# Oxidative degradation of pentachlorophenol by an iron(III)-porphyrin catalyst bound to humic acid via formaldehyde polycondensation

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## Abstract

Introduction of functional groups into humic substances is a novel trend in humic technology. In the present study, a biomimetic catalyst, 5-(p-hydroxyphenyl)-5,10,15,20-tetrasulfonatophenyl porphine iron(III) (FeTPPSOH), was introduced into humic acid via formaldehyde polycondensation. In the presence of KHSO$_5$, the self-degradation of the prepared catalysts, which were called "resol," was retarded. In addition, the catalytic activity, which was evaluated by the percent pentachlorophenol (PCP) disappearance and levels of dechlorination, was significantly greater for the resol catalysts. The results of the present study show that resol catalysts effectively enhance oxidative degradation of PCP. The byproducts of oxidation were investigated by GC/MS analysis of n-hexane extracts of the reaction mixtures. This analysis demonstrated that another advantage of resol catalysts is that they prevent the formation of more harmful dimers, such as octachlorodibenzo-p-dioxin.

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## 1. Introduction

Pentachlorophenol (PCP) has been utilized in the past as a wood preservative and as a component of herbicides. A recent study indicated that chlorophenols, such as PCP, are the primary cause of the health problems observed in humans who live in contaminated areas [1]. Remediation technologies used to treat PCP-contaminated soils include chemical oxidation [2], washing the soil [3] and biological degradation [4]. In particular, oxidative degradation of PCP and other chlorophenols using biomimetic catalysts, such as iron(III)-porphyrin, has received attention as a possible remediation technology for treatment of contaminated soils [5,6]. However, iron(III)-porphyrin catalysts are inactivated by self-degradation in the presence of peroxides, such as H$_2$O$_2$ and KHSO$_5$ [7]. Immobilization of iron(III)-porphyrin catalysts on the surface of clay minerals has been examined for its ability to suppress self-degradation of the catalysts [8,9]. Recently, our research group reported that oxidative degradation of PCP by tetrakis(p-sulfonatophenyl) porphine iron(III) (FeTPPS) was enhanced in the presence of humic acids (HAs), which are the acid-insoluble fraction of humic substances in soil organic matter [10–12]. This effect can be attributed to the fact that self-degradation of FeTPPS in the presence of KHSO$_5$ is suppressed by the formation of supramolecular complexes via hydrophobic interactions between HA and the sulfonatophenyl groups in FeTPPS [13–15]. However, the extent of supramolecular complex formation may be dependent on the type of HA, because the degree of hydrophobic interactions varies significantly, depending on the polar groups in HAs [15].

Recently, hydroquinone groups were covalently introduced into HA using formaldehyde polycondensation to enhance the reducing abilities of HA [16]. The introduction of functional groups into HA is a novel trend in current humic technology. Covalent binding of the iron(III)-porphyrin catalyst to HA would be advantageous, as it would prevent dissociation of the catalyst from the supramolecular complex. Therefore, in the present study, FeTPPS was covalently introduced into HA via formaldehyde polycondensation. In addition, the self-degradation kinetics and catalytic activity of the prepared catalysts were examined.

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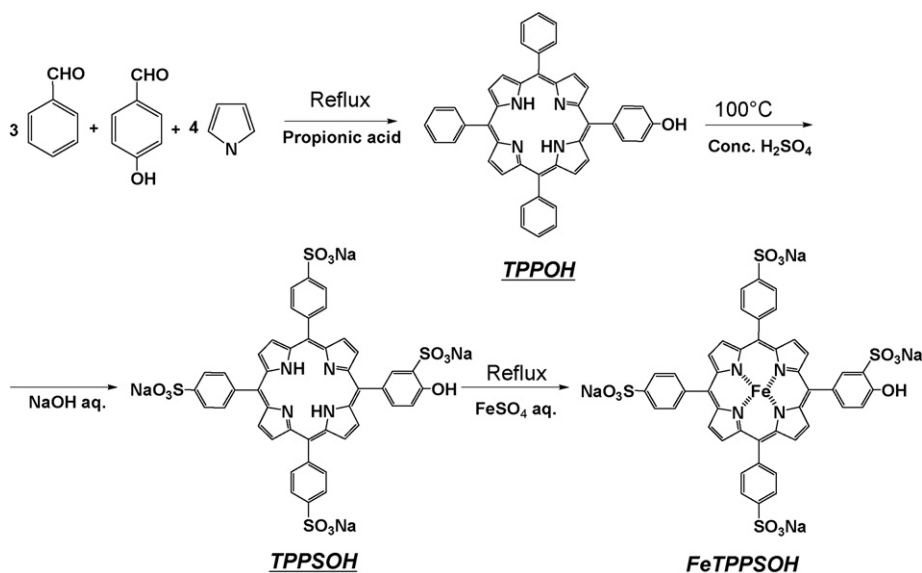
Scheme 1.

