EXTRACTION OF PAHS AND PESTICIDES FROM CONTAMINATED SOILS WITH AQUEOUS CD SOLUTIONS

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ABSTRACT

A new method for the mobilization of organic pollutants from contaminated soils has been developed using aqueous CD solutions. The CD derivatives (methyl, hydroxypropyl, polymer) are able to desorb the lypophylic xenobiotics (pyrene, pentachlorophenol) sorbed on the particles of the soil and to solubilize these organics via inclusion complex formation and make them more accessible for the microorganisms. The CDs themselves do not pollute the environment being biodegradable.

1. INTRODUCTION

CDs have their potential in the reduction of environmental pollution, especially in waste water treatment [1]. Application of CDs in the decontamination of soils seems to be also promising [2].

Recently hydroxypropyl β–CD (HPBCD), was reported to enhance the transport of low-polarity organic compounds through soil [3]. It was found that HPBCD itself is not retarded by the soil, and it decreased the retardation of such compounds as anthracene, pyrene, and trichlorobiphenyl significantly.

The aim of the present work was to enhance the desorption of xenobiotics by aqueous CD solutions.

2. MATERIALS AND METHODS

2.1. Materials

Randomly methylated β–CD (RAMEB); *DS*=1.8 (Wacker Chemie GmbH, Munich), 2-hydroxypropyl β–CD (HPBCD); *DS*= 2.8 (Cyclolab, Budapest), β–CD polymer

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(BCDPS) 55 % CD content, M_W = 4300 (CYL-310, Cyclolab, Budapest), γ–CD polymer (GCDPS) 57 % CD content, M_W = 3800 (CYL-309, Cyclolab, Budapest)

DS= degree of substitution per glucose unit, M_W= weight average molecular weight, measured by gel chromatography on ACA 54 Ultrogel column

2.2. Methods

Desorption experiments were performed on the following way: soil samples (garden soil or clay) were polluted with 0.5 mg/g anthracene, 50.5 µg/g pyrene or 28.4 µg/g perylene or 2.28 mg/g mixture of polycyclic aromatic hydrocarbons (the composition of the mixture is given in Table I) by incubating the sample with a solution containing the pollutant(s) dissolved in heptane then the samples were dried on air for 3 days. 1 g of each sample was stirred with 10 mL solvent (heptane or ethanol or aqueous CD solution) for 15 min at room temperature using magnetic stirrer, then it was left to sediment. In case of individual hydrocarbon pollutants the supernatant was measured spectrophotometrically after filtration and in case of mixtures with HPLC (apparatus: Hewlett-Packard 1050, column: Nucleosil 5 C18 PAH, Macherey Nagel, mobile phase: acetonitrile-methanol-water 55:25:20, UV detection at λ=250 and 300 nm). The extracted pollutant was related to the initial pollutant concentration of the soil.

Table I Composition of the PAH mixture

PAH	1-methyl naphthalene	fluorene	anthracene	fluoranthene	pyrene	perylene	coronene
Conc. (mg/g)	0.56	0.6	0.55	0.14	0.27	0.09	0.07

3. RESULTS AND DISCUSSION

The aqueous solubility of naphthalene and anthracene is increased with increasing concentration of various CD derivatives [4,5]. On the basis of the solubility enhancing effect RAMEB, HPBCD, BCDPS and GCDPS were selected for the soil-extraction measurements.

Soil samples were polluted separately with anthracene or pyrene or perylene and extracted with aqueous CD solutions of 20 % content of the CD derivative.

Table II Pollutants extracted from soil in percent of the pollutant content before extraction

	Anthracene	Pyrene	Perylene
heptane	74	53	79
20 % RAMEB	72	87	32
20 % BCDPS	84	61	25
20% GCDPS	52	95	17
20 % HPBCD	68	65	10

RAMEB was almost as effective in extracting anthracene from soil as heptane, and BCDPS exceeded even the performance of heptane. In case of anthracene the effectivity of RAMEB and GCDPS are nearly double compared to that of heptane. All the studied CD derivatives showed low affinity toward perylene.

Soil samples contaminated with a mixture of PAHs were extracted with 5 - 20 % RAMEB or 96 % ethanol. The extraction efficiency for each of the 7 components increased with increasing RAMEB concentration (Table III). The effect of 10 % RAMEB exceeded that of ethanol in case of naphthalene, fluorene and anthracene. Fluoranthene was extracted with 15 % RAMEB as effectively as with ethanol. For the other three components even 20 % RAMEB could not reach the effectivity of ethanol.

Table III Extraction of soil samples contaminated with a 7 component-PAH mixture

solvent	1-methyl naphthalene (μg/ml)	fluorene (μg/ml)	anthracene (μg/ml)	fluoranthene (μg/ml)	pyrene (μg/ml)	perylene (μg/ml)	coronene (μg/ml)
100 %*	56.5	59.9	54.8	14.3	26.3	8.4	7.1
5% RAMEB	7.1	29.1	18.4	1.9	2.4	<0.5	0.7
10% RAMEB	10.0	44.1	27.6	7.3	13.2	0.6	0.9
15% RAMEB	11.6	50.2	33.2	9.40	21.0	1.0	1.2
20% RAMEB	12.1	50.2	32.0	10.0	23.4	1.5	1.3
ethanol	7.93	36.4	24.5	9.1	25.1	5.9	6.5

* calculated composition of the extract if all the pollutants had been removed

A clay sample contaminated with 0.53 mg/g pentachlorophenol (PCP) was extracted with water, ethanol and aqueous solutions of CD derivatives. The results expressed as percent of the input contaminant are listed in Table IV.

Table IV Pentachlorophenol extracted from clay

solvent	water	20 % RAMEB	20 % HPBCD	20 % GCDPS	ethanol
PCP (%)	37.7	45.3	71.7	54.7	50.9

In this case hydroxypropyl β–CD (HPBCD) was found to be superior to the studied solvents.

4. CONCLUSIONS

Organic contaminants such as lower PAHs and pentachlorophenol can be extracted from soils by aqueous solutions of different CD derivatives. The most effective CD derivative should be found to the target pollutant or a mixture should be used for this purpose.

In the practice the aim would not be the extraction, but the mobilization only of the PAHs and the other xenobiotics. By enhancing the desorption of these organic pollutants probably their microbial decomposition will be facilitated.

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