

# Sorption characteristics of the nonionic surfactant Triton X-100 in soil contaminated with diesel

Shehdeh Jodeh and Mahmood Haitaly

## Abstract

The adsorption of a surfactant to solid surfaces can lower the concentration of free surfactant in aqueous solutions. If the degree of adsorption is high, then surfactant concentration could drop below the CMC (critical micelle concentration), rendering the surfactant solution unable to solubilize. Therefore, the amount of surfactant mass that will sorb should be accounted for when selecting injection concentration. In this study, a nonionic surfactant, Triton X-100, was used to study the sorption characteristics of diesel on to soil below and above CMC. The surface tension is used for calculating this kind of sorption. The results indicated that when the concentration of surfactant was lower than the CMC, the amount of surfactant sorbed on soil increased with increasing surfactant concentration, and the amount of desorbed diesel was relatively low compared to the original amount added to the soil, but that the amount of diesel desorbed from soil at surfactant concentrations above CMC was relatively high.

Key words: contaminant, diesel, isotherm, sorption, surfactant

## 1 INTRODUCTION

Petroleum and products derived from it derived products are considered to be increasingly common pollutants of our environment (Stout *et al.* 2005).

These natural products are introduced to the environment due to various anthropogenic activities, such as accidental spills from transportation processes, leaking underground storage tanks, and poor waste-disposal practices.

These compounds are commonly found in soil and groundwater aquifers in industrialized areas. Some special classes of petroleum hydrocarbons are commonly referred to as nonaqueous-phase liquids (NAPL); they are difficult to recover from the subsurface system, and represent a long-term source of soil and aquifer contamination (Fiorenza *et al.* 2000; Johnston *et al.* 2002; Zhong *et al.* 2003).

Limited solubility of petroleum hydrocarbons is a major constraint on the biodegradation of these compounds. The soluble portion will be degraded at faster rates, while less-soluble or insoluble compounds will have limited bioavailability, thus reducing the degradation rate of these compounds (Paria 2008).

Petroleum hydrocarbons are recalcitrant contaminants in the natural environment that make it difficult to rehabilitate contaminated sites. In addition to their low aqueous solubility, petroleum hydrocarbons have high interfacial tension and a tendency to sorb on to soil particles. The high interfacial tension results in large capillary forces that resist washing by water. One of the most common types of groundwater contamination is from spills of petroleum-based fuels and solvents from underground storage tanks (Sacile 2007).

When the problem of subsurface contamination begins, the initial remediation approach involves removing contaminated soil and pumping the contaminated water for treatment. Pump-and-treat remediation technology was initially prescribed for the clean-up of subsurface contamination from both organic and inorganic contaminants. It is the most commonly used *in situ* remediation technology for contaminated aquifers (Liu and Roy 1992).

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Other conventional treatment technologies for soil contamination involve landfill disposal and incineration. With landfill disposal, only the location of pollutants is changed, and future liability is merely delayed: their complete destruction is not achieved. Incineration of hazardous wastes is both costly and difficult to implement.

It has been known that surfactants are able to improve the mass-transfer of hydrophobic pollutants from the solid or nonaqueous-liquid phase into the aqueous phase by decreasing the interfacial tension, and by accumulating the hydrophobic compounds in the micelles (Tiehm 1994; Volkering *et al.* 1995; Li and Chen 2002; Qin *et al.* 2007). Therefore, surfactants have been extensively studied in recent years with the aim of enhancing the remediation of subsurface contaminants (Liu *et al.* 1992; van der Meeren and Verstraete 1996; Zheng and Obbard 2002).

Surfactant-enhanced subsurface remediation is one of several technologies being developed for the remediation of subsurface nonaqueous-phase liquid NAPL contamination. The removal of total petroleum hydrocarbons (TPHs) was increased by 60% in the presence of surfactants, as compared to water only (Peters *et al.* 1992).

With surfactants, more hydrophobic contaminants, including sorbed and entrapped ones, are mobilized in the aqueous phase. Economic analyses indicate that this technology can be competitive with conventional pump-and-treat, landfill and incineration remediation, if surfactant losses can be minimized; contaminant elution maximized; and surfactant-contaminant separation and surfactant reuse implemented (Sabatini 1995).

