Original Research Article

THE EFFECT OF SURFACTANT CONCENTRATION ON CRUDE OIL REMOVAL FROM CONTAMINATED SOIL

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ARTICLE INFORMATION

ABSTRACT

The extraction efficiencies of three non-ionic surfactants; Tween 80, Brij 35 and Triton X-100 at different concentrations of 0.1-0.5% w/v were investigated. It was observed that for the three surfactants examined, the bulk oil removal increased with increasing surfactant concentration. The results of the investigation also revealed that Brij 35 was effective in the removal of aliphatics while low concentration of Tween 80 did not favour the removal of aromatic hydrocarbons. Triton X-100 seems to be the best amongst the surfactants investigated considering its capability for removing both aliphatic and aromatic hydrocarbons at relatively low concentrations. Concentration of 0.5% w/v for all the surfactants generally produced an appreciable increase in bulk oil removal, aliphatic and aromatic fractions. These results will provide a guideline for evaluating and selecting non-ionic surfactants for the remediation of crude oil contaminated soil.

1. INTRODUCTION

One of the motivating factors in developing crude oil removal technology has been the environmental hazards posed by the continuous presence of spilled crude oil on the subsurface of the soil. This is because of the capacity of crude oil to release to the soil, a wide variety of contaminants such as low molecular mass aromatics like benzene, toluene, ethyl benzene and xylene as well as higher molecular PAHs, some of which possess mutagenic and carcinogenic properties (Chong *et al.,* 2014). As a result of this, the remediation of soils contaminated with crude oil has become an important part of the ongoing quest for a safe environment.

Surfactants are particularly attractive for the removal of organic compounds and have low toxicity and thus are environmentally friendly (Desphane *et al.,* 1999). Types of surfactants include chemical and bio surfactants. Due to biodegradability, bio surfactants are thought to be preferred for remediation purposes (Ying 2006). However, the high cost of their purification has limited the application of bio surfactants (Mulligan, 2005). Among the chemical surfactants, non-ionic surfactants such as Tween 80 and triton X-100 (Chong *et al.,* 2014; Peng *et al.,* 2011) and Brij 35 (Ahn *et al.,*2008) have been used to effectively remediate soil contaminated with petroleum hydrocarbons through column flushing. One of the important properties of surfactants that are directly related to micelle formation is solubilization. This may be defined as spontaneous dissolution of a substance by reversible interaction with surfactant micelles in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 2004). Although the use of surfactant for soil flushing and soil washing has been widely studied, little attention has been given to the use of non-ionic surfactant for the flushing of soil contaminated with crude oil. A previous study investigated the removal of crude oil from soil using two bio surfactants (rhamnolipid and saponin) and a synthetic surfactant (sodium dodecyl sulphate) (Urum *et al.,* 2006). Most of the research work carried out in this area has focused on the use of surfactants to remove heavy metals (Baziar *et al.,* 2013) and petroleum hydrocarbons such as polycyclic aromatics compounds (Baziar *et al.,* 2013; Chong *et al.,* 2014; Khalladi *et al.,* 2009; López-Vizcaíno *et al.,* 2012) while specific hydrocarbons such anthracene have also been removed from petroleum contaminated soils (Cardenas- Aquino *et al.,* 2014). Other researchers have applied surfactants to hydrocarbon-contaminated soil as they solubilize the contaminant, making them available for microbial degradation (Gao *et al.,* 2007)

This study is aimed at assessing the effectiveness of non-ionic surfactants (Triton X-100, Tween 80, Brij 35) in the treatment of crude oil contaminated soil. A mass balance assessment method was used to quantitatively evaluate the quantity of bulk oil, aliphatic and aromatic fractions eluted by the surfactants using different concentrations. The results obtained will provide a guideline for evaluating and selecting non-ionic surfactants for soil clean-up processes.

