

Study of Adsorption Mechanism, Mode, Isotherms, and kinetics, of Dodecyl Sulfate from Raw drinking water on Activated Charcoal using pH Measurements

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Abstract: The adsorption of dodecyl sulfate (DS) from aqueous solution of sodium dodecyl sulfate (SDS) on Activated charcoal (AC) was studied by measuring the change of the pH of the solution. in the light of the adsorption mechanism that, as soon as the (DS) anion is adsorbed on (AC) it is neutralized with one proton of the adjacent adsorbed water molecule leading to adsorbed neutral molecule of hydrogen dodecyl sulfate, and releasing of one hydroxyl anion. Accordingly the solutions pH increases, where one mole increase in hydroxyl anion is equivalent to one mole of adsorbed (DS) molecule. This mechanism is confirmed by the experimental results that show applicability to the Langmuir and Ismail adsorption isotherms indicating Gyps free energy change ΔG equal -14.314, and -14.29 KJ M⁻¹/g(AC) respectively, The coincident of the tow ΔG values confirm the vertical adsorption mode postulated in applying Ismaeel adsorption isotherm. The kinetics of adsorption processes was studied by following the change of the (DS) test solution concentration with time indicating first order adsorption reaction. . The study show the calculation of the charcoal mass. and operation time, needed for treatments of certain amount of water. The pH method of measuring is more suitable than other chemical methods of determination of sulfonate concentration that may affected by the mentioned change of pH due to adsorption processes.

Key Words: Dodecyl Sulfate, Adsorption, Mechanism, Isotherm, Kinetics, Activated Charcoal.

Introduction

Sulfonates are used in large scale as effective detergents, some sulfonates are poorly biodegradable, hence they can reach the bank filtrates used for drinking water production from rivers or underground water. Several sulphonates are detected in the bank filtrates of rivers at concentration of several $\mu\text{g/L}$ during drinking water treatment, such trace compounds should be removed from the raw water effectively. In Germany for many years granular activated carbon (GAC) adsorbent have been operated for that purpose [1-3]. Direct electrochemistry of the cytochrome P450 BM3 heme domain (BM3) by confining the protein within sodium dodecyl sulfate (SDS) adsorbed films on the surface of basal-plane graphite (BPG) electrodes [4]. The effect of co surfactants on sodium dodecyl sulfate micellar structures adsorbed at graphite surface along its crystallographic planes was studied by using solution of 100 mM (SDS). and postulate

that the surfactant molecules initially adsorbed in a tail to tail and head to head fashion as the nucleation sites for the further adsorption and hence the growth of the surfactant micellar hemi cylinders structure [4]

There are different method for determination of sulfonates concentration [1-3], some of which needs time for several steps during which the samples may suffer biodegradable change specially in case of diluted solution[1], and in the others in present of co adsorbate [5,6] we have to avoid interference. Other methods such as colorimetric, infra red methods, or direct volumetric titration method with acid using indicator are affected by any change of the pH of the solution due to adsorption processes .

The adsorption isotherm equations represent the relation between the adsorbate concentration, and the fraction adsorbed at constant temperature. There are several adsorption isotherms such as, Freundlich, Temkin, frumkin, and Langmuir adsorption isotherm [7] from which we can detect the nature of adsorption

processes as the gyps free energy change ΔG value indicating whether it is weak physical adsorption of $\Delta G =$ up to -44KJ/M or strong chemical adsorption of $\Delta G =$ up to -480KJ/M [8]. Some isotherms as Langmuir indicate the number of moles needed to form a mono layer of adsorbate (N_m), and other isotherms such as Jaronice adsorption isotherm [9] that is suitable for the adsorption of poly adsorbate on heterogeneous solid surface illustrate the effect of heterogeneity of the adsorbent surface also concerning the molecular size ratio of each adsorbate with respect to the other [9], and Ismail adsorption isotherm concerning the Deuel competing and enhancing character of one adsorbate with the other, indicate also the adsorption of multi layers, the free energy change ΔG , and the heterogeneity parameter of each layer [10,11]

