Study of the Adsorption of Methylene Blue from Aqueous Solution: a Comparison between Iraqi & English bentonite Activity as Adsorbents

دراسة امتزاز صبغة ازرق المثيلين من المحاليل المائية: مقارنة بين فعالية طين البنتونايت العراقي والإنكليزي كمواد مازة

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Abstract

Background: Methylene blue dye uses as adsorbent to study the ability of different surface activities as adsorbents. The adsorbents can be used in the extraction of certain pollutant substances from solution on solids which is one of the cheapest and easiest separation methods. Furthermore, some of the extracted substances are economically important. In previous work, the ability of English bentonite to extract methylene blue dye from aqueous solution was carried out. In this work, Iraqi locally bentonite was used as a cheaper adsorbent for methylene blue from aqueous solution. The second aim of the present study is to make a comparison between English bentonite and Iraqi bentonite in different parameters of adsorption of Methylene blue dye from aqueous solution. Some practical parameters affecting adsorption process, in both clays, such as initial dye concentration and the thermodynamic parameters ($\Delta H°$, $\Delta G°$, $\Delta S°$) for the adsorption process also computed and compared.

Materials and Methods: Ten milliliters of different concentrations of methylene blue solutions (5, 10, 15, 20, 25, 30, 35, 40, 45, 50 mg/L) were mixed in water shakerbath with 0.05g of bentonite clay. Supernatants were separated by centrifugation. UV-Visible spectrophotometer technique used to follow up the adsorbed quantities after mixing the dye solution with bentonite. The experiment repeated at three different temperatures (5, 25, 45°C) to measure the thermodynamic parameters ($\Delta H°$, $\Delta G°$, $\Delta S°$) for the adsorption process.

Results: The extent of the methylene blue removal by Iraqi bentonite increased with increase in the initial concentration of the dye and with decrease temperature. Thermodynamic parameters, such as $\Delta H°$, $\Delta G°$, and $\Delta S°$ have been calculated by using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations.

Iraqi bentonite :($\Delta H°$=-32.04 KJ.mol^{-1}, $\Delta G°$=-14.78 KJ.mol^{-1}, $\Delta S°$=-٥٧.٩١J.mol^{-1}. °K^{-1}).

English bentonite: ($\Delta H°$=20.21 KJ.mol^{-1}, $\Delta G°$=-5.17KJ.mol^{-1}, $\Delta S°$=85.16 J.mol^{-1}. °K^{-1}).

Conclusion: Both English and Iraqi bentonite clays have ability to adsorb methylene blue. The dye removal increased with increase in the initial concentration of the dye. There is no significant difference in the amounts of dye adsorbed by both clays indicated the possible symmetry in the active sites of bentonite clays even they come from different origin. Thermodynamical data indicate that the adsorption of methylene blue on Iraqi bentonite is exothermic and spontaneous and high heat of adsorption indicates possibility of chemisorption process in addition to other ordinary forces including in adsorption. While same process on English bentonite is endothermic, spontaneous with very low free energy change. In conclusion, Iraqi bentonite clay is cheaper, available and has identical adsorptive activities for methylene blue. This research opens a series of studies for the uses of this Iraqi bentonite as adsorbent for different substances in pollution, medicine, supporter, and different fields in industry.

Keywords: clay, bentonite, adsorption, methylene blue, thermodynamic, $\Delta H°$, $\Delta G°$, $\Delta S°$.

الخلاصة

المقدمة: تستعمل صبغة ازرق المثيلين بكثرة كمادة مازة لدراسة فعالية مختلف ا لسطوح كمواد مازة. أن إزالة المواد الملوثة من المحلول باستعمال المواد ألمازة يعتبر من أسهل وارخص طرق الفصل. كما ان بعض المواد في المحلول تكون ذات أهمية اقتصادية واستخلاصها يعتبر ذو جدوى اقتصادية. في بحث سابق أجريت دراسة الفعالية السطحية لطين البنتونايت الإنكليزي لامتزاز واستخلاص صبغة ازرق المثيلين من المحلول. وفي هذا البحث تم استعمال طين البنتونايت العراقي كمادة مازة رخيصة لاستخلاص صبغة ازرق المثيلين من المحلول كما تمت المقارنة بين البنتونايت العراقي و الانكليزي في قابليتها على امتزاز الصبغة من المحلول المائي. كما تم في هذا البحث حساب ومقارنة تأثير بعض المتغيرات التجريبية على الامتزاز مثل

التركيز الابتدائي ودرجة الحرارة وحساب الدوال الثرموداينمكية (ΔH°, ΔG°, ΔS°) لعملية الامتزاز على كلا السطحين.

