Adsorption of Tetracycline on the Bauxite and Modified Bauxite at Different Temperatures

Israa M. Radhi
Yousif I. Mohammed
Takialdin A. Himdan
Dhefaf H. Badri
Dept. of Chemistry /College of Education for Pure Science(Ibn Al Haitham)/ University of Baghdad

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Abstract

In this study, bauxite and modified bauxite /polymer, which were prepared as an adsorbent surfaces to adsorption of the tetracycline from aqueous solutions. A series of adsorption experiments were conducted to determine the equilibrium time and temperature effect on the adsorption process. The results showed that adsorption was agreed with the Freundlich equation model for the surface of the bauxite. As for the modified bauxite surface, the results were consistent with the Langmuir equation model. The values of the basic thermodynamic functions of the adsorption process were calculated, so the process of adsorption was founded spontaneous and endothermic.

Key word: Bauxite, Modified bauxite, Adsorption, Tetracycline

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Introduction

Antibiotics are widely used in human therapy [1]. Tetracycline is a broad-spectrum antibiotic that works against grampositive and negative bacteria and inhibits their growth. Recently, tetracycline became a concern the trend to the environment[2]. It is detected through contaminated water from water treatment plants [3,4], so that the removing it has a great importance. The removal is done using certain adsorbents such as Montmorellonite [5] where this method is the easiest and the most economical. In this study, bauxite and modified bauxite were used as good adsorbents surfaces to adsorption of the tetracycline from aqueous solutions. Bauxite is the most important type of aluminum ores, it consists of gibbsite, boehmite and diaspore in large quantities, as well as less goethite and hematite and small amounts of anatase [6]. It was first discovered by French geologist Pierre Berthier in 1821[6].

Experimental part

In this study, the following devices were used : 1-Double beam UV- visible spectrophotometer type Shimadzu. 1800, Japan. 2- A water bath shaker Labtech. Korea. 3- Balance (0.0001 g ±) type Sartorius Lab. BL 210 S, Germany.
The chemicals were used (melamine from BDH, urea from Hannover, formaldehyde and hydrochloric acid from Reidel-De Haen). The Bauxite from the general company of geological survey in Iraq. The Tetracycline from SDI- Samarra. The modified bauxite has been prepared previously [7].

Effect of Contact Time

The equilibrium time was determined at a temperature of 293K, taking 50 ml of the tetracycline solution at a concentration of 40ppm and adding it to 0.05g of both adsorbents which were shaken in the shaker water bath. The time period ranged from 10min-180 min, after every 10 minutes separate the solution using a centrifuge at 5000 rpm for 10 minutes. Then the solution was separated and analyzed using a spectrophotometer at the λ_{max}=356 nm. The results indicated that the best time for equilibrium was 2 hours and 3 hours for bauxite and modified bauxite, respectively.

Adsorption Isotherms

A volume of 50 ml. of six different concentrations of tetracycline (20,30,40,50,60 and 70) ppm was shaken with 0.05 g of both adsorbents at acertain temperature in the shaker water bath. After the equilibrium time is elapsed, separate the solution using a centrifuge at 5000 rpm for 10 minutes. After the separation, the absorption of the solution was measured using a spectrophotometer at the λ_{max}. Through absorption values, we can calculate the concentration at equilibrium using the calibration curve.

Results and Discussion

The amount of drug adsorbed at certain conditions of temperatures was calculated from equation:

$$q_e = \frac{V(C_0 - C_e)}{M} \quad \ldots\ldots(1)$$

Where, (V) is the volume of solution in litres, (C_0) and (C_e) are the initial and equilibrium concentration of the drug in milligrams per litre. (M) is the weight of adsorbent which was taken equal to 0.05 g. [8]
The extent of adsorption of tetracycline at (25,30,35,40 and 45) ^{0}C from aqueous solution on bauxite and modified bauxite is given in Figure (1)and (2).

