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≪ **Research Paper** ≫

Surfactant-enhanced Soil Washing using Tween and Tergitol Series Surfactants for Kuwait Soil Heavily Contaminated with Crude Oil

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ABSTRACT

Batch experiments were performed to investigate the feasibility of a surfactant-enhanced soil washing process for soils heavily contaminated with crude oil in Kuwait. TPH concentration of the contaminated soil was 223,754 mg/kg, sampled from the bottom of a vaporized oil extraction pond in the Burgan reservoir field. Commercialized eight nonionic surfactants (Tween and Tergitol series) were used to measure the aqueous solubility for the crude oil. Among them, two Tergitol surfactants were used to evaluate the TPH removal efficiency of the surfactant-enhanced soil washing for heavily contaminated Kuwait soil. The solubility of the crude oil in surfactant solution was in the order Tergitol 15-S-7 > Tergitol 15-S-9 > Tergitol 15-S-12 > Tween-80 > Tween-20 > Tween-60, which showed that the crude oil solubilities of the Tergitol series were higher than those of the Tween series. The TPH removal efficiencies of 2% and 5% Tergitol 15-S-9 solution were 59% and 65%, respectively. Because the residual TPH concentration in the washed soil was still higher than the clean-up level (10,000 mg/kg), the soil washing process was repeated five times. After the fifth washing, the residual TPH concentration in the soil went down to 7,680 mg/kg and its removal efficiency was 97%.

Key words: Crude oil, Soil washing, Surfactant, Tergitol, Tween

1. Introduction

The main environmental concern for crude oil is that, if not handled carefully, it may pose significant hazards to human health and the earth's ecology during all stages of production, the distillation process and consumption (Urum et al., 2006). Among a number of physical and chemical remediation processes, soil washing has been proposed as a promising innovative remediation technology due to its potential for treating not only oil contaminated soils but also those contaminated by heavy metals (Deshpande et al., 1999; Mulligan et al., 2001; Urum et al., 2004). During this process, the washing solution extracts and separates contaminants from the soil, thereby reducing the quantity of contaminant for further treatment (Griffiths, 1995). Because hydrophobic organic contaminants such as crude oil have a low solubility in water, it is difficult to dissolve them by using only water. Therefore, as an alternative, the surfactant-enhanced soil washing has been studied for the removal of organic contaminants by washing out hydrophobic organic compounds from contaminated soil or sediment (Abdul and Gibson, 1991; Yeom et al., 1995; Lee et al., 2005). Several surfactants are particularly attractive because they potentially have low toxicity and favorable biodegradability in the environment. Among them, nonionic surfactants such as the Tergitol, Tween, and Brij series are considered to be suitable for enhancing solubilization of hydrophobic organics (Kuyukina et al., 2005; Park et al., 2009; Lima et al., 2011; Um et al., 2013).

The main objective in this study is to evaluate the feasibility of a soil washing process using a surfactant solution for soil seriously contaminated by crude oil, for which the TPH concentration is more than 200,000 mg/kg. Batch experiments were performed for enhancement in TPH solubility using eight different surfactants (four Tergitol and four Tween series). Using the two studied surfactants that had the best performance for the TPH solubility enhancement, the efficiency of soil washing was studied with a soil

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sample heavily contaminated with crude oil. The results of this study provide meaningful information for the future field application of soil washing to soils seriously contaminated by crude oil.

2. Experimental Methods

2.1. Outline of the research area

Crude oil reserves in the Kuwait territory ranks sixth in the world (about 102 billion barrels) and the petroleum industry in Kuwait is the largest industry, accounting for nearly half of the country's GDP (Simmons, 2002). Due to the arson and bombing by Iraqi troops around oil wells during the Gulf War and by uncontrolled oil separation processes, hundreds of huge oil ponds have been left in ruin (Saenger, 1994). As a result, 700 km of the coastline in Kuwait and Saudi Arabia and 49 km^2 of the desert in Kuwait were contaminated with leaking crude oil (KME, 2011). Table 1 shows typical crude oil contaminated regions and their volumes in Kuwait.

