

REMOVAL OF PCBs FROM POLLUTED AND SPIKED SOILS AND SEDIMENTS USING SURFACTANTS

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EXTENDED ABSTRACT

Polychlorinated Biphenyls (PCBs) share with DDT the distinction of being among the first historically recognized persistent organic pollutants (POPs). Many of the same chemical and physical properties that had made them such desirable industrials, also made them one of the most widespread contaminants in the environment. This paper presents first results from a laboratory study for soil and sediment remediation from PCBs using surfactants.

Various types of soil/sediments were investigated: marine sediment from Thermaikos Gulf, riverine sediment from Axios river, agricultural soil from the area of Halastra and PCBs contaminated soil from an industrial area of Cyprus. The soil and sediment samples were spiked with a transformer oil acetone solution of known PCBs concentration. A gas chromatography analytical technique using Electron Capture Detection, (GC – ECD) has developed both for PCBs in transformer oil and sediments.

Batch experiments were carried out in order to investigate the parameters that affect the desorption behavior and remediation efficiency for spiked and historically polluted samples. Both anionic and nonionic surfactants such as Sodium Dodecyl Benzenesulfonate (SDBS), Polyoxyethylene (4) lauryl ether (Brij 30), Polyoxyethylene (23) lauryl ether (Brij 35), Polyoxyethylene sorbitan monolaurate (Tween 20) and Polyoxyethylene sorbitan monooleate (Tween 80) were examined.

The use of surfactants to enhance remediation efforts has been of considerable interest in recent years. Despite successful laboratory studies, several field demonstrations of surfactant flushing have illustrated potential problems: lower contaminant removal than anticipated and changes in the hydrogeological nature of the aquifer. These reasons predicate the investigation of both surfactant and contaminant nature. The results indicated that in historically polluted samples, the use of surfactants does not sufficiently remove PCBs. In these cases is necessary to enhance remediation efficiency.

Key words: desorption; PCBs; remediation; soil; sorption; surfactants

1. INTRODUCTION

Polychlorinated Biphenyls (PCBs) share with DDT the distinction of being among the first historically recognized persistent organic pollutants (POPs). Many of the same chemical and physical properties that had made them such desirable industrials, also made them one of the most widespread contaminants in the environment. A primary source is PCB-laden oil used in transformers and capacitors because of its excellent dielectric and fire-resistant properties. This oil has in some cases contaminated soil and groundwater with PCBs. PCBs are found as mixtures of chlorinated biphenyls having varying degrees of chlorination and are suspect carcinogens. Their use in most industrial applications has been banned since 1979 [2]. Because of the limitations of pump and treat remediation technology, attention is now focused on the feasibility of surfactant use to increase its efficiency. Surfactants have been studied for use in soil washing and enhanced oil recovery. Although similarities exist between the applications, there are significant differences in the objectives of the technologies and the limitations placed on surfactant use [1]. Surfactants are classified according to the nature of the hydrophilic portion of their molecule. The head group may carry a negative charge (anionic), a positive charge (cationic), both negative and positive charges (zwitterionic), or no charge (nonionic) [1].

A major goal in the in-situ cleanup of a contaminated site using aqueous surfactant solutions is to cause the surfactant solution to reach and permeate the contaminated zone. At actual field sites, getting the solution to permeate the contaminated zone can be a more difficult challenge because the medium is expected to be heterogeneous in composition and hydraulic properties [3]. The objective of this laboratory study was to assess the relative suitability of 5 commercial surfactants to wash PCBs from two grain size fractions (fine and coarse) of soil and sediment samples. Additionally, the difference between the behavior of spiked and old-contaminated samples with PCBs were investigated.

2. EXPERIMENTAL PROCEDURES

Materials. Two types of soils and sediments were investigated, spiked samples and already polluted with PCBs. The samples characterized as spiked were marine sediment from Thermaikos Gulf, river sediment from Axios and agricultural soil from Halastra. Already polluted with PCBs samples were obtained from an industrial area of Cyprus and they were characterized as historically polluted samples [14]. Both sediment and soil samples were air dried and sieved, using a standard mechanical shaker, to separate the fraction under 63 μm (fine fraction) and the fraction between 63 and 250 μm (coarse fraction).

