Adsorption of Triton X-100 Surfactant on Different Agricultural Soils

Shireen I. Hamadamin
Dept. of Chemistry, College of Science, University of Salahaddin
Erbil - Kurdistan -Iraq
E-mail address:shireenhawlery@gmail.com

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Abstract

The extensive utilization of hydrophobic organic compounds such as surfactants generates high environmental pollution levels. Due to their hydrophobicity, this type of compound tends to accumulate in soil organic matter. Distribution coefficient (K_d), Freundlich adsorption coefficient (K_f) and Langmuir adsorption coefficient (K_L) for adsorption of Triton X-100 on three agricultural soil samples with different characteristics were determined. Adsorption of Triton X-100 in solutions was best fitted to the Freundlich equation.

The effects of soil organic matter (OM) content, soil clay content and exchangeable cation content of natural soils on the adsorption capacity of Triton X-100 in water-solid systems were investigated based on the adsorption isotherm analysis. Results showed that, values of K_d and K_f increased with increasing soil OM content, but varied irregularly with clay content, exchangeable cations and pH.

Keywords: Surfactant, Triton X-100, Adsorption isotherms, Fruindlich, Langmuire, OM.

الخلاصة

إن الإستفادة الشاملة من المركبات العضوية الكارهة للماء مثل المواد المختزلة للتوتر السطحي للسوائل (surfactants) ، يولد مستويات عالية من تلوث البيئة. بسبب خاصية الكره للماء فإن هذا النوع من المركبات يميل الى التراكم في المواد عضوية في التربة. إن معامل التوزيع (K_d)، معامل إمتزاز فريندلك (K_f) و معامل إمتزاز لانكمور (K_L) قد حددت لإمتزاز تريتون (Triton X-100) في ثلاث نماذج تربة زراعية ذات خصائص مختلفة. إمتزازية تريتون (Triton X-100) في المحاليل التركيز أظهر توافقها على معادلة فريندلك.

إن تأثيرات محتوى التربة من المواد العضوية، محتوى طين التربة و محتوى الأيون الموجب القابلة للتبادل في الترب الطبيعية على قابلية إمتزاز تريتون X-100 في نظم الماء- التربة تم دراستها على أساس تحليل إمتزاز متساوي الحرارة (adsorption isotherm analysis). أظهرت النتائج بأن قيم كل من (K_d) و(K_f) إزدادت بإزدياد محتوى المواد العضوية للتربة، ولكن تغايرت بشكل غير منتظم مع محتوى طين التربة، الأيونات الموجبة القابلة للتبادل و pH التربة.

Introduction

A better understanding of surfactant adsorption by clays and soils is of great importance due to the wide spread use of these compounds in household and industrial activities.

Surfactants cause foams at sewage treatment plants and polluted underground waters, which are hazardous for health. They exert a solubility effect on many organic compounds and create carcinogenic impacts penetrated in to water and change its quality by causing it to have an unpleasant smell and tests[1]. Surfactant removal from the industrial waste has been the subject of substantial research since the 1950s, when synthetic detergents came in to a widespread use. An intensive data bases have been developed to support new commercial surfactants products for their safety and acceptability in the environment[2].

Natural Adsorbent

Three agricultural soil samples with different physico-chemical characteristics were selected from Erbil (Harer, Khabat and Salahaddin) for the adsorption experiments. The sample depth was a maximum of 10cm, air-dried and sieved through 2-mm mesh. Particle size distributed of clay (<2µm), silt (2-50µm), and sand (0.05-2mm) content was determined for soil using the pipette method[19]. The OC content was determined by the Walkey-Black procedure[20] with the results being multiplied by 1.72 for conversion into OM contents. Soil pH values were measured in a homogeneous paste made in water and 0.01M $CaCl_2$ solution. Soil cation content were measured by atomic absorption spectroscopy (AAS)[21]. Table 1 shows the physico-chemical characteristics of the studied soil samples.

