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Removal of Cetyldimethylbenzylammonium Chloride Surfactant from Aqueous Solution by Adsorption onto Mesoporous Silica

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Abstract: ***In this work, batch adsorption experiments were carried out for the removal of Cetyldimethylbenzylammonium chloride (BAC) as a pollute surfactant from aqueous solutions on mesoporous silica as adsorbents. This silica was prepared from sodium silicate as a precursor and cetyltrimethylammonium bromide (CTAB) as template using sol-gel method. The effects of major variables governing the efficiency of the process such as dosage of mesoporous silica (0.05-0.1, 0.2 and 0.3g) and temperature (298-328 K) were investigated. Equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherm models and isotherm constants were determined. The equilibrium data were best represented by the Freundlich isotherm model. The adsorption kinetic data were analyzed using pseudo-first-order, pseudo-second-order and intra particles diffusion models. The results matched well with Pseudo-second-order and the intraparticle diffusion model suggests that the adsorption process proceeds by surface sorption and intra-particle diffusion. Thermodynamic parameters such as changes in the free energy of adsorption (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated and the results obtained indicate that these systems were spontaneous and exothermic in nature.***

Keywords: Removal from aqueous solution, Cetyldimethylbenzylammonium Chloride, Adsorption, mesoporous silica.

1. Introduction

Cetyldimethylbenzylammonium chloride (BAC) is a cationic surfactant and is a category of Quaternary Ammonium Compounds, other names are Benzylhexadecyldimethylammonium chloride, and Cetalkonium chloride. The structure of its molecule is: CH3 (CH2)15N (Cl)(CH3)2CH2C6H5.It can be produced by the quaternization of the tertiary fatty amine using benzyl chloride [1]. It plays an important role in many industrial fields due to its versatile physico-chemical properties. It is used in leather processing, textile dyeing, and mildew preventive in silicone-based water repellents, compatible with many nonionic detergents; it is active in moderately alkaline solutions, and anti-infective. Such widespread uses also as disinfectants, fabric softening agents, foam depressants, and antistatic agents lead to massive discharge into the environment with its associated concerns [2].

Adsorption of surfactants from aqueous solutions onto colloidal silica[3, 4] and in porous silica [5-7] has been studied extensively in the past in view of its specific porous structure and the excellent textual properties which allow easier diffusion of large molecules into the active sites.

The adsorption of the cationic surfactant benzyl dimethyl hexadecyl ammonium chloride (BAC) has been studied at the hydrophilic and hydrophobic silica-water interface by Raman spectroscopy [8, 9].This study demonstrates the capabilities of the Raman spectroscopy to evaluate thermodynamic and kinetic properties of BAC at the silica-water interface at neutral pH and compare its adsorption behavior with the modified adsorption properties in the presence of four different concentrations of a divalent metal salt.

The purpose of this study is to investigate the adsorption behavior of prepared mesoporous silica (MPS) for removal the surfactant Cetyldimethylbenzyl ammonium chloride (BAC) from aqueous solution. Adsorption equilibrium, adsorption kinetics and thermodynamics parameters were also investigated.

2. Experimental

2.1. Materials

Cetyldimethylbenzylammonium chloride (BAC) purchased from (BDH) Chemicals Ltd., cetyltrimethylammonium bromide (CTAB) was supplied by SCRC-China and sodium silicate (14% NaOH, 27% SiO_2) was purchased from local market.

2.2. Synthesis of Mesoporous Silica

3.75 g of cetyltrimethylammonium bromide (CTAB) was dissolve in 150 ml of distilled water, and put in around bottom flask with 34 ml (1M) HNO_3 with stirring for 1 hour. In 250 ml beaker, 7.5 g of sodium silicate was dissolve in 150 ml of distilled water and was added to the mixture drop by drop from burette for 3 hours. The white precipitate formed spontaneously and then it was recovered by filtration, washed, after aging for one day .The surfactant was removed by calcination at 600^0C for 4 hours. The preparation and characterization of this sample was published in previous work [10]. Table (1) summarizes some of the characterization results of the sample prepared.