طريقة العمل: أخذت ١٠ مليليتر من محاليل صبغة ازرق المثيلين في انابيب محكمة وبتراكيز مختلفة 50 ,45 ,40 ,35 ,30 ,25 ,20 ,15 ,10 ,5 (mg/L) ورجت في حمام مائي هزاز لمدة ساعة واحدة مع ٠,٠٥ غرام من طين البنتونايت العراقي ثم فصل الراشح بجهاز الطرد المركزي. استخدمت تقنية المطيافية فوق البنفسجية لمتابعة الكميات الممتزة بعد مزج محلول الصبغة مع طين البنتونايت. أعيدت التجربة عند ثلاث درجات حرارية (45, 25, 5درجة مئوية وذلك لقياس الدوال الثرموداينمكية (ΔH°, ΔG°, ΔS°) *لعملية الامتزاز*.

النتائج: أظهرت النتائج أن كمية المادة المزالة بالامتزاز على سطح الطين العراقي تزداد بزيادة التركيز الابتدائي ونقصان درجات الحرارة. تم حساب قيم الدوال الثرموداينميكية باستخدام ثوابت الاتزان المستحصلة عند الدرجات الحرارية المختلفة وكانت كالاتي: البنتونايت العراقي: ΔH°=-32.04) KJ.mol^{-1}, ΔG°=-14.78 KJ.mol^{-1}, ΔS°=-57.19 J.mol^{-1}.°K^{-1})(ΔH°=20.21 KJ.mol^{-1}, ΔG°=-5.17KJ.mol^{-1}, ΔS°=85.16 J.mol^{-1}.°K^{-1}):البنتونايت الانكليزي.

الاستنتاج: لطين البنتونايت من كلا المصدرين القدرة على امتزاز واستخلاص صبغة ازرق المثيلين من المحلول. تزداد كمية المادة الممتزة مع زيادة التركيز الابتدائي. كما انه لا توجد فروق معنوية إحصائية في كمية المادة الممتزة لكلا السطحين مما يدل على احتمالية تماثل المواقع الفعالة لطين البنتونايت بغض النظر عن المصدر. تشير النتائج الثرموديناميكية الى أن امتزاز صبغة ازرق المثيلين من المحلول على سطح طين البنتونايت العراقي هو عملية باعثة للحرارة وآنية وان حرارة الامتزاز العالية نسبيا تشير الى احتمالية وجود امتزاز كيميـاوي بالاضـافة الـى القوى المعتادة المسببة لعملية الامتزاز. بينما كانت نفس عملية الامتزاز على البنتونايت الانكليزي عملية ماصة للحرارة وانية وقيم واطئة للطاقة الحرة. يستنتج من هذه الدراسة ان طين البنتونايت العراقي يمتلك قابلية امتزاز مقاربة للبنتونايت الاانكليزي مع ميزة انه متوفر وارخص. ان هذه الدراسة تفتح بابا لسلسلة من الدراسات حول البنتونايت العراقي كمادة مازة لمختلف المواد الملوثة والاستعمالات الطبية وكحامل للمواد في مختلف مجالات الصناعة.

مفاتيح الكلمات: طين البنتونايت-ازرق المثيلين – الامتزاز-الدوال الثرموداينمكية -ΔS° - ΔG° - ΔH°.

INTRODUCTION

Solids have the property of holding molecules at their surfaces either from the gas phase or from solution; this property is quite marked in the case of porous and finely divided materials [1]. The term adsorption refers to the accumulation of atoms, ions or molecules (adsorbate) on a surface of a solid substance (adsorbent) [2-3]. Many factors can influence the process of adsorption; the concentration of adsorbent (substance being adsorbed), surface area of the clay; temperature, pH, ionic strength, solubility, chemical state of both adsorbent and adsorbate molecules and the kinetic effect [1, 2, 4].

The most important application of the surface active substances is as an adsorbent for different water pollutants such as metal ions [5, 6], different industrial dyes [7, 8, 9]. Some active surface materials also have important applications in medicine arises from their high adsorption capability as physical antidotes in the treatment of acute poisoning by toxic substances and drug overdosage [10, 11], as a drug carrier [12], and it used as a component of some pharmaceutical preparations such as calamine lotion.

Some clay materials were studied and found to possess high surface activity such as attapulgite [13], kaolin [14, 15], and bentonite [16].

In previous work [17], carried out in our laboratory, English bentonite (British Pharmacopoeia 2001) [18] used as adsorbent for methylene blue dye (Methylthioninium Chloride) from aqueous solution. The clay showed good adsorptive activity. The British Pharmacopoeia define bentonite as a natural clay containing a high proportion of montmorillonite, a native hydrated aluminium silicate in which some aluminium and silicon atoms may be replaced by other atoms such as magnesium and iron. Montmorillonite, the most abundant mineral of bentonite, showed adsorption ability of bacteria [19], different toxins [20, 21], metal ions [22], different herbicides in environment [23] and used in different agricultural formulations [24].

