

## Thermodynamics and Kinetics of Adsorption of Eriochrome Black-T from Aqueous Media on Rice bran and on its coal

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### Abstract

The commercially rice bran and its coal were used for the adsorption of eriochrome black-T dye from aqueous solutions. The effect of solution pH, initial dye concentration, temperature and adsorption time on dye removal were studied using UV-Visible spectroscopy technique at  $\lambda_{max} = 541 \text{ nm}$ . The equilibrium time was found to be 30 minutes on each surface. The best results were achieved at  $\text{pH}=3$  and  $T= 293 \text{ K}$ . The equilibrium adsorption isotherm have been analyzed by linear Freundlich and Langmuir models. The thermodynamic parameters,  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  were calculated. The negative value of  $\Delta H$  indicates that the adsorption process is exothermic. The kinetic of the adsorption on each surface was analyzed using the pseudo – first order and pseudo second order kinetic models . The adsorption of the dye on rice bran is higher than that on its coal .Key words:- rice bran, coal , Adsorption isotherms. Thermodynamics and Kinetics of dsorption.

### الخلاصة

استخدم سطح قشور الرز وفحمه لدراسة امتزاز صبغة اريو كروم – تي الاسود من المحاليل المائية وتم دراسة تأثير حامضية المحلول pH ، التركيز الابتدائي للصبغة ، درجة الحرارة وزمن الامتزاز على إزالة الصبغة باستخدام تقنية مطيافية الأشعة المرئية – فوق البنفسجية عند الطول الموجي الأقصى للصبغة ٥٤١ نانوميتر. وجد إن أفضل النتائج لعملية الامتزاز هي عند اقل حامضية ( $\text{pH}=3$ ) ودرجة حرارة المختبر ٢٩٣ كلفن . كذلك أوضحت النتائج أن معلومات الاتزان لعملية الأمتزاز كانت في تطابق مع ايزوثيرم فرنديش و لانكماير. وتم حساب قيمالدوال الترموديناميكية  $\Delta G$  و  $\Delta H$  وكذلك  $\Delta S$  وجد أن القيمة السالبة  $\Delta H$  دللت على إن عملية الامتزاز باعثة للحرارة. حلت حركية الامتزاز لكلا السطحين باستخدام نموذجي الحركية الرتبة الأولى الكاذبة والرتبة الثانية الكاذبة وكذلك وجد أن امتزاز الصبغة على سطح قشور الرز هو أعلى مما هو على فحمه.

### Introduction

Textile dyeing process is an important source of contamination responsible for the contamination responsible for the continuous pollution of the environment (1). Colour is a characteristic of waste-water, which is easily detected . Control of water pollution has importance for both organisms , which live in water and those who benefit from water .

Many dyes reaching the water source are difficult to decompose and cause many problems due to their carcinogenicity(2,3). Consequently , it is important to remove these pollutants from wastewater before final disposal.

The method of color removal from industrial effluents includes biological treatment, coagulation ,flotation ,adsorption and hyperfiltration ,Among the treatment options, adsorption has become one of the most effective and comparable low cost method for the decolourization of textile wastewater (4,5).

The largest class of dyes used in textile processing industries are almost azo compounds i.e. molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designated to be chemically and photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic.

Most conventional adsorption use activated carbon which is an expensive material. There is growing interest in using commercially available low-cost materials for the adsorption of dyes including natural clay(6) wood chips(7) cotton and natural cellulose(8).

Rice bran from rice (*Oryza sativa* L.) is a by-product of making polished rice from brown rice. Therefore rice bran is very inexpensive. Rice bran has a good adsorptive activity against different substances including dyes such as neutral red(9). The walls of some plant cells contain the hydrophobic polymer lignin or suberin that may produce surface activity(10). Eriochrome black T dye has been studied using activated charcoal as adsorbent (11).

The present work involves the study of the adsorption of Eriochrome black T by commercial rice bran and its coal at different temperatures and pHs. In addition the kinetic analysis was conducted to investigate the mechanism of dye adsorption.

