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LABORATORY EVALUATION OF MIXED SURFACTANTS SOLUTIONS TO MOBILISE HEXACHLOROCYCLOHEXANE (DNAPL) FROM SARDAS LANDFILL (ARAGÓN, SPAIN)

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Abstract

A laboratory study was conducted to evaluate the suitability of a mixed surfactant solution for removal DNAPL of hexachlorocyclohexane (HCH) and different organochlorinated compounds from a landfill site at Sardas (Aragón, Spain). The commercial surfactants (ionic and nonionic) used for making mixed surfactant solutions were Sorbitan monooleate (Span 80), Polyoxyethylene (20) sorbitan monooleate (Tween 80), Octoxinol (Triton X-100), Dioctyl sodium sulfosuccinate (Aerosol OT), Dihexyl sodium sulfosuccinate (Aerosol MA80), Envirosurf and Envirosurf CC. Based on the properties (hydrophilic/lipophilic balance and emulsifying capacity) of individual and mixed surfactants, the preferred composition for an aqueous mixed surfactant solution was Span 80 (65%) - Tween 80 (35%). The HLB (Hydrophilic-Lipophilic Balance) for HCH DNAPL was calculated and corresponds to a value of 8.0 (lipophilic compound). The emulsion stability tests have shown that mobilisation of free product through micellar solubilisation (stable emulsion) was higher with mix surfactants than with individual surfactants. In addition, we concluded that the best surfactant composition candidates to mobilise HCH DNAPL (higher emulsifying capacity and absence of free product) were Envirosurf CC, Aerosol OT (25%) - Triton X-100 (75%); Span 80 (65%) - Tween 80 (35%). Bath experiments have shown that the sequence of DNAPL removal efficiency was Span 80 (65%) - Tween 80 (35%) > Envirosurf CC and Aerosol OT (25%) - Triton X-100 (75%) > water. The ability of aqueous surfactant solutions to recover DNAPL leachate entrapped in silica soil matrix was evaluated in column experiments. The column studies involved the injection of: a) 5% solution of (Span 80 (65%) – Tween 80 (35%); b) 5% solution of Aerosol OT (25%)-Triton X-100 (75%); c) clean water (Control). Treatment with Aerosol OT (25%)-Triton X-100 (75%) showed high washing efficiency (water solubilisation) after passing 5 volumes of solution though the column. On the other hand, treatment with the surfactant mixture Span 80 (65%) – Tween 80 (35%) mobilise DNAPL in a highly stable emulsion form (micellar solubilisation), although free phase removal was not as effective. Micellar solubilisation of organochlorinated DNAPL is the chosen recovery system for the test trial to be carried out at the Sardas landfill. The tests have revealed a reduction on the DNAPL removal in fine-grained soils. The potential for displacement of HCH DNAPL in natural conditions may be limited due to the presence of high content of silt and clay; therefore, this is a key factor to consider for aquifer remediation. The aim of this study is to choose the best surfactant solution and dosage (concentration and volumes) to develop a field trial test in Sardas landfill.

Key Words
Contaminated site, DNAPL, Emulsifier, Groundwater, HCH, DNAPL, Sardas Landfill, Surfactant.

Materials and methods

Sampling

Soil samples from the unsaturated zone nearby the Sardas landfill were collected including brown silt and marly clays. The two different soil types were mixed (50% each) and physical and chemical properties were determined. Samples of contaminated groundwater (borehole S-37) from the landfill and tap water were collected and chemical properties were determined. DNAPL was collected from the settling tank installed on the landfill site and analysed ate the lab in Bailin. The most common DNAPL compounds are chlorobenzene (21%), Total HCH (17,8%), hexachlorccyclohexane (7,3 %), dichlorobenzene (6,41%), pentachlorocyclohexane (5,8 %), trichlorobenzene (4,8%) and tetrachlorobenzene (3,8%) and benzene (1,2 %).

Surfactant selection

A previous bibliographic study was carried out to select suitable surfactants for DNAPL clean up among different commercial brands according to key characteristics including solubility, emulsification, critical micelle concentration (CMC) and effects on soil dispersion. The following surfactants (ionic and nonionic) were used: Polyoxyethylene (20) sorbitan monooleate (Tween 80), sorbitan monooleate (Span 80), dihexyl sulfosuccinate (Aerosol MA80), dioctyl sulfosuccinate (Aerosol OT), Triton X-100, Envirosurf and Envirosurf-CC.. Tween 80 and Aerosol MA 80 were purchased form Sigma-Aldrich; Span 80 was obtained from Fluka Analytical, Triton X-100 was obtained from Alfa Aesar GmbH and Aerosol OT from Molekula. Envirosurf and Envirosurf CC were obtained from Envirotecnics Global Servicies. All surfactants purchased were laboratory grade. All aqueous solutions were prepared with deionised and distilled water. The properties of the surfactants used are shown in the Table 1.