The selection of methylene blue due to the fact that in medicine, methylene blue used as antidote and in the estimation of adsorptive capacity of Kaolin and attapulgite clays that used for drug formulation [18, 25].

The term adsorption isotherm refers to the relation between the extent of adsorption (Qe) or (X/M) with the equilibrium concentration of the adsorbate in solution (Ce) at constant temperature. (X) is the amount of dye adsorbed in milligrams by (M) grams of the adsorbent [26]. Two main theories have been adopted to describe adsorption isotherms. The first, Langmuir adsorption isotherms which represented by the linear equation:

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{Ce}{a} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

Where (a) represents a practical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate. The constant b is the equilibrium adsorption constant which related to the affinity of the binding sites [27].

The applicability of these equations on the adsorbent-adsorbate (solute) system assume the formation of one layer of adsorbate molecules on the surface while the Freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of more than one layer is probable. The linear form of Freundlich isotherm is:

$$\log Q_e = \log k + \frac{1}{n} \log C_e \qquad \text{------------------ (2)}$$

Where k and n are Freundlich constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively [4, 27].

In this work, a study of Iraqi available bentonite clay as an adsorbent for the methylene blue dye from solution and compare the adsorption capacities, isotherms, and thermodynamical parameter values between English and Iraqi bentonite.

Materials & Methods

(a) Clay Treatment:

The Iraqi bentonite clay was collected from an open mine in Trifawi area and classified as bentonite contains about (75%) of its weight montmorillonite mineral. The analysis showed the chemical components of the bentonite expressed as weight per weight ratios are SiO_2=54.66%, Al_2O_3=14.65%, MgO=6%, Fe_2O_3=4.88%, CaO=4.77%, SO_3= 1.2%, Na_2O=0.65%, and Loss On Ignition=12.56% in addition to other rare ions that were not analyzed. The clay was washed with excessive amounts of distilled water to remove any soluble materials, filtered and dried at $160^°$ C for three hours and kept in an airtight container. The clay was grinded and sieved to a particle size of 75µm and then used in all adsorption experiments.

The English bentonite clay B.P. was obtained from (Evans-Liverpool). The clay was dried at $160^°$ C for two hours and kept in an airtight container. The particle size of clay was equal or less than 75µm and then used in all adsorption experiments.

(b) Adsorption process:

A volume of 10 milliliters of ten different concentrations of methylene blue solutions (5, 10, 15, 20, 25, 30, 35, 40, 45, 50 mg/L) was shaken with 0.05g of bentonite at a certain temperature in a thermostated shaker bath at shaking speed 60cycle/minute for one hour which is measured experimentally as a time needed for reaching the equilibrium state. After the equilibrium time is elapsed, the mixtures were centrifuged at a speed of 3000Xg for 10 minutes. Absorbencies were measured at the maximum wave length (λ_{max}) of methylene blue solution (664nm) using UV-Visible spectrophotometer (Apple® type) and then converted into absolute concentration readings through the calibration curve. The experiments were repeated at different temperatures (5, 25, 45ºC) in order to measure the thermodynamic parameters (ΔHº, ΔGº, ΔSº).

(c) Calculations:

In order to obtain a thermodynamical state of the adsorption process, the adsorption experiments were repeated at different temperatures (5, 25, and 45ºC) to measure the thermodynamic parameters (ΔHº, ΔGº, ΔSº). The equilibrium constant (K) for the adsorption process at each temperature is calculated from division of the quantity of dye adsorbed on the bentonite surface on the quantity of dye still present in solution:-

$$K = \frac{Qe*0.05}{Ce*0.01}$$ --(3)

Where (0.05g) represent the weight of the clay that has been used and (0.01L) represents the volume of the dye solution used in the adsorption process.

The change in free energy (ΔGº) could be determined form the equation:-

$$\Delta G° = -RT \ln K$$ --(4)

Where R is the gas constant (8.314 J.mole^{-1}.ºK^{-1}) and T is the absolute temperature.

The heat of adsorption (ΔHº) may be obtained from the vant Hoff's equation:-

$$\ln K = \frac{-\Delta H°}{RT} + cons \tan t$$ --(5)

Where K is the equilibrium constant when Ce approaches to zero at certain temperature as shown in Figure (1). It obtained from plotting (Ln K) of each concentration against Ce. Plotting (In K) versus (1/T) should produce a straight line with a slope =(-ΔHº/R) from which enthalpy (ΔHº) of the adsorption process is obtained as shown in Figure (2) and Table (1).

