Treatment of Low-level BTEX-contaminated Soils by Anionic Surfactant Washing

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ABSTRACT: Soil contamination generated by petroleum hydrocarbons, including benzene, toluene, ethylbenzene and xylene isomers (BTEX), has raised concern around the world. Soil flushing is the process of treating polluted soils with water, surfactants, or solvents, and it is usually feasible for the remediation of petroleum-hydrocarbon contaminated soils. Surfactant-enhanced flushing was developed from the conventional pump-and-treat method. A mixture of water and surfactants is often applied to polluted soils and groundwater to improve the solubility of the pollutants during soil flushing. The objective of this study was to investigate the effects of applying anionic surfactants flushing on the treatment of low and high level BTEX-contaminated soils. A surfactant, sodium dodecylsulfate (SDS, anionic type), was used as a washing agent in the column experiments. Column studies were conducted to evaluate the efficiency of BTEX removal from unsaturated porous media using different concentrations of SDS for soil flushing. The soil column [4.2 cm (ID) × 12 cm (L)] was packed with low-level BTEX-contaminated soils (100 and 1,000 mg/kg) and DI water was pumped into the column with a flow rate of 11±1 mL/min. Results from the column study show that BTEX removal efficiencies varied from 63 to 95% when 0.5-2% (v/v) of SDS was pumped through the system. Higher BTEX removal efficiency was obtained when the higher surfactant concentration was applied. The results from this study provide insights into the surfactant washing technology, and will be useful in designing a scaled-up system for field applications.

KEYWORDS: Anionic surfactant; Petroleum hydrocarbons; Soil remediation; Soil washing

1 INTRODUCTION

Petroleum hydrocarbons enter ground water systems as the result of spills and leaking underground storage tanks. In ground water systems, gasoline hydrocarbon contaminants can occur as either dissolved or non-aqueous phase liquids (NAPLs). Among the different hydrocarbons present in petroleum, monoaromatic hydrocarbons, including benzene, toluene, ethylbenzene and xylene isomers (BTEX), are a very important category of soil and groundwater contaminants. These volatile compounds are very hazardous because of their fast migration into soil and water bodies and their
acute and chronic toxicities when inhaled or ingested, especially benzene which is a known carcinogenic molecule (U.S. EPA, 2009).

Surfactants including anionic, cationic, zwitterionic, and nonionic forms have been successfully used in groundwater remediation to enhance the solubility and mobility of hydrophobic organic compounds (HOC) in environmental matrices. (He et al., 2008; Lee and Lee, 2010; Nourmoradi et al., 2012; Lee and Lee, 2013) The nonionic surfactant possesses unique characteristics of low critical micelle concentration (CMC) and low adsorption affinity to soil matrix.

The objectives of this work were to evaluate BTEX removal in porous medium through soil column flushing processes using the anionic surfactant (sodium dodecyl sulfate, SDS).

2 MATERIALS AND METHODS

The soil sample was collected from a depth of approximately 0.7–1.5 m below the surface within a farmland located in southern Taiwan. Table 1 shows the basic properties of the soil sample. The texture of this soil was classified as clay. The pH of zero point charge (pHzpc) of soil samples determined by a zeta potential instrument (Pen Kem-Laser Zee 3.0, USA) was about 2.5. The soil pH was measured in water suspensions at 1:1 rate of soil to solution by volume. The cation exchange capacity (CEC) of soil was 13.56 cmole/kg, which was determined according to the method of ASTM D7503. The BET area of soil was 8.43 m²/g. A soil organic matter content of 1.96% was observed by the combustion method (Nelson and Sommers, 1982). After removing the debris, the soil sample was treated with air-dry and pressure steam sterilization (1.2 kg cm⁻² for 5 min). The soil sample was then crushed and sieved to less than 2 mm in diameter. This sieved soil sample was then used for all experiments. The bulk density of soil was 2.45 g/cm³, which was determined according to the method of ASTM D854-92.

Anionic surfactants are usually chosen for soil contaminant flushing treatment because of their lower degree of adsorption on soil compared to cationic and nonionic surfactants (Rouse et al., 1993). Moreover, sodium dodecyl sulfate (SDS, an anionic type) was food grade and was easily biodegradable by soil and/or aquatic microorganisms (Lee et al., 2002). Therefore, SDS with different concentrations (vol/vol) was selected for this study. The characteristic of SDS is shown in Table 1.

Table 1. Chemical and Physical Properties of Selected Commercial Surfactants.

| Surfactant | Formula | Molecular weight | CMC (M) |
|------------|---------|------------------|---------|
| SDS        | C₁₂H₂₅OSO₃Na | 288.38           | 6x10⁻³  |

The BTEX-contaminated soil was prepared by adding amount of BTEX, 100 mL of acetone (as solvent), and 250 g of soil into a 500-mL glass beaker. The mixture was agitated until the acetone was almost completely volatilized. The BTEX in the soil sample was then extracted with dichloromethane and the organic solvent layer was analyzed by gas chromatography. Triplicate soil samples were analyzed for quantification.

