Surfactant-enhanced desorption for recalcitrant hydrocarbons contaminated soils

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Abstract

Hazardous substances produced from industrial sectors have caused serious environmental problems and threatened ecological systems dating back to early 1960’s in Korea. More than 70% of the domestic wastes are disposed to landfills in Korea; however, a number of abandoned landfills and dump sites are poorly managed and are leaking leachate, which are contaminating surrounding soils and groundwater. This study focuses on the feasibility of recovery of the organic-contaminated Nanji-Do soil by applying surfactant-enhanced desorption technique. Nanji-Do landfill is the MSW (municipal solid waste) dump site under service in Seoul between 1978 and 1992. Surfactant-enhanced desorption technique was studied with nonionic surfactant (Triton X-100) and anionic surfactant (SDS) as desorbing solvents for extracting p-Cresol sorbed on soil particles. Sorption characteristics of soil and organic compound were analyzed and the applications of surfactant solution were studied through batch tests and the flexible-wall permeameter tests. The test results show that the surfactant-enhanced subsurface remediation technique can be adequately applicable when the contaminants are hydrophobic and recalcitrant in nature.

1 Introduction

Soils and groundwater exposed to the variety of chemicals and wastes are frequently and heavily contaminated and difficult to be treated and recovered back to normal conditions. This paper focuses on the remediation of the organic-contaminated subsurface by applying the surfactant-enhanced desorption technique. Research
over the last fifteen years has shown that surfactant has potential to increase the rate of remediation of ground water contaminated with hydrocarbon compound pollutants. The main goal of surfactant-based soil remediation is enhanced contaminant extraction. Surfactant molecules consist of a hydrophobic and a hydrophilic part and can interact with polar as well as nonpolar surfaces [1]. Surfactant molecules may exist during the soil flushing process in the following forms: monomers, micelles, precipitates and adsorbed on the soil, etc. When the surfactant concentration is lower than the critical micelle concentration (CMC), the surfactant molecules exist in monomer form [2]. These monomers change some physical properties of the liquid, including the surface tension, interfacial tension and osmotic pressure. Above the CMC surfactant molecules aggregate and form micelles with a hydrophobic center in which partitioning of chemicals is possible. The interior region of micelles is composed of the hydrophobic tails of the surfactant molecules while the outer region is formed by the hydrophilic heads. In general, two major mechanisms are responsible for surfactant-enhanced contaminant removal from porous media. Solubilization refers to partitioning of hydrophobic contaminants into the oil-like interior of surfactant micelles [2], [3], [4] and [5]. Mobilization or displacement of the residual and/or separate oil phases can be achieved by significant reduction of the oil and water interfacial tension (IFT) [6], [7].

The objectives of this study were to (1) investigate the feasibility of surfactant-enhanced desorption by evaluating the removal amount of the representative contaminant, p-Cresol adsorbed onto soils; (2) accomplish laboratory modeling of the effective stresses and flow velocities found in-situ soil-liquid systems using flexible-wall permeameter. This study was to give further information and essential data for applying the surfactant-enhanced desorption technology for the remediation of p-Cresol contaminates sites.

2 Test methods

2.1 Test materials

2.1.1 Test Soil

The test soil was a mixing soil that was homogeneously blended with weathered soil recovered from the vicinity of Nanji-do landfills located near Seoul World-Cup soccer stadium and Jumunjin sand (classified SP by Unified Classification System) and humic soil. For the weathered soil, roots, debris, and stones were removed in the wet condition. The wet soil was then oven dried at 105 °C until the soil was totally dried. The dry soil was sieved through a #40 standard testing sieve (opening size of 0.425mm). This soil was mixing with Jumunjin sand to increase the hydraulic conductivity of the test soil, so that permeation tests could be performed within a reasonable period of time with an induced hydraulic gradient of 40-60. And for the adsorption purpose of the contaminants, humic soil was added to the mixing soils. Mixing soil was blended with Nanji-do soil, Jumunjin sand and humic soil by weight ratio of 2:6:1. Mixing soil has a cation exchange capacity of 25.1 meq/100 g,
and organic content of 6.7%, and a specific gravity ($G_s$) of 2.53. The test soil was classified as SP by Unified Classification System.