Surfactants consist of organic molecules with a hydrophobic and a hydrophilic part and can interact with polar as well as nonpolar surfaces. At low concentrations, surfactants exist solely as monomers; above a critical aqueous concentration, which is specific for each surfactant monomer, called critical micellar concentration (CMC), the surfactant monomers are aggregated in solution to form entities made up of a hydrophobic core and a hydrophilic shell.

Some processes have been employed in order to solve the environmental problems caused by surfactants, including anaerobic and aerobic degradation[3], biodegradation[4,5], and adsorption phenomena[6-18]. Among these, adsorption is one of the effective methods available for such situations.

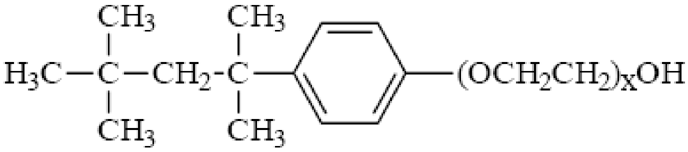
Materials and methods

Table 1: Some physico-chemical properties of the selected soil samples.

Parameter		Soils		
		S_1	S_2	S_3
Region		Harer	Khabat	Salahaddin
OM%		4.50	0.99	2.25
Moisture%		3.07	1.77	2.80
pH in D.W		8.04	7.91	7.68
Sand%		9.848	46.815	38.408
Silt%		53.486	40.485	30.958
Clay%		36.667	12.700	30.633
Texture		Silty Clay Loam	Loam	Clay Loam
Exchangeable basic cations(mg/kg)	Mg^{++}	2796.00	1520.00	2294.00
	K^{+}	586.00	121.00	465.00
	Na^{+}	693.00	823.00	621.00
	Ca^{++}	15353.00	13054.00	13513.00

Surfactants

Octylphenol polyethoxylate with an average ethylene oxide chain length of x= 9.5 (Triton X-100) a non-ionic surfactant, was supplied by BROMMA (LKB, France) with analytical grade (100% purity); its CMC is 150 mg L^{-1} and with molecular weight 624 g mol^{-1}.



Octylphenol polyethoxylate (Triton X-100)

Adsorption Experiments

Adsorption of Triton X-100 by the soils was performed using the batch equilibrium technique. Duplicate 1-g soils samples were equilibrated with 10ml of Triton X-100 solution at 20±2 C? with initial concentrations of 0.75, 1.50, and 50 CMC were equilibrated in thermostated shaker for 24 hour. The preliminary tests excluded adsorption of the studied surfactant to the wall of the test tubes, after which they were centrifuged at 4000×g for 30 min. Triton X-100 concentrations in the supernatants were determined using Uv spectroscopy at 275 nm [22,23] using JENWAY 6405 Uv/vis spectrophotometer. All determinations were performed against a soil blank to correct for possible interferences from the soil in the measurements of the surfactant.

The amount of surfactant adsorbed was calculated from the amount initially present in solution and that remaining after equilibrium with the soil. Distribution coefficients, K_d, as a measure of the adsorption of Triton X-100 by the soils, were obtained from the relationship between the amount of surfactant in the soil and in the equilibrium solution after adsorption.

Results and Discussion

To study the effect of soil characteristics on its affinity to adsorb surfactants, adsorption experiments conducted on the adsorption of Triton X-100 (0.75, 1.50, and 50 CMC) on the selected soil samples at 20±2 C?.

Adsorption coefficient, K_d (ml g^{-1}), is the ratio of surfactant adsorbed by soil (Differences between initial and equilibrium concentration were assumed to be caused to by adsorption) to the surfactant concentration in the solution at equilibrium[24].

$$K_d = \frac{Surfactant \quad adsorbed \quad on \quad soil}{Surfactant \quad in \quad solution \quad at \quad equilibrium} \qquad \text{.........................(1)}$$

$$C_s = K_d C_e \qquad \text{......(2)}$$

where C_s is the concentration of Triton X-100 adsorbed on the soil and C_e the equilibrium concentration of Triton X-100 in the solution.

