

Sorption Equilibrium and Thermodynamics of Triton X-100 removal from aqueous Solutions

Heman A. Smail, Kafia M. Shareef

Dept. of Chemistry, College of Science, Salahaddin University, Erbil, Kurdistan, Iraq

Abstract. One of the major concerns arising from the adsorption of pollutant from wastewater is the simultaneous presence miscellaneous pollutants in wastewater. Therefore, adsorption study for removal of Triton x -100 (Tx-100) from aqueous solution on soils has been carried out under varying experimental conditions such as temperature, PH, initial concentration of Tx-100, concentration of interfering ions (Ca^{+2} & Na^{+1}) and concentration of other surfactants, sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulphonate (SDBS) and their mixture. The spontaneity of adsorption is confirmed from the decrease in ΔG° with increasing the temperature. The positive values of ΔH° & ΔS° indicate the endothermic nature of adsorption process. It was found that the adsorption decreases with PH from 5 – 9, and increases with further increase in PH (9 – 11). This means that the adsorption capacity of the studied soil samples is highly PH dependent. The experimental results showed that the adsorption of Tx-100 onto soil samples was severely restricted in the presence of a mixture of SDS and SDBS.

Keywords: Anionic surfactants, Triton x 100, adsorption, thermodynamic, soil

1. Introduction

The use of surfactants through out the world is increasing at a rate in excess of the pollution growth of generally improved living conditions and processed material availability^[1]. Surfactants cause foams at sewage treatment plants and pollute 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 taste^[2-3].

Some processes have been employed in order to solve the environmental problems caused by surfactants, including adsorption anaerobic and aerobic degradation, and biodegradation^[4].

The effectiveness of surfactant is attenuated if this is adsorbed by the soil, since the amount available for solubilizing the contaminant decreases, and its mobility through the medium to which it is applied is reduced^[5].

Although the adsorption of single surfactants at solid/liquid interface has been investigated intensively, there have been only a few studies of mixed systems. Thus the aim of our investigation was to study the effect of temperature, PH, metal ions and other interfering surfactants on the adsorption of Tx-100 on studied soils.

2. Materials and methods

Batch experiments were carried out to evaluate the potential adsorption of the test soils toward Tx-100^[6-7], in each experiment; 1g of soil was added to 10 ml of surfactant solutions with initial concentrations (C_0) of 0.1, 0.5, 1 and 2 CMC in prewashed centrifuge tubes. The tubes were stirred continuously in a thermostated shaker at 25°C for 24h. The sample tubes were then centrifuged at 4000 rpm for 30 minutes. The absorbance of the supernatant solution was estimated UV visible spectrophotometer (Cecil 3021, ENGLAND) using to determine the residue of surfactant concentration. Blank (soil suspension without surfactant) and Control

(surfactant solution without soil) samples were prepared by identical procedures as the adsorption samples^[8]. All the measurements were done in replicates.

The thermodynamic studies were carried out at 25, 35 and 45°C. To estimate the effect of solution pH, batch experiments were performed at different PH values (5, 7, 9 and 11). The PH was adjusted by addition of NaOH and HCL as needed. All solutions PH were measured by a PH-meter (PW 9421, England).

The effect of the presence of interfering metal ions on the adsorption of Tx-100 was investigated at a concentration range of (0.1 - 0.6) M of Ca⁺²& Na⁺¹ at 25°C. Similarly the effect of SDS, SDBS and mixture of SDS & SDBS on adsorption of Tx-100 was studied from solutions containing (0.5 CMC) Tx-100 in solution containing different concentrations of SDS, SDBS and mixture of SDS & SDBS (0.1, 0.5 and 1 CMC).