Table 1: Values of surface area pore volume, average pore size and diameter for the prepared sample

Single point Surface area ($m^2\ g^{-1}$)	BET Surface Area ($m^2\ g^{-1}$)	Langmuir Surface Area ($m^2\ g^{-1}$)	Pore volume (cm^3/g)	Pore size(A^0)	Diameter (nm)	Average Diameter (nm)
54.0398	55.5421	82.3129	0.126368	91.0069	45-135	94

2.3. Adsorption Experimental

A stock solution of BAC was prepared by dissolving accurately 1g (using accurate and high precision electronic balance) of BAC in 1L of distilled water in a 1 L volumetric flask and then the flask was closed tightly to avoid evaporation. Various concentrations (50, 100-800 mg/L) were prepared for the calibration curve and adsorption processes, the absorbance was measured at the wavelength 263 nm. Batch experiments were conducted by contacting different amounts (0.05, 0.1, 0.2, and 0.3) g of MPS adsorbents with 100 ml of surfactant solution having concentration range (100-600 mg/L). The temperature was fixed at 298K and the agitation speed of thermostatic shaker bath was kept at 200 rpm for all experiments. These samples were shaken well for enough time to reach equilibrium. The particles of MPS were separated from the mixture by centrifugation at 3000 rpm. The concentrations of the surfactant solutions before and after the adsorption were determined by UV-Visible spectrophotometer at λ_{max}263. The experiments were repeated at least twice. The amount of surfactant adsorbed was determined by the equation:

$$q_e = (C_0 - C_t)V/w \quad \ldots\ldots (1)$$

Where C_o is the initial concentration (mg/L), C_t is the equilibrium concentration (mg/L), V is the volume of the solution (L) and w is the amount of MPS (g).

The effect of temperature on the removal of BAC was studied using four temperatures in the range of 298-328 K using the thermostatic shaker bath.

The kinetic study of BAC adsorption was performed by mixing 0.2 g MPS with 50 ml of BAC (100 mg/L) aqueous solution in 250 mL flasks immersed in the thermostatic shaker bath in the temperature 298 K. At various time intervals, one of the flasks was taken and the concentration of solution was determined by measuring absorbance at the maximum wavelength 263

3. Results and Discussion

3.1. Adsorption of BAC on MPS

3.1.1. The Effect of Equilibrium Time

The effect of contact time on the adsorption of BAC on MPS is illustrated in Figure (3-1) which shows the gradual increase in adsorption with increasing contact time up to 95 minutes in which a maximum value of adsorption is attained, so all the experiments of adsorption were done at this equilibrium time.

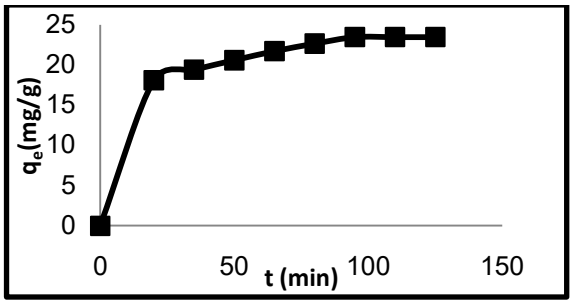


Figure (3-1): The effect of contact time on removal of BAC (100 mg/L concentration, 0.2 g adsorbent)

3.1.2. The Effect of Adsorbent Amount.

The experiment was conducted for 100 mg/L concentration of solution with different amounts (0.05, 0.1, 0.2 and 0.3) g of MPS adsorbent for 50 ml of surfactant BAC, the maximum surfactant removal was achieved within 95 minutes. The removal efficiency, (R %) of the system was calculated accordance to equation (2)

$$R\% = [\,C_0 - C_t\,)/C_0 \qquad 100 \ldots\ldots (2)$$

Figure (3-2) shows the variation of percentage removal (R %) with the amount of adsorbent. The result show that the 0.2 g dose give the best result with R% equal to 93.625, so all the experiments performed with 0.2 g amount of MPS adsorbent.

