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Thermodynamic study of adsorption dye Rh6G on the surface of the Peels Eucalyptus powder in aqueous solution

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ABSTRACT

The main objective of this study Is pollution treatment liquid Industrial waste One of topics threaten the environment. This study is concerned with dye adsorption Rhodamine 6G on the surface of Eucalyptus plant Peels powder, a low-cost and available. Seek time, the primary focus PH, and the temperature on the adsorption, and where the results showed that the equilibrium time 45min, were obtained at the highest adsorption capacity (93.80%) when the weight (0.5gm) of the user surface. And that the effect of the acidic function on the amount of the adsorbent follows (PH = 7, 4, 10). Isotherms studied the adsorption and found to be identical to the equation freundlich Temkin and adsorption in the low-lying degrees heat. The thermodynamic functions (ΔH,ΔS,ΔG) of the dye for their adsorption have been calculated, which show the adsorption is spontaneous and the adsorption is exothermic. The study showed that of Eucalyptus plant Peels powder treated with pollution excellent method.

INTRODUCTION

The discharge of liquid industrial wastes including paints on lands and waters is a serious threat to the environment due to their toxicity and not to analyze biological in nature as well as its failure to change the color and taste of brownish water and list (Paul, E., 2013). To reduce water pollution feces factories that must be addressed before it is put in water bodies is the most important chemical methods used in this field are chemical oxidation (Peyton, G.R. and H.W. Glmze, 1988), reverse Osmosis (Assoc, 1986), ion exchange (Lipezynkak, K.E and J.R. Bolton, 1992), adsorption (Oakes, J. and S. Dixan, 2003).

The adsorption of the effective techniques used in the purification and separation processes is one of the ways that remove material or persistent organic or inorganic of their solutions and the concentrations of low-lying or concentrations cannot be removed chemical means or traditional biological and showed a lot of surfaces usability on adsorption such surfaces mud's porous active, coal (Shaobin, w., *et al*., 2005; Muhammad, J., N. Muhammad, 2007), which has become, inherent in many adsorption processes However study of adsorption and the expansion of its applications, the urgent need to find roofs are available and cheap, such as wood and cellulose (Nagham, A., 2010; Schaffner, L., *et al*., 2006) and zealot And aluminum oxide (Osick, J. and L. Coope, 1982) and silica gel which do not give the ability to adsorption high when used like surfaces adsorbent.

That do not give the ability of adsorption high when used surfaces adsorbent, recent studies have appeared on the high power of some plants on adsorption such as cotton, which has shown high efficiency in adsorption processes (Khan Tabez, A., *et al*., 2009), and also used the pine papers such as the surface of a few adsorbent cost as shown effectiveness for the adsorption Basic red (Kiran mehta, V., 2013), of dye used the roofs of wheat straw for adsorption Astrazon (Carmen, M., *et al*., 2007).

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Eucalyptus plant is one of the most prevalent plants within the family Myrtaceae (Safety, 2004), as it includes this race more than 600 species and native to Australia but were planted more than 200 species in other countries because it provides shade trees and the rapid growth and its resistance to drought.

MATERIALS AND METHODS

In this study used a plant leaf powder peels Eucalyptus surface adsorbent dye, fresh leaves belonging to the plant peels Eucalyptus of gardens of the Baquba city, where he washed the leaves with water brought in and cleaned of dirt, and then dried in the shade for a period of three week and then milled by electric grinder, then Palm sieve 50 µm.

2-1-Adsorbent:

Used as a dye adsorbed in this study is an acid dye (Rhodamine 6G) explained the chemical and physical properties (Table 1). The standard solution was attended by dissolving the dye(0.1gm) from the dye in one liter of distilled water to prepare(100ppm) It is this concentrated solution is prepared dilute solutions (5, 10, 15, 20, 25ppm) scored a nice absorbed using a spectrometer UV – Visible (Uv-Visible Spectrophotometer- Double beam, Shimadzu.pc1950, Japan) For calibration curve after determining the wavelength of the dye (λ_{max}=530)

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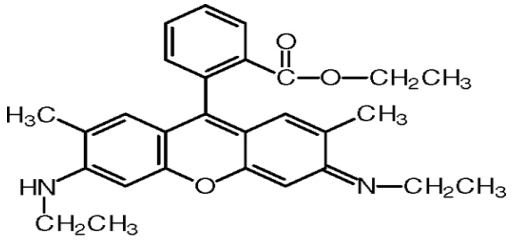

Rhodamine 6G

Table 1: chemical and physical properties of the Rhodamine 6G dye [15].