The adsorption (distribution) coefficients, K_d, obtained for Triton X-100 adsorbed by the soils and the equilibrium concentrations, C_e, expressed in CMC, are shown in Table 2.

The highest K_d coefficients occur when the surfactant is initially in monomeric form (C_i=0.75 CMC), where C_i is the initial concentration upon increasing the concentration of the surfactant to values slightly higher than the CMC (C_i=1.50 CMC), the values of K_d decreased. At higher initial concentration, 50 CMC, that is when a high proportion of the surfactant must be in micellar form, a dramatic decrease in K_d is observed.

The equilibrium concentration values indicate a decrease in the amount of surfactant present in solution as a result of its adsorption by the soils, where the equilibrium concentrations after surfactant adsorption, expressed in CMC of Triton X-100 (Table 2), ranged between 0.0137 and 0.049 at C_i= 0.75 CMC, between 0.0358 and 0.134 at C_i= 1.50 CMC and between 8.047 and 13.90 CMC at C_i= 50 CMC.

Table 2. Distribution coefficients (K_d) and equilibrium concentration (C_e) for the adsorption of Triton X-100 by soils studied.

Soil	C_i = 0.75 CMC		C_i = 1.50 CMC		C_i = 50 CMC	
	K_d	C_e	K_d	C_e	K_d	C_e
1	591.6753	0.0137	154.0025	0.0358	440.0412	8.047
2	450.7828	0.0289	111.0957	0.0414	241.0561	9.782
3	58.2835	0.049	28.9522	0.134	35.8061	13.9

Adsorption models

The Freundlich and Langmuir models were used to quantify the adsorption of Triton X-100 from aqueous solution on selected soil samples.

Freundlich adsorption isotherms

Freundlich proposed the following model:

$$C_s = K_F . C_e^n \quad ....(3)$$

A more convenient form of the above equation is in its linearized form as follows:

$$LogC_s = \log K_F + n \log C_e \quad ....(4)$$

Where K_F is Freundlich *adsorption coefficient,* and n is a *linearity factor*, C_s and C_e is defined previously. Thus, a plot of $\log C_s$ vs. $\log C_e$ will yield a straight line with the slope n and intercept of log K_F. Figure 1 shows the validity of Freundlich isotherm.

Langmuir adsorption model

Adsorption data over the range of Triton X-100 concentration used in this study were utilized to fit the linearized form of Langmuir equation:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_L} + \frac{C_e}{C_m} \quad ....(5)$$

Where C_s and C_e were defined before, C_m is the *maximum amount of surfactant adsorbed (adsorption maxima, µg g^{-1}),* a liner plot of C_e/C_s vs. C_e shows the applicability of Langmuir isotherm (fig.1). The correlation coefficient obtained with both kinds of regressions (linear and non-linear) is shown in Table 3. Based on these parameters the data seem to be best fitted to the Freundlich model rather than the Langmuir model.

