

Complex formation of water-soluble iron(III)-porphyrin with humic acids and their effects on the catalytic oxidation of pentachlorophenol

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Abstract

The effects of peat humic acids (HAs) on the enhancement of peroxosulfate oxidation of pentachlorophenol (PCP) by iron(III)-tetrakis(*p*-sulfonatophenyl)porphyrin (Fe(III)-TPPS) were studied mechanistically. Eight types of cyclodextrins (CDs) were used as model compounds for the polysaccharide moieties in the HAs, and their effects were compared with those for the HAs. The results indicate that the presence of hydroxypropyl- β -CD (HP- β -CD), β -CD, HP- γ -CD, γ -CD and HAs were effective in suppressing the self-oxidation of Fe(III)-TPPS and resulted in an enhanced PCP oxidation. The stabilization of the Fe(III)-TPPS catalyst can be attributed to complexation of the catalyst with non-ionic hydrophobic regions of HAs. The conditional formation constants (K_f) for the complexes of Fe(III)-TPPS with CDs and HAs were evaluated by the changes in UV–vis absorption spectra of the Soret band of Fe(III)-TPPS. The $\log K_f$ values increased with decreasing rate of self-oxidation of Fe(III)-TPPS, showing that the complexation of Fe(III)-TPPS with CDs and HAs plays an important role in stabilizing Fe(III)-TPPS. ^1H NMR studies of D_2O solutions of Fe(III)-TPPS, HAs and mixtures thereof showed that the hydrophobic regions of HAs contributed to the binding of the sulfonatophenyl group in Fe(III)-TPPS. In addition, complexes of Fe(III)-TPPS with HAs were isolated by ultrafiltration.

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1. Introduction

Oxidative enzymes, such as peroxidase and lignase, are able to catalyze the oxidation of chlorophenols [1,2]. Iron(III)-porphyrin complexes have been examined, in an attempt to mimic the enzymatic oxidation of chlorophenols [3,4]. Such biomimetic catalysts have the potential to serve as clean remedial processes for the removal of organic pollutants in soils. In soil environments, humic acids (HAs) are ubiquitous and play important roles in the remediation of organic pollutants via a variety of interactions, including solubilization [5] and electron transfer [6]. However, HAs are heterogeneous compounds and their physicochemical properties vary with the type of soil. Therefore, we investigated the effect of HA type on the catalytic oxidation of pentachlorophenol (PCP) by iron(III)-tetrakis(sulfonatophenyl)porphyrin (Fe(III)-TPPS) and KHSO_5 [7–10]. In these studies, the addition of peat HAs with a lower content of oxygen-containing functional groups was found to

be effective in enhancing PCP oxidation, when the Fe(III)-TPPS/ KHSO_5 catalytic system was used. However, the reasons why the addition of such HAs is effective in enhancing PCP oxidation have not been elucidated. It has been reported that the addition of phenolic acids that are components of HAs are useful in enhancing PCP oxidation in enzymatic oxidation reactions [11]. However, the addition of phenolic acids was not effective in the Fe(III)-TPPS/ KHSO_5 catalytic system [10].

Piccolo [12,13] recently proposed that HAs in solution are supramolecular that relatively small molecules are loosely bound together by self-association, and that the intermolecular hydrophobic interactions are major factors in this process. In this concept, HAs are created by the association of predominantly hydrophobic compounds (e.g., polymethylenic chains, fatty acids, steroid compounds), which are stabilized at neutral pH by hydrophobic dispersive forces (van der Waals, π – π and CH– π bonding). This suggests that HAs have specific hydrophobic domains. Therefore, HAs are able to associate with PCP and/or phenyl-porphyrins, such as Fe(III)-TPPS, which have hydrophobic characteristics, and these interactions may influence the reactivity of Fe(III)-TPPS toward PCP.

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On the other hand, a number of reports on the formation of inclusion complexes with phenyl-porphyrins [14–23] and chlorophenols [24,25] with a hydrophobic core of cyclodextrins (CDs) have been reported. Since HAs contain large amounts of carbohydrate in the form of polysaccharides [26], such interactions with CDs can be used as a model for peat HAs. In the present study, in an attempt to elucidate the effects of HAs on the enhancement of PCP oxidation in the Fe(III)-TPPS/KHSO₅ catalytic system, the influence of peat HAs or CDs on the stability of Fe(III)-TPPS was examined. In addition, the formation of complexes of Fe(III)-TPPS with HAs was investigated by UV–vis spectrometry, ¹H NMR spectroscopy and an ultrafiltration technique.

2. Experimental

2.1. Materials

Fe(III)-TPPS (Na₃C₄₄H₂₅N₄O₁₂S₄Fe·2H₂O, FW 1090.79) was prepared according to the method of Kawasaki et al. [27], and KHSO₅ was purchased from Merck. PCP (99.0% purity) was purchased from Aldrich, and a stock solution (0.01 M) was prepared by dissolving it in acetonitrile. D₂O, D₃PO₄ (85%) and NaOD (40%) for the ¹H NMR studies were purchased from ISOTEC, Inc. In the ¹H NMR measurements, 3-(trimethylsilyl)propionic acid-d₄ sodium salt (TMSP), which was purchased from Aldrich, was used as a reference compound for determining the chemical shifts. HAs, derived from Shinshinotsu (SHA) and Bibai (BHA) peat soils, were extracted and purified according to the protocol of the International Humic Substances Society [28]. Eight types of CDs were used in the present study: α-CD, β-CD and γ-CD (Nacalai Tesque); hydroxypropyl-α-CD (HP-α-CD), HP-β-CD, HP-γ-CD and β-CD sulfate (SO₄-β-CD) (Aldrich); carboxymethyl-β-CD (CM-β-CD) (Fulka). To compare the formation constants for the complexes of Fe(III)-TPPS with HAs or CDs, a tetrakis(sulfonatophenyl)porphyrin (TPPS, C₄₄H₃₀N₄O₁₂S₄·4H₂SO₄·4H₂O), purchased from Dojindo Laboratory (Kumamoto, Japan), was used.

