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Degradation of pentachlorophenol in contaminated soil suspensions by potassium monopersulfate catalyzed oxidation by a supramolecular complex between tetra (*p*-sulfophenyl)porphineiron(III) and hydroxypropyl-β-cyclodextrin

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Abstract

To enhance the catalytic oxidation of pentachlorophenol (PCP) in contaminated soil suspensions using tetra(*p*-sulfophenyl)porphineiron(III) (Fe(III)-TPPS) as a catalyst and potassium monopersulfate ($KHSO_5$) as the single-oxygen donor, the effect of added hydroxypropyl-β-cyclodextrin (HP-β-CD) was examined. At pH 4 and 6, the percentage of PCP disappearance increased substantially in the presence of HP-β-CD. In addition, the self-degradation of Fe(III)-TPPS was significantly retarded in the presence of HP-β-CD. This retarded self-degradation can be attributed to the stabilization of Fe(III)-TPPS via the formation of a supramolecular complex with HP-β-CD. The kinetic constant for the self-degradation of Fe(III)-TPPS in the presence of HP-β-CD at pH 6 was much smaller than that at pH 4, indicating that Fe(III)-TPPS is more stable at pH 6. Thus, the amount of Fe(III)-TPPS, $KHSO_5$ and HP-β-CD required to degrade PCP in contaminated soil suspensions was optimal at pH 6. When PCP-contaminated soil suspensions were treated under the optimized conditions, 12 – 18% and 24 – 28% of the PCP was mineralized to CO_2 in the absence and presence of HP-β-CD, respectively. These results show that the presence of HP-β-CD in the Fe(III)-TPPS/$KHSO_5$ catalytic system is effective in enhancing the degradation of PCP in contaminated soil suspensions.

Keywords: Pentachlorophenol; Soil remediation; Iron(III)-porphyrin; Hydroxypropyl-β-cyclodextrin; Supramolecular complex

1. Introduction

Pentachlorophenol (PCP) has, in the past, been utilized as a wood preservative and in herbicides. A recent study indicated that chlorophenols, such as PCP, are the main cause of detrimental health effects in humans in contaminated areas [1]. In addition, PCP can be converted into more toxic dimers, such as chlorinated dibenzo-*p*-dioxins and dibenzofurans, via a variety of oxidation processes in a soil environment [2, 3]. Thus, the degradation of PCP in contaminated soils could reduce the potential risk of pollution and related health issues. Technologies for the remediation of PCP-contaminated soils include chemical oxidation, washing the soil and biological degradation. The Fenton reaction is used for the chemical oxidation of PCP in contaminated soils [4, 5]. However, the disadvantage of the Fenton reaction is that large amounts of iron(II) and H_2O_2 are required, and an iron(III) hydroxide sludge is produced during the reaction. To overcome such problems, Liou et al. [6] developed an iron-resin catalyst for the degradation of PCP by a Fenton-like system. In soil washing, PCP in the contaminated soil is removed by extraction with organic solvents [7]. However, this may not be an environmentally sound procedure. On the other hand, biological degradation of PCP using microorganisms is known to be a practical process [8, 9]. However, the introduction of non-indigenous microorganisms into contaminated soils is problematic from an ecological point of view.

The use of a chemical catalyst to degrade PCP may circumvent some of the above problems associated with bioremediation. It is known that iron(III)-porphyrins, which are regarded as biomimetic models for active sites in lignase, are able to catalyze the degradation of chlorophenols [10-13]. In general, the catalytic activities of iron(III)-porphyrins are much less sensitive to variations in environmental conditions than are microorganisms and even enzymes *in vitro*. Thus, the use of iron(III)-porphyrins might make the maintenance of reaction conditions a more straightforward procedure. However, iron(III)-porphyrins are unstable in the presence of peroxides, such as H_2O_2 and $KHSO_5$, because they are susceptible to self-degradation [14, 15]. The self-degradation of iron(III)-porphyrins results in a decrease in the oxidation efficiency of the organic substrate. We recently reported that the addition of hydroxypropyl-β-cyclodextrin (HP-β-CD) was effective in stabilizing iron(III)-porphyrin in the presence of $KHSO_5$, due to the formation of a supramolecular complex between HP-β-CD and iron(III)-porphyrin [16]. As shown in Fig. 1, the supramolecular complex is formed by interactions between the sulfophenyl groups in Fe(III)-TPPS and the hydrophobic cavity of HP-β-CD.

A few applications of the catalytic systems using iron(III)-porphyrins for the remediation of PCP-contaminated soils have been reported [17, 18]. However, PCP degradation (mineralization to CO_2) was achieved up to 10% [17]. Fe(III)-TPPS is known to be a non-toxic biomimetic catalyst, and $KHSO_5$, commercially sold as "Oxone", is known to be a stable and environmentally safe oxidant. In addition, HP-β-CD, a biologically derived material, has been used for the extraction of chlorophenols from contaminated soils [19-21]. These facts suggest that combining the Fe(III)-TPPS/$KHSO_5$ catalytic system and HP-β-CD could be a clean and safe process for the remediation of PCP-contaminated soils. The purpose of the present study was to examine the effect of added HP-β-CD on the degradation of PCP in the Fe(III)-TPPS/$KHSO_5$ catalytic system. In order to apply the above system to the treatment of PCP-contaminated soils, the optimal pH and dosage for the reaction were determined. In addition, the mineralization of PCP to CO_2 was examined under optimal conditions.

2. Materials and Methods

2.1. Reagents and Materials

Tetra(*p*-sulfophenyl)porphineiron(III) (Fe(III)-TPPS) was prepared according to a method described in a previous report [22]. $KHSO_5$ was obtained as a triple salt, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Merck). PCP (99.0% purity) was purchased from Aldrich, and a stock solution (0.01 M) was prepared by dissolving it in acetonitrile. ^{14}C-labeled PCP was purchased from American Radiolabeled Chemicals Inc. (0.1 mCi ml^{-1} in ethanol, specific activity 80 mCi $mmol^{-1}$). HP-β-CD (1.0 molar substitution, Mw 1540) was purchased from Aldrich.

Kaolin was purchased from Kukita Yakuhin Kogyo (Tokyo) and was used without further treatment. Commercial Kanuma- and Red-soils for gardening were used in the present study. After air-drying, these soils were ground in a mortar with a pestle and then sieved through a stainless steel sieve (0.22 mm). A particle size below 0.22 mm was employed in the tests. The pH values, bet-N_2 specific surface areas and elemental compositions of the soil samples are summarized in Table 1. The specific surface area for Kanuma-soil was much larger than those for other samples. This can be attributed to the fact that Kanuma-soil includes large amounts of allophane moieties [23].