## 2. Materials and methods

### 2.1. Preparation of catalysts

#### 2.1.1. Synthesis of 5-(p-hydroxyphenyl)-5,10,15,20-tetrasulfonatophenylporphine iron(III) (FeTPPSOH)

The synthesis of FeTPPSOH is described in Scheme 1. Benzaldehyde (22.3 g, 0.21 mol) and 4-hydroxybenzaldehyde (8.55 g, 0.07 mol) were dissolved in propionic acid (500 ml). This solution was placed in a 1-l three-necked flask with a reflux condenser and mechanical stirrer, and then was heated to reflux. After dropwise addition of pyrrole (18.9 g, 0.28 mol), the solution was refluxed for 1 h [17]. After evaporating the propionic acid, the residue was dissolved in chloroform (5 ml). The crude material was then reprecipitated by the addition of 500 ml of methanol. After collecting the precipitate by filtration and drying it under reduced pressure, 1.5 g of crude material was dissolved in chloroform (150 ml). The synthesized 5-(p-hydroxyphenyl)-10,15,20-triphenylporphyrin (TPPOH) was purified using a silica-gel column (Nacalai Tesque, 70–230 mesh, Ø 50 mm × 170 mm) with chloroform; TPPOH was present in the second elute. The TPPOH was reprecipitated in n-hexane, and the powdered sample was obtained under reduced pressure (yield calculated from 4-hydroxybenzaldehyde: 6.1%). $^1$H NMR (CDCl$_3$) 8.84–8.87 ppm (pyrrole), 8.21, 8.22 ppm (dd, o-Ph), 8.05 ppm (d, o-PhOH), 7.72–7.78 ppm (m, m, p-Ph), 7.12 ppm (d, m-PhOH); absorbance (CHCl$_3$) 419, 515, 550, 588 and 647 nm.

Sulfonation of TPPOH was performed using the method of Dixon et al. [18]. TPPOH (C$_{44}$H$_{30}$N$_4$O, 0.3 g, 0.48 mmol) was added to 5 ml of concentrated H$_2$SO$_4$ (90 mmol). The reaction mixture was heated at 100 °C for 10 h, followed by stirring for 2 days at room temperature. Subsequently, ice was added to the green mixture, and the acid was then carefully neutralized with 50% NaOH (aqueous) until the mixture turned red. The pH of the solution was adjusted to 7 and the liquid was evaporated under

reduced pressure. The resulting solid was pulverized and 5-(p-hydroxyphenyl)-5,10,15,20-tetrasulfonatophenyl porphyrin (TPPSOH) was extracted with methanol using a Soxhlet apparatus for 48 h. The purple-colored solution was evaporated under reduced pressure. The crude TPPSOH was dissolved in water, followed by addition of FeSO$_4$·7H$_2$O (0.5 g, 1.8 mmol). The mixture was refluxed for 8 h under N$_2$ atmosphere. Purification of FeTPPSOH was performed using the method of Kawasaki et al. [19]. The yield of FeTPPSOH, calculated from TPPOH, was 18%. Absorption spectra (0.02 M Na$_2$HPO$_4$/NaH$_2$PO$_4$ buffer at pH 6) were as follows: TPPSOH 414, 516, 550, 580, 635 nm and FeTPPSOH 395, 529 nm. Results of the elemental analysis of FeTPPSOH (C$_{44}$H$_{24}$N$_4$O$_{13}$S$_4$Na$_4$Fe·14H$_2$O) were as follows: calculated, %C 39.3, %H 3.9, %N 4.2, %S 9.5 and observed, %C 39.2, %H 3.7, %N 4.2, %S 10.2.

#### 2.1.2. Synthesis of resol catalysts via formaldehyde polycondensation

An HA sample extracted from peat soil (Shinshinotsu, Japan) was purified using the method approved by the International Humic Substances Society [20]. The reaction for binding FeTPPSOH to HA via formaldehyde polycondensation is shown in Scheme 2. In general, compounds that are formed via formaldehyde polycondensation in alkaline solution are termed "resols" [21]. Thus, the catalysts prepared in this study are subsequently referred to as resols.

