

Enhanced solubilization and removal of naphthalene and phenanthrene by cyclodextrins from two contaminated soils

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Received 30 October 2003; received in revised form 20 April 2004; accepted 20 April 2004

Available online 19 June 2004

Abstract

The development of innovative methods for cleaning contaminated soils has emerged as a significant environmental priority. Herein, are investigated the effectiveness of cyclodextrin (CD) to solubilize and to extract organic pollutants from soils. The interactions in the cyclodextrin/pollutant/soil system have been studied “step by step” using two kinds of polycyclic aromatic hydrocarbons (PAH), naphthalene (Nap) and phenanthrene (Phe), cyclodextrins and soils. Inclusion complex formation of PAH with β -cyclodextrin (β -CD) and hydroxypropyl- β -cyclodextrin (HPCD) has been investigated and was proposed as a way to facilitate the pollutant removal from soil. Little effect of ionic strength was observed on CD complex formation for both compounds. The solubility of PAH in 50 g L⁻¹ of HPCD was enhanced 20- and 90-fold for naphthalene and phenanthrene, respectively. Batch experiments were performed to study the adsorption–desorption of two PAH on two soils and the influence of CDs over these processes. These experiments were also conducted with a mixture of two PAH. The batch desorption results indicate that removal capacity of HPCD was higher than that of β -CD. Phenanthrene was strongly sorbed on soils, this led to low desorption rates compared to that of naphthalene, whatever the extracting agent used. When HPCD solution was used as a flushing agent, 80% of naphthalene and 64% of phenanthrene recovery from soil were observed. For both compounds, the slowest desorption rate was found for the soil that had the greatest content of organic matter. CD sorption on soils, was relatively low and depended on soil type. The soil organic matter (SOM) could favor the retention of both CD and pollutant involving the extraction rate to be decreased. A competitive hydrophobic interactions of pollutant between SOM and CD molecules, and co-sorption were expected to be the mechanism for the inhibited desorption.

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Keywords: Naphthalene; Phenanthrene; Cyclodextrins (CDs); Solubilization; Soil organic matter (SOM); Desorption

1. Introduction

Hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAH) are of special interest because they are strongly sorbed to soils or sediments [1,2]. PAHs are receiving increasing attention because of their toxicity (highly carcinogenic) and their continuous release in the environment through human activities associated with combustion and petroleum production [3,4]. The contamination of soil and water by organic pollutants is a widespread environmental problem. Various physical, chemical, biological, and

their combined technologies have been attempted to remediate organic-contaminated soils [5–8]. The in situ microbial degradation of PAH is limited by their low bioavailability and low water-solubility [9]. Improvement of desorption efficiency from soils, mobility and bioavailability in the aqueous phase, of organic pollutants are essential to the remediation of contaminated soils and groundwater. In order to enhance the desorption rate of organic pollutants, various extracting agents have been used: solvent mixtures (ethanol/water, methanol/water, etc.) and surfactant foams such as Triton X-100 [10–12]. More recently, cyclodextrins (CDs) have been proposed as an alternative agent in order to enhance water solubility of hydrophobic compounds [13,14]. Cyclodextrins have a low-polarity cavity within which organic compounds of appropriate shape and size can form inclusion complexes [15]. This property provides CD a capacity

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to increase the apparent solubility of several hydrophobic pollutants such as PAH, chlorinated solvents, pesticides, and nitroaromatic compounds [16–22] and thus their availability for biodegradation [23,24]. Cyclodextrins present several advantages over solvents and non-ionic surfactants such as their lower toxicity and their higher biodegradability.

Moreover, surfactants may form high-viscosity emulsions that are difficult to remove [10,11]. The application of cyclodextrins in several soil remediation technologies has been increasingly studied, but little is known about the soil contents effects on their performance [25,26]. Recently, impact of soil clay content on CD enhanced remediation has been the focus in the study of Jozefaciuk et al. [25]. However, no reports have appeared concerning the soil organic matter effect on CD enhanced extraction process.