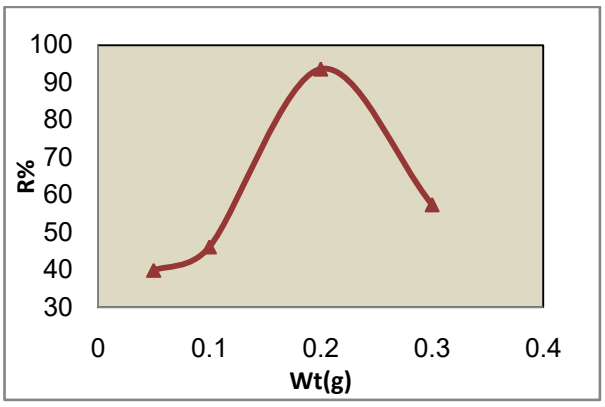


Figure (3-2): Effect of adsorbent dose on removal of 100 mg/L BAC

3.1.3. Adsorption Isotherm

The adsorption isotherm was constructed using Six different BAC surfactant concentrations (100, 200, 300, 400, 500, 600 mg/L) with 0.2g of MPS at different temperatures (298, 308.318, and 328) K.

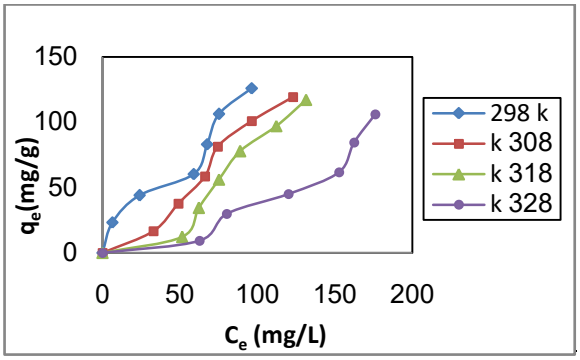


Figure (3-3): Adsorption isotherms of BAC on MPS at different temperatures

As shown in Figure (3-3), the adsorption isotherm of BAC on MPS was nonlinear and typical S-shape curves, indicative of vertical orientation of adsorbed molecules at the surface, and usually appears when three conditions are fulfilled : (a) the solute molecule is monofunctional, (b) has moderate inter molecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another adsorbed species [11].

Also, the results of Figure (3-3) Indicate that the amount of adsorption decreases with increasing the temperature in the range (298-328 K) which confirms that the adsorption process is exothermic and the sorption is mainly adsorption.

In order to investigate the adsorption isotherm, three equilibrium isotherms are analyzed : the Langmuir (equ.3), Freundlich (equ.4), and Temkin (equ.5) .The calculated data to construct the linear plots of the three equations for the adsorption of BAC on MPS at 298, 308, 318, 328 K are listed in Table (2) and shown in Figures [(3-4) - (3-6)]. The linear form ofLangmuir equation [12] can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L . Q} + \frac{C_e}{Q} \dots\dots\dots (3)$$

Where C_e is the concentration of surfactant at equilibrium, q_e is the amount of surfactant adsorbed at equilibrium; Q° (mg/g) and K_L (L/mg) are the Langmuir constants. Q° is the monolayer adsorption capacity and K_L is the constant related to the free energy of adsorption. The Langmuir constants Q° and K_L were determined from the slope and intercept respectively when C_e/q_e was plotted against C_e

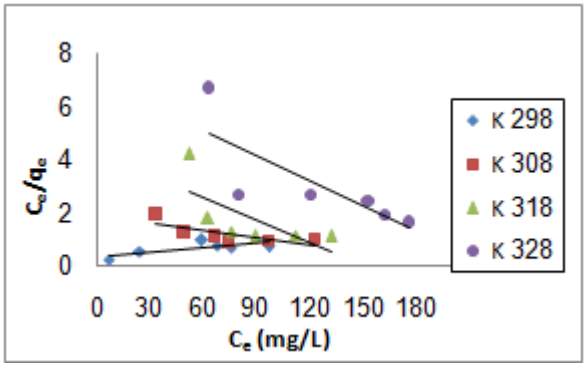


Figure (3-4): The Linear plots of Langmuir models for adsorption of BAC onMPS at different temperatures

Freundlich model [13]is given in its linear form as:

$$\ln q_e = \ln K_f + \frac{1}{n} ln C_e \dots\dots\dots\dots (4)$$

K_f= Freundlich isotherm constant (mg/g)

1/n =dimensionless constant related to the intensity of adsorption, or the heterogeneity factor describes reversible adsorption and is not restricted to the formation of the monolayer.

