ADSORPTION STUDIES OF LINEAR ALKYLBENZENE SULFONATE BY USING IRAQI BENTONITE CLAYS

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Abstract

LAS is the basic material in the industry of liquid and solid detergents, the adsorption of LAS achieved in the concentration 50-1000 mg.l^{-1}.

The adsorption efficiency on bentonite was modified using a cationic surfactant which is Cetyl Pyridinium Bromide (CPB), that raised the adsorption percentage Q(%) from 36% for free bentonite to 81% for modified bentonite at 298 K using 250 ppm LAS solution.

The effect of adding three kinds of inorganic salts was studied; the salts were $Pb(NO_3)_2$, $MgSO_4$, and $CaSO_4$ in the concentration range (100-400) mg.l^{-1}, The results showed a negative effect on the sorption process.

The effect of pH on the sorption of LAS on clay showed that the highest sorption on bentonite was at pH 9, The thermodynamic parameters were calculated, and the kinetics were studied and it followed a pseudo-1st order kinetics.

دراسة امتزاز سلفونات الكيل بنزين الخطية باستخدام اطيان البنتونايت العراقية

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الخلاصة

يعتبر ال LAS المادة الأساس في صناعة المنظفات السائلة والصلبة ,وتم دراسة امتزاز هده المادة على طين البنتونايت بتراكيز تراوحت بين 50–1000ملغم.لتر–1. تم تحسين أمتزاز ال LAS على طين البنتونايت بأستخدام منشط سطح موجب الشحنة وهو مادة بروميد سيتايل البريدين (CPB) والذي رفع النسبة المئوية للأمتزاز من 36% الى 81% بأسخدام 250 ملغم.لتر–1 من محلول ال LAS.

تم دراسة تأثيرأضافة ثلاثة املاح لاعضوية على الأمتزاز وهي $MgSO_4$, $Pb(NO_3)$,$CaSO_4$ وأستخدمت تراكيز من هده الأملاح تراوحت بين 100–400ملغم .لتر–1,وأظهرت النتائج ان تلك الأملاح كانت ذات تأثير سلبي على عملية الأمتزاز

من خلال دراسة تأثير الLAS على عملية الأمتزاز تبين أن أعلى كمية للأمتزاز كانت عند PH تساوي 9 , وقد تم حساب الدوال الثرموديناميكية و دراسة حركيات الأمتزاز وكانت من المرتبة الأولى الكاذبة.

Introduction

Adsorption is the association of an adsorbate compound onto a surface (adsorbent), usually in a liquid-solid or vapor-solid system, while absorption involves the redistribution of a compound from the aqueous phase into a volume of material. In geochemical systems, however, the two are often indistinguishable, and the term adsorption is almost used.

This term is often used when the specific mechanism is not known, and the surface phenomenon could be either absorption or adsorption, or a combination of the two (1).

The adsorption process may also involve the removal of solute molecules from the bulk solution or from the solid surface by a process called "desorption" (2)

Adsorption has traditionally been divided into two kinds: weak physi-sorption, and strong chemi-sorption.

The measurement of the amount of gas adsorbed over a range of partial pressures at a single temperature results in a graph Known as "adsorption isotherm" (3). Many different types of isotherms have been observed in the literatures, these isotherms can have very different shapes depending on the type of adsorbent, the type of adsorbate and intermolecular interactions between the gas and the surface(4).

Langmuir behavior assumes a rapid reversible adsorption, and interaction only between sorbate molecules and a surface site.

The Langmiur equation could be expressed as(5):

$$\left[\frac{Ce}{Q} = \frac{1}{K} + \frac{a}{K} . Ce\right] \qquad \text{.......(1)}$$

where Q is the amount of adsorbate (mg/g), C_e is the equilibrium concentration (mg/l), and a, K are constants related to the binding strength respectively or sometimes called Langmiur constants.

The adsorption isotherm of Freundlich (6) is one of the most important isotherms that deal with adsorption at solid-liquid interface, which has been introduced by (Herbert Max finaly Freundlich) a German scientist in 1926 (6).

Most of the surfaces are heterogeneous, so the change in potential energy is regular, and the adsorption sites are not equivalent in energy (7), hence the multi-layer formation is highly expected.