2.2. Assay for PCP oxidation

A 2 ml aliquot of 0.02 M NaH₂PO₄/Na₂HPO₄/citrate buffer at pH 6 containing 50 mg l⁻¹ of HAs or 2.5 g l⁻¹ of CDs was placed in a 20-ml L-shaped test tube. A 10 μl aliquot of 10 mM PCP in acetonitrile and a 200 μl aliquot of aqueous Fe(III)-TPPS (200 μM) was then added to the buffer solution. Subsequently, a 25 μl aliquot of aqueous 0.01 M KHSO₅ was added, and the test tube was allowed to shake in a Monosin IIA type thermostatic shaking water bath (TAITEC) at 25 ± 0.1 °C. After 60 min reaction period, 1 ml of 2-propanol was added to the test solution. To analyze the level of PCP in the test solution, a 20 μl aliquot of the mixture was injected into a JASCO PU-980 type HPLC pumping system. The mobile phase consisted of a mixture of 0.08% aqueous H₃PO₄ 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. In addition, chloride ions (Cl⁻), released during the oxidation of PCP, were analyzed by means of ion chromatography (DX-500 type, Dionex) using an IonPac AS-11 column (4 mm i.d. × 250 mm, Dionex). All runs were conducted in triplicate.

2.3. UV–vis absorption spectra

UV–vis absorption spectra of a buffer solution at pH 6 (0.02 M NaH₂PO₄/Na₂HPO₄/citrate), containing Fe(III)-TPPS (5 μM) and HAs or CDs, were obtained on a Jasco V-550 type spectrophotometer (Japan Spectroscopic Co.) with a quartz cell (1 cm × 1 cm) at 25 °C. Measurements of the kinetics of decolorization of Fe(III)-TPPS were also performed at 25 °C. A 37.5 μl aliquot of aqueous 0.01 M KHSO₅ was added to 3 ml of the aqueous solution in a 1 cm × 1 cm quartz cell, which contained Fe(III)-TPPS (5 μM) and HAs (50 mg l⁻¹) or CDs (2.0 g l⁻¹) at pH 6, with stirring. The decrease in absorbance was then monitored at 394 nm for periods of up to 120 s by using the kinetic mode of the spectrophotometer. No blank decolorization of Fe(III)-TPPS by only light at 394 nm was observed, even after 5 min of irradiation.

2.4. ¹H NMR spectra

A ¹H NMR spectra of D₂O solutions of Fe(III)-TPPS, HAs and mixtures thereof were obtained on a JEOL Lambda FT-NMR spectrometer (Nippon Denshi) with a resonance frequency for ¹H of 500 MHz. To reduce the large water proton peak (HDO) at 4.76 ppm, the homogate decoupling mode was employed. The spectra were recorded by using a pulse angle of 90° and a 5.0-s pulse delay, with 1024 accumulated scans being collected. A 3.27 mg portion of Fe(III)-TPPS powder was dissolved in 0.6 ml of buffer solution at pD 6.0 (0.02 M D₃PO₄/NaOD). For HAs, 50 mg of HA was dissolved in 5 ml of 0.02 M NaOD and then freeze-dried. Subsequently, the residue was redissolved in 5 ml of D₂O and then freeze-dried. The residue was dissolved in 5 ml of D₂O again and the pD of the solution was then adjusted to 6.0 by adding a D₃PO₄ solution. A mixture of Fe(III)-TPPS and HA was prepared by dissolving Fe(III)-TPPS powder (3.27 mg) in the D₂O solution of HA at pD 6 (0.6 ml). Before transferring the sample solutions to an NMR tube (5 mm Ø), the solutions were passed through a Pasteur-pipette packed with glass wool.

2.5. Ultrafiltration technique

To isolate complexes of Fe(III)-TPPS with HAs, test solutions containing Fe(III)-TPPS (50 μM) and HAs (500 mg l⁻¹) at pH 6 (0.02 M NaH₂PO₄/Na₂HPO₄ buffer) were filtered with simple ultrafiltration filters (Millipore Ultrafree CL filters), having a nominal cut-off of 5000, 30,000 and 100,000 Da. When a 2 ml aliquot of the test solutions for Fe(III)-TPPS + HAs or Fe(III)-TPPS alone were fractionated by ultrafiltration, the iron concentrations in each fraction were measured by using an SPC 3000S type ICP spectrometer (Seiko Instruments, Inc.). In addition, the absorbance at 280 nm and total organic carbon in each

fraction were determined for samples of Fe(III)-TPPS alone, Fe(III)-TPPS + HAs and HAs alone.