The aims of this research are:

- to study the effect of nonionic surfactants in enhancing the remediation of insoluble hydrophobic organic compounds by solubilization and mobilization mechanisms, which in turn increase the bioavailability and hence the biodegradability of petroleum hydrocarbons;
- to study the effect of sorption characteristics of surfactants on soil at different amounts of diesel, in terms of adsorption isotherms, and the effect of these factors (i.e. soil and diesel) on the CMC value of the surfactants, and the interpretation of these effects in term of sorption behaviour; and

- to study different factors that may positively or negatively affect the sorption behaviour of surfactants on to soil.

## 2 MATERIALS AND METHODS

### 2.1 Surfactant analysis and CMC determination

The surfactant used to prepare surfactant solutions was the nonionic surfactant Triton X-100, purchased from Sigma Aldrich. It was used as received at 97% purity. Surface-tension measurements were used to determine the CMC of the surfactant. Surfactant solutions were prepared at ten different concentrations by diluting stock surfactant solution (10% v/v). The selected surfactant solutions as per cent volume by volume were 2.0, 1.0, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001, 0.0005 and 0.0001.

These concentrations range approximately from below CMC to above CMC. Surface tensions of surfactant solutions were measured by a Fisher Surface Tensiometer Model 21, and the procedure of measuring surface tension used ASTM D 1331-89 (reapproved 1995) 'Standard Test Method for Surface and Interfacial Tension of Solutions of Surface-Active Agent'. The room temperature while performing the surface-tension measurement was recorded, and it ranged between  $19.5 \pm 1$  and  $21^\circ\text{C}$  during the entire experimental phase. Each sample was tested at least four times to ensure that consistent values were obtained.

The averages from the measurements of each solution were plotted as a function of surface tension against the logarithm of surfactant concentration, in order to identify the concentration at CMC. The surfactant concentration at which the surface tension no longer decreases significantly with increasing surfactant concentration is taken to represent the surfactant CMC (Kuo 1988).

### 2.2 Soil

Three replicates of agricultural soil were obtained from Al-Jeftlick, north of Nablus city, Palestine. The moisture content of each sample was determined by drying for 24 hours in an Ari J. Levy oven at  $500^\circ\text{C}$ . pH was determined by a Jenway 3510 pH meter. Organic carbon and organic matter of each replicate were determined by the Walkley-Black titration method. The nitrogen percentage of each sample was determined by the Kjeldahl method.

Each soil replicate was analysed in order to evaluate moisture; organic carbon percentage; organic matter; and nitrogen percentage.

Table 1 shows the moisture content, pH, organic carbon percentage, organic matter percentage, and nitrogen percentage of each sample.

After drying, each replicate was sieved and a hydrometer test was performed in order to evaluate the soil texture of each replicate (Table 1).

**Table 1. Moisture content, pH, organic carbon, organic matter, nitrogen and soil texture percentage for three replicates soil sample**

Parameters	Reading
pH	8.42 ± 0.2
Moisture content (%)	24.16 ± 0.8
Organic carbon (%)	1.78 ± 0.02
Organic matter (%)	3.06 ± 0.06
Nitrogen (%)	0.346 ± 0.01
Sand fraction (%)	11 ± 0.8
Silt fraction (%)	57 ± 1.02
Clay fraction (%)	32.6 ± 0.7

### 2.3 Diesel sorption on to soil without surfactant

The task of this experiment was first to study the sorption behaviour of diesel in soil without surfactant. Second it was to determine the amount of diesel sorbed at different diesel concentrations. Three mixtures were prepared by mixing 1 g of soil with a 10-mL solution of diesel dissolved in methanol at three different concentrations: 0.25%, 0.50% and 1.00% (v/v). The mixtures were shaken for two hours, and then left in the fume hood for 24 hours for evaporation of methanol. 500 µL of the liquid phase of each were taken and diluted with methanol in a 10-mL volumetric flask, to test the amount of diesel remaining after completion of the sorption process by UV-visible spectrophotometer at 254 nm.

### 2.4 Surfactant sorption on to soil without contaminant

The purpose of this task was to test the sorption behaviour of the surfactant on to uncontaminated soil. Seven mixtures were prepared, each one consisting of 1 g of uncontaminated soil and 50 mL of surfactant solution with concentrations of 0.0005%, 0.001%, 0.005%, 0.1%, 0.5%, 1.0% and 2.0% (v/v) (i.e. each concentra-

tion for one mixture). The mixtures were shaken for two hours at 300 rpm, and then left for 36 hours for the soil to settle. 30 mL of the aqueous phase of each were taken for surface-tension measurements.

