ADSORPTION OF DYE RHODAMINE B BY IRAQI BENTONITE CLAY

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Abstract

In this study, the adsorption of dye (Rhodamine B) by bentonite clay was investigated. Bentonite clay showed significant adsorption of this dye from aqueous solution.

The langmuir and frendlish isotherm equations were applied to the data and values of parameters of these isotherm equations were evaluated. Kinetics study was made using lagergreen equation and a first order equation was obtained and the rate constant of adsorption was calculated.

Introduction

Widespread contamination of soil and groundwater by synthetic organic chemicals (eg., dyes) has been recognized as an issue of growing importance in recent years. Most of these compounds are potential or known human carcinogens and of considerable health concern, even at low concentrations. For this reason, the fate and transportation of these compounds have been the" subject of much research.

Methods for decolorization have therefore become important in recent years. In principle, decolorization is possible with one or more of the following methods: adsorption, precipitation, chemical degradation, photodegradation and biodegradation [l].

The purification of waste waters contaminated by hazardous pollutants of inorganic and organic nature is among the serious problems of conservation, especially when such toxic materials (eg., dyes) contaminating the environment even in insignificant concentrations, are involved. The elimination of such pollutants from aqueous solution is an important problem not only from a technical but also from an economic point of view. Discoloration in drinking water may be due to the presence of colored organic substances or highly colored industrial wastes. Highly colored, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is not known. Synthetic dyes represent a relatively large group of organic chemicals which are encountered in practically all spheres of our daily life.

It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on humans. In order to minimize the possible damage to people and the environment, several studies have been conducted around the world [2-5].

Adsorption techniques have proven successful in removing colored organic species, with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials[6]. However, due to its high cost and the difficulty of regeneration, effective adsorbents such as bentonite clay derivatives is needed.

Although there is some literature available on equilibrium and kinetic studies on the adsorption of dyes on natural clay, there is only a limited amount of data pertaining to the adsorption of dyes on Iraqi bentonite clay. Valuable data in this field pertains to the adsorption capacities, kinetic studies and adsorption Isotherms of dyes on bentonite derivative adsorbents. No data on parameters, such as initial concentration or starting adsorbent mass, was outlined in the literature[7-8].

Materials and methods

The bentonite clay size 75 μm used in this study was supplied by Geological scanning company and has the following composition (by weight):

% SiO_2	% Al_2O_3	% CaO	% MgO	% K_2O	% Na_2O	% Fe_2O_3	% L.O.I
56.77	15.67	4.48	3.42	0.60	1.11	5	12.49

First, synthetic aqueous dye solution of (100) mgL^{-1} (as stock solution) were prepared for adsorption studies. Then, the synthetic aqueous solution of dyes were diluted to the concentration ranging from 1 to 20 mgL^{-1} , using distilled water.50 ml from each solution of dye was shaked with 0.5 g of bentonite clay for 30 min using a rotary GRIEFIN shaker (100 rpm). All experiments were carried out in a round bottom 250 ml flasks at five temperature in the rang (293-313) K.

To determine the wave length that give highest absorbance (A) for Rhodamine B dye, Shimadzex uv-visible recording spectrophoto-meter type. UV-160 in the wave length ranging (200-1100) nm was used. Fig.(l) show the UV-visible absorption spectrum .for the dyes solution with concentrations ranging (1-20) mgL^{-1} .

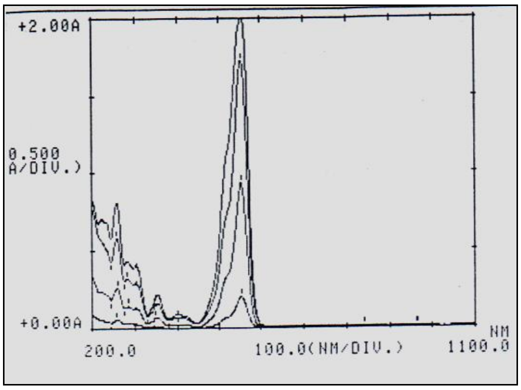


Fig.(1) : UV-Visible absorption spectrum for dyes solutions with concentration ranging (1-20) mgL^{-1}.

A calibration curve Fig.(2). Used to follow the dye concentration before and after adsorption process.