2.2. Batch catalytic oxidation of PCP in soil suspensions

A 0.2 g of soil sample was placed in a 10-ml glass tube. A 2 ml aliquot of 0.02 M NaH_2PO_4/Na_2HPO_4/citrate buffer at pH 4 or 6 was pipetted into the glass tube, and the solution was spiked with a 10 μl aliquot of 0.01 M PCP in acetonitrile. The suspension was then shaken for 24 h to allow the PCP to reach equilibrium with the soil. A 0 – 100 μl aliquot of aqueous Fe(III)-TPPS (200 μM) and a 0 – 50 μl aliquot of aqueous HP-β-CD (100 mg ml^{-1}) were added to the suspension, and a 0 – 50 μl of aqueous 0.01 M $KHSO_5$ was then added. The glass tube was then allowed to shake at room temperature (23 – 25°C). After 1, 3 or 5 days of shaking, 1 ml of 2-propanol was added and the suspension was allowed to shake for a further 2 h. After centrifugation of the soil suspension (2500 rpm for 3 min), the supernatant was filtered through a DISMIC® filter (diameter 13 mm, pore size 0.45 μm, hydrophilic PTFE type, ADVANTEC). It was confirmed that no adsorption of PCP to the filter occurred, when an aqueous solution of PCP (50 μM) in the absence of soil was passed through the filter. A 20 μl aliquot of the filtrate was injected into a JASCO PU-980 type HPLC pumping system.

The mobile phase consisted of a mixture of 0.08% aqueous H_3PO_4 and methanol (20/80 = v/v), and the flow rate was set at 1 ml min^{-1}. A 5C18-MS Cosmosil packed column (4.6 mm i.d. × 250 mm, Nacalai Tesque) was used as the solid phase, and the column temperature was maintained at 50°C. PCP was determined by Uv absorption at a wavelength of 220 nm. The efficiency of extraction of PCP from the contaminated soil suspensions was evaluated (Table 2). In the absence of both Fe(III)-TPPS and $KHSO_5$ ("PCP + buffer" in Table 2), 91 – 101% of the PCP was extracted from the soil suspensions at pH 4 and 6. All runs were conducted in triplicate.

2.3. Mineralization of ^{14}C-labeled PCP

A 0.5 ml aliquot of ^{14}C-labeled PCP in ethanol was evaporated in a stream of dry N_2. The residue was then dissolved in 1 ml of acetonitrile (final concentration of PCP 625 μM). A 19.2 ml aliquot of buffer solution at pH 6 and a 0.8 ml aliquot of ^{14}C-labeled PCP in acetonitrile were mixed with stirring (final concentration of PCP 25 μM). A 0.1 g sample of soil was placed in a 20-ml Erlenmeyer flask. A 1 ml aliquot of the buffer solution, including ^{14}C-labeled PCP, was then added and 25 μl of aqueous Fe(III)-TPPS (400 μM) and 0 or 15 μl of aqueous HP-β-CD (100 mg ml^{-1}) were then added. After adding 25 μl of aqueous $KHSO_5$ (0.01 M), the flask was fitted with a stopper, which contained a polyethylene center well containing a glass wool plug impregnated with 0.4 ml of aqueous 2 M NaOH as a $^{14}CO_2$ trap. After a 5 day reaction period, 1 ml of 2-propanol and 0.4 ml of 1.8 M aqueous H_2SO_4 were injected via a syringe from the top of stopper to release the $^{14}CO_2$ from the soil suspension. After shaking for 1 day, a 2 ml aliquot of the soil suspension was centrifuged (6200 rpm, 1 min), and the supernatant was filtered thorough a DISMIC® filter. A 1 ml aliquot of the filtrate was pipetted into a glass vial including a mixture of methanol (1 ml) and scintillation cocktail (9 ml). The glass wool in the trap was transferred to the glass vial including 1.6 ml of water, and the trap was then washed with 0.4 ml of 2 M NaOH, 0.8 ml of water and 1 ml of 2-propanol. A 1 ml aliquot of this mixture was pipetted into a glass vial including methanol and scintillation cocktail. The radioactivities (dpm) in the vials were determined using an LS 6000 series liquid scintillation counter (Beckman Instruments, Inc). To determine the radioactivity before the reaction (R_{before}), a 1 ml aliquot of buffer solution including ^{14}C-labeled PCP was added to an Erlenmeyer flask containing 0.1 g of soil. After shaking for 5 days, the same procedures, as described above, were carried out. Each experimental run was conducted in duplicate. The percentage of ^{14}C-labeled PCP converted to $^{14}CO_2$ ($\%^{14}CO_2$) was calculated using the equation below:

$$(\%^{14}CO_2) = (R_{\mathrm{before}} - R_{\mathrm{sus}})/R_{\mathrm{before}} \times 100$$

where R_{sus} represents the radioactivities after the reaction in the soil suspension. In addition, the recoveries of ^{14}C were calculated by dividing the sum of the radioactivities in the trap and soil suspension by the radioactivity before the reaction. The recoveries in all experimental runs ($n = 12$) were 92 ± 7%.

2.4. Uv-vis absorption spectra and kinetic measurement

Uv-vis absorption spectra of a buffer solution at pH 4 or 6, containing Fe(III)-TPPS (5 μM) and HP-β-CD, were obtained on a Jasco V-550 type spectrophotometer (Japan Spectroscopic Co.) with a quartz cell (1 × 1 cm) at 25°C. The kinetics of self-degradation were monitored by the decolorization of Fe(III)-TPPS at 25°C. A 37.5 μl aliquot of aqueous $KHSO_5$ (0.01 M) was added to 3 ml of an aqueous solution in a 1 × 1 cm quartz cell, which contained Fe(III)-TPPS (5 μM) and HP-β-CD (1.0 mg ml^{-1}) at pH 4 or 6, with stirring. The absorbance of Fe(III)-TPPS before adding $KHSO_5$ (A_0) was monitored at 394 nm in the absence of HP-β-CD or at 419 nm in the presence of HP-β-CD. After adding $KHSO_5$, the absorbance at arbitrary times (A_t) was determined at 0.2 s intervals up to 180 s using the kinetic mode of the spectrophotometer. No blank decolorization of Fe(III)-TPPS by only light at 394 nm or 419 nm was observed, even after 5 min of irradiation.

3. Results and Discussion

3.1. Control experiments

The mechanism of oxidation of PCP by Fe(III)-TPPS appears to proceed via a peroxide shunt, as described in a previous report [12]. A single-oxygen donor, such as $KHSO_5$, is required to produce the active oxidants from Fe(III)-TPPS (ferryl-porphyrin cation radical and ferryl-oxo species). Such oxidants can be reduced to Fe(III)-TPPS by the oxidation of PCP to a pentachlorophenoxy radical (PCP·). The PCP· is further oxidized, giving rise to a variety of byproducts are produced [10, 11, 13]. Prior to applying the Fe(III)-TPPS/$KHSO_5$ catalytic system to the degradation of PCP in contaminated soil suspensions, the influence of some matrices in the soil suspensions on the disappearance of PCP was examined.