HA and FeTPPSOH were dissolved in 0.1 M NaOH (aqueous). The mixture was transferred to a 300-ml three-necked flask equipped with a reflux condenser and 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 then cooled in an ice bath. The solution was neutralized with aqueous H$_2$SO$_4$. The fraction, including resol, was concentrated by ultrafiltration through a Millipore YM1 ultrafiltration cellulose membrane (nominal cut-off, 1000 Da). After
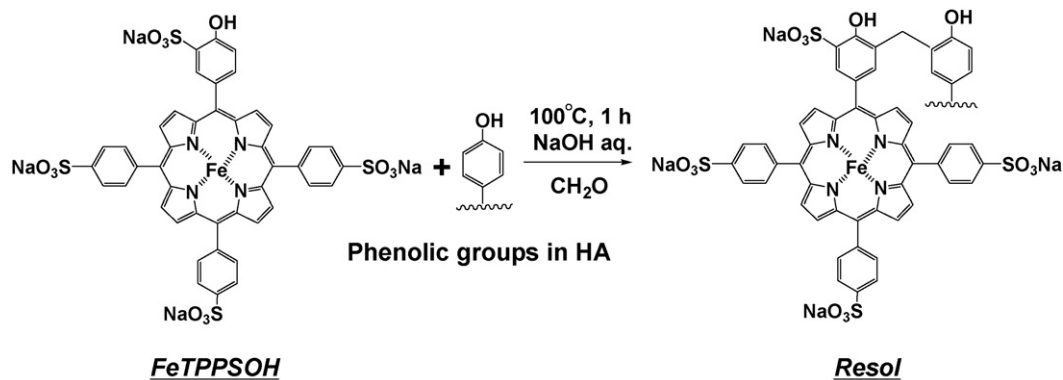
Scheme 2.

washing the resol fraction with water, the concentrated fraction was 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 catalyst in powdered form. In the present study, three types of resol catalysts were synthesized, and a control sample of HA (HA-RBL) without FeTPPSOH was also prepared. The quantities of FeTPPSOH, HA, and formaldehyde in the catalysts and control are summarized in Table 1.

### 2.2. Spectroscopic measurements

FTIR spectra of FeTPPSOH 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 FeTPPSOH and the resol catalysts ($5 \, \mu M$) in a buffer at pH 6 ($0.02 \, M \, NaH_2PO_4/Na_2HPO_4/citrate$) were obtained using a V-630 type spectrophotometer (Japan Spectroscopic Co. Ltd.) with a quartz cell ($1 \, cm \times 1 \, cm$) at $25 \, °C$. Decolorization of the catalysts was monitored using a RSP-1000-02-type stopped-flow spectroscopy system (Unisoku Co. Ltd.).

### 2.3. Test for PCP disappearance

A 2-ml aliquot of $0.02 \, M \, NaH_2PO_4/Na_2HPO_4/citrate$ buffer at pH 6 was placed in a 20-ml L-shaped test tube. The pH of the solution was varied between pH 3 and 7 and was adjusted by adding aqueous NaOH. A 10-$\mu$l aliquot of 10 mM PCP in acetonitrile and a 50-$\mu$l aliquot of an aqueous solution of FeTPPSOH or resol catalysts ($200 \, \mu M$) were then added to the buffer solution. Subsequently, a 10-$\mu$l aliquot of $0.1 \, M$ aqueous $KHSO_5$ was added, and the test tube was shaken in a Monosin IIA-type thermostatic shaking water bath (TAITEC) at

$25 \pm 0.1 \, °C$. After a 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-$\mu$l 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 $H_3PO_4$ 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. $\times$ 250 mm, Nacalai Tesque) was used as the solid phase, and the column temperature was maintained at $50 \, °C$. PCP, and UV absorption was measured at 220 nm.

### 2.4. Analyses of reaction products

#### 2.4.1. $Cl^-$ and total organic carbon (TOC)

Citrate buffer cannot be used for the determination of TOC in the reaction mixture. Thus, the pH was adjusted to pH 6 using a $0.02$-$M \, NaH_2PO_4/Na_2HPO_4$ buffer. In this experiment, neither could acetonitrile be used to prepare the stock solution of PCP. Thus, 10 mg of PCP was dissolved in 50 ml of 0.01 M aqueous NaOH ($750 \, \mu M$), and this solution was then diluted to $37.5 \, \mu M$ with $0.02 \, M \, NaH_2PO_4/Na_2HPO_4$ buffer. A 30-ml aliquot of this solution was placed in a 100-ml Erlenmeyer flask, and a 750-$\mu$l aliquot of the aqueous catalyst ($200 \, \mu M$) was then added. Subsequently, 150 $\mu$l of $0.1 \, M$ aqueous $KHSO_5$ was added, and the flask was then shaken at $25 \, °C$ in a thermostatic shaking water bath. After a 90-min or 1-day reaction period, a 2-ml aliquot of the reaction mixture was mixed with 1 ml of 2-propanol, followed by quantification of PCP 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 $Na_2SO_3$ (1 ml), and the TOC of this solution was analyzed using a TOC-V CSH-type analyzer (Shimadzu).