3. Results and discussion

3.1. Enhancement of PCP oxidation in the presence of HAs or CDs

Fig. 1 shows the influences of HAs or CDs on percent PCP conversion and the concentration of Cl^- released as a result of oxidation by the Fe(III)-TPPS/ KHSO_5 catalytic system. No significant effects were observed for the PCP oxidation in the presence of α -CD, HP- α -CD and SO_4 - β -CD. However, in the presence of HAs, HP- β -CD, HP- γ -CD and β -CD, the percent PCP conversion increased by more than 20%, compared to the absence of additives (Fig. 1a, none). In particular, more than 80% of the PCP disappeared in the presence of HP- β -CD and HAs. The number of chlorine atoms released from PCP was estimated at 1.6–2.0 in the presence of HAs. However, in the presence of HP- β -CD, the PCP completely disappeared after a 60 min reaction period, and the number of chlorine atoms released was increased to approximately 5. These results indicate that HP- β -CD is the most effective additive for the degradation of PCP.

The reason why PCP oxidation might be enhanced by the addition of HAs and CDs is a topic of interest. In general, because PCP and Fe(III)-TPPS are negatively charged in aqueous solu-

tion at pH 6, interactions with anionic HAs would be difficult due to electrostatic repulsion between the molecules. The relatively lower effects of SO_4 - β -CD and CM- β -CD (Fig. 1a) can be attributed to such electrostatic repulsions. These results suggest that the enhancement could be attributed to interactions between HAs or CDs and PCP or Fe(III)-TPPS. It is well known that CDs contain a hydrophobic core in their structures. In particular, β -CDs can form stable inclusion complexes with PCP [24]. For oxidation systems including CDs, the formation of inclusion complexes between aromatic substrates and CDs results in a higher selectivity for substrate conversion [29,30]. In addition, hydrophobic interactions between PCP and HAs have also been reported [31]. However, the stability constants for an inclusion complex of PCP with HP- β -CD (703 l mol^{-1} at pH 3 and 153 l mol^{-1} at pH 7) were smaller than those with CM- β -CD (789 l mol^{-1} at pH 3 and 367 l mol^{-1} at pH 7) [24]. These results are inconsistent with the finding that HP- β -CD was a more effective additive than CM- β -CD. Therefore, interactions between PCP and CDs or HAs are not crucial factors in enhancing PCP oxidation in the Fe(III)-TPPS/ KHSO_5 system.

On the other hand, it has been reported that the loss of catalytic activity of iron(III)-porphyrins can be due to aggregation or the intermolecular self-oxidation of the catalysts [32,33]. Bonchio et al. [34] showed that the photocatalytic activity of TPPS was improved by forming an inclusion complex with the CD, in terms of the photooxidation of L-methionine methyl ester. This finding suggests that hydrophobic interactions between Fe(III)-TPPS and CDs or HAs are factors in enhancing the catalytic activity of Fe(III)-TPPS. Thus, we hereafter focused on interactions between Fe(III)-TPPS and HAs, and compared the findings to cases of CDs.

3.2. Effects of HAs and CDs on the self-oxidation of Fe(III)-TPPS

The deactivation of Fe(III)-TPPS may be due to aggregation and intermolecular self-oxidation. It has been reported that the aggregation of Fe(III)-TPPS can yield μ -oxo species, $\text{O}-(\text{Fe(III)-TPPS})_2$, which are produced in higher concentration of Fe(III)-TPPS and at a higher pH [27]. In our experimental conditions ($5 \mu\text{M}$ Fe(III)-TPPS, pH 6), the wavelength corresponding to the absorption maximum for Fe(III)-TPPS (394 nm) was similar to that at pH 2, where aggregation could not occur. However, at pH 7 the wavelength shifted to 406 nm, indicating the formation of $\text{O}-(\text{Fe(III)-TPPS})_2$ species [27]. These results show that aggregation does not cause the loss of catalytic activity under our experimental conditions. Therefore, we focused on the intermolecular self-oxidation of Fe(III)-TPPS.

The self-oxidation of Fe(III)-TPPS can be conveniently monitored by measuring the decolorization of the catalyst [32]. Fig. 2 shows the kinetic curves for the decolorization. The decay curves could be treated as biphasic kinetics, as reported by Nappa and Tolman [32]. Because the rate constants in the second part of the kinetics were too small, we compared the rate constants in the initial part (k_{obs}). The k_{obs} values are summarized in Table 1. The k_{obs} value for HP- β -CD was the largest of all the additives tested, and this corresponded to the largest effect on PCP oxi-

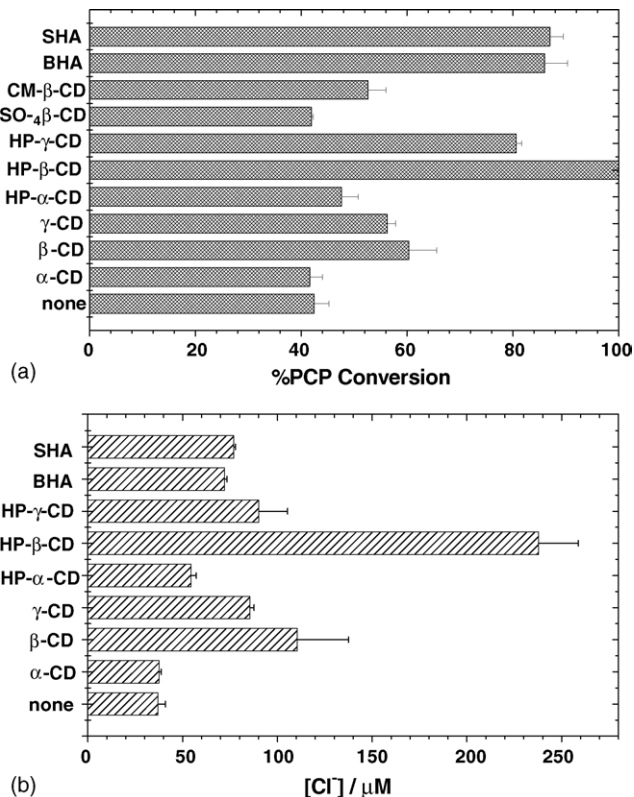


Fig. 1. Influence of HAs and CDs on the percent PCP conversion (a) and on the concentration of Cl^- released from PCP (b) by the Fe(III)-TPPS/ KHSO_5 catalytic system. PCP $50 \mu\text{M}$, Fe(III)-TPPS $5 \mu\text{M}$, KHSO_5 $125 \mu\text{M}$, HAs 50 mg l^{-1} , CDs 2.5 g l^{-1} , pH 6.

