Thermodynamics and Kinetics of Adsorption of Alizarin Yellow 2G From Aqueous Solutions on α-Alumina

Alaa A.Azeez
Chem. Dept. ,College of Education , Univ. Mosul , Mosul, Iraq
(**Received:** 19 / 9 / 2011 ---- **Accepted:** 16 / 10 / 2011).

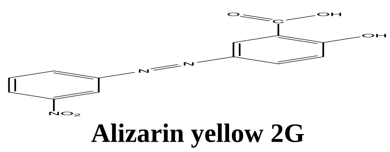
Abstract
α-alumina is used for the removal of the industrial dye (alizarin yellow 2G)from aqueous solution. The effects of contact time ,temperatures , initial concentrations and pH values have been investigated .Langmuir and Freundlich isotherms are fitted on the experimental data of adsorption of the studied system. Depending on the results obtained from the effect of temperatures , the thermodynamic parameters (ΔG°, ΔH° and ΔS°) are estimated.The work also included kinetic study conducted by applying two kinetic models, the pseudo first and second order equations . The results proved that , the studied system follows the pseudo second order model indicated by the agreement between the experimental and calculated values of adsorption capacity (q_e) at equilibrium .The concentration of the adsorbed dye is determined spectrophotometerically .

Introduction
Alumina Al_2O_3 is an industrially important chemical . It is naturally available or prepared in several forms for various commercial applications some of these are

1-α-Alumina (corundum)
2-Activated aluminas,such as γ -alumina, η-alumina and ρ-alumina
3-Hydrated aluminas including aluminum oxide monohydrate Al_2O_3 .H_2O and aluminum oxide trihydrate Al_2O_3 .$3H_2O$ (natural gibbsite)
4-Acidic, neutral and basic alumina (no definite chemical composition made by adding various amounts of water to activated aluminas).**[1]**The α-Alumina represents the stable phase of alumina (Al_2O_3) which is colorless ,rhombic crystals .Its melting point lies in the range between 2005 to 2025ºC.**[2,3]**The major use for alumina is in the production of aluminium metal. Other applications are in ceramics, refractories, abrasives, medicinal ,adsorbents and catalysts.The alumina is used as an adsorbent for the removal of a wide range of industrially important dyes from their aqueous solutions **[4,5]** Water pollution is caused from a discharge of dyes from pickling industries . Dyes are widely used in textile, paper, plastic, food and cosmetic industries. The discharge of the excess of dyes into the environment with the wastewater of such industries represents a great reason of pollution in which its treatment becomes a vital task. The level of pollution by such dyes even it was in a very low concentration is highly visible and will affect aquatic life as well as food web**[6,7]** The colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem**[8]** Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade , furthermore many dyes are toxic to some micro organisms and may cause direct destruction or inhibition of their catalytic capabilities **[9,10]** There are various conventional methods of removing dyes including coagulation, flocculation, ion exchange oxidation or ozonation and membrane separation .These methods are not widely used due to their high cost and economic disadvantage. Chemical and electro chemical oxidations, coagulation are generally not feasible on large scale industries .In contrast adsorption technique is by far the most versatile and widely used. The most common know adsorbent materials are : alumina, silica , metal hydroxides and activated carbon as proved by many researchers.**[11-13]**. Removal of dyes by activated carbon and mineral clay is economically favorable and technically easier.**[14-15]** In this study, the adsorption of alizarin yellow 2G from aqueous solution on the surface of α-alumina as a neutral adsorbent is investigated. The concentration of the adsorbed dye was determined spectrophoto meterically. Factors affecting the adsorption process are studied . Langmuir and Freundlich isotherms are fitted on the experimental data of the studied system. Kinetic study is carried out inorder to determine the type of forces and mechanism of attachment controlling the process .

Experimental
1-Adsorbent
α-alumina supplied by BDH was used as the adsorbent ,Alumina was dried at 250 °C for one hour before use . It has a specific surface area of (111)m^2/g and various pH ,in this work alumina used at pH(5,7and 9).

