THERMODYNAMIC STUDY OF THE ADSORPTION OF ALIZARIN RED ON ATABALGUID

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Abstract:

This study is aimed to test the removal efficiency of the Alizarin Red Dye (ARD) from its acidic medium (pH=5.6) aqueous solution by using a local clay named Atabalguid (ATC). The optimum condition for the adsorption process were investigated, such effect of dose, effect of initial, effect of contact time, and effect of temperature. The study showed that the best amount of ATC used is (0.5gm) in a range of initial concentration that ranged between (24-216mg/l) and at a temperature range ranging between (288-328k°). The study showed that the time required to reach equilibrium was (90) minutes, and for this reason, the time (90) minutes was chosen to test the subsequent studies.

Thermodynamic study was also included. Thermodynamic functions (ΔS^o , ΔH , ΔG°) were calculated at one concentration (24 mg/L) and at several temperatures (288, 298, 308, 318,and 328). The experiment was repeated at several concentrations. (72, 120, 168, and 216 mg/L) The results showed, the equilibrium constant (K) decreases with increasing temperature. This is consistent with the physical nature of the adsorption process. The values of the thermodynamic functions proved that the adsorption system under study is spontaneous, and the forces controlling the bond between the alizarin red dye (ARD) molecules and the available sites on the Atabalguid clay (ATC) surface are physical in nature. The adsorption process leads to more ordered system at a concentration of 24 mg/L, while at higher concentrations the adsorption leads to more random dyes system. This can be attributed to the fact that increasing the concentration increases the number of

remaining molecules in the dye solutions, thus increasing the randomness of the system, especially after equilibration.

Keywords: *Alizarin Red, Atabalguid, Adsorption, Thermodynamic Study.*

Introduction:

Dyes are widely spread organic compounds, having different active groups and multiple substituents. They are easily prepared and have a wide range of color and wave length in the visible region of the UV spectrum. Therefore, they are widely used in textile, rubber, paper mills, leather tanning, plastics, cosmetics ,and many other industries. More than 100,000 of these dyes are known in the literature so far. Anthraquinone dyes, represent the second largest group of prepared dyes. The bulk of these dyes were used in the textile and printing industries, especially after the great industrial development and population explosion at the global level. All the industries mentioned above and others that use dyes leave traces of these dyes that are thrown with industrial wastewater into the surrounding environment, which is often into river water [1]. The danger of these dyes is not limited to high concentrations only, but also to low concentrations, which do not exceed one part per million, as part of them can have a significant effect on the coloration of water, which leads as a result to poor solubility of oxygen in it [2]. This is for dyes that are stable in air and light. The greatest danger lies when dyes or their biological degradation products are dangerous and toxic substances, as they can, through into the water, affect human, animal and plant health through the food chain [3], [4].

For these reasons, the industrial wastewater treatment process has become a vital and essential issue. Accordingly, many of those interested in this field began searching for an efficient, cheap and appropriate way to remove various pollutants. Accordingly, many techniques have been proposed to accomplish this task. Among these methods are photo catalysis, oxidation and biodegradation as well as many other techniques that have been used to remove dyes from wastewater [5], [6], [7], [8]], Among the simplest, most accurate, least expensive, and most direct implementation of these methods is the adsorption technique [9]. Many workers in this field have searched for solid, porous materials with a large surface area that are efficient in removing pollutants and do not affect the environment [10].

Alizarin red is an important organic anthraquinone dye that is widely used in the textile industry because of its dark color. Therefore, they leave large quantities of waste in industrial wastewater, which must be treated and removed from the polluted water. In this study, the Atabalguid clay, one of the local and available clays in Iraq was used, to remove alizarin from its acidic aqueous solution as a cheap adsorbent.

Adsorption isotherm

Freundlich Isotherm

Freundlich equation is one of the well-known isotherm models that can be successfully applied to single-component systems. This model assumes that the surface of the adsorbent material is not homogeneous, due to the irregularity of the potential energy on it as a result of the adsorption sites having varying levels of energy. The strength of the linear relationship can be expressed through the value of the correlation coefficient (R^2), as this value is used in evaluating the possibility of representing the experimental data of adsorption through this isotherm. This model can be expressed by the following linear equation (Eq. No. (1)):

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

Where K_F and n represent the Freundlich isotherm constants, while the value of qe represents the amount of adsorbate (mg) per gram of the adsorbent, which is known as the adsorption capacity (at equilibrium) (mg/g), Ce represents the concentration of the remaining adsorbate, i.e. the not adsorbed dye at equilibrium (mg/L). When drawing the relationship between log qe versus log Ce, it gives a straight line whose slope is equal to (1/n), Where n represents a measure of the intensity of adsorption, and intercept equal to log K_F. The value of K_F is related to the adsorption capacity, while the value of n indicates the preference for the adsorbate-adsorbent system. When the value of n is confined between (1-10), this means preferred adsorption, but when n=1, this indicate to linear adsorption whereas when n>1 is referring to chemical adsorption [10,9].