Observed solubility enhancements of organic pollutants by CDs in water and their desorption rate enhancements from soils could be closely related to the physico-chemical properties of pollutants, CD kinds, solution chemistry, and sorbent nature. The objective of this study is to examine more specifically the contribution of each factor using two kinds of PAH (naphthalene (Nap) and phenanthrene (Phe)), CDs and soils. The solubility of two aromatic pollutants in aqueous CD solutions was measured at various ionic strength conditions. On the other hand, batch experiments were performed to study the adsorption–desorption of these compounds on soils and the influence of CDs over these processes. These experiments were also conducted with a mixture of two PAH in order to test the efficiency of CD enhanced extraction in this case. Potential “loss” of CD due to soil sorption may significantly increase the cyclodextrin doses required to enhance site remediation. Besides, the adsorption of the decontaminant agent could lead to an increased adsorption of the contaminant and therefore, diminish the efficiency of the extracting reagents [27]. Checking this hypothesis on two soils containing different organic matter percentage was also the aim of this paper using a fluorimetry method to determine the CD concentrations. The performance of CD enhanced removal process of organic pollutants from soils is discussed.

2. Materials and methods

2.1. Chemicals and sorbents

β -Cyclodextrin (β -CD) and hydroxypropyl- β -cyclodextrin (HPCD) were obtained from Roquette–Freres (France). All CDs were used without further purification. The solubilities of natural CDs in water are different based on the number of glucose units (6, 7, or 8, respectively for α , β , or γ -CD). β -Cyclodextrin (1135 g mol^{-1}) is the least expensive, but unfortunately, has a limited water solubility (15.8 mmol L^{-1}). HPCD (1420 g mol^{-1}) are the modified CDs the most used and their water solubility are interesting.

Table 1
Physico-chemical properties of naphthalene and phenanthrene [13,14]

	M.W. (g mol^{-1})	Sw at 25 °C (mg L^{-1})	log K_{ow}	M.V. (nm^3)	H_c at 25 °C (atm m^3 mol L^{-1})
Naphthalene	128.17	34.4	3.37	0.232	$4.6 \cdot 10^{-4}$
Phenanthrene	178.23	1.00	4.46	0.310	$1.59 \cdot 10^{-1}$

Naphthalene and phenanthrene were provided from Sigma–Aldrich with a specified purity of 99%. Naphthalene and phenanthrene were chosen in this study for their varying physico-chemical properties and their widespread presence in contaminated sites [3,4]. Some of these properties are showed in Table 1. Sorbents used in this paper are natural soils sampled from La Côte Saint André, Isère, France, whose major characteristics are given in Table 2. The soils are called S1 (culture soil) and S2 (meadow soil). They were aseptically collected, transported to the laboratory in coolers, air-dried, crushed and passed through 2 mm sieve to remove surface plant remains and coarse materials. Numerous investigations have been done on these soils in our laboratory within this framework [28,29].

2.2. Analytical methods

For adsorption and desorption experiments, aqueous supernatants were analyzed by reverse-phase chromatography using a Waters HPLC system (Waters LC-module 1, Waters pumps 600) equipped with a UV–vis detector and a reverse-phase C-18 column ($250 \text{ mm} \times 4.6 \text{ mm i.d.}$, 5 mm). The mobile phase was a mixture of water/acetonitrile (20:80, v/v), with a flow rate of 1.0 mL min^{-1} . The wavelengths (nm) used for detection were 209 for Nap and 250 for Phe. The PAH concentrations were quantified with an external standard method.

Water used for solutions was purified by Milli-Q system (Millipore). The water contents in the used CDs were measured by TG analysis using a Setaram (Labsys) calorimeter. For solubilization experiments, UV–vis spectrophotometer (Perkin-Elmer) was used to follow PAH concentrations.

2.2.1. CD determination by fluorimetric method

This method is based on enhancement of fluorescence intensity of fluorescent probe: 2-(*p*-toluidino)

Table 2
Physico-chemical characteristics of two soils from La Côte Saint-André, Isère, France

Parameter	S1	S2
Sand (%)	39.8	40.9
Silt (%)	42.5	42
Clay (%)	17.7	17.1
OM (%)	2.0	5.0
CEC (meq/kg)	8.6	11
pH water	7.4	6.9

naphthalene-6-sulfonic acid (TNS). The sodium salt of TNS was purchased from Sigma. The TNS fluorescence increases rapidly when cyclodextrin is added to the aqueous solution.

For this aim, a TNS stock solution was prepared and protected from light since TNS is a photosensitive molecule. Aliquots of 5 mL of the TNS solution were pipetted into 10 mL calibrated flasks and diluted to volume with water or with CD solutions at suitable concentration. The solutions were then analyzed by a spectrofluorimeter (KONTRON, SFM 25). The enhancement of fluorescence intensity of TNS in aqueous solutions versus CD concentration led to elaborate the calibration curve [30,31]. This latter allowed to determine the unknown CD concentration in supernatants issued from adsorption experiments.