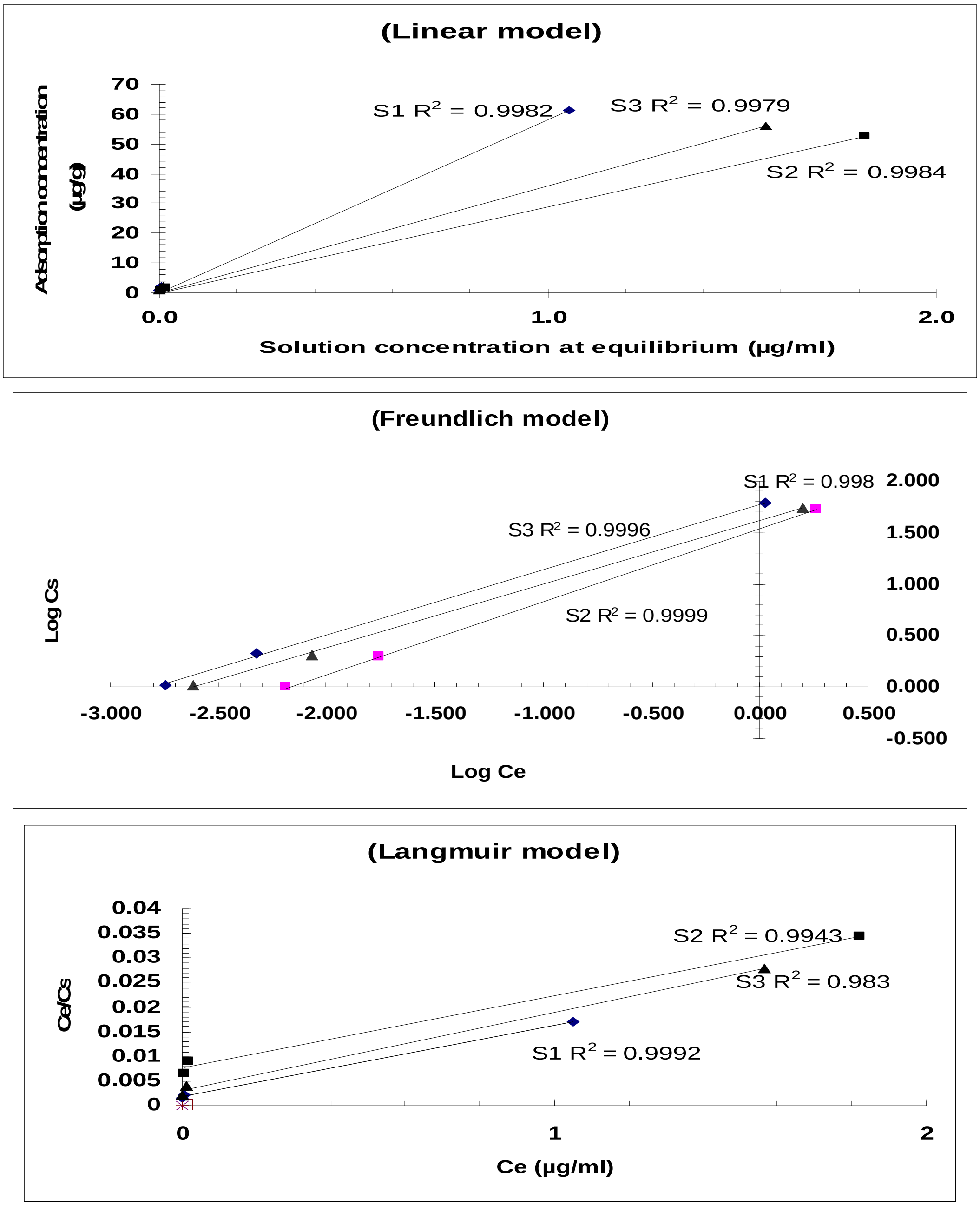


Fig.1: Fitted adsorption isotherm models for adsorption of Triton X-100 on the selected soil samples.

Table 3: Adsorption isotherm parameters for the linear, Freundlich, and Langmuir models for adsorption of Triton X-100 on the selected soil samples.

Models	Parameter	Soils		
		S_1	S_2	S_3
Linear model	K_d(ml/g)	58.293	28.962	35.814
	K_d (ml/g)(calc)	366.913	98.016	238.967
	R^2	0.998	0.998	0.998
Freundlich model	K_F(mL/g)	59.821	34.419	41.921
	K_{OC}(mL/g)	2291.809	5993.773	3212.080
	K_{OM}(mL/g)	1329.356	3476.667	1863.156
	n	0.631	0.705	0.619
	R^2	0.998	1.000	0.999
Langmuir model	K_l (mL/g)	7.631	1.947	5.129
	C_m(μg/g)	68.965	67.567	62.893
	R^2	0.999	0.994	0.983

Effect of soil characteristics on adsorption coefficient

Effect of soil organic matter

Organic matter normalized adsorption coefficient

The Freundlich adsorption coefficients are related to *soil organic carbon (OC*) and *soil organic matter (OM)* by the following equations:

$$K_{OC} = \frac{100K_F}{\%OC} \quad \ldots(6)$$

$$K_{OM} = \frac{100K_F}{\%OM} \quad \ldots(7)$$

$$\%OC = \frac{\%OM}{1.724} \quad \ldots(8)$$

Where K_{oc} is the organic carbon normalized adsorption coefficient and K_{oM} is the organic matter normalized adsorption coefficient.

