

Use of Cyclodextrins as An Environmentally Friendly Extracting Agent in Organic Aged-contaminated Soil Remediation

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Abstract

The removal of Polycyclic Aromatic Hydrocarbons (PAHs) from soil using pure water is quite ineffective due to their low aqueous solubility. Most of present processes are based on organic cosolvents or surfactants, leading to potential environmental hazard. Addition of cyclodextrin (CD) in aqueous washing solutions has been shown to increase the removal efficiency several times, while being non-toxic agents. Herein are investigated the effectiveness of cyclodextrins to remove PAHs occurring in industrially aged-contaminated soil. β -cyclodextrin (BCD), hydroxypropyl- β -cyclodextrin (HPCD) and methyl- β -cyclodextrin (MCD) solutions were used for soil flushing in column test or batch experiments to evaluate some influent parameters that can significantly increase the removal efficiency. The process parameters chosen were CD concentration, ratio of washing solution volume to soil weight, and temperature of washing solution. These parameters were found to have a significant and almost linear effect on PAHs removal from the contaminated soil, except the temperature where no significant enhancement in PAHs extraction was observed for temperature range from 5 to 35 °C. Removal capacity of HPCD and MCD was higher than BCD one. The PAHs extraction enhancement factor compared to water was about 200.

Introduction

Soil matrices contaminated with polycyclic aromatic hydrocarbons (PAHs) abound at the sites of coke-oven gas plants, refineries, and many other major chemical industries. Owing to the persistence of PAHs in soil and sediments and their toxic, mutagenic, and carcinogenic effects, the remediation of PAH-contaminated sites is an important environmental issue.

Sites contaminated by PAHs are widely spread across the world, and are mostly found in or near cities, thus representing a considerable public health hazard. Most of them are former manufactured gas plants (MGP), where PAHs are present as part of coal and oil tars. In the US, the USEPA estimate that there are about 30,000 to 45,000 of these sites [1]. Costs of treatment per site range between \$1 million and \$10s millions [2]. In France, PAHs pollution is present in 17% of contaminated sites [3]. In China some studies have been made and for example, in 10 rivers sediments of Tianjin, the total concentration of 16 PAHs varied

from 0.787 to 1.943 mg/kg dry weight. Coal combustion is suggested as a recent local source of PAHs in this area [4].

Several way of remediating soils contaminated by organic compounds are already used industrially, such as thermal desorption, incineration, venting or bio-remediation, which can be enhanced by using cyclodextrins [5–7]. This study is based on soil washing, which can be either an *in-situ* technique, such as pump-and-treat method, where liquid is injected in the soil and pump from the aquifer, or an *ex-situ* technique, where the soil is excavated and treated off-site.

Currently, soil washing techniques are mostly using co-solvents (methanol, ethanol...) or surfactants to achieve sufficient solubilization of hydrophobic compounds. But this can be a regulatory concern as those molecules can represent a health or environment hazard.

Attempts to increase the solubility of recalcitrant organic contaminants have been made using complexing agents which encapsulate poorly water soluble contaminants and thus may enhance their removal from polluted site. Cyclodextrins appear as a promising complexing agent to enhance organic compounds solubility [8–11], while minimizing environmental

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impact. Indeed, cyclodextrins are now commonly used in drug formulation, and thus, have been approved as a non-toxic compound [12] and also biodegradable [5, 13].

Previous works have focused on the cyclodextrin solubilization of individual compounds and often from lab-contaminated soil, whereas in real situations contaminated soil may contain aged mixtures of organic compounds [14, 15]. Furthermore, desorption from artificially contaminated soils is usually unrealistically high compared to desorption from weathered and aged coal tar-contaminated soil samples [16, 17].

Although CD can effectively remove organic pollutants from subsurface, more laboratory work is needed to understand the limitations of cyclodextrin-assisted remediation at high-scale. In particular, the type, the concentration of CD and the volume of flushing solution necessary to decontaminate some kilograms of polluted soil should be detailed.