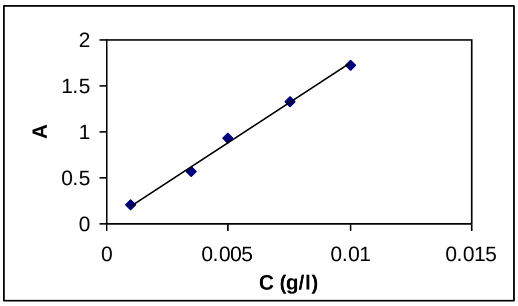
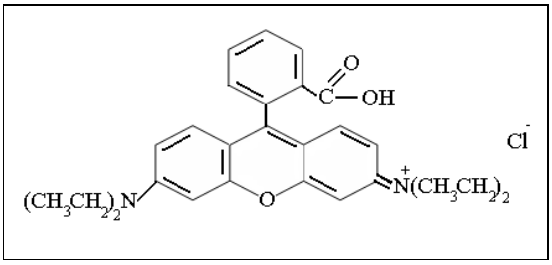


Fig. (2): Calibration curve of adsorption Rhodamine B dye at (λ_{max}=554).

To study the kinetic of dye adsorption, different shaking time including (5, 6, 7, 8, 10, 25, 40, 60) minute at a constant temperature of 298 K have been carried out, this study was repeated at (293, 298 and 303) K. Rhodamime (B) has the following structure:



With Fw=416.87 and X_{max}=554.

Theoretical consideration: Adsorption equations

The Batch Equilibrium Test (BET) is used to determine the adsorption characteristics of bentonite by blotting their adsorption isotherms. From the experimental results, The amount of dye removed from the solution per gram of clay sample Q (mg/g) after 30 min. of testing can be calculated using the equation below[9]:-

$$Q = \frac{V_{soln.}(C_o - C)}{m} \quad ....(1)$$

Where, Co is the initial concentration of dye (mgL^{-1}), C is the equilibrium concentration of dye in solution after the experiment (mgL^{-1}), m is the mass of bentonite (g) *and* V is the volume of solution (L).

Solid-liquid equilibrium can be easily described by adsorption isotherms. The Langmuir equation is the mathematical function most commonly used to describe this process.

The Langmuir isotherm can be expressed as:-

$$Q = \frac{K_L C_e}{1 + aC_e} \quad ....(2)$$

The linear form of the Langmuir isotherm equation is represented in the following formula(10):

$$\frac{C_e}{Q} = \frac{1}{K_L} + \frac{a}{K_L}.C_e \quad ....(3)$$

where Q= amount of dye adsorbed per unit weight of adsorbent (mg g-1), Ce=Concentration of dye remaining in solution at equilibrium (mg L-1), KL=a constant related to the energy or net enthalpy.

The equilibrium removal of dye considered can be mathematically expressed in terms of freundlish adsorption isotherm models as (11):

$$Q = K_f C_e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where:

Kf = sotherm parameters of adsorption capacity.

l/n = isotherm parameters of adsorption intensity.

This model is rearranged to the linear form by taking logarithms on both Sides(11):

$$\mathrm{Log}Q = \mathrm{Log}K_f + \frac{1}{n}\mathrm{Log}C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Results and discussions

The results concerning dye adsorption on bentonite are presented in Fig.(3) (a,b,c,d and e) by plotting the amount of removed dye (adsorbed) from solution (Q in mg/g) against the equilibrium concentration of dye in solution (Ce mg/L).

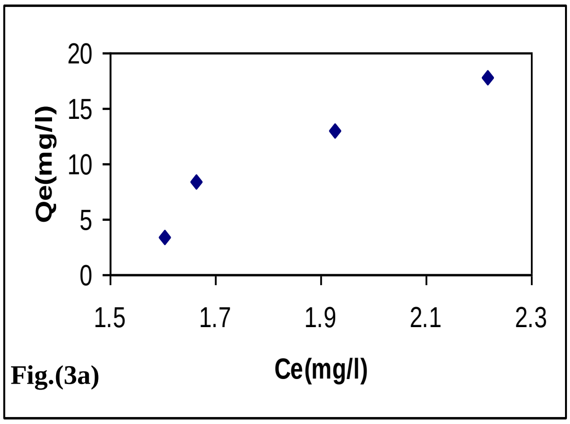


Fig.(3a)

