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The adsorption of skimmed milk and full- fat milk solution on the surface of natural teeth

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Abstract. Method: Synthetic aqueous solution from different milk solution (500ml) and the concentration (24ppm) the stocke solution were diluted by distilled water from (2.5, 5,10,15 and 20 ppm), using (50 ml) from each solution of different milk was shaken with (0.5 g) of teeth surface at different tempratuers and at pH= 7 for (10 min) and measured the absorbance for the different solutions before and after adsorption. Results: Milk in adsorption process equilibrium was rapidly reached after 10 minutes of the contact time, from the amounts adsorbed of different milk almudhish (high fat) and alanen (low fat) on teeth, it was described by the Freundlich adsorption isotherms and we calculated thermodynamic parameter (ΔH, ΔG, ΔS). Conclusion: Studies concerning the factors influencing the adsorption procees Such as adsorbent dosage, pH, contact time and temperature and we found that these the adsorption capacity was increased with increasing initial milk concentrations and with increasing tempratures indicated the formation of dimer layer on the contact region.
Keyword: adsorption process, teeth surface, thermodynamic and milk composition.

1. Introduction

Adsorption is define as adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent [1]. Milk and dairy products play an important role in the daily diet of people all over the world. Several milk proteins of different mammalian are known to be bioactive and to positively effect of various aspects of human health, including reducing the risk of caries [2]. from human and animal studies it is substantial scientific evidence supports for the conclusion that milk play role the anti-cariogenic or cariostatic properties, and that diets including milk and dairy products reduce the risk of dental caries [3,4,and 5]. In the fact, it seems that many of the reported about anti cariogenic properties of milk proteins including such as lubrication, digestion, regulation of the oral micro flora and film formation on oral surfaces are similar to those exerted by saliva proteins [6]. Therefore, in vitro and in vivo experiments have indicated a selective adsorption of different protein species onto hydroxyapatite (HA) surfaces and enamel surfaces in the oral cavity [7]. In addition the morphological features similar to those observed in acquired enamel pellicle have been observed when enamel specimens were incubated in fat free milk, and some of the beneficial properties of milk proteins for oral health and lowering risk of caries may be directly relate to their ability to adsorb to tooth enamel surfaces in the oral cavity. However, to date no information regarding the pellicle forming abilities of proteins in different fluid milk products is available [8].

2. Materials and Methods

The instruments used were UV - VIS Spectrophotometer (UV-1800) Shimadzu, thermo stated Shaker bath/GFL (D-3006), Germany, TDA Electronics Ltd., and electronic Balance/Sartorius Lab. BP 3015. The material used in this process is Anelene and AL- Mudhish Milk as an adsorbent. It is soluble in water, the anelene milk is low fat but the al- Mudhish milk is high fat.

Adsorbents

Teeth used as adsorbent in (figure 1).

Total of 20 teeth were obtained from a private dentist extracted from the patients undertaken to orthodontics treatment .The teeth were keep in normal saline at ($37^{o}c$) until be used.

A stock of (500ml) aqueous solution of (low fat) Anelene and (high fat) AL- Mudhish Milk (24 ppm) was prepared and its (λmax) was determined. The maximum absorbance (λmax) was (454) nm for Anelene milk and the maximum absorbance (λmax) was (458) nm for AL- Mudhish milk. At figure '2and 3'.

Various milk (high fat and low fat) solutions with different concentrations were prepared by diluting the stock solution with distilled water (20, 15,10,5 and 2.5 ppm).

The calibration curve for aqueous solutions for two milks by plotting the absorbance values of these milk solutions were measured at the specific (λmax) by using UV-Vis double beam Spectrophotometer and plotted versus the concentrations of these milk solutions in figure' 4and 5'. For anelene and al-mudhish milk.

The time to reach equilibrium state that is required for full saturation of adsorbent surface at 37 ^{o}C by the adsorbate has been determined by the following procedure:

50 ml initial concentration (24ppm) of adsorbate milk solution was shaken with (18.78 g) of teeth adsorbent. The absorbance of adsorbate solutions were measured by UV/Visible spectrophotometer at different intervals 10, 20, 30 …minutes until reaching equilibrium (no further uptake of adsorbate by adsorbent as the time proceeds).