Molecular formula	C28H31N2O3cl
Molar mass	479.02
the source	Chem. supply
	Xanthan

2-2 Adsorption Process:

The study isotherm adsorption of dye (Rh6G) prepares five concentrations of aqueous solution (5, 10,15,20,25)ppm and placed in contact with the (0.5gm) from the plant powder peels Eucalyptus at (PH) and temperature limited and then placed in the provider a water bath to a Shake (100 rpm)(shsker water bath, jeiotech bs-1) and set the desired temperature. When reaching the equilibrium time (45 min) has offered solutions to the centrifuge (centrifuge, R8C.Bombay,India) quickly (3000 rpm)time (20 m) measure the absorbance using a (Uv-Visible Spectrophotometer) at greatest length (λ_{max}=530) and then calculate concentration of each solution at the expense of equilibrium C_e (mg/L) of the calibration curve. And it returned to the adsorption process experimental range of temperatures and pH.

To calculate the amount of the adsorbent of acidic dye Rh6G, Q_e(mg/g) used the equation (1) [16].

$$Q_e = \frac{(C_\circ - C_e)V}{m} \quad (1)$$

Where :--

(C_0) : the primary conc. of the dye (mg /L) ,

(C_e) :equilibrium conc. of the solution (mg/L),

V: The total V. of solution (L),m= W. Leaves peels Eucalyptus (g), and according R (%) to the percentage removal of the dye of the equation (2).

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2-3 Effect of Adsorption Parameter:

For the purpose of studying the influence of temperature in the adsorption, the study isotherm adsorption of the dye when the extent of thermal grades (278,288,298,308,318K) and also studied the influence of (PH) in the adsorption of dye Rhodamine 6G which has been modified acidic solution using (0.1m) of NaOH and

(0.1m) of (HCl) and measuring function acidic using device (PH-Meter-Hanna-Hl – 8417/England) the impact surface adsorbent weight used in the study was over (0.1,0.2,0.3,0.4,0.5gm).

Resuit & discussion:

3-1 Influence of Touch Time:

Were studied adsorption of dye Rh6G by adding (50ppm) of the dye to the solution (0.4gm) from the surface of plant peels Eucalyptus powder and depending on the amount of adsorption of each (15min) as shown in Figure 1 and the results explained that the adsorption of the dye rate on the user's surface increases with time to reach equilibrium time (45min) and who spoke with him a higher amount of adsorption of the dye. And explain the results to the amount of the adsorbent increases with time to provide number of active sites for the user adsorption surface where the dye molecules move from the solution for surface adsorbent strong influence hydrogen bonds that occurs between the active sites for the dye and the surface, and when you reach a state of equilibrium at the time said to be the active sites in the surface adsorbent occupied by the dye adsorbed molecules.

