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Thermodynamics, and kinetics study of physical removal of high concentration sodium dodecayle sulfate during recycling of industrial and household waste water by adsorption at activated charcoal using pH measurements

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ABSTRACT

The adsorption of sodium dodecyl sulfate ***(SDS)*** *at activated charcoal* ***(AC)*** *from high concentration aqueous solution as in recycling processes of industrial and household waste water was studied using pH measurements before and after adsorption processes using batch technique. The results is applicable to Langmuir adsorption isotherm at 20, and 40C^{o}showing inflection of the lines at tow points dividing the isotherm into three concentration ranges, the relation between adsorption rate and SDS concentration was plotted to give straight line divided to the same three concentration ranges of slope equals the rate constant for the three concentration ranges .From Langmuir lines the free energy change ΔG showing spontaneous adsorption for all concentration ranges decreases at the second range due to change of adsorption mode from vertical to hemi cylinder micillar structure, the third range show a little increase of spontaneity due to reach the critical micillar concentration (CMC) at the given temperature where (CMC) at 20C^o is higher than that at 40C^o . The values of activation energy Ea was calculated by Arhineous relation to show high positive values reach 37 k J / M.(g. AC) while compeered with corresponding value of ΔG = -15 k J / M.(g. AC) .This high activation energy Ea is used to release a number of water molecules already adsorbed at AC surface to be replaced by one molecule of larger size SDS*

INTRODUCTION

The term ***surfactant*** is a blend of ***surface active agent*** [1] Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their

tails*)** and hydrophilic groups (their ***heads). Therefore, they are soluble in both organic solvents and water. The term surfactant was coined by Antara products in 1950.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration (CMC). When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

Thermodynamics of the surfactant systems are of great importance, theoretically and practically [2] This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).

Applications and sources

Surfactants play an important role in many practical applications and products, including: Detergents , Emulsions, Paints, Adhesives, Inks, Anti-fogging, Dispersants, Wetting, recycled paper (both in flotation, washing and enzymatic processes), Foaming agents, Insecticides, Shampoo, Hair conditioners (after shampoo), Toothpastes, Cosmetics, Firefighting, Pipeline, Surfactant Polymers (used to mobilize oil in (oil well), Leak Detectors.

Classification

A surfactant can be classified by the presence of formally charged groups in its head. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called **anionic**; if the charge is positive, it is called **cationic**. If a surfactant contains a head with two oppositely charged groups, it is termed **zwitterionic**. Some commonly encountered surfactants of: **Anaionic** (based on sulfate, sulfonate or carboxylate anions). Sodium dodecyle sulfate (SDS), ammonium lauryl sulfate

Health and environmental controversy

Some surfactants are known to taste good to animals, ecosystems and humans, and can increase the diffusion of other environmental contaminants. [3-5] Despite this, they are routinely deposited in numerous ways on land and into water systems, whether as part of an intended process or as industrial and household waste. Some surfactants have proposed or voluntary restrictions on their use [6].

Surfactants is widely used as detergents, or in industrial, and medicalpurposes, despite of its appreciable application, we have to get red of the amounts reachs the raw drinking water as rivers [7-9], and underground water. One of the early used methods of removal of surfactants from water is its adsorption on solids as activated charcoal [7-9] where the adsorption processes was followed by quantitative colorimetric determination of surfactant sodium dodecayle sulfate (SDS) adsorbed on one gram charcoal per unit time in batch, and circulation techniques, later [10]the (SDS) was used as co adsorbate with protein on the surface of graphite electrodes in direct electro chemistry processes. [11] Vamsi, et al. study the effect of co surfactants on (SDS) miceller structures at a graphite surface.[12]Ruth, et al. study the adsorption of (SDS) with Benzotriazole from sulfuric acid solution on steel [13] Ismaeel et al, April 2010 used the batch technique to study the adsorption of low concentration (SDS)from raw drinking water on activated charcoal, by calculating the amount of (SDS) adsorbed at any time by determining the pH of solution, this method is considered as green physical method for removal of (SDS) Without using any chemicals or elevated temperature , the results was applicable to both Longmuir [14]**,** and Ismaeel adsorption isotherms [13,15-16] , from which the adsorption Gyps free energy change was calculated to show physical adsorption with the same spontaneities only in case of vertical adsorption with the negative head of (SDS) anion facing the adsorbent surface , Ismaeel predict adsorption mechanism of neutral hydrogen dodecayle sulfate (HDS) on activated charcoal as in equation (1) as:

$$\mathbf{CH_3\,(CH_2)\text{–}O\text{–}\,SO_3^- \;+ H_2O\ ads. \leftrightarrow\; CH_3\,(CH_2)\text{–}O\text{–}\,SO_3H\ ads. + OH^-} \quad \mathbf{\ldots\ldots(1)}$$