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In Figure (1), The general pattern of adsorption isotherm of the tetracycline on the surface of the bauxite follows the S_{2max} pattern at low temperatures and then begins to convert to L_{2max} pattern at high temperature. Figure (2) shows that the adsorption of the tetracycline on the modified bauxite surface follows the L_{max} pattern at low temperatures and then changes to the S_{max} pattern at high temperatures (up to 318K). The maximum-adsorption occurs when the adsorbed particles reach a certain level of concentration, which begins by interfering strongly with each other in the solution to form agregations. These agregations increase the solubility of the adsorbent by increasing the concentration and thus decrease the adsorption potential of these molecules [9] .When the literatures were reviewed, it was found that tetracycline tends to form agregations by attracting different charges on the tetracycline molecules itself ,and that these agregations have less adsorption capability. This is due to decreased adsorption and the formation of the maximum end point in the isotherm curve[10,11]. There are several isotherm adsorption models that help to explain the obtained results for isotherm:

Freundlich Isotherm Model

The Isotherm Freundlich equation (2) [12]for tetracycline adsorption was applied to the bauxite and modified bauxite surface at different temperatures as shown in Figure(3) and (4).

$\ln q_e = \ln k_f + 1/n \ln C_e$ ……..(2)

where k_f and n are Freundlich constants, q_e the amount of drug adsorbed (mg/g) and Ce is the equilibrium concentration of tetracycline (mg/L). A plot of log qe against log Ce would give the values of n and k_f from the slope and intercept respectively. The values of Freundlich constants with the correlation coefficients are shown in Table 1. The results shown in the table indicate that the values of the Freundlich constants at different temperatures on the surface of bauxite have an increase in the value of k_f by increasing the temperature, while is fluctuate in value at different temperatures. As for the values of the Freundlich constants on the modified bauxite surface, we observe their variability at different temperatures. This indicates that bauxite corresponds to the model well while modified bauxite has a weak corresponds.

Langmuir Isotherm Model

The Isotherm Langmuir equation (3)[13]for tetracycline adsorption was applied to the bauxite and modified bauxite surface at different temperatures as shown in Figure(5) and (6).

$Ce/qe = 1/a\ k + Ce/a$ ……..(3)

where k and a are Langmuir constants, q_e the amount of drug adsorbed (mg/g) and C_e is the equilibrium concentration of tetracycline (mg/L). A plot of C_e/q_e against C_e would give the values of a and k from the slope and intercept respectively. The values of Langmuir constants with the correlation coefficients are shown in Table 2. The results shown in the table indicate there is a fluctuation in the values of the equilibrium constant or the constant of the adsorption process according to Langmuir in the case of bauxite at different temperatures. In the case of modified bauxite, we observe negative values, which are mainly due to non-typical adsorption and then become positive when the temperature rises. As for the values of the maximum amount of absorbent matter calculated according to the Langmuir model of the bauxite modified bauxite surface, we note that there is a fluctuation of these values at low temperatures followed by a continuous increase at high temperatures. These results indicate that the modified bauxite corresponds to the model well, while bauxite is moderately consistent.

Interpretation of thermodynamic functions

The equilibrium constant (k_{eq}) for the adsorption process at each temperature is calculated from the equation (4):

$k_{eq} = q_m/C_e$ ……..(4)

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Where q_m is the amount of maximum absorbent at equilibrium (mg/g) and Ce is the equilibrium concentration of tetracycline (mg/L).
The change in free energy (ΔG) could be determined from the equation (5):
$\Delta G = -RTlnK$ ….(5)
Where R is the gas constant (8.314 $J.mol^{-1}.K^{-1}$) and T is the absolute temperature The heat of adsorption (ΔH) may be obtained from the equation (6):
$lnk = -\frac{\Delta H}{RT} + constant$ ……..(6)
Where k is the equilibrium constant. Table 3 gives k values at different temperatures. A plot of lnk versus 1/T would give a straight line with a slope = (-ΔH/R) as shown in Figure (7) and (8).
The change in entropies (ΔS) was calculated from Gibbs equation (7):
ΔG = ΔH-TΔS ……..(7)
Table 4 shows the basic thermodynamic values of adsorption of the tetracycline on bauxite and modified bauxite. The values shown in the table indicate that the heat adsorption of tetracycline, whether on the surface of the bauxite or modified bauxite, is positive and this indicates that the adsorption process is andothemic process. This indicates to the possibility of a high absorption process associated with adsorption process and this result agrees with the results of the study[14]. We also note that the values of change in free energy are negative and this indicates that the process of adsorption is spontaneous. As for the values of the change in the entropy, it is positive and its value on the surface of the bauxite is higher than the modified bauxite surface. This is the reason for the possibility of forming the symmetric bond between the neoclophilic groups in the tetracycline molecule with empty orbitals that found in the aluminum atom on the surface of the bauxite. Its value on the modified bauxite surface is lower. This indicates that the formal structures taken by tetracycline molecules when trapped inside the polymer paths and pores are not significantly different from the probability of their arrangement in the aqueous solution.