2. MATERIALS AND METHODS

2.1. Materials

The materials used for this work were soil and silica. Silica was obtained from Fisher chemical company United Kingdom with particle size between 0.2-0.5 mm, and the soil collected at a distance of 500 m from Coalite plant in Chesterfield, United Kingdom. Surfactants used in this study were three non-ionic surfactants: Brij 35 (polyoxyethylene (23) Lauryl ether), Tween 80 (polyoxyethylene (20) Sorbitan monooleate and Triton X-100 (polyoxyethylene (10) Octyphenol. Surfactants were obtained from Acros Organics Company in the United Kingdom and were used as received from the supplier without further purification. The crude oil used to artificially contaminate the soil was North Sea crude. Chromatographic solvents used include Dichloromethane (DCM), n- hexane, toluene, and methanol and all these were obtained from Fisher Chemical Company in United Kingdom.

2.2. Methods

The silica used was activated by keeping them in the oven at 200º C for 12 hours and allowed to cool in a desiccator. This to remove any absorbed water. The soil sample was extracted with DCM for about 12 hours to remove organic matter. All surfactant solutions were prepared using distilled water and stirred using a magnetic stirrer for about 12 hours for complete dissolution of the surfactant in the

water. The surfactant solutions were prepared in terms of percentage weight by volume, (e.g 5 g of surfactant in 1 litre of distilled water is 0.5% w/ v). All chromatographic solvents (DCM, n-hexane, toluene and methanol) were distilled before use.

2.2.1. Impregnation of oil into soil sample
Approximately, 10 ml of DCM was added to 250 mg of oil in a round bottom flask. Shaking the flask for 2 minutes formed a homogenous mixture. A slurry was formed by adding 100 mg of soil to the oil-DCM mixture in the flask. The DCM was removed from the slurry by rotary evaporator at $30^{o}C$ leaving the soil contaminated with crude oil.

2.2.2. Preparation of packed column.
The packed column used for this study was based the chromatographic method for the separation of solid-liquid described by Scott (1995). The column was plugged with a cotton wool at its bottom and 5 g of clean soil were packed into the column (0.5cm internal diameter and 10 cm long). Tapping the column with one finger leveled the soil. The contaminated soil (oil- soil mixture) was added to the top of the clean soil in the column to form a layer of about 3 mm deep. The clean soil was used a packing material for the column so that during surfactant flushing of the contaminated soil placed on top, so that no other contaminant will be found in the result.

2.2.3. Surfactant elution
Approximately 100 ml of each surfactant solution was used to elute the column and was collected in a beaker. In order to ensure that the oil left in the column was free of surfactant, 100 ml of distilled water was used to wash the column down 5 times until no trace of surfactant bubble was seen in the eluted distilled water. Finally, the oil remaining in the column was recovered using methanol / DCM mixture (1:1 v/v ratio). This was carried out for the different surfactant concentrations prepared. The solvent was evaporated and the weight of crude oil recovered after surfactant flushing was taken. Then by mass balance, the percentage of oil extracted with the different surfactant concentration was obtained.

2.2.4. Fractionation of extracts and crude oil
The chromatographic column was plugged with cotton wool at the bottom. A weighed amount of activated silica (5 g) was used as packing for the column after which 10 ml of of DCM was added to crude oil extract obtained from the bottom after surfactant flushing. A known weight of silica (100 mg) was added to the DCM-crude oil mixture to for homogenous mixture and the solvent evaporated using rotary evaporator leaving the silica coated with the crude oil. Then the silica coated sample was placed on top of the silica packed column. The column was eluted with different solvents in order to separate the different fractions namely the aliphatics, aromatics and polars. In order to obtain the aliphatic fractions, 70 ml of hexane was used. This is a colourless eluant and was received into a round bottom flask. Before the column became dry, 70 ml of toluene was added to elute the aromatics. This was generally yellowish in colour. The aliphatic fraction was collected until the aromatic fraction (yellowish colour) was about 1 cm from the bottom of the column, when the flask used for the aliphatics was replaced by a new clean one to collect the aromatics. As the column was about to dry, 70 ml of DCM and methanol (1:1 ratio) was used to elute the polars, which is a dark yellow colour. Again the receiving flask was replaced by a new when the dark yellow colour was also about 1cm from the bottom of the column. Each solvent was evaporated using a rotary evaporator to reduce the volumes and transferred to small pre-weighed vials and blown to dryness by a gentle stream of nitrogen gas. This procedure was carried out for the crude oil sample to obtain the different

fractions in the crude oil so that by mass balance the extraction efficiency of the different surfactants at the different concentration can determined.