2.3. Solubilization experiments

For the solubility measurements, 30 mL of solution containing varying concentrations of CD were poured in 60 mL bottles and the solid compound was added in quantities in excess of the solubility limit. Triplicate tubes were prepared for each CD concentration. Blanks were prepared in an identical manner with the exception that no CD was added. All samples were equilibrated on a reciprocating shaker for at least 3 days in the dark. After equilibration, liquid samples were then extracted from the bottles by syringe and filtered through a 0.22 μm glass fiber filter to remove solid compound. An aliquot of the final filtered sample was withdrawn and diluted with 50:50 methanol/water solution in volumetric flasks. Samples were then analyzed by UV–vis spectrophotometry. The wavelengths used for UV detection of Nap and Phe were 250 and 270 nm, respectively. The role of methanol is to decompose the CD–solute complexes, thereby keeping the UV spectrum unchanged [16].

In order to study the ionic strength effect, the solubilization experiments for PAH were also carried out in pure water, 0.001, 0.01 and 0.1 mol L^{-1} of CaCl_2 aqueous solutions. The pH was checked along the experiments. All experiments were done at room temperature ($22 \pm 2^\circ\text{C}$).

2.4. Equilibrium sorption experiments

All equilibrium sorption experiments were conducted in triplicates, in 30 mL glass vials. The soil samples were mixed with variable PAH concentrations and the vials were sealed and shaken for 24 h in the dark, at constant temperature (22°C). HgCl_2 was added at a concentration of 400 mg L^{-1} to minimize bacterial growth and biodegradation during batch experiments. An incubation period of 24 h was chosen after a preliminary kinetic experiment was conducted for 72 h. For each batch experiment, blank samples were prepared and monitored (i.e. PAH solutions without sediment). The blank samples did not indicate any significant PAH degradation or sorptive losses on the glassware during the course of the experiment. The adsorption was conducted at a solid/liquid ratio of 1/3. Five grams

of soil and 15 mL of background solution were added to each flask. Before analysis, the samples were centrifuged at a constant temperature of 22°C at 3000 rpm for 30 min. The Nap and Phe concentrations in the supernatants were determined by HPLC. The same procedure of equilibrium sorption experiments was carried out to study the behavior of CD on soils. The CD concentration in supernatants was determined by fluorimetric technique as explained above.

2.5. Batch desorption experiments

Extraction experiments were initiated immediately after precedent sorption experiments. After reaching the equilibrium, the suspensions were extracted and the solid was recaptured for desorption experiments.

Once the supernatant was sampled, the remaining solution was removed with a pipette and discarded. The mass of each vial and its content was measured to determine the exact volume of the supernatant removed. The vials were then refilled with de-ionized water or CD solution ($\beta\text{-CD}$ or HPCD) containing 400 mg L^{-1} of HgCl_2 . The flasks were then shaken for 2 days at 22°C in the dark. The content of the flasks was then extracted and the supernatants sampled and analyzed by HPLC to quantify the PAH. After the successive desorption steps, solutions were decanted and the wet sediments left in the vials (actual amounts were determined by weighing).

3. Results and discussion

3.1. Phase solubility studies

The aqueous solubility of Nap and Phe measured in absence of CDs were, respectively, 1.3 and 31 mg L^{-1} which are in agreement with the solubility values reported in literature (Table 1). The relative solubility ($S_r = \text{apparent solubility/aqueous solubility}$) of Nap and Phe was significantly increased in the CDs solutions as shown in Figs. 1 and 2. This increase was linear with respect to CD concentration, and indicates the formation of 1:1 inclusion complexes [13]. The equilibrium constants of both compounds, obtained from linear regression, were also determined at different ionic strength conditions. The constant values reported in Table 3 are close to those found in literature HPCD ($K_{\text{HPCD}} = 700$

Table 3
Equilibrium constants (L mol^{-1}) for naphthalene and phenantrene complexes with CDs at various CaCl_2 concentrations (mol L^{-1})

	$K_{\beta\text{-CD}}$				K_{HPCD}			
	0	0.001	0.01	0.1	0	0.001	0.01	0.1
Naphthalene	471	482	478	520	611	590	610	630
Phenantrene	1226	1205	1220	1280	2749	2730	2766	2840

The error percentage was about 5%.