2-Preparation of stock solution of dye
The Alizarin yellow 2G was of a commercial purity,and it was used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 1000 mg/L. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to different concentrations.



Alizarin yellow 2G

3- Adsorbent dose and equilibrium time
In order to find out the optimum amount of adsorbent , a number of samples of the same concentration of

dye and the various amounts of alumina (0.02-0.12 g) were prepared. (0.1) g of the adsorbent showed optimum adsorption . The time of adsorption equilibrium was determined by preparing 50 ml of same concentration(10 ppm) of dye in eight flasks and (0.1) g of adsorbent is added to each sample . These samples were shaked for (10 -80) minutes using agitation speed (100 rpm) .The adsorption systems reached equilibrium after (1) hour.

4- Effect of concentration

The effect of concentration on the adsorption system was investigated under the optimized conditions of time and adsorbent dose (60 min ,0.1 g). The concentration of dye was varied from 10 – 50 (mg/L).Samples of different concentrations were shaked for (60 min) after addition 0.1g of adsorbent (α-alumina) and the capacity of adsorption is determined by equation(1) in the visible region using a spectrophotometer of (Cecil E1011) type.

$$q_e = \frac{Ci - Ce}{m} \times V \qquad \text{---(1)}$$

Where Ci and Ce are initial and remained dye concentrations (mg/L) at equilibrium respectively , qe is the adsorption capacity(mg/g) at equilibrium ,V is the volume of the dye solution (L) shaked and m is the weight(g) of adsorbent.

5-Effect of temperature

For studying the effect of temperatures ,several samples of the same initial concentrations of dye and by keeping other conditions constant were shaked under various temperatures (298 -328 K) The capacity of adsorption at each temperature was determined spectrophoto metrically .

6- Effect of time

In order to study the effect of contact time, various sample of the same concentration of dye and other optimized adsorption conditions were shacked for different periods between 10 -70 minutes. The samples were then filtered and the concentrations of adsorbed dyes are evaluated.

7-Effect of adsorbent pH

The effect of adsorbent pH on the adsorption system is conducted using three types of α-alumina ; acidic , neutral and basic as adsorbents , in which the natural pH of their aqueous solution are 5,7 and 9 respectively. The preparation of samples were carried out using the same initial concentration and same optimized conditions of adsorption system (amount of adsorbent , temperature and time). The percentage of adsorption at each pH is calculated by employing equation (2).

$$\%Adsorption = \frac{Ci - Ce}{Ci} \times 100 \qquad \text{---(2)}$$

Results And Discussion

As an initial step of this investigation ; a calibration curve is constructed for the alizarin dye at λmax 362 nm using several solutions of the dye of different concentrations .The dye is found to obey Beer's law as shown in Figure(1).

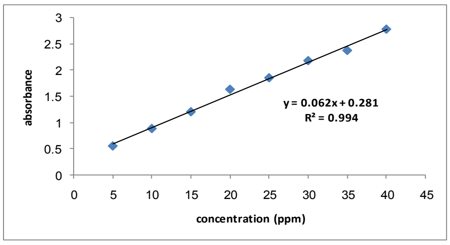


Figure 1: Standard calibration curve of alizarin yellow 2G at different concentrations (5-40 ppm)

Adsorption isotherms

Langmuir isotherm

The Langmuir isotherm is the best known linear model for monolayer adsorption and it is frequently utilized to determine the binding energy of adsorption systems .The Langmuir equation is given as below[16].

$$\frac{Ceq}{qe} = \frac{1}{bQ} + \frac{Ceq}{Q} \qquad \text{---(3)}$$

Where Ceq is the concentration of adsorbate in solution at equilibrium (mg/L) ,qe is the adsorption capacity(mg/g) at equilibrium ,b is the Langmuir constant related to the sorption energy (L/mg) and Q is the maximum amount of adsorbate that can be taken up per unit mass of adsorbent maximum(monolayer capacity) (mg/g) .