Table 1. Properties of the test surfactants

Surfactant commercial name	Abbreviation	Surfactant type	HBL	Molecular Formula
Sorbitan monooleate	Span 80	Nonionic	4,3	$C_{24}H_{44}O_6$
Polyoxyethylene (20) sorbitan monooleate	Tween 80	Nonionic	15	$C_{32}H_{60}O_{10}$
Octoxinol	Triton X-100	Nonionic	13,5	$C_{16}H_{26}O_2$
Dioctyl sodium sulfosuccinate,	Aerosol OT	Anionic		$C_{20}H_{37}NaO_7S$
Dihexyl sodium sulfosuccinate	Aerosol MA80	Anionic		$C_{16}H_{29}NaO_7S$
Ethoxylated fatty alcohol Benzenesulfonic acid	Envirosurf	Nonionic	14	-
Ethoxylated fatty alcohol Benzenesulfonic acid	Envirosurf-CC	Nonionic	9,5	-

HLB determination
To determine the HLB (Hydrophilic-Lipophilic Balance) value for the DNAPL leachate, seven emulsions tests were prepared using different proportions of Sorbitan monooleate (Span 80) and Polyoxyethylene (20) sorbitan monooleate (Tween 80) proportion as shown in Table 2.

Glass bottles (250 ml) were prepared, adding 5 ml of DNAPL leachate, 200 ml of tap water from the site and 5,0 ml of emulsifier solution. The glass bottles were stirred at 50 r.p.m for 1 hour at room temperature. HLB was determined comparing solution stability after leaving to settle for 24 hour.

Table 2. Determination of HLB requirement

HLB	Sorbitan monooleate (Span80)	Polioxietilen 20 sorbitan monooleate (Tween80)
4	100%	0%
6	83%	17%
8	65%	35%
10	46%	54%
12	28%	72%
14	8%	91%
15	0%	100%

Figure 1. Series of jars of nonionic surfactant blends used in the HLB determination

Emulsion stability experiments
Emulsion stability experiments were performed in order to determine the best surfactant composition candidate to mobilize DNAPL. Glass bottles (250 ml) were prepared, adding 5 ml of DNAPL leachate, 200 ml of tap water from the site and 5,0 ml of emulsifier solution (see Table 3). The glass bottles were stirred at 50 r.p.m during 1 hour at room temperature. HLB was determined by solution stability after settling for 24 hours.

Table 3. Emulsion Stability Test

Number	Surfactant 1	%	Surfactant 2	%
1	Aerosol OT	100		
2	Aerosol MA80	100		
3	Triton X-100	100		
4	Envirosurf	100		

Number	Surfactant 1	%	Surfactant 2	%
5	Envirosurf-CC	100		
6	Aerosol OT	50	Triton X-100	50
7	Aerosol MA80	50	Triton X-100	50
8	Triton X-100	25	Span 80	75
9	Aerosol OT	75	Triton X-100	25
10	Aerosol OT	25	Triton X-100	75
11	Aerosol MA80	75	Triton X-100	25
12	Aerosol MA80	25	Triton X-100	75
13	Span 80	65	Tween 80	35

Batch experiments
Batch test were conducted using 350 ml glass bottles, where 100 g of silica sand (20-30–mesh size fraction) or soil from the site previously passed through a 2,0 mm (10-mesh) sieve was added, with 5 g of DNAPL leachate and 300 ml of surfactant solution. The glass bottles were stirred on a rotary stirrer for 3 hours at room temperature. After leaving to settle for 24 hours, the supernatant was decanted and analysed for DNAPL concentration, and then the amount of DNAPL extracted was calculated. From to the previous experimental results (HLB determination and the emulsion stability test), the following surfactant formulations were used in the batch experiments: (1): Span 80 (65%) – Tween 80 (35%); (2) Aerosol OT (25%)-Triton X-100 (75%); (3) Envirosurf CC (100%).

Column experiments
Soil column experiments were conducted to measure the capacity of 5% (w/w) mixed surfactant solutions (Span 80 (65%) – Tween 80 (35%) and Aerosol OT (25%)-Triton X-100 (75%)) to recover DNAPL leachate from calibrated sand.

The experiments were carried out in glass columns (90 mm diameter, 400 mm high, glass thickness 3,3 mm) with a filter disc (Duran- Porosity 0; 160-250 µm) at the bottom. Three soil columns (2 treatments, 1 Control) were packed with 2000 g of nonporous, 20-30–mesh size fraction silica sand acting as a solid matrix. The sand was rinsed with deionised water before use. The soil columns were saturated by adding of 1000 ml of contaminated groundwater from the Sardas landfill (borehole S-37). DNAPL leachate (100 g) was added to the columns to reach an initial concentration of 50.000 mg/kg (DNAPL/soil).

The water level in the columns was kept constant (water saturation conditions) by adding surfactant solution (Treatment 1 and 2) or clean water (Control) at a rate of 3,5 ml/min with a peristaltic pump (inlet) and pumping out the effluent at the same flow-rate (outlet). The effluent was collected and analysed by GC-MS. Soil samples were collected (three samples per column) at the end for lindane analysis. Tests were performed at room temperature (22^{o}C).

