Removal of Methyl Orange From Aqueous Solution By Iraqi Bentonite Adsorbent

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Abstract

The adsorption behavior of methyl orange from aqueous solution on Iraqi bentonite was investigated. The effects of various parameters such as initial concentration of methyl orange, amount of adsorbent, ionic strength and temperature on the adsorption capacity has been studied. The percentage removal of methyl orange increased with the decrease of initial concentration of methyl orange and it increased with the increase of dose of adsorbent. The adsorbed amount of methyl orange decrease with increasing ionic strength and an increase in temperature. The equilibrium adsorption isotherms have been analysed by the linear, Langmuir and Temkin models. The Langmuir isotherms have the highest correlation coefficients. Thermodynamic parameters such as ΔG, ΔH and ΔS for the adsorption process were calculated. The adsorption process was found to be exothermic and spontaneous.

Keywords: adsorption; methyl orange; Langmuir and Temkin isotherms; ionic strength; thermodynamic parameters

Introduction

Environmental pollution control has been a concerned issue in many countries. One of the major environmental pollution is waste water. Water pollution due to colour from dyestuff is a topic of major concern of scientists today. Many industries use dyes extensively in different operations such as textile, leather tanning, paper, plastic, food processing, cosmetics, printing etc. [1, 2, 3].

Numerous techniques have been proposed by various researchers for the treatment of dye effluents [4]. These include ion-exchange, chemical precipitation; chemical oxidation and adsorption have been used for the removal of toxic pollutant from waste water [5, 6, 7].

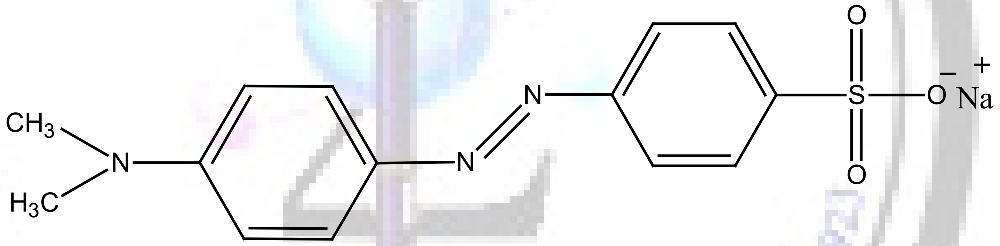
Sorption of colored components from aqueous solution has proven to an excellent way to treat effluent and also a cost effective technique. Several studies have shown that numerous low-cost materials have been successfully applied in the removal of dyes such as rice husk[8],giant duckweed[9],sepiolite[10], modified clays[11,12], oxihumolite[13], fly ash[14] and kaolin[15].

This study is aimed at investigation the possibilities of the use of, a local clay readily available in Iraq for removal of methyl orange from aqueous solution. The system variables studied include sorbent dose, initial concentration of the dye, ionic strength and temperature.

Materials and Method

Materials

The dye, methyl orange,4-[[(4-Di methyl amino)phenyl]azo]benzene sulfonic acid sodium salt, C.I. 13025 ,chemical formula ,MW=327.34 g/mol, λ_{max}= 503 nm(measured value) was supplied by Merck Co.(dye content 85 %) and used without purification. The chemical structure of methyl orange is shown below:



The clay used in this experiments was obtained from tarifawi region in western desert by the state company for Geological survey .The chemical composition of this clay is 54.66 % SiO_2, 14.65%, Al_2O_3, 4.88% Fe_2O_3, 4.77% CaO, 6.00% MgO, 0.65% Na_2O,1.20% SO_3, 12.56% Ignition loss. The particle size was 125 µm.

Method

Adsorption experiments were carried out by shaking 0.2 g bentonite samples with 10 ml aqueous solution of methyl orange of desired concentration at various ionic strengths (0.05 - 0.35 M NaCl solution in water), adsorbent dosage (0.05-0.35g), temperature (25-45) for 1.5 h (the required time for methyl orange to reach the equilibrium concentrations). A thermostated shaker bath was used to keep the temperature constant. The initial concentration of dye solutions, C_o ,were in the range of (10 ppm- 40 ppm). All adsorption experiments were performed at 25 C^o and pH 5 except those in which the effects of temperature were investigated. At the end of the adsorption period, the solution was centrifuged for 5 min at 3000 rpm and then the concentration of the residual methyl orange, C_e, was determined with the aid of CECIL, CE7200 UV-Visible Spectrophotometer (190-900nm). The adsorbed amounts of methyl orange were calculated from the concentrations in solutions before and after adsorption according to the equation (1):

$$Q_e = (C_o - C_e)\frac{V}{W} \qquad (1)$$

Where C_o and C_e are the initial and equilibrium liquid phase concentrations of dye solution (mg/L), respectively; Q_e is equilibrium dye concentration on adsorbent (mg/g), V is the volume of dye solution (L), and W is the mass of bentonite sample used (g).