Freundlich isotherm

The Freundlich isotherm is one of the most known models that is frequently used for determination of adsorption parameters those are indicative to adsorption capacity and intensity of adsorption ,the linear form of the Freundlich model is given by the following equation [17].

$$Ln\ qe = Log\ K + \frac{1}{n}\ Log\ Ce \qquad \text{---(4)}$$

Where K and n are Freundlich constants related to the adsorption capacity and adsorption intensity respectively [18] The results obtained showed that, the adsorption of dye is decreased with increasing temperature, these results are listed in Table (1)

Table (1) : Effect of temperature on adsorption capacity at various initial concentrations

Temp(k°)	Adsorption capacity(qe) of initial concentration				
	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
298	2.39	4.27	5.16	7.18	8.95
308	2.20	4.07	4.93	6.96	8.70
318	1.99	3.56	4.82	6.06	8.49
328	1.85	3.36	4.57	5.77	8.15

The description of the experimental data by the Langmuir and Freundlich isotherms at different temperatures are shown in Figures (2) and(3) respectively

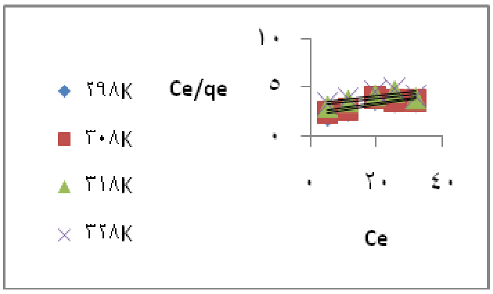


Figure 2: Linear plots of the Langmuir isotherms of the adsorption of alizarin yellow 2G on alumina at various temperatures.

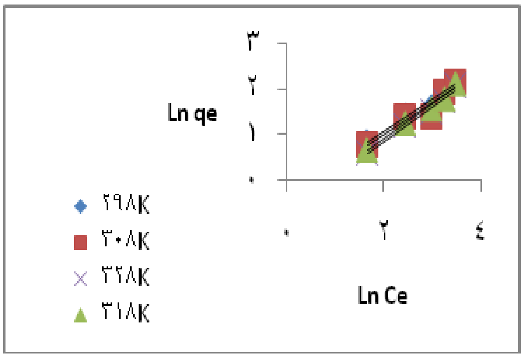


Figure 3: Linear plots of the Freundlich isotherms of the adsorption of alizarin yellow 2G on alumina at various temperatures.

The values of Langmuir constants ***Q*** and ***b*** were calculated from the slope and intercept of the linear plot of C_{eq}/q_e against C_{eq} , The decrease in ***b*** values with the rise in temperature indicates weakening of adsorbate – adsorbent interaction at high temperatures. The maximum monolayer capacity ***Q*** increased with increasing the temperature which could be due to, the increase of temperature activate further positions on the adsorbent surface that attached to the dye molecules. The values of Freundlich constants ***n*** and ***K*** are determined from the slope and intercept of the linear plot of Log q_e against Log C_{eq} respectively. The value of ***K*** is relative to the adsorption capacity of the adsorbent .It is found to increase with increasing temperature while the value of ***n*** describes the adsorption intensity in the adsorption system and reveals the ability of the adsorbate to connect on the rough surface. When the value of ***n*** lies between (1-10) indicates to the best adsorption of the adsorbate on to adsorbent .The values of isotherm constants are given in Table (2).

Table (2): Results of the application of Freundlich and Langmuir isotherms on the adsorption of Alizaren yellow 2G on the alumina

Temp.(Kelvin)	K	n	Q(m/mg)	b(L/mg)
298	1.32	1.44	18.18	0.025
308	1.60	1.38	20.40	0.019
318	2.15	1.25	24.39	0.013
328	2.53	1.20	27.02	0.010

Thermodynamic parameters

Thermodynamic studies are used to decipher any reaction in a better way .In the present study, the thermodynamic parameters, Gibbs free energy ΔG° (kJ/mol), change in enthalpy ΔH° (kJ/mol) and change in entropy ΔS° (J/mol.K) are estimated by employing the following equations.