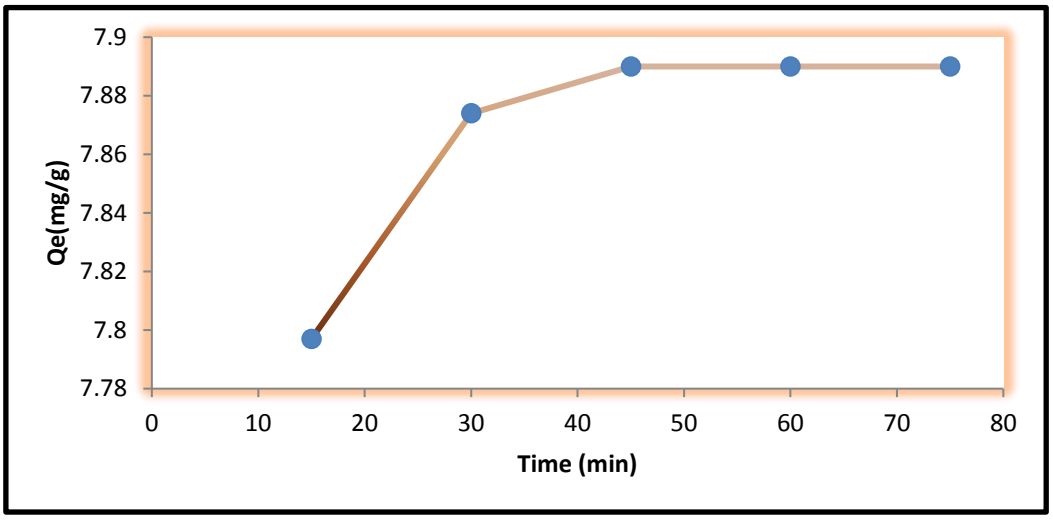

Fig. 1: Contact time dye Rhodamine 6G on leaves powder Caleptos.

2-3 Influence of adsorbent:

Study the influence Eucalyptus Peels powder on the adsorption for dye Rhodamine 6G capacity, where they were taking different weights from the surface adsorbent (0.1,0.2,0.3,0.4,0.5 gm) It was the adsorption of the dye capacity affected by the weight of adsorbent surface within the experimental range (0.1-0.4g) where it was to get a higher adsorption capacity (93.80%) when the weight (0.5gm).

3-3 Influence of PH:

Study the Influence of pH on the adsorption of dye Rh6g on the surface of Eucalyptus Peels at different values of the function acidic (PH=4,7,10), where the results are explained in (Figure 2) explained that the amount of adsorption increases in the order (PH=7> 4> 10) can be explained by the fact that in the solution of equal more likely hydrogen bonds between the active groups on the surface user and group (NH_2)effective in the formula and a tendency to link the surface more than a tendency to link with comet particles. The acid in the solution would gain range (NH_2) and Proton turn into a positively charged ion (Ion Alanallenium) and surface carries a positive charge and a negative attraction occurs between different shipments.

But in the middle basic surface acquires a more negative shipments due to the effect of the ocean and the dye withstand negative shipments also occurs electrostatic repulsion between the cargo and the asymmetric least adsorption (Ozcan, A.S. and A. Ozcan, 2004; Frhan, A. and A. Salah, 2014).

Table 2: Effect of pH function in adsorption (Rh6G) at a temperature (25°C)

C_0 ppm	pH=4			pH=7			pH=10		
	C_e	Q_e	R %	C_e	Q_e	R %	C_e	Q_e	R %
5	1.19	0.49	77.1	1.20	0.51	77.4	4.30	0.13	18.02
10	1.4	1.07	84.2	1.60	1.11	85.2	7.49	0.35	2.116
15	2.6	1.60	85.9	2.07	1.66	87.6	11.50	0.59	28.89
20	2.862	2.19	88.21	2.13	2.29	89.9	12.81	1.09	40.96
25	3.4	2.75	88.90	2.47	2.93	90.41	15.60	1.39	41.97

3-4 adsorption Isotherms:

Is a term that refers to the relationship between the amount of the adsorbent (Q_e) and concentrate remaining at equilibrium (C_e) at a constant the heat. The analysis of the results obtained in this study using three Isotherms.

3-4-1 Langmuir Adsorption Isotherm:

Langmuir model that supposedly active sites obtained by adsorption be uniformly distributed almost (Homogenous) where the area of any site on a constant surface and be energy distribution on a regular surface adsorption and be topical. This makes it clear that the adsorption is a monolayer (Ahlam, M., H. Ammar and M. Akl, 2013).

Linear version of the equation is Langmuir equation:

$$C_e/Q_e = 1K_Lq_{max} + (1/q_{max})Ce \quad (3)$$

where

Q_e : The amount of the adsorbent (mg/g).