The research area for this study is the Burgan field, which contains the largest sandstone reservoir rock in Kuwait. The Burgan field area produces 1.2 million barrels of crude oil per day (Simmons, 2002). Because the final stage of the crude oil producing process uses water to increase the pressure for extracting the crude oil, the crude oil extracted at the final stage contains a large amount of water and it has to be separated for the further use. In the conventional separation process, extracted crude oils were dumped into a pond, and thus the floor and slope area of the pond were seriously contaminated by the crude oil. The study area contains one of the crude oil reservoir ponds in the Burgan reservoir field and the pond soil that was contaminated by the crude oil was sampled for this study. When all of the water had evaporated from the pond, the free phase oil floating above the water had permeated into the bottom or the slop soil.

Table 1. Crude oil contamination in Kuwait (from KME, 2011)

Oil Field Region in Kuwait	Oil contaminated area (km^2)	Oil contaminated soil volume (m^3)
Wafra	3.26	1,956,000
Burgan	25.6	14,520,000
Minagish	0.19	95,000
Umm Gudair	0.27	135,000
Raudhatain	12.28	2,456,000
Sabriya	6.85	3,082,500
Bahra	0.68	408,000
Total	49.13	22,652,500

2.2. Soil properties

The crude oil contaminated soil was carried to Korea by plane for research purposes after the approval by the Korean animal, plant and fisheries quarantine and inspection agency in 2014. Several analyses were performed to identify the physical and chemical properties of the soil particle distribution, pH, water content, and TPH concentration before the experiments. For the analysis of TPH concentration in soils, soil samples were pretreated according to the Korean Soil Pollution standard analytical process, and the ultrasonic wave extraction process was performed. To remove moisture from the soil, 20 g of soil was mixed with anhydrous sodium sulfite in a beaker. A hundred milliliters of dichloromethane solvent was added to the soil, and the crude oil was extracted by an ultrasonic extractor (Sonics, Vibra-cell). The output of the ultrasonic extractor was adjusted to the maximum, and the duty cycle was fixed at 50% for three minutes. The extracted solvent in the beaker was then evaporated to 2 mL and the TPH mass in the 2 mL of the remaining liquid was measured by GC/FID (Gas Chromatography/Flame Ionization Detector; Agilent 6890). The analytical conditions of the GC/FID for measuring the TPH concentration in the soil are shown in Fig. 1. All analyses were repeated three times and their arithmetic average was used as the final result.

The physical and chemical properties of the soil were measured and the results are shown in Table 2. The soil was composed of 96.6% sand and 3.4% silt and clay, which belonged to the category "Sand" in the USDA (United States Department of Agriculture) soil textural diagram, which suggested that the soil washing process would be feasible for the remediation of the soil. Because the pH of the soil was 7.47 (weak base), there was also no limitation to applying the soil washing process. The average TPH concentration of the soil was 223,754 mg/kg, which was much higher than the clean-up level in Kuwait (10,000 mg/kg). From the results of the GC analysis, a noticeable pattern of