In the present work, both column and batch extraction experiments were carried out to evaluate the ability of three types of cyclodextrins (β -cyclodextrin (BCD), hydroxypropyl- β -cyclodextrin (HPCD), methyl- β -cyclodextrin (MCD) to extract three selected PAHs from an industrially aged-contaminated soil.

Temperature can be a driving parameter to improve field performances of a washing process. Up to now, no reports have appeared concerning the temperature effect on CD washing process. In this paper, temperature effect on the contaminant flushing during the treatment of soils was investigated. Enhancement extraction of compounds from soil versus CD amount in flushing solution was also investigated, as well as protocol efficiencies.

Experimental

Chemicals

β -Cyclodextrin (BCD) was obtained from Roquette-Frères (France) and both hydroxypropyl- β -cyclodextrin (HPCD, degree of substitution: 0.8) and methyl- β -cyclodextrin (MCD, degree of substitution: 1.6–2.0) were supplied by Sigma-Aldrich. All CDs were used without further purification.

Soil characteristics

The soil used in this study was obtained from the site of a former manufacturing gas plant in the south of France. It was air-dried, crushed and passed through 2 mm sieve to remove coarse materials. The collected fraction (≤ 2 mm) represented about 70% of the sample. Its major characteristics are given in Table 1. Coal tars are by-products of the coal carbonization process and are often present as contaminants at the sites of coke production and manufactured gas plants [1]. Coal tar is

a denser than water, non-aqueous phase liquid (NAPL) composed of a complex mixture of organic compounds, including abundant polycyclic aromatic hydrocarbons as well as more volatile components such as benzene and alkylated benzenes [18]. The contamination of the studied site is about 30 years-old and is mostly present as NAPL. The total amount of PAHs regarded as the US EPA 16 list was about 655 mg kg^{-1} . PAHs background concentrations in soil were determined in triplicates. The reproducibility of measurement was excellent, informing of the good homogeneity of this soil. The soil was stored at 5°C . Detailed initial state of contamination is given in Table 2.

Analytical methods

During experiments, aqueous samples of washing solutions (about 0.5 mL) were analyzed, (without preparation), by reverse-phase chromatography using a Waters HPLC system (Waters LC-module 1, Waters pumps 600) equipped with a UV-visible detector (UV Autochrom 162 CSI) and a reverse-phase C-18 column (Supelcosil LC-PAH, 250 mm \times 4.6 mm i.d., 5 mm). The mobile phase was a mixture of water/acetonitrile (20:80,

Table 1. Physico-chemical characteristics of the investigated soil (≤ 2 mm fraction)

Water content	0.3%
Organic matter content	2.7%
TOC	0.77%
pH water	8.15
Clay	1.9%
Sand	94.4%
Silt	3.7%

Table 2. Initial concentration of the US EPA 16 PAHs in the studied soil. (triplicates, average of the 3 measurements)

PAH compound	mg kg ⁻¹ of dried soil
Naphthalene	4.4
Acenaphthylene	4.3
Acenaphthene	66
Fluorene	48
Phenanthrene	200
Anthracene	71
Fluoranthene	110
Pyrene	71
Benzo(a)anthracene	21
Chrysene	23
Benzo(b)fluoranthene	11
Benzo(k)fluoranthene	9.0
Benzo(a)pyrene	8.1
Indeno(1,2,3-c,d)pyrene	3.7
Dibenzo(a,h)anthracene	1.3
Benzo(g,h,i)perylene	3.9
Sum of US EPA 16 PAHs	655.2

v/v), with a flow rate of 1.0 mL min^{-1} . Wavelength used for detection was 254 nm. PAHs concentrations were quantified with an external standard method. Water used for solutions was purified by Milli-Q system (Millipore). Acetonitrile HPLC grade (99.99%) was provided by Fluka. Phenanthrene (PHE), anthracene (ANT) and pyrene (PYR), representative of 3-cycles-PAHs, have been chosen as targeted contaminants. The maximal uncertainty of the analytical methods obtained was estimated at about 5%.