Langmuir Isotherm:

This model assumes that the molecules adsorb on a specific number of well-known pores on the adsorbent surface, and these pores are energetically equivalent and each of them can carry only one adsorbate molecule, and that the adsorbate molecules attacking the adsorbent surface do not interfere with each other or with other molecules adsorbed on the adsorbent surface. A single layer of adsorbate particles is formed on the adsorbent surface. According to this model, the adsorption phenomenon is fast in beginning and then become slower until reaches equilibrium which occurs when the velocity rate of adsorption of adsorbate molecules on the surface of the adsorbent material and the rate of their return to the solution are equal [11, 12]. According to this model, the amount of adsorbate material is proportional to the part of the adsorbent surface exposed to adsorption, while the amount of return particles is proportional to the covered part of the surface.

This model can be expressed by linear equation No. (2):

$$C_e/q_e = 1/bQ_{max} + C_e/Q_{max} \quad \ldots\ldots\ldots(2)$$

Where (b) is the Langmuir isotherm constant and indicates to the strength of the dye bond on the surface of the adsorbent, while the value of (Qmax) represents the highest theoretical adsorption capacity of the adsorbent (mg of adsorbate per gram of adsorbent), while the values of Ce (mg/L) and qe (mg/gm) are the remaining concentration at equilibrium, and practical adsorption capacity, respectively. One more dimension less parameter could be estimated by this isotherm indicated by R_L as presented in eq.3.

R_L = 1/ (1+ b Ci) ....(3)

When the value of   (0 < R_L < 1)indicate to physical adsorption

Experimental part:

Adsorbent:

The raw material, which was in the form of a rock, was mechanically crushed into small granules. These granules were then placed in a one-liter beaker filled with distilled water and left to settle. The suspended part was separated from the precipitate by decantation. The suspended part was taken and the sedimented stony part was discarded. The suspension was filtered and washed well with distilled water. It was left to dry in an electric oven at a temperature 105 °C for three hours, were then separated in certain sizes using molecular sieves, then placed in an electric oven at temperatures ranging between (100-400 c⁰) for six hours, and kept in a closed container for subsequent uses.

Analytical method:

Both the adsorption efficiency and capacity are used to express the amount of the adsorbed dye by estimating its remaining amount in the solution. Since the studied substance is a colored material, the spectrophotometric method in the visible region within the range (300-800 nm) was optimal. And the amount of adsorbed dye is calculated from the difference between the initial concentration (Ci mg/L) and the remaining concentration in the solution (Ce) . The calibration curve has been adopted according to Beer Lambert equation (eq.3) to find the concentrations, of the adsorbate, adsorption efficiency and adsorption capacity are found by using equations No. (4,5)

A= ε bCL ....(4)

% Adsorption = $\frac{Ci-Ce}{ci}$ × 100 ....(5)

q_e = $\frac{Ci-Ce}{m}$ × V_L ....(6)

Where (A) represents the absorbance, (ε) the absorption coefficient, (C) the molar concentration, and (L) represents the cell width (L=1cm).

(Ci) is the initial concentration, (Ce) is the remaining dye concentration after adsorption, (Ce - Ci) represents the adsorbed concentration, which is symbolized by (Cads),

while (qe) represents the adsorption capacity, (V_L) the volume of the dye solution, And (m) is the weight of the adsorbent (gm). All concentrations are in (mg/L) ppm.

Effect of the initial concentration:

For the determination of the effect of the initial concentration, the experiment was conducted under specific and constant conditions, with the exception of the initial concentration. (20ml) solutions of different concentrations of ARD were placed in sealed conical glass flasks under the same conditions. Then, certain amount of adsorbent (ATC clay), which were chosen for the completion of this study, were added to it. The flasks were continuously agitated for a specific time and at a shaking rate of (100 cycles/min, (cpm)) using a water-bath vibrator after adjusting the temperature.

Effect of contact time:

Nine solutions containing equal concentrations (1×10^{-4}M) of the dye were prepared and the same amount of adsorbent was added to them (0.1 g) at a constant temperature and after continuous shaking (100 cycles/min), the nine solutions were filtered at different times (10,20, 30, 40, 50, 60, 70, 80, 90)minutes respectively. The adsorbed quantities were estimated using the spectroscopic method and the equation of the calibration curve, which was found at the best wavelength (λ_{max}) .

Temperature effect:

It was studied using the same amount of adsorbent material at a constant shaking speed for a period of 90 minutes and in the range (293-328°K) absolute degrees.

Single Component Batch Method:

All processes for selecting optimal conditions were conducted using this method. For the purpose of completing any study and to determine a specific parameter, all conditions except for the circumstance to be determined were fixed.

Results and Discussion:

Determination of maximum wavelength (λmax) and calibration curve:

The value of the highest wavelength (λmax) was determined at the highest absorption in the ARD solution, (pH=5.6) and in a solvent mixture of (%50v water : Ethanol), by recording the absorption spectrum of the dye solution for any concentration, provided that it is within the measurement limits of the used device. Through which the highest wavelength of the colored dye solution is determined at the highest absorbance value. Then several solutions of the dye were prepared with different concentrations, and then the absorbance of

the solution was measured for those concentrations at the value of (λmax), and then the relationship between the intensity of absorption and the concentrations is drawn, which must be applied to Beer-Lambert law and within the limits of detection. It was found that the value of (λmax) for this dye is (426 nm). The obtained calibration line is shown in Figure (1).
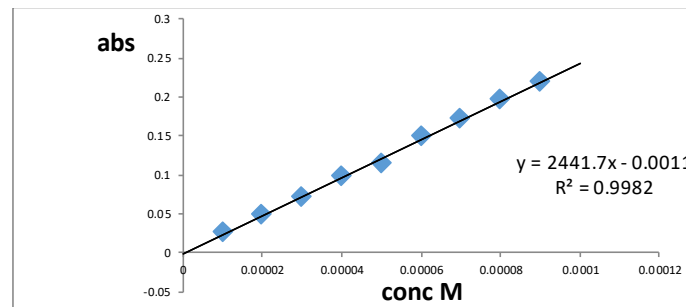