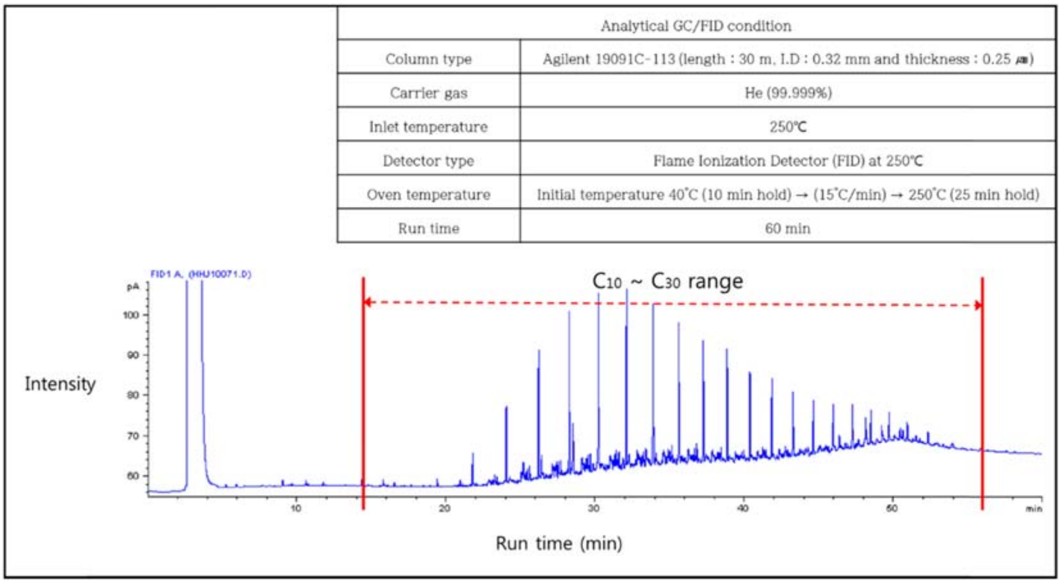

Fig. 1. GC peak of contaminants in the soil and analytical conditions of GC/FID.

Table 2. Soil properties and TPH concentration

Size distribution ratio (%)[a]		pH	Water content (%)	Average TPH concentration (mg/kg)
Sand	Silt & Clay			
96.6	3.4	7.47	7.4	223,754

[a]Done by the dry screening process

GC peaks for contaminants in the soil was very similar to that of diesel; the carbon number mainly ranged from 10 to 30, and the main pollutant in the soil was determined to be diesel according to its composition (Fig. 1).

2.3. Surfactants

The amphiphilic compounds (containing hydrophobic and hydrophilic portions) of a surfactant reduce the free energy of the system by replacing the bulk molecules of higher energy at interfaces (Rosen and Kunjappu, 2012). They contain a hydrophobic portion with little affinity for the bulk medium and a hydrophilic group that is attracted to the bulk medium (Mittal, 1979; Mulligan et al., 2001). Another characteristic of surfactants is the formation of micelles, small aggregates of surfactant molecules (Volkering et al., 1998). The minimum concentration at which this occurs is called the ‘CMC’ (critical micelle concentration). There are two mechanisms of surfactant-enhanced soil washing. The first mechanism, ‘separation’, occurs below the CMC when surfactant monomers increase the contact angle between the soil and the hydrophobic contaminant. The other mechanism, ‘solubilization’, occurs above the CMC when contaminants are partitioned from the soil into the hydrophobic core of surfactant micelles (Deshpande et al., 1999). With these processes, a surfactant can increase the solubility of organic contaminants or lower the interfacial tension to enhance the mobility of the organic contaminants (West and Harwell, 1992).

The most accepted classification of surfactants is based on their dissociation type in water. Anionic surfactants are dissociated in water as an amphiphilic anion group and a cation such as Na^+, NH_4^+ and metals. Cationic surfactants are dissociated in water into an amphiphilic cation group and an anion such as halogen. Nonionic surfactants do not ionize in aqueous solution because their hydrophilic group is the nondissociable type such as alcohol, phenol, ether, ester, or amide. Nonionic surfactants account for about 45% of the world production and a large proportion of nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain obtained by the polycondensation of ethylene oxide (called "polyethoxylated (POE) surfactants") (Rosen and Kunjappu, 2012). Several factors can influence the efficiency of the surfactant-enhanced soil washing. Generally, the surface of the soil particle remains negatively charged and anionic or nonionic surfactants are less likely to be absorbed into the soil and easily bring out the organic compounds from the soil surface. Subsurface water that is too hard may be detrimental to the effectiveness of an anionic surfactant because the anionic surfactant may precipitate, while nonionic surfactants are more likely to adsorb onto clay fractions than anionic surfactants (West and Harwell, 1992; Tsomides et al., 1995). For these reasons, researchers consider that the polyethoxylated (POE) surfactants such as as Tergitol, and Tween series have potential for the remediation of NAPLs (Non Aqueous Phase Liquids) contaminated soils or aquifers (Mulligan et al., 2001; Lee, 2001). Surfactant-enhanced soil washing and the flushing processes that use them have been studied as a promising technology for the remediation of contaminated soils (Paria, 2008; Khalladi et al., 2009; Huguenot et al., 2015). However, even though the use of surfactants in the subsurface was originally developed in the petroleum recovery area to increase the amount of extracted crude oils from the subsurface, the feasibility of the surfactant usage for highly NAPL contaminated soils or aquifer having free products (TPH concentration > 100,000 mg/kg) has not been evaluated yet. In this study, the TPH removal efficiency of the soil washing process using Tween and Tergitol series nonionic surfactants for Kuwait soil seriously contaminated with the crude oil (TPH concentration: 223,754 mg/kg) was investigated in batch experiments.