Values of K_F were plotted against soil OC content; the slope of the linear correlation gives the average values of the corresponding K_{oc} for all studied soil samples. Figure 2 and data in table 3 Reveled that, K_F values increased with increasing soil OM (regression factor; R^2=0.99), our results were in agreement with those previously related by Walker et al. 2001[25].

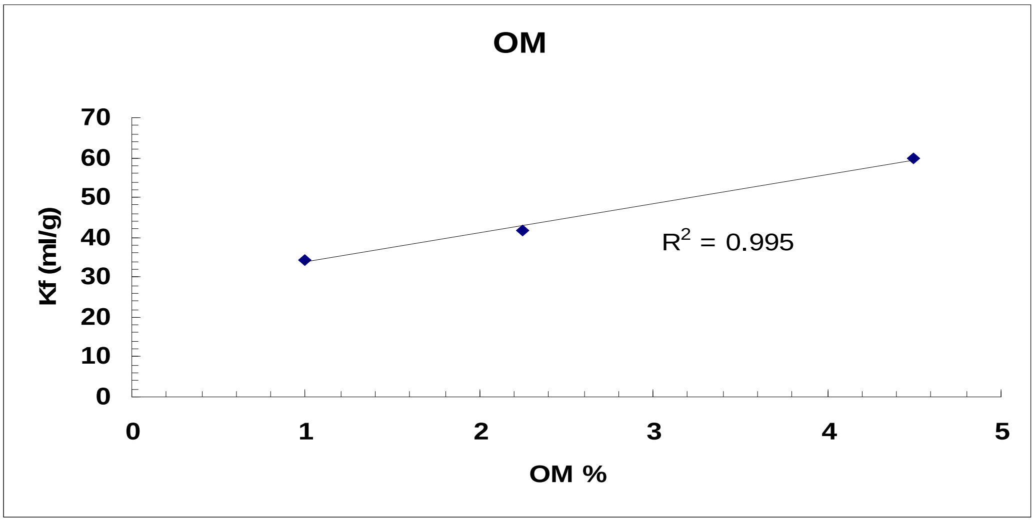


Fig. 2. Relationship of soil organic matter percent and adsorption of Triton X-100 on the selected soil samples.

From the stand point of interactions of non-ionic surfactants with soil OM significant differences in the chemistry of soil OM may be encountered from soil to soil in its polarity, elemental composition, aromaticity and condensation. Therefore the type and the age of soil OM affect the adsorption of non-ionic surfactants.

Adsorption of hydrophobic organic compounds has often been reported to be highly correlated with soil OC and soil OM content and relatively independent of other soil properties[26]. If it is so then one should obtain essentially the same or a narrow range of K_{oc} values for a given surfactant within a group of soils. (Table 3)

Effect of clay content

The dependence of adsorption of Triton X-100 with soil clay content is reported in Fig.3. The adsorption increases with increasing soil clay (R^2= 0.76), this indicates that the clay mineral are especially important in characterizing the soil adsorption capacity. Fig.3 reveled that values of K_F increased with increasing soil clay content. Irregular variation in the values of K_F with soil exchangeable cations.

Our results were in agreement with that reported in literature[27], which states that clay content of soil is not adequate to estimate the adsorption of surfactant but the type of clay mineral have a different cation exchange capacity so the adsorption is different.