C_e : equilibrium concentration of adsorbate in solution after adsorption (mg/L).

q_{max} : Great adsorption capacity when the surface is saturated adsorption entirely.

K_L: Equilibrium constant and associated card adsorption.

The calculated value of (K_L q_{max}) to draw the relationship between (C_e/ Q_e) versus (C_e) on the slope ($1/q_{max}$) and intersections ($1/k_L$ q_{max}) was calculate the value R^2 (Correlation Coefficients) showing Does the equation appropriate to describe the adsorption processes and in the equation for Langmuir by the correlation coefficient values (Separation Factor) of the equation.

$$R_L = 1/(1+k_LC_0) \quad (4)$$

Where (C_0) and the primary concentration (K_L) fixed Langmuir. Of the value of the correlation coefficient (R_L) got information on the nature of adsorption as shown in Table (2)

Table 3: the nature of adsorption and the correlation coefficient

Value R_L	Type of isotherm
R_L > 1	Unfavorable
R =1	Linear
0<R_L<1	Favorable
R_L =0	Irreversible

Table 4: the effect of the equation for the adsorption Langmuir at different temperatures and when (PH = 7)

C_0 ppm	278		288		298		308		318	
	C_e	$\frac{Qe}{Ce}$	C_e	$\frac{Qe}{Ce}$	C_e	$\frac{Qe}{Ce}$	C_e	$\frac{Qe}{Ce}$	C_e	$\frac{Qe}{Ce}$
5	1.2	2.26	1.19	2.49	1.19	2.41	1.49	3.32	1.89	4.79
10	1.48	1.36	1.49	1.46	1.55	1.45	1.99	1.97	2.19	2.15
15	1.70	1.05	1.76	1.09	2.02	1.30	2.12	1.35	2.29	1.36
20	1.99	0.89	2.06	1.09	2.11	0.98	2.15	0.98	2.38	1.09
25	2.35	0.85	2.39	0.89	2.45	0.89	2.61	0.97	2.97	1.11

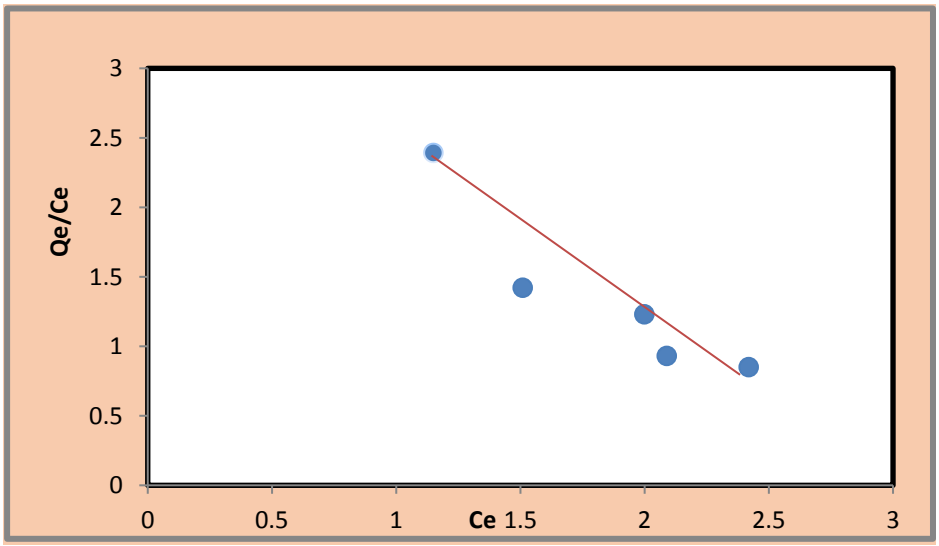

Fig. 2: straight to Langmuir at 298k.