Figure 1: Calibration curve of Alizarin red

Effect of amount of adsorbent:

Usually, the effect of the amount of adsorbent is studied in two ways. The first is conducted by taking a specific amount of the adsorbent and several concentrations of the adsorbate. The second method, it is done by determining a certain concentration of the adsorbent and using several quantities of the adsorbent. This study was carried out using the second method. This was done by taking a certain concentration of the adsorbent (dye) and several quantities of the adsorbent. The solutions were shaken for a period of (90) minutes, then filtered using ash less filtration paper and then calculate the adsorption efficiency and capacity using equations 4 and 5 respectively. The results obtained when studying the effect of the amount of adsorbent are shown in Table No. (1)

compound	Adsorbent	Dose gm/L	qe mg/gm	%Ads.
Alizarin red (AR)	Atabalguid clay (ATC)	0.1	189.8	79.120
		0.3	67.0	83.760
		0.5	42.4	88.400
		0.7	31.1	90.720
		1.0	22.0	91.880

Table (1): The effect of the amount of adsorbent on the efficiency and capacity of adsorption at time 90 minutes,

a temperature of 298 ° K, a shaking speed of 100 cycles / min, and the volume of the dye solution (20)ml

When observing the results listed in table (1), the increase in the amount of the adsorbent is accompanied by an increase in the adsorption rate due to the increase in the active substances present on the surface of Atabalguid. The adsorption capacity, on the

contrary, decreased due to the increase in the number of active sites present on the surface of the adsorbent and the insufficiency of the dye molecules present in a specific concentration for adsorption. With the new and available sites from the increase of adsorbate molecules. This result is consistent with previous findings available in the literature[3].

Effect of contact time:

The effect of contact time study on the adsorption of ARD onto ATC showed that it is highly efficient %75-80 is removed from the aqueous solution of ARD in the first minutes (5-10) minutes as illustrated in Figure (2) a result of the availability of many effective sites eligible for adsorption [15] on the ATC surface. The adsorbate that will be attached to it. As the time is passing on the adsorption process will increase and its speed will slow down due to the occurrence of a great competition among the adsorbate molecules with each other to contact the remaining sites present on the adsorbent surface and with the particles already adsorbed on the surface. The slowdown continued until equilibrium is reached within 90 minutes. In which, the rate of adsorption is almost equal to the rate of desorption.
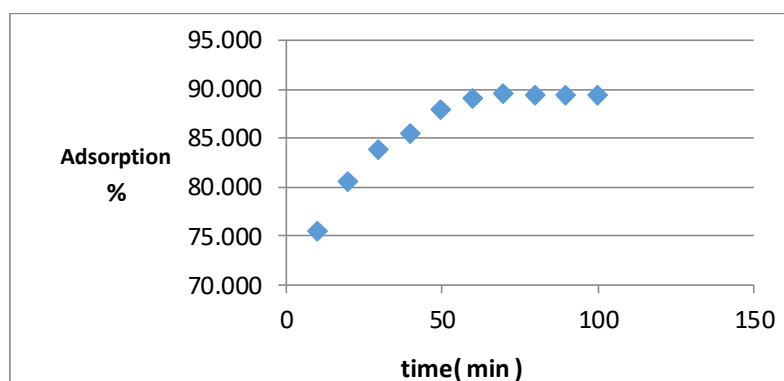
Figure 3: The percentage of adsorption of ARD on ATC variation with time

Effect of Temperature:

The study of temperature facilitates the determination of thermodynamic parameters. It is well known that the adsorption process, whether physical or chemical, is affected by temperature. In the physical adsorption, when the temperature increases, The bonds linking the adsorbate molecules and the adsorbent surface [16-18] causing the loss of heat that returns to the solution, and the process is called exothermic. When the reaction is endothermic, the increase in heat provides the activation energy required to start a chemical reaction, and adsorption is called chemical adsorption [19-21]. It is not necessary for the adsorption to be endothermic in order to be chemical, but most of the cases the adsorption is exothermic process) [22].