Freundlich equation could be written as follows:

$$Q=K_F\, C_e^{1/n} \qquad \text{........ (2)}$$

$$\log Q = \log K_F + (1/n) \log C_e \qquad \text{........(3)}$$

Bentonite clay is widely used in many fields of technology including adsorption of dyes and surfactants (8), refining oils, and treatment of effluents from metal ions and organic pollutants. Moreover, the addition of surfactants to the suspension of bentonite was found to enhance the geological properties of the latter (9).

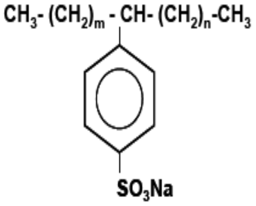
The wide use of bentonite may be attributed to its high surface area, high chemical and mechanical stability and to a variety of surface and structural properties.

Bentonite modified by surfactants was reported to be efficient in the treatment of various pollutants (8).

The ability of surfactant to adsorb at solid-liquid interface is controlled by the chemical nature of the components of the system: the surfactant and the medium.

Linear Alkylbenzene Sulfonate (LAS) is the major anionic surfactant used world wide in detergents and household cleaning product formulations.

The chemical structure of LAS could be shown as follows

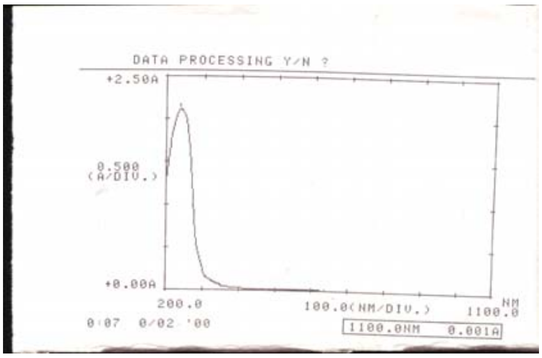


The chemical structure of LAS, where m+n=10.

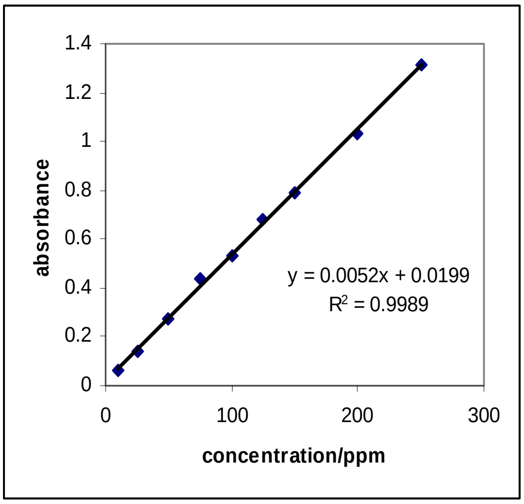
The pollution by detergents is the major problem of industrial progress, since a large amount of those detergents are disposed into the environment and specifically into the rivers and lakes, consequently, the major objective of this research is to minimize the environmental impacts of these detergents via an adsorption study using Iraqi clays.

Experimental Procedures

A sample of 1000 ppm LAS solution was taken and a spectrum scan was measured using UV-VIS Spectrophotometer, Shimadzu-160, and showed a λmax at 239 nm, and as shown in following figure.



The calibration curve was accomplished by measuring the absorbance of solutions (10, 25, 50, 75, 100, 125, 150, 200 and 250 ppm) at 239 nm. Table 2.1 shows the absorbance of each solution, thereafter plotting of absorbance vs. concentration, and as shown below:



The quantity of adsorbate was calculated by using the following, formula.

Qe = Vsol (Co- Ce)/m …… (4)

where:

Qe= Quantity of adsorbate (mg/g).

Vsol= Total volume of adsorbate solution (l).

Co= Initial concentration of adsorbate solution (mg/l).Ce= Concentration of adsorbate solution at equilibrium.

The percentage of adsorption was calculated by using the following formula:

$$\%Q = \frac{(C_o-}{Co} \times 100 \qquad \ldots(5)$$

where:

%Q = Adsorption percentage.

Co= Initial concentration of adsorbate solution (mg/l).

C_f= Final concentration of adsorbate solution (mg/l).

Surfactant-modified bentonite was prepared by mixing equal amounts of bentonite and Cetyl Pyridinium Bromide (CPB), 1g of bentonite mixed with 1g CPB, then a 100mL of distilled water was added to the mixture and stirred overnight at room temperature, thereafter the obtained mixture was filtered and the supernatant was discarded, and the precipitate was washed with distilled water several times to remove the bromide ions, then the precipitate was dried at 90°C in an oven.

