



Introduction of 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphine iron(III) into humic acid via formaldehyde polycondensation

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ABSTRACT

To stabilize an iron(III)-porphyrin catalyst in the presence of peroxide such as KHSO_5 , 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphine iron(III) ($\text{FeTPP}(\text{OH})_4$) was introduced into a humic acid (HA) via formaldehyde polycondensation to produce a “resol” catalyst. $\text{FeTPP}(\text{OH})_4$ can have four phenolic hydroxyl groups for HA-binding. The self-degradation kinetics for prepared resol catalysts using $\text{FeTPP}(\text{OH})_4$ were compared with those synthesized prepared from 5-(*p*-hydroxyphenyl)-5,10,15,20-tetrasulfonatophenylporphine iron(III) (FeTPPSOH) that has one site for HA-binding. In the presence of KHSO_5 , half-lives of the self-degradation was much larger in resol catalysts using $\text{FeTPP}(\text{OH})_4$ (3.4–3.5 s), compared to those using FeTPPSOH (0.08 s). These results show that use of $\text{FeTPP}(\text{OH})_4$ for the synthesis of resol catalysts is useful for stabilization of iron(III)-porphyrin catalyst and retardation of the self-degradation. In addition, the catalytic activity of prepared resol catalysts was evaluated by 2,4,6-trichlorophenol (TrCP) oxidation. In particular, mineralization to CO_2 was significantly greater for the resol catalysts (17–18%) than for $\text{FeTPP}(\text{OH})_4$ alone (4%). These results indicate that resol catalysts effectively enhance oxidative degradation of TrCP due to retardation of catalyst self-degradation.

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1. Introduction

Reactions using metalloporphyrins that mimic the transformation of xenobiotics via ligninases in soil environments have been examined for their ability to oxidize chlorophenols, such as 2,4,6-trichlorophenol (TrCP) [1–4]. However, metalloporphyrins are inactivated by self-degradation in the presence of peroxides, such as H_2O_2 and KHSO_5 [5,6]. Fukushima and Tatsumi [7] reported that a supramolecular catalyst comprised of hydroxypropyl- β -cyclodextrin and *meso*-tetra(sulfonatophenyl) porphineiron(III) significantly retarded self-degradation in the presence of KHSO_5 . This result suggests that formation of supramolecules effectively retards self-degradation of metalloporphyrins.

Humic acids (HAs), which are the primary constituents of soil organic matter, have a variety of modifiable functional groups, such as phenolic hydroxyl groups [8]. Introduction of functionalities into HA for application in environmental technologies is a novel and challenging topic. Perminova et al. [9,10] reported covalent introduction of hydroquinone derivatives into HA using formaldehyde polycondensation to enhance the reducing abilities

of HA. In general, formaldehyde polycondensation has been utilized to synthesize polyphenol compounds. In this reaction, either an acid or base catalyst is used to produce polyphenol compounds termed, “novolacs” and “resols”, respectively [11]. This observation suggests that iron(III)-porphyrin with phenolic hydroxyl groups can be introduced into HA phenolic moieties via formaldehyde polycondensation. However, in the case of iron(III)-porphyrin catalysts, iron(III) slowly dissociates from porphyrin ligands in acidic solutions [12]; novolac-type reactions are not suitable for iron(III)-porphyrin under acidic conditions. Thus, resol-type reactions can be employed in the preparation of supramolecular catalysts containing iron(III)-porphyrins and HA. Using this concept, Fukushima prepared a supramolecular catalyst comprised of 5-(*p*-hydroxyphenyl)-5,10,15,20-tetrasulfonatophenylporphine iron(III) (FeTPPSOH) and HA via formaldehyde polycondensation [13]. However, retardation of self-degradation was minimal compared with that of the original catalyst, FeTPPSOH .

To suppress the inactivation of metalloporphyrin catalysts via self-degradation, polymer-supported metalloporphyrin catalysts have been investigated [14,15]. The introduction of iron(III)-porphyrin into HA may be a reasonable concept. However, the stability influence on catalytic activity of metalloporphyrins bound to polymers has not been examined. In FeTPPSOH [13], there is only one phenolic hydroxyl group for HA-binding. If the number of phenolic hydroxyl groups in the original iron(III)-porphyrin was

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increased, a more stable and/or rigid binding of iron(III)-porphyrin to HA could be formed. In the present study, 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphine iron(III) (FeTPP(OH)₄), which has four phenolic hydroxyl groups for HA-binding, was introduced into HA via formaldehyde polycondensation. In addition, the effects of the prepared catalysts on self-degradation kinetics and catalytic activity of TrCP oxidation were examined.

2. Materials and methods

2.1. Materials

An HA sample was prepared from peat soil (Bibai, Hokkaido, Japan) using a method described by the International Humic Substances Society [16]. TrCP, 2,6-dichloro-*p*-quinone (2,6-DC-*p*-Q), 3,5-dichlorocatechol and pentachlorophenol were purchased from Tokyo Chemical Industry. FeTPP(OH)₄ was synthesized by refluxing 5,10,15,20-tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine (Tokyo Chemical Industry) and FeCl₂·4H₂O (Nacalai Tesque) in *N,N*-dimethylformamide solution under a N₂ atmosphere [17]. After refluxing, the reaction mixture was filtered and the filtrate was then evaporated under reduced pressure. Subsequently, the residue was redissolved in 1–2 ml of methanol and FeTPP(OH)₄ was then precipitated by addition of 200 ml of water. The precipitate was collected by filtration and then washed with water. The obtained FeTPP(OH)₄ was in the dihydrate form (C₄₄H₂₈N₄O₄Fe·2H₂O). Results of elemental analysis are as follows: calculated, C 68.76%, H 4.20%, N 7.29%; observed, C 68.54%, H 4.24%, N 7.65%, Cl was not detected; yield, 56.3%.