A systematic procedure was followed to determine the adsorption isotherms for each of adsorbent and adsorbate systems. A volume of (50ml) of five different concentrations of milk solution (20, 15,10,5 and 2.5 ppm) was shaken with (18.78 g) of teeth adsorbent at a certain temperature in a thermostatic shaker. The speed of shaking was 40 cycles per minute. After the equilibrium time (10 min) elapsed, the absorbencies of the filtrate solutions were measured at (λmax). The equilibrium concentrations of the prepared solutions can be determined from the calibration curve using their absorbencies. Adsorbed amount of the milk solution was calculated at certain conditions from the concentration of solution before and after adsorption according to 'as in equation (1)'

$X_m = (C_o-C_e)\ V / m$…………….. (1), where C_o and C_e are the initial and equilibrium concentrations of milk solution (ppm g/ml) respectively, V is the volume of solution in (ml), X_m= the maximum quantity of adsorbate (in g) that is adsorbed on the adsorbent at certain value of C_e that was fixed for all temperatures used in the study, (m) is the weight of adsorbent in grams.

X_m can be determined 'as in equation (2)'

$Q_e = X_m / m$…………………… (2), where Q_e= is the quantity of adsorbate (in mg) held by (18.78 g) of adsorbent.

The equilibrium constant (k) for the adsorption process at each temperature is calculated 'as in equation (3)'
K = (Q_e) (18.78 g)/(C_e) (0.05 L)……….(3), where (18.78 g) represents the weight of the teeth that has been used, (0. 05 liter) represents the volume of the milk solution used in the adsorption process.
The change in free energy (ΔG) could be determined 'as in equation (4)'
ΔG = - R T ln k……………. (4), where R is the gas constant (8.314 J/mol. deg) and T is the absolute temperature.
The heat of adsorption (ΔH) may be obtained 'as in equation (5)'
In Xm = -ΔH/RT + constant ………. (5)
The change in entropy (ΔS) can be determined 'as in equation (6)'
ΔG = ΔH – TΔS……… (6)

3. Results

Figure 1. Teeth used as adsorbent.

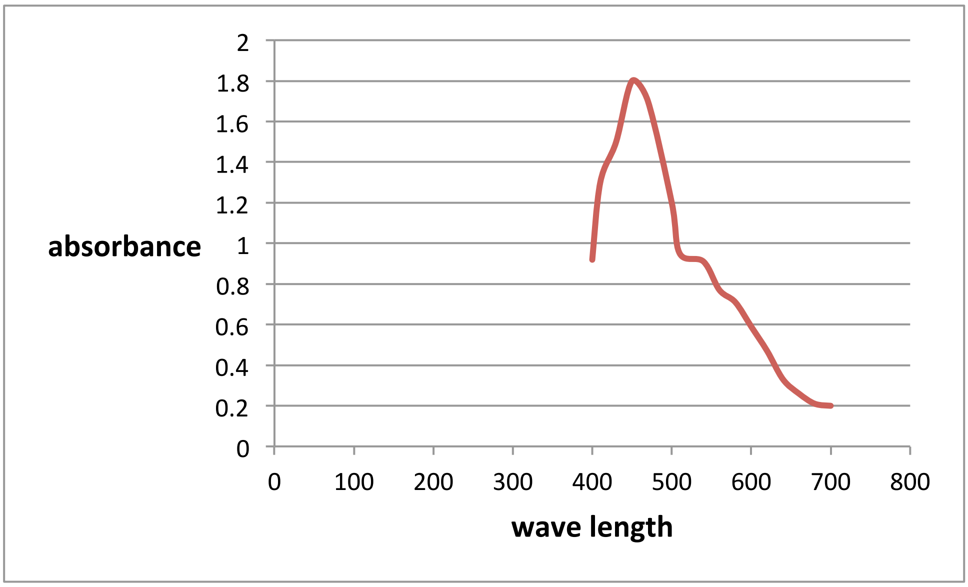

Figure 2. UV Spectra of aqueous solution of Anelene milk at temperature 37°c.