3.Results and Discussion

Figure 1 shows the variation of Qe with the contact time needed for a solution of 1000, 250, and150 ppm LAS to be in an attachment with 0.1 g of bentonite clay.

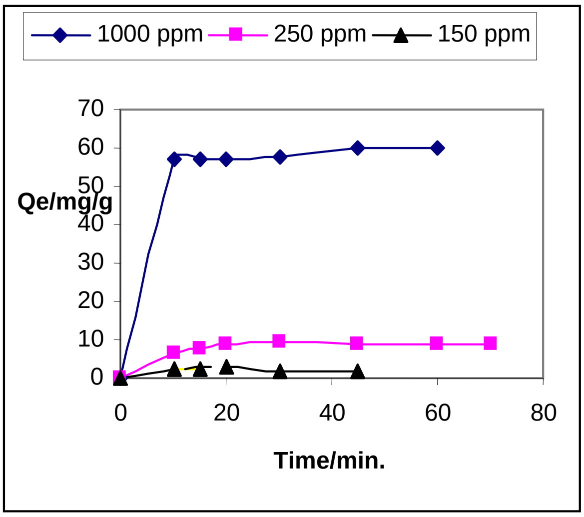


Figure 1:The variation of Q_e with time for 1000, 250, 150 ppm LAS solutions at 298 K.

Figure 2 shows the adsorption isotherm of (50-250) ppm LAS solutions at 298 K, the adsorption isotherm was of Freundlich type

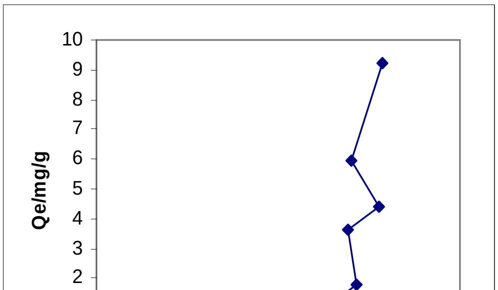


Figure 3 shows the effect of the dose of sorbent on the adsorption process for bentonite clay.

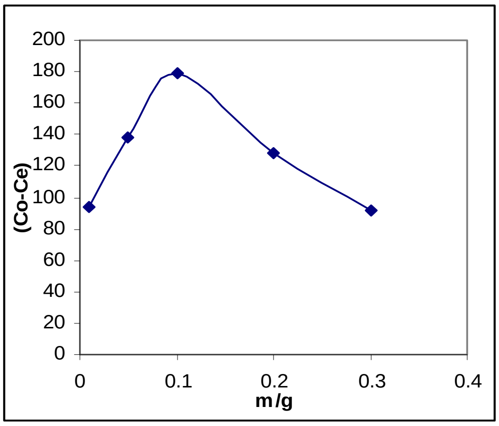


Figure 3:The effect of sorbent dose on the adsorption process at 298 K

According to the above figure the maximum uptake of adsorbent was at 0.1g of bentonite clay.

Figure 4 shows the effect of pH on the adsorption quantity of LAS on the surface of bentonite clay at 298 K, since it was in the maximum at pH 9 while it was in the minimum at pH 4.

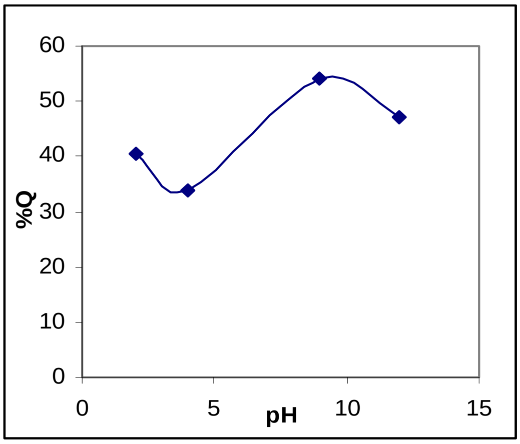


Figure 4 The effect of pH on the adsorption

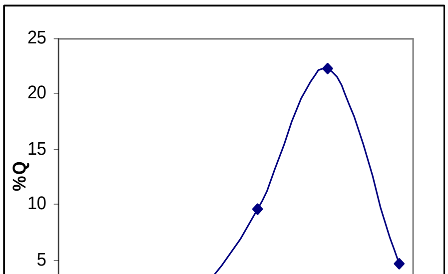


Figure 5 shows that the adsorption percentage increases as the temperature increases, knowing that the adsorption process is an exothermic process (2), while the absorption process is an endothermic process. However, the adsorption process could be exothermic or endothermic depending on the dominant process, in other words the adsorption or absorption or both of them.