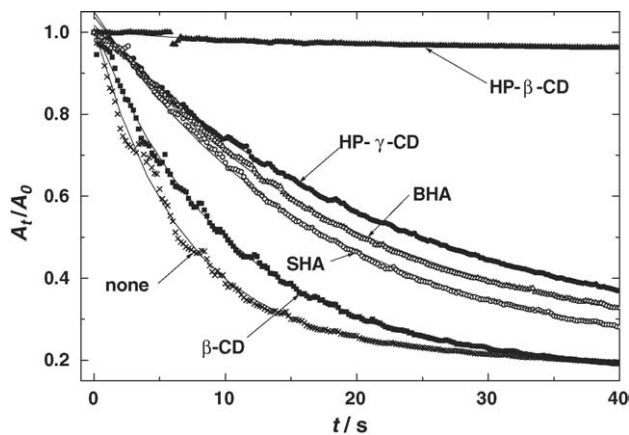
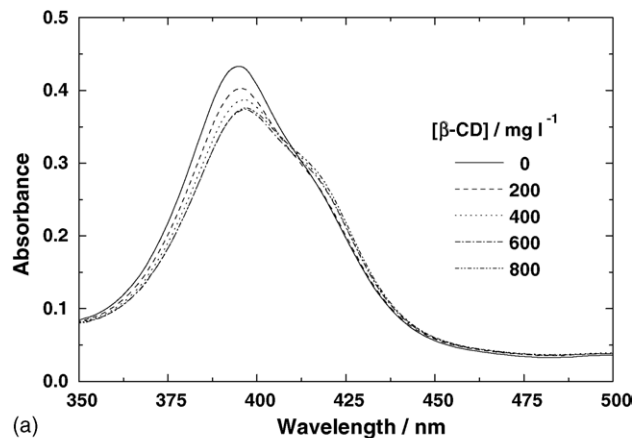


Fig. 2. Influence of HAs and CDs on the kinetics of decolorization of Fe(III)-TPPS. Fe(III)-TPPS 5 μM , KHSO_5 125 μM , HAs 50 mg l^{-1} , CDs 2.0 g l^{-1} , pH 6.

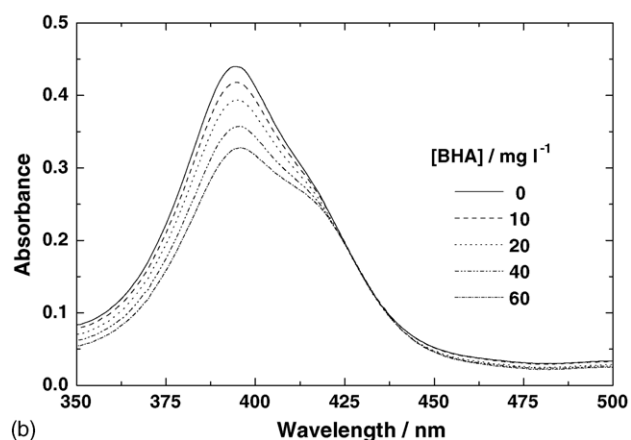
dation. In addition, the addition of HAs and HP- γ -CD, which were effective in enhancing PCP oxidation, led to larger k_{obs} values, by one order of magnitude, compared to k_{obs} in their absence (“none” in Table 1). However, the addition of α -CD, HP- α -CD, CM- β -CD and SO_4 - β -CD, which failed to enhance PCP oxidation, also did not result in an increase in k_{obs} value.

3.3. Influence of HAs and CDs on the UV-vis absorption spectra of Fe(III)-TPPS

It is possible that the suppressive effects on the self-oxidation of the catalyst might be related to complexation between HAs or CDs and Fe(III)-TPPS. The formation of inclusion complexes between CDs and porphyrins or metalloporphyrins has been reported [14–23]. The formation of such inclusion complex could be detected as a decrease in absorption at the Soret band of porphyrins and metalloporphyrins. To further investigate possible complexation between CDs and Fe(III)-TPPS, we first investigated variations in the Soret band of Fe(III)-TPPS in the absence and presence of CDs. UV-vis absorption spectra in the presence of a variety concentration of β -CD are shown in Fig. 3a. In these absorption spectra of Fe(III)-TPPS, a significant red-shift was observed with increasing concentrations of CDs, as reported in previous studies [15,18,19]. In the presence of γ -CD, HP- γ -CD and HP- β -CD, similar variations in absorption



(a)



(b)

Fig. 3. UV-vis absorption spectra of Fe(III)-TPPS in the presence of β -CD (a) and BHA (b). Fe(III)-TPPS 5 μM , pH 6.

spectra were also observed. However, in the cases of α -CD, HP- α -CD, CM- β -CD and SO_4 - β -CD, a red-shift in the Soret band and a decrease in absorption maximum were not significant.