3. Results and Discussion

3.1. Thermodynamic parameters of adsorption

Adsorption experiments were conducted at 25, 35, and 45°C to study the thermodynamic (equilibrium) parameters, associated with the adsorption of Tx-100 on the tested soil samples. The values of ΔG° were calculated at different temperatures were determined using the following equation^[9].

$$\Delta G^\circ = -RT \ln K_d \quad (1)$$

where K_d is the distribution coefficient for the adsorption, ΔG° is the Gibbs free energy, R is the gas constant and T is the absolute temperature. The following relation relates Gibbs free energy change to the enthalpy and entropy change^[10]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

where, ΔH° and ΔS° are the changes in enthalpy and entropy. The values of ΔH° and ΔS° were calculated from the intercepts and slopes of the plot of ΔG° vs. T. The values of ΔG° , ΔH° and ΔS° were summarized in Table 1. The negative values of ΔG° at all temperatures indicate the spontaneous nature of Tx-100 adsorption on soil. Similar results were found in literature^[11-12]. The values of ΔG° for adsorption of Tx-100 on S₁ was from -9.8184 to -10.8525, on S₂ was from -10.2776 to -11.5918, on S₃ was from -11.4487 to -13.5213, and on S₄ was from -12.4535 to -16.0506 KJmol⁻¹ during the temperature change from 25 to 45°C. So, according to the previous results, the adsorption of Tx-100 on the tested soils was predominantly physical adsorption.

The positive values of ΔH° for adsorption of Tx-100 revealed that the process is an endothermic process. This phenomenon may be due to the behavior of Tx-100 in aqueous solution, which displaced more than single water molecule adsorbed previously on soil which leads to endothermic adsorption process.

In addition the small values of ΔH° (5.61 – 41.28 KJ.mol⁻¹) are not compatible with the formation of strong chemical bonds between Tx-100 molecules and the sites on the soil surface. ΔS° is positive since the displaced water molecules gain more translational entropy than is lost by the Tx-100 leading to increase randomness at the solid/solution interface.

Table 1. Thermodynamic parameters for adsorption of Tx-100 on the studied soils.

Soil	ΔH° KJmol ⁻¹	ΔS° Jmol ⁻¹ .K ⁻¹	ΔG° KJmol ⁻¹	Temperature K
S1	5.6105	51.7	-9.8184	298
			-10.2729	308
			-10.8525	318
S2	9.3223	65.7	-10.2776	298
			-10.8796	308
			-11.5918	318
S3	19.497	103.6	-11.4487	298
			-12.2943	308
			-13.5213	318
S4	41.281	179.9	-12.4535	298
			-13.8396	308
			-16.0506	318

3.2. Factors affecting adsorption Capacity

3.2.1. Effect of solution pH

Fig. 2. represents the effect of variation of PH of the solution with adsorption capacity of all soils for Tx-100. The adsorption capacity decrease with PH from 5.0 to 9.0 and then increased with further increase in PH from 9.0 to 11.0 this confirms that the adsorption capacity of soil is highly PH dependent. This effect was attributed to the hydrogen bonding between polar chain of Tx-100 and the active site groups at the soil surface. These results were in agreement with that found by Nasiruddin et al (2004)^[13].

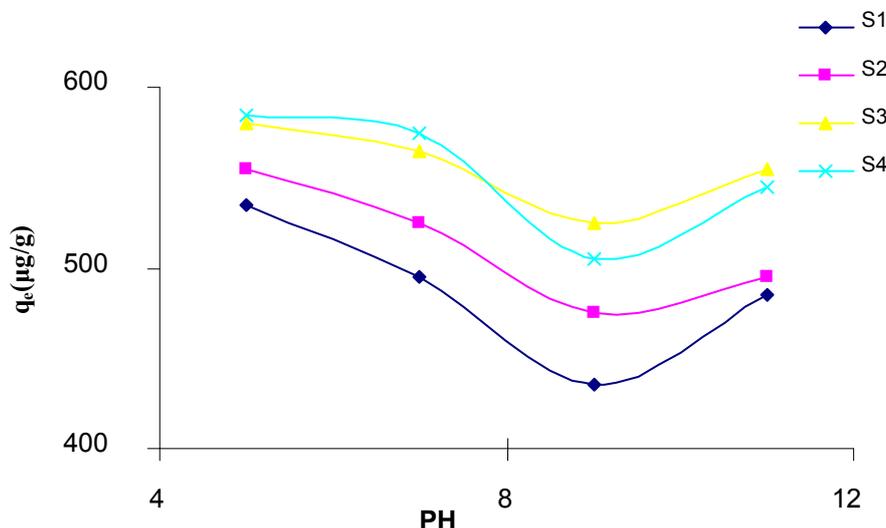


Fig. 1: Variation of amount of Tx-100 adsorbed at equilibrium with PH.

