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Title	Degradation of pentachlorophenol in contaminated soil suspensions by potassium monopersulfate catalyzed oxidation by a supramolecular complex between tetra(p-sulfophenyl)porphineiron(III) and hydroxypropylcyclodextrin.
Author(s)	Fukushima, Masami; Tatsumi, Kenji
Citation	Journal of Hazardous Materials, 144(1-2), 222-228 https://doi.org/10.1016/j.jhazmat.2006.10.013
Issue Date	2007-06-01
Doc URL	http://hdl.handle.net/2115/28125
Туре	article (author version)
File Information	JHM144-1-2.pdf



1	Revised manuscript: HAZMAT-D-06-00673			
2	Degradation of pentachlorophenol in contaminated soil suspensions by potassium			
3	monopersulfate catalyzed oxidation by a supramolecular complex between tetra			
4	(<i>p</i> -sulfophenyl)porphineiron(III) and hydroxypropyl-β-cyclodextrin			
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15				
16	Abstract			
17	To enhance the catalytic oxidation of pentachlorophenol (PCP) in contaminated soil			
18	suspensions using tetra(p-sulfophenyl)porphineiron(III) (Fe(III)-TPPS) as a catalyst and			
19	potassium monopersulfate (KHSO5) as the single-oxygen donor, the effect of added			
20	hydroxypropyl- β -cyclodextrin (HP- β -CD) was examined. At pH 4 and 6, the percentage			
21	of PCP disappearance increased substantially in the presence of HP- β -CD. In addition,			
22	the self-degradation of Fe(III)-TPPS was significantly retarded in the presence of			
23	HP- β -CD. This retarded self-degradation can be attributed to the stabilization of			
24	Fe(III)-TPPS via the formation of a supramolecular complex with HP- β -CD. The kinetic			

1	constant for the self-degradation of Fe(III)-TPPS in the presence of HP- β -CD at pH 6
2	was much smaller than that at pH 4, indicating that Fe(III)-TPPS is more stable at pH 6.
3	Thus, the amount of Fe(III)-TPPS, KHSO ₅ and HP- β -CD required to degrade PCP in
4	contaminated soil suspensions was optimal at pH 6. When PCP-contaminated soil
5	suspensions were treated under the optimized conditions, $12 - 18\%$ and $24 - 28\%$ of the
6	PCP was mineralized to CO_2 in the absence and presence of HP- β -CD, respectively.
7	These results show that the presence of HP- β -CD in the Fe(III)-TPPS/KHSO ₅ catalytic
8	system is effective in enhancing the degradation of PCP in contaminated soil
9	suspensions.

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

13

14 **1. Introduction**

Pentachlorophenol (PCP) has, in the past, been utilized as a wood preservative and in 1516 herbicides. A recent study indicated that chlorophenols, such as PCP, are the main cause 17of 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 1819 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 20and related health issues. Technologies for the remediation of PCP-contaminated soils 2122include chemical oxidation, washing the soil and biological degradation. The Fenton 23reaction 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 H₂O₂ are 24

required, and an iron(III) hydroxide sludge is produced during the reaction. To 1 $\mathbf{2}$ 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 3 soil is removed by extraction with organic solvents [7]. However, this may not be an 4 environmentally sound procedure. On the other hand, biological degradation of PCP $\mathbf{5}$ using microorganisms is known to be a practical process [8, 9]. However, the 6 7 introduction of non-indigenous microorganisms into contaminated soils is problematic 8 from an ecological point of view.

9 The use of a chemical catalyst to degrade PCP may circumvent some of the above 10 problems associated with bioremediation. It is known that iron(III)-porphyrins, which 11 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 12iron(III)-porphyrins are much less sensitive to variations in environmental conditions 1314than are microorganisms and even enzymes in vitro. Thus, the use of iron(III)-porphyrins might make the maintenance of reaction conditions a more 15straightforward procedure. However, iron(III)-porphyrins are unstable in the presence of 1617peroxides, such as H_2O_2 and KHSO₅, because they are susceptible to self-degradation [14, 15]. The self-degradation of iron(III)-porphyrins results in a decrease in the 18 19oxidation efficiency of the organic substrate. We recently reported that the addition of hydroxypropyl-β-cyclodextrin 20 $(HP-\beta-CD)$ was effective in stabilizing iron(III)-porphyrin in the presence of KHSO₅, due to the formation of a supramolecular 2122complex 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 23Fe(III)-TPPS and the hydrophobic cavity of HP-β-CD. 24