In this study, column experiment was performed to evaluate the effectiveness of using the designed SDS on low-level BTEX-contaminated soil (100 and 1,000 mg/kg) remediation. Figure 1 shows the layout of the laboratory-scale column experiment. The column had a length of 12 cm with an inside diameter of 4.2 cm. In this system, a peristaltic pump (Cole Parmer MasterFlex L/S®) was used to deliver the solution. All tubing materials in contact with solution were made of Teflon. The solution was continuously pumped into the columns with an upflow mode under saturated conditions.
by the peristaltic pump. Approximately 109.5 PVs of solution was pumped through
the column system at a flow rate of 11±1 mL/min. The operational characteristics of
the column study are presented in Table 2.

Table 2. Characteristics of Tested soil.

| Characteristics | Values |
|-----------------|--------|
| Texture         | Sandy loam |
| Organic content (%) | 1.96 |
| pH              | 7.25 |
| pH_{zpc}        | 2.5    |
| BET area (m^2/g) | 8.43   |
| CEC (cmole/kg)  | 13.56  |
| Bulk Density (g/cm^3) | 2.45 |

A Hewlett Packard GC/FID (4890D) coupled to a HP7950 purge and trap concentrator
was used for quantitative analysis of BTEX. A HP-5 column (Hewlett Packard, 0.53
μm 30 m) was equipped with GC. The soil/aqueous solutions were purged with nitro-
gen for 11 min and captured in the absorbent of the then desorbed at 225°C for 5 min.
The GC oven temperature was programmed as follows: hold at 40°C for 1 min and
ramp at 5°C for 2 min to 90°C. Injection and detector temperature were set at 200 and
300°C, respectively.
Figure 2. Variations in BTEX cumulative mass vs flushed pore volumes in batch experiment using different SDS concentration solutions with initial BTEX concentration of 1,000 mg/kg. (◆: 2%; □: 1%; △: 0.5%; ×: 0.1%; ○: D.I. water).

Figure 3. Residual BTEX profiles in soil after anion surfactant system treatment with initial BTEX concentration of 100 mg/kg. (◆: benzene; □: toluene; △: ethylbenzene; ○: xylene; L: Length of soil core; L/L: Normalized distance from bottom to top of soil core).

3 RESULTS AND DISCUSSION

Appropriate surfactant injection into the contaminated system would enhance the solubilization and mobilization of the contaminant in the water phase. Fig. 2 and 3 presents the percentage of BTEX cumulative mass vs flushed pore volumes in batch experiment with the initial SDS concentration were 0.1%, 0.5%, 1%, 2% and DI water used. Results show that more than 50% of the BTEX can be removed after 25 PVs of SDS and DI water washing with initial soil BTEX concentration were 100 and 1,000 mg/kg. Approximately 42.24% and 45.43% of toluene recovered efficiencies were observed when 109.5 PVs of 0.1% SDS and DI water were flushing through the 1,000 mg/kg of contaminated soils, respectively. Results also reveal that the 40.83%, 24.47%, 26.99% and 42.89%, 26.36%, 27.06% of ethylbenzene and xylene isomers recovered efficiencies were observed when 109.5 PVs of 0.1%, 0.5% SDS and DI water were flushing through the 1,000 mg/kg of soils, respectively. Benzene, toluene, ethylbenzene and xylene isomers solubility in water were determined to be around 1,780 mg/L, 500 mg/L, 150 mg/L and 181 mg/L at 25°C. During surfactant-enhanced dissolution, the aqueous phase permeability of the contaminated region is increased as the residual BTEX saturation is reduced. It's worth noting that ethylbenzene solubility was similar that xylene isomers. In these experiments, solubility was the dominant
mechanisms of BTEX removal with 100 mg/kg of soil. The solubility of HOCs increases with surfactant concentration (Kalali, et al., 2011). Results reveal that the significant BTEX recovered efficiency was observed after flushing with 0.5% of SDS with 1,000 mg/kg of soil. The SDS concentration was below 0.5% at the end of the experiment. Results indicate that SDS washing is a promising technology to remediate BTEX contaminated soils containing low-level TPH concentrations. Kalali et al. (2011) reported that about 11% removal efficiency of total petroleum hydrocarbon was achieved using distilled water as flushing solvent. As distilled water was replaced by SDS solution with its concentration beyond the critical micelle concentration (CMC), 0.2% (wt/vol) for SDS concentration in this case (Urum, et al., 2004), the micelles in surfactant significantly increases the solubility of HOCs (Kalali, et al., 2011). This would enhance the soil flushing efficiency.