Results and Discussions

Effect of initial dye concentrations

The adsorption capacity of bentonite for methyl orange was determined at different initial dye concentrations (10 ppm- 40 ppm). The results were represented in figure (1{ a,b}) show that the dye amount sorbed increase with the increase of dye concentration but the percent of dye removal decrease at high concentration.

Effect of adsorbent dosage

Removal % of methyl orange on bentonite was studied at different bentonite mass [0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35/10 ml, respectively] keeping initial methyl orange concentration (30 ppm), temperature (25 ^{0}C), pH=5 and contact time (1.5 h) constant. The results showed that the percentage of dye removal increased with the increase of amount of bentonite, but amount of dye adsorbed per unit mass of adsorbent decreased with the increase of amount of adsorbent from (0.05-0.35g/L) figures(2{a,b}). As amount of adsorbent increases, number of active sides available for adsorption also increases thus removal % also increases but as all active sides may not be available during adsorption due to overlapping between the active sides themselves and thus amount adsorbed mg/g of adsorbent decreases [3]. Thus, the adsorption of dye increased with the sorbent dosage and reached an equilibrium value after certain sorbent dosage (0.2-0.3g/L). .

Effect of the ionic strength

Figure (3) shows the influence of ionic strength on the adsorption of methyl orange by bentonite. It has been tested by the addition of sodium chloride to the methyl orange solution. The increase in ionic strength between 0.05 and 0.35 has decreased the amount of adsorption between (0.294 – 0.114 $mg.g^{-1}$). This may be due to the following two reasons:

I - The electrostatic attraction seems to be significant mechanisms, as indicated by the results were at high ionic strength, the increased amount of NaCl can help to swamp the surface of the bentonite, which decreases methyl orange access to the bentonite surface for adsorption [16]. In fact according to the surface chemistry theory developed by Guoy and chapman [17], when solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and methyl orange from approaching. **II-** The relative competition between sodium ions and dye species for the active sites of bentonite can also be an explaining factor.

Adsorption isotherms

Several mathematical models have been applied for describing equilibrium studies for the removal of organic pollutants by adsorption on solid surfaces. Selections of an isotherm equation depend on the nature and type of the system. The Langmuir adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance, and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption occurs at specific homogenous sites with the adsorbent. It is then assumed that once a dye molecular occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent. Theoretical, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur [18]. Figure 4 shows the adsorption isotherms of methyl orange on bentonite at different temperatures.

The saturated monolayer isotherm can be represented as a linear from

$$\mathrm{Qe} = \frac{\mathrm{Qm\ KL\ Ce}}{1+\mathrm{KL\ Ce}} \qquad (2)$$

The above equation can be rearranged to the following linear form:

$$\frac{\mathrm{Ce}}{\mathrm{Qe}} = \frac{1}{\mathrm{KLQmax}} + \frac{\mathrm{Ce}}{\mathrm{Qmax}} \qquad (3)$$

Where C_e is the equilibrium concentration ($mg.L^{-1}$), Q_e is the amount of dye adsorbed ($mg.g^{-1}$), Q_{max} is the maximum amount of dye that can be adsorbed in a monolayer (adsorption capacity $L.g^{-1}$)and K_L is the adsorption equilibrium constant ($L.mg^{-1}$). A plot of C_e/Q_e versus C_e should give a straight line figure (5)

The values of Q_{max} and KL were determined by the slopes and intercepts of figure (5) and have been given in table (1).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in equation [19]:

$$R_L=\frac{1}{1+KLC0} \qquad (4)$$

The value of R_L Indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The initial dye concentrations of (10- 40 mg/L) and the corresponding value of parameter R_L are found to be less than 1 and greater than 0 (0.020- 0.140). These results show that the methyl orange sorption onto bentonite is favorable at all temperatures considered. Figure (6) shows the values of R_L for methyl orange at different temperatures. The R_L values indicate that adsorption is more favorable for the higher initial dye concentration then the lower ones.