3

A few applications of the catalytic systems using iron(III)-porphyrins for the 1 $\mathbf{2}$ remediation of PCP-contaminated soils have been reported [17, 18]. However, PCP degradation (mineralization to CO₂) was achieved up to 10% [17]. Fe(III)-TPPS is 3 known to be a non-toxic biomimetic catalyst, and KHSO₅, commercially sold as 4 "Oxone", is known to be a stable and environmentally safe oxidant. In addition, $\mathbf{5}$ HP-β-CD, a biologically derived material, has been used for the extraction of 6 chlorophenols from contaminated soils [19-21]. These facts suggest that combining the 7 8 Fe(III)-TPPS/KHSO₅ catalytic system and HP- β -CD could be a clean and safe process 9 for the remediation of PCP-contaminated soils. The purpose of the present study was to 10 examine the effect of added HP- β -CD on the degradation of PCP in the Fe(III)-TPPS/KHSO₅ catalytic system. In order to apply the above system to the 11 12treatment of PCP-contaminated soils, the optimal pH and dosage for the reaction were 13determined. In addition, the mineralization of PCP to CO₂ was examined under optimal conditions. 14

15

16 2. Materials and Methods

17 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]. KHSO₅ was obtained as a triple salt, 20 2KHSO₅·KHSO₄·K₂SO₄ (Merck). PCP (99.0% purity) was purchased from Aldrich, and 21 a stock solution (0.01 M) was prepared by dissolving it in acetonitrile. ¹⁴C-labeled PCP 22 was purchased from American Radiolabeled Chemicals Inc. (0.1 mCi ml⁻¹ in ethanol, 23 specific activity 80 mCi mmol⁻¹). HP-β-CD (1.0 molar substitution, Mw 1540) was 24 purchased from Aldrich.

Kaolin was purchased from Kukita Yakuhin Kogyo (Tokyo) and was used without 1 $\mathbf{2}$ 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 3 then sieved through a stainless steel sieve (0.22 mm). A particle size below 0.22 mm 4 was employed in the tests. The pH values, bet-N₂ specific surface areas and elemental $\mathbf{5}$ compositions of the soil samples are summarized in Table 1. The specific surface area 6 7 for Kanuma-soil was much larger than those for other samples. This can be attributed to 8 the fact that Kanuma-soil includes large amounts of allophane moieties [23].

9

10 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 11 NaH₂PO₄/Na₂HPO₄/citrate buffer at pH 4 or 6 was pipetted into the glass tube, and the 1213solution 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 - 10014 μ l aliquot of aqueous Fe(III)-TPPS (200 μ M) and a 0 - 50 μ l aliquot of aqueous 15HP- β -CD (100 mg ml⁻¹) were added to the suspension, and a 0 – 50 μ l of aqueous 0.01 16M KHSO₅ was then added. The glass tube was then allowed to shake at room 17temperature $(23 - 25^{\circ}C)$. After 1, 3 or 5 days of shaking, 1 ml of 2-propanol was added 1819 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[®] 20filter (diameter 13 mm, pore size 0.45 µm, hydrophilic PTFE type, ADVANTEC). It 2122was 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 23aliquot of the filtrate was injected into a JASCO PU-980 type HPLC pumping system. 24

The mobile phase consisted of a mixture of 0.08% aqueous H₃PO₄ and methanol (20/80 1 = v/v), and the flow rate was set at 1 ml min⁻¹. A 5C18-MS Cosmosil packed column $\mathbf{2}$ 3 $(4.6 \text{ mm i.d.} \times 250 \text{ mm}, \text{Nacalai Tesque})$ was used as the solid phase, and the column temperature was maintained at 50°C. PCP was determined by Uv absorption at a 4 wavelength of 220 nm. The efficiency of extraction of PCP from the contaminated soil $\mathbf{5}$ suspensions was evaluated (Table 2). In the absence of both Fe(III)-TPPS and KHSO₅ 6 ("PCP + buffer" in Table 2), 91 - 101% of the PCP was extracted from the soil 7 8 suspensions at pH 4 and 6. All runs were conducted in triplicate.