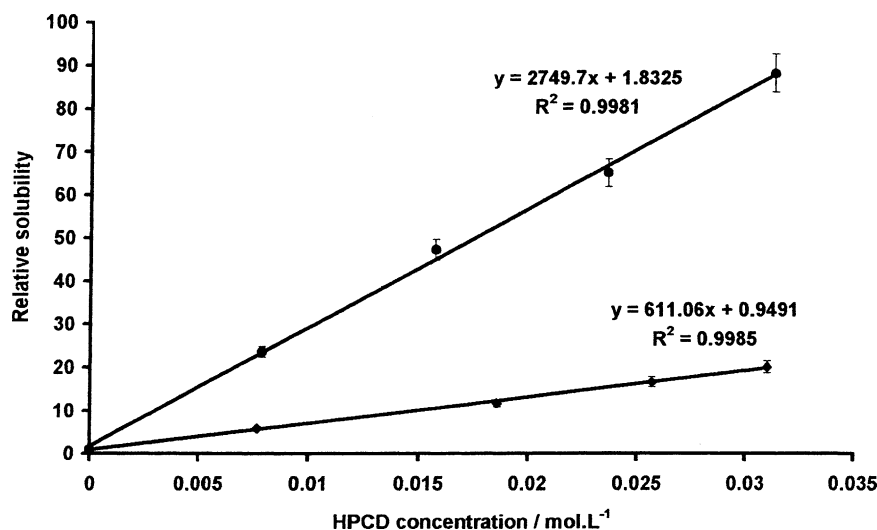


Fig. 1. Plot of the relative solubility vs. HPCD concentration for naphthalene (◆) and phenantrene (●).

and 3200 L mol⁻¹ for Nap and Phe in water, respectively [13,14].

Inspection of Table 3 reveals that the solubility enhancement of Phe was much greater than that of Nap. This is likely due to the greater hydrophobicity of Phe (Table 1), which favors its partition within the low-polar cavity of CD. This is in agreement with the results of Wang and Brusseau [13], where the solubilization of organic compounds in CD solutions was found to be octanol/water partition coefficient dependent. HPCD was found to be more effective to solubilize both compounds than β -CD at the same concentration. Moreover, the higher water solubility of HPCD allowed a greater solubilization of the compounds compared to that of β -CD. As example, the Nap and Phe solubilities increased 20 and 90-fold, respectively, at 50 g L⁻¹ of HPCD. However, a precipitation was observed in solute solutions at about

2 g L⁻¹ of β -CD concentration. This tends to limit the use of β -CD as an extracting agent. The formation of insoluble aggregates, due to low solubility of (β -CD, has been also observed by Hanna et al. [32] and Cao et al. [33].

Little increase in the apparent solubility of both compounds in CD solutions was observed with increasing CaCl₂ concentration (Figs. 3 and 4). K_{CD} values obtained are reported in Table 3. Varying ionic strength conditions exhibited little effect on the aqueous solubility of Nap and Phe and therefore their complex formation with CD, presumably because of the non-polar characteristics of pollutants. This is in agreement with the results of Whitehouse [34] where the aqueous solubilities of PAHs were found to be insensitive to small changes in salinity. At the opposite, in our previous work, the ionic strength significantly influenced the aqueous solubility of pentachlorophenol (weak acid) and

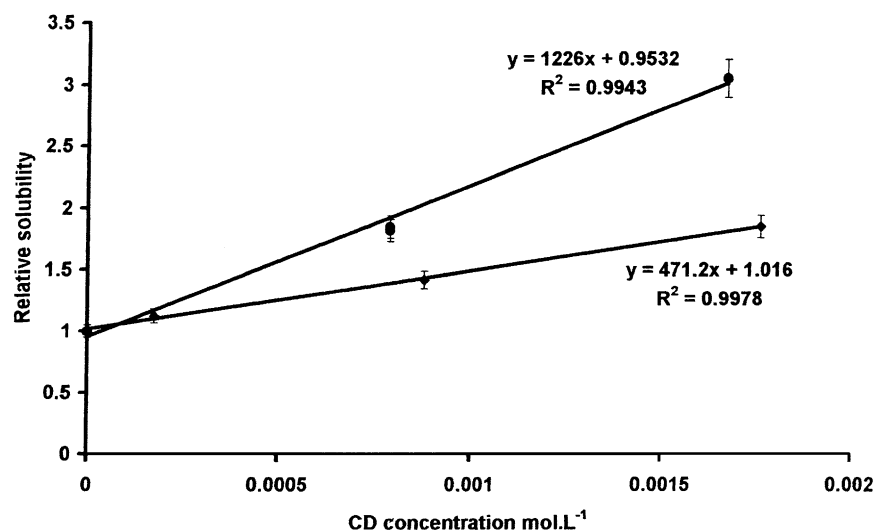


Fig. 2. Plot of the relative solubility vs. β -CD concentration for naphthalene (◆) and phenantrene (●).