Column and batch extraction experiments

Columns experiments were designed to prevent soil mobilization, to measure extraction equilibrium concentrations of contaminants in conditions close to a "pump and treat" process. The columns were purchased from Amersham Biosciences (Germany), glass-made (H: 400 mm, i.d.:26 mm), with two end plates designed to minimize void volume, protected by nylon membranes (pore diameter $10 \mu\text{m}$). All connections and tubing were made of PTFE. The columns were packed in incremental steps with 50 g of dry soil to establish uniform bulk density (about 7 cm height in the columns). One layer of glass beads were used to protect top and bottom nylon membrane from clogging. Columns are placed in a closed-loop circulation of washing solution, in an ascendant flow, with a buffer bottle of solution (typically, for Liquid to Solid ratio of 3, 150 mL of solution). Tracer tests have been conducted using KBr and an online conductivity sensor, and have shown that there are no preferential paths nor accumulation of tracer and that radial diffusion is quite limited (short tailing in tracer response curve).

After packing, experiments began without prior water saturation. For each experiments three columns were used, testing respectively a solution of BCD, HPCD and MCD, added with 0.01 M of CaCl_2 to adjust the ionic strength, and 400 mg L^{-1} of HgCl_2 to prevent microbiological degradation of pollutants and CDs [17]. Extracting solutions are slowly pumped with a Master-Flex peristaltic pump from the buffer bottle through the columns. Flow rate was set at 1 mL min^{-1} . The whole system was placed in a thermostatic room, and buffer bottles were protected from light by an aluminum sheet. Samples for PAHs analysis were collected from those bottles. Three temperatures have been studied (5, 20, $35 \text{ }^\circ\text{C}$) in a thermostatic room with the same concentration of CD, except for BCD which aqueous solubility dropped too low at $5 \text{ }^\circ\text{C}$ to be tested.

To study other types of soil washing processes that can be found on site (such as granulometric washing), batch experiments were also conducted. Vials containing soil and washing solution were placed in a rotary shaker for 48 h, therefore centrifuged and samples were collected in the supernatant phase then analyzed as presented before. This method implies a deconstruction of the soil, and so, a wider exchange area between pollution and the washing solution. To minimize the head

space, glass vials were chosen as close as possible to experimental volume determinate by chosen Liquid to Solid (L/S) ratio.

Results and discussion

Determination of steady-state at 3 temperatures

Batch experiments were conducted, using respectively BCD, HPCD and MCD as flushing agents, to determine the time needed to reach a steady-state and the apparent equilibrium PAHs concentrations. A L/S ratio of 3 was used. Results have shown that CD extraction process of PAHs from soil, as well as their complexation in water, can be considered as a fast process. Furthermore no mobilization peak was observed during the whole experiment (7 days).

The evolutions of extracted concentrations versus time were similar for all experiments, independently from temperature or CD type. Temperature is an important process parameter, so it is really noticeable that the extraction seems not very sensible to temperature variation ($5, 20$ and $35 \text{ }^\circ\text{C}$), as shown in Figure 1. For these three column experiments, time to reach a steady-state, and PAHs aqueous concentration remained relatively constant. This is very interesting for a possible industrial application because others methods (organic solvents, surfactants) present a clear decrease of efficiency with decreasing temperature [19].

As enhancement of aqueous solubility of PAHs is caused by the complexation reaction, this very low dependence to the temperature is probably due to the increase of PAHs aqueous solubility with temperature [20], counterbalanced by a destabilization of PAH/CD complexes. These complexes have a negative enthalpy of formation (about -4 kcal mol^{-1} for anthracene-BCD complex, [21]), and so, tend to be dissociated with the temperature increasing. These two opposite effects result in a relative insensibility of PAHs extraction with temperature variation (within the range of temperature studied), even if more work in this field is needed to confirm this behavior.

