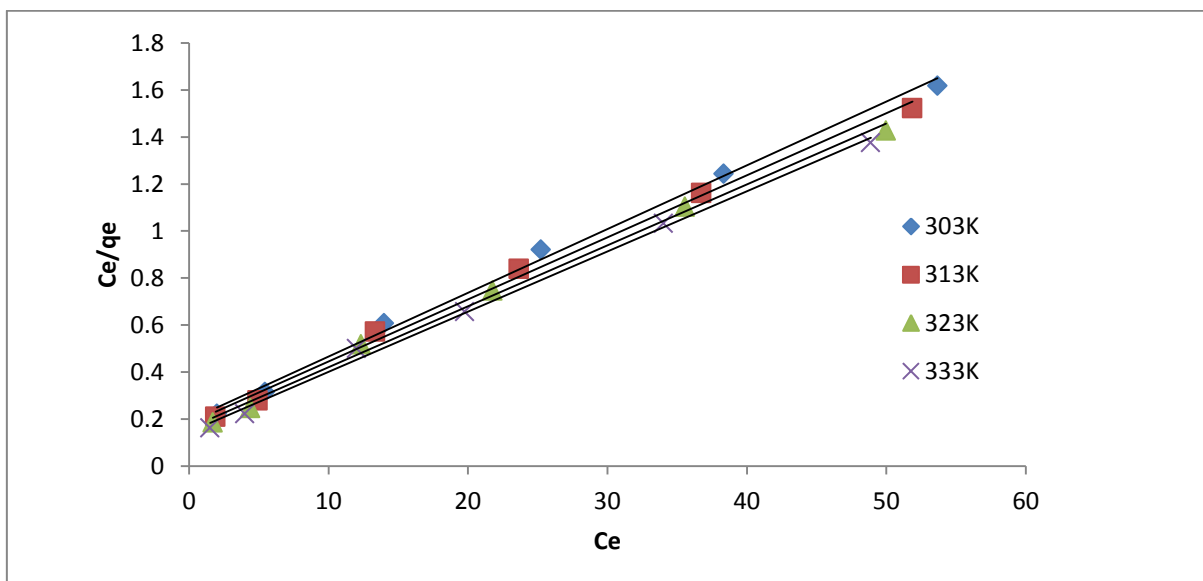

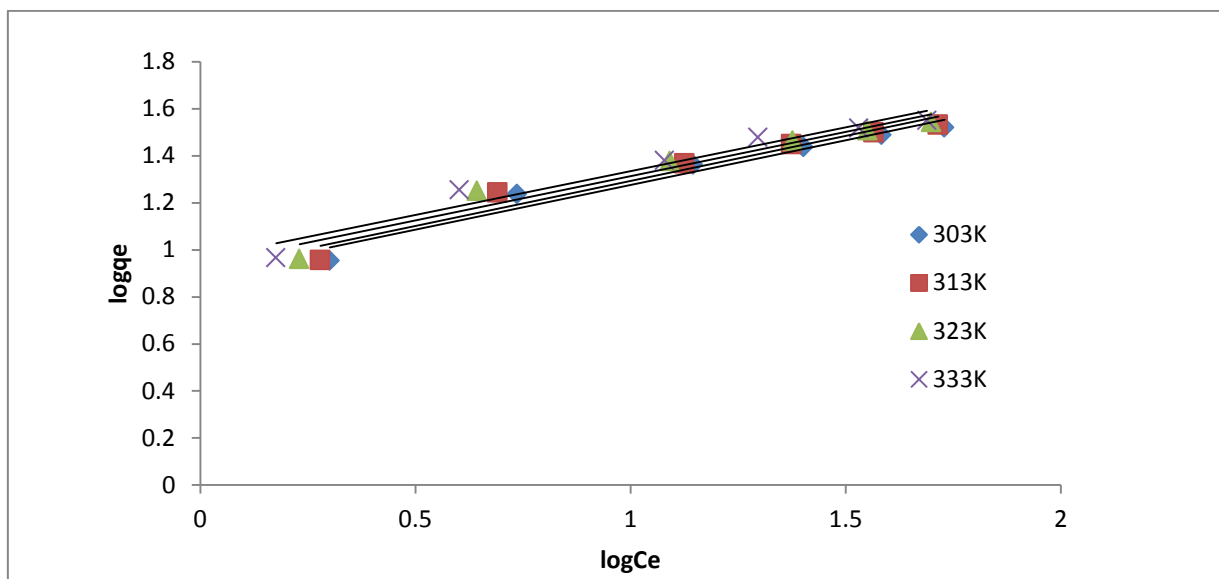*Fig.(7): Langmuir adsorption isotherm of RhB onto Rhamnus stone.*