9

10 2.3. Mineralization of 14 C-labeled PCP

A 0.5 ml aliquot of ¹⁴C-labeled PCP in ethanol was evaporated in a stream of dry N₂. 11 The residue was then dissolved in 1 ml of acetonitrile (final concentration of PCP 625 12 μ M). A 19.2 ml aliquot of buffer solution at pH 6 and a 0.8 ml aliquot of ¹⁴C-labeled 13PCP in acetonitrile were mixed with stirring (final concentration of PCP 25 µM). A 0.1 g 14sample of soil was placed in a 20-ml Erlenmeyer flask. A 1 ml aliquot of the buffer 15solution, including ¹⁴C-labeled PCP, was then added and 25 µl of aqueous Fe(III)-TPPS 16 (400 μ M) and 0 or 15 μ l of aqueous HP- β -CD (100 mg ml⁻¹) were then added. After 17adding 25 µl of aqueous KHSO₅ (0.01 M), the flask was fitted with a stopper, which 18contained a polyethylene center well containing a glass wool plug impregnated with 0.4 19 ml of aqueous 2 M NaOH as a ¹⁴CO₂ trap. After a 5 day reaction period, 1 ml of 202-propanol and 0.4 ml of 1.8 M aqueous H₂SO₄ were injected via a syringe from the top 21of stopper to release the ${}^{14}CO_2$ from the soil suspension. After shaking for 1 day, a 2 ml 22aliquot of the soil suspension was centrifuged (6200 rpm, 1 min), and the supernatant 23was filtered thorough a DISMIC[®] filter. A 1 ml aliquot of the filtrate was pipetted into a 24

glass vial including a mixture of methanol (1 ml) and scintillation cocktail (9 ml). The 1 $\mathbf{2}$ 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. 3 A 1 ml aliquot of this mixture was pipetted into a glass vial including methanol and 4 scintillation cocktail. The radioactivities (dpm) in the vials were determined using an LS $\mathbf{5}$ 6 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 7 ¹⁴C-labeled PCP was added to an Erlenmeyer flask containing 0.1 g of soil. After 8 9 shaking for 5 days, the same procedures, as described above, were carried out. Each experimental run was conducted in duplicate. The percentage of ¹⁴C-labeled PCP 10 converted to ${}^{14}CO_2$ (${}^{14}CO_2$) was calculated using the equation below: 11

$$(\%^{14}\mathrm{CO}_2) = (R_{\mathrm{before}} - R_{\mathrm{sus}})/R_{\mathrm{before}} \times 100$$

where R_{sus} represents the radioactivities after the reaction in the soil suspension. In addition, the recoveries of ¹⁴C 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 $92 \pm 7\%$.

17

18 2.4. Uv-vis absorption spectra and kinetic measurement

19 Uv-vis absorption spectra of a buffer solution at pH 4 or 6, containing Fe(III)-TPPS (5 20 μM) and HP-β-CD, were obtained on a Jasco V-550 type spectrophotometer (Japan 21 Spectroscopic Co.) with a quartz cell (1 × 1 cm) at 25°C. The kinetics of 22 self-degradation were monitored by the decolorization of Fe(III)-TPPS at 25°C. A 37.5 23 μl aliquot of aqueous KHSO₅ (0.01 M) was added to 3 ml of an aqueous solution in a 1 24 × 1 cm quartz cell, which contained Fe(III)-TPPS (5 μM) and HP-β-CD (1.0 mg ml⁻¹) at pH4 or 6, with stirring. The absorbance of Fe(III)-TPPS before adding KHSO₅ (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 KHSO₅, 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.

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8 3. Results and Discussion

9 3.1. Control experiments

10 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 KHSO₅, is 11 12required 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 13oxidation of PCP to a pentachlorophenoxy radical (PCP \cdot). The PCP \cdot is further 1415oxidized, giving rise to a variety of byproducts are produced [10, 11, 13]. Prior to applying the Fe(III)-TPPS/KHSO₅ catalytic system to the degradation of PCP in 1617contaminated soil suspensions, the influence of some matrices in the soil suspensions on the disappearance of PCP was examined. 18

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 KHSO₅ or not, was carried out.



8

1	presence of Fe(III)-TPPS only ("PCP + buffer + Fe(III)-TPPS" in Table 2), the
2	recoveries were in the range of $92 - 99\%$ at pH 4 and 6, indicating no influence of soil
3	components and Fe(III)-TPPS. However, in the presence of KHSO ₅ only ("PCP + buffer
4	+ KHSO ₅ " in Table 2), a significant lower recovery (59%) was observed in the Red-soil
5	at pH 4. As shown in Table 1, the contents of organic carbon and iron in the Red-soil
6	were much larger than those in the other soils. Paciolla et al. [25, 26] proposed that
7	ferryl-oxo species can be formed by the hydrogen peroxide catalysed oxidation by an
8	iron(III)-soil organic matter complex. Thus, it is likely that the lower recovery for the
9	Red-soil in the presence of KHSO ₅ only at pH 4 may be due to the formation of the
10	ferryl-oxo species via a reaction between KHSO5 and iron in the soil.