Following the adsorption percentage in figure 5, reveals that at 288-308 K, the adsorption percentage increased, and then the proposed mechanism is absorption, since it is an endothermic process.

At 318K the adsorption percentage reached a steady state so the probable mechanism is adsorption, and at 328K the probable mechanism is desorption, since the LAS molecules start to leave the surface of bentonite clay.

As a consequence, the behavior of LAS molecules on the surface of bentonite with temperature raise could be explained as a comprehensive mechanism involving three stages, absorption, adsorption, and then desorption.

The thermodynamic functions, ΔH, ΔG, and ΔS were calculated using the following formulas:

$b= a.\exp(-\Delta H/RT)$ ……..(6)

$\ln b = \ln a- (\Delta H/R).1/T$ ..….. (7)

$\ln a= \Delta S/R$ ……. (8)

$\Delta G = \Delta H-T\Delta S$ .... (9)

where b is the maximum adsorption quantity for 250 ppm LAS solution on bentonite and could be obtained from the plot of Ce/Qe versus Ce.

The equation (7) was used to calculate the ΔH, by plotting of ln b versus 1/ T.

Figure 6, showed a linear relationship and the slope represents $-\Delta H/R$, R is the gas constant ($8.314\ j.K^{-1}.mol^{-1}$), and the ΔH values were calculated.

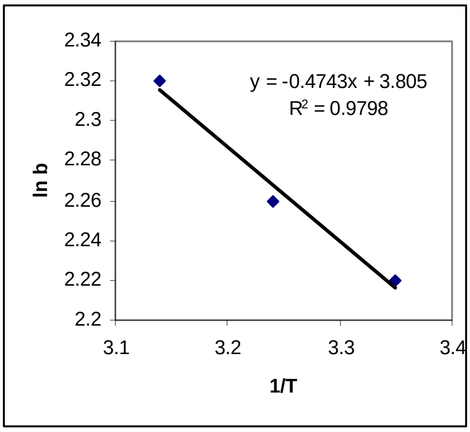


Figure 6: The plot of ln b versus 1/T.

Table 1: The calculated thermodynamic parameters

T/K	*$\Delta H/kJ.mol^{-1}$*	*$\Delta G/kJ.mol^{-1}$*	*$\Delta S/kJ.mol^{-1}K^{-1}$*
298	+0.97	-1927.09	+6.47
308	+0.852	-1974.7	+6.52
318	+2.48	-2663.34	+8.571

Figure 7 shows the effect of salts concentration on the adsorption process of 250 ppm LAS solution containing interfering salts pb(NO3)$_2$, $MgSO_4$, and $CaSO_4$.
All the three salts have reflected a negative impact on the adsorption process.

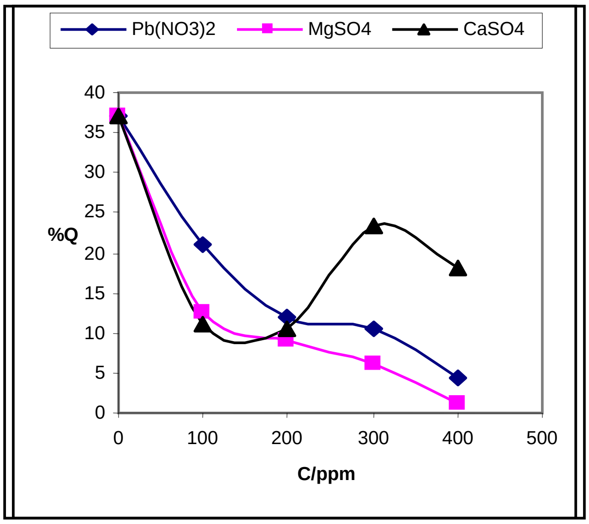


Figure 7:The plot of adsorption percentage versus conc. Of interfering salts

The kinetics of adsorption process were studied via introducing three models at 298 K and at specific periods of time to calculate the rate constant and the energy of activation of adsorption process.