Table 1
Quantities of HA, FeTPPSOH and formaldehyde, and the results of elemental compositions for each sample

| Samples | HA/FeTPPSOH (mg/mg) | CH$_2$O (mmol) | %C | %H | %N | %O | %S | %Ash | C/N | C/S |
|---|---|---|---|---|---|---|---|---|---|---|
| HA (untreated) | – | – | 54.5 | 5.4 | 2.2 | 35.1 | 0.7 | 2.2 | 29.3 | 221 |
| HA-RBL (reaction BL) | – | 6.9 | 51.3 | 5.3 | 2.2 | 34.9 | 1.4 | 4.9 | 27.3 | 98.5 |
| Resol 1 | 60/30 | 1.0 | 41.8 | 4.4 | 2.7 | 34.5 | 6.8 | 9.1 | 18.0 | 16.3 |
| Resol 2 | 60/30 | 6.9 | 44.9 | 4.6 | 2.6 | 35.1 | 5.3 | 7.6 | 20.2 | 22.7 |
| Resol 3 | 20/30 | 6.9 | 40.5 | 4.0 | 3.2 | 35.4 | 7.9 | 8.9 | 14.7 | 13.6 |

### 2.4.2. Analysis of byproducts

A 20-ml aliquot of 0.02 M $NaH_2PO_4/Na_2HPO_4$ buffer at pH 6 was placed in a 100-ml Erlenmeyer flask. A 75-μl aliquot of 0.01 M PCP in acetonitrile and a 500-μl aliquot of an aqueous solution of the catalyst (200 μM) was added to the buffer solution. Subsequently, 100 μl of 0.1 M aqueous $KHSO_5$ was added, and the flask was then shaken at 25 °C in a thermostatic shaking water bath. After a 90-min reaction period, 800 μl of 1 M aqueous ascorbic acid was added, and the pH of the solution was adjusted to 11–11.5 by addition of aqueous $K_2CO_3$. Subsequently, 4 ml of acetic anhydride was added dropwise. This mixture was extracted two times with 10 ml of *n*-hexane, and the combined extracts were dried over anhydrous $Na_2SO_4$. After filtration, the extract was concentrated to 200 μl under a stream of dry $N_2$. A 1-μl aliquot of the extract was introduced into a GC-17A/QP5050 GC/MS system (Shimadzu). A Quadrex methyl silicon capillary column (0.25 mm i.d. × 25 m) was employed in the separation. 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.

### 2.4.3. Chlorine content in the resol fraction

PCP was oxidized as described above, although the volumes in this experiment were 10-fold greater than those in Section 2.4.2. After a 90-min reaction period, 0.2 g of ascorbic acid powder was added, and the fraction including the resol catalyst was concentrated by ultrafiltration through a Millipore cellulose membrane (nominal cut-off, 500 Da), followed by washing with water. The concentrated fraction was freeze-dried and the chlorine content in the fraction was analyzed. Analysis of chlorine was performed at the Center for Instrumental Analysis at Hokkaido University (Sapporo, Japan).

## 3. Results and discussion

### 3.1. Characterization of resol catalysts

The elemental composition of HA and the resol catalysts are summarized in Table 1. The C/N and C/S atomic ratios of the resol catalysts were much smaller than those for HA and HA-RBL, suggesting that FeTPPSOH, which contains nitrogen and sulfur, can be introduced into HA. The Fe content of the resol catalysts is summarized in Table 2. Fe content was determined

Table 2
Fe contents in resol catalysts and percentages of FeTPPSOH bound to HA

| Samples | Fe content (μmol Fe mg$^{-1}$) | %Fe | FeTPPSOH bound[a] (%) |
|---|---|---|---|
| FeTPPSOH | 0.75 | 4.2 | – |
| Resol 1 | 0.17 | 1.0 | 65 |
| Resol 2 | 0.22 | 1.2 | 90 |
| Resol 3 | 0.39 | 2.2 | 86 |

[a] The Fe content before the polycondensation was calculated from amount of FeTPPSOH added as described in Table 1. Thus, percentage of FeTPPSOH bound to HA via the formaldehyde polycondensation is estimated as (Fe content after the polycondensation)/(Fe content before the polycondensation) × 100.
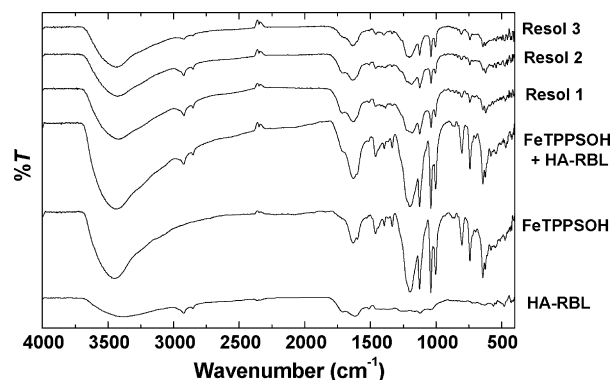