11

12 *3.2. Influence of pH on the disappearance of PCP*

In the presence of both Fe(III)-TPPS and KHSO₅, the influence of pH and HP-β-CD on 13the percentage of PCP disappearance was investigated (Figure 2). It had previously been 14reported that the percentage of PCP disappearance increased with increasing pH up to 1516 pH 7 in an Fe(III)-TPPS/KHSO₅ catalytic system [11, 12]. As expected from the previous reports, the percentage of PCP disappearance at pH 6 was larger than that at 17pH 4 for all soil samples. In addition, the disappearance of PCP was remarkably 1819 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. 20

21

22 3.3. Influence of pH on the stability of Fe(III)-TPPS

23 The deactivation of Fe(III)-TPPS is due to self-degradation via oxidation by KHSO₅ [14,

24 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 1 $\mathbf{2}$ 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 3 6 was 10-times smaller than that at pH 4. In addition, the kinetic constant in the 4 presence of HP- β -CD ($k_{HP-\beta-CD}$) at pH 6 was 17-times smaller than that at pH 4. These $\mathbf{5}$ 6 results indicate that the self-degradation of Fe(III)-TPPS is significantly retarded at pH 7 6 in the absence and presence of HP- β -CD. As shown in Table 3, the ratio of k_0 to $k_{\rm HP-6-CD}$ ($k_0/k_{\rm HP-6-CD}$) at pH 6 was much larger than that at pH 4. This shows that the 8 retardation of Fe(III)-TPPS self-degradation by added HP-β-CD at pH 6 is greater than 9 10 that at pH4.

The stabilization of Fe(III)-TPPS in the presence of HP-β-CD can be attributed to the 11 12formation 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 13for Fe(III)-TPPS at 394 nm in the absence of HP- β -CD was clearly shifted to 419 nm in 14the presence of HP- β -CD (1 mg ml⁻¹), indicating the formation of a supramolecular 15complex. However, at pH 4, a red-shift in the Soret band in the presence of HP-β-CD 1617was 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 18 Fe(III)-TPPS to HP- β -CD. To evaluate the ability of Fe(III)-TPPS to bind HP- β -CD, the 19 formation constants (K_{f}) were determined by a spectroscopic titration method, as 2021described in a previous report [16]. As shown in Table 3, the log $K_{\rm f}$ 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 22addition of HP-\beta-CD is more effective in stabilizing Fe(III)-TPPS than at pH 4. 2324Therefore, the conditions in the Fe(III)-TPPS/HP- β -CD/KHSO₅ 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.

6

7 *3.4. Optimization of dosage*

Figure 5 shows the effect of the concentration of Fe(III)-TPPS in the soil suspension on 8 the percent PCP disappearance. For the Kaolin and Kanuma-soils, the percent PCP 9 10 disappearance increased with increasing concentration of Fe(III)-TPPS up to 5 μ M. However, for the Red-soil, 10 µM of Fe(III)-TPPS was required to reach a plateau. 11 12Figure 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 1314increasing 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 15of Kaolin and Kanuma-soil. As shown in Table 1, organic carbon in the Red-soil 1617(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 18 19 lead to the retardation of the catalytic oxidation of PCP. Thus, the larger dosages of Fe(III)-TPPS and KHSO₅ may be required in the case of the Red-soil. 20

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, KHSO₅ and HP- β -CD in the soil suspensions were set to 10 μ M, 250 μ M and 1.5 mg Γ^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%).

 $\mathbf{5}$

6 3.5. Mineralization of PCP to CO_2

Fe(III)-TPPS/HP- β -CD/KHSO₅ catalytic 7 In the system, tetrachloroquinone, 8 nonachlorodiphenyl ether and octachlorodibenzo-p-dioxin were detected as oxidation 9 products in the initial stage of the reaction (10 min) [16]. However, the levels of these 10 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 11 12[16]. However, because soil samples include large amounts of chloride ions, dechlorination could not be determined in the present study. In remediation technologies 13for soil contaminated with xenobiotics, mineralization of the xenobiotics is highly 14desirable to reduce the potential risks of pollution. Therefore, the mineralization of PCP 15to CO₂ was the major focus in the present study. Figure 8 shows the effect of HP-β-CD 16on the percentage of mineralization of ¹⁴C-labeled PCP to ¹⁴CO₂ for a 5 day reaction 17period. In all soils, the percentages of ${}^{14}CO_2$ in the presence of HP-B-CD (24 – 28%) 1819 were larger than those in the absence of HP- β -CD (12 – 18%). These results demonstrate that added HP-\beta-CD is effective in enhancing PCP degradation in 2021contaminated soil suspensions.

