

Mobilization Assessment and Possibility of Increased Availability of PAHs in Contaminated Soil Using Column Tests

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Surfactants are well known to increase solubility/mobility of hydrocarbons and can be used to remediate contaminated water and soil. We wanted to explore if Ivey sol[®] 106 used at less than the critical micelle concentration (CMC) could effectively mobilize PAH (polycyclic aromatic hydrocarbons) from contaminated soil. The first step was to establish a measurement technique. Hence, a column leaching method was undertaken to investigate mobility of PAH-contaminated soil from a former gaswork facility. The methodology was based on a recycled flow of aqueous solution containing CaCl₂ 0.01M through two different soil columns. In the first column test, the free desorption of hydrocarbons was studied by recycling the solution through the soil column with a peristaltic pump and with a liquid/solid ratio of 2, based on ISO/DIS 18772. The solution was replaced with new solution every three days to aid desorption.

In the second column test, the set-up was similar with the exception of the aforementioned recycling solution. In this case, a second column was filled with a resin, Amberlite XAD-2, which captures PAHs entering the solution through the soil column, cleaning it of hydrocarbons (induced desorption). The results obtained for induced desorption and free desorption with reposition showed that liberation of PAHs in the presence of resins was higher (7%) as opposed to free desorption (below 0.3%). These two experiments demonstrated low mobilization of PAHs.

A third column test was performed using a non ionic surfactant, Ivey-sol[®] 106, 100 µg g⁻¹ of soil below the CMC in the recycling solution. The introduction of Ivey-sol[®] 106 at 0.005%w/v increased desorption of PAHs to 32%, thus demonstrating the potential for increased bioavailability of the PAHs for bioremediation of the soil.

Keywords Hydrocarbons, non-ionic surfactant, bioremediation

Introduction

Industrial activities have led to the deposition and discharge of a number of pollutants in soils. Many of these organic pollutants are persistent in contaminated sites. Among the most widespread, persistent organic pollutants are polycyclic aromatic hydrocarbons (PAHs), which originated from several pyrolysis processes. Due to the persistence of such compounds, the remediation of these sites is an important environmental issue.

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The high hydrophobicity of these compounds results in strong sorption to the soil matrix, hence reducing availability for microorganisms and limiting the rate of their biodegradation (Di Gennaro et al., 2008). Typically, it is assumed that the slow biodegradation of such compounds in soils is caused by the extremely slow desorption or dissolution rates of these hydrophobic organic contaminants. In other words, these hydrophobic organic compounds have low bioavailability for bacteria.

Several different approaches to determine desorption and leaching of hydrophobic organic compounds have been reported. Stirred aqueous batch tests can increase the desorption rate of contaminants. The introduction of a third phase as an adsorbent to the soil/water system is another method, but if it is done in a stirred reactor, over-estimations of desorption rate can take place. To overcome some of these drawbacks, mobility assessment can be determined with the use of column leaching methods (Enell et al., 2004).

Column leaching methods have been thought to be more realistic in simulating the leaching processes occurring in the field. Existing column leaching procedures for organic compounds are often modified standard leaching tests for inorganic compounds. Standard procedures for the determination of leaching of organic compounds from contaminated soil such as the German column leaching test DIN V 19736 (DIN, 1998) are commonly used. Research has been conducted on the PAHs solubilization, mobilization, and biodegradation based on column tests (Hack and Selenka, 1996; Tiehm et al., 1997; Berger et al., 2005).

The use of resins as adsorbents of a hydrophobic organic compound is a well-known practice (Yang et al., 2001; Dongye and Pignatello, 2004; Huesemann et al., 2000). Amberlite XAD-2 is a resin-type styrene-divinylbenzene, which has shown strong affinity to aromatic compounds. The introduction of this resin as a third phase provides an infinite sorption sink to maintain near-zero aqueous-phase PAH compound concentrations, in order to maximize the rate of PAH compound mass transfer out of soil particles (Lei et al., 2004).