Both anionic and nonionic surfactants were used like Sodium Docecyl Benzenesulfonate (SDBS), Polyoxyethylene (4) lauryl ether (Brij 30), Polyoxyethylene (23) lauryl ether (Brij 35), Polyoxyethylene sorbitan monolaurate (Tween 20) and Polyoxyethylene sorbitan monooleate (Tween 80). Some of surfactants properties are represented in Table 1 [4].

Table 1. Abbreviations and properties of the surfactants tested

Trade name or abbreviation	Chemical name	General Structure ²	Molecular weight
SDBS	sodium docecyl benzenesulfonate	C ₁₈ SO ₄ Na	
Brij 30 ¹	Polyoxyethylene (4) lauryl ether	C ₁₂ E ₄	362
Brij 35 ¹	Polyoxyethylene (23) lauryl ether	C ₁₂ E ₂₃	1198
Tween 20 ¹	Polyoxyethylene sorbitan monolaurate	C ₁₂₋₁₈ S ₆ E ₂₀	1225
Tween 80 ¹	Polyoxyethylene sorbitan monooleate	C ₁₈ S ₆ E ₂₀	1310

¹ Trade name; the corresponding chemical name and molecular weight are those of the major component.

² C_n represents a saturated or unsaturated hydrocarbon chain of length n; E_n is n repeating –CH₂CH₂O– groups; and S₆ is a sorbitan ring.

Spiking procedure. Dry soil and sediment samples were placed into glass vials and spiked with the spike solution obtained after the clean-up procedure as described in [9]. The solvent of the spike solution is acetone.

Washing procedure. Batch desorption experiments were conducted for PCBs washing from spiked samples. In each batch test, 1 g of soil and 20 ml of surfactant aqueous solution having concentration 0.5 % w/v were shaken for 12 hours. After shaking, samples were centrifuged at 4000 rpm for 10 min.

PCBs extraction. The wet solid phases were mixed with anhydrous Na₂SO₄ and PCBs were extracted with 3x25 ml of 25 % v/v acetone in hexane. The extraction was assisted by ultrasonication. The extracts were united and evaporated under vacuum till the volume of approximately 1 ml. This concentrate was passed through a column packed with 1 g of partially deactivated silica and alumina. The silica was heated at 180 °C for 24 hours and was deactivated with water (1 % H₂O w/w). The alumina was heated at 450 °C for 4 hours and was deactivated with water (10 % H₂O w/w). PCBs were eluted with 40 ml hexane that was concentrated to approximately 1 ml. This concentrate was filtered through 0,45 µm membrane and dried with anhydrous Na₂SO₄. The hexane was replaced by isooctane (1 ml) and internal standard PCB-209 was added.

PCBs analysis. A Hewlett Packard 5890 Series II GC equipped with an Electron Capture Detector was used for PCBs determination. PCBs were separated on a DB-5 fused silica column (50 m length, 0.32 mm i.d. and 0.17µm film thickness) connected with a precolumn (1 m length). The injection volume was 1 µl. The carrier gas was Nitrogen at a flow rate of 4 ml/min. A standard solution containing seven PCBs (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180) was used for system calibration. PCB-209 was used as internal standard added in both standards and samples. [7, 8, 9, 10, 11, 12, 13].

3. RESULTS AND DISCUSSION

Desorption of the PCBs from soil samples. Figure 1(a) shows a GC-ECD chromatogram of a 1 g soil sample extracted with acetone/hexane (a) without and (b) with washing with 0.5% w/v SDBS for 12 h. There seems a clear reduction of the PCBs content in the washed sample.