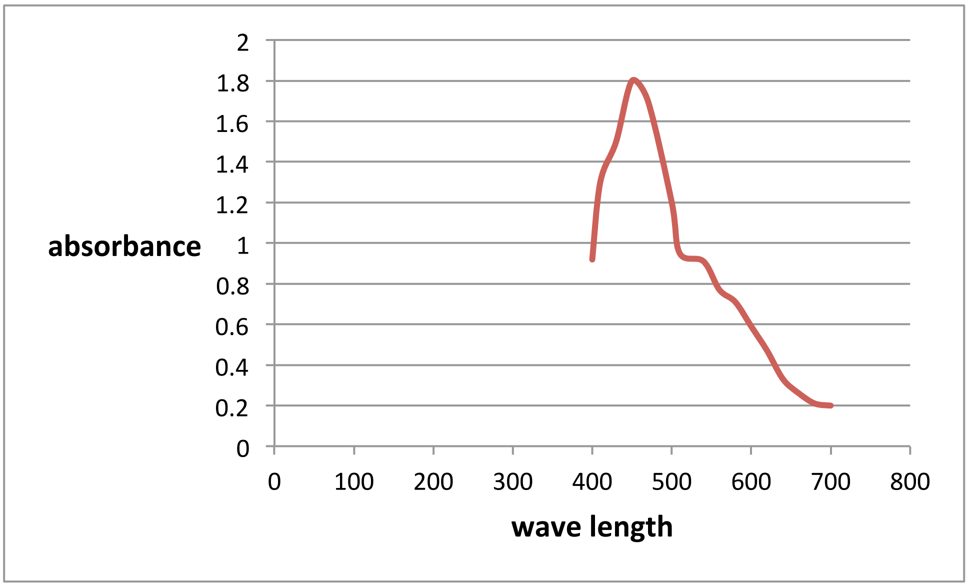

Figure 3. UV Spectra of aqueous solution of AL-Mudhush milk at temperature 37°c.

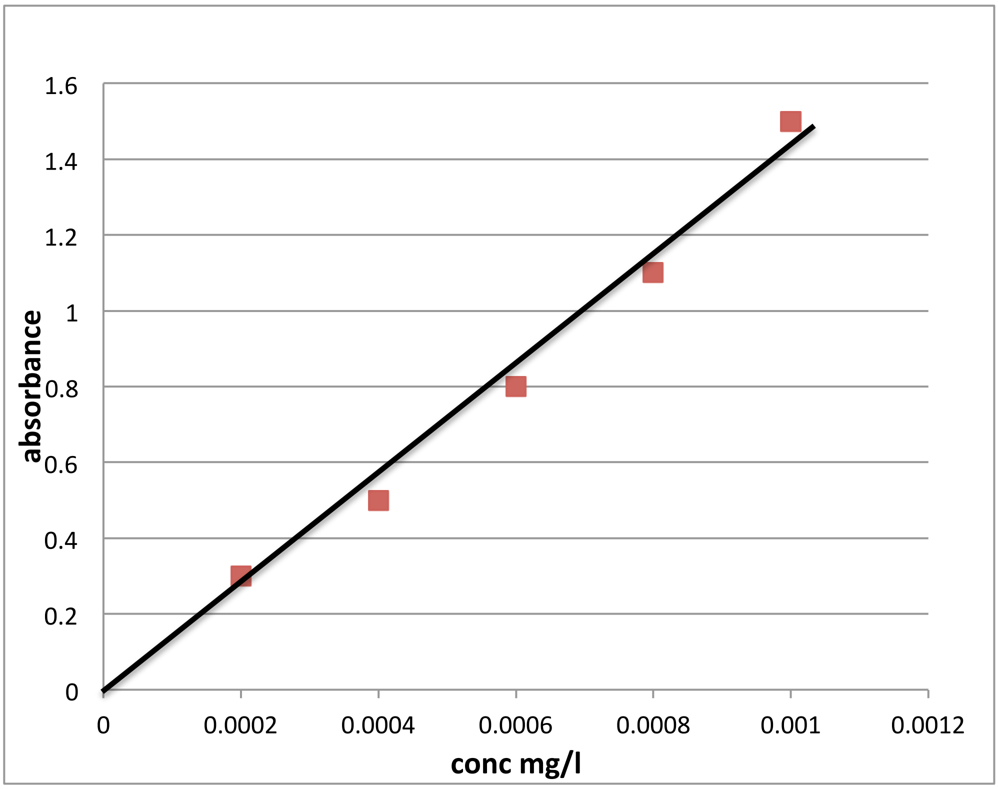

Figure 4. Calibration curve for aqueous solutions of Anelene milk at temperature 37°c