Surfactant-enhanced ground water remediation and soil washing are technologies previously shown to enhance the removal of organic contaminants (Yeom et al., 1995). The use of surfactants should therefore be considered as a possible solution in an experimental and modelling study of washing organic contaminated soil (Mulligan et al., 2001). Liu et al. (1991) and Yeom et al. (1996) have previously demonstrated the use of anionic and non-ionic surfactants as washing solutions, resulting in increasing the PAH desorption rate and mass transfer from soil. The application of many types of surfactants on PAH has been reported (Zheng and Obbard, 2002; Zhou and Lizbong, 2007, 2008). Ivey-sol[®] 106 surfactant is a proprietary, non-ionic formulation that has been used successfully in various situations (Ivey and Craft, 2005; Ivey, 2006).

Volkerling et al. (1995) described using non-ionic surfactants for the solubilization of PAHs and demonstrated that if the substrate was in the micellar phase it was not available for degradation by microorganisms, thus causing inhibition. In a separate study by Laha and Luthy (1991), the use of non-ionic surfactants below the CMC demonstrated no inhibitory effects during biodegradation. These are two examples for specific analytes, surfactants, and microorganisms demonstrating the advantages of working below the CMC. Other advantages of working below surfactant CMC would include cost of remediation as well as compatibility with analytical testing procedures used to measure the effluent. In this study, we used an optimized formulation of Ivey-sol[®] 106 at 0.005%w/v below the CMC of 0.02%w/v (pure surfactant) to investigate its ability to mobilize PAH contamination. We used a column leaching method to measure mobility of PAHs from contaminated soil that originated from an old gaswork facility based on ISO 18772 (International Standard, 2008).

Comparative column free desorption, induced desorption (using resin Amberlite XAD-2), and surfactant desorption tests (using a non-ionic surfactant, Ivey-sol[®] 106), were studied with the objectives of evaluating the mobility of PAHs or quantification of the desorbable PAHs and the possibilities to increase desorption and bioavailability.

Materials and Methodology

Design of Column Leaching Tests

The method set-up is based on a recycled flow of an aqueous solution of CaCl₂ 0.01 M through three soil columns with different leaching procedures.

In the first column test, free desorption of hydrocarbons was studied by recycling the solution through the soil column with a peristaltic pump (Watson-Marlow) and with a Liquid:Solid ratio of 2 L/kg. The solution was replaced daily with a new solution during duration of test to aid desorption (Figure 1a).

In the second column test, the set-up is similar, with the exception of the previously used recycling solution. In this test, a second column was filled with resin Amberlite XAD-2 that captures PAHs, which enter the solution as it passes through the soil column and removes the hydrocarbons (induced desorption) from the soil (Figure 1b).

In the third column, the set-up was the same as with the free desorption, but the leaching media now contained a non-ionic surfactant formulation, Ivey-sol[®] 106 in an optimal concentration, that was determined by a previous stirred desorption test. This test was carried out, varying the Ivey-sol[®] 106 surfactant concentration in solution from 0–1000 $\mu\text{g g}^{-1}$ of soil (0–0.05%w/v). Samples of 2 g of soil were put in contact with 40 mL of Ivey-sol[®] 106 surfactant solutions in 50-mL Teflon-lined screw-cap glass centrifuge tubes and stirred. The test lasted four days. At the end of the test, samples were centrifuged, the supernatant solution was retired, and a new solution of only fresh water was introduced and

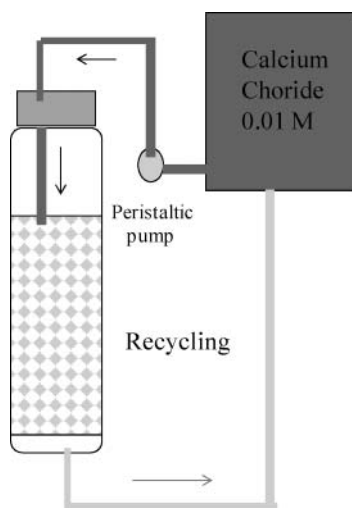


Figure 1a. Desorption in free column.