The constant $K_f$is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process

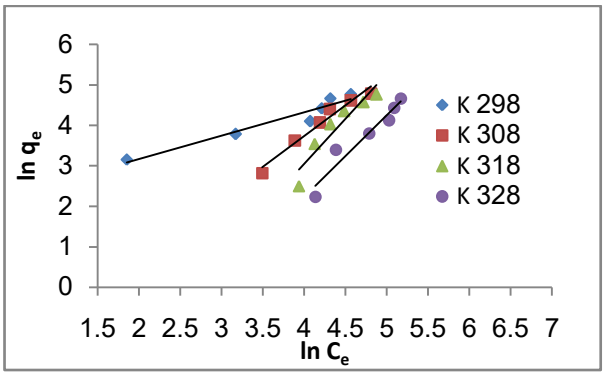


Figure (3-5): The Linear plots of Freundlich models for adsorption of BAC on MPS at different temperatures

The result of n and K_f is determined from the slope and intercept of the plots and are presented in Table (3-2).

And it show that the Freundlich constant is more than 1 at 298 K which is an indication that MPS has a high affinity for BAC molecules, and has high heterogeneity of the adsorbent sites, while at 308, 318, and 328 K is less than 1 indicate that MPS has a low affinity for BAC adsorption.

The linear form of Temkin model [14] is given by the following equation:

$$q_e = B ln K_t + B \ln C_e \dots\dots.(5)$$

Where K_t is the Temkin constant, which related to binding energy and B is Temkin constant equal to RT/b_T;b_T is corresponding to heat of adsorption, R is the universal gas constant and T= Temperature.

Table (3-2): The parameters of Langmuir, Freundlich and Temkin equations for adsorption of BAC at different temperatures

Constant of equations		298 K	308 K	318 K	328 K
Langmuir	Q_0	181.821	-112.3595	-36.1011	-31.646
	K_L	0.01456	-0.00476	-0.00658	-0.00452
	R^2	0.5725	0.5481	0.4811	0.6228
Freundlich	n	1.74	0.660	0.4507	0.494
	K_f	7.548	10.205	339.95	349.778
	R^2	0.936	0.9627	0.8859	0.9304
Temkin	B	33.212	81.017	110.45	79.624
	K_t	4.379	28.705	45.439	58.059
	R^2	0.7738	0.9769	0.9969	0.8829

The result of B and $K_t$are determined from the slope and intercept of the plots and are presented in Table (3-2).

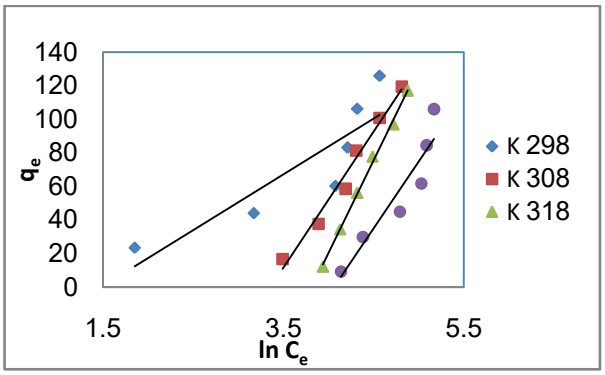


Figure (3-6): The Linear plots of Temkin models for adsorption of BAC on MPS at different temperature

From the results in Tables (3-2), it is obvious that the values of correlation coefficient R^2 obtained from Freundlich equation are higher than values obtained from Langmuir and Temkin equations which indicate that the Freundlich model was the best to analyze the experimental data of the adsorption process of BAC on sample of MPS prepared.