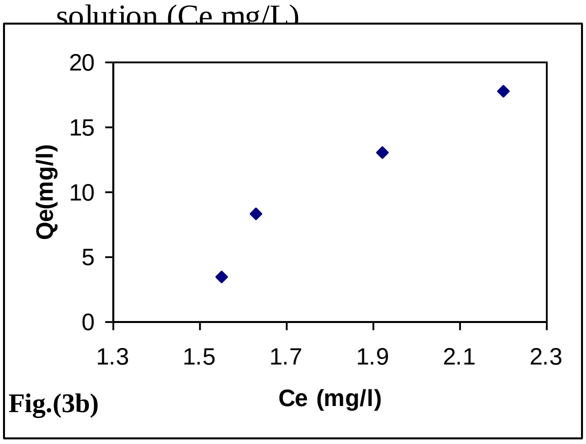


Fig.(3b)

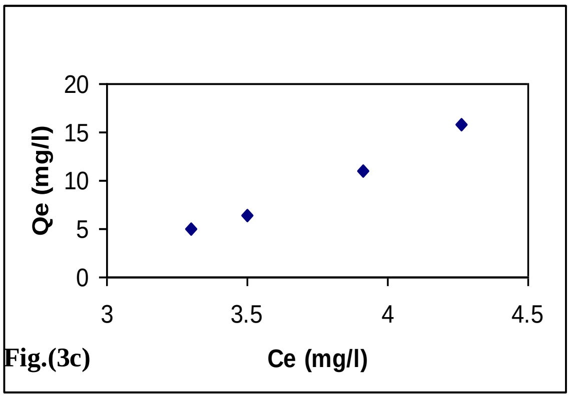


Fig.(3c)

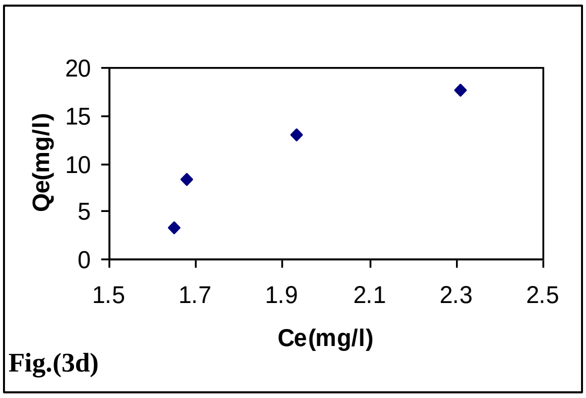


Fig.(3d)

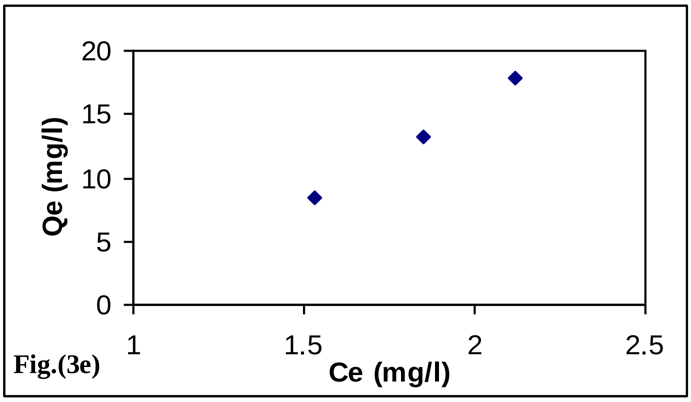


Fig.(3e)

Fig.(3): Adsorption isotherm of Rhodamine B on bentonite at different temperatures.((3a) at 293 K, (3b) at 298 K, (3c) at 303 K ,(3d) at 308 K, (3e) at 313 K.)

It is obvious from fig.3 that the adsorption isotherms of Rhodamine B dye on Iraqi bentonite are S-type according to the Giles classification [(12)]. Plotting the experimental data Table (1) using eqn. (3) and (5) are shown in Fig. (4) and (5) (a,b,c,d and e) that both models give good fit for the data.

Table (1)
Adsorption isotherms parameter Ce, Q of Rhodamine B on bentonite at different temperatures.