2.4. Batch experiment for the solubility increase of the crude oil

The solubility of NAPLs in washing solution is directly proportional to the removal capacity of the soil washing process for the contaminated soil (Mittal, 1979). Batch experiments to measure the solubility increase of the crude oil were performed for eight commercialized nonionic surfactant solutions (Tween-20, Tween-60, Tween-80, Tween-85, Tergitol 15-S-7, Tergitol 15-S-9, Tergitol 15-S-12, and Tergitol 15-S-30) which were purchased from Ilshinwells Co., Ltd. The physical and chemical properties of the surfactants used in the experiment are shown in Table 3. The crude oil used in the experiment was provided by the Korea Petroleum Quality & Distribution Authority. A hundred milliliters of distilled water was mixed with each surfactant solution of 0.01%, 0.05%, 0.1%, 0.2%, 0.5%, 1%, 1.5%, 2%, 3%, and 5% concentration. Ten milliliters of crude oil and 30 mL of each surfactant solution were mixed using a rotator mixer in a 40 mL vial for 1 hour, and then the mixed solution was separated to two distinct liquid phases (the aqueous phase and the crude oil phase) (Fig. 2). The surfactant solution of 2 mL sampled from only the aqueous phase was mixed again with 10 mL of dichloromethane in a 20 mL vial using a rotator mixer for 1 hour to extract the crude oil dissolved in the aqueous phase. Two milliliters of extracted dichloromethane was analyzed with the GC/FID to calculate the solubility of the crude oil for each surfactant solution.

2.5. Batch experiment for the surfactant enhanced soil washing

Soil washing experiments with various surfactant solu-

Table 3. Physico-chemical properties of surfactants used in the experiment (from Yang et al., 2008)

Trade name	Chemical name	CMC (mM)	M.W.[a] (g/mol)	HLB[b]
Tween-20	POE(20)[c] sorbitan monolaurate	0.06	1,228	16.7
Tween-60	POE(20)[c] sorbitan monostearate	0.022	1,309	14.9
Tween-80	POE(20)[c] sorbitan monooleate	0.012	1,310	15
Tween-85	POE(20)[c] sorbitan trioleate	0.06	1,839	11
Tergitol 15-S-7	POE(7)[c] secondary alcohol	0.039	515	12.1
Tergitol 15-S-9	POE(9)[c] secondary alcohol	0.056	584	13.3
Tergitol 15-S-12	POE(12)[c] secondary alcohol	0.11	738	14.7
Tergitol 15-S-30	POE(30)[c] secondary alcohol	0.56	1,400	17.4

[a]Average molecular weight, [b]Hydrophilic-Lipophilic Balance, [c]Polyoxyethylene ($-OCH_2-CH_2$) number