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Table (1): Experimental Freundlich constants and correlation coefficient values for tetracycline adsorption on bauxite and modified bauxite/polymer surfaces

Adsorbent	293 K			298 K		
	k_f(L/mg)	n	R^2	k_f(L/mg)	n	R^2
Bauxite	0.173421	1.418795	0.562	0.201857	1.339008	0.4753
Polymer	17.13394	-2.50705	0.3629	9.495273	-6.37004	0.1404
Adsorbent	303 K			308 K		
	k_f(L/mg)	n	R^2	k_f(L/mg)	n	R^2
Bauxite	0.681169	2.245408	0.5677	0.625257	2.013136	0.7775
Polymer	2.816479	-328.961	0.0003	4.219827	-52.0096	0.0024
Adsorbent	313 K			318 K		
	k_f(L/mg)	n	R^2	k_f(L/mg)	n	R^2
Bauxite	0.479041	1.626741	0.863	0.950128	2.002192	0.8115
Polymer	1.644996	3.318814	0.5465	2.814918	4.765777	0.1161

Table (2): Experimental Langmuir constants and correlation coefficient values for tetracycline adsorption on bauxite and modified bauxite/polymer surfaces

Adsorbent	293 K			298 K		
	k(L/mg)	a (mg/g)	R^2	k(L/mg)	a(mg/g)	R^2
Bauxite	0.017015	6018.494	0.3394	0.015168	8610.754	0.2434
Polymer	-0.04119	1816.136	0.8352	-0.1248	4194.708	0.8808
Adsorbent	303 K			308 K		
	k(L/mg)	a(mg/g)	R^2	k(L/mg)	a(mg/g)	R^2
Bauxite	0.029652	6602.84	0.6555	0.026525	7845.14	0.7839
Polymer	0.825802	2828.241	0.9534	-0.12732	3323.093	0.9214
Adsorbent	313 K			318 K		
	k(L/mg)	a(mg/g)	R^2	k(L/mg)	a(mg/g)	R^2
Bauxite	0.01515	12579.92	0.8031	0.022848	12818.22	0.7769
Polymer	0.065825	7134.041	0.9396	0.163886	7107.203	0.5995

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Table (3): Constant equilibrium values at different temperatures for tetracycline adsorption on the bauxite and modified bauxite/polymer surfaces

Adsorbents	T/K	1/T K^{-1}	k	Ln k
Bauxite	293	0.0034	60.09	4.09
	298	0.0034	81.77	4.40
	303	0.0033	78.89	4.37
	308	0.0032	82.61	4.41
	313	0.0032	95.98	4.56
	318	0.0031	131.53	4.88
Polymer	293	0.0034	69.84	4.25
	298	0.0034	104.38	4.65
	303	0.0033	69.28	4.24
	308	0.0032	131.45	4.88
	313	0.0032	79.53	4.38
	318	0.0031	133.88	4.89

Table (4): Values of thermodynamic functions the adsorption of the tetracycline on the bauxite and modified bauxite/polymer surfaces

T (K)	Bauxite		
	ΔG ($kJ.mol^{-1}$)	ΔH ($kJ.mol^{-1}$)	ΔS ($J.mol^{-1}.K^{-1}$)
293	-9.97		100.91
298	-10.91		102.35
303	-11.00	19.59	100.96
308	-11.30		100.30
313	-11.87		100.53
318	-12.89		102.16
T (K)	Modified bauxite		
	ΔG ($kJ.mol^{-1}$)	ΔH ($kJ.mol^{-1}$)	ΔS ($J.mol^{-1}.K^{-1}$)
293	-10.34		81.74
298	-11.52		84.30
303	-10.67	13.61	80.14
308	-12.49		84.74
313	-11.38		79.85
318	-12.95		83.50