The degree of decrease in absorption maximum (ΔA) corresponds to the concentration of complex species of Fe(III)-TPPS with CDs and can be calculated as follows:

$$\Delta A = (\text{absorption at 394 nm in the absence of CDs}) - (\text{absorption at 394 nm in the presence of CDs at arbitrary concentration}) \quad (1)$$

Assuming a 1:1 complexation of porphyrins (Por) with CDs according to Mosinger et al. [20], the complexation equilibrium and conditional formation constant (K_f) can be written as follows:



$$K_f = \frac{[\text{Por-CD}]}{[\text{Por}][\text{CD}]} \quad (3)$$

The total concentrations of Por and CD (C_{Por} and C_{CD}) can be represented as follows:

$$C_{\text{Por}} = [\text{Por}] + [\text{Por-CD}] \quad (4)$$

Table 1

The k_{obs} values for Fe(III)-TPPS self-oxidation

Additives	k_{obs} (s^{-1})
None	$(1.6 \pm 0.1) \times 10^{-1}$
α -CD	$(1.4 \pm 0.1) \times 10^{-1}$
β -CD	$(1.1 \pm 0.1) \times 10^{-1}$
γ -CD	$(1.3 \pm 0.1) \times 10^{-1}$
HP- α -CD	$(1.5 \pm 0.2) \times 10^{-1}$
HP- β -CD	$(4.3 \pm 0.7) \times 10^{-3}$
HP- γ -CD	$(4.8 \pm 0.4) \times 10^{-2}$
SO_4 - β -CD	$(2.6 \pm 0.1) \times 10^{-1}$
CM- β -CD	$(2.6 \pm 0.2) \times 10^{-1}$
SHA	$(6.6 \pm 0.5) \times 10^{-2}$
BHA	$(5.7 \pm 0.3) \times 10^{-2}$

$$C_{\text{CD}} = [\text{CD}] + [\text{Por} - \text{CD}] \quad (5)$$

The ΔA is related to the concentration of complex species and molecular extinction coefficient (ε):

$$\Delta A = [\text{Por} - \text{CD}] \cdot \varepsilon \quad (6)$$

To compare the K_f for a variety of CDs, C_{CD} was normalized to molar concentration of dissolved organic carbon in CDs (C_{DOC}) by the following equation:

$$C_{\text{DOC}} = \frac{\%C/100 \times C_{\text{CD}}(\text{g l}^{-1})}{12.011} \quad (7)$$

Combining Eqs. (3)–(7), the following relationship between ΔA and C_{DOC} can be derived:

$$\Delta A = \frac{\varepsilon}{2} \times \left[\left(C_{\text{Por}} + C_{\text{DOC}} + \frac{1}{K_f} \right) - \left\{ \left(C_{\text{Por}} + C_{\text{DOC}} + \frac{1}{K_f} \right)^2 - 4C_{\text{Por}}C_{\text{DOC}} \right\}^{1/2} \right]$$

The symbols in Fig. 4a represent the data set for ΔA and C_{DOC} for the CDs. The K_f values can be calculated by a non-linear least square regression analysis of the data points.

In the cases of HAs, the spectra of the mixture of HA and Fe(III)-TPPS were subtracted from those for HA alone, as

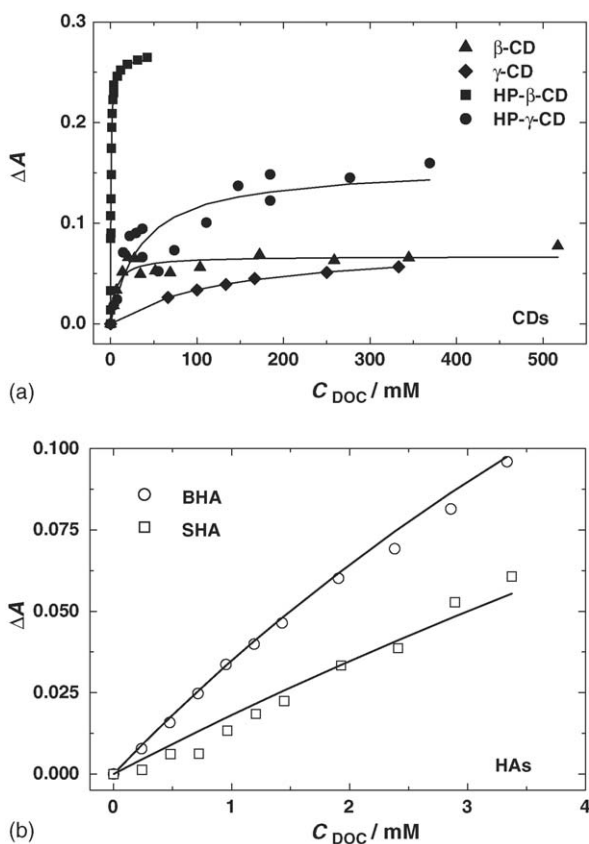


Fig. 4. Relationship between C_{DOC} and ΔA for CDs (a) and HAs (b). The symbols and solid lines represent experimental data and calculated curves based on Eq. (8).

