UVC photolysis of phenanthrene in cyclodextrin solutions generated from contaminated soil washing

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ABSTRACT

Ultraviolet-C (UVC; 254 nm) photolysis was applied to achieve simultaneous removal of phenanthrene and recovery of the extraction ability of cyclodextrin (CD) in soil washing solutions. β-cyclodextrin (β-CD) and hydroxypropyl-β-cyclodextrin (HPCD) were found to have comparable abilities to solubilize phenanthrene in aqueous solutions and extract phenanthrene from spiked agricultural soil or kaolinite. Only loosely bound phenanthrene is extractable to CDs, and approximately 30% of initially spiked phenanthrene is non-extractable. β-CD and HPCD showed comparable retardation effects on the UVC photolysis of phenanthrene, and HPCD was more persistent than β-CD during UVC photolysis of soil extraction solutions. After three extraction–UVC photolysis cycles, the extraction efficiency of the regenerated β-CD and HPCD solutions were 77% and 93% of the corresponding fresh CD solutions. In contrast, the apparent photolysis kinetic constant of phenanthrene in regenerated HPCD extraction solutions decreased significantly more than that in regenerated β-CD extraction solutions. 9,10-Phenanthrenequinone and its hydroxylation derivate, and three other oxygenated products were the detected intermediates that were generated during the UVC photolysis of phenanthrene, and CD or leached soil organic matter did not alter the degradation pathway. A combination of enhanced extraction and UVC photolysis is a promising method for treatment of extraction solutions from soil contaminated by phenanthrene or other polycyclic aromatic hydrocarbons.

Keywords: Cyclodextrin; Phenanthrene; Regeneration; Soil extraction; UVC photolysis

1. Introduction

Soil washing or flushing based technology was one of the most promising ways for soil remediation. Organic solvent, surfactant, or other solubilizer were added to enhance the removal efficiency of pollutants from the extraction solutions of contaminated soils [1–5]. Cyclodextrin (CD) and its derivates are typical host molecules that have been widely used in the removal of polycyclic aromatic hydrocarbons (PAHs) [6–8], polychlorinated biphenyls (PCBs) [9–11], pesticides [11], and non-aqueous phase liquids from contaminated soils [12–14]. These hydrophobic organic compounds (HOCs) are captured by the cavity in CD, resulting in the formation of a host–guest supermolecule in the washing or flushing solution. Post-treatment of the washing or flushing solution is necessary to eliminate pollutants and enable reuse of the washing or flushing agent.

Since washing/flushing agents are usually expensive, establishing novel methods for simultaneously achieving the elimination of pollutants and regenerating the washing agents with almost same extraction capacity is a subject of significant research interest. Existing methods for the removal of pollutants from the soil washing or flushing solution can be divided into two categories. The first focuses on the fast and efficient removal of pollutants and application of various advanced oxidation technologies while paying less attention to the regeneration of the flushing reagent. Villa et al. [15]

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investigated the degradation of *p,p′*-DDT, *p,p′*-DDE, and diesel in a Triton X-100 soil washing solution by solar photo-Fenton. The degradation efficiencies obtained for *p,p′*-DDT, *p,p′*-DDE, and diesel after 6 h of irradiation were 99%, 95%, and 100%, respectively, and more than 95% of the dissolved organic carbon was removed, indicating that Triton X-100 also decomposed in the process of degradation of the target pollutants. A synergic degradation of petroleum from SDS washing solution was observed when UV photolysis and sonolysis were coupled with boron-doped diamond electrolysis [16]. UVC (λ = 254 nm) photolysis combined with electrolysis showed an efficient performance in removing oxyfluorfen from SDS soil washing solution [17]. However, surfactant also decomposed that prevents its reuse.

The second category pays much more attention to the reuse of washing agents in the post-treatment process. Liquid–liquid extraction, electrochemical technologies, and selective oxidation process are used to achieve this goal. The reuse of methyl-β-cyclodextrin in a washing solution has been achieved by liquid–liquid extraction with colza oil [7]. The extracted solution was equally able to remove PAHs from contaminated soil compared with a newly prepared methyl-β-cyclodextrin solution. However, the PAHs in colza oil still required further treatment. Electrochemical technology has been applied to regenerate the extraction ability of soil washing solution [18,19], which demonstrated that 50% of TW80 and 90% of HPCD were recovered by an electro-Fenton process but without providing the performance of the regenerated washing solutions [19]. Long et al. [20] found that UV/$S_2O_8^{2-}$ could efficiently remove toluene in sodium dodecyl sulfate (SDS) solution while most SDS was maintained after three cycle use. Trellu et al. [21] found selective degradation of PAH in TW80 soil washing solution can be achieved using anodic oxidation with low density when TW80's concentration was high.

CD and its derivatives have no spectral absorption in the ultraviolet region from 210 to 400 nm, while HOCs usually have strong absorption (see below). Thus, theoretically, UV photolysis of the washing solution could decompose HOCs without destroying CD. The ring cleavage intermediates of HOCs have lower affinity than their parent compounds for forming an inclusion complex with CD; thus, the CD cavity is available, and the extraction ability of a CD washing solution can be regenerated by UV photolysis. However, it is notable that some soil organic matter (SOM) could also dissolve in the washing solution during the soil remediation process. SOM shows either enhancement or retardation effect on the photolysis of organic pollutants, which reflects the combined effects of photosensitization, competition in light harvesting (the inner filter effect), and radical scavenging [22,23]. Although the effects of HA on UV photolysis of various pollutants have been widely investigated over the last few decades [24–26], no systematic study has been performed regarding the effects of HA on UV photolysis of a host–guest complex. Kamiya et al. [27] found that CD could promote the photodegradation of organophosphorus pesticides in humic acid water because the reaction of the pesticide with reactive radicals generated by the humin photosensitizer could be catalyzed by the form of the pesticide/CD complex. Moreover, CD-trapped reactive radicals could

also contribute to the degradation of pesticides. Cai et al. [28] reported that methyl-β-CD favored the hydrolysis of diclofop-methyl in pH 8.0 deionized water and natural aquatic systems, whereas methyl-β-CD showed retardation effects on diclofop-methyl hydrolysis in soil dispersion.