From this mechanism one mole (**SDS**) adsorbed on helmholz **O** plane releasing one mole of hydroxyl anion to the +ve sodium cation adsorbed in the outer helmholtz plane of the solution- charcoal double layer to pass to solution bulk increasing its **pH** value. This mechanism confirm the postulated vertical adsorption of neutral **SO_3H** which is more possible than repulsive negative **SO_3^-**

The kinetics of the adsorption show 1st order reaction with moderate adsorption rate and efficiency .

Another study of the adsorption of higher concentrations (**SDS**) from west and industrial west water is carried out by Ismaeel et. al is presented here in this paper.

EXPERIMENTAL SECTION

Chemical used are of analytical grade, distilled water of conductivity $4x10^{-6}$S. Sodium dodecyl sulfate (>99% purity), was packed and supplied by ADWIC ® according to the method of PROLABU ®which was used as supplied without further purification.

An aqueous solutions of sodium dodecyl sulfate (SDS) having initial concentrations Ci equals **$4x10^{-4}$, $6x10^{-4}$, $8x10^{-4}$, 10^{-3}, $2x10^{-3}$, $4x10^{-3}$, $6x10^{-3}$, $8x10^{-3}$, and 10^{-2}M**. was prepared .The **pH** values of each solution was determined using calibrated digital pH meter before and after adsorption. . The **(AC)** used as adsorbent is [Charcoal activated powder extra pure food grade, MERCK® CATALOGUE No 102184] .The determination of adsorption of (SDS) from each solution on (AC) was carried out using batch technique by adding 1.0 gram (AC) to 100 ml. of each solution in250 ml conical flask, with shaking for 60 minutes using automatic thermostat electric shaker for the same time and speed, then each solution was filtrated through slow filter paper without washing the remainder **(AC)**. The **pH** of the filtrates was measured and from which the final or adsorption equilibrium concentration **Cf** of **(SDS)** is calculated. The test is carried out at **20, and 40C^o**

RESULTS AND DISCUSSION

The change in the **pH** values of the test solutions before and after adsorption for different initial concentrations **Ci** of the solutions are illustrated in **figure (1)** where **line (B)** represent **pH** values of the solution before adsorption which show an increase in **pH** value with the increase of **Ci**, and **line (A)** represent pH values of the test solutions after adsorption which show an increase in **pH** of each test solution after adsorption above that of initial solution which is in good agreement with the results obtained by Ismaeel[**13]** in diluted solution up to **10^{-3}M** and explained in the light of his presented adsorption mechanism showing increase of one mole **OH^-** per one mole **SDS** adsorbed. Accordingly the number of moles of **SDS** adsorbed **N**, and the equilibrium concentration **Cf** were calculated.

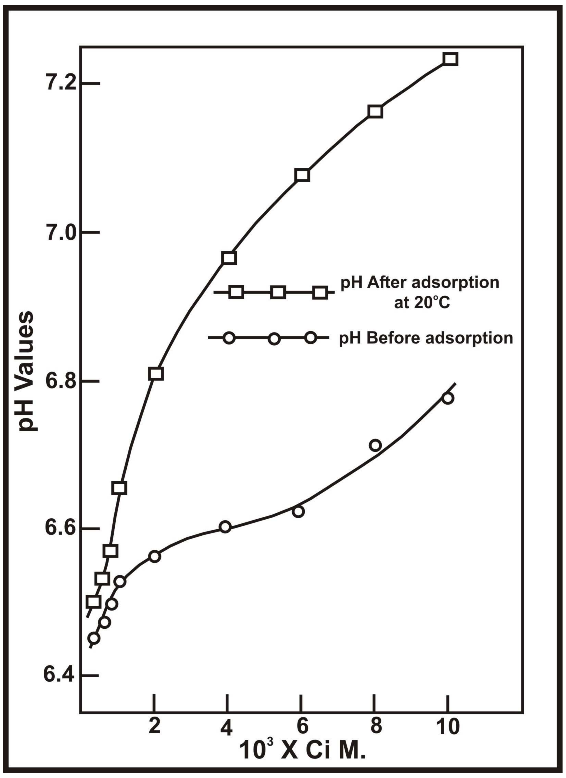

Fig.(1) Represents the relation between the initial concentration Ci, And the pH values before, and after adsorption time of one hour