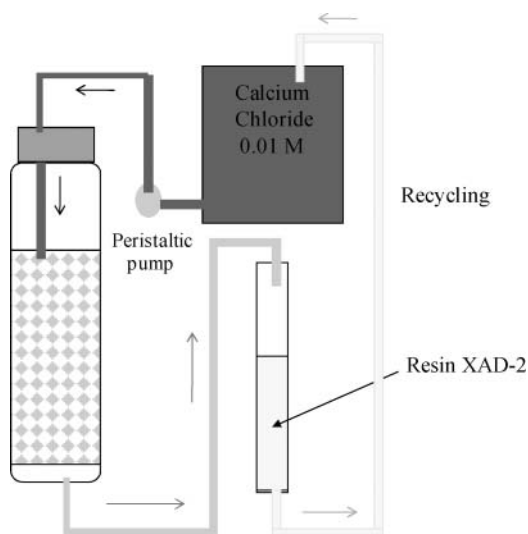


Figure 1b. Desorption in column with resin.

stirred over 24 hours. At the end of the test, the initial washing solutions were analyzed for PAHs to determine the optimal Ivey-sol[®] 106 surfactant concentration. The tests were performed in a thermostatic chamber at 25°C and under darkness. An additional desorption test was carried out using only water for comparison with the surfactant-aided desorption process.

In the surfactant desorption column test, two cycles of conducting included one leaching step (4 days of leaching) plus one washing step (4 days of washing). In the washing steps, the washing solution (aqueous solution of CaCl₂ 0.01 M) was changed daily.

The three soil-containing columns were identical, with their characteristics summarized in Table 1. The column containing the resin was smaller, with a diameter of 25 mm and a height of 40 cm. The quantity of resin Amberlite XAD-2 used was half of the soil sample, therefore the resin:soil weight ratio was 1:2.

Table 1
Column test conditions

Material of column	Glass
Diameter of column (mm)	75
Filling heights (cm)	35
Tubing materials	Viton
Flow rate (ml/min)	0.46
Test conditions	Room temperature
Leaching solution (mL)	500
Soil sample (g)	250
Duration of test (days)	16

Table 2

Main physical-chemical characteristics of soil samples. In Table 2, it takes in all values, the points corresponding to decimals.

Parameter		Value
Humidity	(%)	0.92
Water holding capacity	g H ₂ O 100 g ⁻¹	23.06
pH H ₂ O		8.3
Hydraulic conductivity	cm h ⁻¹	20.1
Porosity		0.46
Conductivity	μS cm ⁻¹	390
Carbon	Total C (%)	19.1
	Black C (%)	7.7
	Total Organic C (%)	5.7
	Total Inorganic C (%)	5.7
Nitrogen	(%)	0.35
Phosphorus	mg/Kg	210

Soil Sample

Contaminated soil samples were extracted from an old gaswork facility. For the column test, a size fraction of less than 4 mm was used. The soil was saturated into the column and a bulk density of 1.2 g/cm³ (porosity of 0.46) was achieved. The main physical-chemical characteristics of the soil prior to testing were performed following standard procedures (Gutián-Ojea and Carballas, 1976), with black carbon (Oen et al., 2006) and hydraulic conductivity applying (U.S. EPA Method 9100, 2008). These results are summarized in Table 2.

PAHs analyses were carried out by HPLC (high performance liquid chromatography) with a fluorescence detector. The conditions of the fluorescence detector and analytical procedure have been previously reported (García-Alonso et al., 2008). Briefly, solid samples were previously homogenized by grinding followed by extraction with methylene chloride and sonication. Extraction was carried out using sub-samples of 0.5 g and 20 mL of dichloromethane for 20 minutes twice to assure maximum extraction efficiency. Extracts were separated by centrifugation and then concentrated under nitrogen stream to adjust the final volume to 1 or 10 mL (acetonitrile) according to the level of concentration sample. An Agilent series 1200 chromatograph equipped with a C18 supelcosil thermostated column (250 × 4.6 mm) at 37°C and a series 1100 fluorescence detector were used for analysis. The operating conditions were gradient-mode starting with acetonitrile/water (45:55) at 1.5 mL.min⁻¹, programmed up to 100% of acetonitrile over 23 minutes, and holding for 10 minutes for column washing. The column was equilibrated for 6 minutes at the starting conditions prior to each injection. PAH concentrations of initial samples are displayed in Table 3.