3-4-2 Freundlich Isotherm:

It is one of the most important isotherm equations used when the surfaces unequal So are the potential energy changes irregular due to the occurrence of adsorption sites at varying levels of energy. Freundlich developed an equation to represent the change in the magnitude of the adsorbent (Q_e) per unit area or mass of adsorbent material with Daft or equilibrium concentration (C_e) and can be written Freundlich equation as follows (Huang, R. and *et al*, 2011).

$$Q_e=K_F C_{e1/n} \quad (5)$$

Where : –

Qe : quantity adsorbed at equilibrium in (mg / g).

Ce: The equilibrium conc. of the adsorbate in (mg / 1).

K_f:The Freundlich constant.

N=The value of a constant value expresses intensity of adsorption affinity depends on the surface adsorbent type and nature of the adsorbent and the temperature and take the Logarithm both sides of the equation (5) read as follows:

$$\text{Log}Q_e = \text{Log } K_F + 1/n \text{ Log} \quad (6)$$

When you draw (log Q_e) versus (log C_e) we get a linear relationship penchant amount (1 / n) and the intersection (logK_f) as shown in Figure(3)

Table 5: the effect of the adsorption equation Freundlich different temperatures and at (PH = 7)

C_0 ppm	288		298		308		318		328	
	Log C_e	Log Q_e	Log C_e	Log Q_e	Log C_e	Log Q_e	Log C_e	Log Q_e	Log C_e	*Log Q_e*
5	0.07	-0.2	0.68	-0.29	0.08	-0.30	0.18	-0.32	0.29	*-0.38*
10	0.19	0.32	0.20	0.029	0.21	0.026	0.32	0.00	0.33	*-0.006*
15	0.25	0.25	0.27	0.25	0.32	0.22	0.34	0.21	0.37	*0.26*
20	0.31	0.36	0.34	0.37	0.34	0.36	0.35	0.37	0.39	*0.37*
25	0.38	0.46	0.39	0.47	0.41	0.47	0.44	0.45	0.48	*0.48*

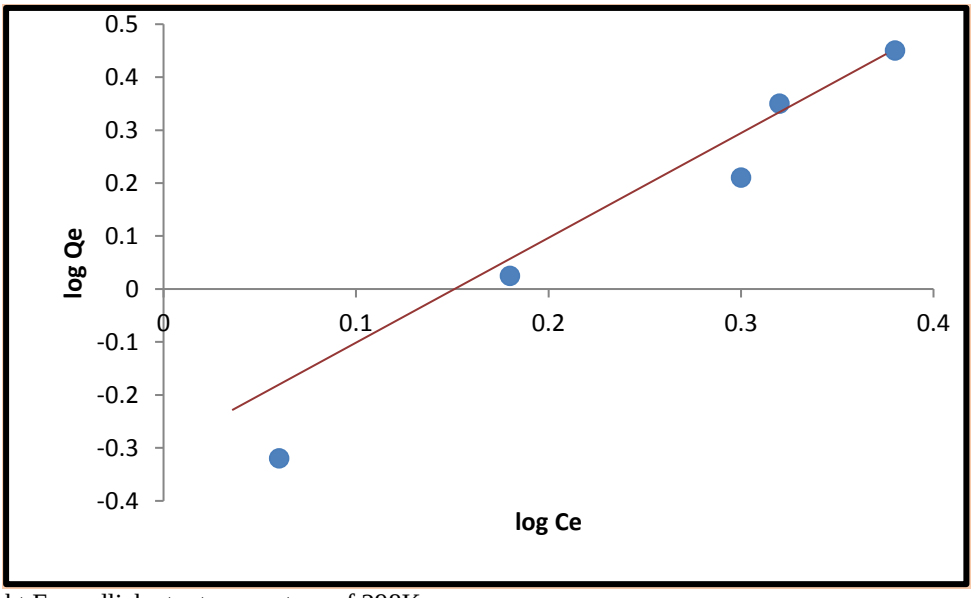

Fig. 3: Straight Freundlich at a temperature of 298K.