The aim of our work is :

- 1- To use direct, accurate, simple, fast, and instantaneous method for determination of the amounts of moles of (DS) removed by adsorption on activated charcoal during physical green chemistry purification processes of raw drinking water.
- 2- To illustrate the adsorption mode, and mechanism, and to indicate the suitable applicable adsorption isotherm for determination of the adsorption ΔG to know the type of adsorption [8].
- 3- Determination of the number of moles adsorbed / g (AC) (N) and that needed to form mono layer of the adsorbate (N_m) / g (AC), also to calculate the needed mass of (AC) for the treatment of certain amount of water.
- 4- The study of the kinetics of the adsorption processes to identify the time needed for treatment of certain amount of water having certain adsorbate concentration
- 5-To tack this study as a base fore the forthcoming work in case of higher (SDS) concentration in case of recycling the industrial, and agriculture waist water

The Experimental Methods

Chemical used are of analytical grade, distilled water of conductivity $4 \times 10^{-6}\text{S}$. 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 C_i equals 10^{-3} , 8×10^{-4} , 7×10^{-4} , 6×10^{-4} , and $5 \times 10^{-4}\text{M}$. 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 0.5 gram (AC) to 50 ml. of each solution in 250 ml conical flask, with shaking for 45 minutes using 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 C_f of (SDS) is calculated.

Results and Discussion

The change in the pH values of the test solutions before and after adsorption for different initial concentrations C_i of the solutions are illustrated in **figure (1)** where line (B) represent pH values of the solution before adsorption which show a decrease in pH value with the increase of C_i as a result of acidity of (S DS) sample, and line (A) represent pH values of the test solutions after adsorption which show an increase in pH of each test solution after adsorption. this experimental fact lead us to consider the following

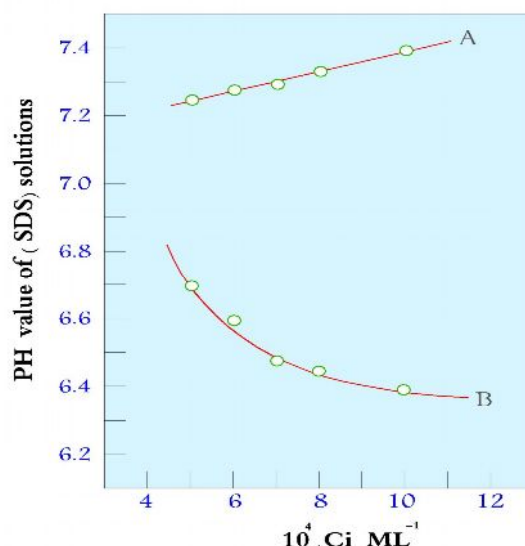
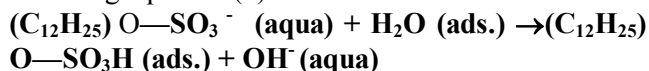


Fig. (1) Represents the change of pH of (SDS) solutions with its Concentration C_i (M L^{-1}), before (line B) and after (line A) adsorption at activated charcoal at 30°C

Adsorption Mechanism, and Mode

The adsorption mechanism of (DS) on (AC) surface that, the hydrated negative dodecyl sulfate anion move with its negative sulfate end facing to graphite surface due to the electrostatic attraction with partial positive charge on the hydrogen of the molecules of primary water layer adsorbed on graphite surface at the Helmholtz O plane. this attraction in addition to The Van der Waals force lead to vertical adsorption of neutral molecule of hydrogen dodecyl sulfate, formed by accepting one proton from adjacent adsorbed water molecule prior to adsorption, and releasing one negative hydroxyl anion to one of the positive sodium anions hydrated in the outer Helmholtz plane of the solution – charcoal double layer, the adsorption mechanism is illustrated by the following equation (1)



The liberated hydroxyl anion increase the pH value of solutions after adsorption, where the adsorption of one mole of dodecyl sulfate is equivalent to an increase of one mole hydroxyl ion as indicated by equation (1) so, we can determine the decrease of concentration ΔC of (DS) which equals to $(C_i - C_f)$ to be equal to the increase of hydroxyl ion concentration calculated from the mentioned increase of pH values of solution due to adsorption.