Liquid Sampling Collecting

Samples of the supernatant and washing solutions in the tubes (desorption test), as well as leaching samples, were taken during the column tests. All samples were analyzed for PAHs

Table 3
PAHs content of initial soil sample

PAH	Content (mg/kg soil)
Fluorene	29
Phenanthrene	139
Anthracene	36
Fluoranthene	156
Pyrene	224
Benzoanthracene	66
Chrysene	69
Benzo(b)fluoranthene	61
Benzo(k)fluoranthene	38
Benzo(a)pyrene	58
Dibenzo (a,h)anthracene	8
Benzo (g,h,i)perylene	47
Σ PAHs	931

by HPLC solvent extraction with methylene chloride. During column tests, liquid samples were taken from the leaching media daily.

PAH Desorption Yield

PAH desorption yields were calculated based on analysis of final solid samples from columns after desorption tests, which are compared with the content of the initial sample, as described by the following equation:

$$\text{PAHs desorption (\%)} = [(I - F) * 100] / I$$

being

I: PAH concentration (mg kg^{-1}) in initial sample.

F: PAH concentration (mg kg^{-1}) in final solid residues from column desorption tests.

Results and Discussion

Surfactant Aided Desorption

Preliminary testing of the Ivey sol[®] 106 was required to obtain the optimized concentration for PAH desorption. The results obtained using a range of Ivey-sol[®] 106 surfactant concentrations by batch desorption test in tubes are represented in Figure 2. It was observed that PAH solubilization is diminishing at concentrations greater than $100 \mu\text{g g}^{-1}$ of soil. This may be explained by the surfactant approaching the effective critical micelle concentration. Taking into account these results, a concentration of $100 \mu\text{g g}^{-1}$ of soil was chosen as optimal and was applied in the leaching media for surfactant-aided desorption.

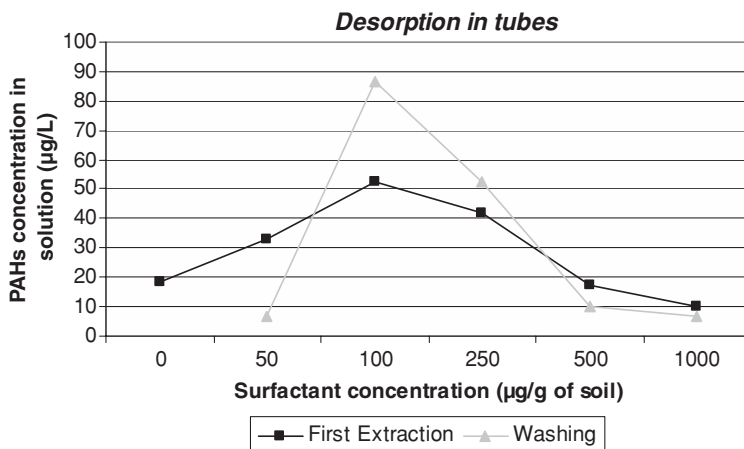


Figure 2. Optimization of dose of Ivey-sol[®] 106 surfactant by batch desorption in tubes.

Free and Induced Desorption

Figure 3 represents a graphical display of the results for each soil sample after free desorption, induced desorption, Ivey sol 106[®], and initial PAH measurements. This data was used in the equation previously mentioned, to calculate percent desorption, displayed in Figure 4.