22

23 4. Conclusions

24 The addition of HP- β -CD to the Fe(III)-TPPS / KHSO₅ catalytic system was found to be

1	useful for enhancing the degradation of PCP in contaminated soil suspensions. Although
2	Fe(III)-TPPS was stabilized by forming a supramolecular complex at pH 4 and 6, a pH
3	of 6 was selected as optimal for the degradation conditions because the self-degradation
4	of Fe(III)-TPPS was retarded to a greater extent. The combined processes of PCP
5	extraction with some CDs and the degradation of PCP using a TiO ₂ photocatalyst [20]
6	and electrochemical method [21] have recently been reported. Thus, the Fe(III)-TPPS /
7	$HP-\beta-CD/KHSO_5$ catalytic system, examined in the present study, may also be useful
8	for the treatment of extracts of PCP-contaminated soils with aqueous HP- β -CD.
9	
10	Acknowledgment
11	This work was supported by Grants-in-Aid for Scientific Research in Japan Society for
12	the Promotion of Science (18201013). Authors wish to thank to Dr. H. Tamura

13 (Graduate School of Engineering, Hokkaido University) for useful advice concerning
14 the measurement of the bet-N₂ specific surface area.

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1	Figure Captions
2	
3	Fig. 1. Chemical structures of Fe(III)-TPPS and HP- β -CD, and the formation of a
4	supramolecular complex.
5	
6	Fig. 2. Influence of pH and HP- β -CD on the percentage of PCP disappearance. Soils 0.2
7	g, [PCP] 50 μ M, [Fe(III)-TPPS] 10 μ M, [KHSO ₅] 250 μ M, [HP- β -CD] 2.5 mg ml ⁻¹ ,
8	reaction period of 1 day.
9	
10	Fig. 3. Influence of pH and HP- β -CD on the kinetics of the self-degradation of
11	Fe(III)-TPPS. [Fe(III)-TPPS] 5 μ M, [KHSO ₅] 125 μ M, [HP- β -CD] 1.0 mg ml ⁻¹ .
12	
13	Fig. 4. Influence of pH and HP- β -CD on the uv-vis absorption spectrum of Fe(III)-TPPS
14	(5 μM).
15	
16	Fig. 5. Influence of Fe(III)-TPPS concentration on percent PCP disappearance. Soils 0.2
17	g, [PCP] 50 μ M, [KHSO ₅] 250 μ M, [HP- β -CD] 2.5 mg ml ⁻¹ , reaction period of 1 day,
18	kaolin, ● Kanuma-soil, ▲ Red-soil.
19	
20	Fig. 6. Influence of KHSO ₅ concentration on percent PCP disappearance. Soils 0.2 g,
21	[PCP] 50 μ M, [Fe(III)-TPPS] 10 μ M, [HP- β -CD] 2.5 mg ml ⁻¹ , reaction period of 1 day,
22	■ kaolin, ● Kanuma-soil, ▲ Red-soil.
23	
24	Fig. 7. Influence of HP- β -CD concentration on percent PCP disappearance. Soils 0.2 g,
25	[PCP] 50 μ M, [Fe(III)-TPPS] 10 μ M, [KHSO ₅] 250 μ M, reaction period of 1 day,
26	kaolin, ● Kanuma-soil, ▲ Red-soil.
27	
28	Fig. 8. Effects of HP- β -CD on percent ¹⁴ C-labeled PCP mineralization to ¹⁴ CO ₂ . Soils
29	0.1 g, [PCP] 25 μ M, [Fe(III)-TPPS] 10 μ M, [KHSO ₅] 250 μ M, [HP- β -CD] 1.5 mg ml ⁻¹ ,
30	reaction period of 5 days.



Fe(III)-TPPS

HΡ-*β* -CD

Fig. 1

(HAZMAT-D-06-00673)



Fig. 2 (HAZMAT-D-06-00673)



Fig. 3

(HAZMAT-D-06-00673)



Fig. 4 (HAZMAT-D-06-00673)



Fig. 5

(HAZMAT-D-06-00673)



Fig. 6

(HAZMAT-D-06-00673)



Fig. 7 (HAZMAT-D-06-00673)





(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
AI (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-N₂ 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 + KHSO₅	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

рН	<i>k</i> ₀ (s⁻¹)	$k_{\text{HP-}\beta\text{-}\text{CD}}$ (s ⁻¹)	k ₀ /k _{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

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