2.2. Formaldehyde polycondensation

The reaction for FeTPP(OH)₄-binding to HA via formaldehyde polycondensation is shown in Scheme 1. In the present study, the prepared catalysts are referred to as “resol catalysts.” Fifty milligrams of HA and FeTPP(OH)₄ were dissolved in 30 ml of aqueous 0.1 M NaOH. The mixture was transferred to a 300-ml, three-necked flask equipped with a reflux condenser and a mechanical stirrer. After addition of aqueous formaldehyde and 0.5% aqueous NaOH (10 ml), the mixture was heated at 100 °C for 1.5 h. Subsequently, the reaction mixture was transferred to a 300-ml beaker and was then cooled in an ice bath. The solution was neutralized with aqueous H₂SO₄. The fraction that contained the resol catalyst was concentrated and deionized by ultrafiltration through a Millipore YM1 ultrafiltration cellulose membrane (nominal cut-off, 1000 Da). After washing the resol fraction with water, the

Table 1

Quantity of added formaldehyde, and the results of elemental compositions for each sample

Samples	CH ₂ O (mmol)	C (%)	H (%)	N (%)	O (%)	S (%)	Ash (%)	C/H	C/N
HA	–	51.86	5.61	2.95	35.22	0.63	3.73	0.78	20.50
Resol 1	0.5	57.31	5.10	4.94	25.83	0.67	6.15	0.94	13.53
Resol 2	22.0	55.02	4.94	4.72	24.23	1.60	9.49	0.93	13.59

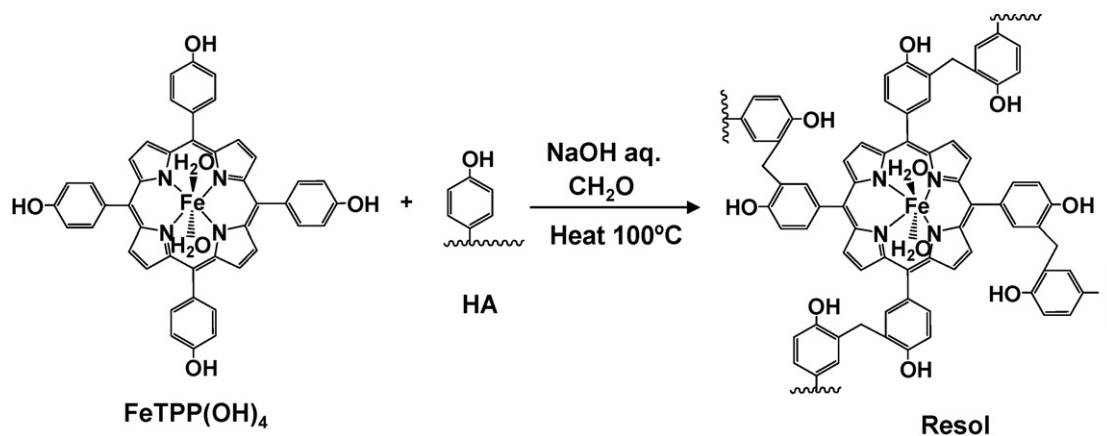
concentrated fraction was further dialyzed against water using a Spectra/Por cellulose ester membrane (nominal cut-off, 500 Da). Finally, the resol catalyst was freeze-dried to yield the sample in powdered form. In the present study, two types of resol catalysts were prepared by varying the amounts of added formaldehyde, as shown in Table 1. The molar concentrations of resol catalysts were determined by analyzing the Fe concentration in the aqueous solutions using an ICP-AES (SPS7800-type, SII NanoTechnology Inc.).

2.3. Spectroscopic measurements

FTIR spectra of FeTPP(OH)₄ and the resol catalysts were recorded using an FT/IR 600 type spectrometer (Japan Spectroscopic Co. Ltd.) with KBr pellets. UV–vis absorption spectra of FeTPP(OH)₄ and the resol catalysts (10 μM) in phosphate buffers at pH 3 and 6 were obtained using a V-630 type spectrophotometer (Japan Spectroscopic Co. Ltd.) with a quartz cell (1 cm × 1 cm) at 25 °C. Decolorization of the catalysts was monitored using a RSP-1000-02-type stopped-flow spectroscopy system (Unisoku, Co. Ltd.) at a detection wavelength of 420 nm.

2.4. Test for TrCP disappearance

Two-milliliter aliquots of 0.02 M phosphate buffer at pH 3–7 were placed in a 20-ml, L-shaped test tube. The pH of the solution was adjusted by addition of either aqueous NaOH or H₃PO₄ to aqueous NaH₂PO₄. A 10–40 μl aliquot of 0.01 M TrCP in acetonitrile and a 50-μl aliquot of either aqueous FeTPP(OH)₄ or resol catalysts (200 μM) were then added to the buffer. Subsequently, a 10-μl aliquot of 0.1 M aqueous KHSO₅ was added, and the test tube was shaken in a T-22S type thermostatic shaking water bath (Thomas Kagaku Co. Ltd.) at 25 ± 0.1 °C. After a 60-min reaction period, 1 ml of 2-propanol was added to the test solution. To determine the TrCP concentration in the test solution, a 20-μl aliquot was injected into a PU-980 type HPLC pumping system (Japan Spectroscopic Co. Ltd.). The mobile phase consisted of a mixture of 0.08% aqueous H₃PO₄



Scheme 1.

and methanol (30/70, 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. UV absorption of TrCP was measured at 220 nm.