Temkin isotherm, which considers the effects of the heat of adsorption that decreases linearly with coverage of the adsorbate and adsorbent interactions, is given as[20] :

$$Q_e = B\ln AC_e \qquad (5)$$

And linearized as

$$Q_e = B\ln A + B\ \ln C_e \qquad (6)$$

Where A (L/g) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B= (RT/b) is related to heat of adsorption. The Temkin isotherm plot between $\ln C_e$ and Q_e is shown figure (7) enables the determination of the B and A from the slope and intercept Table (1). These results in table(1) show the Langmuir model was found to fit data significantly better than the Temkin model which shows the more homogeneous nature of bentonite powder.

Effect of temperature

Temperature has important effects on the adsorption process. The effect of temperature on the adsorption isotherm of the methyl orange on bentonite was studied at 298,308 and 318 K the results were displayed in figure (4). The results revealed that the amount of adsorption decreased from (0.905 to 0.381mg.g^{-1}) with temperature increase from 298 to 318 K. This decrease in amount adsorption with temperature is due to the enhancement of the desorption step in the adsorption mechanism indicating that the process is exothermic. It is known that the decrease of amount adsorption with the increase of temperature is mainly due to the weakening of sorptive forces between the active sites on the bentonite and methyl orange species, and also between adjacent dye molecules on the sorbed phase [21]

Estimation of thermodynamic parameters

Thermodynamic parameters such as Gibb's free energy (ΔG) (J/mole), enthalpy (ΔH) (J/mole) and entropy (ΔS) (J/mole.K) changes can be determined by the following equations:

$$\Delta G = -RT\ \mathrm{Ln}\ K_0 \qquad (7)$$

$$LnK_0 = -\Delta G/ RT \qquad (8)$$

$$LnK_0 = \Delta S/R - \Delta H/RT \qquad (9)$$

Where R is universal gas constant (8.314 J. $mole^{-1}.K^{-1}$) and T is absolute temperature in Kelvin.

Gibb's free energy change ΔG, is calculated using K_0 obtained from the method suggested by khan and Singh[22] by plotting Ln Q_e/C_e versus Q_e figure(8) and extrapolating to zero . The enthalpy and entropy changes are respectively determined from the slope and intercept of the plot Ln K_0 against 1/ T figure (9).

Thermodynamic parameters for the adsorption of methyl orange on bentonite are given in table (2). As shown in the table, the negative value of ΔG confirms the feasibility of the process and spontaneous nature of adsorption. The values of ΔH and ΔS are found be (-29.98) kJ/mole and (-83.31) J/mole.K respectively. The enthalpy implying that the adsorption process is exothermic, and lower temperature makes the adsorption easier. Enthalpy change due to chemisorption takes value between 40-120 KJ/mole, which is larger than that due to physisorption [23]. Therefore, the adsorption of the methyl orange dye under examination onto bentonite is likely due to physisorption. This result shows that the interaction between the dye and the bentonite is mainly electrostatic interactions [23]. The negative value of **ΔS** suggests decreasing randomness at the solid/liquid interface during the adsorption of methyl orange on bentonite in the aqueous solution.

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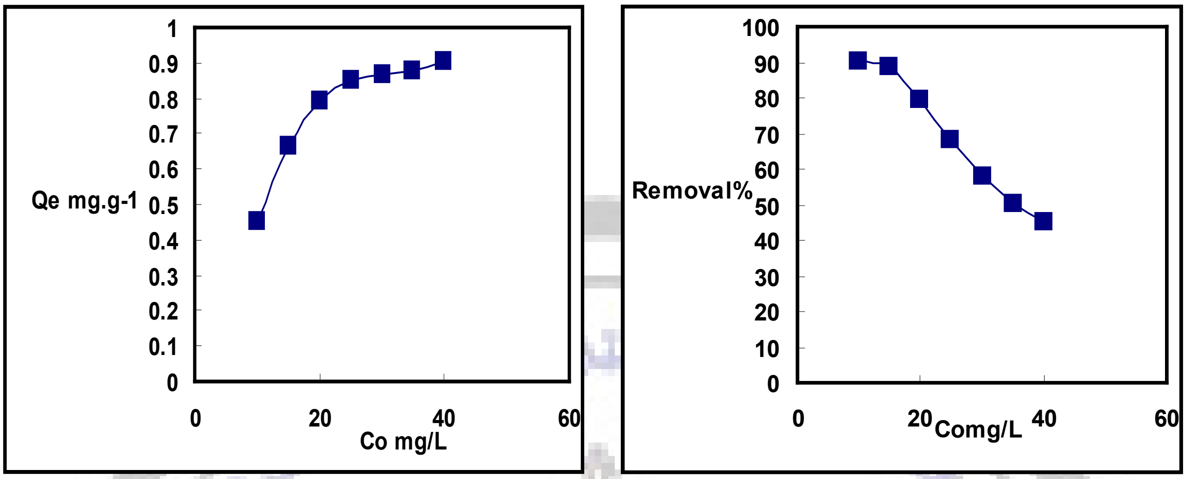
Table (1): isotherm constants for adsorption of methyl orange on bentonite at different temperature.