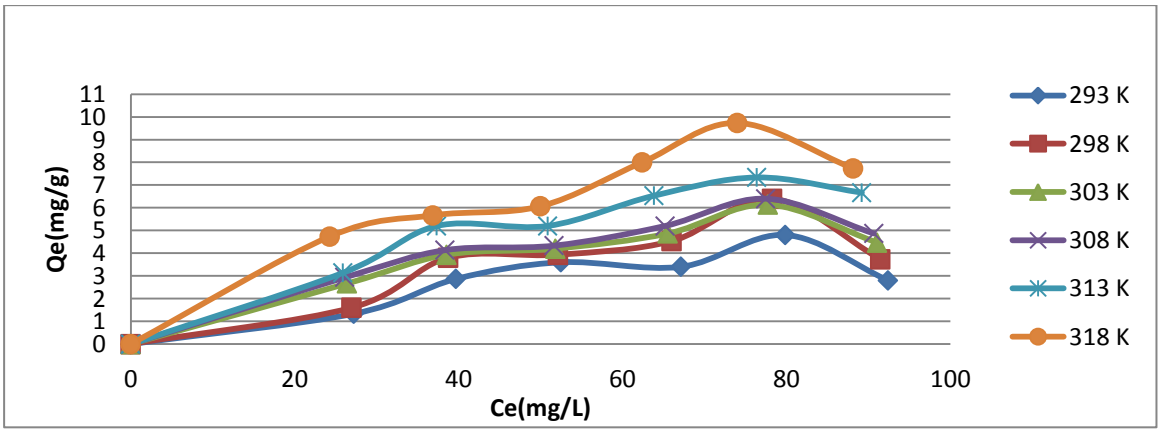

Figure (1): Isotherm adsorption of tetracycline on the surface of bauxite

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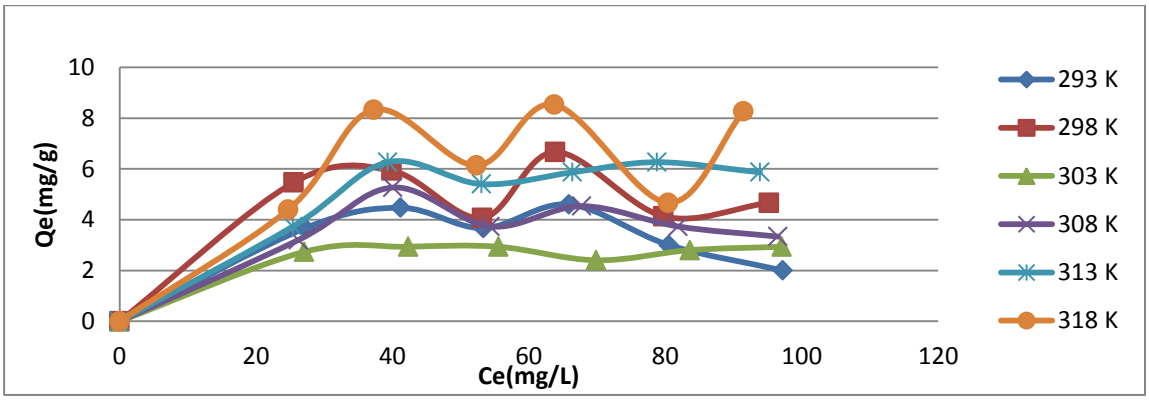

Figure (2): Isotherm adsorption of tetracycline on the surface of modified bauxite