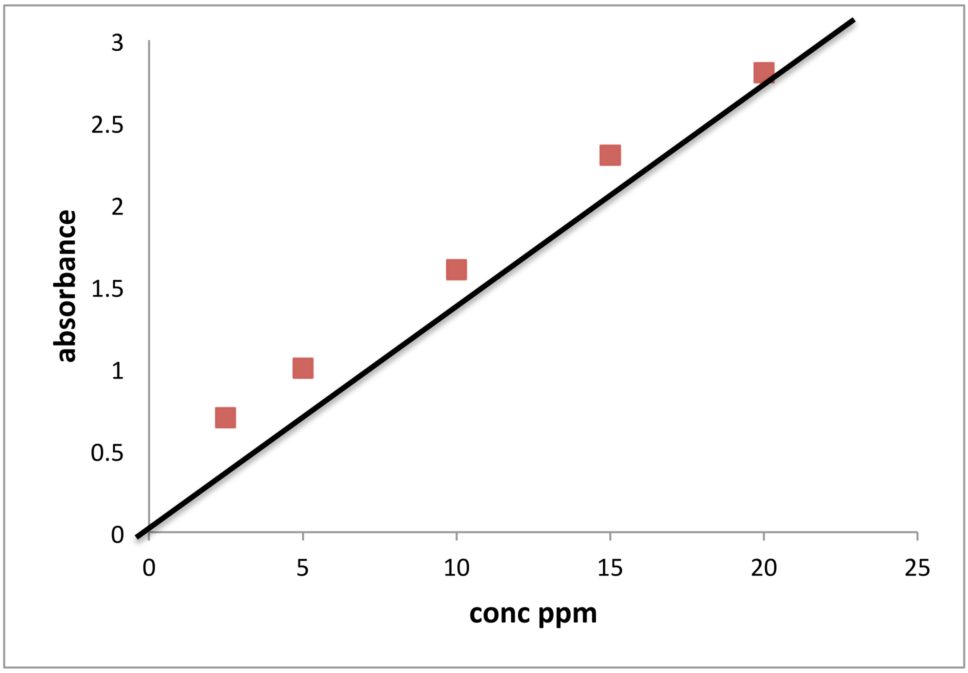

Figure 5. Calibration curve for aqueous solutions of al-Mudhish milk at temperature 37^{o}c

Temperature effects and thermodynamic parameters: -

The general shapes of the adsorption of two milk on teeth at three different temperatures (30, 32 and 37°c) are given in figures (6 and 7). Figures show that the adsorption of milk increases at 37 $^{\circ}$c temperature.

The adsorption isotherms of Anelene and AL- Mudhush Milk on teeth at different temperatures are shown in figures '6 and 7', as indicate of frundlich isotherm depend on Giles classification.

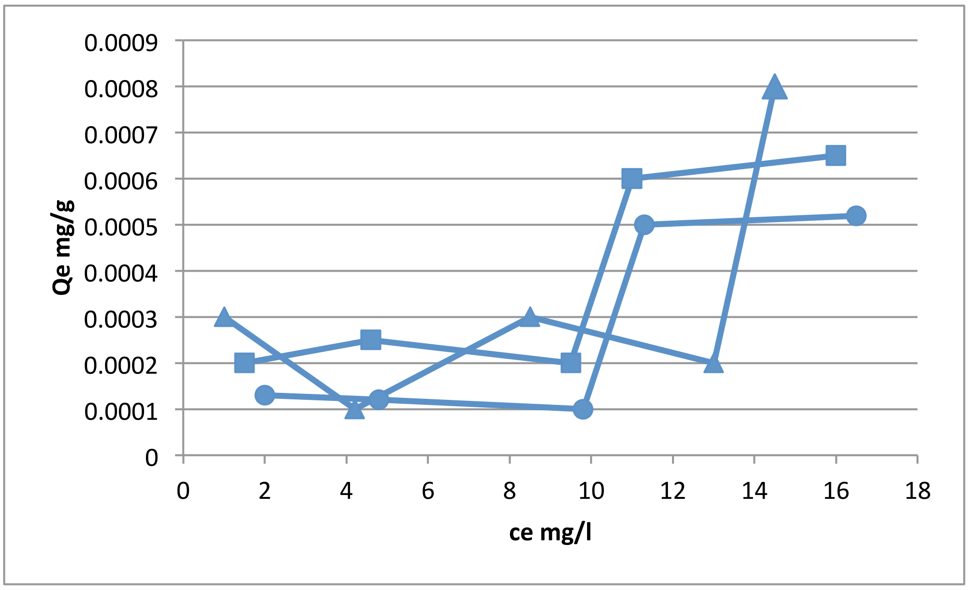

Figure 6. Adsorption isotherms of Anelene milk on teeth at different temperatures (●30, ■ 32 and ▲37^{o}c)