The rate constant k_{sorp} was determined from the following pseudo-1st order rate expression, which could be expressed as follows(11):

$$\ln(qe-qt)=\ln qe-ksorp\ t \qquad \ldots\ldots (10)$$

Where q_t and q_e (mg/g) are the amount sorbed at time t (min.) and at equilibrium successively, and k_{sorp} (min^{-1}) is the rate constant.
A linear relationship was obtained via plotting ln (q_e-q_t) versus t (min.), and as shown in figure 8.

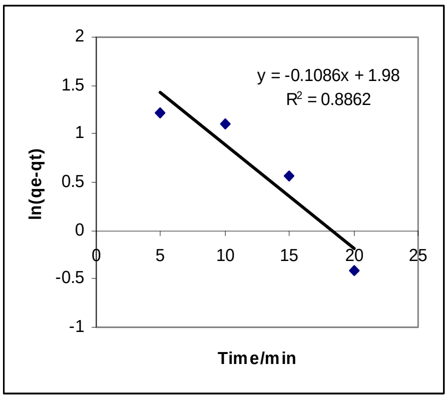
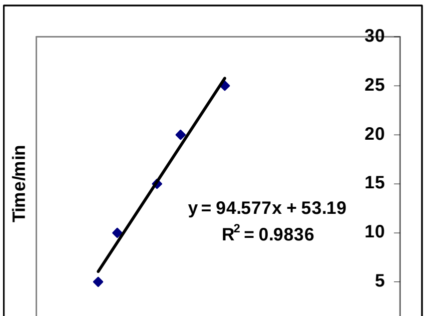


Figure 8:The Lagergren Kinetic model for 250 ppm LAS at 298K.

The Reichenberg kinetic model was proposed to discuss the behaviors of many adsorption processes in solutions, and Reichenberg has introduced the following formula:

$$F = [1- (6/\pi^2)]\ e^{-Bt} \qquad \ldots\ldots (12)$$
$$Bt = -0.4977-\ln (1-F) \qquad \ldots\ldots (13)$$
$$F = q_t/q_e \qquad \ldots\ldots (14)$$

Figure 10 shows a linear relationship with relatively acceptable R^2 value.
According to this model, it characterized the rate determining mechanism which was a diffusion process for the LAS molecules in the bulk solution and absorption occurred.



The modification of bentonite clay has been accomplished to activate the surface of it, and to get a better adsorption process for LAS molecules in the solution, the Cetyl Pyridinum Bromide (CPB) was adsorbed on the surface of bentonite clay in the form of CP^+ CP^+ molecules which were attached to the bentonite, While for the adsorption of LAS molecules on the surface of bentonite, the molecules orient themselves in a pattern that is completely different.

Figure 11 shows the time needed for the adsorption of LAS on the surface of modified bentonite, and it was 30 minutes, since the amount of adsorbate Q_e reached the steady state at the period 30-40 minutes, and thereafter the best agitation time was 30 minutes. A higher agitation time may lead to a desorption process, which is unfavorable.

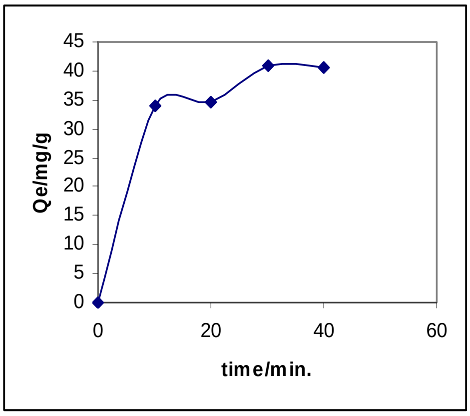
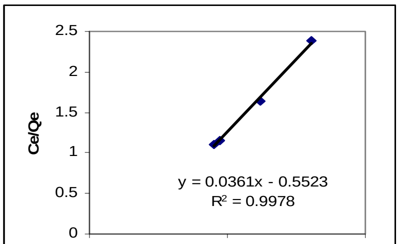


Figure 11: Varation of the contact time of 250 ppm LAS on the modified bentonite at 298 K.

Figure 12 represents the linear relationship between C_e/Q_e and C_e of the Langmuir isotherm, the adsorption of the CPB and LAS on the modified bentonite clay occurrs at the solid-liquid interface and may depend upon many factors, some depend on the solution properties and others depended on the surface characteristics like pore size (11).



The adsorption was expected to be taken place at the external and internal surfaces of the modified bentonite clay, and as previously mentioned.