### 2.5 Surfactant sorption on to contaminated soil at different diesel concentrations

The purpose of this task is to determine the effect of diesel concentration on surfactant sorption on to soil. Sixty-three samples were prepared in 250-mL Erlenmeyer flasks, and separated into three groups for each soil replicate, 1, 2 and 3 (i.e. 21 samples for each soil replicate). The diesel concentrations were 0.25%, 0.50% and 1.0% (v/v) dissolved in methanol. Methanol was the preferred solvent because it showed no effect on surfactant solubilization; higher molecular weight alcohols would affect CMC values significantly (Edwards *et al.* 1991).

Seven surfactant concentrations were used in this test, 0.0005%, 0.001%, 0.005%, 0.1%, 0.5%, 1.0% and 2.0% (v/v). The surfactant solutions used in this test were prepared and measured for surface tension.

In each group of soils, the samples were separated into three diesel concentrations, 0.25%, 0.50% and 1.0% (v/v).

The artificially contaminated soil was made by adding 10 mL of diesel dissolved in methanol to 1 g soil at different diesel concentrations. The artificially contaminated soils in the flasks were closed by Teflon screw caps and shaken for two hours to make sure that the contaminant was completely adsorbed on the soil. After shaking, the contaminated soil samples were opened and left in the fume hood for 24 hours to evaporate the methanol. The amount of contaminant evaporated with methanol in each sample was assumed to be equal in every group sample. 50 mL of surfactant solution were added to the artificially contaminated soil after methanol was evaporated for 24 hours, and 0.7 mL of mercuric chloride (corresponding to 18 mg) was added to each sample to inhibit the biodegradation process during the experiment. The samples were shaken for two hours, and left to settle for 36 hours. The supernatants were taken from the samples and centrifuged for 15 minutes. 30 mL of the supernatant were placed in 100-mL beakers to measure the surface tension at room temperature (it was between 20.5 and 22.5°C). The results from the surface-tension readings

were plotted versus the logarithm of surfactant concentration in mol/L.

### 3 RESULTS AND DISCUSSION

#### 3.1 Surface-tension measurements and CMC determination

Surface-tension measurement is a well-established method for determining the CMC of surfactants. The surface tension for each concentration of surfactant Triton X-100 was measured at least four times. The sur-

face-tension curve is composed of two linear segments; the intersection of the two linear portions represents the CMC (Zheng and Obbard 2002).

From the result in Figure 1, the CMC was found as the point  $(-3.47, 35.2)$  where the concentration of surfactant solution is  $3.388 \times 10^{-4}$  mol/L, and the surface tension of the surfactant mixture is 35.2 dynes/centimetre. The range of CMC determined by other researchers was from  $6.89 \times 10^{-5}$  to  $3.3 \times 10^{-4}$  mol/L (Liu *et al.* 1991; Liu *et al.* 1992; Zhao and Brown 1996; Zheng and Obbard 2002).

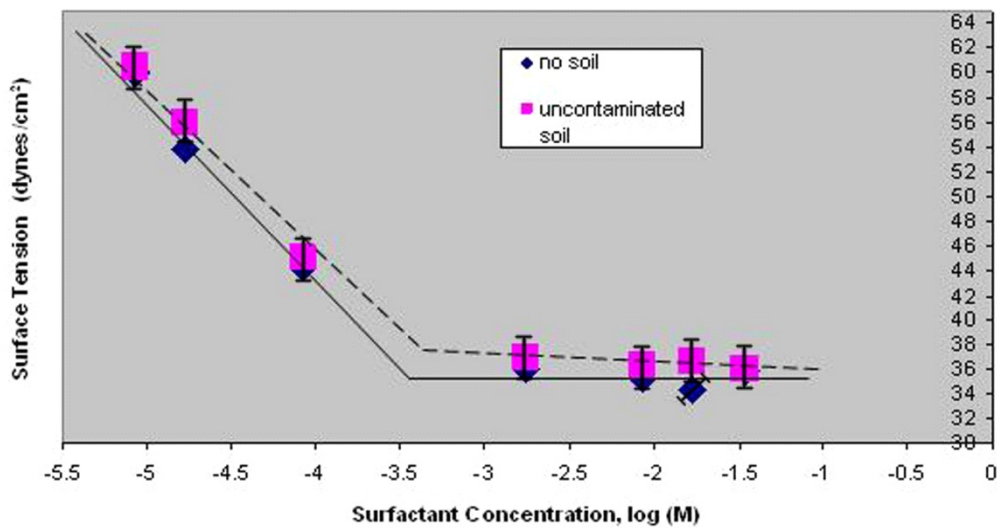


Figure 1. Comparison of surface tension of surfactant with and without uncontaminated soil