As shown in Table 1, the soil samples contained small amounts of manganese. It is known that manganese is present as manganese dioxide in soils, and that it is capable of oxidizing xenobiotics such as PCP [24]. Thus a control experiment to determine, whether the PCP in the soil suspension is degraded in the absence of both Fe(III)-TPPS and $KHSO_5$ or not, was carried out.

The recoveries of PCP from the soil suspensions are summarized in Table 2. In the presence of Fe(III)-TPPS only ("PCP + buffer + Fe(III)-TPPS" in Table 2), the recoveries were in the range of 92 – 99% at pH 4 and 6, indicating no influence of soil components and Fe(III)-TPPS. However, in the presence of $KHSO_5$ only ("PCP + buffer + $KHSO_5$" in Table 2), a significant lower recovery (59%) was observed in the Red-soil at pH 4. As shown in Table 1, the contents of organic carbon and iron in the Red-soil were much larger than those in the other soils. Paciolla et al. [25, 26] proposed that ferryl-oxo species can be formed by the hydrogen peroxide catalysed oxidation by an iron(III)-soil organic matter complex. Thus, it is likely that the lower recovery for the Red-soil in the presence of $KHSO_5$ only at pH 4 may be due to the formation of the ferryl-oxo species via a reaction between $KHSO_5$ and iron in the soil.

3.2. Influence of pH on the disappearance of PCP

In the presence of both Fe(III)-TPPS and $KHSO_5$, the influence of pH and HP-β-CD on the percentage of PCP disappearance was investigated (Figure 2). It had previously been reported that the percentage of PCP disappearance increased with increasing pH up to pH 7 in an Fe(III)-TPPS/$KHSO_5$ catalytic system [11, 12]. As expected from the previous reports, the percentage of PCP disappearance at pH 6 was larger than that at pH 4 for all soil samples. In addition, the disappearance of PCP was remarkably enhanced at pH 4 and 6 when HP-β-CD was added. In the presence of HP-β-CD, the percentage of PCP disappearance at pH 6 was also larger than that at pH 4 for all soils.

3.3. Influence of pH on the stability of Fe(III)-TPPS

The deactivation of Fe(III)-TPPS is due to self-degradation via oxidation by $KHSO_5$ [14, 15]. The kinetics of the degradation of Fe(III)-TPPS were monitored at pH 4 and 6 in the absence and presence of HP-β-CD (Fig. 3). The kinetic constants for the self-degradation of Fe(III)-TPPS, calculated from curve-fitting to the data points in Fig. 3, are summarized in Table 3. The kinetic constant in the absence of HP-β-CD (k_0) at pH 6 was 10-times smaller than that at pH 4. In addition, the kinetic constant in the presence of HP-β-CD ($k_{\text{HP-β-CD}}$) at pH 6 was 17-times smaller than that at pH 4. These results indicate that the self-degradation of Fe(III)-TPPS is significantly retarded at pH 6 in the absence and presence of HP-β-CD. As shown in Table 3, the ratio of k_0 to $k_{\text{HP-β-CD}}$ ($k_0/k_{\text{HP-β-CD}}$) at pH 6 was much larger than that at pH 4. This shows that the retardation of Fe(III)-TPPS self-degradation by added HP-β-CD at pH 6 is greater than that at pH 4.

The stabilization of Fe(III)-TPPS in the presence of HP-β-CD can be attributed to the formation of a supramolecular complex [16]. Figure 4 shows the influence of pH and HP-β-CD on the uv-vis absorption spectrum of Fe(III)-TPPS. At pH 6, the Soret band for Fe(III)-TPPS at 394 nm in the absence of HP-β-CD was clearly shifted to 419 nm in the presence of HP-β-CD (1 mg ml^{-1}), indicating the formation of a supramolecular complex. However, at pH 4, a red-shift in the Soret band in the presence of HP-β-CD was not clearly observed, but the band was broadened. The broadening of the peak at pH 4 may be due to the contribution of both unbound and bound species of Fe(III)-TPPS to HP-β-CD. To evaluate the ability of Fe(III)-TPPS to bind HP-β-CD, the formation constants (K_f) were determined by a spectroscopic titration method, as described in a previous report [16]. As shown in Table 3, the log K_f at pH 6 (5.1) was larger than that at pH 4 (4.6). These results lead to the conclusion that, at pH 6, the addition of HP-β-CD is more effective in stabilizing Fe(III)-TPPS than at pH 4. Therefore, the conditions in the Fe(III)-TPPS/HP-β-CD/$KHSO_5$ catalytic system for degrading PCP in contaminated soil suspensions were optimal at pH 6. As indicated in Table 1, the pH values of soil suspensions were around 6, except for the case of kaolin, which can be regarded as a control soil sample. It has been reported that pH values of soils are in the range of 3 – 7 [27]. Thus, pH control may be required, if the pH of the soil is in the acidic region.

3.4. Optimization of dosage

Figure 5 shows the effect of the concentration of Fe(III)-TPPS in the soil suspension on the percent PCP disappearance. For the Kaolin and Kanuma-soils, the percent PCP disappearance increased with increasing concentration of Fe(III)-TPPS up to 5 μM. However, for the Red-soil, 10 μM of Fe(III)-TPPS was required to reach a plateau. Figure 6 shows the influence of the concentration of $KHSO_5$ in a soil suspension on the percent PCP disappearance. Although the percent PCP disappearance increased with increasing concentration of $KHSO_5$ in all soils, a higher concentration of $KHSO_5$ was required in the Red-soil to reach the percent PCP disappearance comparable to the cases of Kaolin and Kanuma-soil. As shown in Table 1, organic carbon in the Red-soil (1.58%) was much higher than those in other soils. Because soil organic matter related to humic substances includes a variety of phenolic compounds [28], its presence may lead to the retardation of the catalytic oxidation of PCP. Thus, the larger dosages of Fe(III)-TPPS and $KHSO_5$ may be required in the case of the Red-soil.

Figure 7 shows the influence of the concentration of HP-β-CD in the soil suspension on the percent PCP disappearance. In all soils, the percent PCP disappearance increased with increasing concentration of HP-β-CD up to 1.0 mg ml^{-1} and then reached a plateau. In the present study, because the dosages should be reduced as much as possible, the concentrations of Fe(III)-TPPS, $KHSO_5$ and HP-β-CD in the soil suspensions were set to 10 μM, 250 μM and 1.5 mg l^{-1}, respectively. Although the influence of the reaction period (1, 3 and 5 days) was investigated under optimal dosages, the percent PCP disappearance did not vary significantly in any of the soils (89 – 96%).