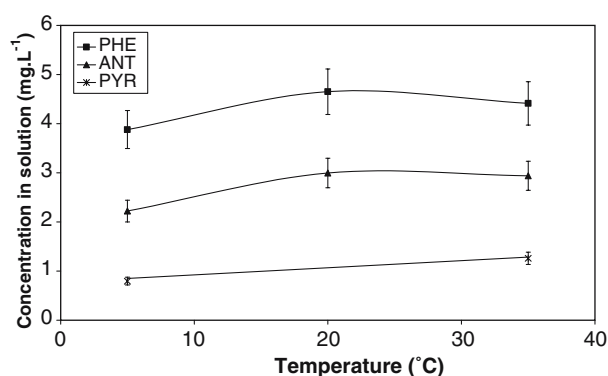


Figure 1. Equilibrium PAHs aqueous concentrations with HPCD (15 g L^{-1}) for different temperatures, L/S ratio of 3, column protocol.

Effect of CD concentration

CD concentration effect on PAHs extraction was studied within a CD aqueous concentration range of 10–100 g L⁻¹ with a L/S ratio of 2. BCD was excluded from those experiments due to its low aqueous solubility (18.6 g L⁻¹ at 20 °C).

In Figure 2, a quasi linear relation can be observed for PAHs release with CD concentration. It is necessary to quoted here that the apparent linearity observed is valuable in our own experimental conditions (soil and CD concentration from 10 to 100 g L⁻¹, i.e. 1–10 %w). Nevertheless, the apparent linearity of PAHs removal can be an interesting factor for industrial application, as it simplifies technical approach of the extraction process.

Effect of liquid to solid mass ratio

Experiments on L/S ratio were carried out to test BCD, which cannot be tested in a concentration range due to its low aqueous solubility. For column protocol, successive extractions were performed with the three types of cyclodextrin. Each column was circulated by a closed-loop flow of CD for 48 h then the solution was removed and replaced by a fresh one, with exactly the same characteristics, to wash the same sample of soil. As a consequence, volumes of extracting solution were cumulated so data is based on cumulated L/S ratio steps. Figure 3a shows the cumulated amount of PAHs extracted after each flushing step. L/S ratios flushing steps of 2 were used (50 g of soil and steps of 100 mL of solution), 5 extractions have been done.

Figure 3b represents L/S ratio experiments using batch protocol. In this case, actual quantities extracted from soil at different L/S ratio were tested instead of cumulated volume, and this leads to comparable results. Cumulated quantities of extracted PAHs (Figure 3a) or actual quantities (Figure 3b) seem to follow again a linear trend with the increase of washing solution used. This confirms previous experiments, because PAHs extracted quantities increased almost linearly with the overall quantity of CD used, whether this amount is provided by an increased concentration of CD at the same L/S ratio or increased L/S ratio.

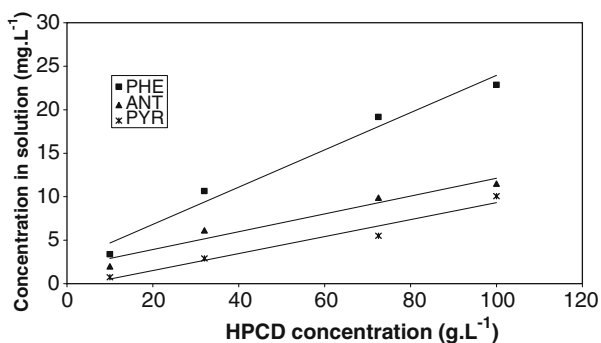


Figure 2. Equilibrium PAHs aqueous concentrations with HPCD at different concentrations, L/S ratio of 2, $T = 22$ °C, column protocol.

These experiments have also allowed to verify that BCD has the same extracting behavior than modified CDs even if its aqueous solubility is very limited. The specificity of this product is that PAHs aqueous concentration remained fairly constant at every flushing steps, whereas with HPCD and MCD, PAHs aqueous concentrations dropped slowly. This is probably mainly caused by the very low concentrations extracted by BCD opposed to quite large ones obtained with HPCD and MCD: there is maybe a depletion of the easily extractable fraction of PAHs.