Minimal desorption rates for individual PAHs were observed in the case of free desorption; only chrysene and benzo(k)fluoranthene showed significant mobility at approximately

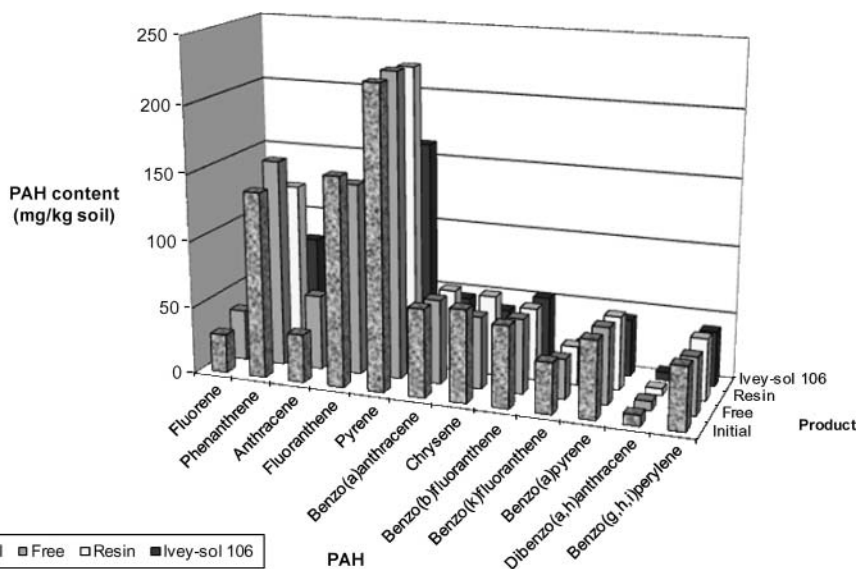


Figure 3. Comparative results of analysis of PAHs (final solids) for desorption column tests.

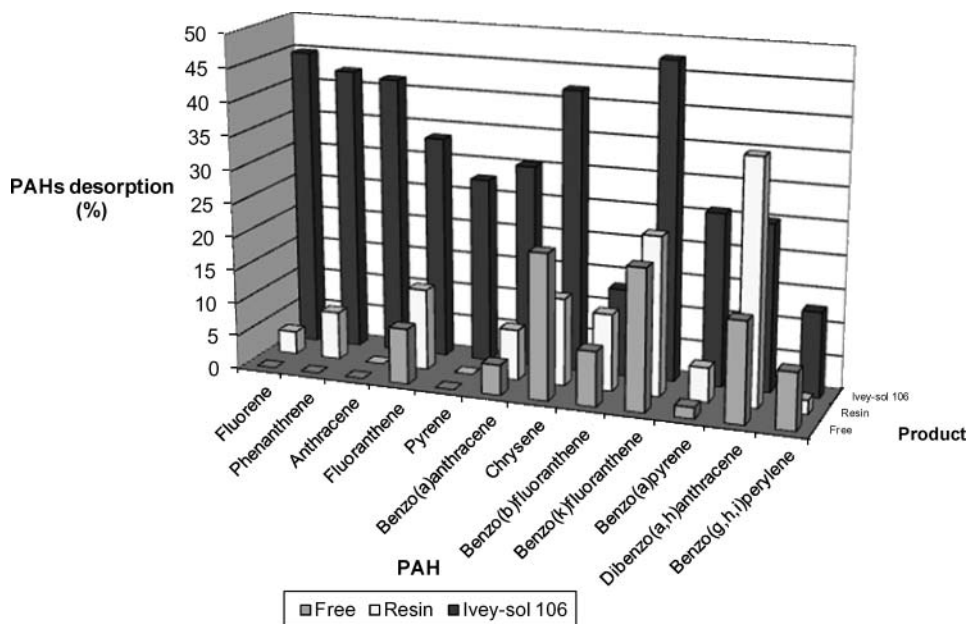


Figure 4. Comparative desorption (%) for PAHs in all tests.

20%. The desorbable fraction obtained with free desorption showed very low mobility (below 0.3%) of contaminants in this soil.