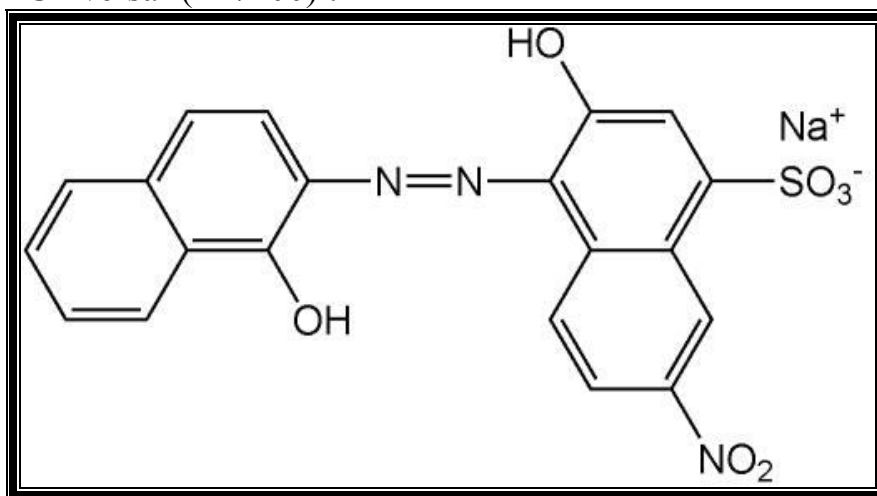
## **Experimental**

### **Material and Apparatus**

**Adsorbates:** dye were used as adsorbates Eriochrome black – T (EBT) was supplied by Fluka (scheme -1). pH values of (3-11) were prepared using (0.01)M of buffer solution (ammonium hydroxide, acetic acid and ammonium).

**Adsorbents:** A commercial rice bran was supplied from locally market.

**Apparatus:** All absorbance measurements were carried out on a Shimadzu UV-VIS 1700 digital double beam recording spectrophotometer using 1cm glass cells, Japan. A digital pH meter, 720 WTW 82362 Denmark was used. Centrifuge tubes, Hettich Universal (D-7200).



1-[1-hydroxy-2-naphthol azo]-6-nitro-2-Naphthol-4-sulphonic acid sodium salt

**Scheme 1- Structure of EBT**

**Adsorption studies**

Commercial rice barn (*Oryza sativa* L.) was cleaned, washed with excessive amount of water and dried at 50° c for one hour and kept in an airtight container . The coal of rice bran was prepared by taking an amount of rice bran was burned in an oven at 300° c for two hours , cooled to room temperature and kept in an airtight container .

Solutions of different concentrations of erichrome black T dye ( 3-18 ppm) were prepared by serial dilution . Absorbance values of these solutions were measured at  $\lambda_{\text{max}} = 541 \text{ nm}$  and plotted against the concentration values . The calibration curve in the concentration range that falls in the region of applicability of Beer – Lambert's law was employed .

**Effect of contact time**

For the purpose of finding out the equilibrium time , experiments were performed using a 30 ml aqueous solutions of the dye ( 9.0 ppm) and was shaken together with ( 0.05) g of each adsorbent for different intervals of time ranging from 10 to 60 minutes . The absorbance of the supernatant was measured by the spectrophotometer at the  $\lambda_{\text{max}}$  of the dye . The adsorption of the dye increased with increasing the shaking time and then attain constant value when equilibrium was established . The equilibrium time was found to be 30 minutes which was used for all further adsorption studies.

**The weight of the adsorbent**

Portions of the dye solutions (30 ml) of known initial concentrations (9.0 ppm) and varied amounts of each adsorbent (0.01 – 0.29) were added in the flasks . The absorbance values of these solutions' were measured at  $\lambda_{\text{max}} = 541 \text{ nm}$  after 30 minutes (equilibrium time) . The best weight of each adsorbent was found to be ( 0.05) g.

**Calculation the quantity adsorbed**

The quantity of the dye adsorbed on each surface was calculated according to the following equation(12):-

$$Q_e \text{ or } x/m = \frac{V(C_0 - C_e)}{m}$$

x : the quantity adsorbed

m : weight of the adsorbent (g)

C<sub>0</sub> : initial concentration(mg /l)

C<sub>e</sub> : equilibrium concentration (mg / l)

V : volume of solution ( l ) .