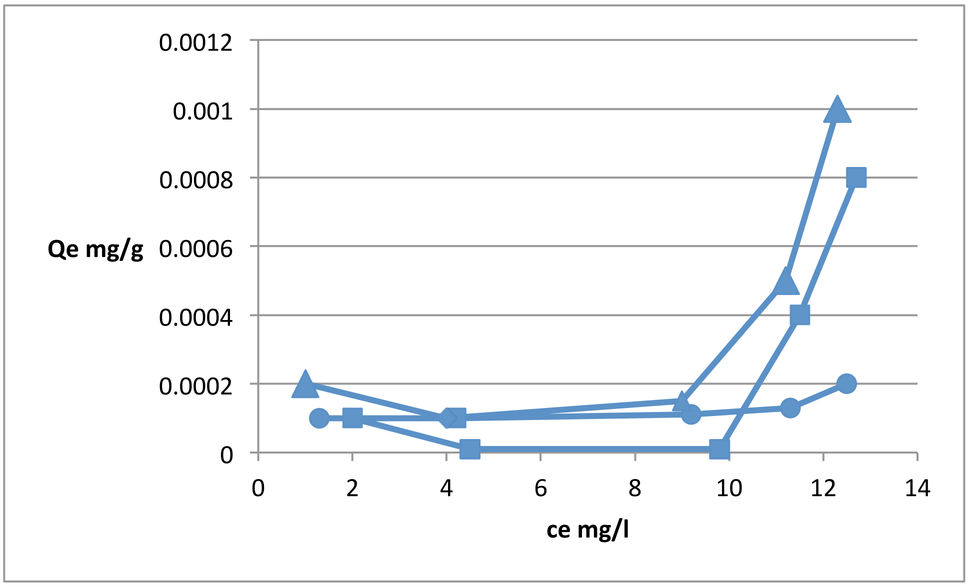

Figure 7. Adsorption isotherms of AL-Mudhish milk on teeth at different temperatures (●30, ■32 and ▲37°c).

Table 1. Effect of temperature on the maximum adsorbed quantities of Anelene and AL- Mudhish Milk on teeth.

Table 1. Gives X_m values at different temperatures.

Adsorbent	T.c°	T.k°	1000/T. °k^{-1}	X_m(mg)	In X_m
Anelene (low fat)	30 32 37	303 305 310	3.30 3.27 3.22	0.01 0.01 0.015	-4.6 -4.6 -4.19
AL-Mudhish (high fat)	30 32 37	303 305 310	3.30 3.27 3.22	0.01 0.02 0.01	-4.6 -3.91 -4.6

Where X_m is the maximum uptake of adsorbate at certain value of (C_e) for all temperatures. Plotting (In X_m) versus 1000/T produced a straight line with a slope = - ΔH/R as shown in figures‘ 8 and 9’.