3.5. Mineralization of PCP to CO_2

In the Fe(III)-TPPS/HP-β-CD/$KHSO_5$ catalytic system, tetrachloroquinone, nonachlorodiphenyl ether and octachlorodibenzo-*p*-dioxin were detected as oxidation products in the initial stage of the reaction (10 min) [16]. However, the levels of these compounds decreased with increasing reaction time and the numbers of chlorine atoms released from the PCP were 2.8 – 3.1, suggesting the further oxidation of the byproducts [16]. However, because soil samples include large amounts of chloride ions, dechlorination could not be determined in the present study. In remediation technologies for soil contaminated with xenobiotics, mineralization of the xenobiotics is highly desirable to reduce the potential risks of pollution. Therefore, the mineralization of PCP to CO_2 was the major focus in the present study. Figure 8 shows the effect of HP-β-CD on the percentage of mineralization of ^{14}C-labeled PCP to $^{14}CO_2$ for a 5 day reaction period. In all soils, the percentages of $^{14}CO_2$ in the presence of HP-β-CD (24 – 28%) were larger than those in the absence of HP-β-CD (12 – 18%). These results demonstrate that added HP-β-CD is effective in enhancing PCP degradation in contaminated soil suspensions.

4. Conclusions

The addition of HP-β-CD to the Fe(III)-TPPS / $KHSO_5$ catalytic system was found to be useful for enhancing the degradation of PCP in contaminated soil suspensions. Although Fe(III)-TPPS was stabilized by forming a supramolecular complex at pH 4 and 6, a pH of 6 was selected as optimal for the degradation conditions because the self-degradation of Fe(III)-TPPS was retarded to a greater extent. The combined processes of PCP extraction with some CDs and the degradation of PCP using a TiO_2 photocatalyst [20] and electrochemical method [21] have recently been reported. Thus, the Fe(III)-TPPS / HP-β-CD / $KHSO_5$ catalytic system, examined in the present study, may also be useful for the treatment of extracts of PCP-contaminated soils with aqueous HP-β-CD.

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Figure Captions

Fig. 1. Chemical structures of Fe(III)-TPPS and HP-β-CD, and the formation of a supramolecular complex.

Fig. 2. Influence of pH and HP-β-CD on the percentage of PCP disappearance. Soils 0.2 g, [PCP] 50 μM, [Fe(III)-TPPS] 10 μM, [$KHSO_5$] 250 μM, [HP- β-CD] 2.5 mg ml^{-1}, reaction period of 1 day.

Fig. 3. Influence of pH and HP-β-CD on the kinetics of the self-degradation of Fe(III)-TPPS. [Fe(III)-TPPS] 5 μM, [$KHSO_5$] 125 μM, [HP-β-CD] 1.0 mg ml^{-1}.

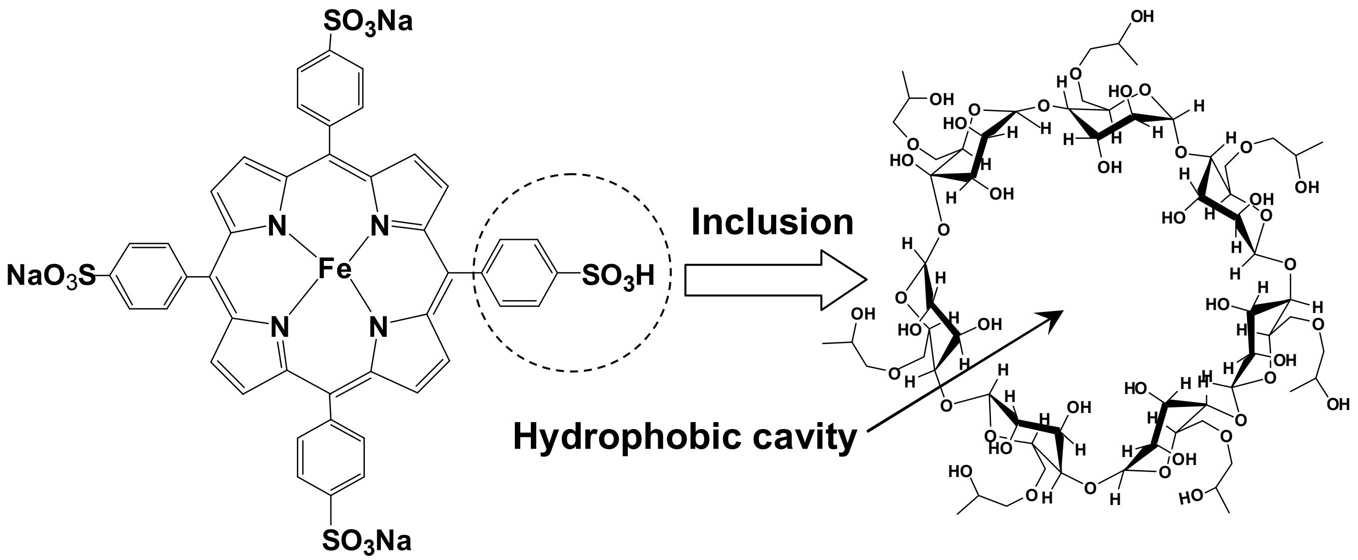
Fig. 4. Influence of pH and HP-β-CD on the uv-vis absorption spectrum of Fe(III)-TPPS (5 μM).

Fig. 5. Influence of Fe(III)-TPPS concentration on percent PCP disappearance. Soils 0.2 g, [PCP] 50 μM, [$KHSO_5$] 250 μM, [HP- β-CD] 2.5 mg ml^{-1}, reaction period of 1 day, ■ kaolin, ● Kanuma-soil, ▲ Red-soil.

Fig. 6. Influence of $KHSO_5$ concentration on percent PCP disappearance. Soils 0.2 g, [PCP] 50 μM, [Fe(III)-TPPS] 10 μM, [HP- β-CD] 2.5 mg ml^{-1}, reaction period of 1 day, ■ kaolin, ● Kanuma-soil, ▲ Red-soil.

Fig. 7. Influence of HP-β-CD concentration on percent PCP disappearance. Soils 0.2 g, [PCP] 50 μM, [Fe(III)-TPPS] 10 μM, [$KHSO_5$] 250 μM, reaction period of 1 day, ■ kaolin, ● Kanuma-soil, ▲ Red-soil.

Fig. 8. Effects of HP-β-CD on percent ^{14}C-labeled PCP mineralization to $^{14}CO_2$. Soils 0.1 g, [PCP] 25 μM, [Fe(III)-TPPS] 10 μM, [$KHSO_5$] 250 μM, [HP- β-CD] 1.5 mg ml^{-1}, reaction period of 5 days.