Fig. 1. FTIR spectra of HA-RBL, FeTPPSOH, FeTPPSOH + HA-RBL, and the resol catalysts obtained with a KBr pellet.

by dissolving the catalyst in water and then analyzing the solution using an ICP-AES spectrophotometer. The weight percent of Fe (%Fe in Table 2) in FeTPPSOH was 4.2%, which was in good agreement with the calculated value (4.3%). Thus, molar concentrations of FeTPPSOH and resol catalysts in the aqueous solutions were calculated based on the Fe content. The phenolic hydroxyl group content in the HA sample was reported to be 13.5 mmol g$^{-1}$ [15]. The phenolic hydroxyl group content of the HA used in this study ranged from 0.27 to 0.81 mmol. Thus, the phenolic sites in HA were present in excess of the added FeTPPSOH (0.02 mmol). The Fe content and %Fe of resol 3, which had the lowest HA/FeTPPSOH ratio, were relatively greater than the other resol catalysts. In addition, a higher formaldehyde content (resols 2 and 3) resulted in higher percentages of bound FeTPPSOH.

Fig. 1 shows the FTIR spectra of HA-RBL, FeTPPSOH, FeTPPSOH + HA-RBL, and of the resol catalysts. The following peaks were evident in the FeTPPSOH sample: at approximately 3470 cm$^{-1}$, phenol O–H stretching; 1620 and 1550 cm$^{-1}$, C=C ring stretching; 1468 cm$^{-1}$, pyrrole C=N stretching; 1338 cm$^{-1}$, phenol O–H bending; 1209 cm$^{-1}$, phenol C–O stretching; 1128, 1041 and 1004 cm$^{-1}$, sulfonate groups symmetric O=S=O stretching; 807 and 743 cm$^{-1}$, out-of-plane C–H bending and 646 cm$^{-1}$, out-of-plane ring C=C bending. For the mixture of FeTPPSOH and HA-RBL, the peaks observed were nearly identical to those observed in the spectrum of FeTPPSOH alone, although the peaks at 2938 and 2881 cm$^{-1}$ for alkyl C–H stretching in HA and the shoulder at approximately 1720 cm$^{-1}$ for carbonyl C=O stretching in HA were unique to the mixture. For the resol catalysts, peaks at approximately 1430–1330 cm$^{-1}$ were broadened and/or disappeared. In addition, peaks for C–O stretching at approximately 1220 cm$^{-1}$ were more broad than those observed in the spectra of FeTPPSOH alone and of the mixture of FeTPPSOH and HA-RBL. When a phenol resin forms via formaldehyde polycondensation, significant broadening and disappearance of the peaks corresponding to phenol O–H stretching and C–O stretching occur [22]. Thus, the FTIR spectra of resol catalysts indicate the formation of phenol-resin-like compounds via formaldehyde polycondensation between FeTPPSOH and HA.

Table 3
Absorption coefficients and self-degradation kinetic constants of catalysts at pH 6, [catalyst] 5 μM, and [KHSO$_5$] 500 μM

| Samples | Absorption data | | Self-degradation kinetic constants (s$^{-1}$) |
|---|---|---|---|
| | $\lambda_{max}$ (nm) | $\varepsilon$ (cm$^{-1}$ M$^{-1}$) | |
| FeTPPS | 394 | 89,900 | 14.1 ± 0.3 |
| FeTPPSOH | 395 | 97,900 | 8.7 ± 0.1 |
| Resol 1 | 395 | 102,700 | 6.9 ± 0.1 |
| Resol 2 | 395 | 99,300 | 6.6 ± 0.2 |
| Resol 3 | 395 | 94,600 | 7.8 ± 0.1 |

### 3.2. Self-degradation kinetics of the catalysts

Iron(III)-porphyrin catalysts are rapidly inactivated by self-degradation in the presence of peroxides, such as KHSO$_5$. The self-degradation kinetics of iron(III)-porphyrin can be evaluated by monitoring the decolorization of the Soret band [7,14,15]. The maximal absorption wavelengths ($\lambda_{max}$) and molar absorption coefficients ($\varepsilon$) for the Soret band of FeTPPSOH and resol catalysts are summarized in Table 3. Previously reported values for FeTPPS were used in the comparison of the different catalysts [13]. The $\lambda_{max}$ values for FeTPPS, FeTPPSOH and resol catalysts were not different. However, the $\varepsilon$ for FeTPPS was less than the values for FeTPPSOH and the resol catalysts. It was expected that $\varepsilon$ of the Soret band would be greater in the resol catalysts than in FeTPPSOH alone because of the additional absorbance due to HA. However, there were no differences between FeTPPSOH and the resol catalysts. These results may be attributed to the polycondensation between HA and FeTPP-SOH.