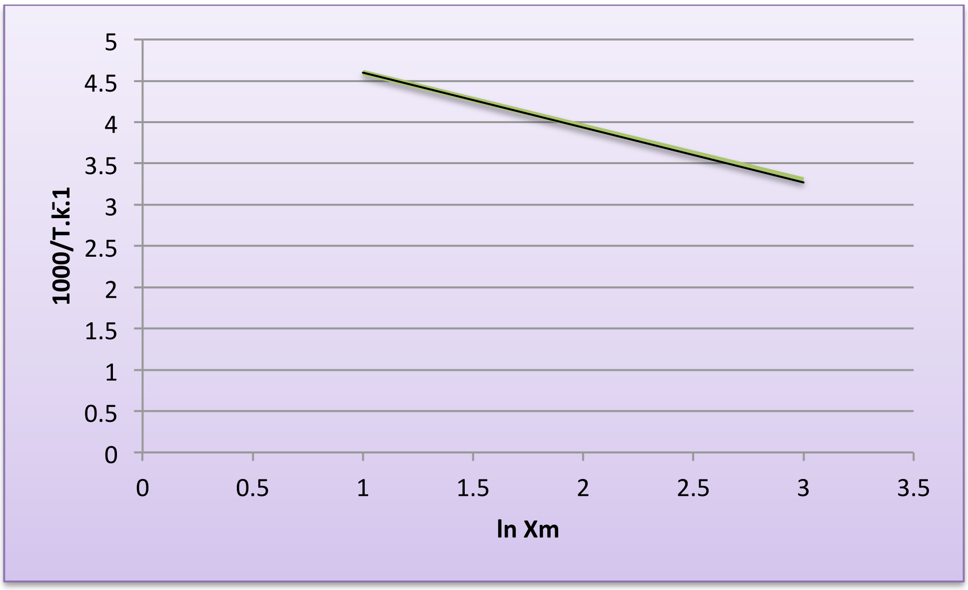

Figure 8. ln Xm plotted against reciprocal absolute temperature for the adsorption of anelene milk on teeth at different temperatures (30, 32 and 37°c).

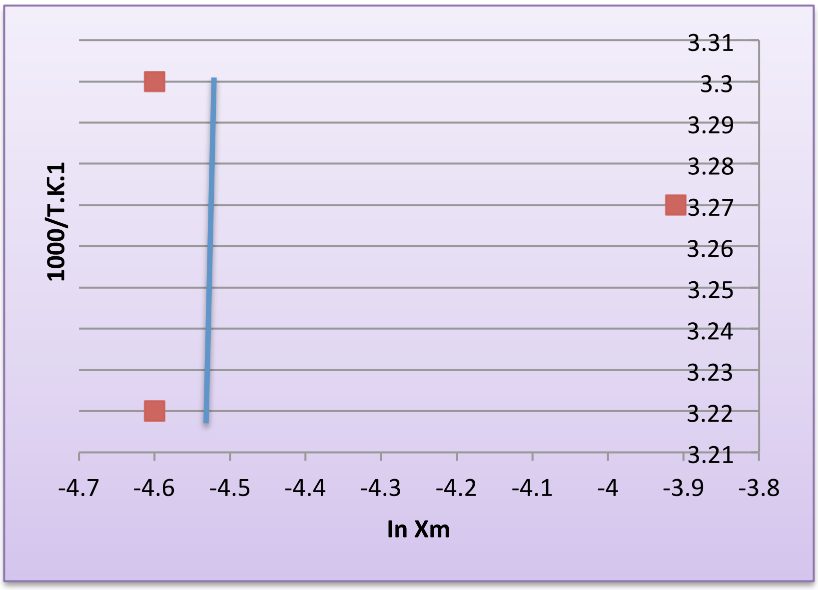

Figure 9. ln Xm plotted against reciprocal absolute temperature for the adsorption of al-Mudhish milk on teeth at different temperatures (30, 32 and 37°c).

The study of the temperature effects on adsorption helps in finding the basic thermodynamic functions (ΔH, ΔG, ΔS) of the adsorption processes. Show as that in table 2.

Table 2. Shows the basic thermodynamically values of adsorption of anelene and al- Mudhish Milk on Teeth.

Adsorbate	ΔH (kJ / mol)	ΔG (kJ / mol)	ΔS (J/ mol k)	Temperature C^0
Anelene	+11.58 +11.66 +10.79	+11.03 +11.2 +10.07	+0.0018 +0.0015 +0.0023	30 32 37
AL-Mudhush	+11.58 +9.91 +11.85	+10.4 +10.47 +11.8	+0.0038 - 0.0018 +0.00016	30 32 37

- The positive values of the ΔG for the adsorption of these milks on teeth indicated that the adsorption process of is nonspontaneous.

- The positive values of ΔH at different temperatures indicated an endothermic reaction.
- The positive values of ΔS for the adsorption of two milk on teeth indicated increase in the degree of freedom of the adsorbed species.
- The negative value of ΔS for the adsorption of al-mudhush milk on teeth at 32°c indicated to the favorable adsorption.