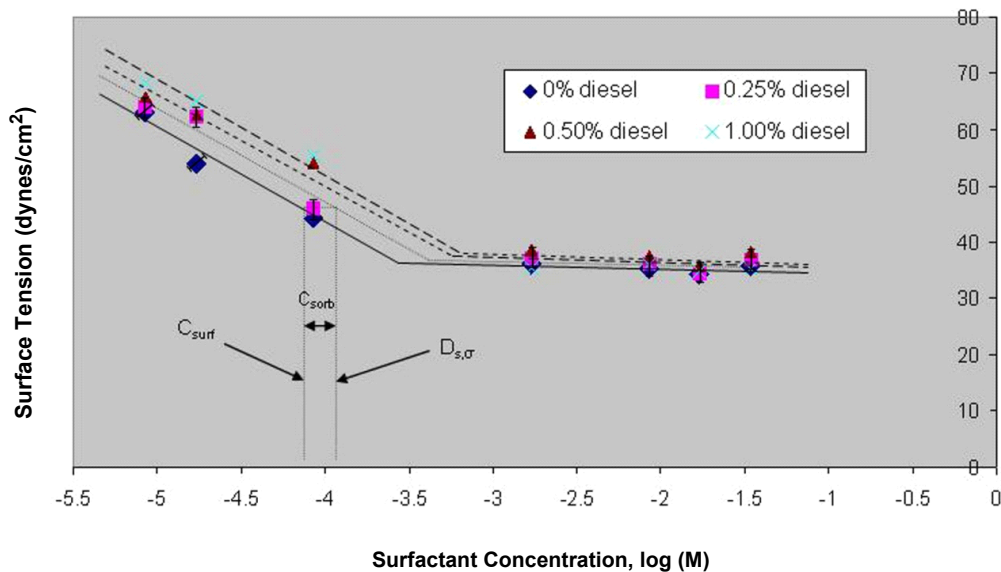


Figure 2. Comparison of surface-tension measurements for systems with and without soil contaminated with diesel at different concentrations

**Table 2: Surface tension of surfactant solutions mixed with diesel-contaminated soil at different concentrations**

% (v/v) diesel	Surfactant concentration (% (v/v))	pH	Temp (°C)	Surface tension (dynes/cm)
0% diesel	0.0005	6.08	21	63.2 ± 2.1
	0.001	6.09	21	53.9 ± 1.9
	0.005	6.06	21	44.3 ± 1.4
	0.1	6.11	21	36.1 ± 1.3
	0.5	6.32	21	35.2 ± 1.3
	1	6.23	21	34.3 ± 1.3
	2	6.42	21	35.9 ± 1.4
0.25% diesel	0.0005	5.99	21.5	64.2 ± 2.2
	0.001	6.02	21	62.3 ± 2.1
	0.005	6.07	22	45.9 ± 1.5
	0.1	5.93	20.5	37.1 ± 1.4
	0.5	6.21	21	36.1 ± 1.4
	1	6.13	21.5	34.2 ± 1.3
	2	6.06	21.5	35.7 ± 1.4
0.50% diesel	0.0005	6.08	22	65.8 ± 2.4
	0.001	6.12	22	62.6 ± 2.3
	0.005	6.01	21.5	54.1 ± 1.9
	0.1	5.97	22	36.1 ± 1.4
	0.5	5.86	20.5	37.5 ± 1.4
	1	5.94	20.5	35.9 ± 1.4
	2	6.11	21	38.3 ± 1.5
1.00% diesel	0.0005	5.93	20.5	67.4 ± 2.4
	0.001	5.87	20.5	64.2 ± 2.2
	0.005	6.02	21	57.2 ± 2.1
	0.1	6.07	20.5	38.1 ± 1.4
	0.5	5.86	21.5	39.2 ± 1.5
	1	5.91	21	37.8 ± 1.4
	2	6.04	21	37.3 ± 1.4

The variation in this number depends on the different techniques used to test CMC and the room temperature during measurements.