3.1.4. The Kinetics Study

The adsorption kinetic behavior was studied on the adsorption of 100 mg/L for BAC onto MPS at 298 K and the result obtained are given in Table (3-3). Three of the most widely used kinetic models; Lager gren-first-order equation, pseudo-second-order equation and intraparticle diffusion equation have been used to research the adsorption kinetic behavior.

The equations of these kinetic models are given in the following:

-The linear form of the pseudo-first order kinetic model of [15] can be expressed as follows:

$$\ln(q_e - q_t) = lnq_e - (k_1/2.303)\, t \ldots\ldots(6)$$

Where k_1 is the rate constant of the pseudo-first order kinetics (min^{-1}). q_e and q_t are the amounts of BAC adsorbed on the surface of the adsorbent at equilibrium and at any time (mg g^{-1}) respectively. The q_e and k_1 are calculated from the intercept and the slope of plots of log (q_e - q_t) vs. tand the results obtained are given in Table (3-3) and illustrated in Figure (3-7).

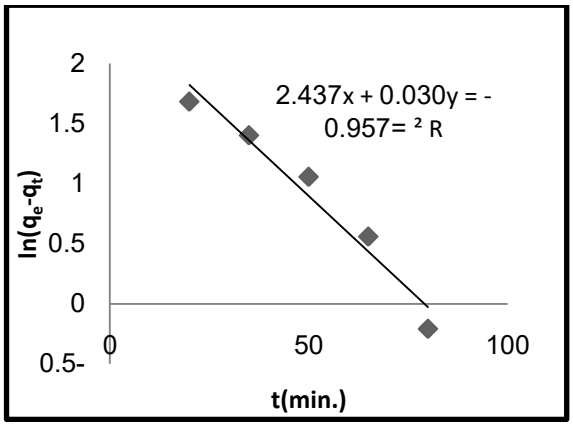


Figure (3-7): The pseudo-first order kinetic plot for adsorption of BAC on MPS at 298 K

Table (3-3): The values of t, qt, lnqe-qt , t/qt and t1/2 for the adsorption of BAC on MPS at 298 K

t(min)	qt	ln (q_e- q_t)	t/q_t	t ^{½} (min)
20	18.093	1.681	1.105	4.472
35	19.406	1.401	1.803	5.916
50	20.593	1.056	2.428	7.071
65	21.718	0.559	2.992	8.0622
80	22.656	-0.208	3.531	8.944
95	23.468		4.048	9.746

Pseudo-second-order equation model [16] is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \ldots\ldots\ldots\ldots (7)$$

Where k_2 is the rate constant of the pseudo-second order kinetics (g mg^{-1} min^{-1}). k_2 and $q_e$are calculated from the intercept and the slope of plot of t/q_t against t respectively [Figure. (3-8)], and the result obtained are given in Table (3-3)

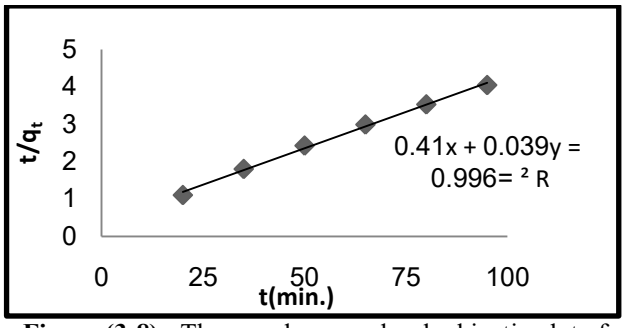


Figure (3-8): The pseudo-second order kinetic plot of BAC adsorption on MPS at 298 K.

The intra-particle diffusion model of Weber and Morris [17] can be expressed as follow:

$q_e = k_d t^{1/2} + C$……..(8)

Where, k_d is intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$), and C is intercept. This model reflects that pore diffusion occurs due to the porous nature of adsorbent.