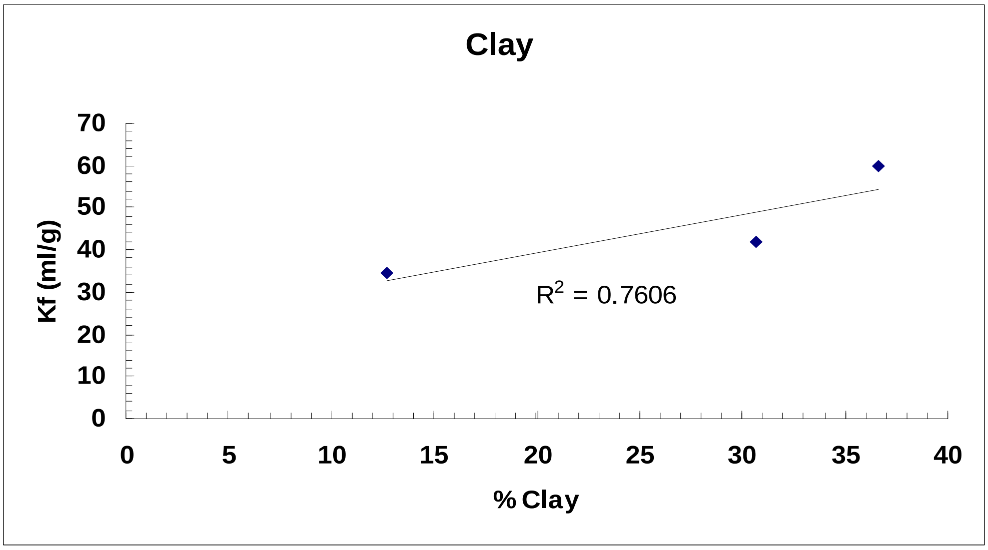


Fig. 3. Relationship of soil clay percent and adsorption of Triton X-100 on the selected soil samples..

Effect of pH

The role of hydrogen ion concentration was examined at different pH. The results given in fig.4 show that, the adsorption capacity decrease till pH reach to 7.9 and increase with further increase in pH at 8.

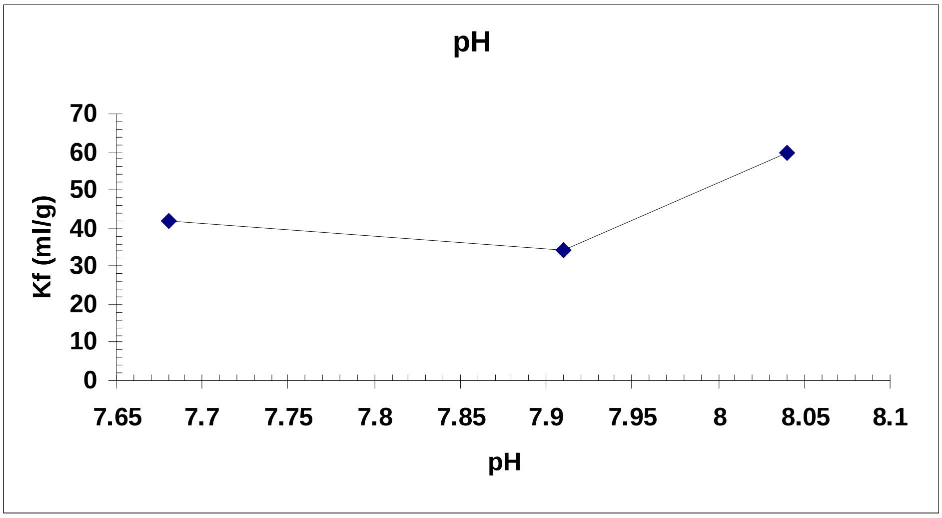


Fig. 4. Effect of pH on the adsorption of Triton X-100 on the selected soil samples.

Effect of exchangeable cations

The presence of Na^+ and Ca^{2+} ions very common in soil and vary from soil to soil. Therefore the effect of the presence of both ions on the adsorption of Triton X-100 was investigated. Fig. 5 showed that, the higher concentration of Ca^{2+} ions provide a favorable condition in the removal of the non-ionic surfactant. However, as it is observed from Fig. 6 while the presence of increasing amount of sodium ions to 700 mg kg^{-1} increased the adsorption of surfactant, a further increase in the concentration to 825 mg kg^{-1} decreased the amount of adsorbed surfactant. This may be due to relative competition between sodium ion and surfactant species on the active center of soil, owing the greater affinity of the Na^+ ions at higher concentrations.