### 3.2 Diesel sorption on to soil without surfactant

The experiment in this part of the research was to evaluate the amount of diesel sorbed on to soil at the three concentrations of diesel: 0.25%, 0.50% and 1.00% (v/v). 500 µL of solution of diesel dissolved in methanol were taken after the sorption process had equilibrated, and were diluted with methanol in a 10-mL volumetric flask. The cell of the UV-visible spectrophotometer was filled from the diluted solution, and tested. The

results were compared with the calibration curve from the UV-visible spectrophotometer. The comparison showed that the amount of diesel sorbed on the soil ranged from 7% to 13% of the original amount. These amounts of sorbed diesel were slightly low; this was probably due to the low organic content of the soil itself, which decreased the tendency of diesel to be sorbed on to it.

### 3.3 Surfactant sorption on to soil without diesel

The results of this experiment showed that the seven surfactant concentrations: 0.0005%; 0.001%; 0.005%; 0.1%; 0.5%; 1.0%; and 2.0% (v/v), mixed with 1 g soil were slightly sorbed on to it. The surface tension of the

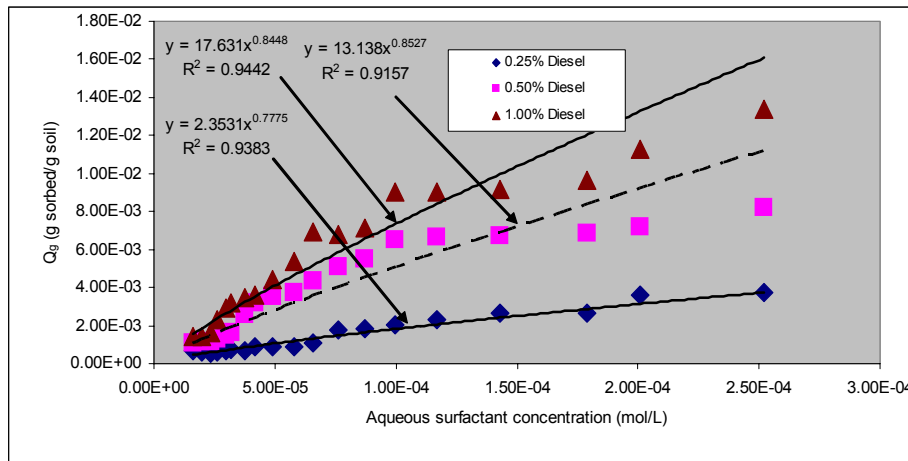


Figure 3. Linear equations for the surfactant Triton X-100 sorbed on soil at different diesel concentrations

supernatant of each sample mixture was measured and compared with the surface tension of the surfactant solution without soil, in order to determine the amount of surfactant sorbed at each concentration:  $Q_g$ . Figure 1 shows the comparison between surface-tension measurements with and without soil. From Figure 2 we can calculate  $C_{\text{sorb}}$ , and  $Q_g$  can be determined by the equations proposed (Liu *et al.* 1992). It was observed that the  $Q_g$  of the surfactant ranged between 9% and 15% for all seven concentrations.

This small amount of sorbed surfactant was probably due to the low organic content of the soil itself. This conclusion may be attributed to the postulate that says 'the greater the organic content of a soil, the greater the tendency for an organic substance to be sorbed on it'.

### 3.4 Effect of contaminant on surfactant sorption on soil

The experiments in this section were performed in batch mode. Diesel dissolved in methanol was used as a contaminant in soil at different concentrations (0.25%, 0.50% and 1.00% (v/v)) in order to study how the contaminants affect the amount of surfactant sorbed on to soil. The contaminant was mixed with soil to produce an artificially contaminated soil, and surfactant solutions were added and agitated for the sorption process to equilibrate. Then the aqueous phase was removed from the sample and the surface-tension measurements were performed.

The average surface-tension results for each sample of aqueous phase removed from contaminated soil at different diesel concentrations are shown in Table 2. The

average surface-tension readings from each sample were found for each soil at 0.25%, 0.50% and 1.00% (v/v) diesel concentration. The results have shown that the presence of diesel with surfactant in solution together enhance the sorption for each one on to soil, especially at a surfactant concentration lower than the CMC.