Fe(III)-TPPS

HP-β-CD

Fig. 1

(HAZMAT-D-06-00673)

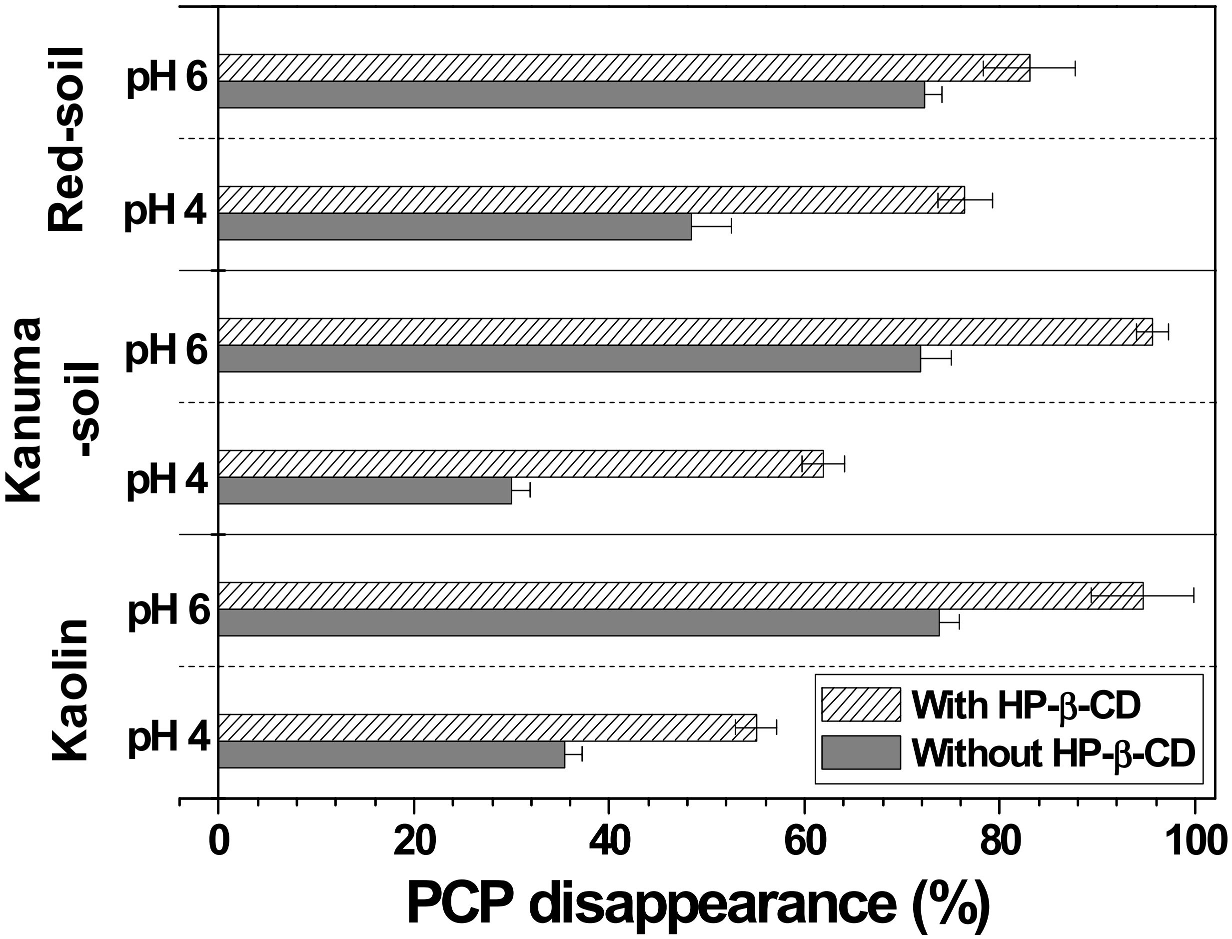


Fig. 2

(HAZMAT-D-06-00673)