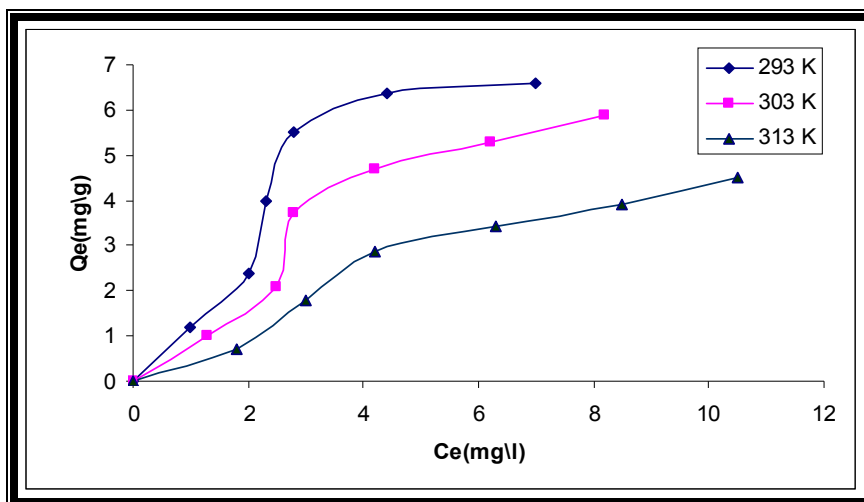
**Kinetic studies**

The kinetic studies was performed by adding a 0.05g of each adsorbent was added to 30 ml of the dye solution with initial concentration ( 9 ppm) and stirring . The temperature was held constant at 30°c with a thermostatic shaker . After different time intervals (5-30 minutes ), the absorbance of filtrate at each time was measured spectrophotometrically.

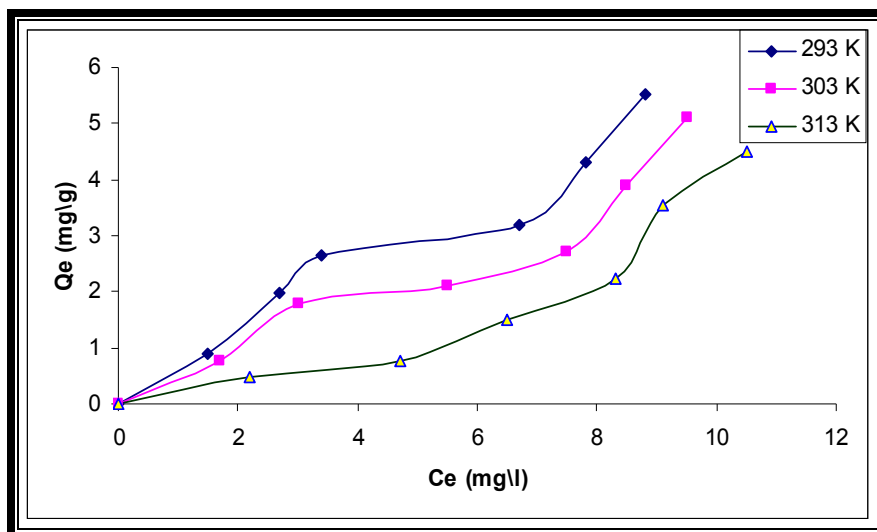
**Result and Discussion**

**Adsorption Isotherms**

The amount of dye adsorbed  $x/m$  (mg.g<sup>-1</sup>) is plotted against the equilibrium concentration  $C_e$  (ppm) to obtain the adsorption isotherm. The adsorption isotherms of the dye on each surface at 293 , 303 and 313 K are represented in figure 1 .and 2. The adsorption isotherm of dye on rice bran is of type S2 and on its coal of S3 .