Fig. 2 shows the kinetic curves for the self-degradation of FeTPPS, FeTPPSOH and the resol catalysts (5 μM) in the presence of KHSO$_5$ (500 μM) at pH 6. $A_0$ and $A_t$ in $y$-axis represent the absorbance, which corresponds to the catalyst concentration, before and after the addition of KHSO$_5$, respectively. Pseudo-first-order kinetic constants, calculated from the kinetic curves, are summarized in Table 3. The kinetic constant for FeTPPS was much larger than those for FeTPPSOH and resol catalysts, indi-
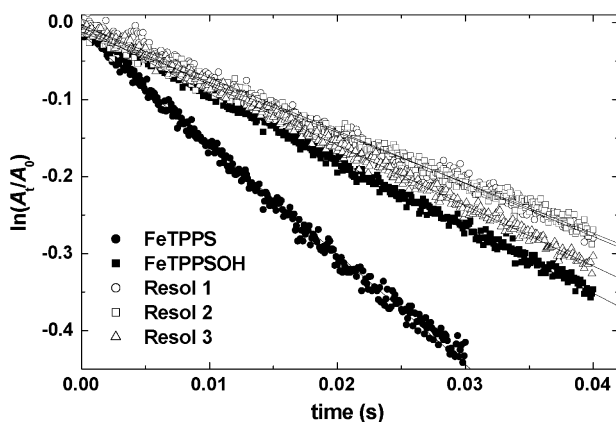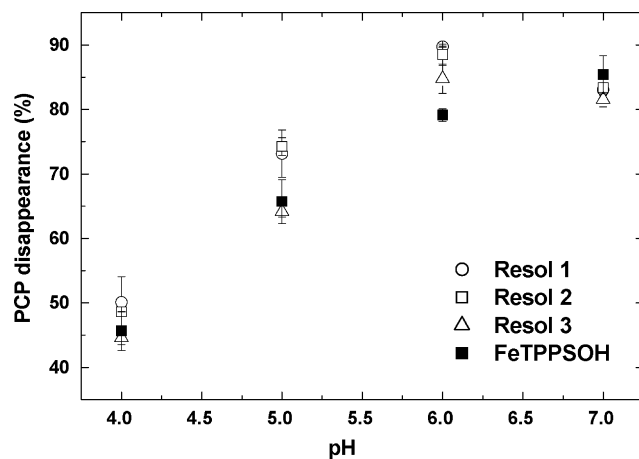
Fig. 3. Influence of pH on %PCP disappearance. The reaction conditions were as follows: [PCP]$_0$, 50 μM; [catalysts], 5 μM; [KHSO$_5$], 500 μM and reaction time, 60 min.

cating that FeTPPS is less stable than the FeTPPSOH and resol catalysts. The kinetic constant for FeTPPSOH was larger than those for the resol catalysts, among which the kinetic constants for resols 1 and 2 were larger than that for resol 3. Thus, resols 1 and 2 appear to have higher catalytic activity than FeTPPS, FeTPPSOH and resol 3.

### 3.3. Degradation characteristics of PCP

To evaluate the activity of the catalysts, oxidation characteristics of PCP were investigated. Reaction conditions, such as pH, KHSO$_5$ and substrate (i.e., PCP) concentrations influence the oxidation of PCP. Our research group investigated the influence of pH on PCP disappearance (Fig. 3). For FeTPPSOH and the resol catalysts, the percent PCP disappearance increased with increasing pH, as reported in a previous study of FeTPPS [10]. As shown in Fig. 3, PCP disappearance was enhanced by resol catalysts at pH 4–6. At pH 6, percent PCP disappearance for resols 1 and 2 were 10% greater than that for FeTPPSOH. Resol 3 enhanced PCP disappearance to a lesser degree than resols 1 and 2, consistent with the self-degradation kinetics (Table 3).

Fig. 4 shows the influence of KHSO$_5$ concentration on the percent PCP disappearance. Percent PCP disappearance increased with increasing KHSO$_5$ concentration until 250 μM KHSO$_5$, at which point the percent PCP disappearance plateaued. In the absence of KHSO$_5$, there was no evidence of PCP disappearance in the presence of FeTPPSOH or resol alone. In addition, in the absence of catalysts, PCP disappearance was not observed in the presence of either 500 μM or 1 mM KHSO$_5$. These results confirm that PCP disappearance requires both a catalyst and KHSO$_5$.