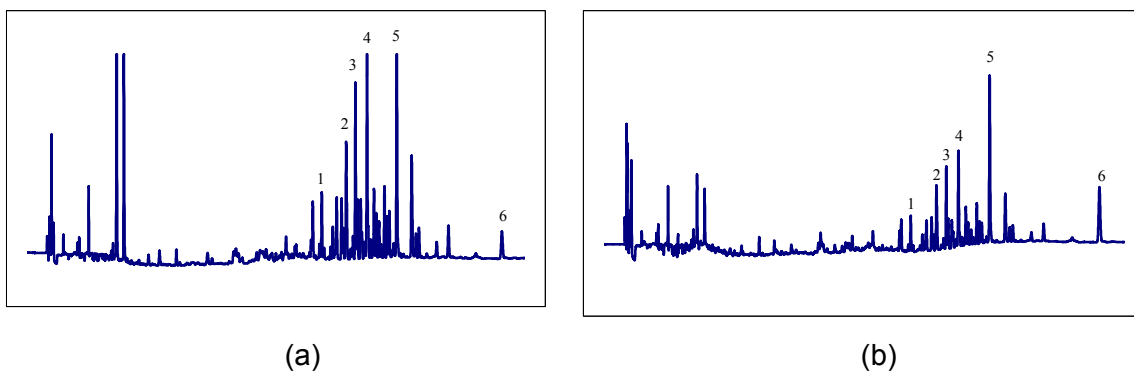


Figure 1: GC-ECD chromatogram of 1 g soil extract (a) before and (b) after 12 h washing with 0.5% w/v SDBS. (1: PCB-101, 2: PCB-118, 3: PCB-153, 4: PCB-138, 5: PCB-180 and 6: PCB-209)

On the contrary samples that had been polluted historically with PCBs since 2000, showed relatively small removal of PCBs after washing with surfactants as shown in Figure 2.

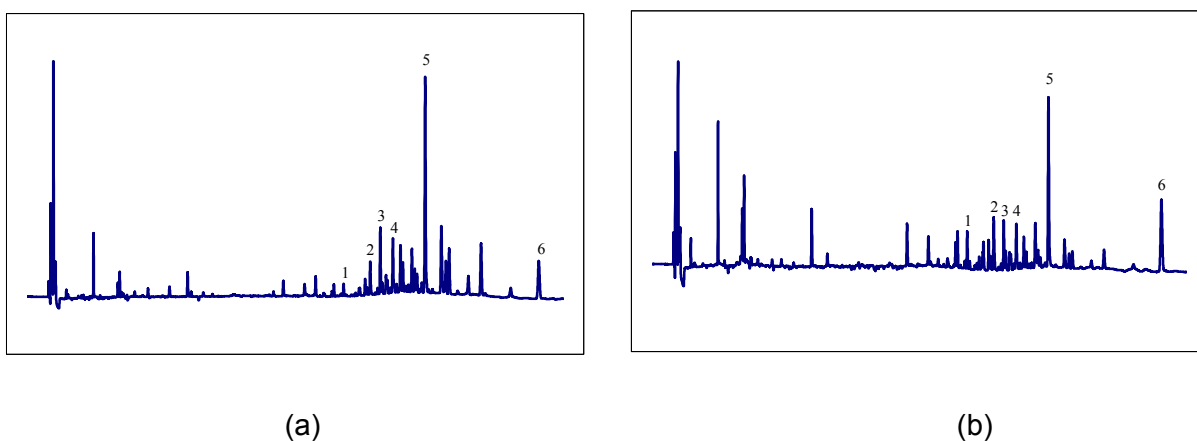


Figure 2: GC-ECD chromatogram of 1 g polluted soil (a) before and (b) after 12 h washing with 0.5% w/v SDBS. (1: PCB-101, 2: PCB-118, 3: PCB-153, 4: PCB-138, 5: PCB-180 and 6: PCB-209)

The PCBs removal obtained with different surfactants are shown in Figure 3.

SDBS appears to be more effective in PCBs removal for both spiked and historically polluted samples than any other surfactant.

4. CONCLUSIONS

A soil treatability study was conducted using particle-size separation and soil washing to reduce the volume of material contaminated with polychlorinated biphenyls (PCBs) at several sites like Halastra area, Axios river, Thermaikos Gulf and an industrial area of Cyprus. Soil washing using different kinds of surfactants concerning the charge (anionic and nonionic) was effective at removing in average 72% of total amount of PCBs into fine and coarse spiked material. Additionally at historically polluted soils the removal in average was less than 65% of total amount of PCBs into fine and coarse material. Results indicate that even though the soils samples were high-polluted (concentrations of PCBs over 1000 µg/kg) surfactants had high efficiency of removal without any addition of co-solvents. There were not any significant differences in the PCBs removal of fine or coarse fractions.

The main conclusion derived is that surfactants by themselves are effective only when the soil/sediment sample has polluted with PCBs recently. In historically polluted samples, the use of surfactants only does not sufficiently remove PCBs. In these cases is necessary to enhance remediation efficiency.

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