The change in entropy (ΔSº) was calculated from Gibbs equation:

$$\Delta G°= \Delta H° - T\Delta S°$$ -- (6)

Results and Discussion:

Ability of Adsorption:

The adsorption processes still the most interested field for research because its applicability and minimum requirement for work in laboratories. Furthermore, different important applications use this process for pollution treatment [5, 9, 27] or in medicine [11, 12] as mentioned in the introduction. Many substances used as adsorbents for different dyes in order to obtain cheep, available, non toxic adsorbents for removing dyes from aqueous solutions in different industries [28, 29, 30]. The adsorption amounts may explained by dependency of adsorption on the relative energies of adsorbent-adsorbate, adsorbate-solvent, and adsorbate-adsorbate interactions [4]. These findings may be applied for the adsorption of dye on bentonite surface in our study. In comparison, it's noticed that there is no statistical significant differences in the amount of methylene blue dye adsorbed by English or Iraqi bentonite clays. This may be due to the fact that the adsorption on active sites is related to the backbone of bentonite clay regardless the origin of the clay.

Adsorption Isotherm

Adsorption isotherm shape of methylene blue dye on Iraqi bentonite depends on temperature as shown in Figure (3). According to the Giles interpretation [31] for the adsorption isotherm shapes, the adsorption isotherm of the dye molecules on the Iraqi bentonite surface obeyed Langmuir adsorption isotherm (L2 type) at 5 and 25**ºC** indicating saturation process for the most active sites of the bentonite surface; i.e adsorption at 5 and 25**ºC** occurs mainly on the highest energy active sites and one adsorbed layer formed only. At 45ºC the both adsorption isotherm equations, Freundlich and Langmuir are applied as shown in Table (2). These results concluded from the applicability of linear form of both equations expressed in equations (1 & 2) as shown in Figure (4 & 5) respectively. This result may indicate that at 45ºC the most active sites for adsorption have equal energy of activation and can adsorb

dye molecule in a mechanism differ from the adsorption mechanism that occur at lower temperature. The Freundlich equation, unlike Langmuir one, does not become linear at low concentrations but remains convex to the concentration axis; nor it does show a saturation or limiting value [32].

In comparison, adsorption of methylene blue dye on bentonite from English origin obeyed Freundlich adsorption isotherm (S3 type) at all temperatures. The pure applicability of Freundlich equation may indicate the heterogeneity of the English bentonite surface and the presence of different types of forces between the dye molecules and the surface active sites [32].

Adsorption isotherms of different dyes (malachite green dye) on bentonite [33] and (Acid Red 57 and Acid Blue 294, and Acid Blue 193 dyes) on different modified bentonites [34, 35] were also obeyed Freundlich isotherm indicating heterogeneity of bentonite surface [4, 26]. While the adsorption isotherm of methylene blue on Iraqi bentonite obeyed Langmuir isotherm as mentioned previously.

Mechanism of adsorption

The process of adsorption from solution is more complicated than the corresponding process of gas adsorption on solid surface. The solvent effect and the complicated interaction between solvent molecules and dye molecules to be adsorbed have to be taken into account [32].

The study of the adsorption process of dye on bentonite clay requires taking the nature of the surface and chemical structure of the adsorbed dyes into consideration. Bentonite surface consists of small patches of various kinds of active sites which are different in physical and chemical nature or in the steric orientation of molecules towards the surface [36]. On the other hand the chemical structure of methylene blue showed the presence of phenothiazine ring that carry the positive charge on the sulfur atom of the ring. This fact may indicate the possibility of ion exchange or chemisorption process mechanisms in addition to the well known physical adsorption mechanism.
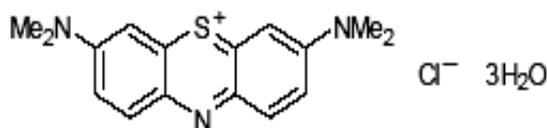
Methylene Blue (3,7-Bis(dimethylamino)phenothiazin-5-ium chloride trihydrate)

In one research, the adsorption of malachite green from aqueous solutions on bentonite has been carried out by physical adsorption concluded from the calculated thermodynamic parameters [33].

The mechanisms of adsorption of any adsorbent on different bentonites were best described with a model that included; cation exchange, surface complexation of ion forms of the compounds, solution speciation, the presence of other competitor ions in bentonite, and the exchangeable pore waters may also affect [37].