$$Ln\ K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{---(5)}$$

$$\Delta G^\circ = -RT\ \text{Ln}\ K \quad \text{--------(6)}$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \text{---(7)}$$

Where K is the equilibrium constant ,R is the universal gas constant (J/mol.k) ,T is the temperature in kelvin .The values of ΔH° and ΔS° were calculated at different initial concentrations (10 ,20 and 30 ppm) from the slope and intercept respectively of the plots of Ln K versus the reciprocal of temperature (1/T) using Vant Hoff equation(Figures (4-6)).The thermodynamic parameters are given in Table (3).

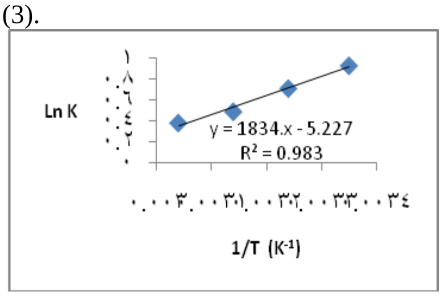


Figure 4: The relationship between Ln K and 1/T at 10 ppm

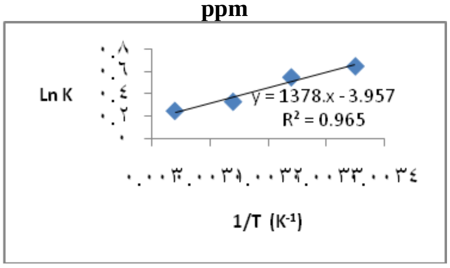


Figure 5: The relationship between Ln K and 1/T at 20 ppm

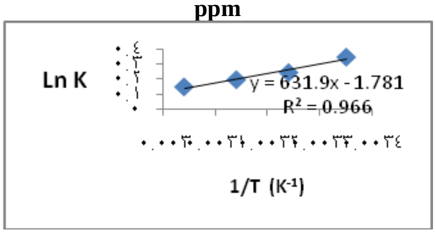


Figure 6: The relationship between Ln K and 1/T at 30 ppm

Table (3): Thermodynamic parameters of adsorption of Alizaren yellow 2G on alumina at pH 5.

Initial Conc(ppm)	Temp. °K	K	ΔH ($kJ.mol^{-1}$)	ΔG° ($kJ.mol^{-1}$)	ΔS° ($J.mol^{-1}.K^{-1}$)
10mg/L	298	2.54	-15.247	-2.309	- 43.42
	308	2.04		-1.823	
	318	1.63		-1.290	
	328	1.46		-1.030	
20 mg/L	298	1.91	-11.456	-1.602	- 32.89
	303	1.73		-1.403	
	318	1.39		-0.869	
	328	1.28		-0.670	
30mg/L	298	1.42	-5.253	-0.867	- 14.80
	303	1.28		-0.629	
	318	1.22		-0.523	
	328	1.15		-0.409	

The negative values of ΔG° at all different temperatures show that, the adsorption process is spontaneous .The negative values of ΔH refer to the exothermic nature of the studied system , while their values (< 40 KJ/mole) indicate that , physical forces are controlling the attachment between the dye and solid surface of adsorbent. The negative values of ΔS indicate the increase of the order in solid / solution interface due to the adsorption .

Kinetic of adsorption

Kinetic of adsorption is one of the most attractive characteristics to be responsible for the efficiency of adsorption ,both the Lagergren first order and pseudo second order kinetic models have been applied at different initial concentrations (10,20 and 30 ppm) for the experimental data to predict the adsorption kinetics . The adsorption capacity at various time (10-50 min) are given in Table (4).