Thermodynamic studies:

Thermodynamic functions are among the important variables that give a distinctive interpretation when studying the adsorption process. It explains the nature of the studied system as well as the type of forces that controlling the adsorption process, in addition to that it can give an idea of the type of molecular interactions that can occur during the adsorption process, which have a major role in determining its efficiency. The heat of adsorption can be found from the Van 't Hoff Equation, which represents the relationship between temperature and the equilibrium constant:

$$K = K_o e^{-\Delta H / RT} \dots\dots\dots\dots(7)$$

Where (ΔH) represents the heat of adsorption, while (K) represents the equilibrium constant of adsorption, while (K_o) represents a constant value. The linear form of the Van't Hoff equation is presented in eq.(8)

$$Ln\ K = lnK_o - \Delta H / RT \dots\dots\dots\dots(8)$$

The value of ΔH can be found by drawing the relationship between ln (K) against the reciprocal of temperature (1/T), which gives a straight line with a slope equal to ($-\Delta H/R$). The equilibrium constant for adsorption, which can be found from the ratio between The concentration of the adsorbed to the (free dye) residue in the solution (Eq. 9)

$$K = C_{ad} (mg/L) / C_e (mg/L) \dots\dots\dots\dots(9)$$

It is possible to find the value of ΔH and then find other thermodynamic functions (ΔS^o, ΔG^o) through the following

equations:

$$\Delta G^o = -RT\ ln\ K \dots\dots\dots\dots(10)$$

$$\Delta G^o = \Delta H - T\Delta S^o \dots\dots\dots\dots(11)$$

$$\Delta S^o = (\Delta H - \Delta G^o)/T \dots\dots\dots(12)$$

In this work the values thermodynamic functions have been conducted by the calculating the values of the

equilibrium constants from various sources as follow :

1- K is calculated from the ratio between   K= Cads/Ce   at certain concentration and various temperatures.

2- K is represented as K_F since it is related to adsorption capacity

3- K is determined from Langmuir isotherm as $K_L = Qmax \times b$

The results of the thermodynamic parameters obtained after considering the points 1,2,and3 are listed in Tables (2), (3), and (4) respectively

Table 2: values of equilibrium constants and thermodynamic functions at equilibrium for adsorption of ARD on clay at different initial concentrations and temperature range (283-328 ^{o}K)

Ci mg/L AR	Temp. K^o	K	ΔH (KJ.mol^{-1})	ΔG^o(KJ.mol^{-1})	ΔS^o(J.mol^{-1}.K^{-1})
24	288	8.0770		-5.002	-34.966
	298	7.1662		-4.879	-34.204
	308	5.2769	-15.0723	-4.259	-35.107
	318	4.3196		-3.868	-35.232
	328	3.9933		-3.775	-34.440
72	288	7.1481		-4.709	-50.793
	298	6.5594		-4.660	-49.254
	308	5.1607	-19.3378	-4.202	-49.141
	318	3.0945		-2.986	-51.419
	328	3.0270		-3.020	-49.748
120	288	6.7318		-4.565	-52.204
	298	5.8626		-4.381	-51.070
	308	4.3570	-19.6008	-3.768	-51.402
	318	2.7232		-2.648	-53.308
	328	2.8404		-2.846	-51.079
168	288	6.7318		-4.565	-55.948
	298	4.8958		-3.935	-56.187
	308	3.2740	-20.6791	-3.037	-57.279
	318	2.4889		-2.410	-57.447
	328	2.5616		-2.565	-55.225
216	288	4.3481		-3.5192	-40.277
	298	4.0999		-3.4957	-39.001
	308	3.1393	-15.1180	-2.9294	-39.573
	318	2.2755		-2.1738	-40.705
	328	2.2274		-2.1839	-39.433

Table 3: Thermodynamic functions obtained from Freundlich constants using ATC clay

as an adsorbent for a range of concentrations (24-216) mg/L

Adsorbent and dye	Temp K°	K_F	$\Delta G°(kJ.mol^{-1})$	ΔH $(kJ.mol^{-1})$	$\Delta S°(J.mol^{-1}.K^{-1})$
Alizarin red	288	2.185	-1.871		-42.118
	298	1.911	-1.605		-41.598
	308	1.544	-1.113	-14.001	-41.846
	318	1.228	-0.544		-42.319
	328	1.118	-0.304		-41.761

Table 4: Thermodynamic functions obtained from Langmuir constants using ATC clay

as an adsorbent for a range of concentrations (24-216) mg/L

dye	Adsorbent	Temp K°	K_L	$\Delta G°(KJ.mol^{-1})$	ΔH $kJ.mol^{-1}$	$\Delta S°(J.mol^{-1}.K^{-1})$
Alizarin red ARD	Atabalguid clay ATC	288	1.774	-1.373		-57.615
		298	1.564	-1.108		-56.570
		308	1.182	-0.429	-17.966	-56.938
		318	0.814	0.544		-58.207
		328	0.783	0.664		-56.801

If we look at tables (3, 4 and 5), it can be seen that the three tables show the same indications that the adsorption system occurs spontaneously and that the forces dominate the adsorption are of a physical nature and that it is an exothermic process. The results indicate also that, the adsorption process leads to a less random system.

It is worth noting that the thermodynamic functions calculated by the three methods agree in their tendencies and directions, and that their numbers agree in their ranges. Although the values of thermodynamic functions are calculated in a way that differs from the application of isotherms, both of them occur at equilibrium. Thermodynamic functions are practically applied by selecting a reaction at equilibrium at one concentration, and the effect on the location of the equilibrium constant is studied when the temperature changes. As for the isotherms, they are applied using several initial concentrations and studying the equilibrium position at a certain constant temperature.