**Fig: 1-Effect of temperature on the adsorption capacity of(EBT)dye with rice bran at pH=7.**



**Fig: 2-Effect of temperature on the adsorption capacity of(EBT)dye with coal of rice bran at pH=7.**

The experimental equilibrium adsorption data were analyzed by using Freundlich and Langmuir isotherms(equations 1 and 2)

Freundlich isotherm  $q_e = KF C_e^{1/n}$  ----- (1)

Langmuir isotherm  $q_e = (ab C_e) / 1 + bC_e$  ----- (2)

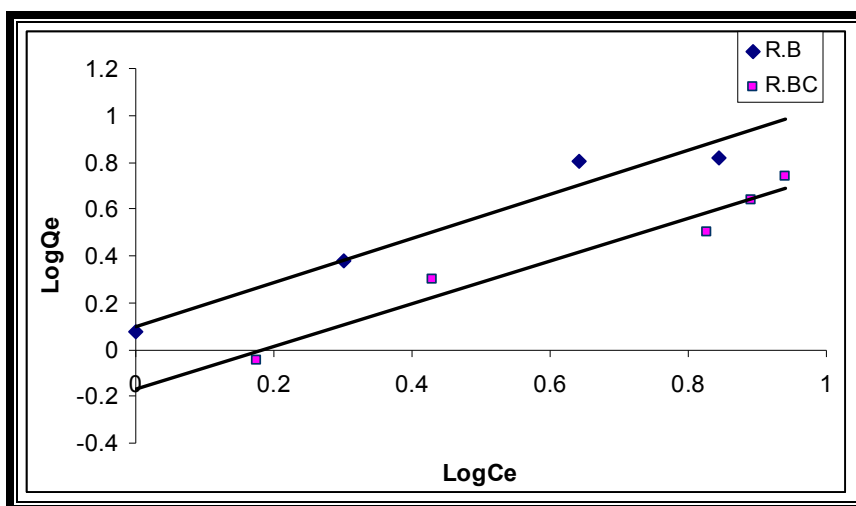
Where (KF) parameter is relative to the adsorption capacity and (n) is a measure of adsorption intensity . The constant (a )represents practical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate. The constant( b) is the equilibrium adsorption constant which related to the affinity of the binding sites ( Table 1 ) .

The Freundlich and Langmuir adsorption parameters were determined by converting the corresponding equations in the linear forms (equations 3 and 4)

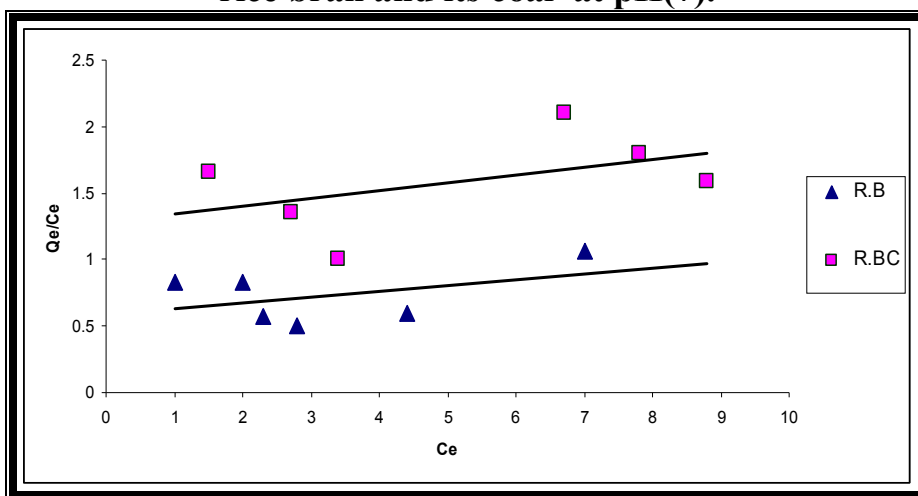
$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ log } C_e \text{ ----- (3)}$$

$$C_e / q_e = 1 /ab + C_e /a \text{ -----(4)}$$

The results show the applicability of Freundlich and Langmuir equations as indicated from Figures 3 and 4.



**Fig :3- Freundlich adsorption isotherm of (EBT)dye with rice bran and its coal at pH(7).**



**Fig :4- Langmuir adsorption isotherm of (EBT)dye with rice bran at pH(7).**

Binding parameters of the adsorption of dye on each rice bran and its coal , calculated from intercepts and slopes of these plots , are represented in Table 1 together with the correlation coefficients ( R<sup>2</sup>) as a goodness of fit criterion .