Table (4): Effect of time on adsorption capacity at different initial concentrations

Time(min)	Adsorption capacity qt of initial concentration		
	10 ppm	20 ppm	30 ppm
10	1.34	2.83	3.93
20	1.70	3.15	4.28
30	1.80	3.33	4.60
40	1.91	3.51	4.93
50	2.01	3.67	5.27

The Lagergren first order kinetic model equation can be written as follows:

$$\text{Ln}\,(q_e - q_t) = \text{Ln}\,q_e - K_1 t \text{---}(8)$$

Where q_e is adsorption capacity at equilibrium , q_t is mg of dye adsorbed per g of alumina at time (t), K_1 is the Lagergren first order rate constant (min^{-1}) of the adsorption. The value of K_1 is calculated from the slope of the plots of Ln(q_e-q_t) versus time (t), as shown in Figures (7-9)

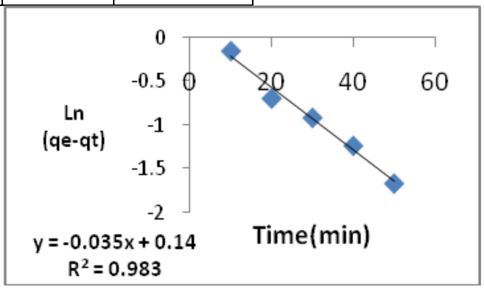


Figure 7: Lagergreen first order rate plot for the adsorption of alizarin yellow 2G by alumina at 10 ppm

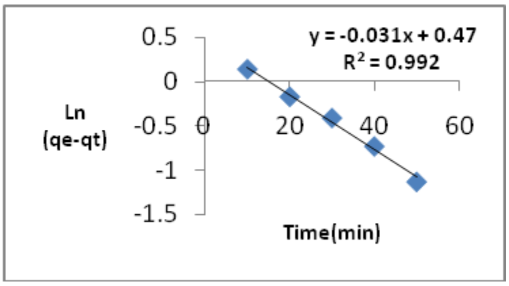


Figure 8: Lagergreen first order rate plot for the adsorption of alizarin yellow 2G by alumina at 20 ppm

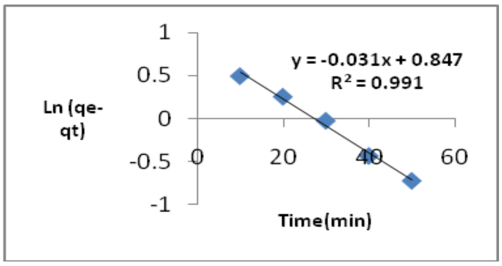


Figure 9: Lagergreen first order rate plot for the adsorption of alizarin yellow 2G by alumina at 30 ppm

The pseudo second order kinetic model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\,t \quad \text{---}(9)$$

Where K_2 is the pseudo second order rate constant. Value of K_2 is calculated from the slope and intercept of the plots of t/q_t against time (t) as presented in Figures (10-12).

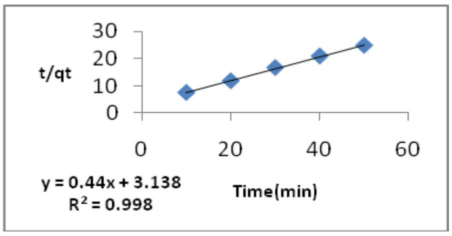


Figure 10: Pseudo second order rate plot for alizarin yellow 2G adsorption by alumina at 10ppm

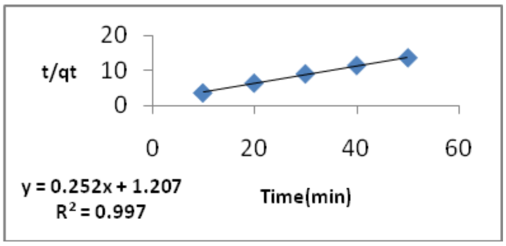


Figure 11: Pseudo second order rate plot for alizarin yellow 2G adsorption by alumina at 20ppm