Figure 13 shows the linear relationship between the log Q_e and log C_e, and the values of Freundlich parameters have been calculated via applying equation (3), thus K_F =143.51, and n= -3.043, regarding these values as important factors on the adsorption process on the modified bentonite clay. The moderate KF value indicated a moderate adsorption capacity, i.e. though the surface of bentonite was almost fully occupied with cationic and anionic surfactant, the surface still having some vacant sites, and the high value of **n** indicated the adsorption intensity, a higher dependence of adsorption on the concentration of the entire surfactant (LAS).

The adsorption percentage of LAS on the modified bentonite has significantly increased, due to the strong interactions between the LAS molecules and the modified surface and the adsorption percentage exceeds 81%, while the adsorption of LAS on the free bentonite clay at 298K is about 36%, so the modification process is profitable, and was increased the capacity of bentonite clay to accommodate LAS molecule on the surface of bentonite.

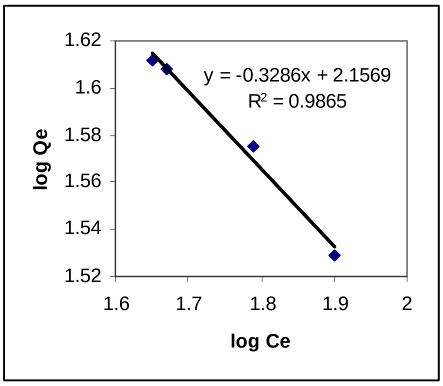


Figure13:The Freundlich linear relationship between log Q_e and log C_e.

1. The adsorption of LAS on bentonite was of monolayer at low and very low concentrations, about 10-50 $mg.l^{-1}$, and this indicates that LAS

has been attached on the bentonite surface in one line, while in higher concentrations, about 200-1000 mg.l^{-1}, the results showed that the adsorption was of Freundlich type, and this indicates that a multi-layer has formed, and LAS molecules are in a bent form on the surface of bentonite.

2. The adsorption increment of LAS at alkaline pH 8-10, indicated that the ion-exchange process is highly expected between the negative portion of LAS and the hydroxide ions in alkaline medium, while in acidic pH the increment in adsorption is due to the ion-pairing process, since the negative portion of LAS may attach with the positive sites on the clay.

Sometimes the adsorption isotherms take irregular forms, which the recent literatures called "hysterical forms", according to IUPAC classification, and this indicates that there was a weak interaction between LAS and the surface, but when the surface was modified by reacting it with Cetyl Pyridinium Bromide (CPB), a big difference in the adsorption percentage observed, since the adsorption percentage raised from 36% to 81% , and this was attributed to the new positive sites on the surface of bentonite that qualified the surface to be attached to the negative portion of LAS molecules that were diffused from the bulk solution into the surface of clay.

The positive value of ΔH indicates that the absorption process is dominating rather than the adsorption, however most of literatures assure that bentonite has a weak binding forces between its internal layers, and this enables aqueous solution to penetrate inside the pores, and so LAS ions may also enter inside the surface. The negative value of ΔG indicates that the adsorption process is spontaneous and it has led to an increment in the disorder of LAS arrangement on the bentonite surface, since ΔS value was positive.

The detailed kinetic study has revealed the following observations:

1. Lagergren model has been employed to investigate the rate and order of the reaction, however the results showed a big match with this equation, in other words, the adsorption process has followed a pseudo-1st order reaction kinetics, and the rate constant was calculated at three different temperatures (298, 308, 318) K.
2. Arrhenius equation has been employed, and the rate of the adsorption process didn't give a good match with this equation, the plot of lnk versus 1/T was of anti-Arrhenius type, since the rate decreased as the temperature increased, which indicates that there was a change in the pattern of LAS molecules in the solution which is due to the micelle formation. Micelles have large molecular weights, so their motion in the bulk solution is slow, which in turn decreases the rate constant of adsorption with increasing the temperature.
3. Morris-Weber model has been employed and the results showed a good match with the straight line equation, which indicates that the rate limiting step of adsorption is the diffusion, this justification coincide with the former one, since the micelles are slow in motion, so the rate limiting step is the diffusion of LAS molecule from the bulk solution into the surface of bentonite.
4. The latter kinetic model assures that three processes have occurred (absorption, adsorption, and desorption). The existence of interfering inorganic salts, may decrease the efficiency of removal of LAS from solutions, so it is preferred to remove or get rid off these salts before the treatment of LAS.

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