From the results of surface-tension measurements, soil with 0.25% diesel reached CMC at  $(-3.315, 35.12)$  or the surfactant Triton X-100 dose  $4.84 \times 10^{-4}$  mol/L; soil with 0.50% diesel reached CMC at  $(-3.23, 36.31)$  or  $5.89 \times 10^{-4}$  mol/L; and soil with 1.00% diesel reached CMC at  $(-3.11, 37.64)$  or  $7.76 \times 10^{-4}$  mol/L.

Figure 2 shows the graph plotted to compare the results of surface tensions in the presence of soil containing different diesel concentrations: 0.25%; 0.50%; and 1.00% (v/v), and the surface tensions of surfactant solution without soil.

The data show that the greater the diesel concentration in the soil, the greater the amount of surfactant that needs to be added into the system in order to reduce the surface tension by a given amount. The amount of surfactant sorbed on soil at any aqueous-phase-surfactant concentration can be calculated by using the data from surface-tension plots (Liu and Roy 1992; Zheng and Obbard 2002).

Referring to Figure 2, the abscissa for a selected data point on the surface-tension curve for the aqueous system without soil gives an aqueous-phase-surfactant concentration,  $C_{\text{surf}}$  ( $-4.03$  from Figure 3 or  $9.33 \times 10^{-5}$  mol/L). The corresponding ordinate, a particular

Table 3. Surfactant sorbed on to soil at different diesel concentrations in g/g soil (uncertainty  $\pm 0.3E-7$ )

Surface tension (dynes/cm)	Surfactant concentration (mol/L)				$C_{\text{sorb}}$ (g surf/g soil)		
	Soil-free surfactant solution	0.25% diesel	0.50% diesel	1.00% diesel	0.25% diesel	0.50% diesel	1.00% diesel
55	1.63E-5	3.76E-5	5.02E-5	6.18E-5	6.65E-04	1.06E-03	1.42E-03
54	1.99E-5	3.89E-5	5.62E-5	6.61E-5	5.93E-04	1.13E-03	1.44E-03
53	2.37E-5	4.07E-5	6.03E-5	7.59E-5	5.30E-04	1.14E-03	1.63E-03
52	2.63E-5	4.68E-5	6.76E-5	1.00E-4	6.40E-04	1.29E-03	2.30E-03
51	2.95E-5	5.13E-5	7.76E-5	1.23E-4	6.80E-04	1.50E-03	2.92E-03
50	3.19E-5	5.48E-5	8.32E-5	1.34E-4	7.14E-04	1.60E-03	3.19E-03
49	3.78E-5	6.03E-5	1.21E-4	1.48E-4	7.02E-04	2.60E-03	3.44E-03
48	4.17E-5	6.92E-5	1.45E-4	1.58E-4	8.58E-04	3.22E-03	3.63E-03
47	4.89E-5	7.76E-5	1.62E-4	1.91E-4	8.95E-04	3.53E-03	4.43E-03
46	5.81E-5	8.71E-5	1.78E-4	2.29E-4	9.05E-04	3.74E-03	5.33E-03
45	6.57E-5	1.00E-4	2.04E-4	2.88E-4	1.07E-03	4.31E-03	6.94E-03
44	7.64E-5	1.32E-4	2.40E-4	2.95E-4	1.73E-03	5.10E-03	6.82E-03
43	8.72E-5	1.45E-4	2.63E-4	3.16E-4	1.80E-03	5.48E-03	7.14E-03
42	9.96E-5	1.66E-4	3.09E-4	3.89E-4	2.07E-03	6.53E-03	9.03E-03
41	1.17E-4	1.91E-4	3.31E-4	4.07E-4	2.31E-03	6.68E-03	9.05E-03
40	1.43E-4	2.27E-4	3.73E-4	4.36E-4	2.62E-03	7.18E-03	9.14E-03
39	1.79E-4	2.63E-4	3.98E-4	4.89E-4	2.62E-03	6.83E-03	9.67E-03
38	2.01E-4	3.16E-4	4.37E-4	5.62E-4	3.59E-03	7.36E-03	1.13E-02
37	2.52E-4	3.72E-4	4.79E-4	6.31E-4	3.74E-03	7.08E-03	1.18E-02

value of the surface tension,  $\sigma$  (43 dynes/cm), is then located on the surface-tension plot for the soil/aqueous system.