Fig.(8):Freundlich adsorption isotherm of RhB onto Rhamnus stone.

Table (1)
Isotherms constants and correlation coefficient.

Temp. (K)	Langmuir isotherm			Freundlich isotherm		
	K_L(L/mg)	q_m(mg/g)	R^2	K_F(mg/g$(\frac{L}{mg})^{1/n}$)	$1/n$	R^2
303	0.1391	36.90	0.9963	7.8578	0.3811	0.9594
313	0.1454	37.88	0.9962	8.1508	0.3828	0.9541
323	0.1602	38.61	0.9964	8.6716	0.3757	0.9533
333	0.1764	39.06	0.9963	9.1854	0.3720	0.9514

Kinetic studies

To understand the mechanism of adsorption reaction, the kinetics experimental observation data was fitted to pseudo-first order (Lagergren equation), and (Ho and McKay) pseudo-second order. The linear form of Lagergren equation formulated as the following [16]:

$$\text{Log } (q_e\text{-}q_t) = \log q_e - \frac{k_1}{2.303} t \quad .... (7)$$

Where q_e and q_t the adsorption capacity at equilibrium and time t respectively. From the plots of log $(q_e\text{-}q_t)$ against the time t for 20mg/L concentration of RhB dye at 303K (Figure.9), the value of k_1 rate constant, calculated equilibrium uptake q_e and correlation coefficient obtained and listed in Table (2).

The (Ho and McKay 1999) pseudo-second order equation written as follows [17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad .... (8)$$

A linear plot of $\frac{t}{q_t}$ against time give the straight line and from the slope and intercept value of k_2 and q_e can be calculated. The initial adsorption rate h_o at various initial concentrations is related in the following equation [14]:

$$h_o = k_2 q_e^2 \quad .... (9)$$

The determination of suitable kinetic model for the adsorption reaction by comparing the correlation coefficient is restricted to linear kinetic model. Therefore, the sum of error squares used to indicate the most suitable kinetic mode [18]:

$$\text{SSE (\%)} = \sqrt{\frac{\Sigma(q_{e,exp} - q_{e,cal})^2}{N}} \quad .... (10)$$

Where SSE is sum of error squares, $q_{e,exp}$ experimental equilibrium uptake, $q_{e,cal}$ calculated equilibrium uptake and N number of data point. The result in table.2 shows

correlation coefficient close to 1 and sum of error squares close to zero for pseudo-second order model that conform the adsorption of RhB dye onto Rhamnus stone is follows pseudo-second order under the condition used in this study.
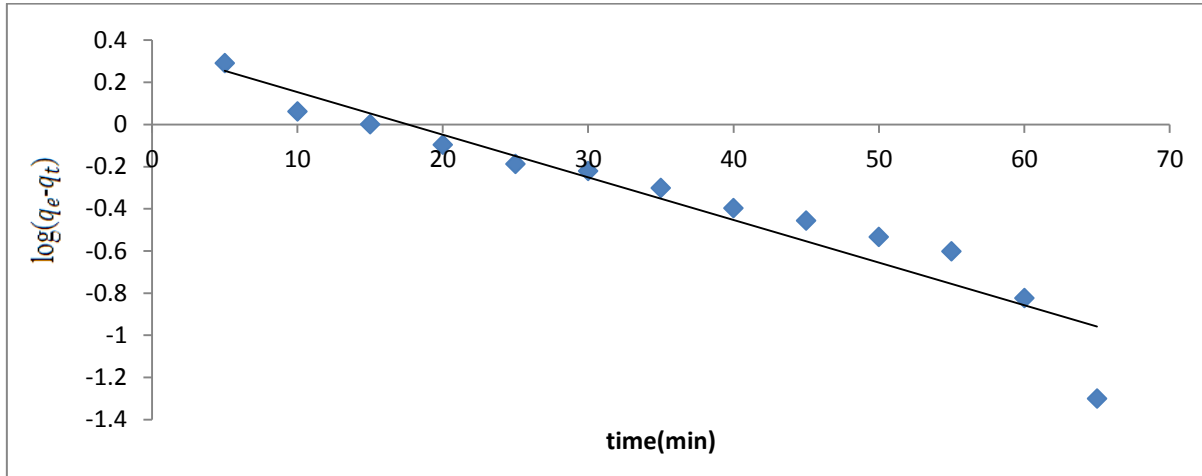

