Cyclodextrin-extraction of soils for modelling bioavailability of contaminants

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Abstract

Aqueous cyclodextrin solutions were applied for the extraction of organic contaminants from soil to estimate their bioavailability. Cyclodextrin derivatives of high solubility and high solubilizing potential such as randomly methylated beta-cyclodextrin (RAMEB) and hydroxypropyl beta-cyclodextrin (HPBCD) were compared. These cyclodextrins can reduce the octanol-water partition coefficient of various organic contaminants.

Soils contaminated with hydrocarbons, like diesel oil and black oil (the distillation residue of raw oil) were extracted with aqueous cyclodextrin solutions to characterize the fractions solubilized by cyclodextrins. Gas chromatographic analysis of the extracts showed that the components in the lower molecular weight region are extracted by cyclodextrin solutions compared to the exhaustive extraction by organic solvents. It was a general observation that compounds in higher concentration and in a wider molecular weight region were extracted by RAMEB than by HPBCD.

The results of extraction were compared with those of several biological and ecotoxicological tests characterizing the bioavailability and biodegradability of the contaminants. A good correlation was obtained with the CD extracted hydrocarbon content and the results of the biotests.

Introduction

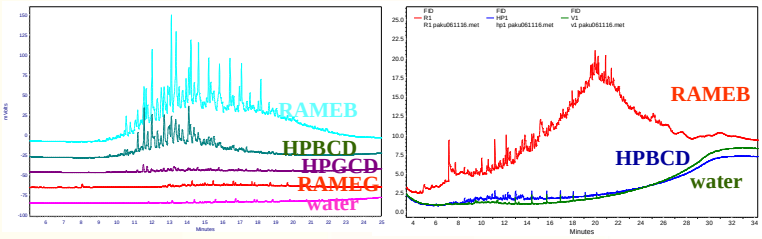
The success of bioremediation of contaminated soils is determined by the bioavailability of the contaminants. The compounds bound strongly to the soil are less available for the microbes. The usual chemical analysis based on exhaustive extraction by organic solvents gives information on the total contaminant content, while there is a great need for assessment of the biologically available fraction.

Reid *et al.* (2000) proposed the „non-exhaustive" extraction of soils contaminated with phenanthrene using aqueous HPBCD solution. The HPBCD extraction and microbial degradation of phenanthrene showed good correlation. The method was validated for various soils contaminated with various PAHs (Sabate *et al.* 2006, Stokes *et al.* 2005).

As cyclodextrins can form inclusion complexes with the petroleum hydrocarbon contaminants as well, we tried the cyclodextrin-extraction for some typical mixtures of petroleum hydrocarbons, such as diesel oil and black oil. Diesel oil is composed of mostly easily biodegradable linear and branched hydrocarbons, while black oil contains less biodegradable large molecules of complicated structure.

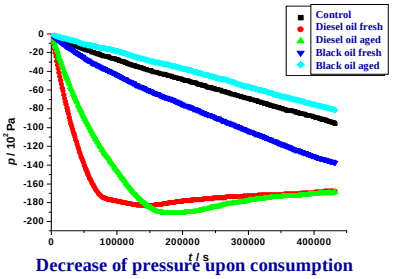
It was not clear from the literature why HPBCD was selected among cyclodextrins. We compared the extracting efficiency of HPBCD with that of RAMEB.

Dissolution of hydrocarbon mixtures in CD solutions



Chromatograms of diesel oil and black oil dissolved in aqueous CD solutions

Biological tests



Decrease of pressure upon consumption of O_2 during biodegradation of contaminants by the soil microbes in closed vessel (Oxy Top)

The rate of O_2 consumption is higher for the soil contaminated with easily biodegradable diesel oil than for the soil contaminated with black oil. The lower bioavailability of the aged contamination results in slower O_2 consumption.

Reduction of octanol/water partition coefficient

	Kow	
	Diesel oil	*Black oil*
Octanol/water	5.0	3.1
Octanol/10% HPBCD solution	4.3	2.3
Octanol/10% RAMEB solution	3.6	1.7

Extraction of soil

Contamination of soil	Extracted by hexane: acetone (2:1) EPH, mg/kg	Extracted by 10% RAMEB solution REH, mg/kg	Extracted by 10% HPBCD solution HEH, mg/kg	REH/EPH (%)	HEH/EPH (%)
Control	75	244	61	325	81.3
Diesel oil fresh	24835	8276	1405	33.3	5.7
Diesel oil aged	22872	7133	1155	31.2	5.1
Black oil fresh	38489	3518	325	9.1	0.8
Black oil aged	3661	1490	20	40.6	0.6

Contamination of soil	Aerobic heterotrophic cells	Oil degrading cells	Toxicity by *Folsomia candida* lethality test
	CFU *10⁶/g soil	*10⁴ cell/g soil	LD_{50} (g soil)
Control	298	0.93	
Diesel oil fresh	8831	210	1.64
Diesel oil aged	6048	2100	2.52
Black oil fresh	1263	93	2.93
Black oil aged	750	1.5	9.80

Experimental

Soils: forest soil was spiked with diesel oil and black oil to obtain freshly contaminated soil samples; the aged diesel oil-contaminated soil was spiked 2 months before the experiments; the soil samples contaminated with aged black oil were from a contaminated site in Budapest.

Extractions: soil samples were extracted by hexane-acetone (2:1) (5 g/ 20 ml) in ultrasonic bath for 2x10 min and measured by gas chromatography to get the total oil content (extractable petroleum hydrocarbon content –EPH) according to EPA SW-846 8270C (1996). Soil samples were extracted with 10% aqueous HPBCD or RAMEB solution (3 g/50 ml) in ultrasonic bath for 120 min, 40 ml of the extract was adsorbed on SPE (Isolute TPH), eluted by hexane and measured by gas chromatography to get HEH and REH, respectively.

Gas chromatography: Shimadzu 17A gas chromatograph equipped with HP-1 (13 m x 0,22 mm x 0,1 µm) column and FID detector was used with oven temperature of 60 ºC for 3 min, rising by 5 ºC/min till 300 ºC, hold for 10 min. The temperature of injector/detector was 280 ºC/320 ºC.

Soil respiration test was performed using Sensomat Oxy Top system.

Concentration of the aerobic heterotrophic cells was measure according to Hungarian Standard 21470/77, 1988.

Concentration of the oil-degrading cells was measured by the most probable number technique (Lorch *et al.*, 1995)

Toxicity test: *Folsomia candida* mortality test was performed according to ISO/FDIS 11267, 1998.

CONCLUSIONS

•More hydrocarbon contaminants can be dissolved and extracted from the soil by aqueous solution of RAMEB than of HPBCD.

•HPBCD dissolves and extracts from the soil the lower molecular weight compounds.

•The biological tests (O_2 consumption, cell concentrations, toxicity) show the higher bioavailability of diesel oil compared to black oil and of the fresh contamination compared to the aged one.

•The non-exhaustive extraction of contaminants by HPBCD relative to the exhaustive extraction by organic solvents show good correlation with the results of the biological tests

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