Table 2

Conditional formation constants (K_f) for complexation between Fe(III)-TPPS or TPPS and HAs or CDs

Additives	$\log K_f$ for Fe(III)-TPPS	$\log K_f$ for TPPS
β -CD	1.54 ± 0.07	1.45 ± 0.14
γ -CD	0.64 ± 0.08	0.87 ± 0.02
HP- β -CD	3.59 ± 0.02	3.27 ± 0.03
HP- γ -CD	1.89 ± 0.06	2.23 ± 0.14
BHA	2.16 ± 0.03	1.94 ± 0.07
SHA	1.87 ± 0.06	1.64 ± 0.02

described in a previous study [10]. The subtracted spectra of BHA are shown in Fig. 3b. The absorbance at 394 nm for Fe(III)-TPPS decreased with increasing BHA concentration and the Soret band for Fe(III)-TPPS alone was slightly shifted to higher wavelength, showing that BHA can bind Fe(III)-TPPS via any interactions. The K_f values for the HAs were also calculated from the relationships between ΔA and C_{DOC} by curve-fitting, as shown in Fig. 4b. The calculated $\log K_f$ values are summarized in Table 2. The K_f values for HAs and CDs were negatively correlated to k_{obs} values ($r^2 = 0.882$). This indicates that Fe(III)-TPPS is stabilized by the complexation with HAs or CDs.

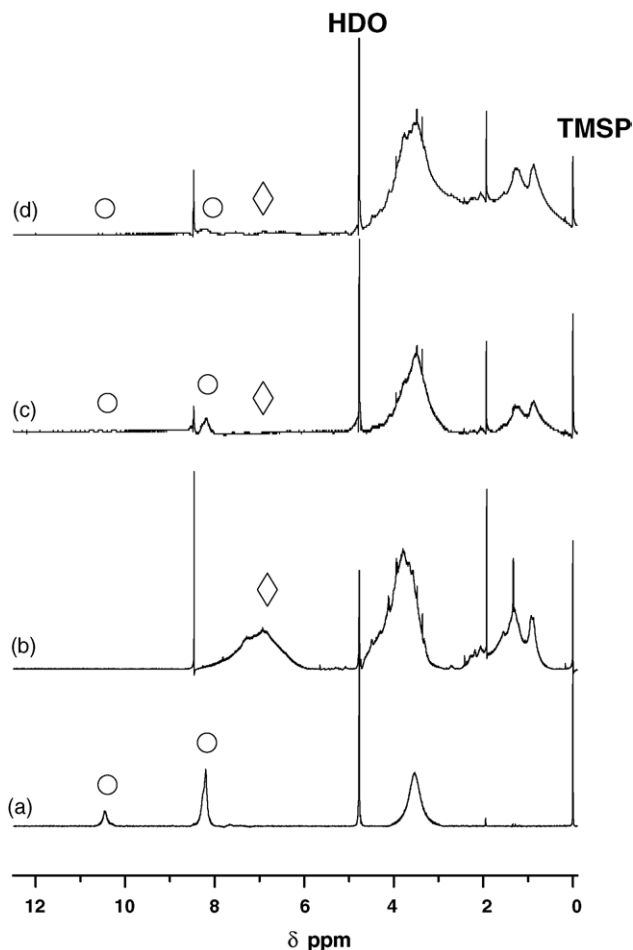


Fig. 5. ^1H NMR spectra of Fe(III)-TPPS in the absence and presence of BHA. pD 6 by 0.02 M $\text{D}_3\text{PO}_4/\text{NaOD}$, (a) 5 mM Fe(III)-TPPS, (b) 10 g l⁻¹ BHA, (c) 5 g l⁻¹ BHA + 5 mM Fe(III)-TPPS and (d) 10 g l⁻¹ BHA + 5 mM Fe(III)-TPPS.

3.4. Confirmation of complexation between Fe(III)-TPPS and HAs

To confirm complexation between Fe(III)-TPPS and HAs, ^1H NMR spectra were recorded. Fig. 5 shows the ^1H NMR spectra of Fe(III)-TPPS, BHA and a mixture thereof. In the spectrum of Fe(III)-TPPS (Fig. 5a), sharp peaks at 8.2 and 10.4 ppm, which corresponds to the *ortho*- and *meta*-protons in the sulfonatophenyl group of Fe(III)-TPPS [35], were observed. In the spectrum of BHA alone (Fig. 5b), broad peaks at around 1–2.5, 3–4.5 and 7 ppm are observed, corresponding to methyl, carbohydrate and aromatic protons, respectively. Focusing on the variations in the *ortho*- and *meta*-protons in Fe(III)-TPPS (\circ in Fig. 5), we notice that these peaks were largely reduced and disappeared with an increase in the concentration of BHA. In the case of SHA, the same spectral changes were also observed. These results clearly demonstrate the occurrence of complexation between Fe(III)-TPPS and HAs. In addition, the broad peak for the aromatic protons in BHA at around 7 ppm (\diamond in Fig. 5) disappeared in the presence of Fe(III)-TPPS. This indicates that the sulfonatophenyl groups in Fe(III)-TPPS are mainly bound to aromatic regions of the HAs via hydrophobic interactions.

If Fe(III)-TPPS was mainly bound to HAs by hydrophobic interactions with the sulfonatophenyl groups in the porphyrin, complexation would also be observed in the case of a non-

metal porphyrin, such as TPPS. For β -CD and HP- β -CD, some reports on the complexation between these CDs and TPPS have been reported [20,23,34]. Consistent with these reports, spectral change in TPPS by the addition of β -CD was observed, as shown in Fig. 6a. The K_f values were evaluated by ΔA at a maximum wavelength of 414 nm for TPPS using Eq. (8). In the case of BHA (Fig. 6b), the spectrum of TPPS was significantly shifted to a higher wavelength region, and similar spectra were obtained for SHA. These results indicate the occurrence of complexation between TPPS and HAs. The K_f values for TPPS were evaluated by curve-fitting to the data set of ΔA and C_{DOC} (Table 2). The K_f values for TPPS were positively correlated to those for Fe(III)-TPPS ($r^2 = 0.935$). These results support the view that sulfonatophenyl groups in porphyrin contribute to the complexation with HAs or CDs.