2.5. Cl⁻ and total organic carbon (TOC)

Acetonitrile cannot be used to prepare the TrCP stock solution for TOC analysis. Thus, 14.8 mg of TrCP was dissolved in 50 ml of 5 mM aqueous NaOH (1.5 mM), and this solution was then diluted to 150 μM with 0.02 M phosphate buffer (pH 3). A 25-ml aliquot of this solution was placed in a 100-ml Erlenmeyer flask, and a 750-μl aliquot of the aqueous catalyst (200 μM) was then added. Subsequently, 150 μl of 0.1 M aqueous KHSO₅ was added, and the flask was shaken in a thermostatic shaking water bath at 25 °C. After a 60-min reaction period, a 2-ml aliquot of the reaction mixture was mixed with 1 ml of 2-propanol, followed by quantification of TrCP and Cl⁻ with HPLC and ion chromatography (ICS-90 type, Dionex), respectively. Another 20-ml aliquot of the reaction mixture was mixed with 1 M aqueous Na₂SO₃ (1 ml), and the TOC of this solution was analyzed using a TOC-V CSH-type TOC analyzer (Shimadzu). The detection limit of the TOC analyzer was estimated to be 52 μg l⁻¹.

2.6. By-product analysis

A 25-ml aliquot of 0.02 M phosphate buffer (pH 3) was placed in a 100-ml Erlenmeyer flask. A 375-μl aliquot of 0.01 M TrCP in acetonitrile and a 625-μl aliquot of an aqueous solution of the catalyst (200 μM) were added to the buffer solution. Subsequently, 125 μl of 0.1 M aqueous KHSO₅ was added, and the flask was then shaken at 25 °C in a thermostatic shaking water bath. After a 60-min reaction period, 2 ml of 1 M aqueous ascorbic acid was added to reduce the quinone derivatives that resulted from phenol oxidation. Subsequently, a 50-μl aliquot of 0.01 M pentachlorophenol in acetonitrile was added as an internal standard. This mixture was extracted two times with 10 ml of diethyl ether, and the combined extracts were dried over anhydrous Na₂SO₄. After filtration, the extract was evaporated under a stream of dry N₂ at 35 °C. The residue was redissolved in 500 μl of methanol, and a 200-μl aliquot of the acetic anhydride and pyridine mixture (7/3, v/v) was then added as an acetylation reagent. A 1-μl aliquot of the sample solution was introduced into a GC-17A/QP5050 GC/MS system (Shimadzu) that included a Quadrex methyl silicon capillary column (0.25 mm i.d. × 25 m). The temperature protocol was as follows: 65 °C for 1.5 min; 65–120 °C at a heating rate of 35 °C min⁻¹; 120–300 °C at 7 °C min⁻¹; and 300 °C for 5 min.

3. Results and discussion

3.1. Characteristics of prepared catalysts

The elemental composition of HA and the resol catalysts is summarized in Table 1. The C/N atomic ratios for the resol catalysts were less than those for HA, suggesting that FeTPP(OH)₄, which contains nitrogen atoms, can be introduced into HA. The Fe content of the resol catalysts is summarized in Table 2. The weight percent of Fe in FeTPP(OH)₄ was 7.4%, which was in good agreement with the calculated value (7.3%). Thus, molar concentrations of FeTPP(OH)₄ and resol catalysts in aqueous solutions were determined based on the Fe content of the prepared samples. The phenolic hydroxyl group content in the HA sample was 14.5 ± 0.1 mmol g⁻¹. The phenolic hydroxyl group content of the 50-mg HA sample used in

Table 2
Iron contents in resol catalysts and percentages of FeTPP(OH)₄ bound to HA

Samples	Fe content		FeTPP(OH) ₄ bound ^a (%)
	μmol Fe mg ⁻¹	wt. %	
Resol 1	0.64	3.6	49
Resol 2	0.69	3.9	53

^a (Fe content after the polycondensation)/(Fe content in FeTPP(OH)₄ added) × 100.

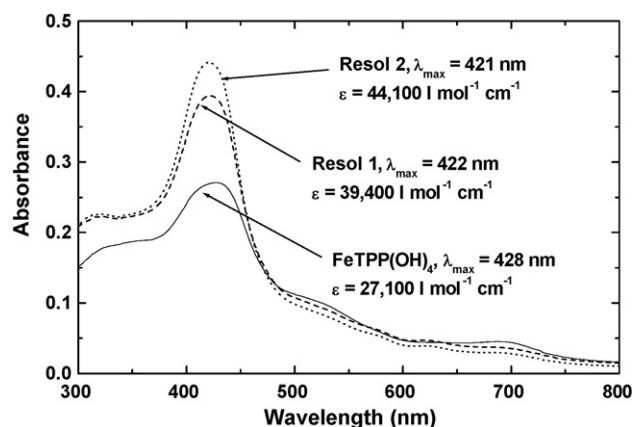


Fig. 1. UV-vis absorption spectra of FeTPP(OH)₄ and resol catalysts in aqueous solution at pH 3. Concentration of the catalysts: 10 μM.

this study was calculated to be 0.72 mmol. Thus, the number of phenolic sites in HA was 2.8-fold greater than the number of sites in the added FeTPP(OH)₄ (0.26 mmol). In the resol catalysts, approximately 50% of Fe was bound to HA via formaldehyde polycondensation (Table 2). However, the formaldehyde content of the resol catalysts was not related to bound FeTPP(OH)₄.