Our mechanism of vertical adsorption of neutral hydrogen sulfate is in agreement with authors [6] where they used solution of 100m M (SDS) and postulate that the surfactant molecules initially adsorbed in a tail to tail and head to head fashion as the nucleation sites for the further adsorption and hence the growth of the surfactant hemi cylinders [6]

, since the head to head adsorption fashion is impossible or difficult to occur due to the repulsion between the head negative charges on $-\text{SO}_3^-$, so our mechanism of vertical adsorption of neutral hydrogen dodecyl sulfate is confirmed. We prove latter that the formation of surfactant hemi cylinders dose not reached in our low concentration 10^{-4}M compared with there concentration of 10^{-1}M .

Adsorption Isotherms :

The number of moles (N) of (DS) adsorbed per one gram graphite is given by equation

$$N = \Delta C \times V / [1000 \times m] \quad \dots\dots\dots(2),$$

where (V) is the volume of test solution in(ml), (m) is the mass of graphite in gram,

Applying Langmuir adsorption isotherm [7-9] represented by the equation,

$$C_f / N = C_f / N_m + 1 / (N_m \times K) \quad \dots\dots\dots(3),$$

where (N_m) is the number of moles of adsorbate needed to form mono layer per one gram (AC), and K is adsorption equilibrium constant. This isotherm is applicable to our results as by plotting C_f with C_f/N it give straight line shown in **figure (2)** with slope equals $1/N_m$, and intercept equals $1 / (N_m \cdot K)$ from the values of slope and intercept $N_m = 10^{-7}$ mole / gram graphite, and the adsorption equilibrium constant $K = 291.944$, the gyps free energy change was calculated as $\Delta G = -2.303 RT \log K$, where R is the general gas constant, T is the temperature in Kelvin = 303.15 K° so $\Delta G = -14.314 \text{ KJ} / \text{M}$ The specific adsorption aria A in $\text{m}^2 / \text{gram} (\text{AC}) = N_a \cdot 10^{-20} \cdot N_m \cdot \sigma$, where N_a is Avogadro number, and σ is the adsorbed aria in A^{02} by one molecule per one gram (AC) so $A = 6.02 \times 10^{23} \times 10^{-20} \times 10^{-7} \times 15.7637$
 $A^{02} = 95 \times 10^{-4} \text{ m}^2 / \text{g} (\text{AC})$.

The value of $\sigma = 15.7637 \text{ A}^\circ$

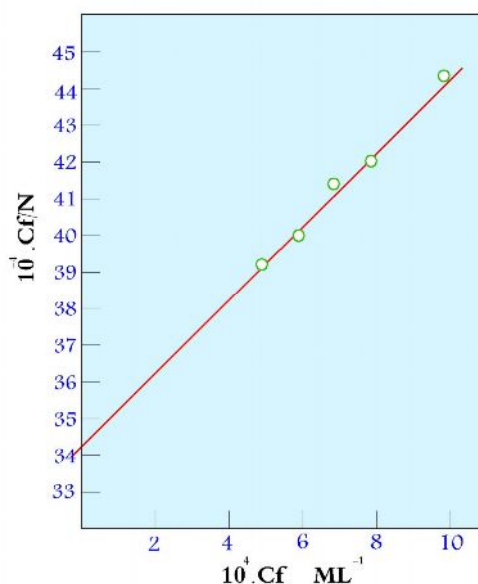


Fig.(2) Langmuir adsorption isotherm illustrate the relation between the final (equilibrium) Concentration C_f (ML^{-1}), and C_f/N at 30°C where N is number of moles (DS) adsorbed /gram (AC).