To isolate complexes of Fe(III)-TPPS with the HAs, test solutions containing Fe(III)-TPPS and HAs were filtered by ultrafiltration. Fig. 7 shows the molecular weight distributions of Fe(III)-TPPS and the absorptivity at 280 nm (e_{280}). To avoid large changes in the complexation equilibrium, the concentrated fractions on the filter were not further washed with buffer solution. Thus, in the presence of Fe(III)-TPPS alone, 75% of the Fe(III)-TPPS was found in the fraction below 5000 Da. For Fe(III)-TPPS + BHA and Fe(III)-TPPS + SHA, the percentages of Fe(III)-TPPS in the fractions below 5000 Da decreased to 25–31%, and 64–74% of the Fe(III)-TPPS was found in the higher molecular weight fractions (30,000–100,000 Da and 100,000 Da and more). The molecular weight distributions of

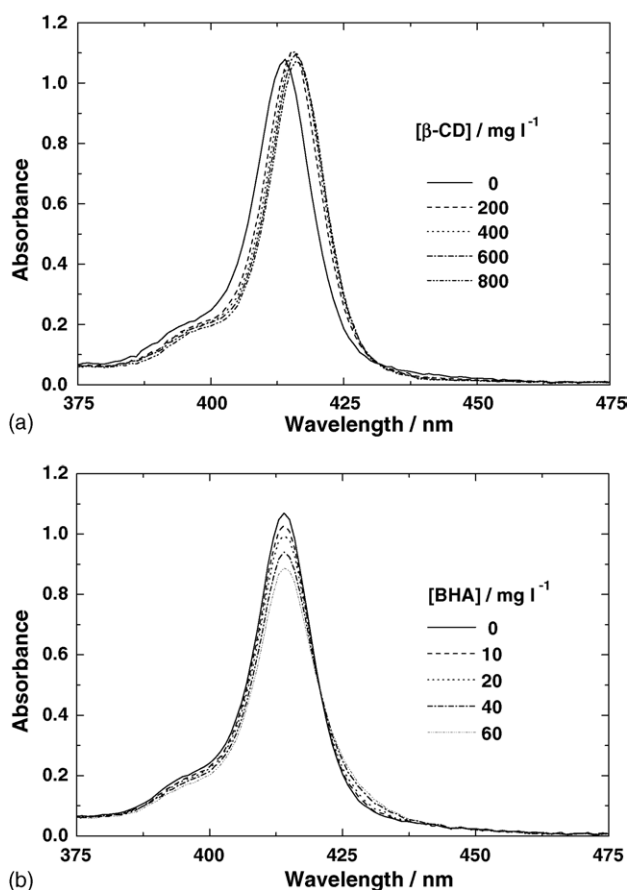


Fig. 6. UV-vis absorption spectra of TPPS in the presence of β -CD (a) and BHA (b). TPPS 2 μM , pH 6.

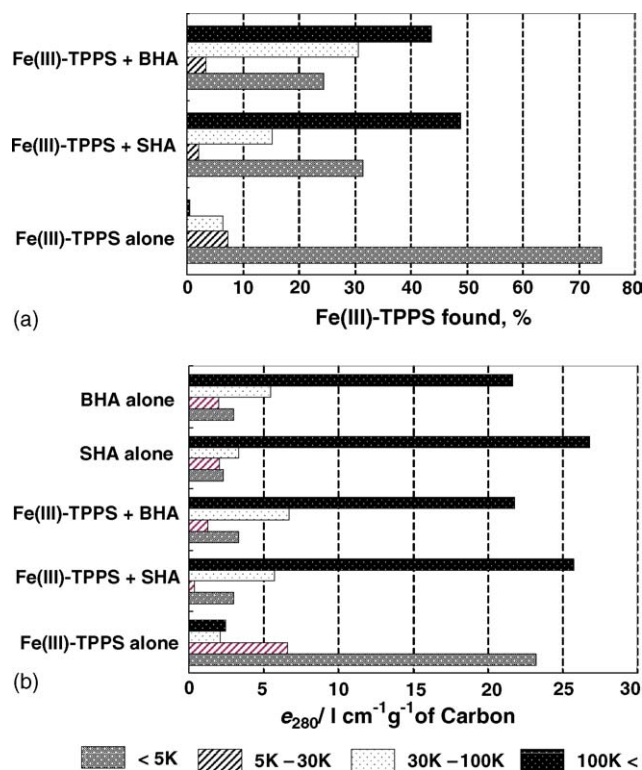


Fig. 7. Molecular weight distribution of Fe(III)-TPPS (a) and absorptivity at 280 nm (b) for Fe(III)-TPPS alone, Fe(III)-TPPS + HAs and HAs alone. pH 6, HAs 500 mg l⁻¹, Fe(III)-TPPS 50 μM .

Fe(III)-TPPS in Fig. 7a were similar to those of the e_{280} values in Fig. 7b. In addition, the molecular weight distributions of the e_{280} values for Fe(III)-TPPS + HAs were also similar to those for HAs alone (Fig. 7b). These results clearly demonstrate complexation between Fe(III)-TPPS and HAs.