Co mg/l	293 K		298 K		303 K		308K		313 K	
	C_e mg/l	Q mg/l	C_e mg/l	Q mg/l	C_e mg/l	Q mg/l	C_e mg/l	Q mg/l	C_e mg/l	Q mg/l
1	0	0	0	0	0	0	0	0	0	0
5	3.30	5.10	1.65	3.35	1.604	3.40	1.55	3.45	0	0
10	3.50	6.5	1.68	8.32	1.663	8.34	1.634	8.365	1.53	8.47
15	3.91	11.09	1.93	13.07	1.926	13.07	1.917	1.308	1.85	13.15
20	4.26	15.74	2.31	17.69	2.22	17.78	2.197	1.78	1.12	17.88

Table (2)
Frendlish and langmiur parameter at different temperature.

T (K)	r	n	K_f	K_L	a x 10^3	r
293	85460.	0.1236	3.445×10^{-17}	0.0498	0.2083	0.9858
298	0.8087	0.2139	2.174×10^{-10}	0.2188	0.3202	0.7905
303	0.9529	0.1894	4.9581×10^{-12}	0.1750	0.3672	0.7873
308	0.8690	0.2351	2.0×10^{-9}	0.1940	0.3578	0.8904
313	0.9960	0.3944	1.063×10^{-4}	0.3080	0.3007	0.9960

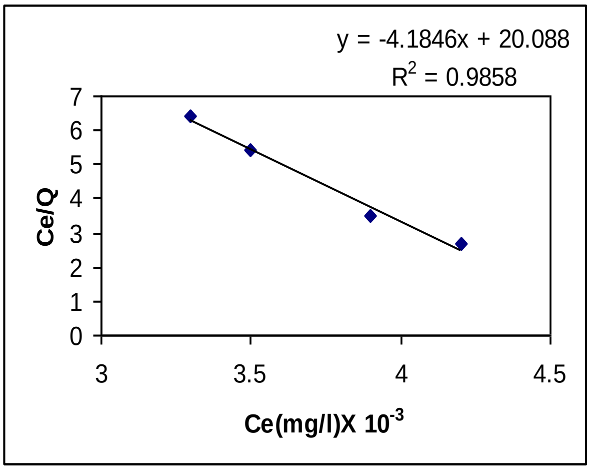


Fig.(4a)

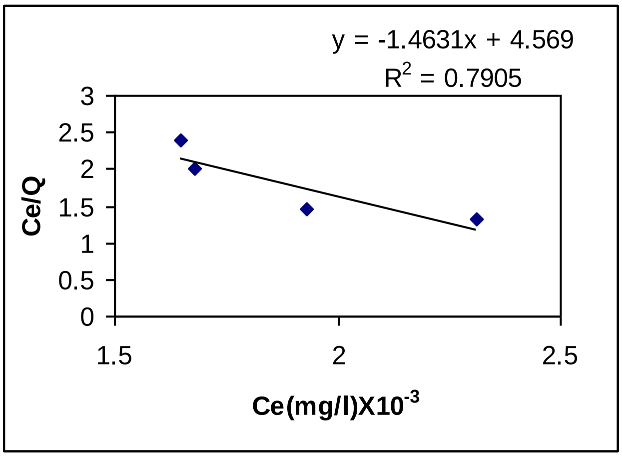


Fig.(4b)

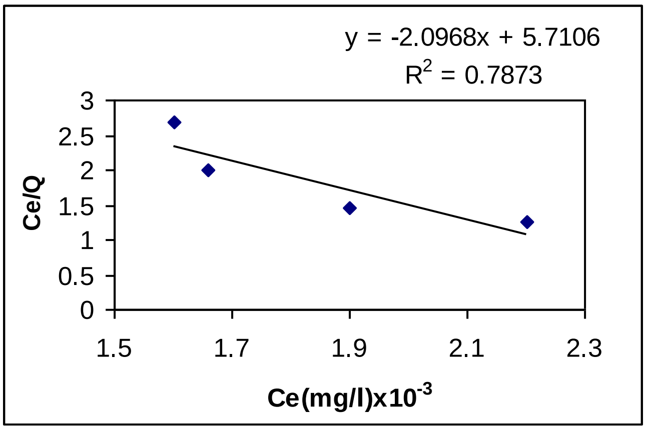


Fig.(4c)