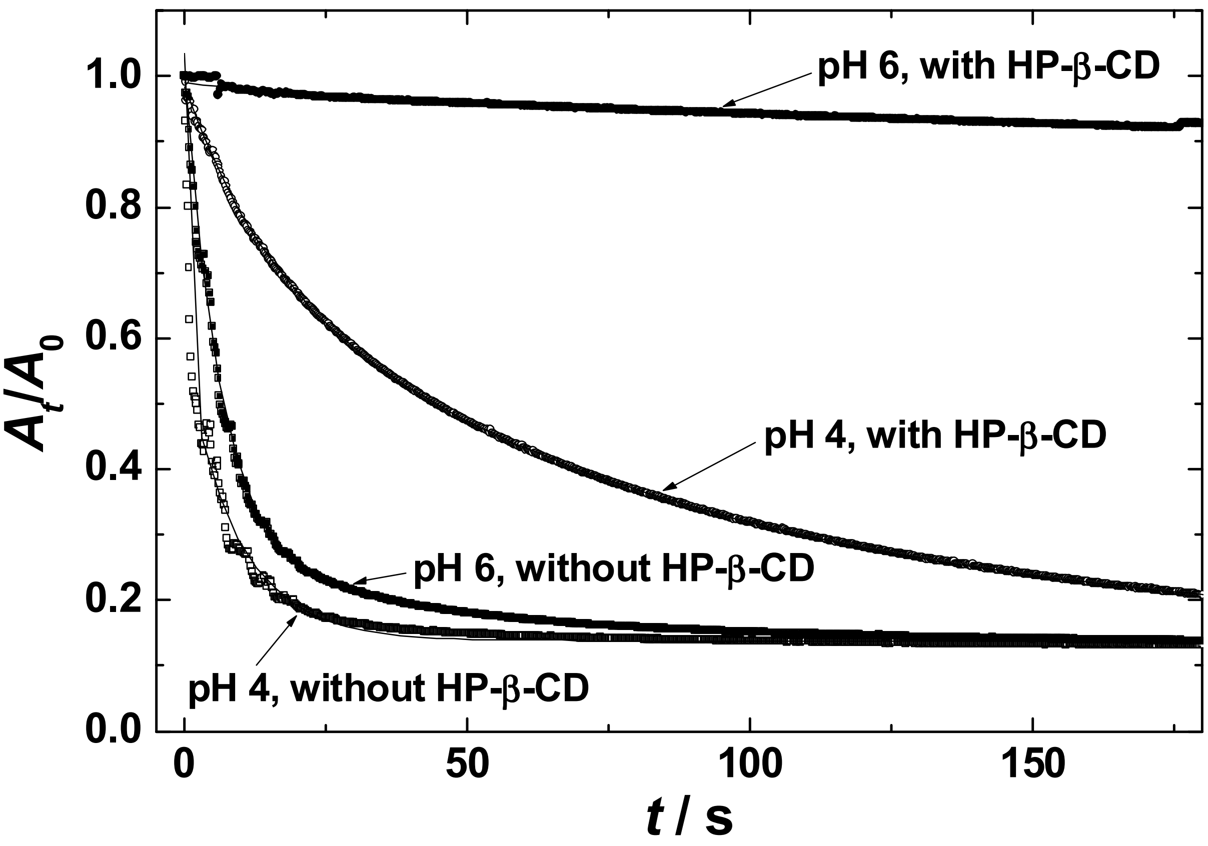


Fig. 3

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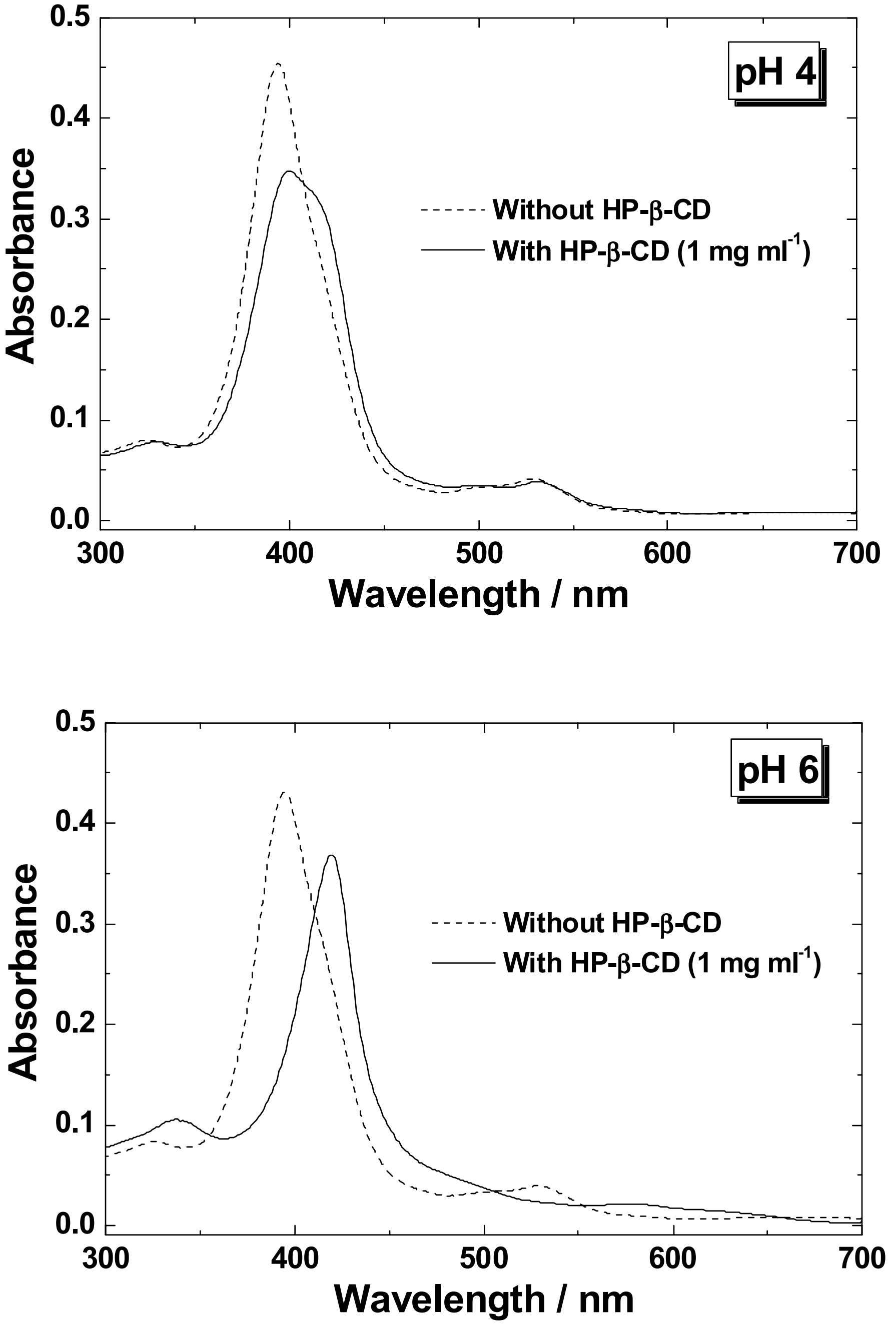

Fig. 4

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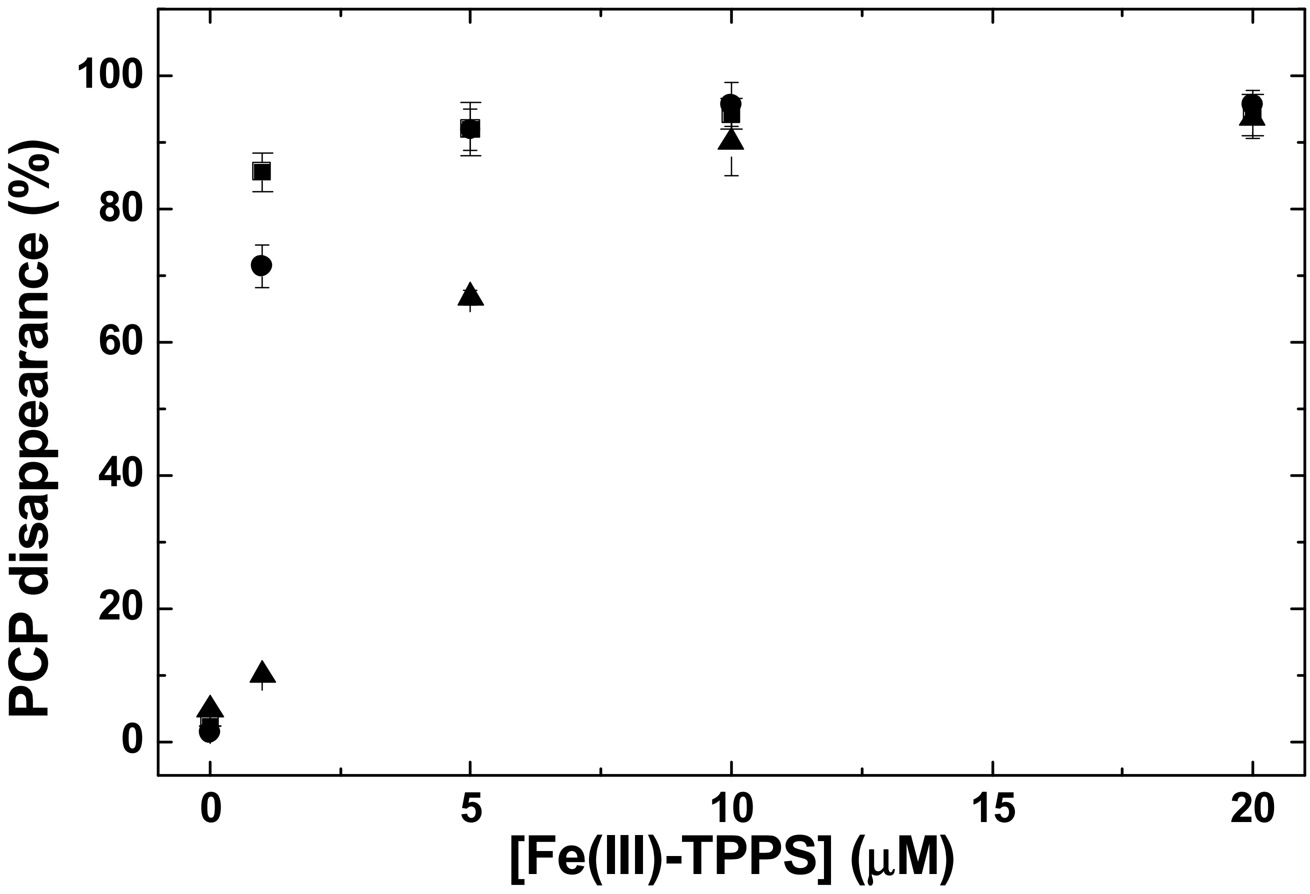