**Table/1- Freundlich and Langmuir constants for the adsorption of riochrome Black T on using residual of rice bran and its coal .**

Adsorbent	Eriochrome Black T					
	Freundlich con.			Langmuir con.		
	R <sup>2</sup> F	n	KF	R <sup>2</sup> L	a	b
rice bran	0.908	1.06	1.20	0.90	0.1	0.129
Coal	0.908	1.09	0.67	0.9623	0.40	6.6-

It is clear from Figure 1 and 2 that adsorption decreased with increasing temperature, indicating exothermic process . This may be explained on the basis that the solubility of the dye is increased at higher temperature and adsorbate – adsorbent interactions decreased resulting into decreased adsorption .This also indicated that desorption steps increase at higher temperature than adsorption(13 ,14).

The eriochrome black T dye is consisting of polar and non – polar portions .

The sulphonic acid group is susceptible to electrostatic interactions with the adsorbent surface , whereas , non polar portions play an important role in hydrophobic interactions ( Van der Waals bonds)(15) .

Due to the negatively charged characteristics of rice bran in aqueous media , the anionic dye should be adsorbed more rapidly than cationic dye .The results obtained here indicate the effect of coulombic interactions between the adsorbent and dye

### Thermodynamic Study

In order to fully understand the nature of adsorption ,the thermodynamic studies play an important role. removal of eriochrome black T using rice bran and its coal has been studied at 293to 313K. determine the adsorption isotherms and thermodynamic parameters, thermodynamic parameters, i.e free energy ( $\Delta G$ ) enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ). changes were also calculated using Eqs. (5-7) .

$$\Delta G = - RT \ln K \quad \text{----- (5)}$$

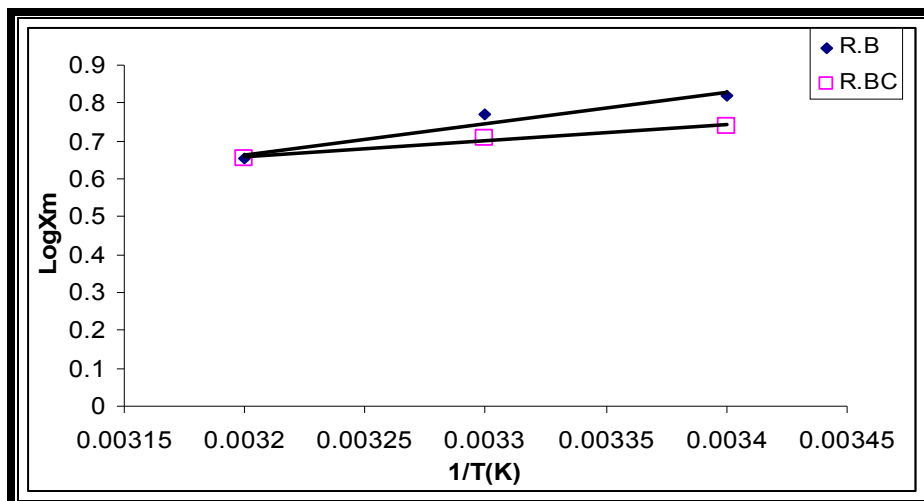
$$\log X_m = \frac{\Delta H}{2.303 RT} + \text{constant} \quad \text{-----(6)}$$

$$\Delta S = (\Delta H - \Delta G) / T \quad \text{----- (7)}$$

Where R is the gas law constant and T is the absolute temperature .  $\Delta H$  for each adsorbent was calculated from the slope of linear dependence of  $\log X_m$  on  $1/T$  ( Figure 5 ). The values of parameters are represented in Table 2 .

The positive value of  $\Delta G$  confirms that the adsorption of EBT on rice bran and its coal is non spontaneous process. The negative values of apparent enthalpy change show an exothermic physical adsorption(16,17).