The rate constant of the intra-particle diffusion (k_d) can be estimated from the slope of the linear portion of the plot of the amount of solute adsorbed (q_e) against square root of time ($t^{1/2}$) [equation (8)], and the results obtained are given in Table (3-3) and illustrated in Figure (3-9).

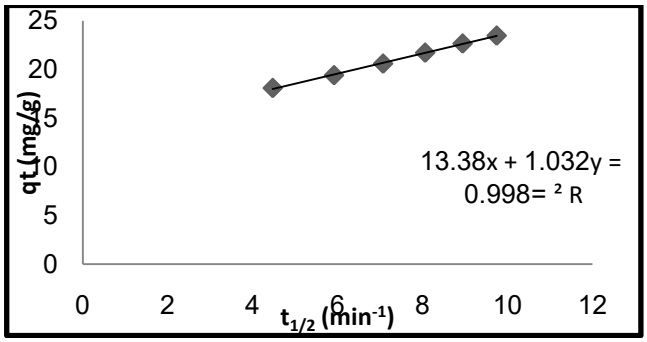


Figure (3-9): The intra-particle diffusion model of BAC adsorption on MPS at 298 K.

Table (3-4): Kinetic parameters for adsorption of BAC on MPS at 298 K

Model	Parameters	The value
Pseudo first order	q_e (calc.) mg /g	11.447
	K_1 (mg g^{-1} $min^{-1/2}$)	0.0308
	R^2	0.9575
Pseudo second order	q_e (calc.) mg /g	25.641
	K_2	0.0037
	R^2	0.9968
Diffusion model	K_d (mg g^{-1} $min^{-1/2}$)	1.0327
	R^2	0.9987

From results in Table (3-4), the correlation coefficient (R^2) values obtained from pseudo-second order kinetic model is higher than that of pseudo first-order, these indicate that the adsorption perfectly complies with pseudo-second order model. The values of q_e (calc.) from the pseudo first order kinetic is not in agreement while the values of q_e (calc.) from the pseudo second order is in agreement with experimental data q_e (exp.) These confirms that the adsorption perfectly complies with Pseudo- second order reaction. And it can be seen the plot of intra-particle diffusion model is linear and did not pass through the origin, this indicates that the adsorption involved intra-particle diffusion but is not the only rate controlling step and determining step [18, 19].

3.1.5. Thermodynamic Analysis

The values of the standard free energy (ΔG°) of adsorption calculate from the equation:

$\Delta G^{\circ} = -RT \ln K_{eq}$ ……. (9)

The standard enthalpy change ΔH° and standard entropy change ΔS° have been calculated according to the Van't Hoff equation (eq. 10) [20] by plotting of ln (K_{eq}) versus 1/T which are given in Figure (3-10).

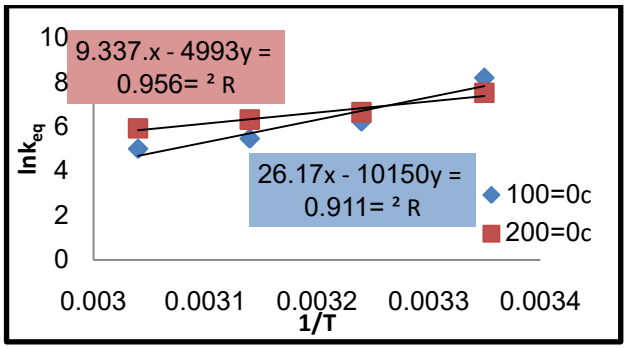
$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ldots\ldots\ldots (10)$$

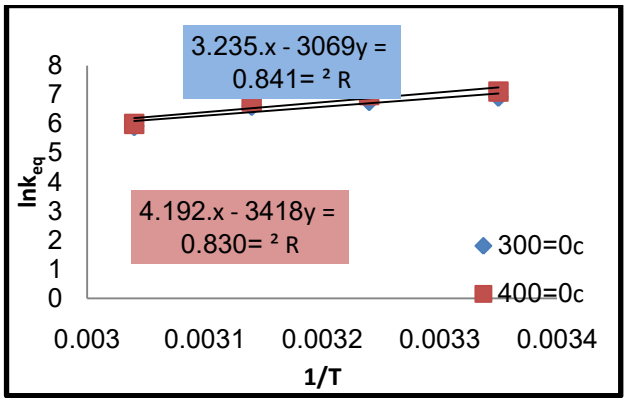
Where: R is the gas constant (8.314 J/K.mol), T is the temperature (K), and K_{eq} is the equilibrium constant

The results obtained for K_{eq} are listed in Table (3-5) and thermodynamic parameters ΔG°, ΔH°, and ΔS° are listed in Table (3-6).