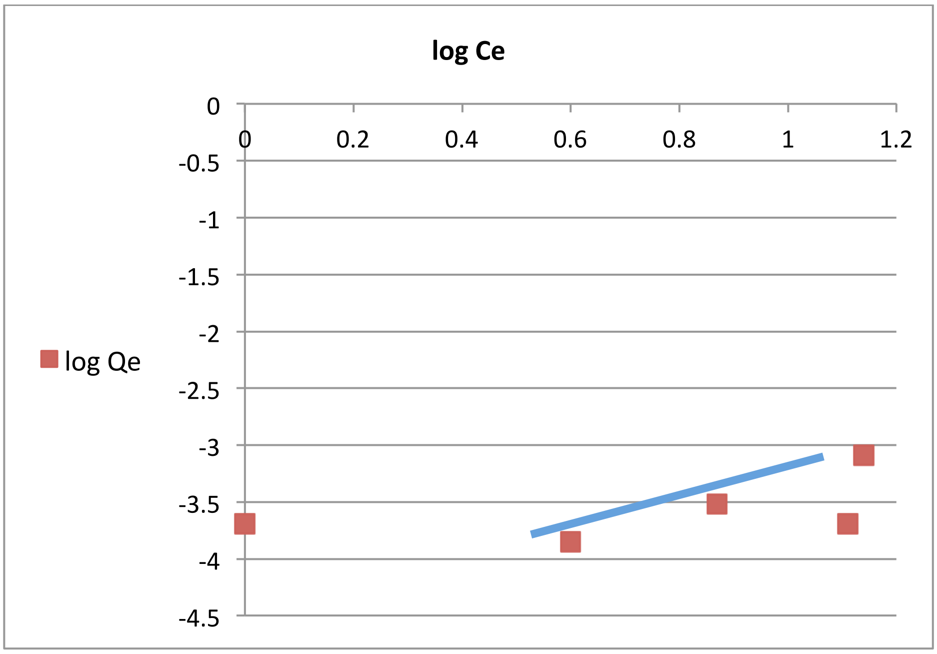

Figure 10. Linear form of frundlich isotherm of anelene milk adsorbed on teeth at 37 °c.

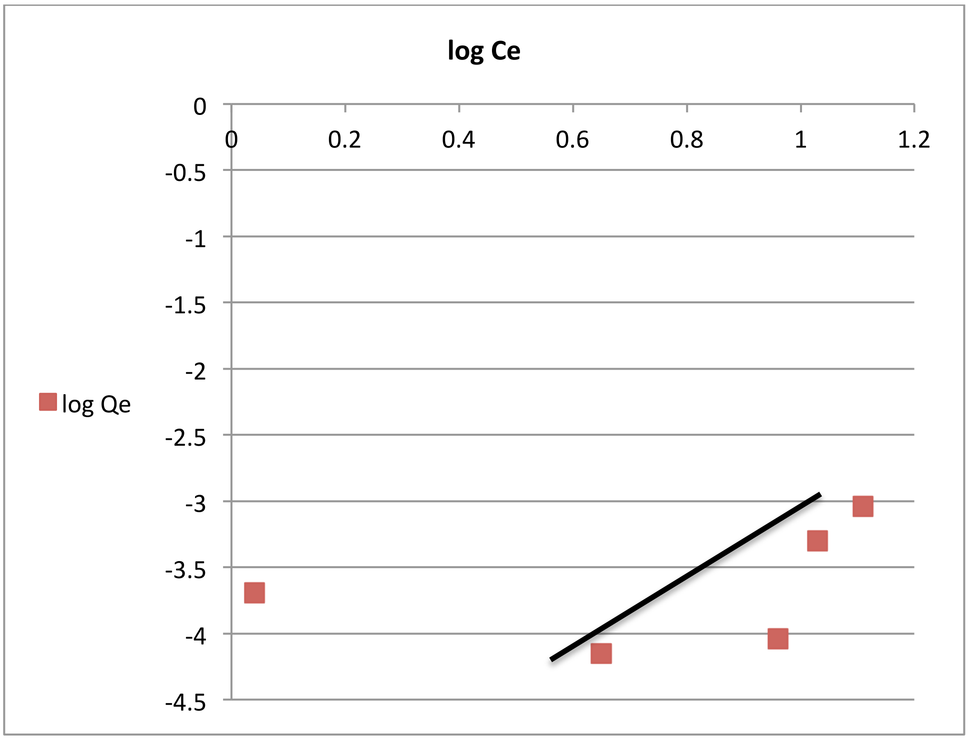

Figure 11. Linear form of frundlich isotherm of al-mudhish milk adsorbed on teeth at 37 °c