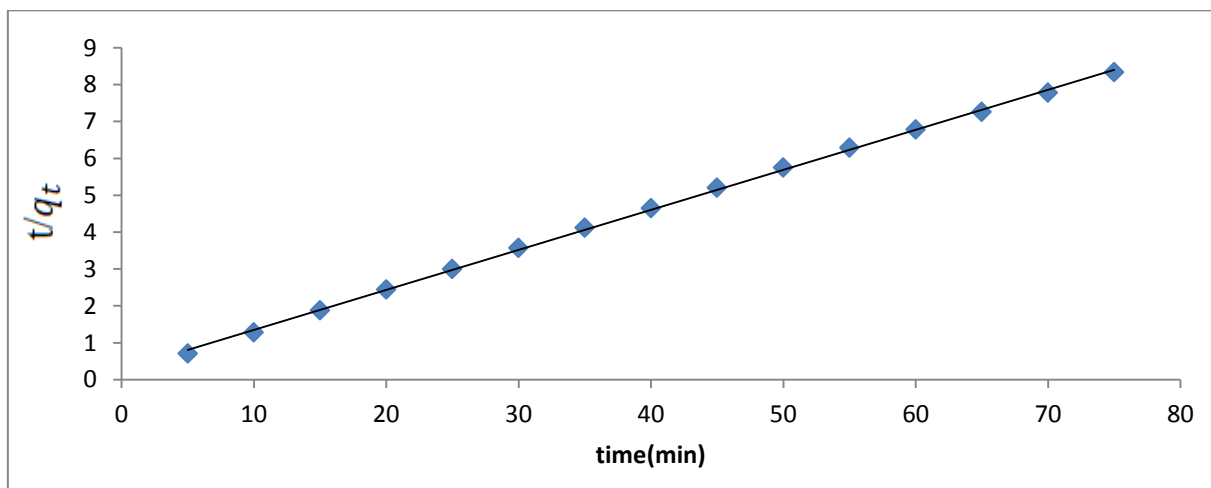*Fig.(9):Pseudo-first order of RhB dye onto Rhamnus stone at 303K using 20mg/L RhB.*

Fig.(10): Pseudo-second order of RhB dye onto Rhamnus stone at 303K using 20mg/L of RhB.

Table (2)
Kinetic results of 20mg/L RhB dye on Rhamnus stone at 303K.

$q_{e,exp}$ mg/g	Pseudo-first order				Pseudo-second order			
	$k_1(min^{-1})$	$q_{e,cal}$ mg/g	R^2	%SSE	k_2 $g.mg^{-1}.min^{-1}$	$q_{e,cal}$ mg/g	R^2	%SSE
9	0.0465	2.26	0.907	6.73	0.0456	9.2	0.999	0.2

Thermodynamic studies

Thermodynamic parameters are calculated by following equations [10]:

$$K_c = \frac{C_{ads}}{C_e} = \frac{C_o - C_e}{C_e} = \frac{C_o}{C_e} - 1 \dots\dots\dots\dots (11)$$

$$\Delta G^o = -RT\ln K_c \dots\dots\dots\dots\dots\dots (12)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \dots\dots\dots\dots\dots\dots\dots (13)$$