Thermodynamic parameters

The thermodynamical parameters values for the adsorption of methylene blue from aqueous solution by both clays are as follow:

Iraqi bentonite: (ΔH°=-32.04 KJ.mol^{-1}, ΔG°=-14.783 KJ.mol^{-1}, ΔS°=-5.166 J.mol^{-1}.$^\circ$K^{-1}).

English bentonite: (ΔH°=20.21 KJ.mol^{-1}, ΔG°=-5.17KJ.mol^{-1}, ΔS°=85.16 J.mol^{-1}.$^\circ$K^{-1}).

Thermodynamical data indicate that the adsorption of methylene blue on Iraqi bentonite is exothermic and spontaneous and high heat of adsorption indicates possibility of chemisorption process in addition to other ordinary forces included in the adsorption process. Other adsorption processes on bentonite clay was also exothermic processes [38]

While the adsorption of methylene blue process on same English bentonite is endothermic, spontaneous with very low free energy change. Hence it may be entropically derived in addition to the change in energy associated the adsorption process. These values are low and indicated a spontaneous adsorption process as seen in the adsorption of other substances on bentonite [39, 40, 41]. It is supposed from the thermodynamic values that, weak and nonspecific interaction occurs between dye molecules

and the active sites of bentonite clay surface. The main differences in the adsorption of methylene blue on Iraqi and English bentonite clays are shown in Table (3).

Conclusion:

Adsorption of on English bentonite is endothermic process with very low thermodynamic parameters values. While same process is exothermic on Iraqi bentonite. It can be concluded from the results of the present study that the process of adsorption of Methylene blue on both types of bentonite may be used effectively to remove the dye from aqueous medium. Iraqi bentonite clay is cheaper, available and has identical adsorptive activities for methylene blue. Furthermore, the thermodynamical data indicate higher binding forces between Iraqi bentonite and dye molecules than English clay. Therefore, this research open a series of studies for the uses of this Iraqi bentonite clay as adsorbent for different substances in pollution, medicine, supporter, and different fields in industry.