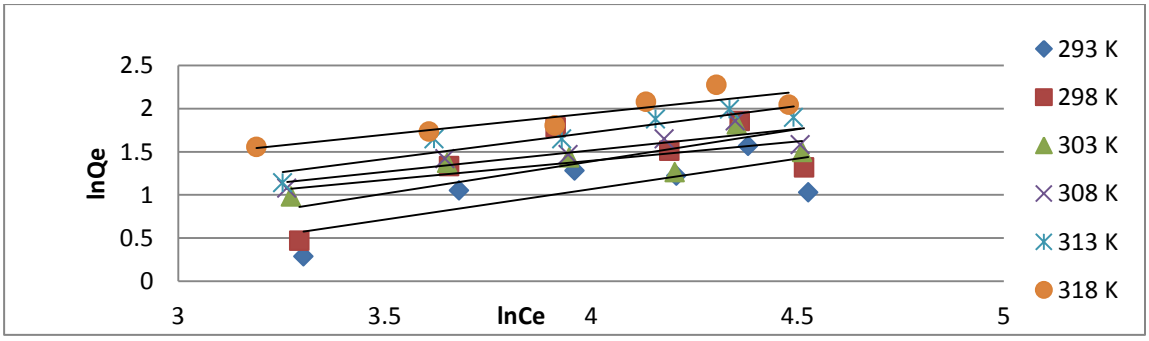

Figure (3): Isothermic Freundlich for tetracycline adsorption on the surface of bauxite

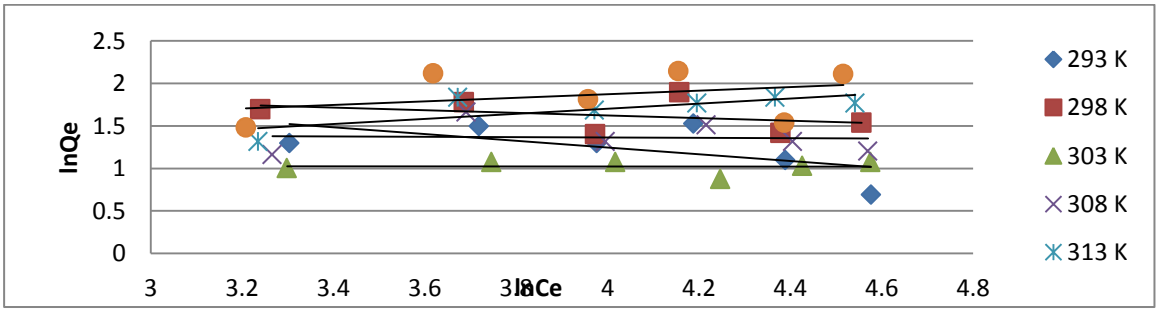

Figure (4): Isothermic Freundlich for tetracycline adsorption on the surface of modified bauxite

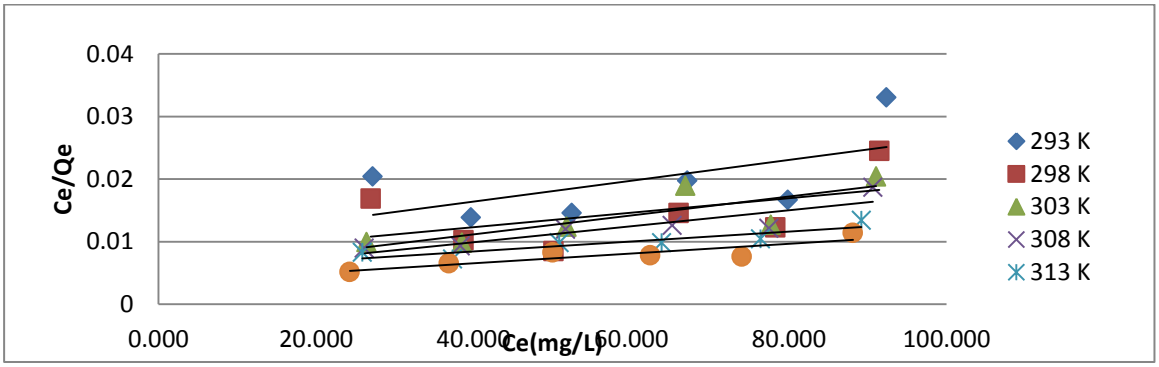

Figure (5): Isothermic Langmuir for tetracycline adsorption on the surface of bauxite