Freundlich Isotherm:

Freundlich equation is better fitted to the experimental results of the system under consideration than Langmuir isotherm so this result refer to that, this models can be successfully applied to single-component systems and according to this result and the surface of the adsorbent is not homogeneous. The strength of the linear relationship can be expressed by the value of the correlation coefficient (R^2). This value is used for evaluating the possibility of representing the experimental data of adsorption through this isotherm.

The values of Freundlich isotherm [10, 23] constants,(those listed in Table (6)) were determined from plotting log qe against logCe gave linear relation illustrated in (Figure 4). Since all of the n values are in the range between (1-10), this means that the adsorption is good and preferred, and physical in nature.

Table 6: Freundlich and Langmuir isotherm constants resulted from the Adsorption Isotherm applications of AR dye on clay as adsorbent

Isotherm		Freundlich isotherm			Langmuir isotherm		
Compound	Temp K^o	n	K_F	R^2	Q_{max} (mg/g)	b(L/mg)	R^2
Alizarin red	283	1.245	1.9884	0.984	67.79	0.0262	0.9794
	288	1.251	1.9119	0.990	74.28	0.0211	0.9946
	298	1.273	1.5446	0.985	66.185	0.0179	0.9586
	308	1.264	1.2287	0.999	63.001	0.0129	0.926
	318	1.264	1.1180	0.998	67.739	0.0116	0.9578

Table 7: R_L and b Constants of Langmuir equations for Adsorption of Alizarin red at 298°K

Compound	b(L/mg)	C_i(mg/I)	R_L
Alizarin red	0.0262	24	0.6142
		72	0.3467
		120	0.2415
		168	0.1853
		216	0.1503

The results of table (7)are pointing out the values of R_L were all lie in the range $0 < R_L < 1$ giving indication to preferred adsorption.
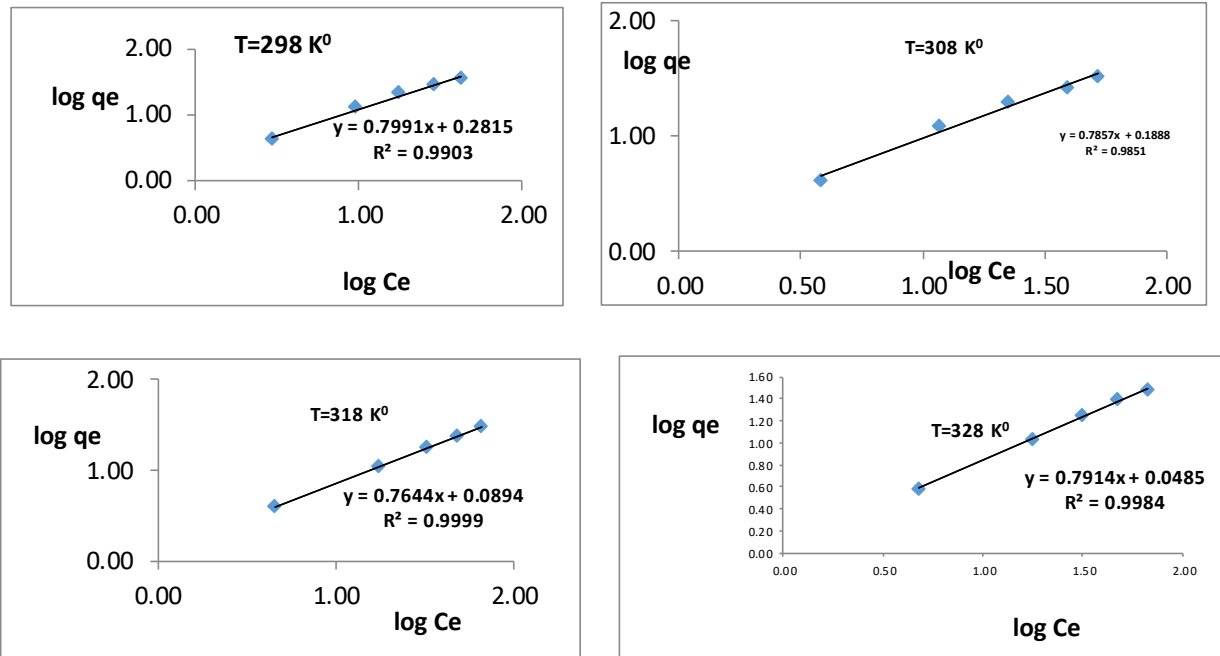
Figure 4: Application of Freundlich isotherm on Alizarin red dye