The uv-vis absorption spectra for FeTPP(OH)₄ and resol catalysts (Fig. 1) indicated that the absorption coefficients (ε) of Soret bands for the resol catalysts were much higher than those for FeTPP(OH)₄. In addition, although broad Q-band signals were observed in FeTPP(OH)₄ at approximately 520 and 700 nm, these signals were not evident in the resol catalysts. These results suggest the formation of FeTPP(OH)₄ and HA supramolecules.

Fig. 2 shows the FTIR spectra of HA, FeTPP(OH)₄, mixture of FeTPP(OH)₄ and HA (FeTPP(OH)₄ + HA), and the resol catalysts. The following peaks were evident in the FeTPP(OH)₄ sample [18,19]: at approximately 3470 cm⁻¹, phenol O–H stretching; 1611 and 1516 cm⁻¹, C=C ring stretching; 1476 cm⁻¹, C=C stretching in porphyrin ring; 1338 cm⁻¹, phenol O–H bending; 1270 cm⁻¹, phenol

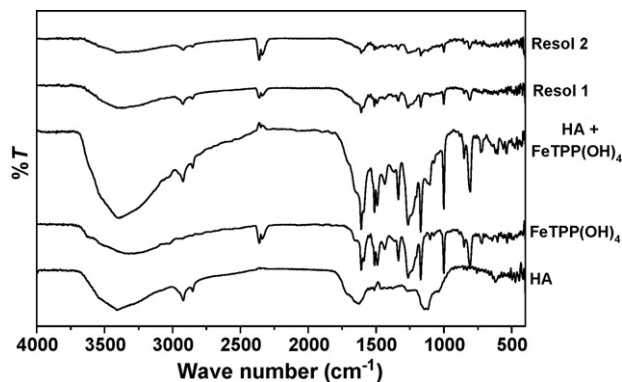


Fig. 2. FTIR spectra of HA, FeTPP(OH)₄, FeTPP(OH)₄ + HA, and the resol catalysts obtained with a KBr pellet.

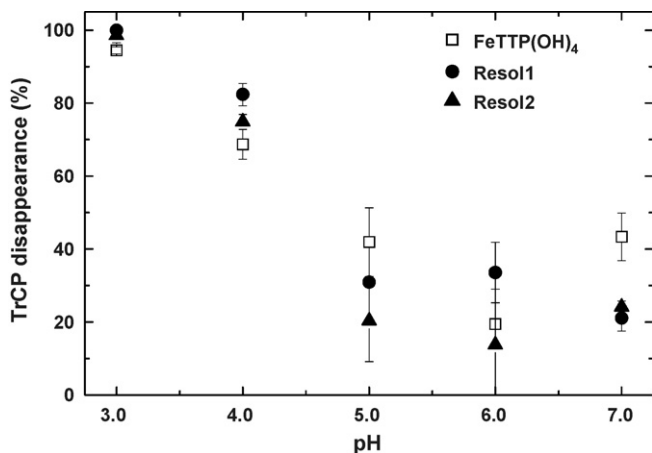


Fig. 3. Influence of pH on percent TrCP disappearance. The reaction conditions were as follows: $[\text{TrCP}]_0$, 50 μM ; [catalysts], 5 μM ; $[\text{KHSO}_5]$, 500 μM ; reaction time, 60 min.

C–O stretching; and 1004 cm^{-1} and 807 cm^{-1} , out-of-plane C–H bending. The peaks observed in the spectrum of the $\text{FeTPP}(\text{OH})_4$ and HA mixture were similar to those observed in the spectrum of $\text{FeTPP}(\text{OH})_4$ alone, although the peaks at 2940 and 2889 cm^{-1} for alkyl C–H stretching in HA [20] were unique to the mixture. Peaks in the resol catalyst spectra were broadened and/or reduced compared with those in the spectra of $\text{FeTPP}(\text{OH})_4$ and the mixture. In addition, peaks for C–O stretching at approximately 1220 cm^{-1} were broader than those observed in the spectra of $\text{FeTPP}(\text{OH})_4$ alone and the spectra of the mixture of $\text{FeTPP}(\text{OH})_4$ and HA. When a phenol resin forms via formaldehyde polycondensation, significant broadening and reduction of the peaks corresponding to phenol O–H stretching and C–O stretching occur [21]. In other papers for the IR spectra of phenol and phenol resins [22,23], reduction and broadening of peaks at 1610 cm^{-1} for C=C ring stretching and at 1270 cm^{-1} for phenol C–O stretching were observed. Thus, the FTIR spectra of resol catalysts in Fig. 2 indicate the formation of phenol-resin-like compounds via formaldehyde polycondensation between $\text{FeTPP}(\text{OH})_4$ and HA.

3.2. Degradation characteristics of TrCP

Catalytic activity was evaluated by measuring oxidation characteristics of TrCP. Reaction conditions, such as pH and substrate concentration might influence TrCP oxidation. First, the influence of pH on TrCP disappearance was investigated (Fig. 3). For both $\text{FeTPP}(\text{OH})_4$ and the resol catalysts, the percent TrCP disappearance increased with decreasing pH. Labat et al. [24] observed a similar tendency for the oxidation of veratryl alcohol in an iron(III)-porphyrin/ KHSO_5 system. These investigators proposed that the decrease in oxidation efficiency with increasing pH could be attributed to the formation of an inactive μ -oxo iron(III)-porphyrin species. As shown in Fig. 2, TrCP disappearance was enhanced by the resol catalysts at pH < 4. At pH 3, 100% of added 50- μM TrCP disappeared for $\text{FeTPP}(\text{OH})_4$ and resol catalysts.