Isotherm constants							
T(C^o)	Langmuir				Temkin		
	K_L(L.mg^{-1})	K_0	$Q_{max(}$ mg.g^{-1})	R^2	A	B	R^2
25	1.233	8.17	0.931	0.9995	73.92	0.127	0.8774
35	0.615	5.21	0.528	0.9998	58.26	0.069	0.9205
40	0.650	3.82	0.402	0.9984	90.65	0.050	0.8535

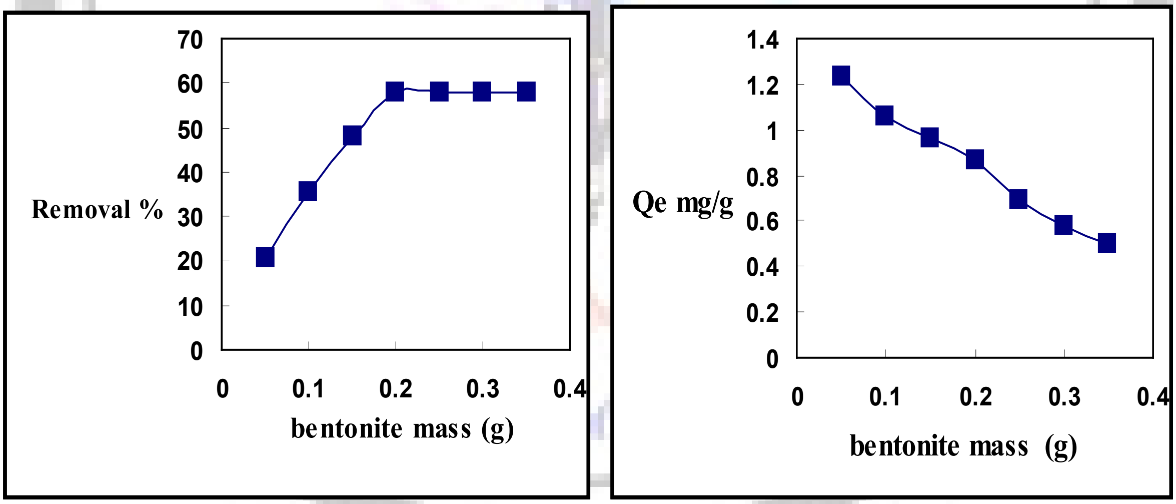
Table (2) : Thermodynamic parameters for methyl orange on bentonite

Temperature (K)	K_0	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS(J/K.mol)
298	8.17	-5.20	-29.98	-83.31
308	5.21	-4.23		
318	3.82	-3.54		



(a) (b)

Fig.(1a,b): The influence of initial dye concentration on the adsorption of methyl orange dye on bentonite (T=25 C^{o}, pH= 5,p.size 125µm).



(a) (b)

Fig.(2a,b): Effect of adsorbent dosage on methyl orange adsorption(T=25^{0}C,pH=5,p.size 125µm) .

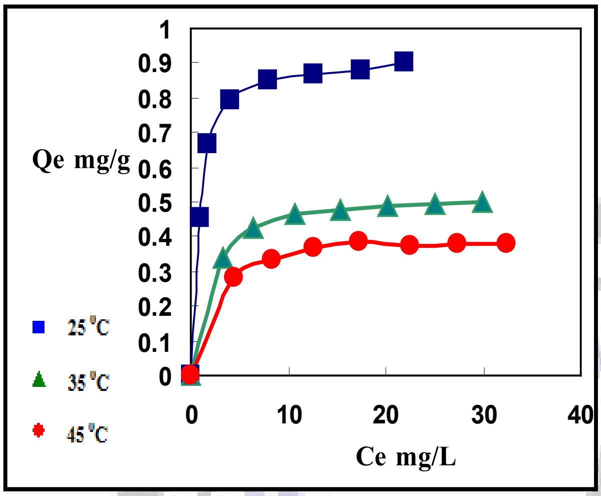


Fig. (4): The adsorption isotherms of the methyl orange on bentonite at different temperatures (pH=5, p.size 125µm