Table (3-5): Values of ln (Keq) and 1/T for adsorption of BAC on MPS

1/T	Ln K_{eq}					
	C_0=100 mg/L	C_0=200 mg/L	C_0=300 mg/L	C_0=400 mg/L	C_0=500 mg/L	C_0=600 mg/L
0.00335	8.208	7.51	6.931	7.113	7.254	7.175
0.00324	6.235	6.65	6.784	6.998	6.953	6.878
0.00314	5.466	6.318	6.617	6.774	6.762	6.793
0.00304	5.005	5.924	5.925	6.004	6.253	6.399





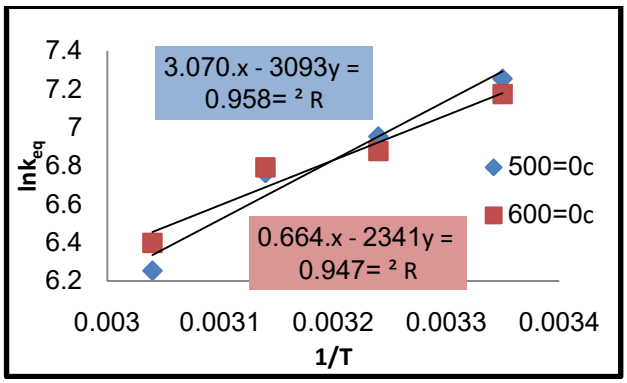


Figure (3-10): Van't Hoff plots for estimation of thermodynamic parameters at different initial concentration

Table (3-6): Thermodynamic parameters ΔGo, ΔHo and ΔS0for adsorption of BAC on MPS

C_o	$-\Delta H^o$ (KJ.mole^{-1})	$-\Delta S^o$ (J.mole^{-1} .K^{-1})	- ΔG^o (KJ.mole^{-1})			
			298 K	308 K	318 K	328 K
100	84.38	217.61	20.33	15.96	14.45	13.64
200	41.51	77.63	18.62	17.028	16.70	16.15
300	25.52	26.89	17.17	17.37	17.49	16.15
400	28.42	34.85	17.62	17.91	17.90	16.37
500	25.71	25.52	17.97	17.80	17.87	17.05
600	19.46	5.52	17.77	17.61	17.95	17.45

From the results in Table (3-6), the values of ΔG° are negative and between (-20 and 0), this indicate the adsorption process of BAC on MPS is spontaneous and physical adsorption [21]. As temperature increase from 298 to 328 K, ΔG° almost decreases suggesting that adsorption is less spontaneous at high temperature.

The negative values of ΔH^o indicate that the adsorption process is exothermic process. The magnitude of ΔH^o<(84 KJ/mole) also suggest that the adsorption process is driven by a physisorption .Entropy has been defined as the degree of disorder of a system [22], the negative values of (ΔS^o) suggest the decrease in randomness at the solid

/liquid interface during the adsorption of BAC on the surface of MPS [23].

4. Conclusions

The study of adsorption of BAC surfactant onmesoporous silica indicates the following:

- The adsorption isotherm of BAC on mesoporous silica is best fitted with the Freunlich model and show favorable adsorption.
- The adsorption is physisorption, this is reflected by the values of ΔH^{o} obtained from Vants Hoff.
- Kinetics investigation have reflected that pseudo-second order kinetics equation is found as the best model for fitting kinetics data and intraparticle diffusion model is necessary through rate determining step reaction
- Thermodynamic data results obtained has indicated that the adsorption processes are spontaneous and exothermic in nature.

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