To date, it is unclear to what extent CD could be simultaneously eliminated under UVC photolysis in the presence of HA or other SOM, which could subsequently influence the regeneration of CD washing/flushing solutions. This study focuses on the removal of phenanthrene from agricultural soils by CD washing and investigates the performance of UVC photolysis in the elimination of phenanthrene and recovery of the extraction ability of CD in soil washing solutions. Moreover, this study proposed the possible reasons for the loss of extraction ability, and also analyzed the transformation products of phenanthrene and the results facilitate the establishment of a novel method for the regeneration of washing agents.

2. Materials and methods

2.1. Chemicals

Phenanthrene (≥98%) was purchased from Aladdin Industrial, Inc. (Shanghai, China) and used as received. Kaolinite (chemical grade), β-cyclodextrin (β-CD, 98%, MW 1,135), and hydroxypropyl-β-cyclodextrin (HPCD, 98%, average MW 1,436) with a 5.2 degree of substitution were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received. Crude humic acid (HA) was purchased from Aladdin Industrial (Shanghai, China) and purified according to the recommended method before use [29]. Agricultural silt loam (10.0% sand, 64.6% silt, 25.4% clay, 1.65% organic matter; pH: 7.02; cation exchange capacity: 11.78 cmol kg^{-1}) was collected from the 0–15 cm soil profile from a site near Wuhan, China. The soil samples were then air dried and sifted using a 2 mm screen mesh. The soils were stored in the dark for 1 month before use. The final spiked concentrations of phenanthrene in agricultural soil and kaolinite were 0.44 and 0.31 mg/g, respectively. Ultrapure water (resistivity: >18.0 MΩ cm) was used during sample preparation.

2.2. Solubilization of phenanthrene

Approximately 0.4 g phenanthrene was added to either a 20 mL β-CD or a 20 mL HPCD (0–10 g/L) aqueous solution in which the phenanthrene dosage was higher than the maximum solubility. The flasks were shaken at 200 rpm in the dark at 20°C for 48 h, chosen based on preliminary kinetic studies. Then, the suspensions were centrifuged twice at 6,000 rpm for 20 min, and the supernatant properly diluted for concentration analysis.

2.3. Batch extraction of phenanthrene

Approximately 1.0 g phenanthrene spiked soil or kaolinite was added to either 100 mL of β-CD (0–9 mM) or 100 mL of HPCD (0–7 mM) aqueous solution, and the suspension was shaken at 20°C for 48 h. Bach extraction was also conducted at different soil mass/extraction solution volume ratios. Samples

(3 mL) were taken and centrifuged twice at 6,000 rpm for 20 min. The concentration of phenanthrene (c_{phe}, mg/L) in supernate was then determined by high-performance liquid chromatography (HPLC) with a Cosmosil 5C18-MS-II column (5 μm, 4.6 mm × 150 mm). The mobile phase was an acetonitrile/water (75/25, v/v) solution, and the flow rate was 0.8 mL min⁻¹. An ultraviolet detector (Waters 484) was applied for detection and the wavelength of 251 nm was utilized. The extraction efficiency (*E*, %) was calculated using Eq. (1):

$$E\ (\%) = (c_{phe} \times v)/m \tag{1}$$

where *v* and *m* are the extraction volume and the total phenanthrene content in the soil, respectively.

2.4. Regeneration and reuse of cyclodextrin washing solution by UVC photolysis

1.0-g samples of phenanthrene-spiked agricultural soil or 1.2-g samples of phenanthrene-spiked kaolinite were added to 30 mL of 10 g/L β-CD (8.81 mM) or HPCD (6.96 mM) aqueous solution. Then, the dispersion was shaken for 48 h. The extraction solution was separated from the soil by centrifugation and then irradiated using a Philips (Pabianice, Poland) TUV PLS lamp (9 W), and the incident irradiation intensity was 0.513 mW/cm² that was measured using an Ocean Optics USB2000 spectroradiometer (Largo, USA). Samples were withdrawn at different time intervals and the concentration was monitored using HPLC. The enantiomer's concentration over time. The pseudo-first-order rate equation (Eq. (2)), which has been used to simulate the UVC photolysis of various pollutants in the absence and presence of CDs [30,31], was applied to fit phenanthrene's concentration over photolysis time,

$$c_t = c_0 \times e^{-k_{obs} \times t} \tag{2}$$

where c_0 and c_t are the initial concentration of phenanthrene and the concentration at a reaction time *t*, respectively. k_{obs} (min⁻¹) is the observed kinetic constant for the irradiation of phenanthrene in the soil extraction solution.

After nearly complete elimination of phenanthrene ($c_t/c_0 < 0.05$), new phenanthrene-spiked agricultural soil or kaolinite was added to the UVC-regenerated extraction solution to repeat the extraction-UVC photolysis cycle.

2.5. Analysis of phenanthrene transformation products

After irradiation for 180 min, more than 90% of the initial phenanthrene was decomposed and the accumulated concentration of intermediates was high. Then, the UVC treated soil washing solution was analyzed using liquid chromatography-mass spectrometry (LC-MS) to identify the transformation intermediates. The analysis was performed on an Agilent 1200 series HPLC system combined with a triple quadrupole mass spectrometer (G6410B: Agilent, Santa Clara, CA, USA). The same separation conditions applied to LC-MS were also used for HPLC. Electrospray ionization (ESI+) full-scan mode (50–1,000 m/z) was applied for mass spectrometry measurements. The ion spray voltage was set to 2.5 kV. Nitrogen was used as the drying and nebulizing gas. The dry gas flow was 10 L/min, and the drying temperature was 350°C. The nebulizer pressure was 40 psi.