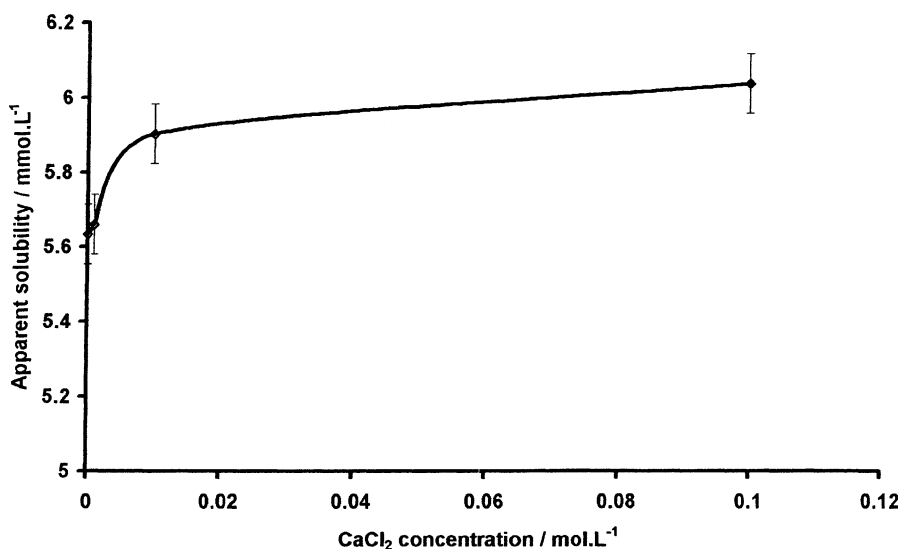


Fig. 3. Apparent solubility of Nap in HPCD solution (5%) vs. CaCl₂ concentration.

therefore, its complex formation with CDs [35]. The small increase in PAH–CD complexation with increasing ionic strength (Table 3) appears to be within statistical limits of the estimated 6% increase expected due to PAH “salting out” [36]. Similar results have been previously reported for PAHs partitioning to micelles formed by the non-ionic surfactant Tween 80 [36]. Wang and Brusseau [37] have reported that the presence of CaCl₂ has a negligible effect on the solubilization of anthracene by CD. They also affirmed that the solubilization capacity of CD for non-ionisable organic compounds is not affected by high concentrations of salts in the aqueous phase, because cations do not interact significantly with the low-polarity cavity of CD. In contrast, solution ionic strength played a major role in the partitioning of PAHs to SDS micelles (anionic surfactants), presumably because the micelle structure itself was changing [36].

3.2. Batch experiments

Adsorption isotherms were determined for Nap and Phe used separately and in mixture, on two types of soil (S1, S2), at 22 °C. They were obtained by plotting the amount of PAH adsorbed by the soil versus the respective concentration in equilibrium. The adsorption isotherms obtained are practically straight lines (two examples are shown in Figs. 5 and 6), so in this case it is appropriated to use the distribution coefficient (K_d) as a measurement of adsorption capacity of the soil. This coefficient represents the relationship between the amount of PAH adsorbed by the soil at equilibrium, and the equilibrium concentration in solution (Table 4). Adsorption rates of compound in mixture are lower than those of each compound used separately. In fact, when both pollutants are in contact with soil, a competition