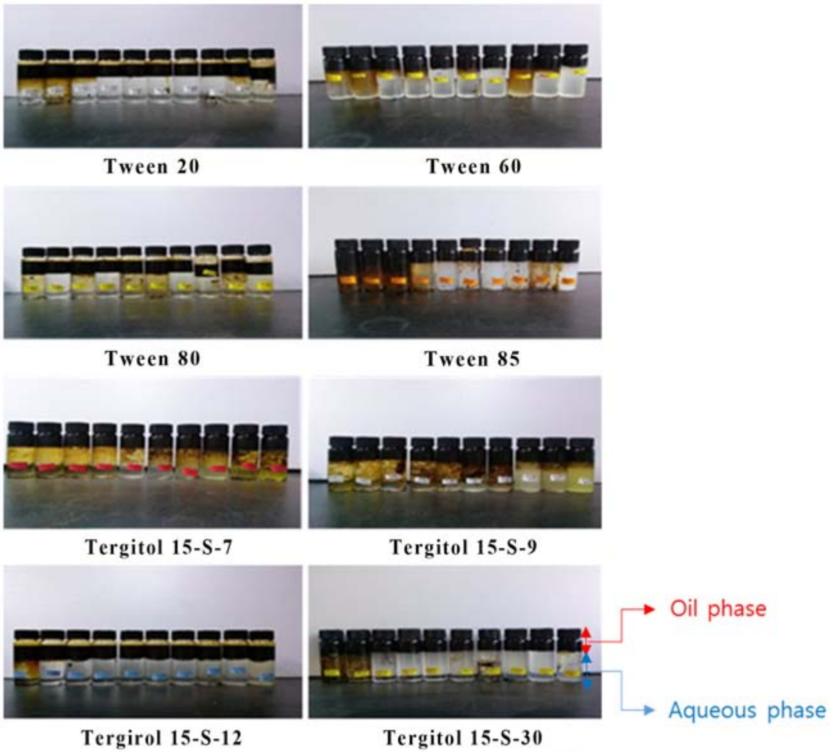

Fig. 2. Separated crude oil phase (top) and aqueous phase (bottom) of the mixed surfactant solution in a vial.

tion were performed to investigate the removal efficiency of TPH for each surfactant-enhanced washing solution and to determine the optimum washing conditions. The contaminated soil with high TPH concentration (223,754 mg/kg) was used for the batch experiments. Two surfactants belonging to the Tergitol series (Tergitol 15-S-7 and Tergitol 15-S-9) were used because they had a high degree of crude oil solubility determined from the previous batch experiment (See 3.1 section). Distilled water and each surfactant were mixed for making 1%, 2%, 3%, and 5% surfactant washing solution (100 mL). Ten grams of the contaminated soil and 30 mL of surfactant solution (1 : 3 ratio, w/v) were mixed in a 50 ml of glass vial again and the mixture was shaken at 150 rpm for 1 hour. After the batch experiment, the washed soil was separated from the solution and the TPH concentration in the washed soil was analyzed on the GC/FID. The measurement of the TPH concentration was performed in triplicate and its arithmetic mean was used to calculate the TPH removal efficiency. The TPH removal efficiency of each surfactant washing solution was calculated from Eq. (1).

$$\textit{Removal efficiency}\ (\%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad (1)$$

where C_i and C_e are the initial and final TPH concentrations of the soil, respectively (mg/kg).

2.6. Batch experiment for the repeated washing

The soil washing was repeated because the TPH concentration of the washed soil after the surfactant-enhanced washing was still higher than the clean-up level in Kuwait (10,000 mg/kg). Two washing solutions with Tergitol 15-S-7 and Tergitol 15-S-9 were used to investigate the increase of the TPH removal efficiency during the repeated washing process. Two percent of surfactant solution was used because the TPH removal efficiency for the washing solution did not increase significantly at above 2% of surfactant concentration (See 3.2 section). Fifty grams of the contaminated soil and 150 mL of surfactant solution (1 : 3 ratio w/v) were mixed in a 200 ml of glass vial and was washed using a rotary shaker at 150 rpm and at 25°C for 1 hour. After the supernatant washing solution was removed from the soil, the washed soil was consecutively washed again with the new 2% surfactant solution at a 1 : 3 ratio (w/v), which was repeated four times (a total of five washings). Ten grams of washed soil for each washing time was sampled from the washed soil and then its TPH concentration was analyzed on the GC/FID to calculate TPH removal efficiency for different washing times.