3.2.2-Effect of interfering metal ions

The effect of the presence of both ions (0.1 – 0.6M) on the adsorption of Tx-100 was investigated. The results showed that the removal of Tx-100 increases with increasing the concentration of Ca^{+2} . Because Ca^{+2} "salts out" Tx-100 this would probably increase its adsorption. At the same time the observed increase in adsorption capacity can be explained by an increase in lateral interactions between polar chains when Ca^{+2} concentration increases^[14].

While the presence of increasing amount of Na^{+} ions in the range of 0.1 – 0.3M slightly increased the adsorption of Tx-100, a further increase in the concentration from 0.3 – 0.6M decreased the amount of Tx-100 adsorbed. This may be due to relative competition between Na^{+} and surfactant species on the active center of the soil surface, owing to the greater affinity of the Na^{+} ions at higher concentrations. This can be explained by the strong adsorption of Na^{+} on the polar surface and the resulting displacement of the nonionic surfactant Tx-100 molecules.

3.3. The Effect of Co-Sorbates

3.3.1. The effect of SDS on adsorption of TX-100

Results of the adsorption of Tx-100 onto the studied soil samples from individual and mixed surfactant solutions are tabulated in Table 2. Maximum amount of Tx-100 adsorbed were decreased with increasing the concentration of SDS in the mixtures. The maximum amount of Tx-100 adsorbed, q_e , were 505, 445, 385 and 215 as the concentration of SDS increase from 0, 0.1, 0.5 and 1 CMC for soil 1. Both compounds SDS and Tx-100 are hydrophobic but their chemical structures are very different. So, the effect decreasing q_e with increasing SDS concentration can be explained by the suggestion of, the weak steric self – repulsion for the nonionic surfactant was weakened and will be replaced by ion – dipole attraction interaction of two different hydrophilic groups of anionic and nonionic surfactants^[15].

3.3.2. The effect of SDBS

Data in Table 2 indicated a decrease in the values of q_e with increasing SDBS concentration. Values of q_e were 505, 465, 415 and 275 in the presence of 0, 0.1, 0.5 and 1CMC of SDBS respectively. Surface imply the increased electrostatic repulsions between surfactant micelles and the negatively charged soil surface,

which could inhibit the hydrogen bonding and electrostatic attraction between Tx-100 in mixed surfactant micelles and the soil surface then reduce the sorption of Tx-100 onto soils^[16].

3.3.3. The effect of mixture of SDS and SBDS

It was found that Tx-100 was adsorbed negligibly from a mixture of 1CMC of each surfactant SDS and SBDS (Table 2). This is because the hemimicellization concentration of the surfactant shifts towards lower concentration. Adsorption of Tx-100 onto soils could be attributed to the hydrogen bonding and electrostatic attraction between the negatively charged soil surface and the TX-100 molecule with slight positive charges^[15,17].

Table 2: Equilibrium adsorption parameters for Tx-100 and Tx-100 mixed surfactants onto studied soils.