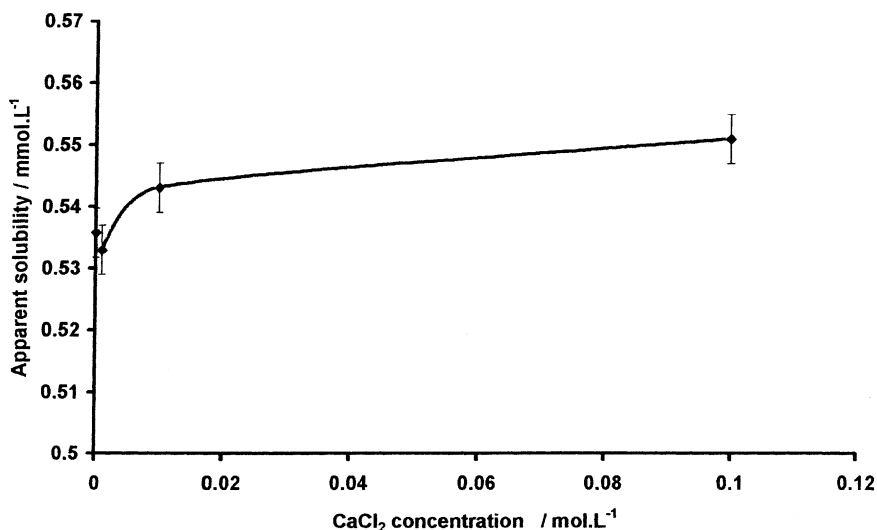


Fig. 4. Apparent solubility of Phe in HPCD solution (5%) vs. CaCl₂ concentration.

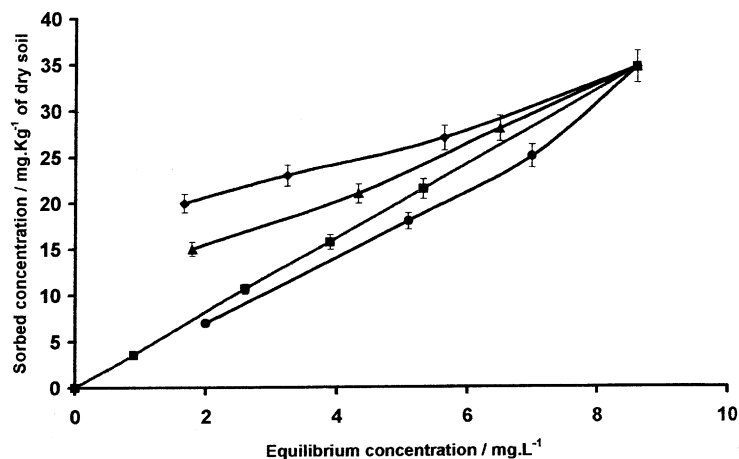


Fig. 5. Naphthalene adsorption (■) and desorption isotherms on S1 soil employing as desorbent (◆) deionized water (▲)β-CD solution (5 g L⁻¹) (●) HPCD solution (5 g L⁻¹).

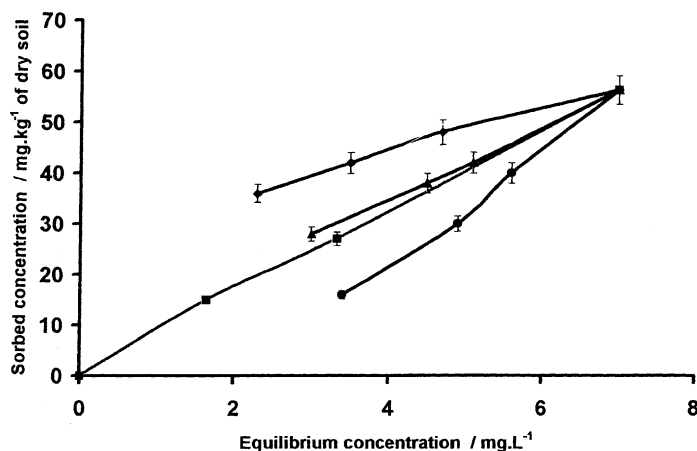


Fig. 6. Naphthalene adsorption (■) and desorption isotherms on S2 soil employing as desorbent (◆) deionized water (▲)β-CD solution (5 g L⁻¹) (●) HPCD solution (5 g L⁻¹).

is expected between them for sorption sites. In the sorption isotherms, the presence of Phe exhibited a significant sorption competition over Nap, regardless of the concentration. Figs. 5 and 6 show the Nap adsorption–desorption isotherms on S1 and S2, respectively. The desorption isotherms obtained show a hysteresis with respect to the adsorption one whatever extracting agent used. The same behavior was observed for Phe (data not shown). This phenomena was also observed with Perez-Martinez et al. [21] and Huang et al. [38]. Desorption of Nap and Phe using HPCD is more easy than (β-CD or deionized water). It is corroborated by Figs. 7 and 8, in which the percentages of PAHs desorbed with deionized water and CDs solutions are presented. The efficiency of CD extraction of pollutants decreases when two compounds are previously sorbed on soil indicating a competition occurred between the two compounds for the extracting agent. In this case, the fraction of desorbed pollutant was significantly increased as shown in Figs. 7 and 8.