Fig. 4 shows the effect of substrate concentration ($[\text{TrCP}]_0$) on percent TrCP disappearance for $\text{FeTPP}(\text{OH})_4$ and the resol catalysts at pH 3. For all catalysts, percent TrCP disappearance decreased with increasing $[\text{TrCP}]_0$. At $[\text{TrCP}]_0 = 100, 150$ and $200\text{ }\mu\text{M}$, TrCP disappearance was enhanced with the resol catalysts. These results indicate that oxidative degradation of TrCP is enhanced by $\text{FeTPP}(\text{OH})_4$ -binding to HA via formaldehyde polycondensation. At $[\text{TrCP}]_0 = 150\text{ }\mu\text{M}$, the influence of reaction duration on percent TrCP disappearance was examined. For $\text{FeTPP}(\text{OH})_4$

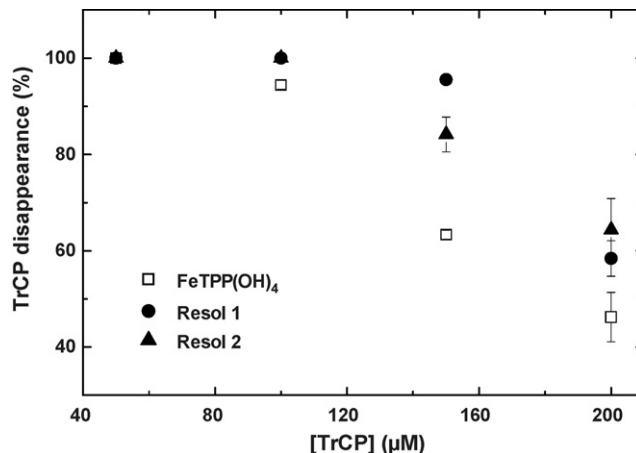


Fig. 4. Influence of substrate concentration ($[\text{TrCP}]_0$) on percent TrCP disappearance. The reaction conditions were as follows: [catalysts], 5 μM ; $[\text{KHSO}_5]$, 500 μM ; pH 3.0; reaction time, 60 min.

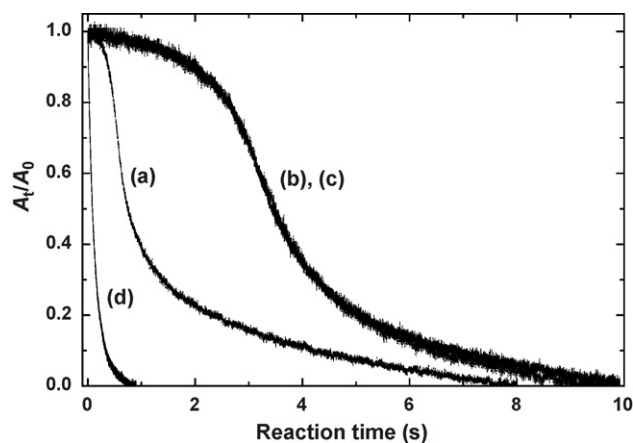


Fig. 5. Self-degradation kinetic curves for $\text{FeTPP}(\text{OH})_4$ and the resol catalysts under the following conditions: [catalysts], 5 μM ; $[\text{KHSO}_5]$, 500 μM ; pH 3.0; observed wavelength, 420 nm; reaction temperature, 25°C : (a) $\text{FeTPP}(\text{OH})_4$, (b) resol 1, (c) resol 2, and (d) resol prepared from FeTPPSOH previously [13].

and the resol catalysts, 60–90% of the TrCP disappeared within 1 min. TrCP in the reaction mixture decreased gradually with reaction duration, reaching a plateau after reactions of 5 min or longer.

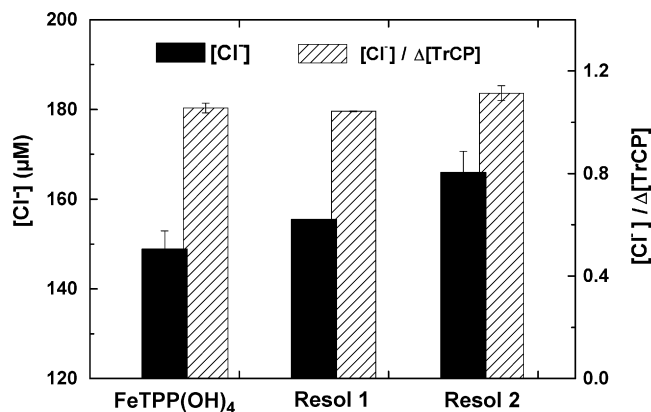


Fig. 6. Concentrations of chloride ions and the numbers of chlorine atoms released from TrCP during the oxidation. pH 3.0; $[\text{TrCP}]_0$, 150 μM ; [catalyst], 5 μM ; $[\text{KHSO}_5]$, 500 μM .