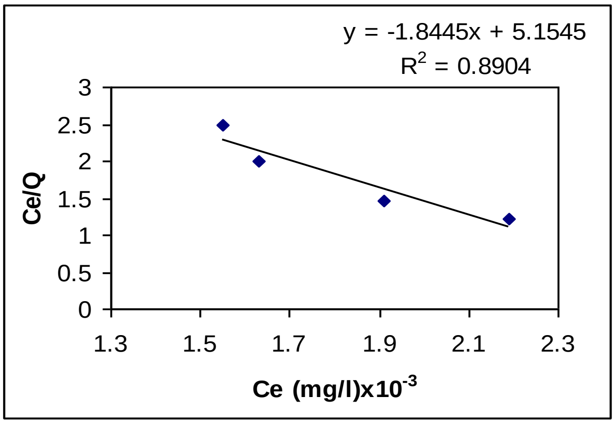


Fig.(4d)

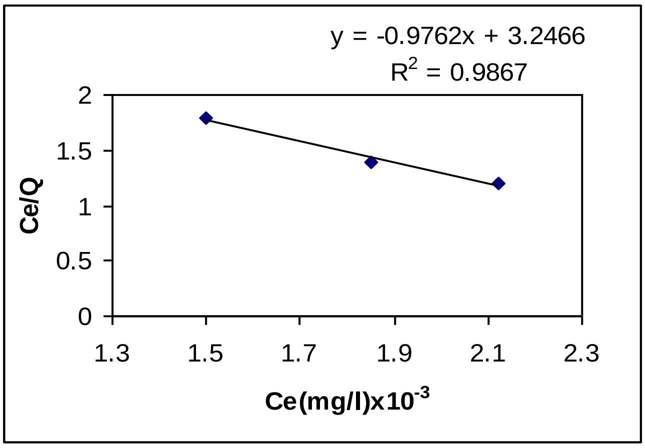


Fig.(4e)

Fig. (4): Langmuir plots bentonite /dye system at different temperature.((3a) at 293 K, (3b) at 298 K, (3c) at 303 K ,(3d) at 308 K, (3e) at 313 K.)

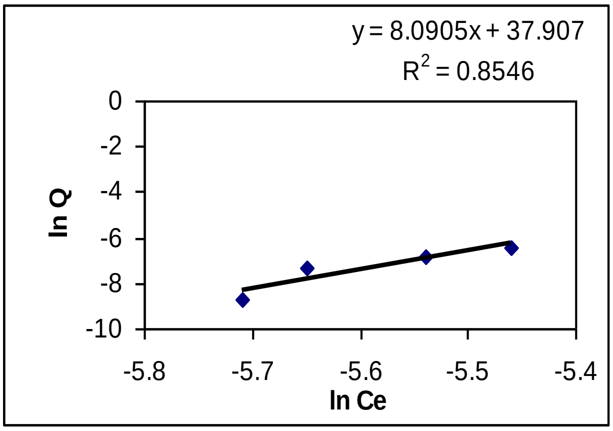


Fig.(5a)

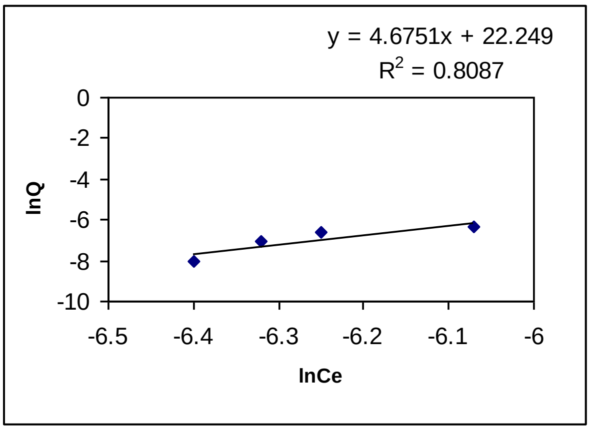


Fig.(5b)