Due to its higher hydrophobicity, Phe is strongly sorbed on both soils (Table 4), this leads to low desorption rates compared to that of Nap whatever the extracting agent used

(Figs. 7 and 8). For both compounds, S2 has a greater sorption capacity towards the hydrophobic compounds due to its relatively higher organic matter content [39–41]. This explains the lower release of pollutants from this soil (S2), whatever flushing solution used. This implies competitive hydrophobic interactions of contaminants between total soil organic matter and CD molecules.

The lower desorption on S2 may also be due, in part, to an adsorption of the CD molecules on this soil preferentially. This hypothesis has been verified by carrying out batch ad-

Table 4
 K_d values for naphthalene and phenantrene used separately and in mixture on S1 and S2 soils

	S1	S2
Naphthalene	4.0 ± 0.2	10.4 ± 0.5
Phenantrene	46.7 ± 2.3	74.4 ± 3.7
Naphthalene in mixture	3.1 ± 0.1	5.4 ± 0.3
Phenantrene in mixture	25.0 ± 1.3	31.1 ± 1.6

For sorption isotherms lines, $R^2 = 0.98$ – 0.99 .

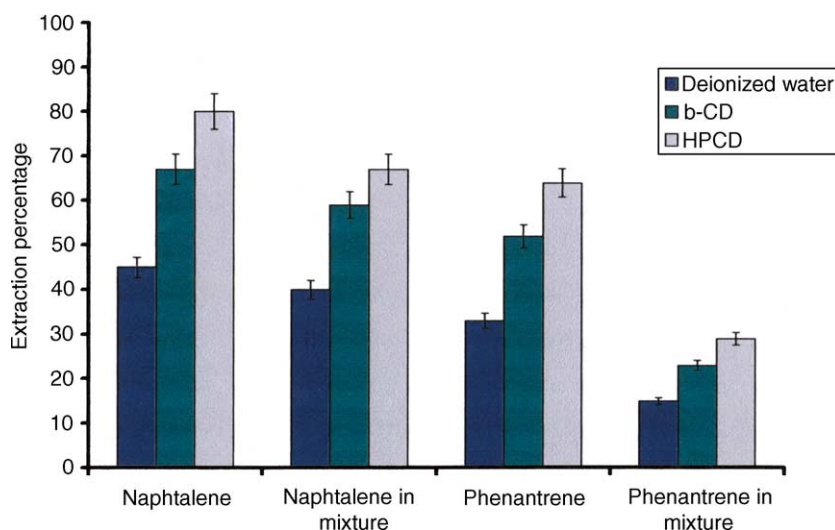


Fig. 7. Extraction percentages of pollutants from S1 using various flushing solutions.

sorption experiments of both CDs on S1 and S2. Results show that the affinity of CDs is relatively low for both soils and β -CD is more sorbed than HPCD (Fig. 9). This may stem from the low water solubility of β -CD (compared to HPCD) which may favor the interactions with soil organic matter (OM). The sorption of β -CD has been shown in several studies using as sorbent (soil: 25% slit and 1.4% OM) [21,42]. Other works shown that HPCD (that has negligible surface activity) was not significantly sorbed by kaolinite, illite or topsoil [14,22]. In recent studies, the sorption capacity of soils towards CD was found to be clay content dependent [25,26]. In this work, both S1 and S2 have the same clay content, but their organic matter content are clearly different (Table 2). Inspection of Fig. 9 reveal that both CDs are more sorbed on S2 (5% OM) than on S1 (2% OM). This affirms that the soil organic matter favors the CD sorption as

well as the retention of organic compounds. Because the soil sorption of organic contaminants is usually predominated by interactions with organic matter (f_{om}) [39–41], sorbed CD molecules which increase the effective f_{om} of the soil, could also increase contaminant sorption. Therefore, it may make less easy the contaminant release from soil and diminish the performance of CD enhanced removal process.

The sorption of CD by soils is much less than that of many surfactants [27]. This is beneficial for situations when strong decontaminate sorption by porous media is undesirable. CD is also non-toxic and biodegradable, thus posing no hazard to the ecosystem. As the application of CD to in situ soil bioremediation, could be suitable, we are looking to see whether increased percolation of complexed pollutants results in increased groundwater pollution and how this can be reduced.