The negative entropy values suggesting an increase in orderliness of the system



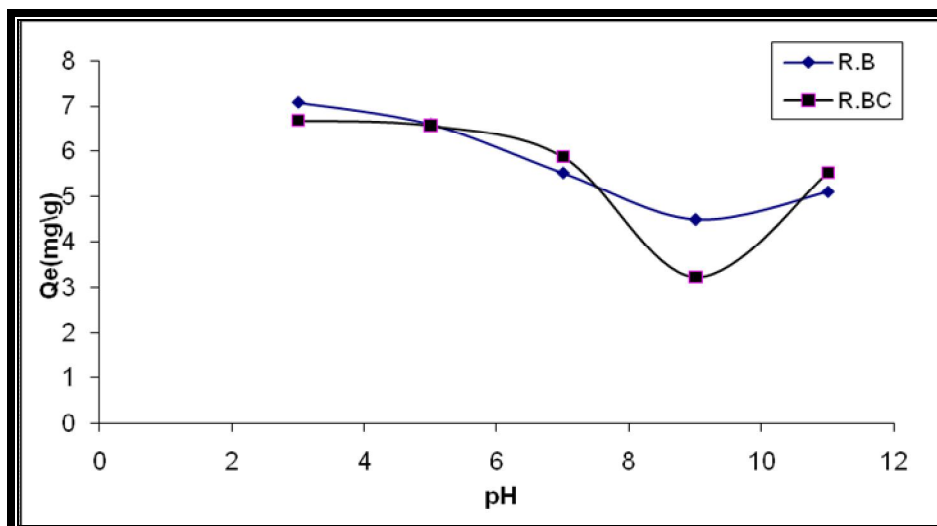
**Fig 5:-Relationship between the Log Xm and 1/Tof dye with rise bran and its coal**

**Table/3- Thermodynamic values of Eriochrome Black T in aqueous solution using residual of rise bran and its coal as an adsorbents .**

Adsorbent	H KJ.mol- $\Delta 1$	G KJ. mol- $\Delta 1$	S J.mol- $\Delta 1.k-1$	Cos.
rice bran	-10.56	0.14	53.6-	-1.9
coal	-8.4	1.13	-32.56	-0.75

**Effect of pH**

The adsorption capacity of the dye on each surface over a broad range of pH at room temperature is shown Figure 6. At high pH the sulphonic acid group is completely deprotonated which make the dye molecule more soluble in water, and so the adsorption is decreased with increasing pH. It may be is also that the surface properties of rice bran are depended on pH of the solution



**Fig: 6-The relation of the amount of adsorbent with different pH of solution of(EBT)dye at293K.**

**Kinetic study**

The kinetics of the dye adsorption onto each rice bran and its coal was investigated using two different models ,the pseudo-first order and pseudo-second order kinetics.

The pseudo-first order (Lagregren model) ,traditionally used for describing adsorption kinetics, is generally expressed by the following equation :

$$\log (q_0 - q_t) = \log q_0 - k_1 t \text{-----(8)}$$

where  $k_1(\text{min}^{-1})$  is Lagergren rate constant of the first order adsorption , evaluated from the slope of the plot  $\log (q_0 - q_t)$  versus  $T$  (Figure 7).

According to the pseudo – second order model, the dye adsorption kinetic is described by the following equation :

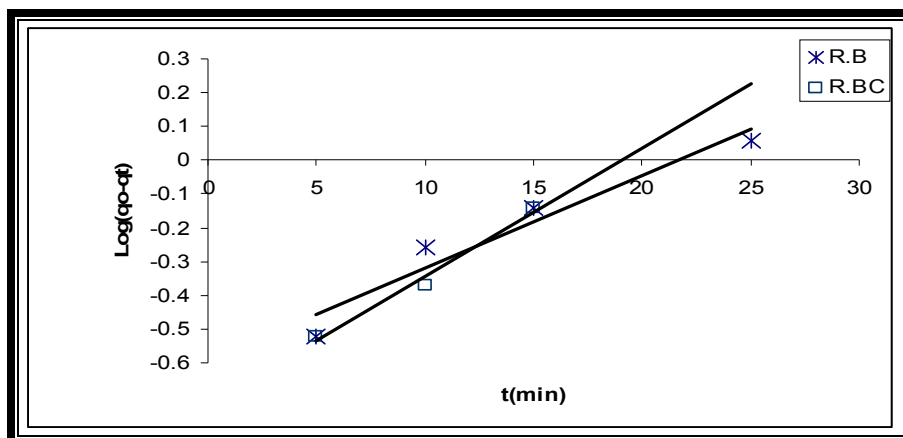
$$t / q_t = 1 / k_2 q_0^2 + t / q_0 \text{----- (9)}$$