T=288 K⁰

$y = 0.0148x + 0.5636$
$R^2 = 0.9794$

T=298 K⁰

$y = 0.0135x + 0.6393$
$R^2 = 0.9946$

T=308 K⁰

$y = 0.0151x + 0.8457$
$R^2 = 0.9586$

T=318 K⁰

$y = 0.0159x + 1.2285$
$R^2 = 0.926$

T=328 K⁰

$y = 0.0148x + 1.2761$
$R^2 = 0.9578$
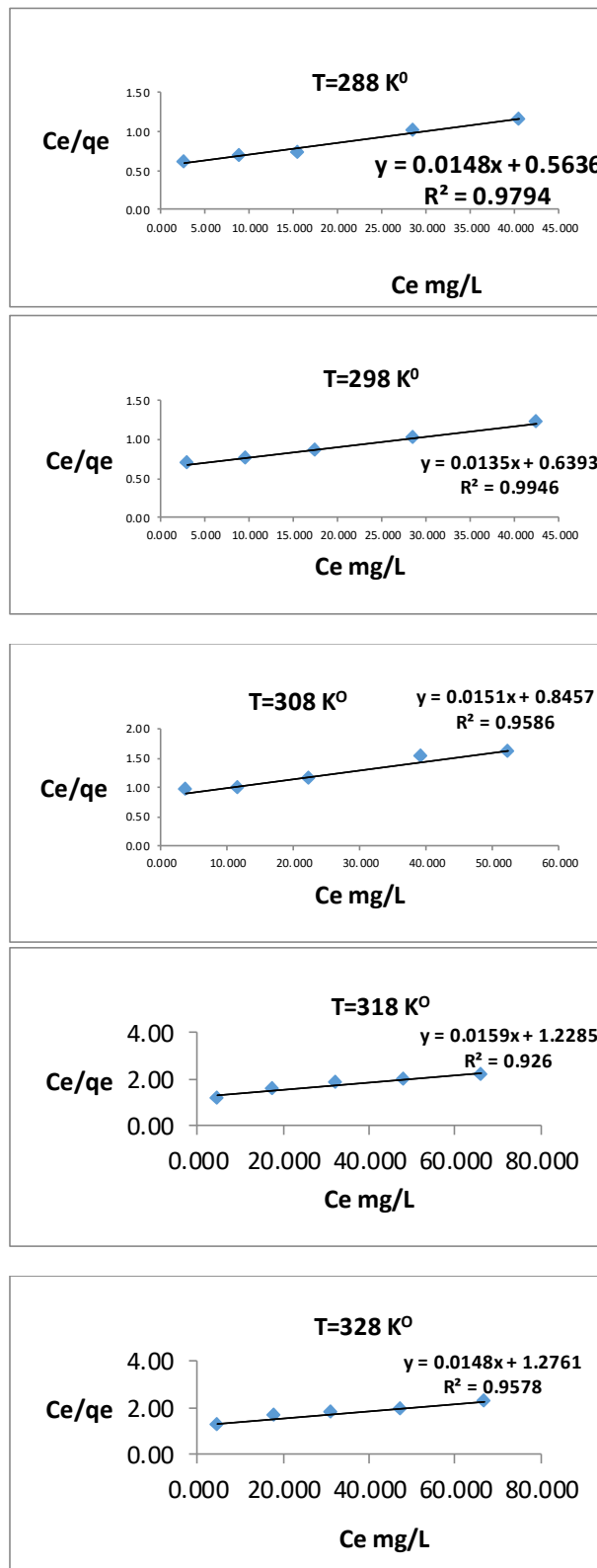
Figure 5: Application of Langmuir isotherm on Alizarin red dye