Fig. 5

(HAZMAT-D-06-00673)

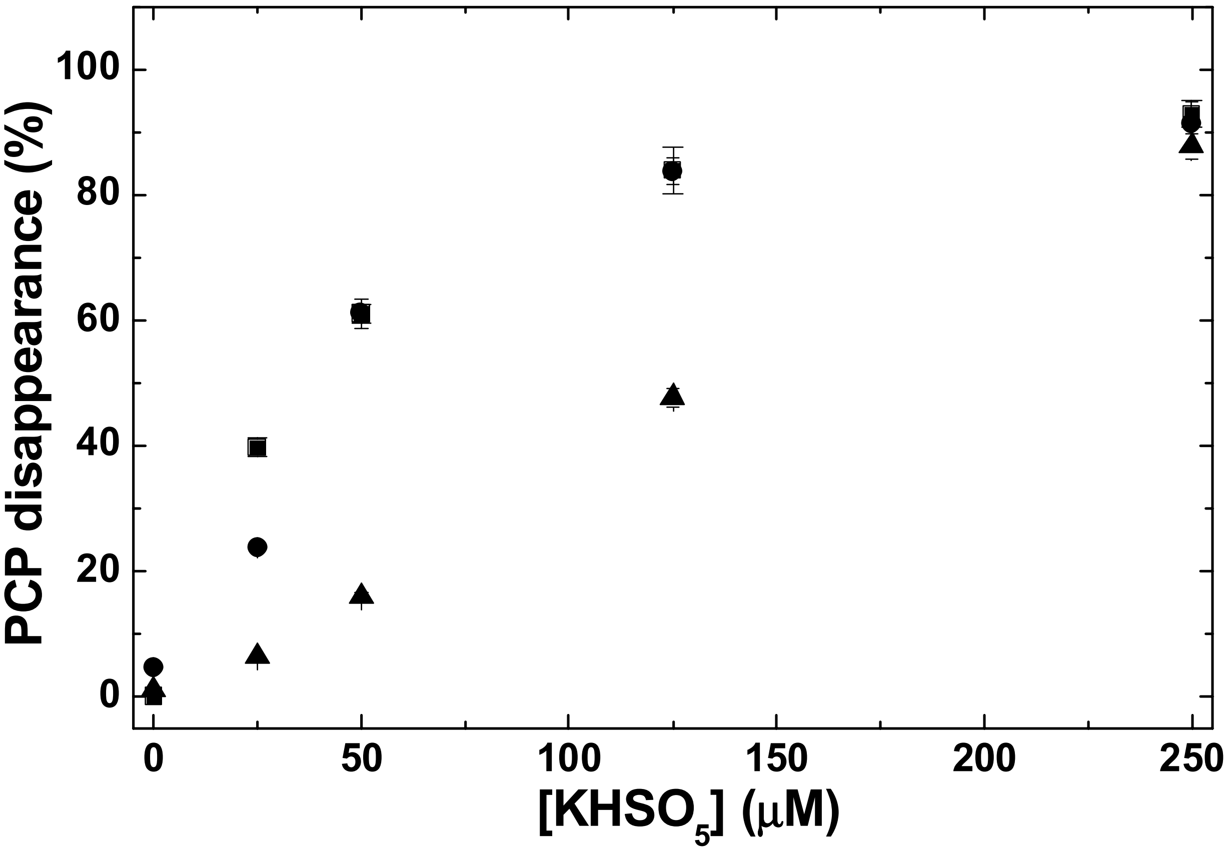

Fig. 6

(HAZMAT-D-06-00673)