Where  $k_2$  is the rate constant of second order adsorption ( $\text{g} / \text{mg} \cdot \text{min}$ ) and  $k_2 q_0^2 = h$  is the initial adsorption rate ( $\text{mg} / \text{g} \cdot \text{min}$ )

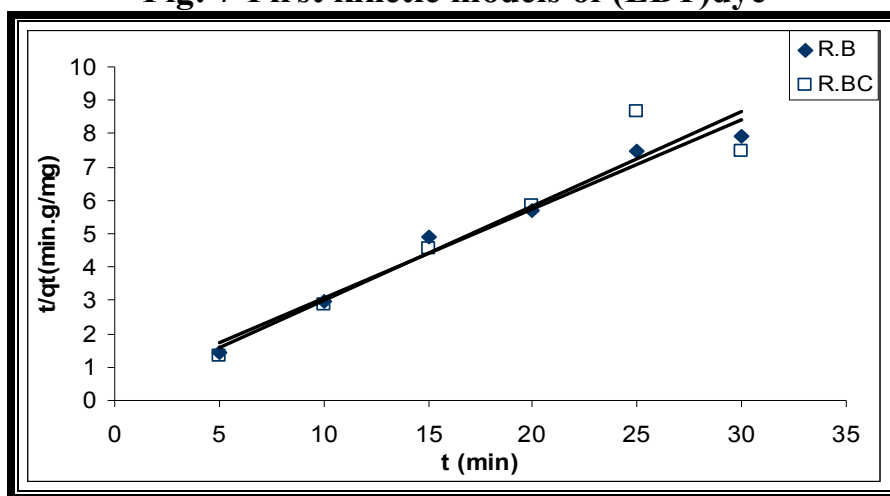
By plotting  $t / q_t$  versus  $t$  (Figure 8) a straight line could be obtained and  $q_0$  ,  $k_2$  and  $h$  can be calculated .

The experimental kinetic data were adjusted according to the indicated models and the coefficients of correlation as well as the kinetic parameters of the dye adsorption on each rice bran and its coal are given in Table 3 .





**Fig: 7-First kinetic models of (EBT)dye**



**Fig: 8-Second kinetic models of (EBT)dye**

**Table/3- The Kinetics parameters of Eriochrome Black T on rise bran and its coal.**

Adsorbent	Pseudo-first kinetic model		Pseudo-Second kinetic model		
	k (min-1)	R2	k (g /mg. min)	h (mg/g.min-1)	R2
rise bran	0.087	0.98	1.8	26.2	0.97
coal	0.62	0.93	2.32	37.2	0.90

The adsorption capacity on coal is much higher than that of the rice bran . The rate of adsorption Eriochrome Black T on coal was found to be greater than those for rice bran. The results of Table(3) showed that second order equation model provided the best correlation with experimental results. It can be said that the adsorption process may involve more than one step ,calling upon the transfer by a diffusion layer, or an interface of diffusion, and the intraparticle diffusion .The intraparticl diffusion step of the adsorption processes ,which certainly should affect the adsorption of dye on the substrates .

### **Conclusions**

Rice bran is efficiently utilized as an adsorbent more than its coal for the removal of eriochrome black T dye from the aqueous solution. The adsorption of the dye was found to decrease with the increase in temperature and pH. The negative values of  $\Delta H$  show that the adsorption on each surface is exothermic, and spontaneous on rice bran (negative  $\Delta G$ ) but non spontaneous on the coal of rice bran (positive  $\Delta G$ ). The process of adsorption is relatively fast and kinetic adsorption data fitted well to the second order kinetic model, indicating an intraparticle diffusion mechanism.

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