The abscissa on this plot that corresponds with this value of  $\sigma$  yields a value for  $D_{s,\sigma}$  ( $-3.76$  from Figure 2 or  $1.74 \times 10^{-4}$  mol/L), the bulk surfactant dose in the soil/aqueous system that produces a surface tension of  $\sigma$  in the supernatant. The difference between this value of  $D_{s,\sigma}$  and the selected value of  $C_{\text{surf}}$  is equal to  $C_{\text{sorb}}$  ( $8.07 \times 10^{-5}$ ), the number of moles of surfactant sorbed per litre of solution, evaluated at the particular bulk-solution surfactant concentration. The product of  $C_{\text{sorb}}$  and the ratio  $V_a$  to  $W_{\text{soil}}$ , the volume of the aqueous solution in litres divided by the weight of the soil in grams, yields a value for  $Q_{\text{surf}}$  ( $4.035 \times 10^{-3}$  g/g of soil), the number of moles of surfactant sorbed per gram of soil or gram surfactant per gram of soil can be calculated (Dzombak and Luthy 1984).

Surfactant sorption may also be expressed as  $Q_g$ , the number of grams of non-ionic surfactant sorbed per grams of the soil, using the Freundlich isotherm:

$$Q_g = K \cdot C^n \quad (4.1)$$

where  $K$  is a measure of sorption capacity; and  $1/n$  is an indicator of the curvature of the isotherm.

Table 3 shows the amount of surfactant sorbed per gram of soil contaminated with diesel at different concentrations calculated by parameterizing the equations of Liu *et al.* 1992, using the data from the current experiment. This is the surfactant sorption at sub-CMC level, and the surfactants that sorb on to soil are in the form of surfactant monomers.

Figure 3 shows the number of grams of surfactant sorbed per gram of soil at 0.25%, 0.50% and 1.00% (v/v) diesel. Using the Freundlich isotherm, the values of  $K$  and  $n$  were found.

$$\begin{aligned} \text{At 0.25\% diesel} & \quad y = 2.3531x^{0.7775} & \quad R^2 = 1 \\ \text{At 0.50\% diesel} & \quad y = 13.138x^{0.8527} & \quad R^2 = 1 \\ \text{At 1.00\% diesel} & \quad y = 17.631x^{0.8448} & \quad R^2 = 1 \end{aligned}$$

However, in many environmental applications, the linear form of the Freundlich isotherm applies (Dzombak and Luthy 1984). For the linear adsorption iso-

**Table 4. Surfactant doses required for micelle formation and amount of surfactant sorbed on to soils with different diesel concentrations in the soil–water systems**

Diesel concentration in contaminated soil (%)	Surfactant doses for micelle formation (CMC <sub>eff</sub> ) Uncertainty (±0.5; ±0.5E-6)		Surfactant adsorbed onto soil Uncertainty (±0.3E-7; ±2%)		Q <sub>max</sub> (g/g soil) uncertainty (±1.5E-5)
	log (M)	mol/L	mol/L	%	
0	-3.47	3.89E-4			
0.25	-3.32	4.84E-4	9.50E-5	19.6	2.96E-3
0.50	-3.23	5.89E-4	2.00E-4	33.9	6.24E-3
1.00	-3.11	7.76E-4	3.87E-4	49.9	1.21E-2

therm,  $1/n = 1$ . From the result, the values of  $n$  at 0.25%, 0.50% and 1.00% (v/v) diesel are close to 1. If the value of  $n$  is assumed to be 1, then the following linear equations are obtained:

At 0.25% diesel  $y = 14.972x + 0.0003 \quad R^2 = 0.9579$

At 0.50% diesel  $y = 36.76x + 0.0014 \quad R^2 = 0.8303$

At 1.00% diesel  $y = 50.488x + 0.0018 \quad R^2 = 0.9066$

Table 4 shows CMC values at different levels of diesel, 0.25%, 0.50% and 1.00% (v/v). The CMC values increase as the diesel concentration increases. Since the higher diesel concentration tends to adsorb more surfactant monomers, the amount of surfactant monomer left to form micelles is reduced. Therefore, the CMC of the higher diesel concentration in soil is reached at the higher surfactant concentration.