2.1.2 Contaminant
The p-Cresol was chosen for the research because it is generally considered as one of the recalcitrant halogenated aromatic compounds. It can be generally found in landfill and industrial wastes containing cresols are somewhat difficult to treat by biological methods [8]. It melts at 34.7°C and has a vapor pressure $1.10 \times 10^{-1}$ mmHg. Its solubility in water is about $2.15 \times 10^4$ mg/L and $K_{ow}$ is 1.94. It has purity greater than 99% and was purchased from Sigma Chemical Co. USA.

2.1.3 Desorbing Solutions (Decontaminants, Surfactants)
Commercially available two surfactants (anionic and nonionic) were selected as washing fluids for the contaminated mixing soil: (1) SDS (sodium dodecyl sulfate); (2) Triton X-100 (octylphenol polyoxyethylene). Table 1 shows the structures, molecular weights, and CMCs of the selected anionic SDS and nonionic TX-100 surfactants tested with various concentrations at their natural pH and room temperature (approximately 20 °C).

<table>
<thead>
<tr>
<th>Commercial Name</th>
<th>Surfactants</th>
<th>Structure</th>
<th>CMC (mM)</th>
<th>MW</th>
<th>HLB [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
<td>C$<em>{12}$H$</em>{25}$O$_2$SNa</td>
<td>8 [9]</td>
<td>288</td>
<td>N/A</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>POE(10)octylphenol</td>
<td>C$<em>{6}$PE$</em>{10}$</td>
<td>$1.7 \times 10^{-1}$ [3]</td>
<td>646</td>
<td>13.5</td>
</tr>
</tbody>
</table>

C : alkyl chain length (-CH$_2$)  P : phenol ring (-C$_6$H$_5$)  E : ethoxylate group  
MW : molecular weight  HLB : Hydrophile/Lipophile Balance  N/A : Not Available

2.2 Analysis method
The concentration of p-Cresol was analyzed by Gas Chromatography(6890 Series, Hewlett Packard Co. USA) with HP-5(capillary column coated with crosslinked 5% phenyl methyl siloxane, 320mm thickness, 30m length, 0.25mm diameter) and FID(flame ionization detector).

2.3 Test methods
To achieve the objectives of this study, the following tests were performed in the laboratory.
2.3.1 Batch sorption tests

Laboratory batch sorption tests were conducted to evaluate the sorption characteristics of the selected organic contaminant onto mixing soil. Batch adsorption tests included adsorption rate and adsorption isotherm tests. These tests were conducted on duplicate or triplicate samples to maintain the quality assurance of the tests.

Batch adsorption rate test was carried out to establish the equilibrium time required for adsorption of contaminant onto the mixing soil. The adsorption rate test for p-Cresol showed that adsorption equilibrium was achieved within 48 hours. Thus, 48-hour contact time was used for later successive reverse isotherm tests and in establishing adsorption equilibrium for preparation of desorption tests.

The adsorption isotherm test method for p-Cresol was as follows: 5g samples of mixing-soil were placed in the centrifuge tube (16×100mm Culture c-tube with teflon-faced cap, Wheaton Co., USA) and mixed with aqueous p-Cresol solution at various concentrations (5-100mg/L) with head space free. These tubes were stored in the thermohygrostat at 20±1°C on a rotary shaking position. After more than 48 hours contact time, mixture samples were centrifuged (Maraton® 8K, Fisher Scientific, USA), and the supernatant solution were taken in vial and analyzed by GC-FID.