3. RESULTS AND DISCUSSION

A comparative analysis of the effect of surfactant concentration on crude oil removal from contaminated soil has been investigated with a view to determining the effectiveness of surfactant treatment. Table 1 shows the fractionation of the crude oil which was used to compare bulk oil and fractions removed by surfactants.

Table 1: Fractionation of crude oil

Experiment No	Aliphatics (mg)	Aromatics (mg)	Polars (mg)	Total recovery (mg)
1	108.4	27.2	2.8	138.4
2	115	25.6	2.6	143.2
3	115	28	2.5	145.5
4	119.7	25.4	2.7	147.8
5	132.4	19.2	3.5	155.1
6	137	20.8	2.5	160.3
7	142	26	4	172
8	143.5	25	3.5	172
Total	1013	197.2		
Mean	126.6	24.7		
Standard deviation	14	3		

The total extractable oil could not balance with the starting oil due to the fact that lighter components of the oil could have been lost during rotary evaporation. Table 1 also shows the percentage bulk oil extracted. Experimental errors were calculated by means of standard deviation from the mean for the aliphatic and aromatic fractions. The errors for aliphatic fractions were higher than those for the aromatic fractions. The inability to estimate accurately exact boundary between aliphatic and aromatic fractions may be presumably responsible for the experimental errors. Therefore, error bars were used to represent percentage standard deviation of the recoverable fractions in the starting oil.

The results of the efficiency of the bulk oil removal by Tween 80, Brij 35 and Triton X-100 are shown in Figure 1. The removal efficiency increased with increase in concentration for the surfactants considered. However, the extraction efficiency of Triton-100 was higher even at lower surfactant concentration (50 %) and increased up to 60% as surfactant concentration increased to 0.5% w/v. Brij 35 seem to have lower extraction efficiency than Triton-100 and Tween 80 at surfactant concentrations below 0.25% w/v. However, the extraction efficiency increased from 0.3%w/v (50%) to about 56% at 0.5% w/v. The extraction efficiency of Tween 80 increased from 45% at 0.1%w/v to about 49% at 0.5%w/v. During soil flushing, the role surfactants play is to concentrate at the interface of the soil and reduce the interfacial tension at the soil/ organic phase and water organic phase (solubilisation) (Paria 2008). The surfactants then desorb or detach the organic molecules from the soil and encapsulate the organic molecules within the micelles at a concentration greater than the critical micelle concentration (Lee et al., 2005).
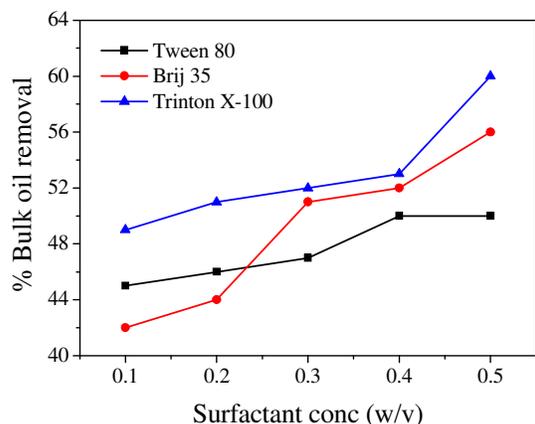
Figure 1: Comparison of extraction efficiency of crude oil by Tween 80, Brij 35 and Triton X-100
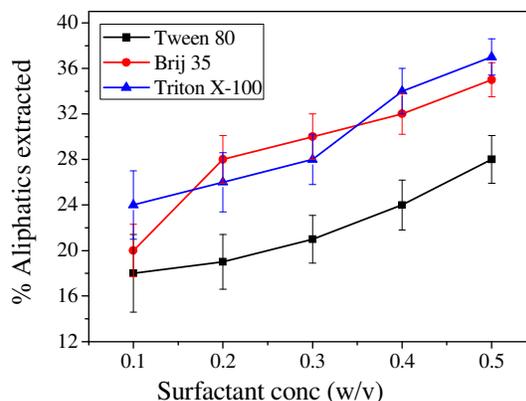
Figure 2: Comparison of extraction efficiency of aliphatics by Tween 80, Brij 35 and Triton X-100