4. Conclusions

The results reported here lead to the conclusion that the complexation of Fe(III)-TPPS with CDs or HAs play an important role in suppressing the intermolecular self-oxidation of the catalyst and this results in an enhanced peroxosulfate catalyzed oxidation of PCP. In the free species of Fe(III)-TPPS, random collisions between catalyst molecules would occur in aqueous solution, leading to self-oxidation. However, with complexation, the collision between the Fe(III)-TPPS molecules would be suppressed, thus preventing or inhibiting self-oxidation. Therefore, the complexation of Fe(III)-TPPS with HA or CD contributes to the stabilization of the catalyst, resulting in an enhancement in PCP oxidation.

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References

- [1] J.-M. Bollag, *Environ. Sci. Technol.* 26 (1992) 1876.
- [2] V.M. Sumokyszyn, J.P. Freeman, K.R. Maddipati, R.V. Lloyd, *Chem. Res. Toxicol.* 8 (1995) 349.
- [3] S. Hasan, J.-G. Cho, K.L. Sublette, D. Pak, A. Maule, *J. Biotechnol.* 24 (1992) 195.
- [4] S.-T. Chen, D.K. Stevens, G. Kang, *Water Res.* 33 (1999) 3657.
- [5] M. Fukushima, K. Oba, S. Tanaka, K. Nakayasu, H. Nakamura, K. Hasebe, *Environ. Sci. Technol.* 31 (1997) 2218.
- [6] G.P. Curtis, M. Reinhard, *Environ. Sci. Technol.* 28 (1994) 2393.
- [7] M. Fukushima, H. Ichikawa, M. Kawasaki, A. Sawada, K. Morimoto, K. Tatsumi, *Environ. Sci. Technol.* 37 (2003) 386.
- [8] M. Fukushima, A. Sawada, M. Kawasaki, H. Ichikawa, K. Morimoto, K. Tatsumi, M. Aoyama, *Environ. Sci. Technol.* 37 (2003) 1031.
- [9] M. Fukushima, A. Sawada, M. Kawasaki, K. Tatsumi, *Toxicol. Environ. Chem.* 85 (2003) 39.
- [10] S. Rismayani, M. Fukushima, A. Sawada, H. Ichikawa, K. Tatsumi, *J. Mol. Catal. A* 217 (2004) 13.
- [11] K. Morimoto, K. Tatsumi, *Chemosphere* 34 (1997) 1277.
- [12] A. Piccolo, *Adv. Agron.* 75 (2002) 57.
- [13] P. Conte, A. Piccolo, *Environ. Sci. Technol.* 33 (1999) 1682.
- [14] J.S. Manka, D.S. Lawrence, *J. Am. Chem. Soc.* 112 (1990) 2440.
- [15] H. Hirai, N. Toshima, S. Hayashi, Y. Fujii, *Chem. Lett.* (1983) 643.
- [16] S. Mosseri, J.C. Mialocq, B. Perly, *J. Phys. Chem.* 95 (1991) 2196.
- [17] S. Mosseri, J.C. Mialocq, B. Perly, *J. Phys. Chem.* 95 (1991) 4659.
- [18] S.K. Sur, R.G. Bryant, *J. Phys. Chem.* 99 (1995) 4900.
- [19] S.K. Sur, R.G. Bryant, *J. Phys. Chem.* 99 (1995) 7172.
- [20] J. Mosinger, M. Deumić, K. Lang, P. Kubát, D.M. Wagnerová, *J. Photochem. Photobiol. A* 130 (2000) 13.
- [21] K. Kano, R. Nishiyabu, T. Asada, Y. Kuroda, *J. Am. Chem. Soc.* 124 (2002) 9937.
- [22] S. Hamai, *Bull. Chem. Soc. Jpn.* 75 (2002) 2371.
- [23] X.-P. Wang, J.-H. Pan, S.-H. Shuang, Y. Zhang, *Supramol. Chem.* 14 (2002) 419.
- [24] K. Hanna, C. de Brauer, P. Germain, *J. Environ. Manage.* 71 (2004) 1.
- [25] K. Hanna, C. de Brauer, P. Germain, *J. Hazard. Mater.* B100 (2003) 109.
- [26] K. Tsutsuki, R. Kondo, *Jpn. J. Soil Sci. Plant Nutr.* 68 (1997) 45.
- [27] M. Kawasaki, A. Kuriss, M. Fukushima, A. Sawada, K. Tatsumi, *J. Por. Phthal.* 7 (2003) 645.
- [28] R.S. Swift, in: D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, P.N. Soltanpour, M.A. Tabatabai, C.T. Johnson, M.E. Summer (Eds.), *Methods of Soil Analysis. Part 3. Chemical Methods*, Soil Science Society of America, Madison, 1996, pp. 1018–1020.
- [29] E. Rizzarelli, G. Vecchio, *Coord. Chem. Rev.* 188 (1999) 343.
- [30] H. Sakuraba, *Nippon Kagaku Kaishi* (1992) 1463.
- [31] F.D. Paolis, J. Kukkonen, *Chemosphere* 34 (1997) 1693.
- [32] M.J. Nappa, C.A. Tolman, *Inorg. Chem.* 24 (1985) 4711.
- [33] J.R.L. Smith, in: R.A. Sheldon (Ed.), *Metalloporphyrins in Catalytic Oxidations*, Dekker, New York, 1994, p. 326.
- [34] M. Bonchio, T. Carofiglio, M. Carraro, R. Fornasier, U. Tonellato, *Org. Lett.* 4 (2002) 4635.
- [35] M.A. Ivanca, A.G. Lappin, R. Scheidt, *Inorg. Chem.* 30 (1991) 711.