3. Results and discussion

3.1. Solubilization of phenanthrene by cyclodextrin

The solubilization effects of β-CD and HPCD on phenanthrene are shown in Fig. 1. The apparent concentration of phenanthrene (c_{phe}) increased linearly with increasing CD concentration. The apparent solubility of phenanthrene was 0.81 (±0.03) mg/L at 20°C, and increased to 12.0 (±0.03) and 12.6 (±0.04) mg/L in the presence of 10 g/L β-CD (8.81 mM) and HPCD (6.96 mM), respectively. The linear increase in phenanthrene solubility with increasing CD concentration indicated the formation of a 1:1 inclusion complex between phenanthrene and CD. The linear correlation was then fit by Eq. (3):

$$c_{phe} = 1 + k \times c_{CD} \tag{3}$$

where c_{CD} (mM) is the conducted CD concentration, and *k* is the slope. As shown in Fig. 1, the data were well fitted by Eq. (3) that the adjusted correlation coefficient square (r^2_{adj}) was larger than 0.995. According to the widely applied Higuchi–Connors equation [32], the inclusion constants (K_c) based on phase-solubility data can be calculated by Eq. (4):

$$K_c = \frac{k}{178.23 \cdot S_0 \cdot (1-k)} \tag{4}$$

where S_0 (M) is the saturated concentration of phenanthrene in aqueous solution, and 178.23 is the molecular weight of phenanthrene, respectively. K_c of phenanthrene/β-CD and phenanthrene/HPCD was 1,600 ± 200 M⁻¹ and 2,200 ± 200 M⁻¹, respectively. Value of K_c obtained in this study was in line with the reported values (1,200 and 2,700 M⁻¹) [33].

3.2. Effects of cyclodextrin concentration on extraction efficiency

The effects of CD concentration on extraction efficiency were investigated for concentrations from 0 to 10 g/L (Fig. 2).
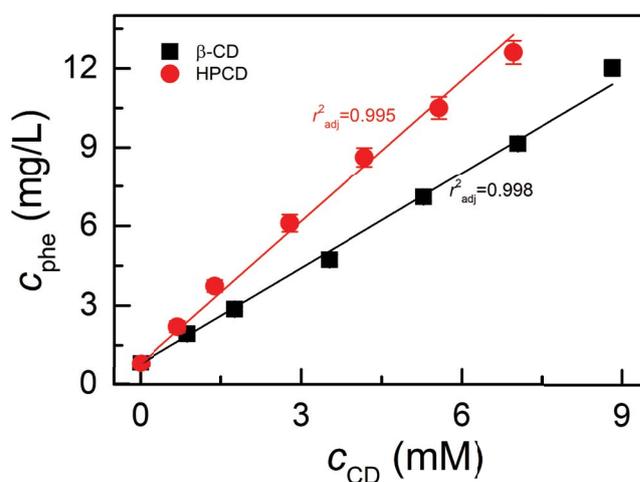
Fig. 1. Phenanthrene solubility in the presence of β-CD and HPCD at 20°C, and the lines were the fit of data by Eq. (3).

The extraction efficiencies of phenanthrene from agricultural soil and kaolinite using pure water were 17.0% and 23.8%, respectively. This poor extraction performance for water or electrolyte aqueous solution has also been observed for other HOCs, including PCBs, pyrene, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans, due to their low aqueous solubility [11,34,35]. The corresponding aqueous concentration of extracted phenanthrene was approximately 0.74 mg/L, which is close to its aqueous solubility. Therefore, the extracted concentration or the extraction efficiency cannot be further increased at a fixed soil mass–extraction volume ratio.

The presence of β-CD or HPCD increased the extraction efficiency significantly. The presence of 1 g/L β-CD (0.881 mM) or HPCD (0.696 mM) increased the extraction efficiencies to 43.0% and 46.5% from agricultural soil and to 74.9% and 74.6% from kaolinite, respectively. The promotion of extraction mainly results from the solubilization effect of CDs, which was supported by the relative higher extraction efficiency of HPCD that has a larger inclusion constant with phenanthrene relative to that of β-CD. The extraction efficiency of phenanthrene from agricultural soil and kaolinite increased linearly with increasing CD concentration to approximately 1.5 mM. A further increase

in the CD concentration only increased the extraction efficiency slightly.

3.3. Extractable and non-extractable phenanthrene in spiked soils

In the presence of a low CD concentration (less than 1.5 mM), the extraction concentration of phenanthrene from both agricultural soil and kaolinite was quite close to the apparent solubility of phenanthrene in the corresponding CD solution. However, the extracted concentration only increased slightly with a further increase in β-CD or HPCD concentration. In the 100-mL extraction solution with 10 g/L β-CD (8.81 mM), the extracted concentrations of phenanthrene from agricultural soil and kaolinite were 3.0 and 2.6 mg/L, or 68% and 83% of the total spiked phenanthrene, respectively (Fig. 2). Analogous results were obtained in the presence of HPCD. Notably, the extracted concentrations were smaller than the theoretical concentrations that all the spiked phenanthrene was extractable (4.4 and 3.1 mg/L). The probable reasons for the smaller extractable concentration relative to theoretical values are some parts of CDs adsorbed to soil or kaolinite that led to reduced solubilization, soil leached materials from soil decreased the solubilization effect of CDs, and/or some portion of the spiked phenanthrene was non-extractable to CD.