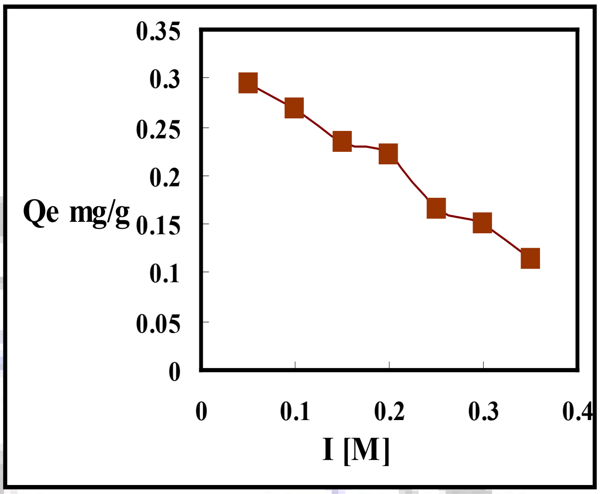


Fig. (3): Effect of ionic strength on the Adsorption methyl orange on bentonite ($T=25^0C$, pH=5, p.size 125µm)

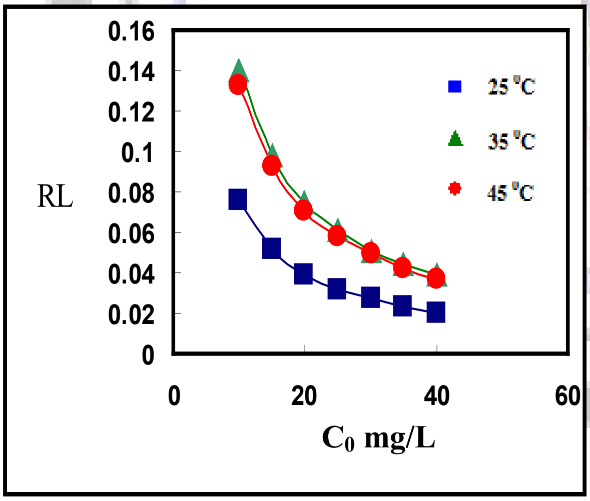


Fig. (6): plot of R_L against initial methyl orange concentration at various temperatures.

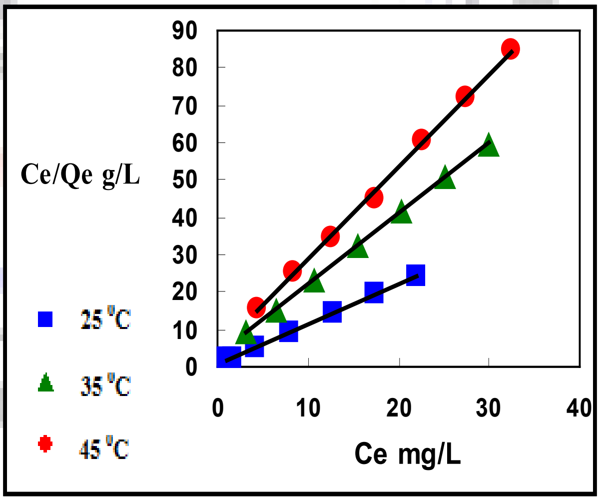


Fig. (5): Langmuir plots for the adsorption of methyl orange onto bentonite at various temperatures.