A post-rinsing with pure water was done, and has shown that the pollutant is available after treatment. 0.31 mg L⁻¹ of phenanthrene and 0.20 mg L⁻¹ of anthracene were found in this water flush after MCD treatment, instead of 0.13 and 0.04 mg L⁻¹ respectively during a water flush done without prior treatment. This last point puts the emphasis on the necessity of a post-rinsing after a treatment with CD. Despite the fact that CDs are biodegradable and non-toxic, persistence of these compounds in the soil will make residual PAHs more mobile and bioavailable than before treatment, causing a probable dispersion of these contaminants.

Comparison between the removal efficiencies of three CDs

Prior to compare the removal efficiency of three types of CD, the concentrations of CD in flushing solutions were

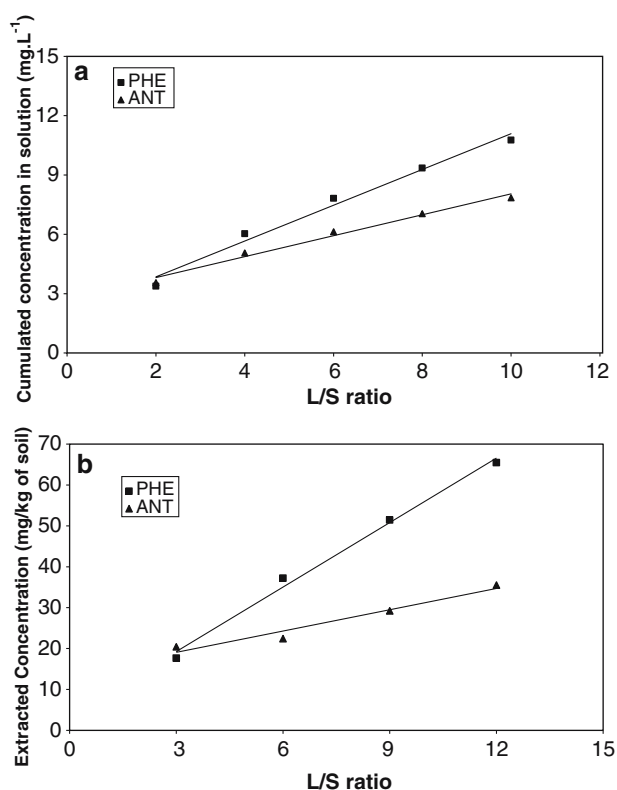


Figure 3. (a) Cumulated equilibrium aqueous concentrations for PHE and ANT with HPCD (10 g L⁻¹) at cumulated L/S ratios, $T = 22$ °C, column protocol. (b) Extracted concentrations from soil of PHE and ANT with MCD (15 g L⁻¹) different L/S ratio, $T = 22$ °C, batch protocol.

expressed in mmol by kg of dry soil. The removal percentage of PHE using three types of CD extracting solutions is reported in Figure 4. Data was extracted from both concentration and L/S ratio experiments, and confirmed the linearity observed for the variation of amount extracted versus CD quantity in flushing solution. Inspection of Figure 4 reveals that cyclodextrins are efficient agents to remove PAHs from soil and that the cleaning capacity increases quasi-linearly with CD concentration (within the range of concentration studied).

For both compounds, the removal efficiencies of CDs can be ranked in the following order : MCD > HPCD >> BCD. The modified CDs were more efficient than the BCD for PAHs removal. When MCD solution at 10% was used as a flushing agent, 31% of PHE and 43% of ANT recovery from soil were observed. Thus, methyl- β -cyclodextrin or hydroxypropyl- β -cyclodextrin could be more suitable for remediation of PAH-polluted soils.

Figure 5 shows a similar extraction behavior for both column and batch protocols, consequently destructure of soil did not influence washing mechanism. A slight efficiency difference (about 10%) was observed between these two protocols, a wider exchange area could explain batch better performances. Practically there is no drop in performance when using an in-situ technology.

Table 3 indicates the enhancement extraction factor of three PAHs by HPCD and MCD compared to water used alone. In column experiments, PAHs recovery from soil was improved by respectively a 160, 270 and 270 times factor for PHE, ANT and PYR, when using MCD flushing solution at 10%w as compared to a pure water flushing solution. Batch results are slightly better (less than 10%) for PHE and ANT.