### Table 3. Variations in BTEX recovery Efficiency vs. flushed batch experiment different mixed surfactant concentration (0.1 to 2% of SDS) solutions.

| Test NO. | Concentration of BTEX soil (mg/kg) | Wash time (hr) | Average Flow Rate (ml/min) | Recovery Efficiency [%] |
|----------|-----------------------------------|---------------|----------------------------|------------------------|
|          |                                   |               |                            | B         | T         | E         | X         |
|          |                                   | 100           | 5±0.2                     | 11±1      |           |           |           |
| 1        | D.I. water                         |               |                            | 5.19      | 94.37     | 4.64      | 54.90     | 11.09     | 65.82     | 11.58     | 84.51     |
| 2        | 0.1%                              |               |                            | 10.01     | 77.37     | 9.86      | 87.53     | 21.27     | 57.58     | 22.11     | 58.64     |
| 3        | 0.5%                              |               |                            | 7.49      | 83.33     | 10.47     | 86.83     | 29.36     | 48.77     | 26.25     | 53.70     |
| 4        | 1.0%                              |               |                            | 7.11      | 84.50     | 4.77      | 95.14     | 9.10      | 88.54     | 6.53      | 93.79     |
| 5        | 2.0%                              |               |                            | 3.42      | 92.65     | 1.79      | 56.25     | 7.35      | 88.03     | 10.70     | 87.72     |
| 6        | D.I. water                         | 1000          |                            | 3.34      | 60.62     | 24.86     | 45.41     | 47.59     | 26.99     | 44.71     | 27.06     |
| 7        | 0.1%                              |               |                            | 5.64      | 64.36     | 22.65     | 42.24     | 37.72     | 24.47     | 37.01     | 26.36     |
| 8        | 0.5%                              |               |                            | 4.04      | 72.66     | 29.32     | 59.96     | 29.40     | 40.83     | 29.47     | 42.89     |
| 9        | 1.0%                              |               |                            | 6.63      | 86.50     | 23.22     | 78.08     | 30.65     | 66.36     | 25.22     | 72.28     |
| 10       | 2.0%                              |               |                            | 1.01      | 85.72     | 2.32      | 84.93     | 5.32      | 80.63     | 5.04      | 88.09     |

Table 3 summarizes the results of BTEX recovered efficiency at column experiment for all tests. The recovered efficiency of BTEX for column experiment during 1,000 mg/kg of contaminated soils were 1.01-5.4%, 2.32-29.12%, 5.32-37.72%, and 5.04-37.01%, respectively. Furthermore, it was found that the recovered efficiency of the 2% of SDS concentration was better than 0.1-1% during 1,000 mg/kg of contaminated soils and the increase of surfactant concentrations tends to increase the removal efficiency. This is largely because the anionic surfactant (SDS) was conducted at higher concentration (2%), which was above CMC. The recovered efficiency of BTEX for column experiment during 100 mg/kg of contaminated soils were 3.42-5.01%, 1.79-10.41%, 7.35-26.26%, and 6.51-26.25%, respectively. The surfactant concentration would no significantly increase recovered efficiency of 100 mg/kg of contaminated soils.

Table 3 also summarizes the results of BTEX removal efficiency at column experiment for all tests. The removal efficiency of the 2%, 1%, 0.5% and 0.1% of SDS concentration on the 1,000 mg/kg of contaminated soils were in the order of 95%, 75%, 70%, and 63% at optimized experimental conditions. Results from the column experiment indicate that approximately 90% of benzene and toluene and 73% of ethylbenzene and xylene isomers could be removed during 100 mg/kg of contaminated soils. One mole of SDS was removed by using 191.2, 159.3, 249.8 and 289.9 mg of BTEX.

Figure 4-5 show that BTEX residual concentration on top and bottom soil was higher than middle prior the column experiment. Results show that BTEX were mainly adsorbed onto finer particles (e.g., silt, clay), and thus, less BTEX can be adsorbed onto sand particles.
CONCLUSIONS

This study suggested that the effective removal of benzene, toluene, ethylbenzene and xylenes (BTEX) from contaminated soil by SDS was carried out in column experiment using different SDS concentration and contaminated soil level. Several conclusions are described as the following:

- Results from the column study show that BTEX removal efficiencies varied from 63 to 95% when 0.5-2% (v/v) of SDS was pumped through the system. Higher BTEX removal efficiency was obtained when the higher surfactant concentration was applied.
- These studies have shown that both soil rollup and solubilization mechanisms were active during soil washing, with the magnitude of each effect being a function of the extent of surfactant sorption and the soil grain size distribution.
- The interaction between SDS concentration and BTEX removal efficiency is significant.

In full scale remediation projects, technology involving recovery and reuse of the surfactant can be part of the whole soil flushing remediation system for reducing the expense of surfactants.
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