The negligible adsorption of β-CD and HPCD to kaolinite (<5 μmol/g) demonstrated that the low extractable phenanthrene concentration was not because of the loss of "functional" CDs in bulk solutions. The extraction experiment was investigated under a higher soil/extraction solution ratio (1.0 g vs. 20 mL extraction solution) in the presence of different CDs. The extracted concentrations of phenanthrene increased linearly with increasing CD concentration (Fig. 3), and the slopes were comparable with that in CD aqueous solutions in the absence of kaolinite or soil (Fig. 1). The result indicated that leached soil materials did not decrease the solubility of phenanthrene in CD solutions. Solubilization of phenanthrene by CDs in soil extraction solutions also proved
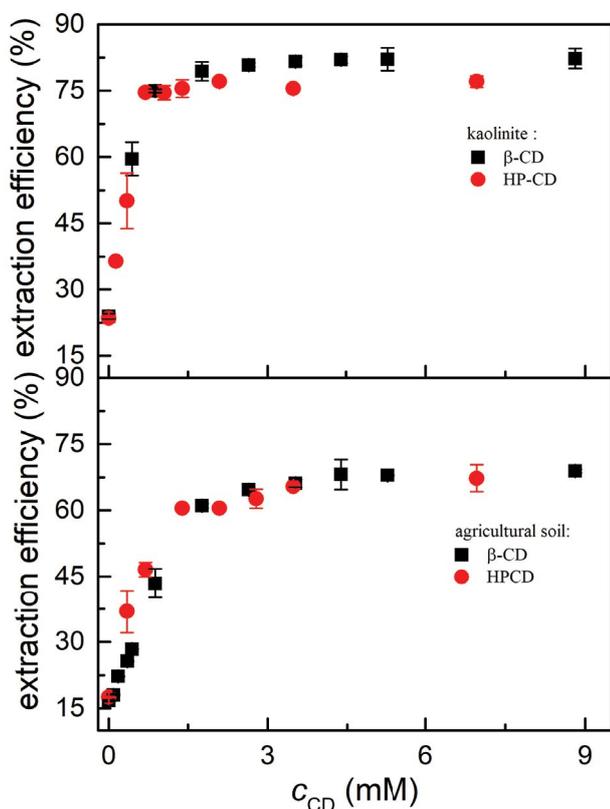
Fig. 2. Effects of cyclodextrin concentrations on the extraction efficiency of phenanthrene from kaolinite (upper panel) and agricultural soil (lower panel). The mass of soil and kaolinite were 1 g, and the volume of extraction solution was 100 mL.
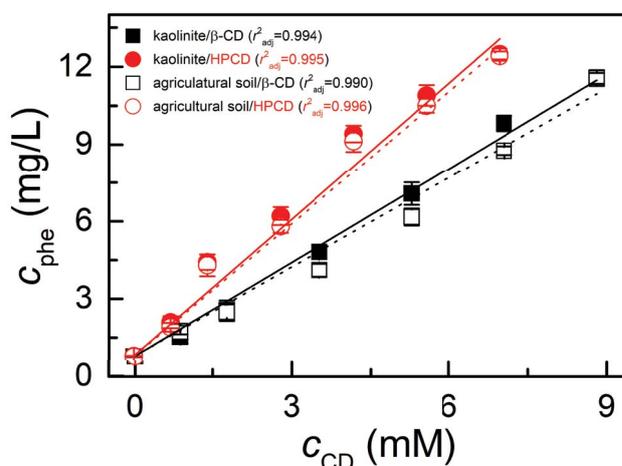
Fig. 3. Effects of cyclodextrin concentrations on the extracted concentration of phenanthrene from agricultural soil and kaolinite, the mass of soil and kaolinite were 1 g, the volume of extraction solution was 20 mL, and the lines were the fit of data by Eq. (3).

that soil leached material does not influence solubilization (data not shown).

Batch extraction was further investigated in a 10 g/L β-CD solution (8.81 mM) at soil mass/extraction volume ratios of 1/50, 1/200, and 1/300 g/mL; the extracted phenanthrene concentrations were 5.6, 1.5, and 1.0 mg/L, respectively, which are all equal to 67% ± 2% of the total spiked phenanthrene concentrations in the soil samples. The results indicated that some portion of the spiked phenanthrene was not extractable to CD; otherwise, the extraction efficiency would increase with a decreasing soil/extraction solution ratio. It has been reported that phenanthrene and other PAHs could adsorb to different energy sites in soils and that SOM plays a vital role in phenanthrene sorption and desorption processes [36]. The extractable phenanthrene was mainly from physically mixed or loosely bound fractions, and the non-extractable phenanthrene in agricultural soil was approximately 30% that of the total spiked dose. Notably, phenanthrene contaminated soil that was used in this study was a relative newly spiked soil sample (aged for one month), the non-extractable phenanthrene proportion in real PAHs contaminated soil could be different. He et al. [37] found that up to 30%–57% of total PAHs was non-extractable in some soil samples.