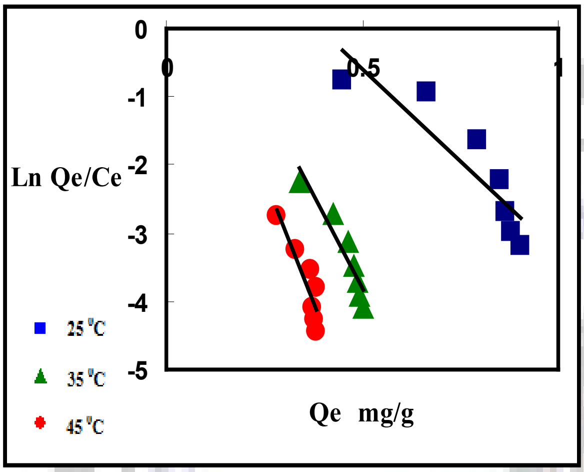


Fig. (8): Plot of Ln Q_e/C_e versus Q_e

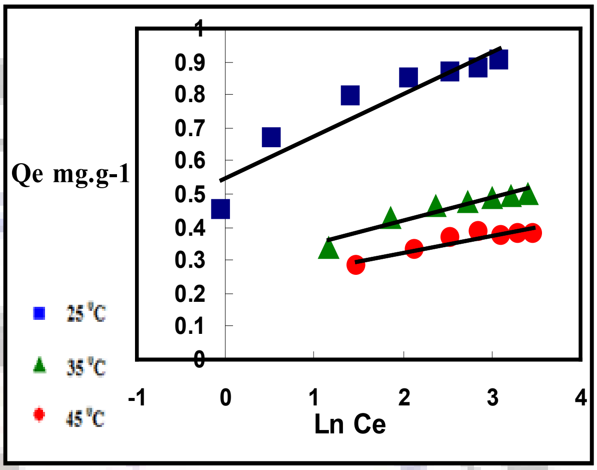


Fig. (7): Temkin isotherm plot of Q_e versus Ln C_e

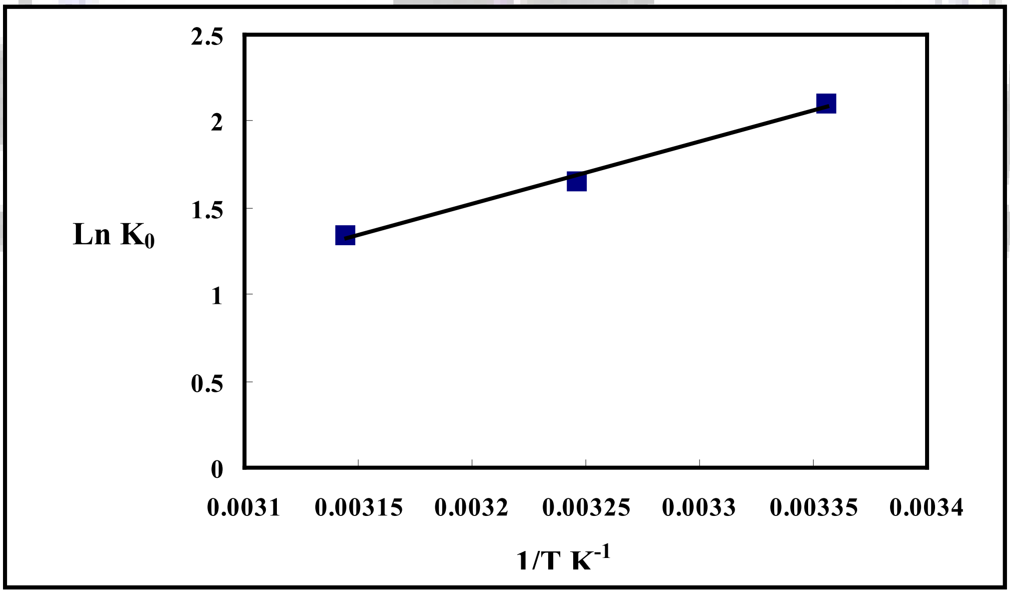


Fig. (9) Plot Ln K_0 versus 1/ T for the estimation of thermodynamic parameters.

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إزالة المثيل البرتقالي من المحلول المائي بواسطة البنتونايت العراقي

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الكلمات المفتاحية: الامتزاز، المثيل البرتقالي ، ايزوثيرم لانكماير وتمكن ، الشدة الايونية ، الدوال الثرموديناميكية

الخلاصة

يتناول موضوع البحث دراسة سلوك امتزاز المثيل البرتقالي في المحاليل المائية على سطح البنتونايت العراقي . أجريت دراسة العديد من العوامل ألمؤثره في عملية الامتزاز مثل التركيز الابتدائي وكمية المادة المازه والشدة الأيونية ودرجة الحرارة على سعة الامتزاز. أوضحت النتائج ان نسبة إزالة المثيل البرتقالي تزداد مع نقصان التركيز الابتدائي للمثيل البرتقالي وتزداد مع كمية المادة المازه. كذلك امتزاز المثيل البرتقالي يقل مع زيادة الشدة الأيونية وزيادة درجة الحرارة وأوضحت نتائج الاتزان لايزوثيرمات الامتزاز أنها مطابقة لمعادلة لانكماير وتمكن(Temkin) وان معامل الارتباط لمعادلة لانكماير كان أكثر مقارنة بمعادلة تمكن(Temkin) . وتم حساب الدوال الثرموديناميكية مثل ΔG و ΔH و ΔS واتضح ان عملية الامتزاز للمثيل البرتقالي هي عملية تلقائية وباعثة للحرارة.