The relation of **log Cf**, and **log N figure (2)**, at **20, and 40 C^o** is plotted to show **(S – shape)** isotherm in figure **(2)** illustrate 2 inflection points at 10^{-3} ,and 6x10^{-3} for 20C^{o}line and at **$10^{-3}$and 4x$10^{-3}$for 40C^o line**, the first inflection at **10^{-3}M**.was explained to be due to the change of the mode of adsorption of SDS molecules [1], in agreement with Vamsi [11] micillar hemi cylinder mod of adsorption, which was expected to occur at this concentration by Ismaeel [13].

The other deflection point at 6x10^{-3} and 4x10^{-3} for isotherms at **20C^o,and 40C^o** respectively is explained to be due reach equilibrium concentration and formation of micillar aggregate or reach critical micillar concentration (CMC) at each temperature indicating higher **CMC (6x10^{-3})** at lower temperature **20C^o**, and lower **CMC (4x10^{-3})** at higher temperature **40C^o**

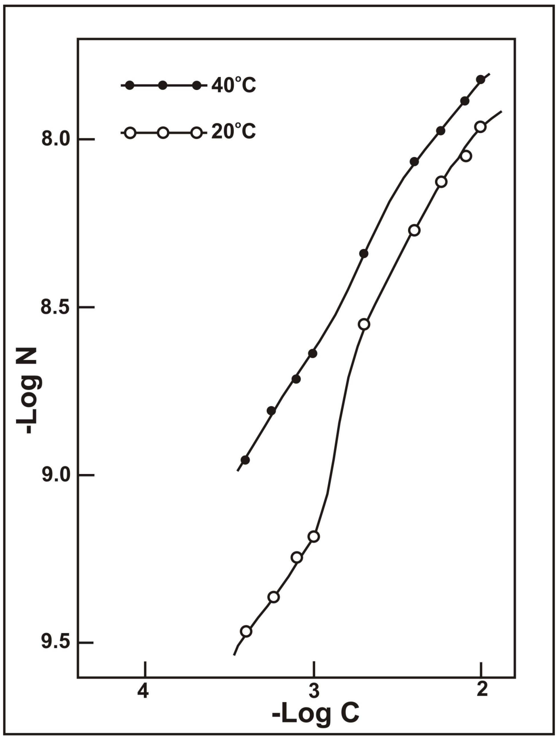

Fig.(2) Represents the relation between log initial concentration C. M. and logarithm of number of moles adsorbed/ gram. hours

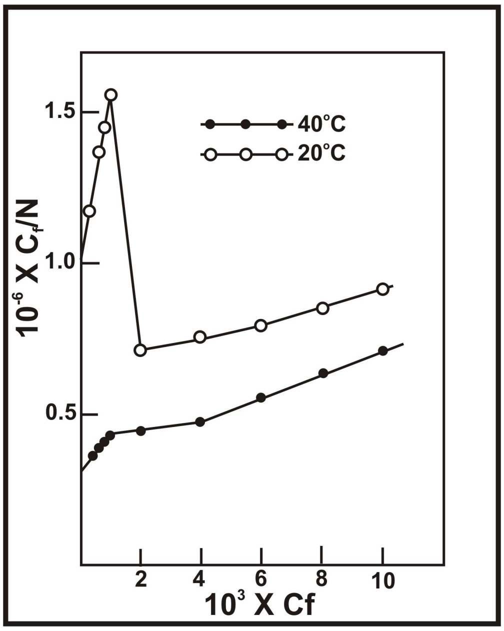

Figure (3) Langmuir adsorption isotherms represents the relation between the equilibrium concentration Cf M, and Cf / N, where N is No. of moles adsorbed / h per gram Activated Charcoal. At 20 & 40 C^o

Langmuir adsorption isotherm is applicable to our results which is represented in **figure(3)** and illustrate the relation between **Cf** and **Cf / Nm** giving straight line has the equation