Fig. 5 shows the influence of substrate concentration ([PCP]$_0$) on the percent PCP disappearance for FeTPPS, FeTPPSOH and the resol catalysts. For all catalysts, the percent PCP disappearance decreased with increasing [PCP]$_0$. At [PCP]$_0 = 25$, 37.5 and 50 μM, PCP disappearance was enhanced with the resol catalysts, although this effect was less with resol 3 than with resols 1 and 2. These results can be attributed to the fact that
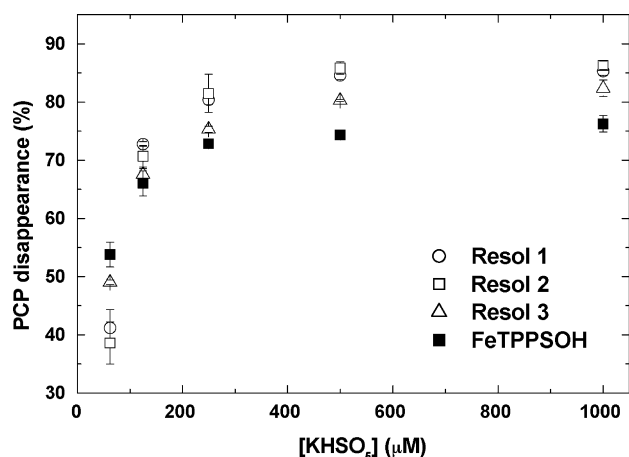
Fig. 2. Self-degradation kinetic curves for FeTPPS, FeTPPSOH and the resol catalysts under the following conditions: [catalysts], 5 μM; [KHSO$_5$], 500 μM; observed wavelength, 395 nm and reaction temperature, 25 °C.

Fig. 4. Influence of [KHSO$_5$] on %PCP disappearance. The reaction conditions were as follows: [PCP]$_0$, 50 μM; [catalysts], 5 μM; pH 6.0 and reaction time, 60 min.
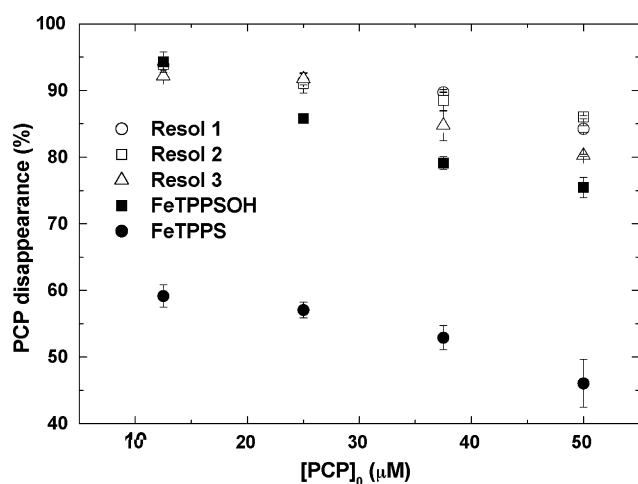


Fig. 5. Influence of substrate concentration ([PCP]$_0$) on %PCP disappearance. The reaction conditions were as follows: [catalysts], 5 μM; [KHSO$_5$], 500 μM; pH 6.0 and reaction time, 60 min.

self-degradation of FeTPPSOH is retarded by binding to HA via formaldehyde polycondensation. The influence of the duration of the reaction period on percent PCP disappearance was examined under the following reaction conditions: pH 6; [PCP]$_0$, 37.5 μM; [catalysts], 5 μM and [KHSO$_5$], 500 μM. For FeTPP-SOH and the resol catalysts, 70–80% of the PCP disappeared within 1 min. PCP in the reaction mixture decreased gradually with duration of the reaction, reaching a plateau at reaction periods of 20 min or longer.
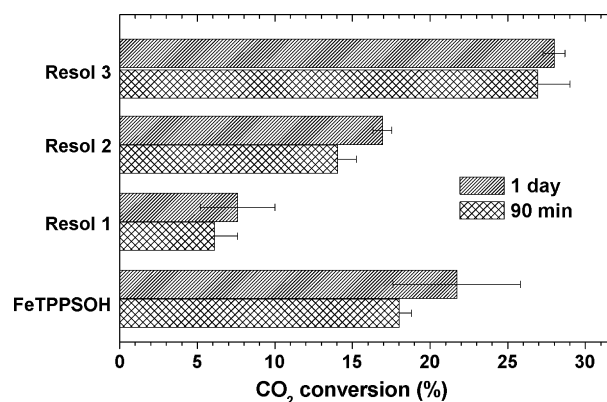


Fig. 6. Percentage CO$_2$ conversion as a result of oxidation with FeTPPSOH or the resol catalysts. The reaction conditions were as follows: [PCP]$_0$, 37.5 μM; [catalysts], 5 μM; [KHSO$_5$], 500 μM and pH 6.0.