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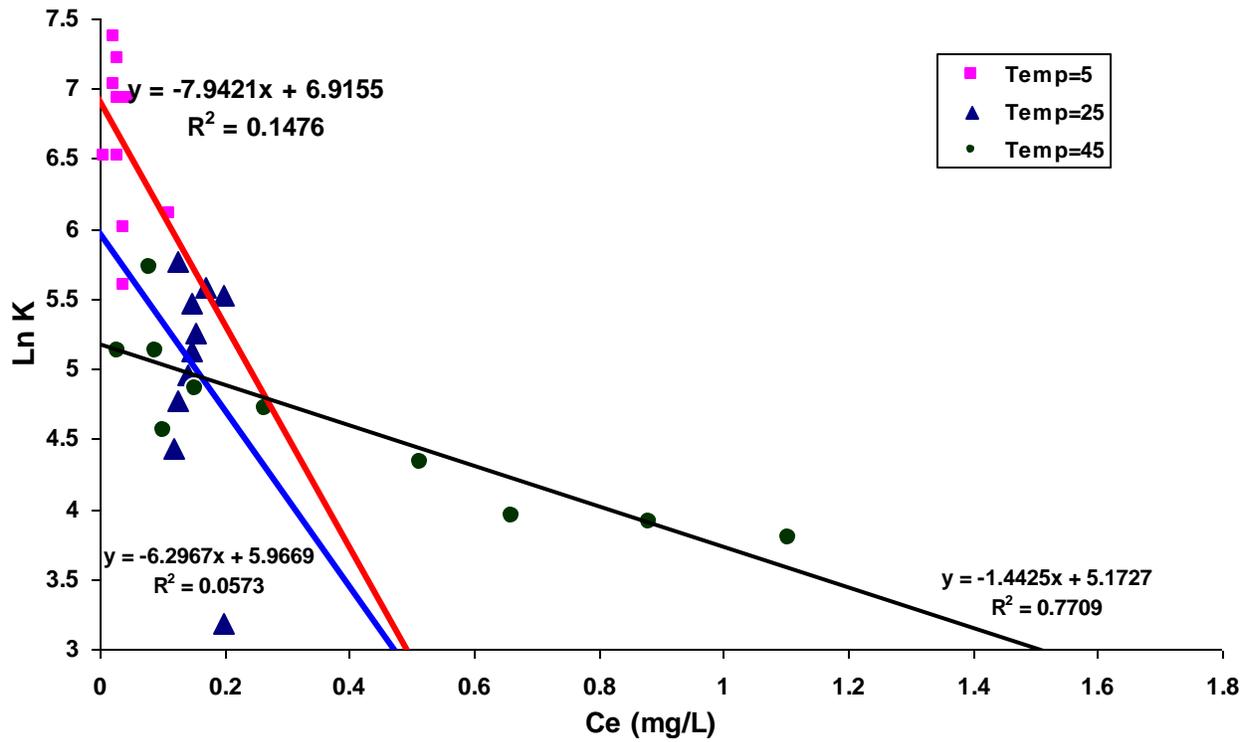
Figure (1): Natural logarithm of equilibrium constants (LnK) against equilibrium concentration (Ce) of adsorption of methylene blue on bentonite clay surface. The intercept represent the (LnK) when Ce approaches to zero at certain temperature.
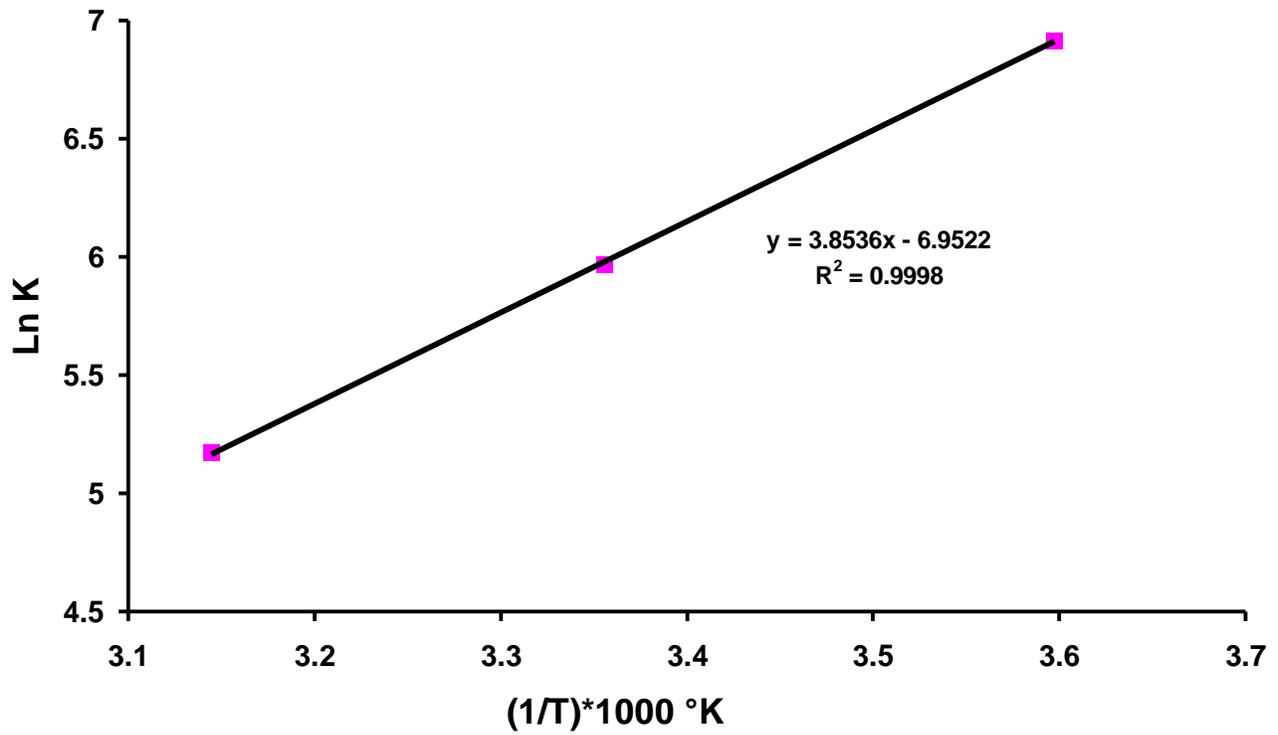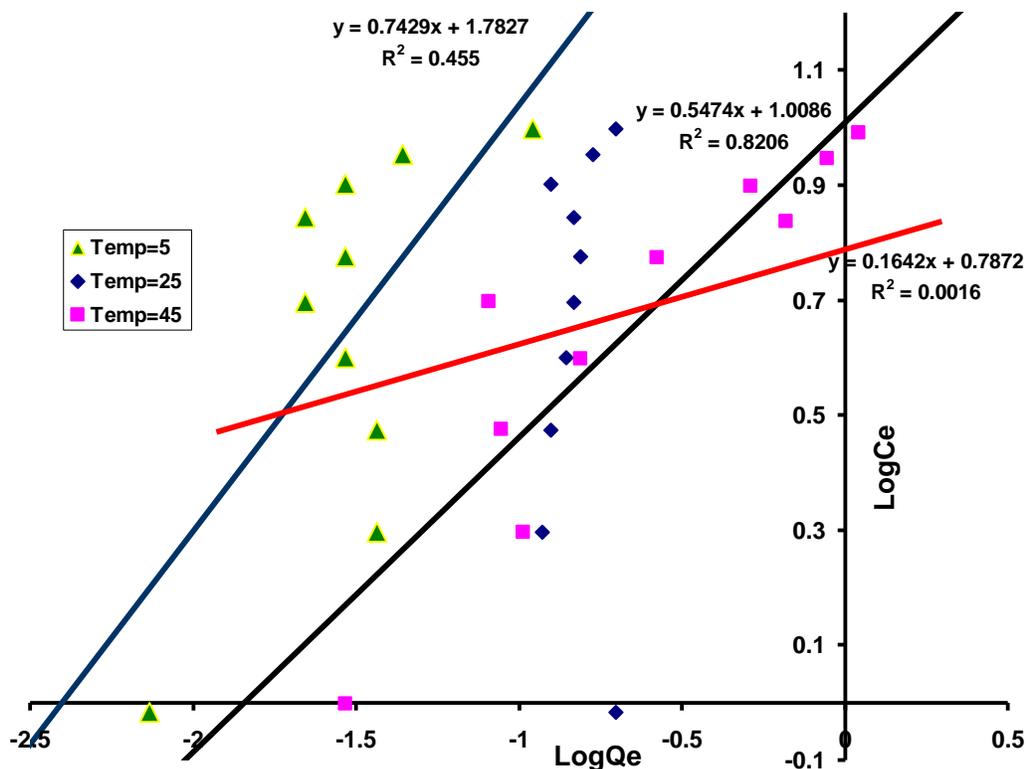