Whatever CD used as flushing solution, removal percentages were ranked as followed: ANT > PHE > PYR. This ranking is based on the initial state of contamination, and is different from extracted concentration ranking (PHE > ANT > PYR), based on apparent aqueous concentrations of PAHs in presence of CDs for this soil.

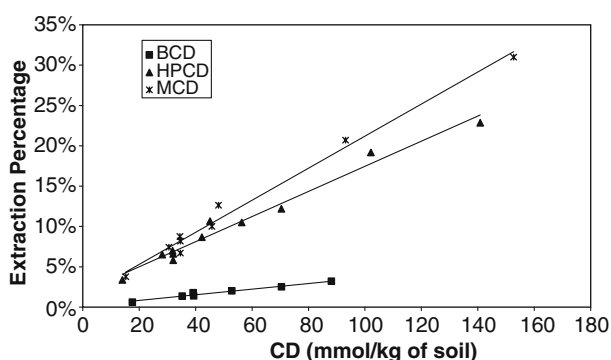


Figure 4. Efficiency comparison between cyclodextrins for PHE column extraction (percentage of recovery, $T = 22\text{ }^{\circ}\text{C}$).

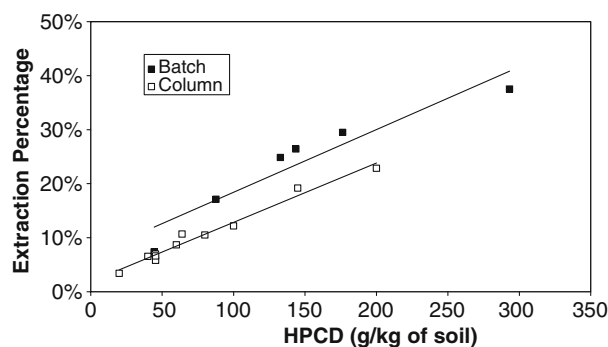


Figure 5. Efficiency comparison between batch and column protocol, for PHE extraction by HPCD (percentage of recovery, $T = 22\text{ }^{\circ}\text{C}$).

These results indicate that CDs showed a strong efficiency for PAHs solubilization and removal from soil. While surfactants may obtain comparable results, reduction of interfacial tension may cause partial mobilization of immiscible liquid [22, 23] and frequently emulsification that may increase solution viscosity [24, 25]. Furthermore there is no problem of minimal active concentration, contrary to surfactants critical micelle concentration [26]. Cosolvent flushing (e. g. ethanol/water) has also shown mobilization at the beginning of the treatment [23] and need a minimal concentration to have a significant solubilization effect [27]. All these phenomena were not observed for CDs during this study.

Conclusion

Results of this work show that CD has a great potential for PAHs extraction. The use of CDs as a solubility-enhancement agent is effective for PAH compounds on aged-contaminated soils. Kinetic studies have shown that PAHs solubilization by CDs is a fast process. On our soil, improvement of PAHs extraction was directly proportional to CD concentration in our experimental conditions. This linearity is observed whether CDs amounts are increased by higher concentration or higher volumes of solution.

A very interesting point of this study is the apparent temperature independence of the extraction between 5 and 35 $^{\circ}\text{C}$, which could be industrially decisive (almost constant efficiency with changing weather conditions).

Costs problematic has not been investigated in this paper but represents an important optimization parameter, as the cheapest form of cyclodextrin, BCD, is far less efficient than substituted ones (HPCD, MCD).

Table 3. Enhancement extraction factors compared to pure water for PHE, ANT and PYR with modified CDs in column experiments, at 10%w concentration

Type of CD	PHE	ANT	PYR
HPCD	120	210	210
MCD	160	270	270

These two derivatives have close performances and the choice between them should be greatly determined by their respective costs.

Based on published data, it would appear that CDs are becoming comparable in cost with surfactants but a detailed costs comparison between surfactants, organic cosolvents and CDs for polluted-site remediation has to be done. However, since the cost of CDs has continuously decreased in recent year, investigations regarding their technical merit for subsurface remediation are justified, as they represent an ecological alternative to classical washing agents.

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