Soil	0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	0.1CMC SDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	0.5CMC SDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	1CMC SDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)
S ₁	505	445	385	215
S ₂	527	435	355	175
S ₃	567	485	405	165
S ₄	580.5	465	335	115
Soil	0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	0.1CMC SBDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	0.5CMC SBDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	1CMC SBDS+ 0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)
S ₁	505	465	415	275
S ₂	527	475	405	215
S ₃	567	515	435	225
S ₄	580.5	485	385	165
Soil	0.5CMC TX-100 ($q_e \mu\text{g.g}^{-1}$)	0.1CMC (SBDS+SDS)+ 0.5CMC TX-100 (q_e $\mu\text{g.g}^{-1}$)	0.5CMC (SBDS+SDS)+ 0.5CMC TX-100 (q_e $\mu\text{g.g}^{-1}$)	1CMC (SBDS+SDS)+ 0.5CMC TX-100 (q_e $\mu\text{g.g}^{-1}$)
S ₁	505	425	235	0
S ₂	527	395	205	0
S ₃	567	345	145	0
S ₄	580.5	315	75	0

4. References

- [1] M. Kafia and S. George. Sorption kinetics of 2,4-D and Carbaryl in selected agricultural soils of northern Iraq: application of a dual-rate model. *Chemosphere* (2008) 72 (1): 8-15.
- [2] P. Somasundaran and L. Huang. Adsorption/Aggregation of Surfactants and their mixtures at Solid-Liquid Interfaces *Adv.Colloid interface Sci.* 2000, 88:179.
- [3] P. Rao and L. He Adsorption of anionic and nonionic surfactant mixtures from synthetic detergents on soil J. *Chemospher* 2006, 63:1214-1221.
- [4] W. ZhouZhu. Enhanced soil flushing of phenanthrene by anionic-nonionic mixed Surfactant. *J. water Research.* 2008,42:101-108.
- [5] N. Okamoto and T. Yoshimura. Effect of pH on solubilization of single and binary organic solutes into a cationic hydrocarbon surfactant adsorbed layer on silica *J.Colloid interface Sci.*2004,275:612-617.
- [6] M. Kafia and A. Lawen. Competitive Adsorption of Heavy Metals by Natural Soils. 1st International Conference on Engineering, Environment, Economy, Safety and Health, 10th SENVAR. Manado, Indonesia, 26-27 November 2009.
- [7] M. Kafia. Agricultural wastes as low cost adsorbents for Pb removal: Kinetics, Equilibrium and Thermodynamics. *International Journal of Chemistry.* 2011,3 (2).
- [8] M. Kafia and Y Huda. Rice husk as a low-cost adsorbent for Cu, Ni and Zn removal from polluted water, 10th International Conference on Materials Chemistry (MC10), University of Manchester, United Kingdom. 2011.
- [9] R. Rrakhshae and M. Khosravi. Kinetic modeling and thermodynamic study to remove pb(n) , Cd(n), Ni(n) and Zn(n) form aqueous solution using dead and living *Azolla filiculoides*. *J.Hazardous materials.* 2006,134:120-129.
- [10] T. Anirudhan and P. Radhakrishnan. Thermodynamics and kinetics of dsorption of Cu(n)form aqueous solutions onto a new cation exchanger derived from tamarind fruit shell *J.Chem. Thermo.* 2008,40:702-709.
- [11] M. Ronak and M. Kafia. Thermodynamic adsorption of Herbicides on eight Agricultural Soils, *International Journal of Scientific and Engineering Research*, Vol. 2 (6): 2011.

- [12] M. Nasiruddin and U. Zareen. Adsorptive Removal of non-ionic surfactants form water using Granite sand. J. Iranian chemical society. 2004, 1(2):152-158.
- [13] I. Penfold, R. Thomas, E. Staples and R. Schuermann. Structure of fixed anionic/nonionic surfactant micelle : experimental observations relating to the role of head group electrostatic and steric effect and the effects of added electrolyte. J.phys.chem. 2005, B109: 10760-10770.
- [14] Q. Zhou and M. Rosen. Molecular interactions of surfactants in mixed monolayers at the air/aqueous solution interface and in mixed micelles in aqueous media the regular solution approach. Langmuire. 2003, 19: 4555-4562.
- [15] M. Reson. Surfactants and interfacial phenomena. 2004,thirded,wiley, Hoboken.
- [16] V. Gramus. Formation of mixed micelles in salt-free aqueous solutions of sodium dodecyl sulfata and Tritonx-100. 2003,19: 7214-7218.