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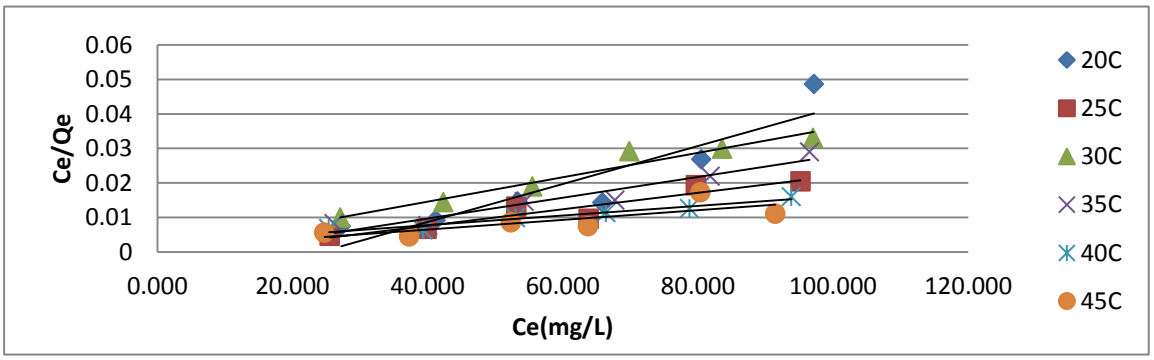

Figure (6): Isothermic Langmuir for tetracycline adsorption on the surface of modified bauxite

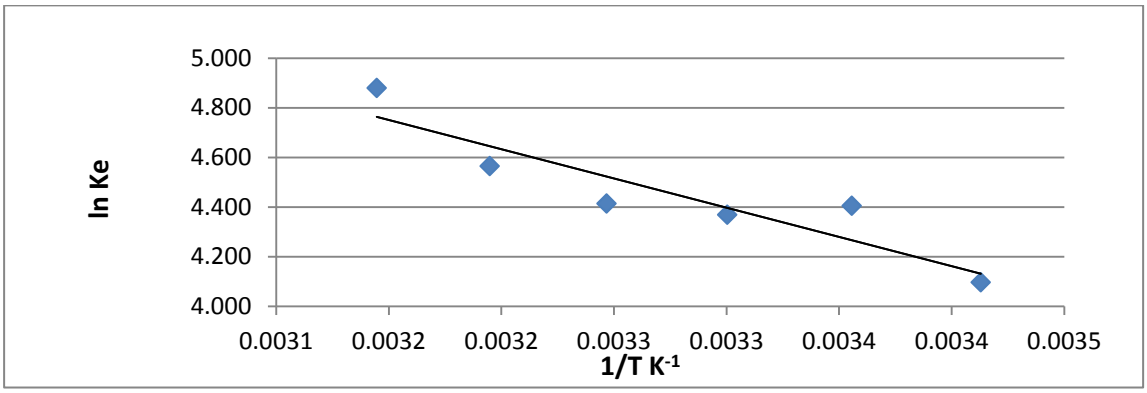

Figure (7): The Van Huff's curve for tetracycline adsorption on the surface of bauxite

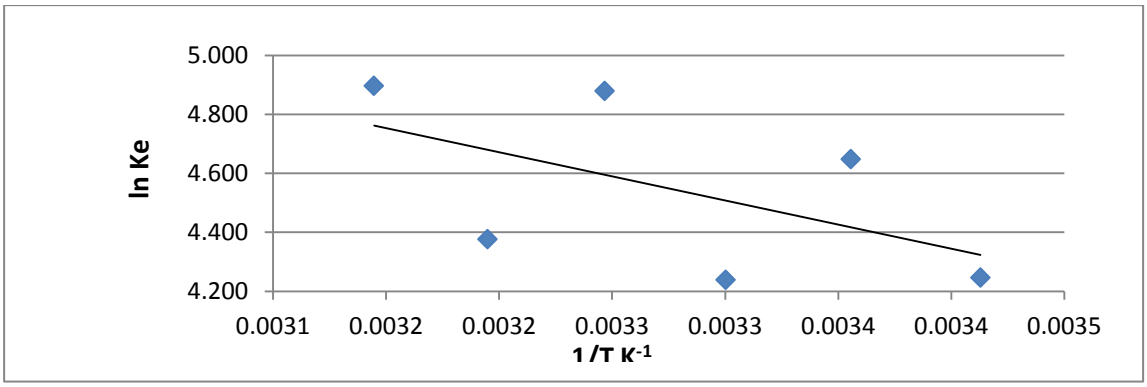

Figure (8): The Van Huff's curve for tetracycline adsorption on the surface of modified bauxite

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