24 mg/L

$y = 1812.9x - 4.1845$
$R^2 = 0.9698$

72 mg /L

$y = 2325.9x - 6.0225$
$R^2 = 0.9134$

120 mg/L

$y = 2357.6x - 6.232$
$R^2 = 0.9219$

168 mg/L

$y = 2487.3x - 6.7859$
$R^2 = 0.932$

216 mg/L

$y = 1818.4x - 4.7868$
$R^2 = 0.932$
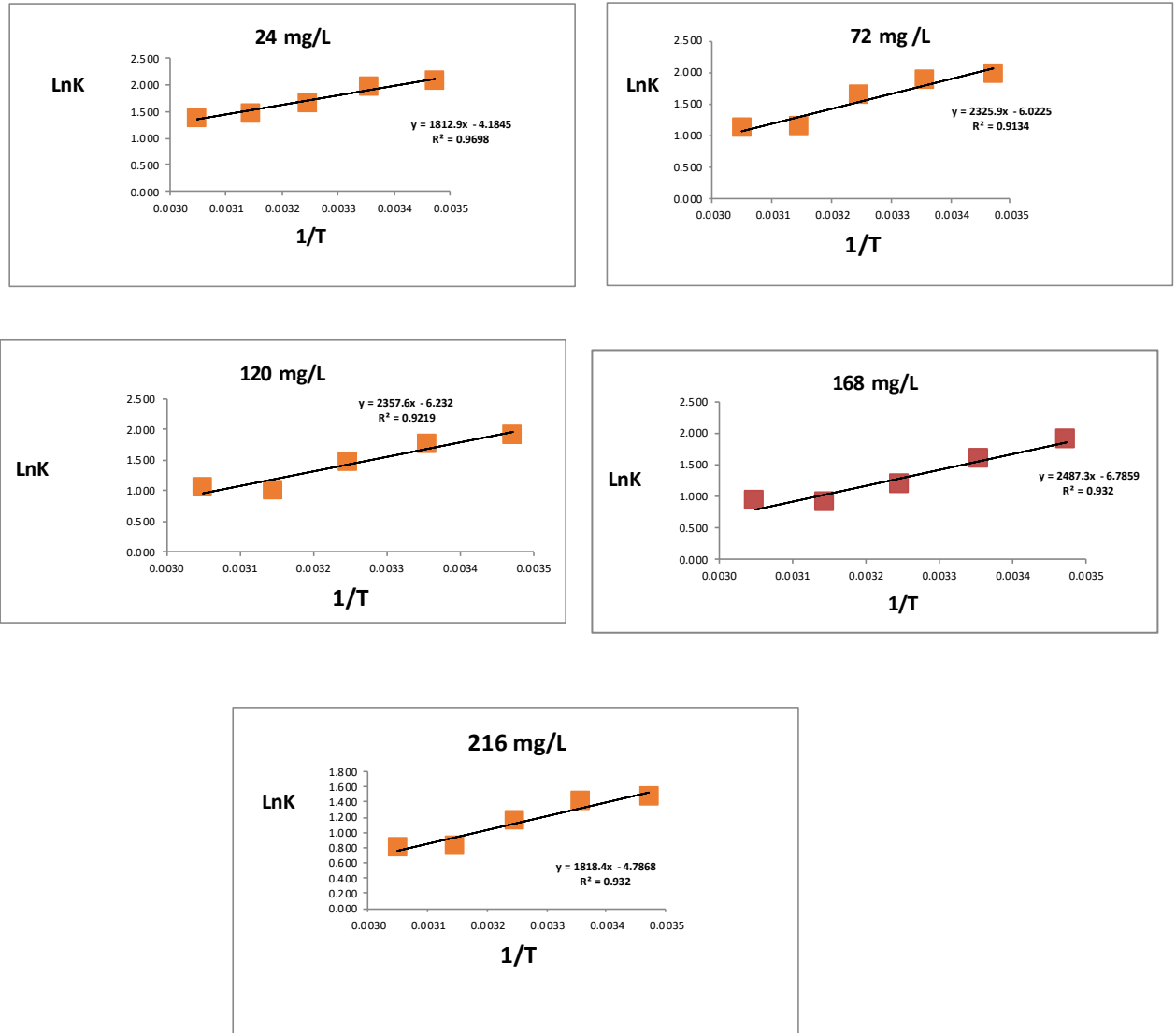
Figure (6) :The relationship between lnK (equilibrium constant) versus 1/T for Alizarin red dye

$y = 1684.1x - 5.0431$
$R^2 = 0.9851$
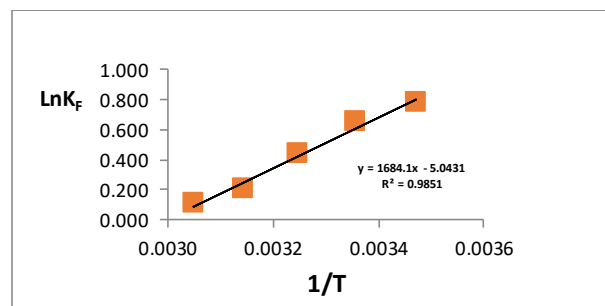
Figure (7) : Relationship of LnK_F to Frendlich's constant vs. 1/T
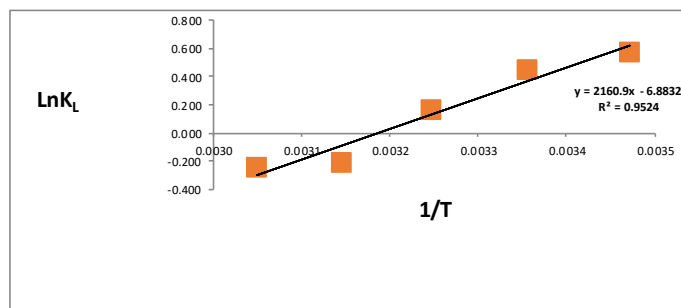
Figure (8):Relationship of LnK$_L$ to Langmuir's constant vs. 1/T

Refrences:

1-A.M. Rheimaa, R. S. Mahmoodb , D. H. Hussainb , Z. S. Abbas, 2021, Study The Adsorption Ability Of Alizarin Red Dye From Their Aqueous Solution On Synthesized

Carbon Nanotubes, Digest Journal Of Nano-materials And Bio-structures Vol. 16, No. 1, P. 11 – 18.

2-Zhifeng Zhang, Huijuan Chen, Wenmei Wu, Wenting Pang, Guiqin Yan, 2019, Efficient removal of Alizarin Red S from aqueous solution by poly ethylene imine functionalized

magnetic carbon nanotube. Bioresour Technolgy, 2019 Dec;293:122100. doi: 10.1016/j.biortech.2019.122100. Epub 2019 Sep 3.

3- Y. El maguana, N. Elhadiri, M. Benchanaa, and R. Chikri, (2020), Activated Carbon for Dyes Removal: Modeling and Understanding the Adsorption Process, Journal of

Chemistry https://doi.org/10.1155 / 2020/ 2096834.

4-S. Kumar, C. Patra, S. Narayanasamy, and P. V. Rajaraman, (2020) Performance of acid activated water caltrop (Trapa natans shell in fixed bed column for hexavalent chromium

removal from simulated wastewater," Environmental Science and Pollution Research, vol. 27, no. 22, pp. 28042–28052.

5-Y. El maguana, N. Elhadiri, M. Bouchdoug, M. Benchanaa، and A. Boussetta, (2018), "Optimization of preparation conditions of novel adsorbent from sugar scum using response

surface methodology for removal of methylene blue," Journal of Chemistry, Article ID 2093654, 10 pages.