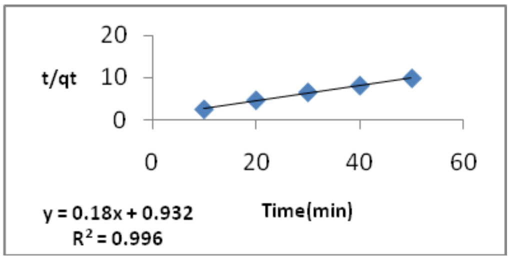


Figure 12: Pseudo second order rate plot for alizarin yellow 2G adsorption by alumina at 30ppm

Table (5): Comparison of first-Order second-Order adsorption rate constants, calculated (qe) and and experimental (qexp) values for different initial dye concentrations

Conc. (mg/L)	**q_e (expermental)**	**Lagergren first order**			**Pseudo second order**		
		K_1 (min^{-1})	R^2	q_e (theoretical)	K_2 (g/mg.min)	R^2	q_e (theoretical)
10	2.20	0.035	0.983	1.15	0.061	0.998	2.27
20	3.99	0.031	0.992	1.59	0.052	0.997	3.96
30	5.57	0.031	0.991	2.33	0.034	0.996	5.55

The results in Table (5) show the kinetic rate constant , values of experimental (q_e) , theoretical (q_e) , correlation coefficients of Lagergren first order and pseudo second order for the adsorption system obtained from the kinetic study . It can be seen that, the pseudo second order equation provided the best correlation coefficient (R^2) and agreement between the calculated q_e(theoretical) (from the plots) and the experimental q_e values, therefore the studied adsorption system under consideration follows pseudo second order kinetic model.

Effect of initial pH on adsorption efficiency

The initial pH of adsorbent is an important factor that may affect the uptake level of the adsorbate . The chemical characteristics of both adsorbate and adsorbent are changing with pH .This study is carried out in order to investigate the effect of pH in the range of (pH5-pH9) which are represented by the natural aqueous solutions of three types of α-alumina, acidic , neutral and basic employed as adsorbent.The results showed that,the percentage of adsorption is decreased with increasing the pH of adsorbent . The lowest percentage of adsorbed dye was recorded at (pH 9) 47.8% and at(pH7) 54.2% while the highest percentage of adsorption was noticed at (pH5) 71.8% which may be attributed to the difference between the dye molecules and alumina surface those have negative and positive charges respectively, which facilitate various type of electrostatic force between the adsorbate and adsorbent surface .which may be due also to basic characterstics of Al_2O_3. Accordingly acidic alumina is the best adsorbent for such dye adsorption system . The values of percentage of adsorption are given in Table (5).

Table (5): Effect of type alumina pH on the percentage of adsorption at various concentrations.

Conc.(ppm)	**pH (5)**	**pH (7)**	**pH (9)**
10	71.8	54.2	47.8
20	63.5	48.3	42.7
30	68.5	52.3	37.7
40	65.3	49.9	35.9
50	57.4	49.8	35.7