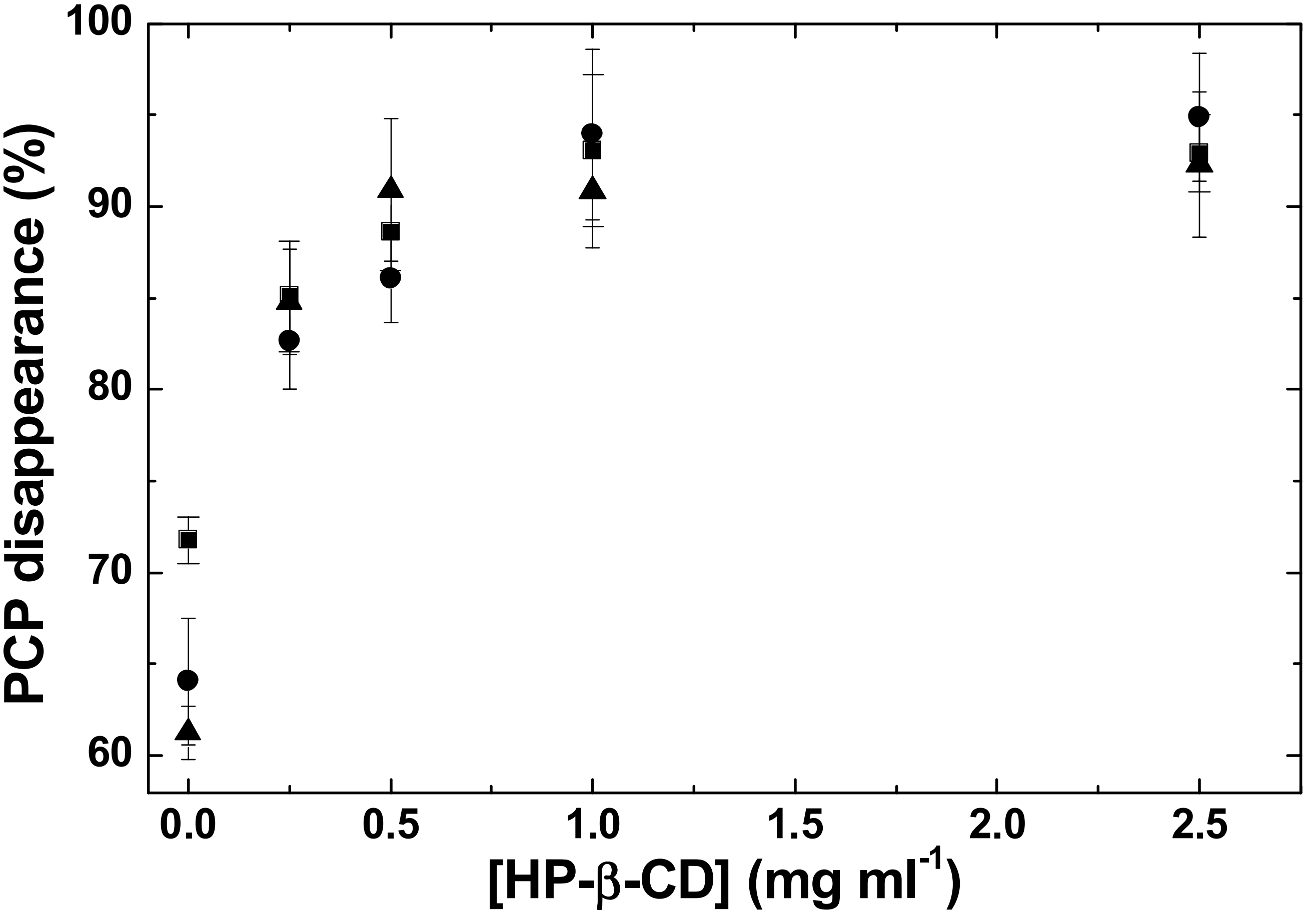

Fig. 7

(HAZMAT-D-06-00673)

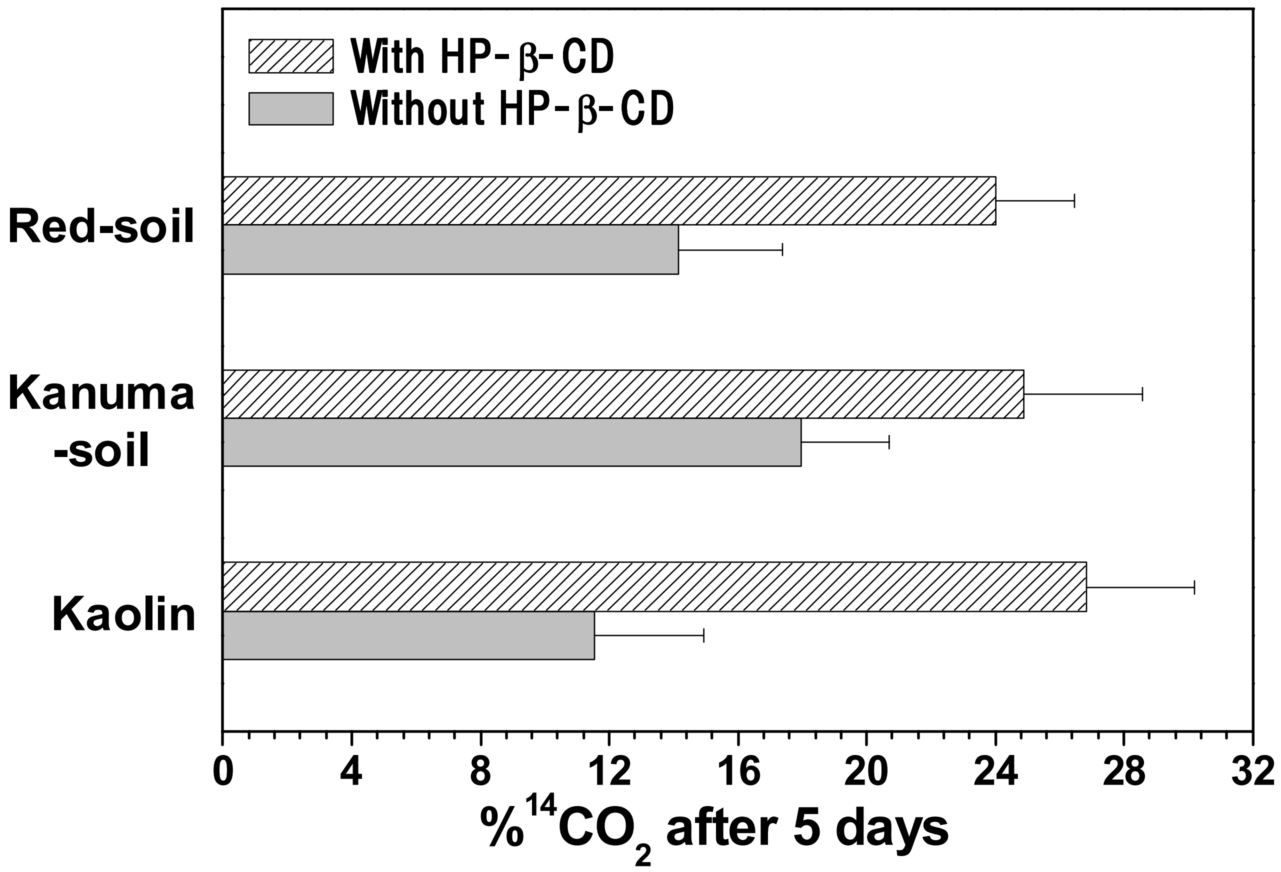

Fig. 8

(HAZMAT-D-06-00673)

Table 1

The pH values, bet-N_2 specific surface areas and elemental compositions for soil samples.

Soil samples	Kaolin	Kanuma-soil	Red-soil
pH [a]	7.71	6.27	6.01
SSA (m^2 g^{-1}) [b]	2.72	106	26.3
OC (wt %) [c]	nd [d]	0.16	1.58
Al (wt %)	8.6	10.1	9.3
Si (wt %)	35.3	16.0	12.8
Ca (wt %)	0.09	0.77	0.36
Fe (wt %)	0.11	0.97	4.69
Mn (wt %)	0.002	0.020	0.079

[a] The pH of the soil slurry was determined for a mixture of soil and water at a ratio of 1 : 2.5 (soil : water = w/w) [18].

[b] Bet-N_2 specific surface area.

[c] Organic carbon

[d] Not detected

Table 2

Extraction efficiencies (%) of PCP from contaminated soil suspensions for three controls.

Patterns of control	Kaolin	Kanuma-soil	Red-soil
pH 4			
PCP + buffer	94 ± 5	101 ± 6	99 ± 3
PCP + buffer + Fe(III)-TPPS	97 ± 4	97 ± 5	99 ± 6
PCP + buffer + $KHSO_5$	88 ± 7	99 ± 4	59 ± 3
pH 6			
PCP + buffer	91 ± 3	97 ± 7	96 ± 2
PCP + buffer + Fe(III)-TPPS	92 ± 4	96 ± 2	97 ± 3
PCP + buffer + $KHSO_5$	94 ± 2	93 ± 4	89 ± 4

Table 3

Kinetic constants for the self-degradation of Fe(III)-TPPS (k_0 and $k_{\text{HP-β-CD}}$) and the formation constants of the supramolecular complex (K_f) at pH 4 and 6.

pH	k_0 (s^{-1})	$k_{\text{HP-β-CD}}$ (s^{-1})	$k_0/k_{\text{HP-β-CD}}$	log K_f
4	1.3	7.3×10^{-2}	18	4.6
6	0.16	4.3×10^{-3}	36	5.1