3. Results and Discussion

3.1. Batch experiment for the solubility increase of the crude oil

The experimental results for the crude oil solubility of eight surfactant solutions at different surfactant concentrations are shown in Fig. 3. As the surfactant concentration in the solution increased, the crude oil solubility proportionally increased, and it ranged in descending order, Tergitol 15-S-7 > Tergitol 15-S-9 > Tergitol 15-S-12 > Tergitol 15-S-30 > Tween-80 > Tween-20 > Tween-60 > Tween-85. The crude oil solubility of the Tergitol series was much higher than that of the Tween series, suggesting that the hydrophobic group of secondary alcohol (Tergitol's formula) has more affinity for the crude oil than sorbitan (Tween's formula)(Heo, 2015). In the Tergitol series, the surfactant with a low number of oxyethylene (OE: $-OCO_2-CH_2-$) had the highest crude oil solubility in solution, which shows that the Tergitol series with a low OE number (< 10) is more attractive to the crude oil. The increase in the crude oil solubility depended on the number of oxyethylene in a surfactant monomer and the hydrophilic-lipophilic balance (HLB), which has a molecular structure similar to that of the crude oil. The results revealed that the Tergitol 15-S-7 surfactant solution had the highest solubility for the crude oil. At 2% of surfactant concentration, the crude oil solubility increased up to 5,689 mg/L, which was more than 1,700 times that with only distilled water. And 2% solution of Tergitol 15-S-9 increased the crude oil solubility more than 930 times in comparison with only distilled water. These results suggest that the surfactant-enhanced soil washing is feasible for soils seriously contaminated by crude oil, and thus two surfactants (Tergitol 15-S-7 and Tergitol 15-S-9) with high crude oil solubility were used in the subsequent soil washing experiments.

3.2. Batch experiment for the surfactant enhanced soil washing

For the two surfactants, batch experiments with various washing solutions were performed to determine the surfactant type and its optimal concentration in the washing solution. The TPH removal efficiency of each surfactant solution was investigated and is shown in Fig. 4. The TPH removal efficiency of the washing solution was proportional to the amount of surfactant in the solution. However, at above a 2% concentration of the surfactant, the increase in TPH removal efficiency was moderated. The TPH removal efficiency of 5% Tergitol 15-S-7 and Tergitol 15-S-9 solution was 64% and 65%, respectively. Considering the cost and the viscosity of the surfactant, it was not suitable to use in the washing solution with a high percent of surfactant (> 5%) for actual field sites. Then it was determined that the optimal surfactant concentration for the soil washing pro-

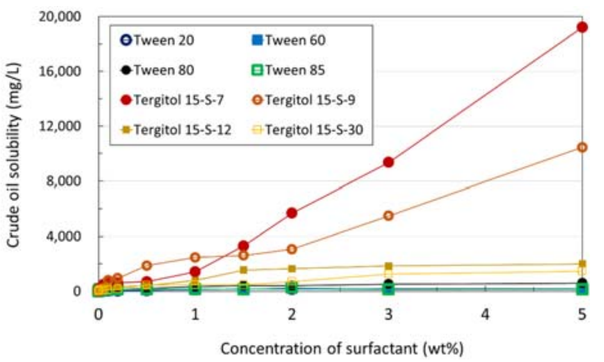

Fig. 3. Results of the crude oil solubility experiment for eight surfactant solutions.

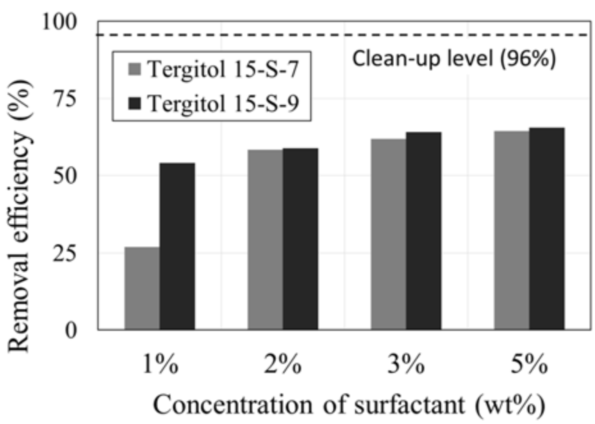

Fig. 4. Removal efficiency of the washing solution with different surfactant concentrations.

cess to remove the crude oil is around 2%. Even though the TPH removal efficiency of the washed soil was 59%, which was the highest TPH removal efficiency with the 2% washing solution (Table 4), it was lower than the clean-up level (96%) in Kuwait.