According to other researchers (Kuo 1988; Liu *et al.* 1991; Zheng and Obbard 2002), the smallest surfactant dose that corresponds to the minimum plateau values of surface tension for the soil/aqueous system gives, after subtracting the CMC and multiplying by the ratio of  $V_a$  to  $W_{soil}$ , a specific value for  $Q_{surf}$  that is equal to  $Q_{max}$ , i.e. the maximum value of sorption for surfactant on

that particular soil. From  $Q_{max}$ , the effective CMC,  $CMC_{eff}$ , can be estimated using the surface-tension technique (Zheng and Obbard 2002) as the following:

$$CMC_{eff} = CMC + Q_{max} \left( \frac{W_{soil}}{V_{aq}} \right) \quad (4.2)$$

$Q_{max}$  is an important parameter in predicting surfactant solubilization of organic contaminants. From the data, the  $CMC_{eff}$  and CMC were determined. Therefore, the amount of surfactant sorbed on to soil and  $Q_{max}$  can be calculated from Equation 4.2. Table 4 shows the amount of surfactant sorbed on soil (Mol/L) and by percentage loss in the contaminated soil. The amount of  $Q_{max}$ , which predicts the surfactant solubilization, was also found. The amounts of surfactant sorbed on soil are 19.6%, 33.9% and 49.9%, and the  $Q_{max}$  are 2.96E-3, 2.24E-3 and 1.2E-2 g/g of soil, for the diesel concentrations 0.25%, 0.50% and 1.00% (v/v) respectively.

The surfactant dose required for micelle formation in a soil–water system ( $CMC_{eff}$ ) is shown in Table 5, at different concentrations of diesel.

**Table 5. Surfactant doses required for micelle formation and amount of surfactant sorbed on to soils with different diesel concentrations in the soil–water systems**

Diesel concentration in contaminated soil (%)	Surfactant doses for micelle formation (CMC <sub>eff</sub> )		Surfactant adsorbed on to soil		Q <sub>max</sub> (g/g soil)
	log (M)	mol/L	mol/L	%	
0	-3.47	3.89E-4			
0.25	-3.32	4.84E-4	9.50E-5	19.6	2.96E-3
0.50	-3.23	5.89E-4	2.00E-4	33.9	6.24E-3
1.00	-3.11	7.76E-4	3.87E-4	49.9	1.21E-2



#### 4 CONCLUSIONS AND RECOMMENDATIONS

The amount of surfactant Triton X-100 sorbed on to the soil increased with increasing surfactant concentration. After the sorption process had been completed, the additional amount of surfactant added into a soil/aqueous system was no longer sorbed by the soil, but formed micelles which play an important role in the solubilization of hydrophobic organic compounds. From the experiments performed in this study, it was observed that the  $CMC_{eff}$  value increased with increasing diesel concentration in the soil. In soil/aqueous systems with no contaminant present in the soil, the  $CMC_{eff}$  depends on the organic content of the soil itself. The CMC of surfactant Triton X-100 in an aqueous system without soil and contaminant was  $3.88E-4$  mol/L, and  $CMC_{eff}$  values of soil–water systems in the presence of diesel at concentrations of 0.25%, 0.50% and 1.00% (v/v) were  $4.84E-4$  mol/L,  $5.89E-4$  mol/L and  $7.76E-4$  mol/L respectively.

In this investigation, the amount of surfactant sorbed on to soil at surfactant concentrations below the CMC was calculated, and the relationship between diesel concentrations and the amount of surfactant sorbed on the soil was developed. In the soil–water system, the Freundlich isotherm and the linear equation could be applied to all three types of soil with 0.25%, 0.50% and 1.00% (v/v) diesel.

Not only is the  $CMC_{eff}$  value for each soil type important, but the amount of surfactant sorbed on each soil type is also crucial for utilizing the surfactant to enhance soil remediation. The amount of surfactant sorbed on to soil can be calculated as the per cent surfactant lost due to sorption on soil and the grams of surfactant sorbed per gram of soil at any surfactant concentration and also the maximum grams of surfactant sorbed per gram of soil,  $Q_{max}$ . The amount of surfactant Triton X-100 sorbed on to soil with no contaminant present ranged from 9% to 15%. However, the amount of surfactant Triton X-100 tends to be sorbed to a greater degree on to contaminated soil. Also, the amount of surfactant sorbed on the soils contaminated with diesel ranged from 19.6% to 49.9%. These results indicate that the presence of organic contaminants may result in greater surfactant sorption on to the soil, thereby further increasing chemical costs in possible surfactant-enhanced subsurface remediation applications.

Overall, the results of this study suggest that the addition of aqueous surfactant solutions to contaminated soils may facilitate the removal of organic contaminants from soil. However, surfactant losses due to sorption on to soil appear to be significant and may increase due to the presence of organic contaminants.

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