Figure (2): Correlation of equilibrium constants, when Ce approaches to zero of adsorption of methylene blue on bentonite clay surface at (5, 25, and 45ºC) according to the vant Hoff's equation.
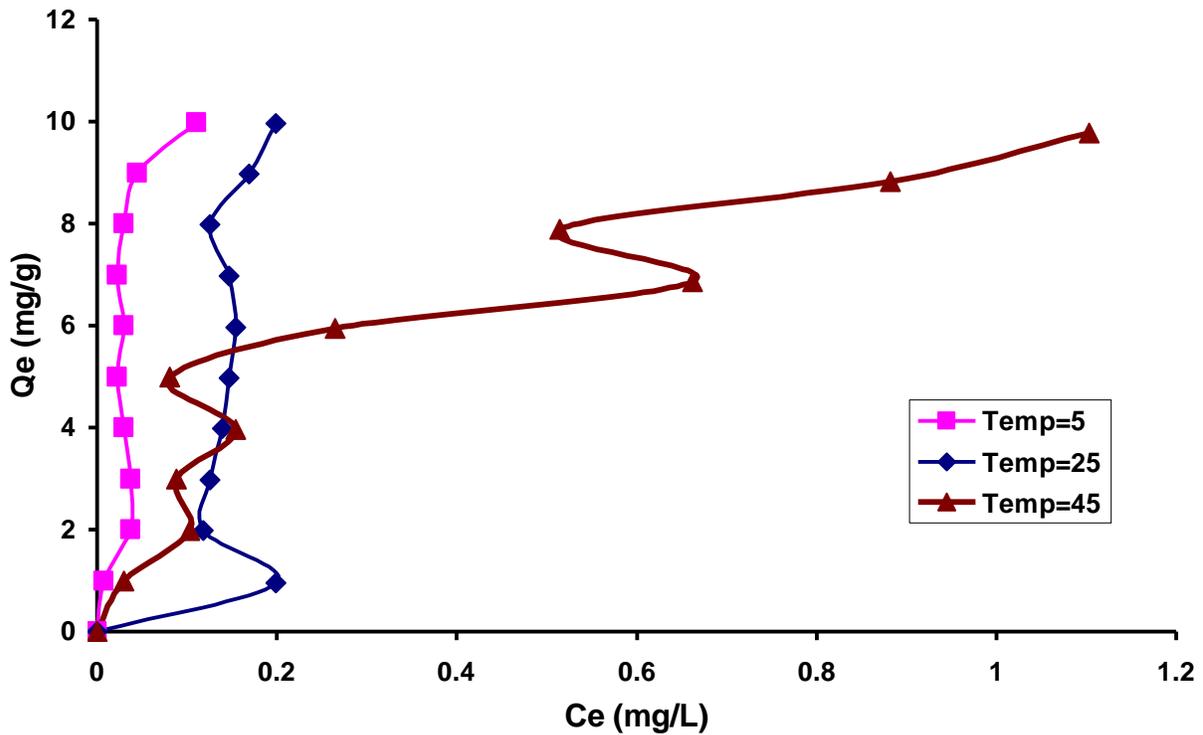
Figure (3): Adsorption isotherms of methylene blue on Iraqi bentonite clay surface at (5, 25,and 45ºC).
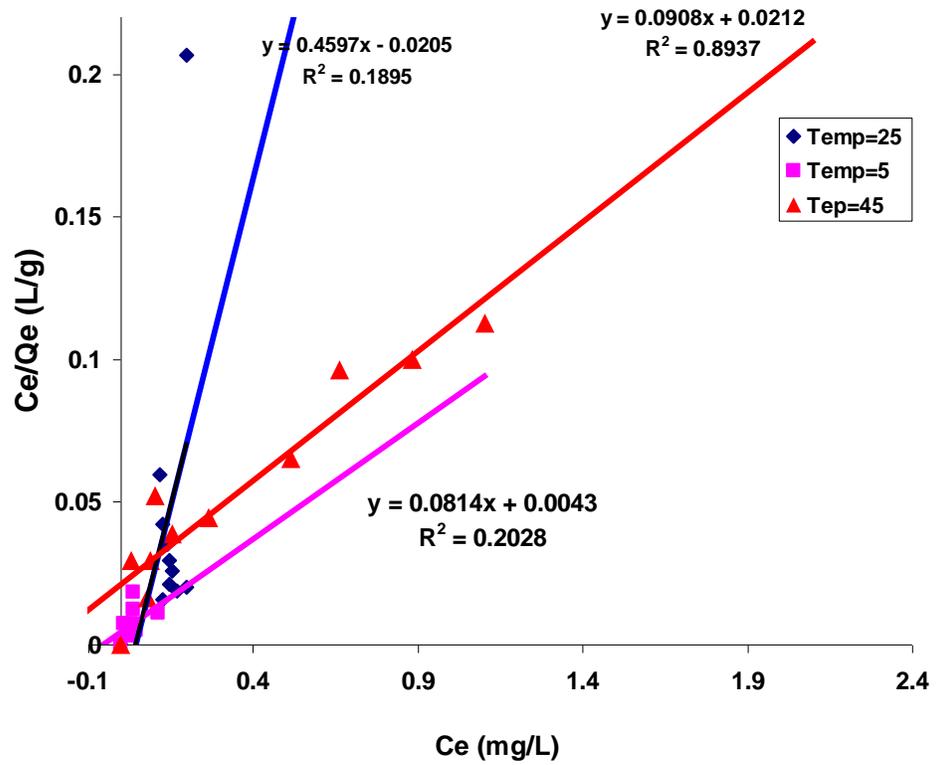
Figure (4): Langmuir lines for the adsorption of methylene blue on Iraqi bentonite clay surface at (5,25, & 45 ºC)

