

## A Study of surfactant-based remediation for removal of toluene and PCE in contaminated water

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### Abstract

The purpose of this study was to assess the effect of surfactant on the rate of NAPLs(non-aqueous phase liquids) solubilization. The experimental variables were surfactant type, NAPLs type and water type. The main experimental designs were consists of two phases. The solubilization rate is sensitive to surfactant type based on this test. Used aqueous surfactants were solubilized and removed 72.77 to 89.90% of toluene, PCE(tetrachloroethylene) from the contaminated water during the test, respectively. T60 has higher and stable recovery ratio than SDS in surfactant type but, the micelle of the T60 is more weaker than that of SDS based on this study's results. And the solubilization rate in used water type was almost same.(deionized water, surface water)

**key word** : surfactant, solubility, NAPLs, toluene, PCE.

### 1. Introduction

The problem regarding contamination has come to occupy an important position in environmental system. NAPLs can be persisted as a long-term source that contaminated soils and water due to their low aqueous solubility and slow rates of dissolution and degradation of most NAPLs contaminants. From the viewpoint of motion and these classification, migration of NAPLs have been caused by gravity and capillary forces. Pump and treat processes were inefficient to recover the NAPLs from the aquifer due to low solubilities, high interfacial tensions and mass-transfer limits of the chlorinated solvent [1]. Each of these problems was interesting as an object of surfactant flushing. Surfactant flushing was circulates surfactant solution through water to recover NAPLs [1]. In recent years, surfactant enhanced remedial methods have been employed to remove NAPLs from contaminated soils and water.

The main experimental designs in this study were (1) experiment 1: determination of solubility rates from experiment of each condition - compares DI water with surface water by surfactant reaction. The experimental variables are surfactant types (anionic, non-ionic) and NAPLs types (DNAPLs, LNAPLs). (2) experiment 2: batch experiment - estimate dissolution of NAPLs concentration vs. time. Both shaker and centrifugal separator were used in this experiment for the contract of time-scale to equilibrium in nature conditions. The objectives of this study were to use above methods to evaluate the remediation condition in water, to consider in caused problem of surfactant flushing remediation method and conduct research about the best method of remediation in soil and water contaminated by NAPLs.

## 2. Materials and methods

### 2.1. Surfactant selection

The two surfactants selected for this study, one was polyoxyethylene sorbitan monostearate(T60), and the other was sodium n-dodecyl sulfate(SDS). T60 is a nonionic surfactant, which has been noted for their unfavorable tendency to sorption to aquifer solids, but it was selected for its low CMC(critical micelle concentration), which would maximize surfactant retention during filtration [2]. Nonionic surfactant has the character that it does not have the group of ionic dissociated in solution of contaminant materials. SDS, anionic surfactant was chosen because it had been previously tested and data showed that superior surfactant of result could be examined. Anionic surfactants were usually chosen for surfactant based remediation because of their lower degree of adsorption in soil than that by cationic and nonionic surfactants[3-6]. The characteristics of T60 and SDS are shown in Table 1.

Table 1. The characteristics of used surfactants

Trade name	T60 <sup>a</sup>	SDS <sup>b</sup>
Chemical name	polyoxyethylene sorbitan monostearate	sodium n-dodecyl sulfate
Molecular weight	1310	288
HLB <sup>c</sup>	14	40
CMC <sup>d</sup>	8	30
Formula	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOCO(CH <sub>2</sub> ) <sub>8</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SO <sub>3</sub> Na
Type	nonionic	anionic
Phase	gel solution	powder

<sup>a</sup> data come from Carol. (2002) and Lee, (2002)

<sup>b</sup> HLB: hydrophile-lipophile balance

<sup>c</sup> CMC: critical micelle concentration.