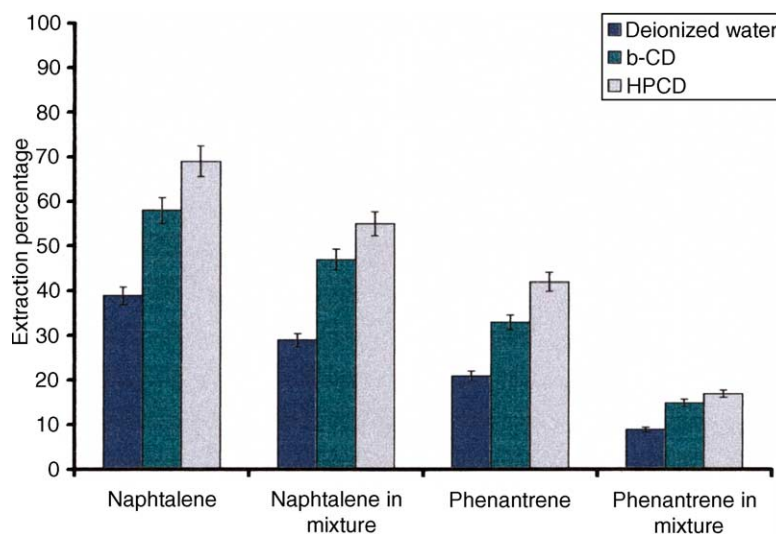


Fig. 8. Extraction percentages of pollutants from S2 using various flushing solutions.

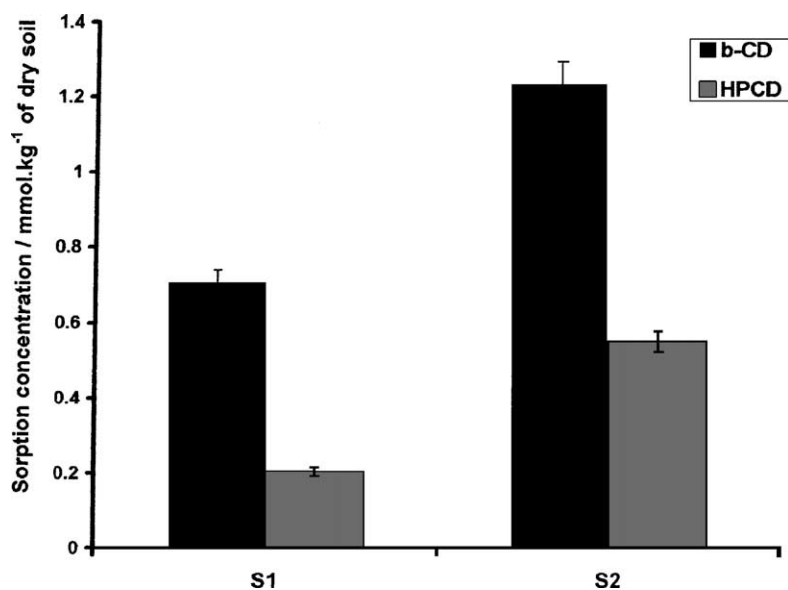


Fig. 9. Sorption concentrations (g kg^{-1} of dry soil) of β -CD and HPCD on S1 and S2.

4. Conclusion

Results of this paper affirm that CD complex formation has great utility as a rapid way of dissolving organic pollutants, making easier their removal from porous media. Overall process of site decontamination is found to be closely related to pollutant hydrophobicity, CD and soil types. The solubilization power of HPCD as well as its removal capacity from soil were greater than those of β -CD. The higher solubility of HPCD allowed a greater increase of the solute solubility in water. Varying ionic strength conditions exhibited little effect on the complex formation. It was also observed that the desorption rate of PAH compounds from soils depended on their hydrophobicity and on CD type. Low desorption rates were found for phenanthrene and especially on S2, whatever the extracting agent used. Desorption for both compounds was significantly inhibited for S2 that had the greatest content of organic matter (5% OM). SOM impacted desorption as evidenced by a 30% decrease in desorbed Phe fraction compared with when the soil only contained 2% OM (S1). In the case of Nap, the SOM caused a decrease of average 13% in desorbed fraction compared with S1. This could be explained by competitive hydrophobic interactions of pollutant between SOM and CD molecules. Thus, the soil organic matter content is an important element which can favor the sorption of both contaminant and decontaminant and therefore, affects the performance of cyclodextrin-aided pollutant remediation.

The solubilization power of CD is midway between that of miscible organic solvents and surfactants [11]. Nevertheless, CD may have several advantages over surfactants in practical uses as described above. Based on published data, it would appear that CDs are becoming comparable in cost with surfactants [43]. A detailed comparison on the costs

of surfactants and CDs for polluted-site remediation is not found in the literature. However, since the cost of CDs has continuously decreased in recent years [43], investigations regarding their technical merit for subsurface remediation are justified.

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