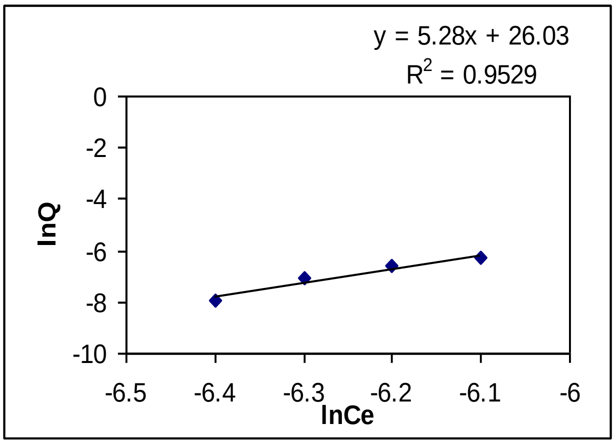


Fig.(5c)

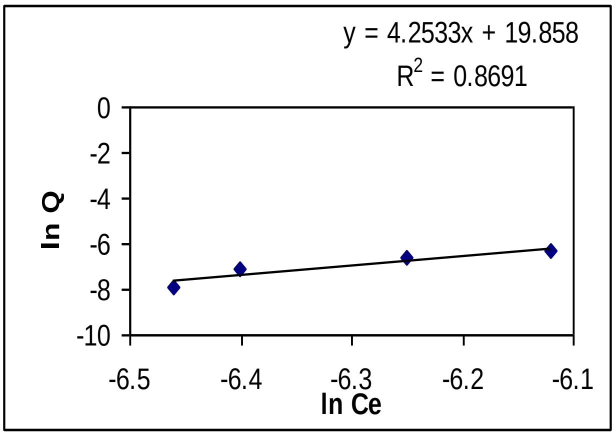


Fig.(5d)

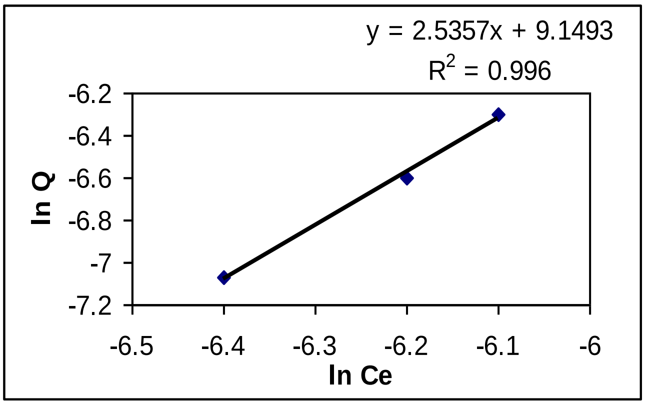


Fig.(5e)

Fig.(5): Friendlish plots for bentonite/dye system at different temperature.
((3a) at 293 K, (3b) at 298 K, (3c) at 303 K ,(3d) at 308 K, (3e) at 313 K.)

The values of K_L, a, K_f and (1/n) that best fitted the data as well as the corresponding correlation coefficients are presented in table 2. As it can be seen most of the adsorption isotherms fitted the Langmuir and frendlish equation with correlation coefficients reach to r>0.99. Many experimental isotherms conforming to a Langmuir isotherms involve monolayer coverage. The Langmuir model assumes that:

(a) Adsorption energy is constant and independent of surface coverage.

(b) Adsorption occurs at localized sites with no interaction between various ions in the solution.

(C)Maximum adsorption occurs when clay surface is covered by monolayer cations.

Langmuir equation, provide the parameter of maximum adsorption (a) and a constant related to bonding-energy of the adsorbate to the adsorbent (K_L). The highest maximum adsorption value took place at 303 K which equal to 367.17 and the lowest at 293 K equal to 208.31.

Values of K_L, was highest at 313 K equal to 0.308 and lowest at 293 K equal to 0.04978.

Table(3)
Kinetic data of adsorption (0.01mg/L) dye / bentonite at temperature rang (298-303)K and for (5,6,7,8,10) mints.

q_e (10^{-2})	Temp K	q_t (10^{-2})	qe-q_t (10^{-3})	-(lnq_e-q_t)
8.310	298	8.09	2.200	8.4219
		8.123	1.870	8.5807
		8.15	1.60	8.7403
		8.174	1.360	8.8959
		8.21	1.00	9.2103
8.3010	301	8.040	2.606	8.2525
		8.068	2.308	8.365
		8.088	2.128	8.455
		8.126	1.750	8.65
		8.173	1.128	8.965
8.2920	303	7.984	3.08	8.0854
		8.003	2.8914	8.1480
		8.008	2.84	8.1665
		8.069	2.224	8.4107
		8.129	1.63	8.718

The adsorption rate of dye which calculated from lagergreen equation [13] and first order equation was obtained at time ranging from 5 mints to equilibrium times shown in Table (3) and Fig.(6).