3.3. Batch experiment for the repeated washing

Although the TPH removal efficiency of surfactant-enhanced soil washing was high (Table 4), the residual TPH in the washed soil was 77,388 mg/kg, which was still higher than the clean-up level in Kuwait (10,000 mg/kg), which demonstrated that it is hard to reach the clean-up level using only one washing. Thus, the soil washing process with two surfactant solutions was repeated five times and results are shown in Table 5 and Fig. 4. After three washings with a 2% surfactant solution, the TPH removal efficiency increased to 89% (Fig. 5). After five washings, the TPH removal efficiency increased to more than 97% and the residual TPH concentration in the soil was 7,680 mg/kg, which was below the 10,000 mg/kg soil clean-up level in Kuwait (Table 5). Therefore, it was concluded that repeated washings with 2% Tergitol 15-S-7 and Tergitol 15-S-9 solution could be successfully used to additionally remove TPH from soil seriously contaminated with crude oil (TPH concentration > 220,000 mg/kg).

Table 4. Results of the soil washing experiment with different surfactant concentrations in the solution (the initial TPH concentration of the soil: 223, 754 mg/kg)

Surfactant name	Concentration of surfactant in washing solution (wt%)	TPH concentration remained in washed soil (mg/kg)
Tergitol 15-S-7	1	163,285
	2	93,338
	3	85,587
	5	79,803
Tergitol 15-S-9	1	102,941
	2	92,332
	3	80,606
	5	77,388

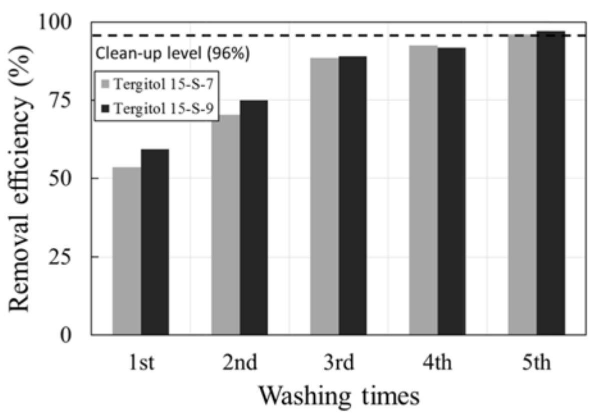

Fig. 5. Removal efficiency of the repeated washing solution (2% surfactant solution).

Table 5. Results of the repeated washing experiment with a 2% surfactant solution

Washing times	Surfactant type	TPH concentration remained in washed soil (mg/kg)
1st	Tergitol 15-S-7	103,754
	Tergitol 15-S-9	91,402
2nd	Tergitol 15-S-7	66,236
	Tergitol 15-S-9	55,925
3rd	Tergitol 15-S-7	25,798
	Tergitol 15-S-9	24,422
4th	Tergitol 15-S-7	16,956
	Tergitol 15-S-9	18,459
5th	Tergitol 15-S-7	8,012
	Tergitol 15-S-9	7,680

4. Conclusion

In our batch experiments, more than 97% of the crude oil in the soil was removed by five soil washings using 2% Tergitol series surfactant solution. Our investigation confirmed that the Tergitol series-enhanced soil washing process has a great potential for remediating sites seriously contaminated by crude oil. Our results give additional insight into evaluating the feasibility of using the surfactant-enhanced soil washing process to treat real oil spill sites and also provide valuable information on the development of effective and safe surfactant remediation technologies.

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