Figure (5): Freundlich lines for the adsorption of methylene blue on Iraqi bentonite clay surface at (5, 25, & 45 ºC)

Table (1): Vant Hoff's parameters including reciprocal of absolute temperature and natural logarithm of equilibrium constant.

T	(1/T)*1000	Ln K
278	3.597	6.9155
298	3.356	5.9669
318	3.145	5.1727

Table (2): Correlation coefficients (r-value) of the Freundlich and Langmuir lines that represented in Figures (1 and 2)

Freundlich		Langmuir	
Temperature (ºC)	r-value	Temperature(ºC)	r-value
5	0.514	5	0.675
25	0.040	25	0.435
45	0.911	45	0.945

Table (3):Comprehensive comparison between English bentonite and Iraqi bentonite for the adsorption of methylene blue from aqueous solution.

Parameter		English bentonite	Iraqi bentonite
Adsorption Isotherm		Obey Freundlich at all temperatures	Obey Freundlich & Langmuir at 5 & 45ºC and obey Langmuir at 25ºC
Equilibrium Constant (K)	5	4.003224	1007.775
	25	8.044591	390.2939
	45	11.96517	176.3904
Maximum Quantity adsorbed (Q)	5	9.322854 mg/g	9.977941 mg/g
	25	9.484885 mg/g	9.960294 mg/g
	45	9.680774 mg/g	9.77941 mg/g
$\Delta H°$ at 25ºC		20.212 KJ.mol^{-1}(Endothrmic)	-32.04KJ.Mol^{-1}(Exothrmic)
$\Delta G°$ at 25ºC		-5.166 KJ.mol^{-1}	-14.783KJ.Mol^{-1}
$\Delta S°$ at 25ºC		85.16 J.mol^{-1}.ºK^{-1}	-5.166J.Mole^{-1}.K^{-1}
Giles Classification of adsorption isotherm		(S3) type at all temperatures	(S1) type at 5 & L2 type at 25 & 45 ºC