is calculated by considering that the (DS) anion adsorbed vertically with its head negative charge facing the (AC) surface and get σ dimensions from bonds angles and lengths of SO_3^- [10-12]

The previously mentioned Langmuir adsorption isotherm dose not include any term related to other factors affecting the adsorption processes as surface homogeneity, competing or enhancing adsorbate with (DS) anions in the solution, Ismail adsorption isotherm [10,11] consider these factors which is represented by the following equation

$$\text{Log} [\theta / (1 - \theta)] = C_1 \cdot C_2 \cdot r_{12} \cdot m \cdot \text{Log} K + \text{Log} [r_{12} / m C_2] \dots\dots\dots(4)$$

where θ is the surface coverage fraction by (DS) = N / N_m , and C_1 is the molar concentration of (DS), C_2 is the concentration of competing water molecules tends to be adsorbed at (AC) surface, r_{12} is the size ratio of (DS) anion to that of water molecule, m is the surface heterogeneity parameter, and K is adsorption equilibrium constant .

Ismail adsorption isotherm is applicable to our results as the relation between C_1 and $\text{Log}[\theta / (1 - \theta)]$ give straight line illustrated in **figure (3)**

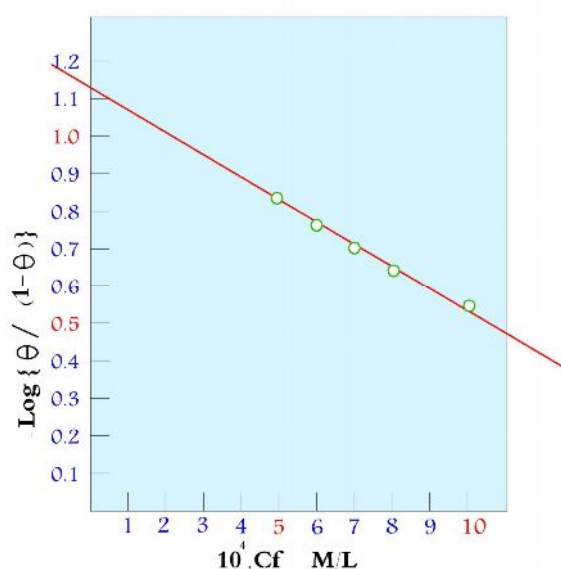


Fig.(3) Ismaeel adsorption isotherm illustrate the relation between the equilibrium concentration $C_f \text{ ML}^{-1}$ and $\text{Log} [\theta / (1 - \theta)]$ for the adsorption of (DS) on (AC) at 30°C .

as we consider $C_2 = 1$ since water exists in excess, its concentration is considered constant, the size ratio $r_{12} = 4.3$ calculated in case of vertical adsorption of (DS). By substituting C_2 and r_{12} in the intercept value $= \text{Log} [r_{12} / m C_2]$, we get the value of (m.) Substituting the values of C_2 , r_{12} , and m in the value of the slope of the line $= C_2 \cdot r_{12} \cdot m \cdot \log K$ from which $\log K$ is calculated to give Gyps free energy change $\Delta G = -14.288 \text{ KJ M}^{-1} / \text{g(AC)}$. This value is nearly identical to that obtained from Langmuir adsorption isotherm confirming our postulated vertical adsorption mode of (DS).