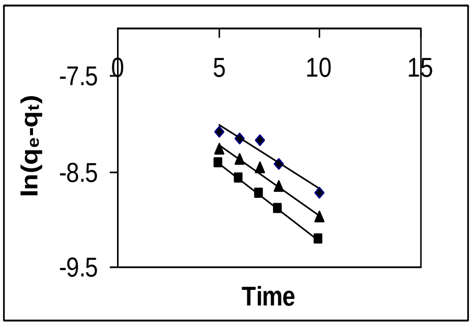


Fig. (6) : Relation between ln(q_e-q_t) and time.

Lagergreen equation has the following formula:-

$$Ln(q_e - q_t) = Lnq_e - K_{ad}t \quad ....(6)$$

Where q_e= The amount of removed dye at equilibrium

q_t = The amount of removed dye at (t) time

K_{ad}= rate constant of adsorption.

Rates adsorption experiment carried out at initial concentration equal to 0.01 mg/L of dye solution and at three temperatures (298,301 and 303)K. the values of K_{ad} at those temperature were:

T/K	298	301	303
K_{ad}/min^{-1}	0.1313	0.1444	0.1576

The activation energy (E_a) for dye adsorption can be obtained from the relation between ln (K_{ad}) and (1/T) when T=temperature (K).

As shown in Fig.(7) from the slope of Fig.(7) E_a can be obtained and it has little value 27.100 kJ which indicates physical adsorption between dye molecules in solution and the dye adsorbed at bentonite surface.

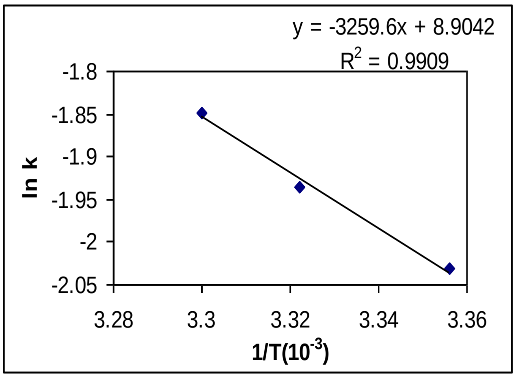


Fig.(7) : Arrhenns equation of adsorption of dye/bentonite.

Thermodynamic Results

The values of maximum adsorption (b) for dye/ bentonite at five temperatures (293, 298, 303, 308, 313) K, are reported in Table (4). Anther langmuir from equation [(14)]:

$$\frac{C_e}{Q} = \frac{1}{b} + C_e \text{ ....(7)}$$

Was used which give good fit for various temperatures.

Table (4)
Maximum adsorption at different temperature

$1/T^* 10^{-3}$	$b \times 10^3$	Log b
3.41	0.2083	2.3187
3.35	0.3202	2.5054
3.3	0.3672	2.5649
3.25	0.3578	2.5537
3.19	0.3007	2.4781

The thermodynamic parameters (ΔG, ΔH and ΔS_a) for dye/ bentonite adsorption can be calculated from the the following equations:

$$b = a\exp(-\Delta H_a / RT) \text{ ....(8)}$$

$$a = \exp(\Delta S_a / R) \text{ ....(9)}$$

$$b = \exp(-\Delta H_a / RT).\exp(\Delta S_a / R) \text{ ....(10)}$$

$$\mathrm{Logb} = \frac{-\Delta H_a}{2.303RT} + \frac{\Delta S_a}{2.303R} \text{ ....(11)}$$

$$\Delta G = \Delta H - T\Delta S \text{ ....(12)}$$

Fig.(8) show the relation between Log (b) and (l/T). Positive values of ΔH_a, indicate to existe of absorption process with adsorption (physical) and all sorption processes.

A diffusion process was occur inside the bentonite crevices and pores, so endothermic process was occurred.