Table 2. The characteristics of used chemicals

Chemical name	toluene	tetrachloroethylene	n-hexane
Formula	C <sub>7</sub> H <sub>8</sub> CH <sub>3</sub>	Cl <sub>2</sub> C=CCl <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>
Molecular weight (g/mol)	92.14	165.83	86.17
Specific gravity (20°C)	0.8669	1.6227	0.678
Vapor density (g/l)	3.18	5.83	2.97
Boiling point (°C)	111	121	69
Freezing point (°C)	-95	-22.35	-95
Ignition point (°C)	480	-	225
Solubility (g/100g water)	0.045	0.015	0.1
Volatility (%)	100	100	-

<sup>a</sup> data come from MSDS

### 2.2. Chemicals selection

Toluene(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) and PCE(Cl<sub>2</sub>C=CCl<sub>2</sub>) are frequently detected in industrially site of Korea and raise a problem of environmental systems. Toluene, PCE were selected as the LNAPLs, DNAPLs model substance, respectively. The characteristics of toluene, PCE were shown in Table 2. Also, n-hexane was selected for gas chromatography analysis procedure (Table 2.)

### 2.3. Exp. 1: Determination of solubilization rate

The experiment put in operation to calculate the solubility rates of surfactants. Make eight solutions in constant temperature laboratory and the characteristics of eight solutions were represented in Table 3. And then put mixing solutions into separate funnels and funnels were placed on stands for 90h at room temperature and the left standing 90h to separate the three different layers, namely, aqueous layer, middle layer and contaminant layer. Volume of each layer was measured for five times at 6h, 12h, 24h, 48h and 90h. The samples of each layer were acquired into vials and diluted with n-hexane for analysis with a gas chromatography system.

Table 3. The characteristics of eight solutions

Solutions number	water type (150ml)	contaminant type (15ml)	surfactant type (50ml)
Sample 1.	distilled water	toluene	T60 <sup>a</sup>
Sample 2.	distilled water	PCE <sup>b</sup>	T60
Sample 3.	surface water	toluene	T60
Sample 4.	surface water	PCE	T60
Sample 5.	distilled water	toluene	SDS <sup>c</sup>
Sample 6.	distilled water	PCE	SDS
Sample 7.	surface water	toluene	SDS
Sample 8.	surface water	PCE	SDS

<sup>a</sup> PCE: tetrachloroethylene

<sup>b</sup> tween #60: polyoxyethylene sorbitan monostearate

<sup>c</sup> SDS: sodium n-dodecyl sulfate.

### 2.4. Exp. 2: Batch experiments for dissolution of NAPLs concentration vs. time

Twenty batch experiments were conducted in a constant temperature laboratory. It was conducted by two methods that were changed velocity of shaker and centrifugal separator and changed the sample volume. First, 9ml of each sample from experiment 1 were pipetted into 10ml centrifugal vials(Wheaton). The vials were tumbled at a 50rpm rolling rate for 17h. End of times, vials centrifuged for 34min at 2000rpm to ensure the

separation of contaminant layer from the aqueous layer. Second experiment conducted to 1.2 ml of each samples were pipetted into centrifuge tube (1.3ml, Wheaton) and filled with distilled water. The tubes were tumbled at a 100rpm rolling rate for 8.5h. and centrifuged for 7min at 10000rpm.

### 3. Results and discussion

#### 3.1. Separatory funnel experiments for solubilization rate

A total of 90h runs were completed over the course of solubility experiments. The volume of the toluene solution decreased 21.02% of contaminants layer, 2.56% of aqueous layer and the volume of PCE solution decreased 7.32% of contaminants layer, 2.44% of aqueous layer as average. The result of this experiment showed the equilibrium was done about 18h. In the T60 surfactant solutions, sample 1 to 4, there was nothing attentive

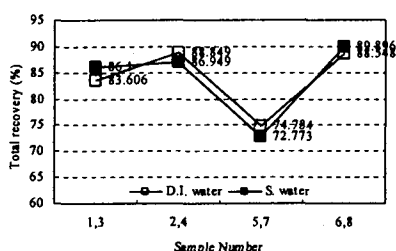


Figure 1. Graph of compared with distilled water and surface water for solubility experiment