3.4. Performance of UVC photolysis in the regeneration of cyclodextrin washing solution

Direct UVC photolysis of cyclodextrin washing solution was investigated to assess the performance in simultaneously removing phenanthrene and recovering the washing ability of cyclodextrin. The concentration of phenanthrene in the washing solution rapidly decreased with increasing irradiation time in both the β-CD and HPCD washing solutions, as shown in Fig. 4. The observed first-order kinetic constants (k_{obs}) for the elimination of phenanthrene in 10 g/L β-CD (8.81 mM) and HPCD (6.96 mM) solutions generated from kaolinite were 0.034 and 0.026 min^{-1} in the first cycle, respectively. Direct photolysis kinetic constant and the sum of its reaction with radicals constitute k_{obs} for the UVC elimination of phenanthrene in soil washing solutions. Because the ratio of the phenanthrene inclusion complex to total phenanthrene was approximately the same in β-CD (0.97) and HPCD (0.95) solutions, the difference in k_{obs} mainly resulted from the different photolysis behaviors of the phenanthrene/ β-CD complex and the phenanthrene/HPCD complex. In contrast, k_{obs} was 0.014 min^{-1} in both the β-CD and HPCD washing solutions generated from agricultural soil. The decrease in k_{obs}
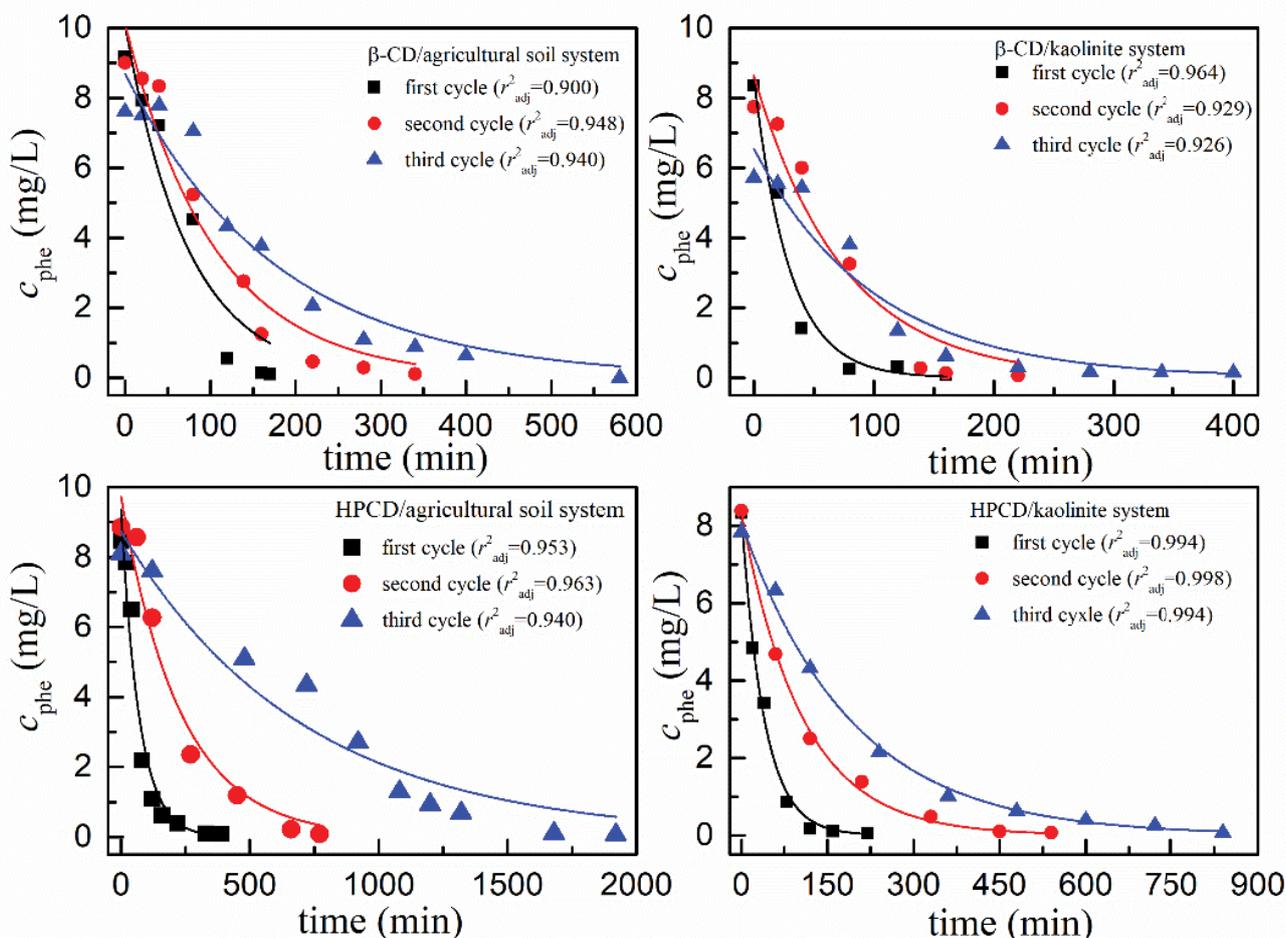
Fig. 4. Cycling performance of cyclodextrin extraction and UVC photolysis in the removal of phenanthrene and the regeneration of cyclodextrin extraction ability.

was probably because leached SOM from the agricultural soil inhibited the degradation of phenanthrene in both solutions. It has been reported that direct UVC (254 nm) photolysis of phenanthrene was suppressed in the presence of humic acid [38]. Competition for irradiation photons and those generated radicals between leached SOM and phenanthrene could lead to a decrease in k_{obs}.

After the concentration of phenanthrene decreased to approximately zero, the irradiated solution was reused to treat spiked soil or kaolinite. The fourth time extraction efficiencies of the β-CD solution after three extraction-UVC photolysis cycles were 48% and 44% for agricultural soil and kaolinite, respectively, corresponding to 77% and 66% of the efficiencies in the first extraction cycle. Conversely, the extraction efficiency decreased to 5% and 3% for agricultural soil and kaolinite when β-CD solution was not regenerated by UVC photolysis. On the other side, the extraction efficiencies of the HPCD solution after three extraction-UVC photolysis cycles for agricultural soil and kaolinite were 54% and 60%, respectively, which was close to the corresponding extraction efficiencies in the first cycle (58% for agricultural soil and 67% for kaolinite). The results showed that the regeneration of the HPCD solution was better than the regeneration of the β-CD solution, partly because the loss of HPCD (7% after three cycles) during UVC photolysis was smaller relative to that of β-CD (12% after three cycles). It has been reported that HPCD was more stable relative to TW80 during a 180-min electro-Fenton oxidation [19]. Elimination of CDs mainly resulted from the attack of reactive species generated in the irradiated solutions, because direct UVC photolysis of β-CD or HPCD was negligible. Decomposition of the cavity of HPCD was more difficulty relative to β-CD because of the steric hindrance.