2.3.2 Desorption kinetics studies by successive reverse isotherm (SRI) method

Desorption test was conducted to assess the effectiveness of the extraction solution for the contaminant with the potential desorbing solutions by simple contact shaking of the contaminated soil with an aqueous solution of the extracting agent. This test method is termed the SRI procedure [10]. In the SRI test, soil was mixed with contaminant solution (20mg/L). After 48 hours of contacting time, the contaminated soil was washed successively by agitation in the decontaminated solution for more than 30 minutes, centrifuging, decanting the supernatant solution, replacing the decanted solution with fresh decontaminant solution, and repeating the process several times until the contaminant could not be measured in the decanted supernatant solution. The cumulative weights of the desorbed contaminants, determined through gas chromatography, were added to obtain the total weight of contaminant removed. SRI tests were performed to allow a comparison between the washing of the contaminated soil with simple deionized water (DI water) and treatment by the various decontaminant solutions.

2.3.3 Flexible wall permeameter test

The modeling of in-situ flow of a decontaminating solution through a contaminated soil mass requires similitude of hydrological and geotechnical aspects of the sites such as fluid velocity, soil stress conditions etc. Such modeling was performed in this study by employing macrohomogeneous cylindrical compacted soil samples that were confined in flexible-wall permeameter. The soil samples were compacted by Harvard miniature compacter and tamping using pore water with a 100mg/L concentration of the organic contaminant. The test specimens had a coefficient of Darcian permeability, k of $10^{-6}$ cm/s and were tested under a hydraulic gradient of 50-60. Oven-dried mixing-soil was blended with the p-Cresol solutions (the
concentration of 100mg/L) at a moisture content of 16%, which is slightly higher than the optimum moisture content. The system consists of a flexible-wall permeameter, an influent reservoir called an accumulator, a buret to collect the effluent, and an air supply to provide pressure. Pressure is applied to the system with compressed nitrogen gas that passes through two manifolds and three pressure regulators before being applied to the permeant. Permeant liquid from the influent accumulator flows upward from the bottom of the soil specimen to the top to help in the removal of air bubbles from the soil pores. The effluent line carries the permeant liquid to the buret, which is also used to measure the flow volume. The confining cell pressure of 0.7 kg/cm² (10psi) is representative of an element of submerged soil at a depth of 2-4m.

3 Results and discussion

3.1 Adsorption isotherm tests

For p-Cresol, adsorption equilibrium was achieved within 48 hours. The amount of contaminant sorbed onto the mixing-soil after adsorption equilibrium was calculated. From the adsorption isotherm test the linear equilibrium partition coefficients $K_p$ values of p-Cresol was found 1.21.

3.2 Desorption tests

To evaluate the desorption of p-Cresol which sorbed onto the soil, desorption tests were conducted by solution with several surfactant concentrations. Figure 1 shows that the amount of desorption increased from 25% to 43% as the concentration of TX-100 increased from 0.05% to 0.1% (approximately from 5CMC to 10 CMC). But the desorption amount was from 56% to 60% in case of the concentration of TX-100 increasing from 1% to 2%, and this increasing rate was almost negligible. In case of SDS, 52% of p-Cresol was removed by 1% SDS(4CMC) solution, while DI water desorbed only 18% of p-Cresol.

![Figure 1: Desorption of p-Cresol with TX-100 and SDS](image-url)
In case of SDS, which is anionic surfactant, the CMC can be lowered by the addition of NaCl. Electrolyte ions stick to the surface of micelle so that the electric double layer is compressed [1]. Then the force of repulsion between surfactant ions is weakened and as a result micelle is stabilized and CMC is lowered. If 0.4M NaCl is added to SDS solution, the concentration of CMC formation changes from 8mM to 1mM. In this study 0.05M, 0.1M, 0.2M, 0.4M NaCl solution was added to 1 CMC SDS solution and a desorption experiment was conducted with each solution. The results are shown in Figure 2. Desorption was promoted by the addition of 0.4M NaCl solution from 41% to 50%. Up to 0.2M NaCl the improvement of desorption was proportional to the NaCl concentration. But the addition beyond 0.4M NaCl to 1CMC SDS solution, precipitation occurred after 2-3 weeks. It is assumed that the precipitation was due to the low solubility of the complexes formed by divalent cations and the anionic surfactant ions, that is Ca(DS)_2 [9].