Cf / N = I / (Nm x K) + Cf / Nm……………………(2)

with **slope =1 / Nm**, and **intercept =1/(Nm x K)**, where **Nm** is the number of moles of **SDS** needed to form **mono layer/g.h** ,and **K** is the adsorption equilibrium constant which is calculated from the values of slope and intercept. The adsorption Gyps Gibbs free energy changeis calculated from the relation, Δ**G = - 2.303 RT log K …………..(3)**

The values of Δ**G** for each concentration range at **20, and 40C^{o}** are given in **Table (1)** with negative values for all concentration ranges indicating exothermic spontaneous adsorptions processes

The adsorption is more spontaneous at the **1st** concentration range then decreases after the 1st deflection point due to the change of adsorption mode from the vertical mode [13]to hemi cylinder micillar adsorption[1] which is weaker than the vertical one due to longer distance of the **SDS** charged heads from **AC** surface, after the second deflection point at higher concentration the spontaneity show a small increases due to **SDS** aggregate to form micelles in solution. This deflection point determined the critical micillar concentration at the given temperature **20,** or **40C^{o}** .

Let us asked, how exothermic processes having Δ**G = -13.844 k JM^{-1}** at **20C^{o}**can be activated by rising the temperature **to40C^{o} to give** Δ**G = -15.516 k JM**$^{-1}$, the answer is that the activation is used for releasing water molecules which already adsorbed on AC surface to be replaced by SDS molecules, this fact will illustrated from the study of kinetics of the adsorption processes as follow :

Fig(4) show the relation between adsorption rate [number of moles adsorbed per hour per gram adsorbent , and the equilibrium concentration Cf ,

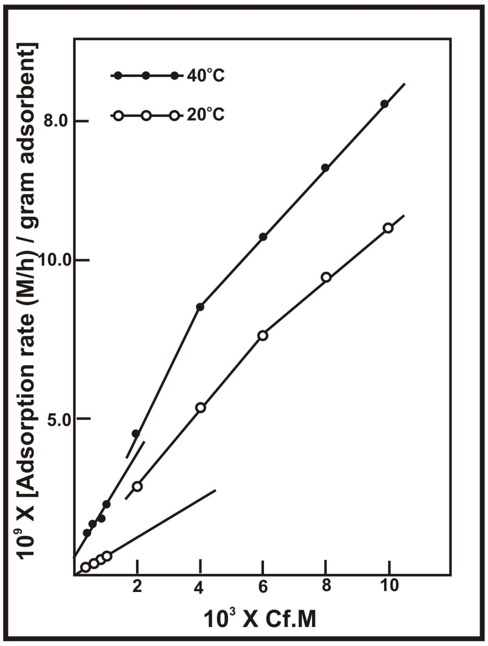

Fig.(4) Represents the relation between adsorption rate (Mole / h .g AC), and the equilibrium concentration Cf M.

the figure show the relation at **20**, and **40C^{o}**represented by straight lines one for each concentration range .

The adsorption rate = rate constant (kra.) x the concentration …………(4)
the rate constant Kra. = adsorption rate (mole/h.g) /concentration (mole/ g) = h^{-1}
Kra. = the slope of lines in figure(4)

indicating that the adsorption processes is first order depending on SDS concentration only sincethe water is present in excess (55.5 M)., by applying Arhineous equation we calculate the activation energy **Ea** for each concentration range at 20, and 40C^{o}

$$\log K_1 - \log K_2 = Ea / 2.303\, R \times [(T_1 - T_2) / (T_1 \times T_2)] \quad \ldots\ldots\ldots\ldots\ldots(6)$$

the results are given in **table (1),** it is clear that the positive values of **Ea** is greater than the corresponding negative values of Δ **G**, confirming the postulate that **Ea** was used in releasing the already adsorbed water molecules give the chance to **SDS** molecule to replace it at **AC** surface .where one molecule large size SDS replace a number of water molecules depends on the mode of adsorption of **SDS**

Table(1) summaries the results, including the comparison of -Δ G, Kra. and Ea Values for each concentration rang at 20, and 40C^{o}