The efficiency of any surfactant is its ability carry out these processes. From the above results, the higher extraction efficiency of Triton X-100 was because the solubilisation and the rate of desorption of the contaminants was higher for Triton X-100 than Brij 35 and Tween 80. Secondly, the increase in concentration will increase surfactant performance because it is when concentration is above the critical micelle concentration of a surfactant that micelles are formed. The micelles formed increase the solubility of the desorbed organic contaminants so that they are encapsulated within the cores of the micelles when concentration is above the critical concentration and different surfactants have different critical micelle concentration so it will lead to differences in their efficiencies (Zhou and Zhu, 2007). The comparison of the extraction efficiencies of aliphatic fractions by the surfactants is shown in Figure 2.

The extraction efficiency of Triton-100 increased from 24% at surfactant concentration of 0.1 %w/v to about 37% at 0.5v%w/v while Brij 35 efficiency increased from 20% to about 33% at 0.5%w/v. It was observed also that Brij 35 had higher efficiency than Triton X-100 at concentration between 0.18 % w/v and 0.35%w/v. The reason could be that it's desorption and encapsulation rate for aliphatic fractions are higher at those concentrations than for Triton X-100.

Tween 80 had the lowest extraction efficiency of aliphatic fractions of 18% at 0.1%w/v to about 24% at 0.5%w/v. Also, the extraction efficiency of Triton X-100 for aliphatic fraction was also higher than the extraction efficiencies of Brij 35 and Tween 80 for all the concentrations considered. About 23% of aliphatic fractions were extracted by Triton X-100 at 0.1w/v and increased to 43%w/v at 0.5 %w/v. The reason for the relative efficiencies of the different surfactants is that they have different solubilisation or desorption capacity for aliphatic fractions at the different concentrations. Similarly, the extraction efficiencies of the aromatic fractions by the three surfactants were compared and presented in Figure 3. Triton X-100 showed higher extraction efficiency than Tween 80 and Brij 35. Brij 35 extracted 8% at 0.1 %w/v to 35% at 0.5 %w/v. The extraction efficiency of Tween 80 at 0.1 %w/v was 0%. This means that solubility of aliphatic fraction in Tween 80 at such low surfactant concentrations were minimum so there was no interaction. However, as the concentration increased, there was slight increase in removal of aliphatic fraction to about 10% at 0.5 %w/v.
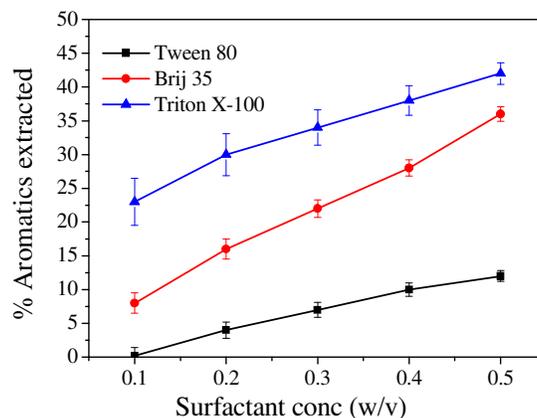
Figure 3: Comparison of extraction efficiency of aromatics by
Tween 80, Brij 35 and Triton X-100

4. CONCLUSION

The current investigation into the effectiveness of using Tween 80, Brij 35 and Triton X-100 to remove crude oil from contaminated soil has led to the following conclusions:

Both aliphatic and aromatic fractions can be effectively removed from contaminated soil by surfactant treatment. However, aliphatic fractions in relation to aromatic fractions are more amenable to removal. Brij 35 can be used to remove both fractions especially at higher concentrations. Triton X-100 is the most favourable in removing both fractions even at low concentrations. A concentration of 0.5% w/v for all the surfactants generally produced an appreciable increase in bulk oil removal, aliphatic and aromatic fractions. The above results suggest that there is a great potential in using non-ionic surfactants in soil remediation and should be considered as a cost effective option to clean up crude oil contaminated soil.

5. ACKNOWLEDGMENT

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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