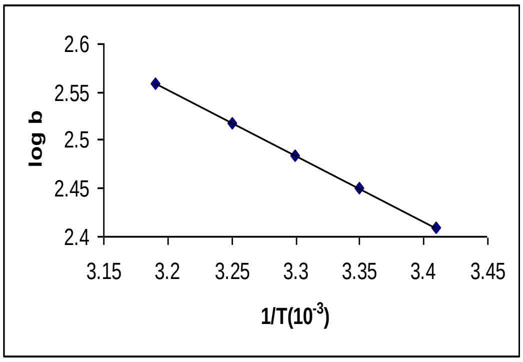


Fig. (8) : Relation of log b against (1/T) where (T/K).

Table (5): Thermodynamic parameter ΔG, ΔS and ΔH of dye/ bentonite adsorption at temperature rang (293-313) K.

T (K)	Δ G KJ mol^{-1}	ΔH KJ mol^{-1}	ΔS J $mol^{-1} K^{-1}$
293	-13.4147	13.200	90.835
298	-13.8683	=	=
303	-14.323	=	=
308	-14.777	=	=
313	-15.231	=	=

Conclusion

Rhodamine B can be removed completely from wast water specially in low concentration. The adsorption processes occur between the dye (with its spherical shape and positive charge) and negative site of hydroxyle group in the bentonite site surface.

The sorption (adsorption+absorption) process was endothermic and its not need to any activation energy.

At the end of adsorption studies, it can be said that bentonite may be used as an adsorbent for adsorption or decolorization of some textile dyes from waste solutions and modification of bentonite with some organic compound, requires further investigations to increase the bentonite adsorption capacity to remove anionic dyes and inorganic compounds.

References

[1] H. Zollinger, Color Chemistry, VCH publicshers Inc. New York (1991).
[2] R. Deoraj, R.D.Guy, clays and clay miner, Vol. 29, No. 3 , 1981, 205-212.
[3] G. S. Gupta, S.P. shuckla, G. Prasad, V.N. Singh, Environ. Tech.,Vol.13, 1992, 925-936.
[4] J. Ceners and Schoonheydt, Proceedings of the 9th International Clay Conference, Strasbourg, Vol. 85, 1990, 15-23.
[5] L. Margulies, H. Rozen, S.Nir, Clays and Clay Miner Vol. 36, 1988, 270-276.
[6] R.S. Juang,, Wu, F.C., and R.L., Tseng, "The ability of activated clay for the adsorption of dyes from aqueous solutions", Environmental Technology, Vol. 18, 1997, 525-531.
[7] H. K Lekaa. "Adsorption of some dyes on surface of white Iraqi Kaolin clay", Msc. Thesis, college of Education woman, University of Kufa, 2005.
[8] G. S Dawood "Adsorption study of lead ions on the surfaces at ion-exchange resin and some Iraqi clays." Msc. Thesis, college of science, Baghdad University, 2006.
[9] C. Ozlem and B.Demet, Turk. J.chem. Vol. 25, 2001,193-200.
[10] D.Ahmet, G. Ahmet and D. Eyyup, 155 N 0378-4738 : water SA Vol. 28 No.3 July 2002.
[11] MI. Bright Geological Society Engineering Special Publication Vol. 11: 1996, 159-164.
[12] C.H Giles, T.H. Macewan, S.N. Nakhwa, D. Smith, J. Chem. Soc, 1960, 3973- 3993.
[13]. N. T. Basta and M.A.Tabafabai: Effect of cropping systems on adsorption of metals by soils : п effect of PH. Soil Sci. Vol. 153, 1992, 195-204,.
[14] A.S. Khulood and J.M Saleh Ph.D. Thesis, College of Science University of Baghdad October 1997.

الخلاصة

تمت دراسة إمتزاز صبغة الرورامين B على طين البنتونايت العراقي وأظهرت النتائج كفاءة واضحة لامتزاز هذه الصبغة على طين البنتونايت العراقي وقد تم تطبيق النتائج على متساويات الحرارة للنكماير وفرند لش وتم حساب ثوابت هذين المتساويين الحراريين من معادلتي لنكماير وفرند لش . كما وتم متابعة حركيات الامتزاز باستخدام معادلة لكاكرين والتي تتبع المعادلة من الدرجة الاولى وتم حساب ثابت سرعة عملية الامتزاز على طين البنتونايت .