3.3. Self-degradation kinetics of prepared catalysts

Iron(III)-porphyrin catalysts are rapidly inactivated by self-degradation in the presence of peroxides, such as KHSO_5 . The kinetics of iron(III)-porphyrin self-degradation can be evaluated by monitoring decolorization of the Soret band [6]. Fig. 5 shows the kinetic curves for self-degradation of $\text{FeTPP}(\text{OH})_4$ (a) and the resol catalysts (b and c) in the presence of KHSO_5 (500 μM) at pH

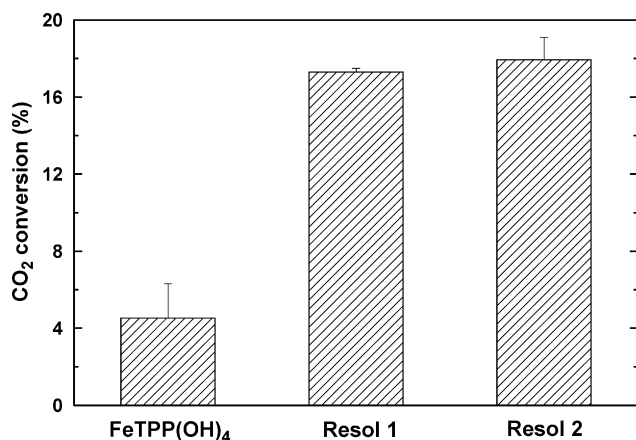


Fig. 7. The percent CO_2 conversion for $\text{FeTPP}(\text{OH})_4$ and the resol catalysts under the following conditions: pH 3.0; $[\text{TrCP}]_0$, 150 μM ; [catalyst], 5 μM ; $[\text{KHSO}_5]$, 500 μM ; reaction temperature, 25 $^\circ\text{C}$.

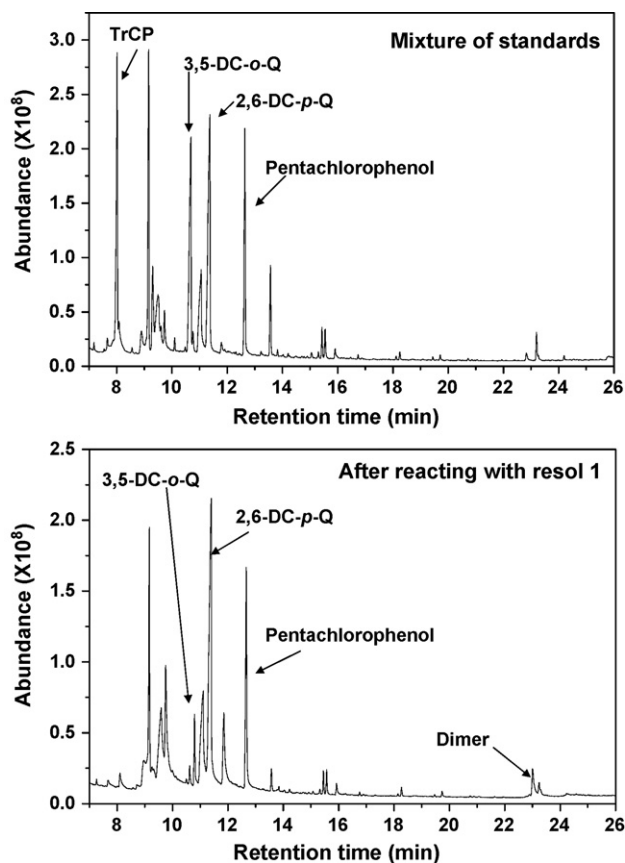


Fig. 8. The GC/MS chromatograms of the extracts of the standard solutions (50 μM of TrCP, 3,5-DC-*o*-Q and 2,6-DC-*p*-Q) and the reaction mixture after reaction with resol 1 (reaction conditions: pH 3.0; $[\text{TrCP}]_0$, 150 μM ; [catalyst], 5 μM ; $[\text{KHSO}_5]$, 500 μM).

3. A_0 and A_t on the y-axis represent the absorbances that correspond to the catalyst concentration before and after addition of KHSO_5 , respectively. As shown in the kinetic curves in Fig. 5, after an initial period of gradual catalyst degradation, the catalysts were rapidly degraded. The kinetic curve for resol 1 was nearly identical to that of resol 2. Due to the complicated nature of the catalyst degradation reactions, the overall reactions could not be elucidated. However, the half-lives, estimated at $A_t/A_0 = 0.5$, for resol catalysts (3.45 ± 0.03 s for resol 1; 3.49 ± 0.02 s for resol 2) were significantly longer than the half-life of $\text{FeTPP}(\text{OH})_4$ (0.75 ± 0.01 s). These results indicate that the formation of resol catalyst retards self-degradation in the presence of KHSO_5 . The half-life for the resol catalyst, which was previously prepared from FeTPPSOH [13], was estimated to be 0.08 s (Fig. 5(d)). These results show that resol catalysts using $\text{FeTPP}(\text{OH})_4$ having four phenolic hydroxyl groups are more stable than those using FeTPPSOH having only one site for HA-binding.

3.4. Cl^- release and mineralization

Oxidative dechlorination has been observed during degradation of TrCP by iron(III)-porphyrin catalysts [1,3]. Therefore, Cl^- was analyzed in the reaction mixtures during the 60-min reaction period (Fig. 6). Concentrations of Cl^- released in the presence of resol 1 and 2 were significantly greater than that in the presence of $\text{FeTPP}(\text{OH})_4$. These results show that disappearance of TrCP can be attributed to oxidative dechlorination. The number of chlorine atoms released from TrCP was estimated from the ratio of $[\text{Cl}^-]$ to the decrease in