Notably, the elimination proportions of CDs were small, which means the loss of CDs was not the only reason for the decreased extraction capacity. On the other side, the intermediates generated during UVC photolysis could also decrease the extraction ability of CD because of their potential occupation of the CD cavity. The decrease in extraction efficiency for agricultural soil was less than that for kaolinite (Table 1). This may be because the accumulated SOM leached from agricultural soil promotes desorption of phenanthrene, which compensated for the loss of CD to

some extent. As shown in Fig. 5, the presence of humic acid applied as an SOM proxy increased the extraction concentration of phenanthrene from agricultural soil and kaolinite, which demonstrated that phenanthrene has a high affinity for HA or other SOM components. The partition coefficient of phenanthrene to SOM ranged from 1.2 to 4.2 × 10⁴ L/kg [39]. Therefore, it is reasonable to postulate that phenanthrene can bind to SOM in agricultural soils, and parts of these bound fractions could be transported to the washing solution during SOM leaching.

The values of k_{obs} obtained for the regenerated β-CD and HPCD solutions decreased with an increase in the number of cycles, especially for the HPCD solution (Table 1). The k_{obs} for the third time photolysis of phenanthrene in HPCD soil washing solution was only 10% that of the value obtained for the first cycle, and k_{obs} was 41% of the original value for the β-CD soil washing solution. In the case of kaolinite system, k_{obs} for the third cycle was 29% and 20% that of the first cycle in β-CD and HPCD washing solution, respectively. The decrease in k_{obs} in solutions generated from kaolinite is mainly due to the competition for irradiation photons
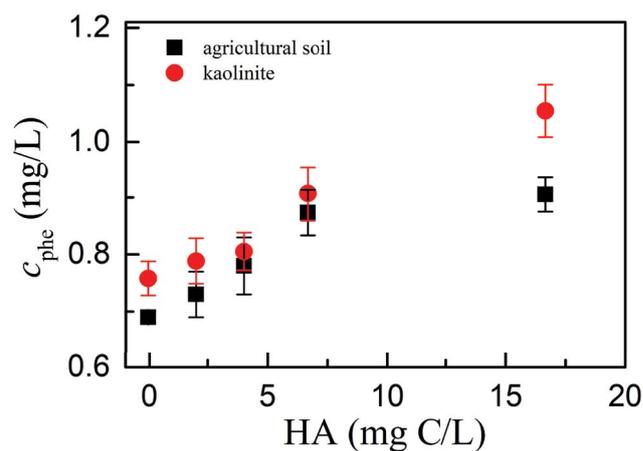
Fig. 5. Effects of dissolved humic acid (HA, mg C/L) concentration on the extraction concentration of phenanthrene. The mass of soil and kaolinite were 1.0 g, and the volume of extraction solution was 20 mL.

Table 1
Performance of UVC photolysis in the regeneration of CD washing solutions, c_0 (mg/L) and k_{obs} (min⁻¹) represent initial concentration and the observed UVC photolysis of phenanthrene in different cycling using times, respectively

CD cycling use		Soil	1st time	2nd time	3rd time	4th time
β-CD	c_0	Agricultural soil	9.2 (62%)[a]	9.0 (61%)	7.6 (51%)	7.2 (48%)
		Kaolinite	8.3 (67%)	7.7 (62%)	5.7 (46%)	5.5 (44%)
	$k_{obs} \times 10^2$	Agricultural soil	1.36	0.95	0.56	—[b]
		Kaolinite	3.41	1.36	1.00	—
HPCD	c_0	Agricultural soil	8.4 (58%)	8.6 (59%)	8.1 (56%)	7.9 (54%)
		Kaolinite	8.3 (67%)	8.4 (68%)	7.8 (63%)	7.4 (60%)
	$k_{obs} \times 10^2$	Agricultural soil	1.42	0.43	0.14	—
		Kaolinite	2.55	0.95	0.52	—

[a]Values listed in the parenthesis represent the extraction efficiency;
[b]"–" indicates that the experiment was not performed.

between phenanthrene and generated intermediates (see details in next section), and the decrease in k_{obs} in agricultural soil washing solutions was the overall effects of leached SOM and these transformation intermediates. The differences in
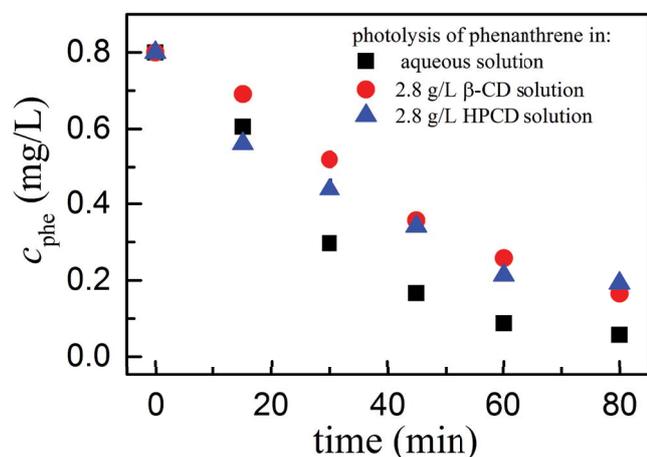
Fig. 6. Effects of β-CD and HPCD on the UVC photolysis of phenanthrene, initial concentration of phenanthrene was 0.8 mg/L.

the decreases in k_{obs} in β-CD and HPCD soil washing solutions were in line with the smaller decomposition proportion of HPCD relative to β-CD. Otherwise, as both solutions have comparable retardation effects on the photolysis of phenanthrene (Fig. 6), it is reasonable to expect the same decomposition intensity for β-CD and HPCD leading to identical decreases in k_{obs}.