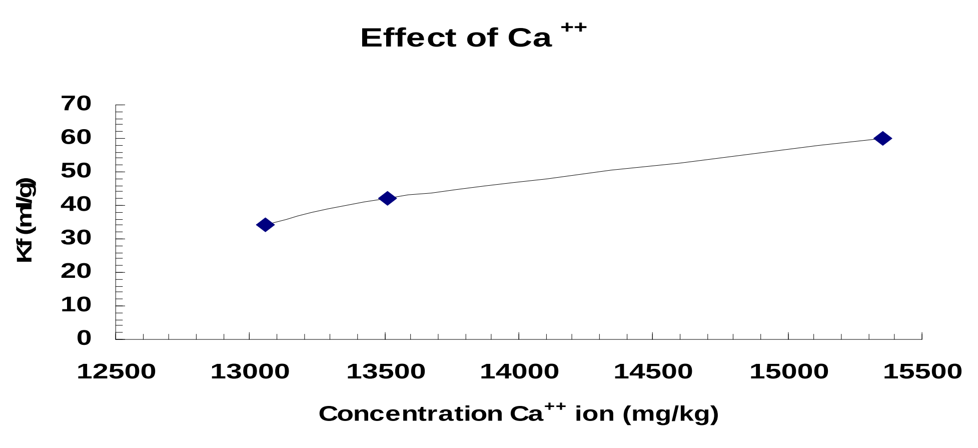


Fig. 5. Effect of Ca^{2+} ion on the adsorption of Triton X-100 on the selected soil samples.

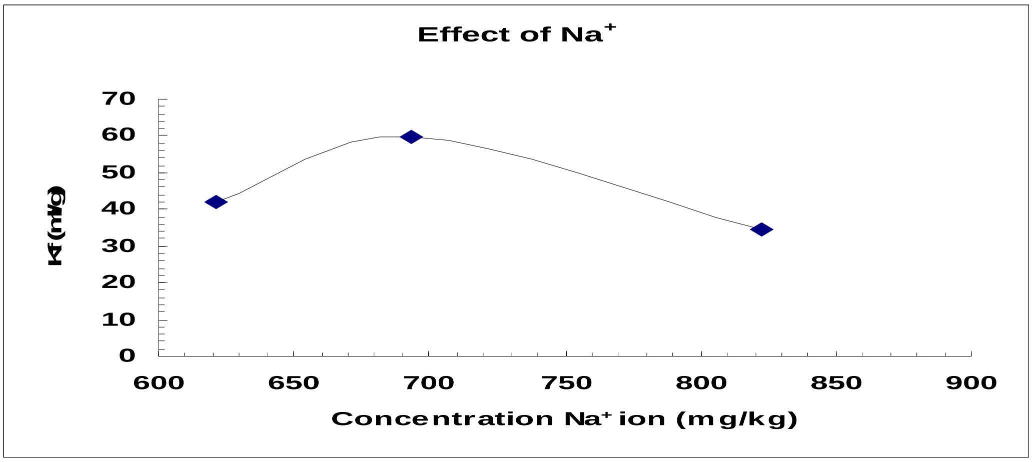


Fig. 6. Effect of Na^+ ion on the adsorption of Triton X-100 on the selected soil samples.

Conclusions

Non-ionic surfactant (Triton X-100) is physically adsorbed, differ from many other surfactant in that, quite small changes in concentration of the adsorbent can have a large effect on it's adsorption to the soil samples. This is due to adsorbate-adsorbate and adsorbate-solvent interaction, which causes surfactant aggregation in bulk solution and which leads to change in orientation and packing of surfactant at the surface.

In environments such as soil and sediments, adsorption of surfactants to surfaces results in much higher total surfactant concentrations being necessary to achieve micellisation in pore water than would be necessary in clean water system.

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