![Figure 2: Effect of NaCl addition for p-Cresol desorption](image)

The results of the SRI (Successive Reverse Isotherm) test on the mixing soil contaminated with p-Cresol are shown in Figure 3 and 4. Figure 3 shows the desorption removal amount with TX-100 at various concentrations. On the successive desorption experiment with TX-100 solution, desorption amount was 56% after the first washing and 95% after the 7th washing. Figure 4 shows the results of SRI test with SDS 2% and DI water. In case of SDS 2% solution, desorption amount was 52% after the first washing and 91% after the 7th washing. When treated with water, desorption amount was only 18% by the first washing and 58% after the 7th washing. To investigate the mixing effect of anionic and nonionic surfactants, 2 CMC of each surfactant (TX-100: 2CMC=0.02%, SDS: 2CMC=0.5%) were mixed together. Figure 4 shows that 35% of p-Cresol was removed by the first washing and 86% by the 7th washing. This means that the
mixed system with anionic surfactant and nonionic surfactant improves the effect of desorption.

Figure 3: SRI test for p-Cresol with TX-100

Figure 4: SRI test for p-Cresol with SDS and TX-100

3.3 Results of desorption experiments with permeameter test

Flexible wall permeameter tests were conducted to simulate the desorption under the hydrogeological and stress conditions in situ. Figure 5 shows that 87% of p-Cresol was removed by 2% TX-100 in the permeation tests, which means TX-100 recovered 1.7 times better than DI water. Permeameter experiment with DI water shows that the recovery of p-Cresol was 18% when the hydraulic conductivity was $8 \times 10^{-6}$ cm/sec, but it was 51% when the hydraulic conductivity was $8 \times 10^{-7}$ cm/sec. This means that the contact time between soil and desorbing solution is very important factor when the desorbing solution flows through matrix of soil.
As seen on Figure 7, the total recovery was 75% in flexible-wall permeameter desorption experiment with 0.5% SDS solution. With 2% SDS solution, total recovery was 87% in the permeameter experiment. But in the permeameter experiment with SDS solution in Figure 6, the permeation coefficient declined to $1.5 \times 10^{-7}$ cm/sec and less as time passed. It can be considered that SDS has a strong dispersion effect that blocks the void by distributing soils [11]. Permeameter and SRI test results are summarized in Figure 7. As you can see in this figure, water desorbed only 50% of the p-Cresol, while surfactant solution removed up to 90% of the adsorbed p-Cresol onto soil.

![Figure 5: Permeameter test for p-Cresol](image1)

![Figure 6: Hydraulic conductivity in permeameter tests](image2)

### 4 Conclusions and further study

Following conclusions are drawn from the test results:

1. For TX-100, suitable concentration to recover the p-Cresol contaminated soil was found to be between 0.1% and 1% in the p-Cresol desorption experiment.
(2) For the effect of NaCl to enhance the decontamination of SDS, desorbing capacity changed from 41% to 50% when 0.4M NaCl was added to 1 CMC SDS solution in the batch SRI experiment.

(3) Washing with TX-100 2% solution was 1.7 times higher than washing with DI water in the desorption experiment of contaminated soil using flexible wall permeameter. Recovery in washing with 0.5% SDS solution was 75%, and 87% with SDS 2% solution. But as time passed by, the decline of the hydraulic conductivity coefficient was observed with SDS.

The task of extracting contaminants from contaminated soil is complex; however, the results of this study provide encouraging visions of how to remediate organic-contaminated soils in situ by aqueous solution extraction. Aqueous solution extraction produced physically by applying induced hydraulic gradient can be a promising technique for soil remediation. This method has some limitations and problems. The most serious problem is the secondary contamination by the aqueous solution itself. But this problem can be reduced if biodegradable solutions are used. Further study is necessary for this part of the application.
References