When we consider the horizontal mode of adsorption recommended by [6] leading to micellar structures on graphite the size ratio of (DS) to water molecule $r_{12} = 17.2323$ which give adsorption free energy change $\Delta G = -921.675 \text{ J/M /g(AC)}$ ie. very weak adsorption which is not in agreement with that of Langmuir or with Ismaeel when considering horizontal adsorption mode [$r_{12} = 17.2323$], we explained this contradiction in the light of [6] hypothesis that the adsorption of (DS) occurred at first, then it act as nucleation of forming the hemicylindrical micelle structures, this confirm our postulate that the molecule is physically adsorbed vertically at first with $\Delta G = -14.288 \text{ KJ / M}$ at our low (DS) concentration (10^{-4} ML^{-1}), where no multi layers formed unless the first layer had been

completed [13], then may acting as a nucleation of forming the hemi cylinders structure as a multilayer indicated by [6] at higher concentration 10^{-1} M of (SDS) .

The kinetics of adsorption:

The study of the kinetics of adsorption processes is don by determining the average adsorption rate [$\text{M L}^{-1} \text{ S}^{-1}$] for each starting concentration C_i (M L^{-1}) of (SDS) solution by calculating of the time of the change of solution concentration from C_i to C_f .

Figure (4) represent the relation between the adsorption rate and the initial concentration C_i which give straight line represented by the equation,

$$\text{Adsorption rate} = K \times C_i \dots \dots \dots (5)$$

The rate constant $K = \text{Rate} (\text{M L}^{-1} \text{ S}^{-1}) / \text{Conc.} (\text{M L}^{-1}) = 1.0625 \times 10^{-7} \text{ S}^{-1}$ indicating that the adsorption processes is first order which is in agreement with the fact that the reaction

rate depends only on the (SDS) concentration because water present in excess and its concentration is nearly constant. We can make use of the kinetic study to calculate the mass of (AC), and the time needed to purify certain volume of water having known (SDS)Coc..

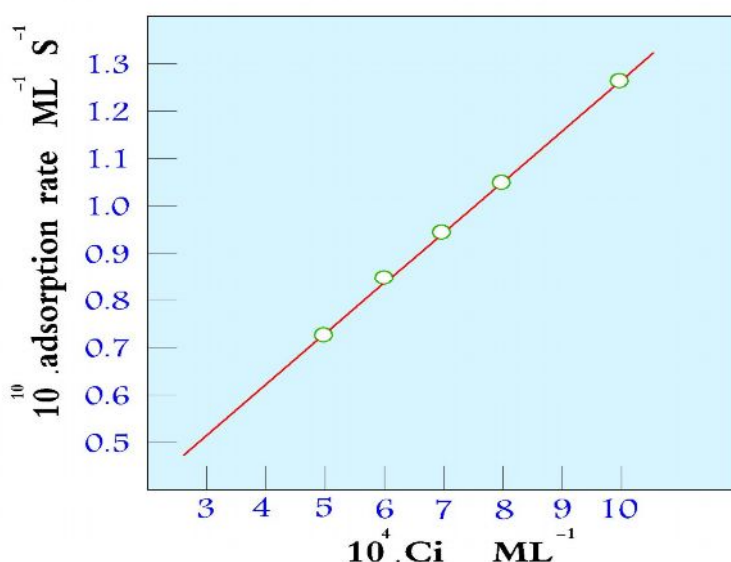


Fig. (4) Represents the relation between the average adsorption rate $\text{ML}^{-1} \text{ S}^{-1}$ and initial concentration C_i in ML^{-1} for adsorption of (DS) on (AC) at 30°C .

Conclusions

1- Using the pH measurements as a green physical, direct, accurate, simple, and fast, method for determination of the amounts of moles of (SDS) removed by adsorption on activated charcoal during green physical chemistry purification processes of raw drinking water, to avoid the error occurred in other measuring methods which affected by the increase of pH due to adsorption, and to avoid the

interference in case of the present of other co adsorbate.

2- This method can be used for identifying the adsorption mode, mechanism, isotherms, and kinetics of any other surfactants.

3- We can use this method in the study of adsorption of (SDS) of higher concentration in case of purification of industrial, and agriculture waste water.

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