3.5. Degradation mechanism of phenanthrene in soil washing solutions

Several intermediates were detected during the UVC photolysis of phenanthrene, as shown in Fig. S1. The major intermediates were the same in both cyclodextrin solutions, although their distributions differed. Liquid chromatography-mass spectrometry analysis of the phenanthrene solution after 180 min of irradiation indicated five major compounds and one other intermediate with an unknown structure (Figs. S2 and S3). Intermediate P1 with molecular weight (MW) 208 was assigned as 9,10-phenanthrenequinone (Fig. 7). P1 is a signature oxygenated derivative found during the biological transformation, photooxidation, and chemical oxidation of phenanthrene [40–42]. Barbas et al. [42] found UVC photolysis of phenanthrene adsorbed on silica gel leading to
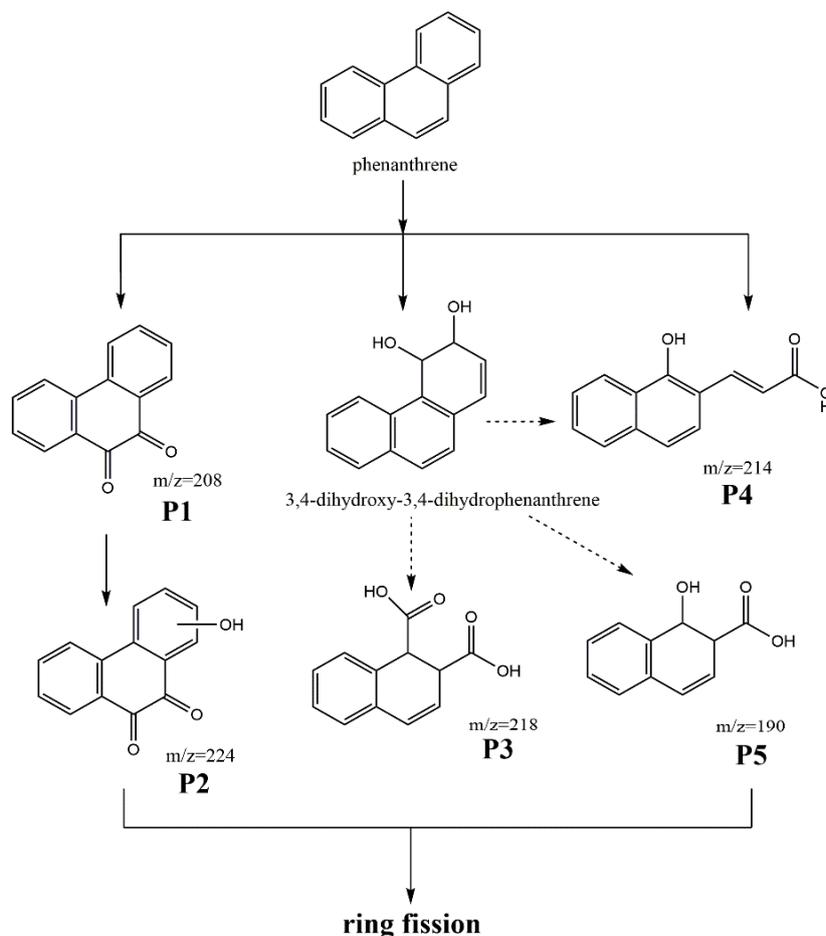
Fig. 7. Transformation pathway of phenanthrene under UVC photolysis.

the formation of 9,10-phenanthrenequinone. The addition of the hydroxyl radical ($^{\bullet}$OH) to P1 led to the formation of P2 (MW = 224). However, the substitution position was unknown due to limited information. Oxidation of phenanthrene at the C3 and C4 position could lead to the formation of intermediate 3,4-dihydroxy-3,4-dihydrophenanthrene. 1,2-Dihydronaphthalene-1,2-dicarboxylic acid (P3) with MW = 214, 3-(1-hydroxynaphthalen-2-yl)acrylic acid (P4) with MW = 190 and 1-hydroxy-1,2-dihydronaphthalene-2-carboxylic acid (P5) with MW = 218 may be the subsequent oxidation products of 3,4-dihydroxy-3,4-dihydrophenanthrene. More future work is needed to confirm these preliminary transformation structures. Further photolysis/oxidation products such as single benzene compounds, etc. can be formed during the oxidation of these detected intermediates that still has absorbance around 254 nm.

4. Conclusions

This study focused on the extraction of phenanthrene from agricultural soils using cyclodextrin (CD), and achieved degradation of phenanthrene and regeneration of CD in the soil washing solutions by UVC photolysis simultaneously. The results suggested that approximately 70% of the spiked phenanthrene was removed by washing with CD solution, and the residues were non-extractable. β-CD and HPCD solutions possessed comparable ability to remove phenanthrene from soil samples when using the same dose. Direct UVC photolysis simultaneously removed phenanthrene and recovered the washing ability of CDs. The degradation of phenanthrene became more persistent with increase of reuse times for both β-CD and HPCD washing solutions, particularly for HPCD. The presence of β-CD or HPCD did not alter the phenanthrene degradation path. The results obtained indicate that a combination of solubilization and direct UVC photolysis provides a promising method for the remediation of organic-contaminated soils. The choice of washing/flushing agent should take into account both extraction efficiency and its influence on the post-treatment of organic pollutants in washing/flushing solutions.

Supporting Information

HPLC and LC-MS spectra for the transformation intermediates were provided as the supporting information.