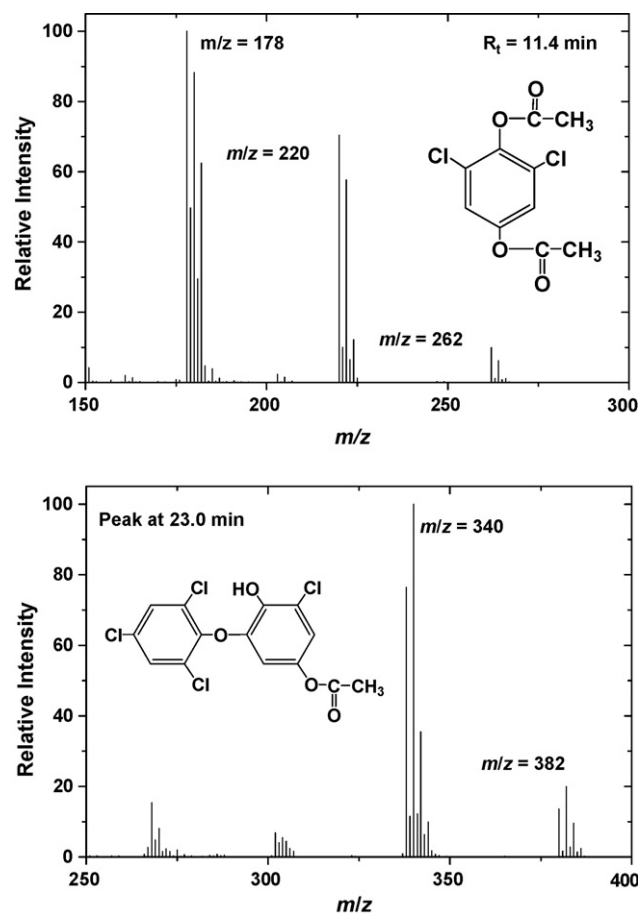


Fig. 9. Mass spectrum of the peak with a retention time of 23.0 min in the chromatogram.

TrCP concentration ($\Delta[\text{TrCP}]$) (Fig. 6). The $[\text{Cl}^-]/\Delta[\text{TrCP}]$ ratios of the $\text{FeTPP}(\text{OH})_4$ and resol catalysts were similar (1.0–1.2).

For the oxidative degradation of TrCP using metallophthalocyanines, Sorkin et al. [25] reported that TrCP oxidation included a variety of aromatic ring cleavage products. In addition, further oxidation of these products by metallophthalocyanines and their supported polymers can lead to mineralization to CO_2 during TrCP oxidation [26,27]. Therefore, we investigated the mineralization of TrCP to CO_2 as a result of oxidation by either $\text{FeTPP}(\text{OH})_4$ or resol catalysts. Because the detection limit of the TOC analyzer was 0.052 mg l^{-1} , the carbon concentration in the reaction mixture included $150 \mu\text{M}$ TrCP (11 mg l^{-1}) and could precisely be analyzed using the TOC analyzer. We evaluated percent CO_2 conversion in the $\Delta[\text{TrCP}]$ by the loss of TOC before and after oxidation. The loss of TOC (ΔTOC) was calculated by subtracting the TOC in the reaction mixture after a 60-min reaction period from the TOC of the mixture before adding KHSO_5 , as described in the following equation:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{\Delta\text{TOC}}{\Delta[\text{TrCP}] \times 6} \times 100.$$

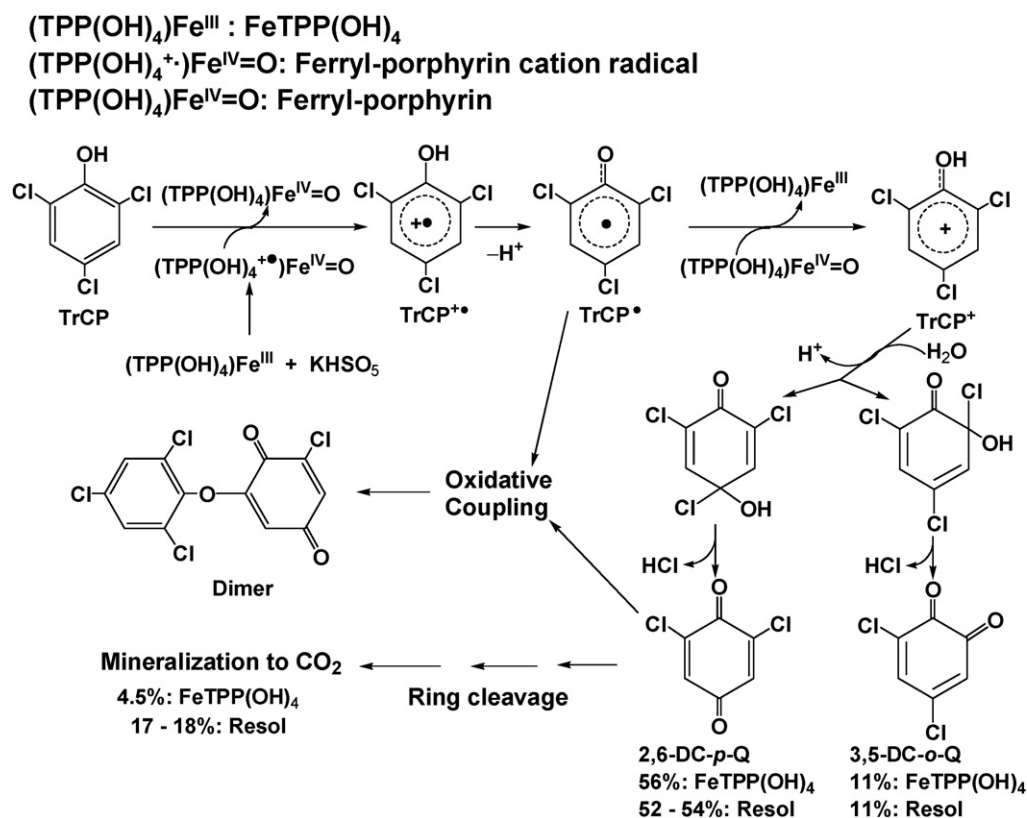
In the absence of TrCP, the reaction mixtures included background organic compounds, such as $\text{FeTPP}(\text{OH})_4$ and resol catalysts. Thus, the TOC in the reaction mixture including $\text{FeTPP}(\text{OH})_4$, or the resol catalyst alone, was analyzed as a control. However, TOC before the reaction with KHSO_5 (3.9 mg l^{-1} for $\text{FeTPP}(\text{OH})_4$; 4.7 mg l^{-1} for resol 1 and 2) was unchanged after a 60-min reaction period. Thus, the decrease of TOC in the presence of TrCP could be due to the loss of TOC from TrCP as a result of oxidation. The units of ΔTOC and $\Delta[\text{TrCP}]$ are molar concentrations of the carbon, and $\Delta[\text{TrCP}]$ is calculated from the HPLC analysis. The rates of CO_2 conversion with resol 1 and 2 (17% and 18%, respectively) were significantly greater than conversion using $\text{FeTPP}(\text{OH})_4$ alone (4.5%) (Fig. 7). Therefore,