Where, K_c equilibrium constant, C_o(mg/L), C_{ads}(mg/L), and C_e(mg/L) represent the dye original dye concentration, concentration of adsorbed dye and remaining concentration in solution at equilibrium, respectively. The ΔG^o,

ΔH^o and ΔS^o are change in free energy, enthalpy and entropy respectively. R gas constant (8.314J.$mol^{-1}.K^{-1}$) and T (K) solution absolute temperature. The ΔG^o obtained have negative sign that indicates the adsorption process was spontaneous and from slope and intercept of van't Hoff plot Fig.(11),

ΔH^o and ΔS^o are calculated. The thermodynamic results summarized in Table(3) shows positive value of enthalpy indicates endothermic adsorption reaction and positive value of entropy indicate increase in randomness.
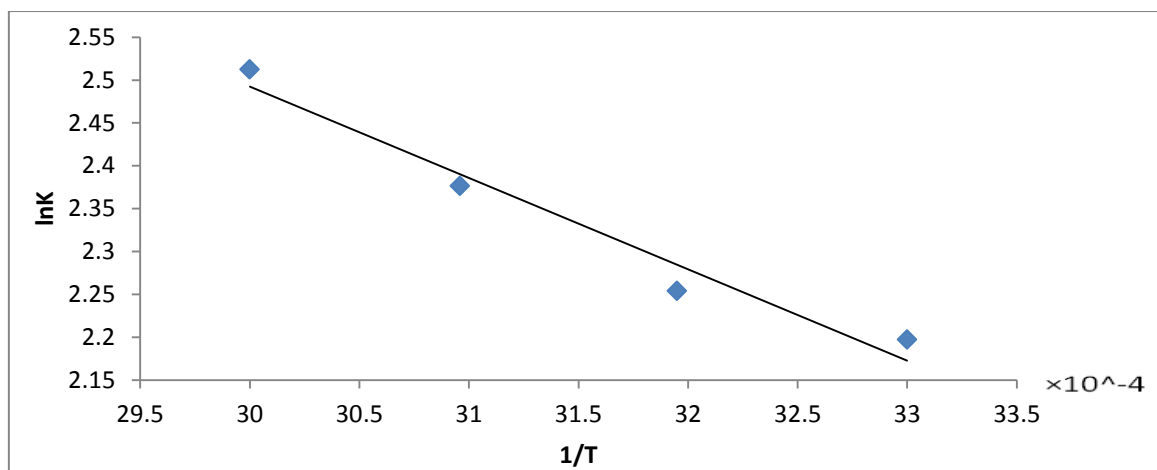
Fig.(11): Van't Hoff plot of RhB dye onto Rhamnus stone.

Table (3)
Values of thermodynamic parameters for the adsorption of RhB on the Rhamnus stone at different temperatures.

T(K)	ΔG(kJ.mol^{-1})	ΔH(kJ.mol^{-1})	ΔS(J.$mol^{-1}.K^{-1}$)
303	-5.535		
313	-5.865	+ 8.8	+ 47.27
323	-6.381		
333	-6.955		

Conclusion

The results exhibit that Rhamnus stone is an excellent new low cost adsorbent for removal of RhB dye from aqueous solution. The experimental equilibrium data obeyed for Langmuir as well as Freundlich isotherms with better fit to Langmuir isotherm. Thermodynamic studies shows the adsorption process spontaneous and endothermic.

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الخلاصة

تم في هذه الدراسة استعمال نوى النبق كمادة مازة لأمتزاز صبغة الرودامين B من المحلول المائي. و تم دراسة العوامل المؤثرة على الامتزاز مثل كمية المادة المازة، زمن التماس، الدالة الحامضية و تركيز المادة الممتزة بطريقة الوجبة. كذلك تم دراسة حركية الامتزاز و وجد انها تخضع للمعادلة الحركية من الدرجة الثانية الكاذبة. و بعدها تم تحليل بيانات الاتزان باستخدام ايزوثرمات لانكماير و فروندليش واشارت النتائج الى ان الامتزاز يطيع كلا المعادلتين و ينطبق بصورة اكبر مع معادلة لانكماير. الدوال الثرموديناميكية اشارت الى ان التفاعل تلقائي و ماص للحرارة.