Acknowledgment

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Supplementary information
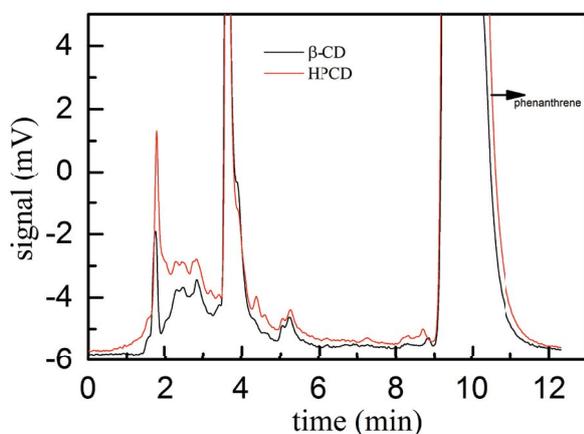
Fig. S1. HPLC chromatograph of samples withdrawn from the UV photolysis of β-CD or HPCD agriculture soil flushing solutions.
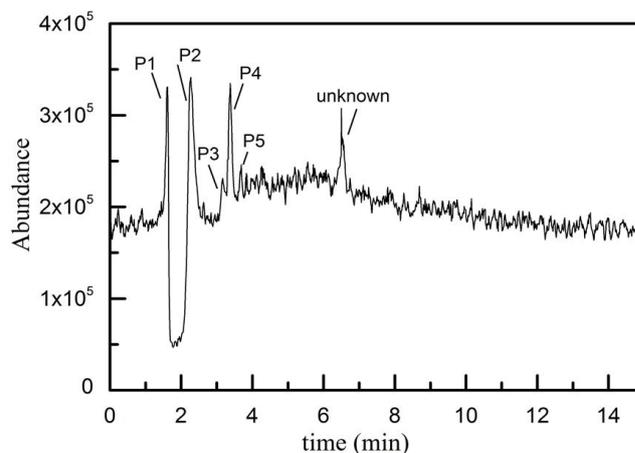
Fig. S2. Positive ion LC/ESI-MS total ionization chromatograph of UV photolysis sample of agriculture soil flushing solution in presence of β-CD.
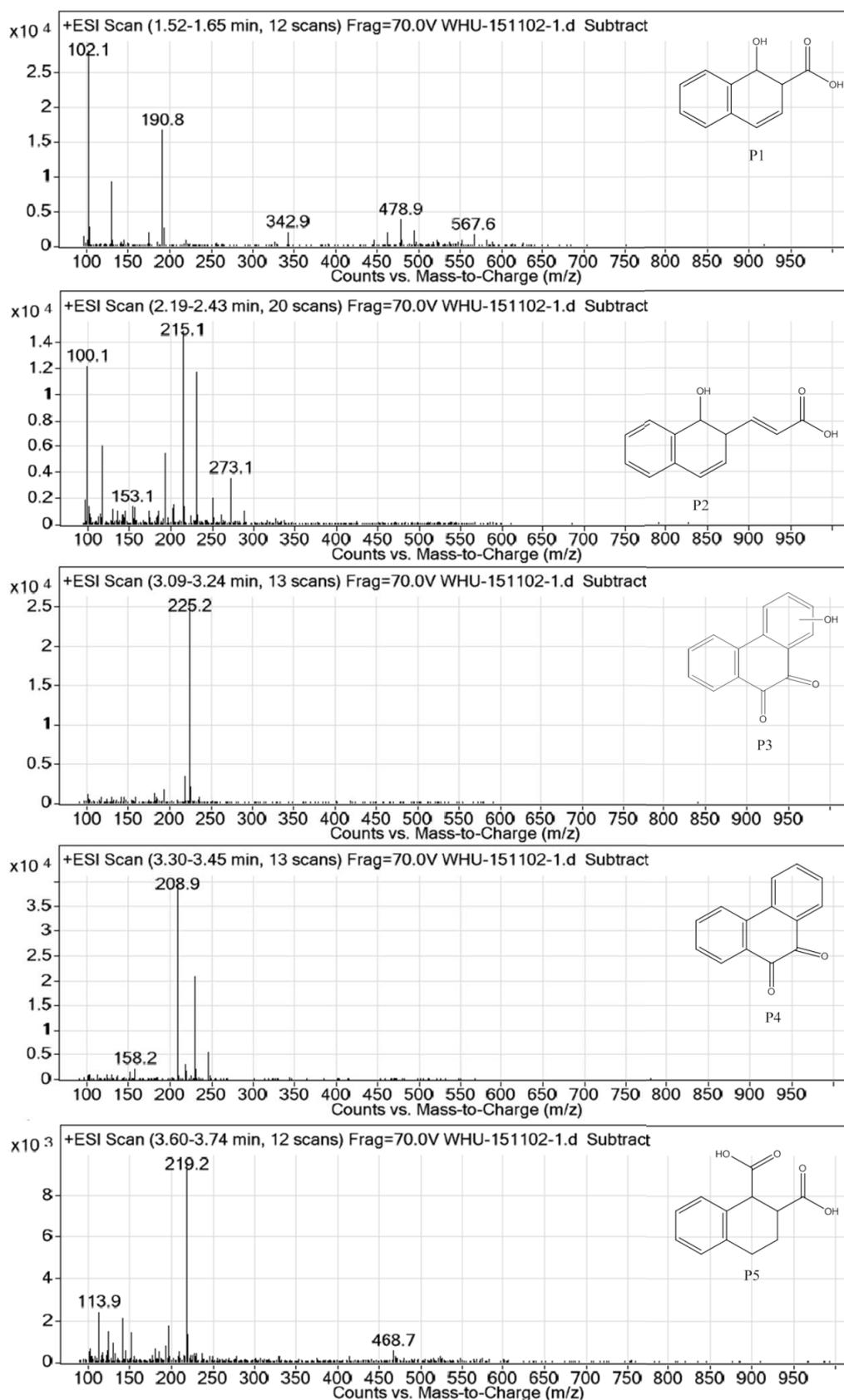
Fig. S3. HPLC mass spectrogram of UV photolysis sample of phenanthrene in presence of β-CD.