4. Discussion

The aim of the study was to show were the effect of food, drink or drug intake on the formation of tooth discoloration or caries [9]. Therefore, the adsorption experiments should be carried out by testing the effect of different types of high-fat and low-fat milk on the surface of the tooth and determining its effect. Milk is a very important source of calcium supplying well over half the daily requirement and intake for children in many countries. The next most important inorganic components are iodine and phosphorus, followed by potassium and magnesium, zinc and selenium. Milk is not a significant source of iron or copper. There is some variation in the concentration of nutrients in milk between seasons and countries, and national food tables should be consulted for more precise information [10].

The tooth surface is unique among all body surfaces in two ways. First, it is a hard surface and the second surface is introduced into the human mouth during the first years of life [11, 12].

The mineral in our teeth and bones is composed of a highly substituted hydroxyapatite (HAP), it described as a calcium-deficient carbonated HAP. A simplified formula that helps to understood this is Ca_{10}_x Nax $(PO4)_6$_y(CO_3)z $(OH)_2$_u Fu in contrast to HAP which has the perfect formula $Ca_{10}(PO_4)_6(OH)_2$.[(12)] The adsorption was studied by incubating bovine enamel in a peptide Solution for different periods of time. The amount of peptide adsorbed was calculated from the differences in peptide concentration in solution before and after adsorption [13].

In another meaning**,** the amount of adsorbed matter was quantity measured by the indirect method, in which the concentration of adsorbed matter is measured before and after the test [14] this is related with the materials it have smaller particle sizes and larger specific surface areas illustrate markedly better properties [15].

The solid/solution ratio between them is an important factor determining the capacity of adsorbent in a batch adsorption. Increasing the sample dose provides high surface area and larger number of adsorption sites and hence enhancement of milk uptake [16].

The factor of temperature was studied it has effects of on the adsorption process. Increasing the temperature is known to increase the rate of diffusion from the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, lead to the decrease in the viscosity of solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a molecules adsorbate [17, 18].

We found from the adsorption studies of two milk onto teeth at three different temperatures (30, 32 and 37 °C) and at pH =7. The results when the temperature increased the adsorption capacity increased from 0.0001mg/g to 0.001mg/g for the Al-mudhish milk (high fat) and 0.0002mg/g to 0.0008mg/g for the alanine milk (low fat) Therefore, higher temperature facilitated the adsorption of high fat milk and low fat milk on teeth . Also, we studied the values of thermodynamics.

The values of ΔH increased with the increase of surface coverage showing a maximum value. This might be due to the occurrence of structural rearrangement in the adsorbate molecules. Adsorption interaction between adsorbate molecules and solid surface generally modifies the state of solid and the magnitude of this modification depends on the high energy adsorption sites capable of specific interactions. Adsorption on adsorbents involves the adsorbent and adsorbate as equal

Partners of the adsorption process [19].

ΔH used in distinguish between chemical and physical adsorption the values of enthalpy +10.79 kJ/ mol for anelene milk while for al-mudhush milk is+11.85 kJ/ mol. The low values of ΔH give clear evidence that the interaction between two milk and teeth was weak and this is indicate to physical adsorption process. A diffusion process was occur on the teeth pores, lead to endothermic process [18, 20].

The positive values of the ΔG indicate that the adsorption process is nonspontaneous due to the small values less than 1 of the equilibrium constant [21].

Also, the positive values of ΔS related to an increased in degree of randomly of molecules at the solid/liquid interface during the adsorption of two milk onto teeth [18].

The Freundlich isotherm is a good evidence in the experimental adsorption process it suggests the heterogeneous of active sites on the adsorbent surface and physical adsorption [22]. In other word, it was may be that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed on surface increases with an increase in the concentration of adsorbate [23].

5. Conclusion

The aim of this study was to investigate the effect of different milk on teeth surface. We found initial milk concentration and temperature effect on the adsorption process its increase with increasing temperature.From thermodynamic results we found that the adsorption process is non-spontaneous due to physical adsorption and endothermic reaction. Also, a positive value for the entropy which indicates that adsorbed of molecules (milk) on adsorbent (teeth) remain randomly on the surface. Finally,from the adsorption of different milk on teeth surface it has no significant or high effect on tooth decay through the practical results obtained.

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