6-A. M. Elgarahy, K. Z. Elwakeel, G. A. Elshoubaky, and S. H. Mohammad, (2019) "Untapped sepia shell–based composite for the sorption of cationic and anionic dyes," Water,

Air, & Soil Pollution, vol. 230, p. 217.

7-A. Kausar, M. Iqbal, A. Javed et al., (2018), "Dyes adsorption using clay and modified clay: a review," Journal of Molecular Liquids, vol. 256, pp. 395–407.

8-K. Z. Elwakeel, A. A. El-Bindary, A. Ismail, and A. M. Morshidy, (2016), "Sorptive removal of Remazol Brilliant Blue R from aqueous solution by diethylenetriamine

functionalized magnetic macro-reticular hybrid material," RSC Advances, vol. 6, no. 27, pp. 22395–22410.

9-A. A. Yakout, M. A. Shaker, K. Z. Elwakeel, and W. Alshitari, (2019), "Lauryl sulfate@magnetic graphene oxide nano sorbent for fast methylene blue recovery from aqueous

solutions," Journal of Dispersion Science and Technology, vol. 40, no. 5, pp. 707–715.

10- Theyab G Hussein Al-Joubory, Emad A Saleh Al-Hyali and Mustafa R Al-Hadeethi, (2023), Study of the factors affecting the adsorption efficiency of some chemical pesticides

activated carbon at the nano scale, International Journal of Advanced Chemistry Research 2023; 5(1): 89-98.

11- Theyab G Hussein Al-Joubory, Emad A Saleh Al-Hyali and Mustafa R Al-Hadeethi, (2023), Preparation and diagnosis of nano-activated carbon from falling sidr leaves

International Journal of Advanced Chemistry Research 5(1): 99-105.

12-Wu, C. H. (2007). Adsorption of reactive dye onto carbon nanotubes; equilibrium, kinetics and thermodynamics. Journal of hazardous materials, 144(1-2), 93-100.

https://doi.org/10.1016/j.jhazmat.2006.09.083

13- Losso, J. N., Ng, C., Marshall, W.E.,& Rao, R.M.(2002).Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water

system. Bioresource technology, 85(2), 131-135.

14- AL-Sayd Toohi, H.T.(2019). Thermodynamic and kinetic study of the adsorption of Azo dyes derived from (4-aminoantiparerine) on activated carbon prepared from

mixtures of (asphalt polymer) and development of the rhrological properties of these mixtures. Ph.D. thesis, College of Education for Pure Sciences, University of Mosul

/ Iraq.

15- Al-Taey, S.I. (2017), ''preparation of new types of activated carbon and testing their efficiency by the adsorption of some dyes, Thermodynamic and Kinetic studies'' ,

Ph.D. Thesis, University of Mosul.

16- Theivarasu C.,Mylsamy S.,Sivakumar N.,(2011),"Cocoa shell as Adsorbent for the Removal of Methylene Blue from Aqueous solution: Kinetic and Equilibrium Study",

Universal. J.Envir.Res. &Tec., Vol.1, pp.70-78.

17- Mohamed , H . F. (2017) Preparation of Nano scale Adsorbent Material From pomegranate peels and ceratonia Mixture and used it to Adsorb Number of Drugs from their Water

Solutions . Master Thesis. University of Samarra .

18- Acharya, J., Kumar, U., & Rafi , P . M.,(2018), Removal of heavy metal ions from wastewater by chemically modified agricultural waste material as potential adsorbent-a

review. International Journal of Current Engineering and Technology, 8(3), 526-530.

19- Al-Abady Ra'ed T. Gh., Saleem N. H., Al-Hyali Emad A.S.,(2021), "Kinetic and Equilibrium Studies of the Adsorption of Dichalcones on Activated Carbon", Samarra J. Pure

Appl. Sci.; 3 (4): 41-55.

20- Aldbouni, S. A., Alkazraji, A. A., & Alhyali, E. A. (2019). kinetic study of adsorption of some azo dyes on a thermally catalyzed local bentonite clay. Journal Of Education And

Science, 28(4):pp.1-17.

21- Al-Hyali, E.A, S., Al-Dubuni,A., and Ramadhan,O.M., (2015), "The effect of temperature, pH and concentration on the adsorptive properties of aromatic amines and their

substituents", Accepted for Publication by the National Journal of Chemistry, Vol. 16. p68-79.

22- Al-Hyali, E.A.S., AL-Memary, K. A.O.,and AL-Sayd Toohi, H. T. S.,(2020),Preparation of Activated Carbon From ((Asphalt:Polymer)) Mixtures and Improving its Adsorption

Properties by Thermal Fusion Carbonization and Microwave Technique, Journal of Education and Science, Vol. 29, No.1, pp.233-241.

23-Ali, D.J. (2016). "Adsorption, desorption and theoretical study of propranolol hydrochloride on the surface of chitosan and cellulose di acetate ". M.Sc. thesis, College of Science,

University of AlMustansiriyah, Iraq.

24-Ali, R. M., Hamad, H. A., Hussein, M. M., & Malash, G. F. (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics,

isotherm, thermodynamic, mechanism and economic analysis. Ecological Engineering, 91,pp. 317-332