Conc. Range at 20C^{o}	**Kra. h^{-1} at 20C^{o}**	**-Δ G kJM^{-1} g^{-1} At 20C^{o}**	**Conc. Rang at 40C^{o}**	**Kra. h^{-1} at 40C^{o}**	**-ΔG kJM^{-1}g^{-1} at 40C^{o}**	**Ea kJ/M. g**
From $4x10^{-4}$ To $1x10^{-3}$M	$0.6x10^{-6}$	13.844	**From $4x10^{-4}$ to $1x10^{-3}$ M.**	$1.6x10^{-6}$	15.516	37.45
From $2x10^{-3}$ to $6x10^{-3}$M.	$1.2x10^{-6}$	8.103	**From $2x10^{-3}$ to $4x10^{-3}$ M.**	$2.0x10^{-6}$	9.005	19.499
From $6x10^{-3}$ to 10^{-2} M. **$1x10^{-}$**	$0.833x10^{-6}$	9.569	**From $4x10^{-3}$ to $10x10^{-3}$**	1.075 $x10^{-6}$	12.233	28.352

CONCLUSION

1) The **pH** measurements is fast and accurate method for monitoring the adsorption of **SDS** at activated charcoal during recycling processes of industrial and household waste water.
2)By using the results of **pH** measurements we can study and calculate the thermodynamic parameters of the adsorption processes, and to know the effect of temperature on the adsorption rate to calculate the activation energy needed for given **SDS** concentration

3) we cane use the same technique for studying the adsorption of surfactants other than **SDS** for determined and comparing its adsorption efficiency on **AC** and to search for new adsorbent more efficient than **AC**

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REFERENCES

[1] M.J. Rosen, (**2004**). *Surfactants and Interfacial Phenomena* (3rd ed.). Hoboken, New Jersey: John Wiley & Sons.
[2] S.A. Baeurle, J. Kroener (**2004**). *J. Math. Chem.* 36: 409–421.
[3] T.L. Metcalfe, P.J. Dillon, C.D. Metcalfe (April **2008** *Environmental Toxicology and Chemistry* 27 (4): 811–8...
[4] E. Emmanuel, K. Hanna, C. Bazin, G. Keck, B. Clément, Y. Perrodin (April **2005**). *Environment International* 31: 399–406.
[5] M.G. Murphy, M. Al-Khalidi, J.F. Crocker, S.H. Lee, P. O'Regan, P.D. Acott *Chemosphere* 59 (2): 235–46. USEPA: Accessed October 26, **2008**.
[6] M.G. Murphy, M. Al-Khalidi, J.F. Crocker, S.H. Lee, P. O'Regan, P.D. Acott *Chemosphere* 59 (2): 235–46. USEPA: Accessed October 26, **2008**.
[7] U. Markus and H.H. Wolfgang, Removal of aromatic sulfonates by granular activated carbon .comparison of pilot plant data. RSSCT results, and mathematical model predictions. Proceeding of the Chemviron Carbon Award Meeting, university of Leuven(1997)
[8] U. Markus, K. Andreas, G. Hans-Jurgen, und H. H. Wolfgang, *Gwf Wasser* 141 (**2000**) 5, 293-299
[9] O.E. Maguire et al. **1962**. *JAWWA* 54:665.
[10] K. U. Andrew,. G. H Michael, and. B. G. Harry, *Langmuir*.**2006**, December 5, 22 (25) : 10854 -10857.
[11] K. P. Vamsi, N. Jakub,. O. S. Dinesh, D. M. Jan, *Eng. Aspects* 272 (**2006**)157–163
[12] F.V. Ruth, Villamil, Paola Corio, J. C. Rubium, M.L. Silvia.Agostinho, *J. of electro analytical chemistry* 472(**1999**) 112 – 119
[13] A. R. Ismaeel, K. M.Edbey, and A M. Sagluf, *International Journal of Chem. Tech. Research,*Vol.2 No.2,pp1214-1219, April-june 2010
[14] Cz Lesek., R. B. Mieczyslaw., Ewa Komorowska-Czeprska., *Internet Journal of Chemistry,***2000**,3,14 [ISSN:1099 – 8292] Article 14
[15] A.R. Ismaeel.., *Asian Journal of Chemistry*, Vol.18, No.3 (**2006**), 2081 – 2088
[16] A. R Ismaeel.., *Asian Journal of Chemistry*, Vol. 19 , No. 5 (**2007**), 3688 – 3696