formation of resol catalysts effectively enhanced the catalytic oxidation of TrCP.

3.5. By-products

To identify by-products derived from TrCP, the reaction mixture was extracted with diethyl ether, and the extract that was replaced by methanol was then injected into a GC/MS after addition of an acetylation reagent. The GC/MS chromatograms of the extracts from the standard solution and the reaction mixture for resol 1 are shown in Fig. 8. Patterns of by-products in the GC/MS chromatograms for the $\text{FeTPP}(\text{OH})_4$ and resol catalytic systems were similar. As a result of catalytic reactions, peaks corresponding to 3,5-dichloro-*o*-quinone (3,5-DC-*o*-Q) diacetate (10.8 min) and 2,6-DC-*p*-Q diacetate (11.4 min) were evident (Fig. 8). In addition, the small peak at 23.0 min, which appeared in both $\text{FeTPP}(\text{OH})_4$ and resol catalytic systems, was assigned to the dimer, 4-chloro-6-(2,4,6-trichlorophenoxy)-1-hydroxy-4-acetyl-phenol, based on the results of mass spectroscopy shown in Fig. 9. Although the assigned by-products were present in the acetate form, these compounds may exist as quinone derivatives in the reaction mixture.

Based on the results described above and the known reactivity of iron(III)-porphyrins activated by KHSO_5 [28], possible TrCP degradation pathways were proposed (Scheme 2). Initially, KHSO_5 reacts with $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{III}}$ in the catalysts to generate an oxoiron(IV)porphyrin radical cation, $(\text{TPP}(\text{OH})_4)^+\text{Fe}^{\text{IV}}=\text{O}$. This active species reacts with TrCP and gives oxoiron(IV)porphyrin $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{IV}}=\text{O}$ and the radical cation (TrCP $^{\bullet}$). Removal of a proton from the TrCP $^{\bullet}$ yields the trichlorophenoxy radical (TrCP $^+$). This species interacts with $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{IV}}=\text{O}$ to produce cationic TrCP (TrCP $^+$) and regenerate $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{III}}$. TrCP $^+$ can react with H_2O to produce 2,6-DC-*p*-Q and 3,5-DC-*o*-Q. The concentrations



Scheme 2. $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{III}}$: $\text{FeTPP}(\text{OH})_4$; $(\text{TPP}(\text{OH})_4^+)\text{Fe}^{\text{IV}}=\text{O}$: ferryl-porphyrin cation radical; $(\text{TPP}(\text{OH})_4)\text{Fe}^{\text{IV}}=\text{O}$: ferryl-porphyrin.

of 2,6-DC-*p*-Q and 3,5-DC-*o*-Q were estimated from peak areas in the GC/MS chromatograms using standard reagents. Percentages of TrCP converted to 2,6-DC-*p*-Q and 3,5-DC-*o*-Q were estimated to be 52–56% and 11%, respectively. During oxidation of chlorophenol, chloroquinones are further oxidized to maleic acid derivatives [25]. Although these compounds were not identified in the present study, the unknown products present in both systems might be the ring-cleavage products of 2,6-DC-*p*-Q and/or 3,5-DC-*o*-Q. This type of ring cleavage results in mineralization to CO₂. In the present study, mineralization of TrCP was observed, and percent TrCP conversion to CO₂ when the resol catalysts were used (17–18%) was significantly greater than that observed for FeTPP(OH)₄. Other possible TrCP oxidation pathways are coupling reactions between TrCP• and quinones, which yield a variety of dimers [29]. In the present study, we found small peaks attributed to a dimer in both the FeTPP(OH)₄ and resol catalytic systems.

4. Conclusion

Introduction of functionalities into HA is a novel and, apparently, effective trend in current humic substance technology. Because half-life for the resol catalyst prepared from FeTPPSOH, having only one phenolic hydroxyl group for HA-binding, were much smaller than those for the catalysts prepared from FeTPP(OH)₄, having four phenolic hydroxyl groups for HA-binding. Thus, the increase of phenolic hydroxyl groups in iron(III)-porphyrin for HA-binding resulted in forming more stable resol catalysts. The prepared resol catalysts using FeTPP(OH)₄ also exhibited retarded self-degradation compared with degradation in FeTPP(OH)₄ alone. Percent CO₂ conversion, an index of catalytic activity, was significantly greater with the resol catalysts. Thus, resol catalysts prepared from FeTPP(OH)₄ effectively enhanced catalytic activity due to the reduction in self-degradation.

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