The desorption rates for individual PAHs obtained in the induced desorption test were higher than free desorption mainly for phenanthrene, fluoranthene, and dibenzo(a,h)anthracene. Although the desorbable fraction was increased, PAH mobility only increased a further 7%. This data is consistent with prior literature confirming the inefficient mobilization of these contaminants in soil (Hong et al., 2003; Johnsen et al., 2005). The result is very limited availability of PAHs and consequently unlikely positive remediation.

Figure 3 also contains the comparative results of analysis for PAHs (final solids) and for Ivey-sol[®] 106 surfactant desorption. Figure 4 displays desorption rates for all tests.

Figure 4 shows that surfactant-aided desorption clearly increased desorption yields for almost all PAHs. Specifically, anthracene and pyrene went from close to zero up to 42 and 27% desorption, respectively. The PAHs can be classified according to benzene ring number. When this ring number increases more difficult is to degrade the compound and consequently it is more persistent in environment. Grouping aromatic compounds by ring numbers, Figure 5 compares desorption of PAHs for all tests. These results show that there is a notable increase in all PAH desorption rates with respect to free and induced desorption (desorption being higher for 3- and 4-ring PAHs).

The sum of PAHs for initial conditions was $931 \mu\text{g}\cdot\text{g}^{-1}$, whereas soil, post-free, resin and surfactant treatment were $929 \mu\text{g}\cdot\text{g}^{-1}$, $869 \mu\text{g}\cdot\text{g}^{-1}$, and $632 \mu\text{g}\cdot\text{g}^{-1}$, respectively. These results indicate that free desorption was only 0.24% and induced desorption was 6.7%.

The use of Ivey-sol[®] 106 surfactant at 4 times below the CMC of 0.02%w/v resulted in a 32% desorption rate, thus significantly increasing the bioavailability.

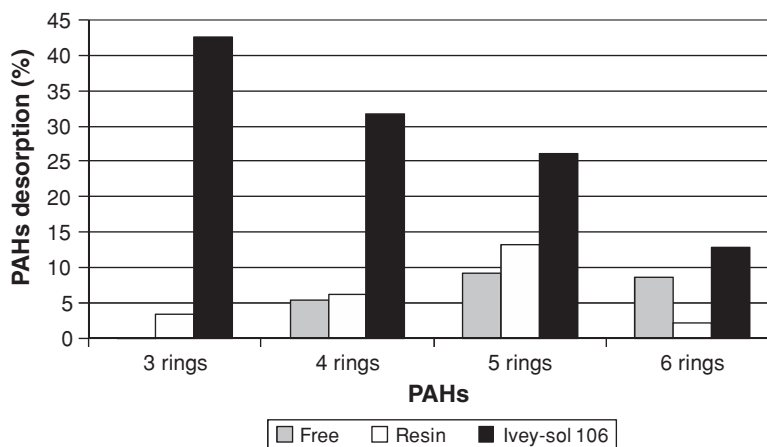


Figure 5. Comparative desorption (%) for PAHs grouping by ring numbers in all tests.

Conclusions

The column leaching method was an appropriate means to measure mobility of organic pollutants in soil. This methodology is also adequate to select optimal conditions to increase availability and consequently bioavailability of contaminants such as PAHs.

The use of this non-ionic surfactant Ivey-sol[®] 106 below the CMC increased desorption yield of t-PAHs by 32% compared to free and induced desorption techniques at 0.3 and 7%, respectively. This significant increase in PAH desorption yields for Ivey-sol[®] 106 make it promising for improving bioremediation of contaminated soil. Taking into account the results of the bioremediation tests of contaminated soil (in which the PAH contaminants are desorbed and made more bioavailable), it is possible to conclude that applying adequate conditions of humidity, nutrients, Ivey-sol[®] 106 surfactant, and aeration would improve the efficacy and enhance bioremediation processes. Future work will involve using this column method to optimize real-world testing of Ivey-sol[®] 106 surfactant in conjunction with bioremediation.

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