3-4-3 Temkin Adsorption Isotherm:

The use of the equation in many adsorption processes and can be written to the image-linear equation Timken as follows (Ghosh, D. and K. Bhattacharyya, 2002).

$$Q_e=B_T \text{In}(A_T.Ce) \quad (7)$$

After we got a rearranged equation:-

$$Q_e=B_T \text{In } AT+B_T \text{In } C_e \quad (8)$$

Where :

Q_e= is the amount adsorbent in (mg / g)

C_e= focus when the unbalance in (g / L) or (mg / L)

R= Constant gases " 8.314 j. mol $^{-1}$. K^{-1}. "

T = absolute T. in (K)

B, A represent constants can be calculated for (B = RT / b), the value of B, A calculated value of the pieces and the sloop to draw in a row against the value of the value of Q_e , $logC_e$ as in Figure (4)

Table 6: The effect of the equation Temkin on adsorption at different temperatures and at(PH = 7)

C_0	288		298		308		318		328	
	lnC_e	Q_e	lnC_e	Q_e	lnC_e	Q_e	lnC_e	Q_e	lnC_e	Q_e
5	0.098	0.51	149	0.49	0.144	0.48	0.371	0.43	0.66	0.40
10	0.400	1.09	0.411	1.08	0.415	1.07	0.662	1.1	0.77	1.001
15	0.525	1.69	0.570	1.68	0.697	1.65	0.736	1.62	0.84	1.71
20	0.697	2.26	0.710	2.27	0.735	2.26	0.751	2.26	0.88	2.25
25	0.839	2.84	0.863	2.86	0.885	2.82	0.955	2.84	1.11	2.80

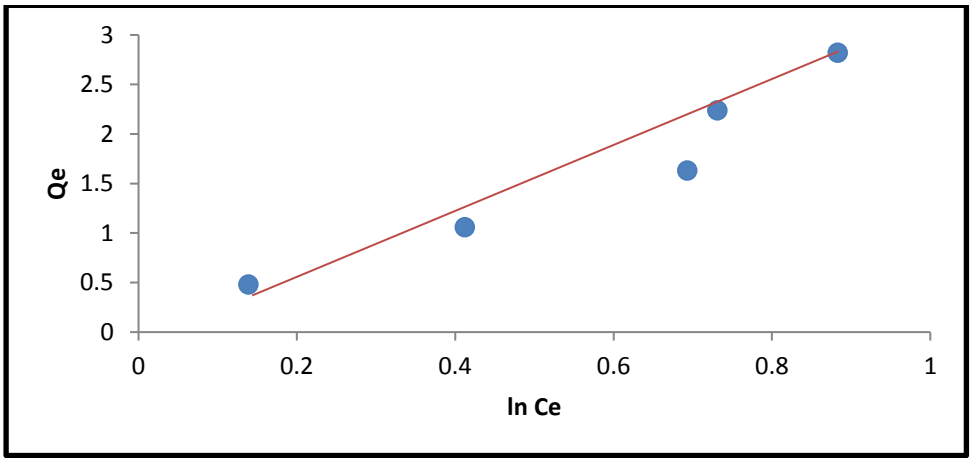

Fig. 4: A straight Temkin at a temperature of 298k.

Table 7: values Constants linear equations (Freundlich, Langmuir , Temkin) for adsorption.

T (k)	Freundlich			Langmuir				Temkin		
	N	K_f	R^2	q_{max}Type	K_L	R_L	R^2	b_T	lnA_T	R^2
308	0.256	0.056	0.817	2.85	0.044	0.39	0.506	501.21	-1.970	0.898
303	0.295	0.126	0.939	2.84	0.061	0.37	0.824	602.11	-3.285	0.89
298	0.427	0.362	0.982	2.83	0.102	0.378	0.819	820.39	-37.73	0.95
293	0.402	0.377	0.986	2.82	0.105	0.37	0.82	721.78	-23.10	0.989
288	0.418	0.429	0.987	2.78	0.110	0.359	0.87	734.95	-141.2	0.981

3-5 Study the thermodynamic variables:

Calculated thermodynamic values (ΔS, ΔG, ΔH) where values are calculated (a) of the equation (9) (Mahmood, M., *et al*., 2012).

$$\Delta G = - RT \text{ IN } K \quad (9)$$

Where:-

ΔG= Is the free energy of change (k.J.mol^{-1})

R= Is the gas Constant " 8.314 j. mol $^{-1}$. K^{-1}. "

K=Is the thermodynamic equilibrium constant

T= The absolute T. in (K)

It calculated the amount of heat associated with adsorption (ΔH) to draw Logarithm (K) Versus inverted temperature (1 / T) by equation (10)

$$\text{Ink} = \frac{H}{RT} + \text{constant} \quad (10)$$

Where the expense of a mile straight linear relationship

Through the use of the equation (11) It was calculated ΔS

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Table 8: Thermodynamic values of the adsorption at (308k -288 k)

T	- ΔG	-ΔH	ΔS
278	5459.3	10.234	18920
288	5505.3		18754
298	5524.9		18510
308	5416.1		17841
318	5095.8		16511

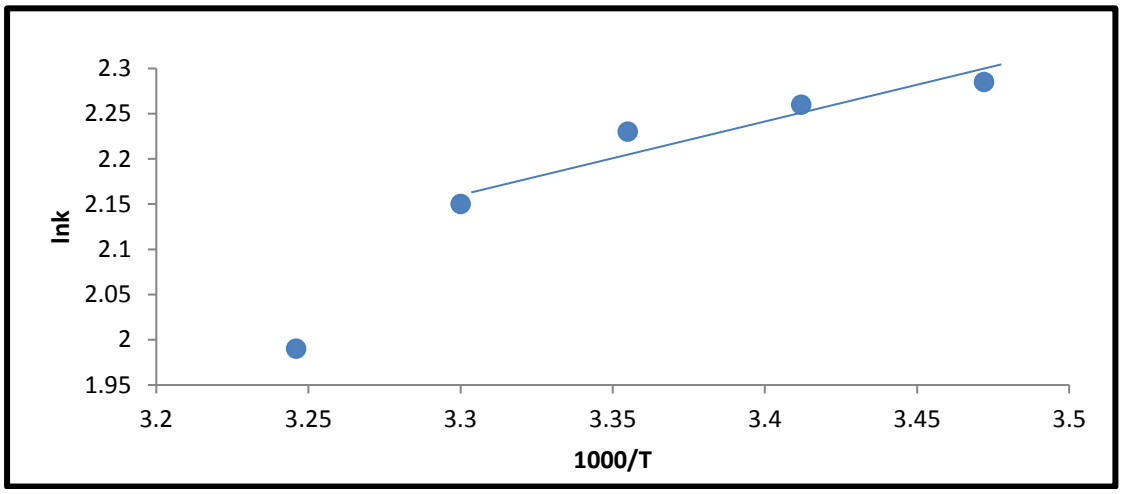

Fig. 5: Represents a relationship in k versus inverted temperature adsorption within the range of thermal (288K-328)

notes the negative value of the adsorption of the dye on the surface of Peels Eucalyptus exothermic (physical adsorption) This explains the decrease in the adsorption with increasing (T) and that of the separation of links between the surface adsorbent and adsorbent particles. And the values of entropy (S) cationic indicate continues mobility. And also the values of (G) Negative indicates that Spontaneous adsorption experimental conditions.

Conclusions:

Proved Leaves powder Peels Eucalyptus his efficiency surface adsorbent a low-cost and available and is harmless to the environment in the adsorption of dye Rh6G , the study showed that the process of adsorption affected by all of the surface weight, a time of adsorption, the primary concentration , PH and temperature, also showed that the adsorption is subject isotherms Freundlich and Temkin in low temperature ,thermodynamic studies in this research show that the adsorption Spontaneous and process exothermic.

5- Future studies:

1-The use of other types of waste plants in pollution treatment.
2-Use Eucalyptus plant Peels powder in sewage treatment and recovery of heavy metals.
3-Use other types of dyes in pollution treatment.

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