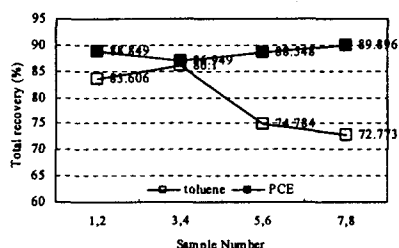


Figure 2. Graph of compared with toluene and PCE recovery for solubility experiment

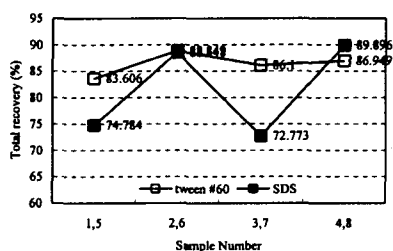


Figure 3. Graph of compared with tween #60 surfactant solution and SDS surfactant solution for solubility experiment

variables among the water types and contaminants types. Total recovery was maintained 83.61% to 88.85%. T60 was a nonionic surfactant that nonionic surfactants in non-polar solvents possess low critical micelle concentration(CMC) values. In the partition coefficient, we could see the suitability as the water types were based on surfactant types. Both T60 and SDS surfactant solutions have no connection with water types and T60 has more suitability that toluene contaminated remediation and SDS was suitable for PCE contaminated remediation than T60. As we could see the classification of water type in Figure 1, the graph showed trend of samples, but there was no difference with water type. It was considered that surfactant solutions were not influenced on ionic difference between distilled water and surface water. About the result of Figure 2 and 3, sample 5 and 7 were low values relatively and its values were 74.78% and 72.77%. Toluene solubility was approximately treble higher than PCE solubility in water. As it were that PCE hydrophobicity was higher than that of toluene. Surfactant had a character to applicable as high as hydrophobicity. So, we could determine the T60 had a predominant and stable recovery ratio during initial 90h.

#### 3.2. Batch experiments for dissolution of NAPLs concentration vs. time

The percent was meant the ratio of contaminants in the aqueous layer with the passage of definite time and the values of percentage were detected below 1% on an average. As we have seen results of sample 17 to 20 could be used standard samples, both

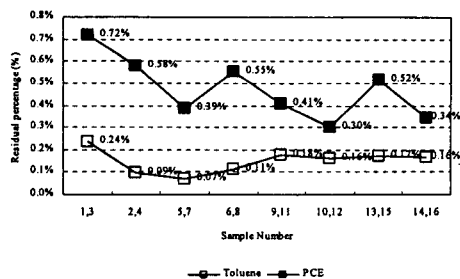


Figure 5. Graph of compared with toluene and PCE recovery for batch experiment

T60 and SDS had predominant results of remediation in LNAPLs such as toluene then, the whole results were detected low values at DNAPLs. Figure 4 showed comparison of distilled water and surface water values. As the comparison with water type, it had a fixed trend similar that of solubility experiment. In Figure 5, the graph was complete divided by contaminants type but, it was a contrary

result for initial solubility experiment results trend. For this result, we considered that the result changed by different volatility of each contaminant. And this showed the experimental example that DNAPLs remediation was difficult and caused the contaminant source by DNAPLs in aquifer and groundwater. The case of Figure 6, it compared with T60 and SDS that caused by different of CMC. The result showed the micelle of T60 was more weaker than that of SDS. Consequently, SDS showed more stable curve in Figure 6.

#### 4. Conclusions

As we could see the result of solubility experiment, PCE has the higher recovery ratio than toluene during initial 90h and they are no difference by water types. Used surfactants were effectively worked in surface water. Also, T60 has higher and stable recovery ratio than SDS in surfactant types. In the result of batch experiment, similarly there are no connection with water types. T60 and SDS result are high values of remediation. In the comparison of surfactant types, SDS has slowness slope width and tendency of these are alike. So, the micelle of T60 was more weaker than that of SDS.

#### 5. References

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