The experimental work was conducted at the Environtecnics Laboratory (Girona, Spain) and analytical determinations were carried out at the SARGA laboratory (Bailín, Spain) using internal methods.

Results and discussion

HLB determination

Prior to surfactant tests, the HLB requirements of the HCH leachate were determined. Different HLB solutions were prepared (from 4 to 15), adding purified water, DNAPL and HLB solutions, and were shaken for 1 hour. The results after leaving to settle for 24 hours showed good emulsion stability in HLB mixtures 6, 8 and 10. HLB mixtures 7 and 9 were prepared following the same experimental procedure to select the most stable emulsion. It was found that HCH leachate (mixture of chlorobenzene, dichlorbenzene, pentachlor cyclohexene and hexachlorocyclohexane) has an HLB value of 8,0.

Figure 2. Determination of the required HLB for HCH DNAPL

Emulsion stability experiments

Emulsion stability experiments were conducted using different types of surfactant (ionic and nonionic) and surfactant mixtures with contaminated water from the site amended with DNAPL to a final concentration of 0,25%. The most stable mixture from the HLB determination (Span 80 -65%- + Tween 80 – 35%) was also tested (Table 3, number 13). The solutions were gently mixed on a shaker at 50 r.p.m for 1 hour in a temperature-controlled room maintained at $23 \pm 0,1^{o}C$. The results were assessed following equilibration and settling for 24 hours.

The test resulted in the formation of a stable emulsion when nonionic surfactants were used, except for Triton X-100 which gave a brownish solution with a high HCH concentration. Additionally, the solutions were tested for the absence or presence of organochlorinated mixture as a free product (DNAPL) at the bottom of the glass flasks.

The best surfactant composition candidates to mobilize DNAPL (higher emulsifying capacity and absence of free product) were Envirosurf CC, Aerosol OT (25%) + Triton X-100 (75%); Span 80 (65%) + Tween 80 (35%).

Batch experiments

Batch experiments were conducted using the best surfactant candidates from the emulsion stability tests, modifying surfactant concentration (0%, 2,5% and 5,0%), solid matrix (natural soil and silica sand) and aqueous phase (deionised water and groundwater contaminated from S-37).

The properties of surfactants used (surface tension, HLB, solubility) and environmental characteristics (soil properties, sorption of surfactants on soils, temperature and flow velocity of the surfactant solution) impacted on the effectiveness of the removal efficiency of DNAPL in soil.

Free lindane showed up in glomerular form in the silica soil matrix in control samples (without surfactant solution). In natural soil, lindane is sorbed by the silt and clay and is not visible in the soil matrix. The batch tests also revealed that higher surfactant concentrations were required when natural soil was used as compared to silica soil. We can conclude that silt and clay content in natural soil may represent a key limiting factor in the effectiveness of the lindane removal process.

During the batch testss we observed that the surfactant solutions with the highest emulsion capacity were Span 80 (65%) - Tween 80 (35%), followed by Envirosurf CC and Aerosol OT (25%) - Triton X-100 (75%). We will confirm these observations after reception and study of analytical results from the aqueous samples. Although Aerosol OT (25%) - Triton X-100 (75%) didn't show DNAPL mobilisation through the formation of a stable emulsion, we believe this particular surfactant mixture could be highly efficient when the decontamination method of choice is dilution in the aqueous phase.

Column experiments

Columns experiments were conducted to assess the effect of adding different surfactant solutions to mobilise DNAPL in water saturated conditions. Soil columns (silica soil matrix) contaminated with DNAPL were tested using 5% (w/w) of mixed surfactant solutions (Span 80 (65%) – Tween 80 (35%) and Aerosol OT (25%)-Triton X-100 (75%) and compared to a control column (clean water). The effluent throughout testing and soil samples resulting after the tests were monitored by GC-MS in order to compare the DNAPL removal efficiency.

Treatment with an Aerosol OT (25%)-Triton X-100 (75%) surfactant mixture showed a high washing efficiency after passing 5 volumes of solution though the column, as DNAPL could not be detected visually in the soil column. Effluent samples did not show evidence of an emulsion, leading to the conclusion that lindane had been removed through solubilisation in aqueous phase. The use of Span 80 (65%) – Tween 80 (35%) solution (nonionic surfactant mixture) to remove lindane was seen to be less effective as lindane drops were detected in the soil column. However, the effluent from this column was a stable emulsion. Studies are under progress to break up the emulsion for subsequent laboratory analysis.

Mobilization was shown to be an effective means of removing residual HCH from silica soil by using different surfactant mixtures. Based on the efficient recovery of HCH from the lab experiments, we considered the appropriate surfactant for the Surfactant Enhanced Aquifer Remediation (SEAR) in situ trial in the Sardas landfill, the surfactant solution Span 80 (65%) – Tween 80 (35%) at 5%. Further investigation of the de-emulsion process will be required to design properly the effective surfactant remediation strategy.

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