References

1. Pradyot and Patnaik ," Hand book of organic chemicals " copyright by the McGraw –Hill companies ,Inc.p.11 (2003).
2. James F.,S and Robert H.,D., "Ceramic and glass materials", Springer Science ,Business Media, LLC, p. 1-4, (2008).
3. Wade. K., and Banister A.J., "Aluminum ,Gallium ,Indium and Thallium", Pergamon Press, p.1034, (1973).
4. Riaz Q. and Sumeera I., "Cobalt Impregnated Alumina :Nitrogen Adsorption Study at 77K", Turk. J. Chem., 29(2005).
5. Muhammad N.A., "Thermodynamics and Kinetics of Adsorpton of Dyes From Aqueous Media onto Alumina" J. Chem. Soc. of Pakistan ,Vol.32, 4(2010).
6. Aparna S.G, Vanjara A.K and Sawant M.R., "Removal of Disperse Dyes from Water Using Surfactant Treated Alumina" Journal of the Chinese Chemical Society.,52 ,907-913(2005).
7. Hajira T.,Muhammad S. and Qazi J.,"Removal of Basic Dye Methylene blue by Using Bioadsorbent Ulva Lactuca and Sargassum", African Journal of Biotechnology, Vol 7.,2649-2655(2008).
8. Gautam K.N. and Vikram S.G."Removal of Janus Green Dye From Aqueous Solution by Phosphoric Acid Carbonized Agro-industrial waste"Science Asia ,37 ,38-42 (2011).
9. Elass, K., Laachach, A. and Azzi, M., "Removal of methylene blue from aqueous solution using ghassoul, a low-cost adsorbent", Applied ecology and environmental research, 153-163,(2010).
10. Sharma. Y.C., Uma S.N. and Gode F. ,"Adsorptive Removal of Basic Dye from Water and Wastewater by Activated Carbon " Journal of Applied Sciences in Environmental Sanitation, Vol. 4,21 -28(2009).
11. Klimiuk E., Filipkowska U. and Wojtasz A. ,"The Effect of pH and chitin preparation on adsorption of Reacitve dyes", Polish Journal of Environmental Studies ,12.,575-588(2003).
12. Yavuz O. and Aydin A.H., "Removal of Direct Dyes from Aqueous Solution using various Adsorbent ", Polish Journal of Environmental Studies ,15.,155-161(2006).
13. Nwabanne J.T. and Mordi M.I., "Equilibrium uptake and Sorption Dynamics for the Removal of a basic dye using bamboo", African Journal of Biotechnology, Vol 8.,1555-1559(2008).
14. Yamin Y., Mohd Z.H. and Faujan H.A. ,"Adsorption of methylene blue onto treated activated carbon ",Malaysian Journal of Analytical Sciences, 11., 400-406 (2007).
15. Daniela S. and Doina B., "Equilibrium and kinetic Study of Reactive Dye Brilliant red HE-3B Adsorption by Activated Carbon", Acta Chim.Slov.,52,73-79 (2005).
16. Hefne .J.A., Mekhemer W.K. and Alandis N.M."Kinetic and thermodynamic study of the adsorption of pb^{+2} from aqueous solution to the natural and treated bentonite", International Journal of Physical Sciences,Vol.3,281-288(2008).
17. Ahmet S. and Mustafa S., "Equilibrium and Thermodynamic of Stearic Acid Adsorption on Celtek Clay"J.Serb.Chem.Soc.,72,485-494(2007).
18. Bouguerra W., Sik M.B. and Hamrouni B., "Equilibrium and Kinetic Studies of Adsorption of Silica onto Activated Carbon ",Desalination 206,141-146(2007).

ثرموداينميكية وحركية أمتزاز الالزارين الصفراء من المحاليل المائية على الألفا ألومينا 2G

علاء عبدالعزيز احمد

قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق

(تاريخ الاستلام: ١٩ / ٩ / ٢٠١١ ---- **تاريخ القبول:** ١٦ / ١٠ / ٢٠١١)

الملخص

استخدمت في هذه الدراسة مادة الالفا ألومينا كمادة مازة لإزالة الصبغة الصناعية 2G (Alizarin yellow) من المحاليل المائية وعند أزمان رج ودرجات حرارية مختلفة وتراكيز ابتدائية تراوحت بين (10- 50 mg/L) ودالات حامضية مختلفة ومن خلال دراسة تأثير درجة الحرارة تم تطبيق ايزوثيرمات لانكماير وفرندلخ وكذلك حساب الدوال الثرموداينمكية ($\Delta G°,\Delta H°$ and $\Delta S°$) كما تضمن البحث انجاز دراسة حركية من خلال تطبيق نموذجين حركيين هما قانون المرتبة الأولى الكاذبة وقانون المرتبة الثانية الكاذبة وأظهرت البيانات العملية لنظام الامتزاز أنها أكثر انطباقا على قانون المرتبة الثانية ، وأستدل على ذلك من خلال تطابق قيم سعة الامتزاز(q_e) المحسوبة عمليا مع تلك المقدرة نظريا عند تطبيق قانون المرتبة الثانية فضلا عن قيمة (R^2) .وقد تم تقدير تراكيز الصبغة الممتزة طيفيا