### 3.4. Reaction products

#### 3.4.1. Cl$^-$ release and mineralization to CO$_2$

Dechlorination is observed during the oxidative degradation of PCP by iron(III)-porphyrin catalysts [10–12]. Therefore, Cl$^-$ was analyzed in the reaction mixtures for the 90-min and 1-day reaction periods (Table 4). Cl$^-$ concentrations increased in proportion to the percent PCP disappeared (Δ[PCP]). In addition, Cl$^-$ release with resols 1 and 2 was significantly greater than that with FeTPPSOH and resol 3. These results show that disappearance of PCP can be attributed to oxidative dechlorination. As indicated in Table 3, the numbers of chlorine atoms released from PCP, were estimated from the ratio of [Cl$^-$] to Δ[PCP] (2.8–3.0). These values were similar to those reported for a photo-Fenton system, in which mineralization to CO$_2$ is expected [23].

To estimate the percentage of CO$_2$ conversion in the Δ[PCP], the TOC of the reaction mixture after the reaction was subtracted from the TOC of the mixture before the reaction. The TOC in the absence of PCP was also analyzed as a control. Thus, the loss of TOC as a result of catalytic oxidation (ΔTOC) was estimated taking the control data into account. Percent CO$_2$ conversion was calculated as follows:

$$CO_2 \text{ conversion } (\%) = \frac{\Delta TOC}{\Delta[PCP] \times 6}$$

where the units of ΔTOC and Δ[PCP] are molar concentrations, and Δ[PCP] is calculated from the HPLC analysis. Fig. 6 shows the percentages of CO$_2$ conversion. The rate of CO$_2$ conversion with resol 3 was significantly greater than the conversion using

Table 4
The release of chloride ions at pH 6, [PCP]$_0$ 37.5 μM, [catalyst] 5 μM, and [KHSO$_5$] 500 μM

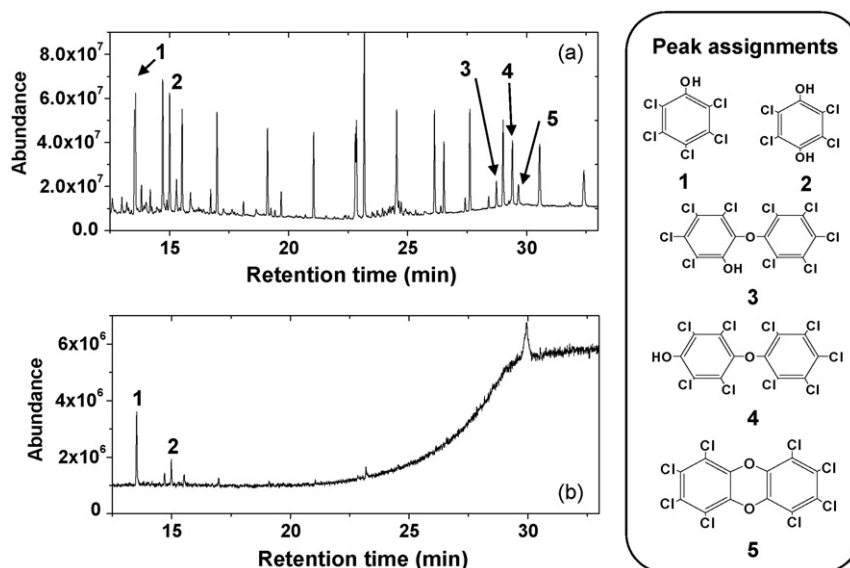| Samples | Δ[PCP][a] (μM) | | [Cl$^-$] (μM) | | [Cl$^-$]/Δ[PCP] | |
|---|---|---|---|---|---|---|
| | 90 min | 1 day | 90 min | 1 day | 90 min | 1 day |
| FeTPPSOH | 26.7 ± 0.7 | 32.0 ± 0.6 | 76.5 ± 0.6 | 92.4 ± 1.1 | 2.87 ± 0.06 | 2.88 ± 0.03 |
| Resol 1 | 30.9 ± 0.1 | 34.3 ± 0.1 | 85.5 ± 0.7 | 101 ± 2.1 | 2.77 ± 0.02 | 2.93 ± 0.06 |
| Resol 2 | 31.1 ± 0.6 | 36.3 ± 0.2 | 88.2 ± 2.4 | 111 ± 3.2 | 2.84 ± 0.13 | 3.06 ± 0.09 |
| Resol 3 | 29.3 ± 0.6 | 33.2 ± 0.2 | 82.4 ± 0.2 | 93.1 ± 0.7 | 2.81 ± 0.05 | 2.80 ± 0.02 |

[a] Δ[PCP] = [PCP]$_0$ − [PCP]$_t$.

Fig. 7. GC/MS chromatograms of hexane extracts of the reaction mixtures: (a) FeTPPSOH and (b) resol 2. The reaction conditions were as follows: $[PCP]_0$, 50 µM; [catalysts], 5 µM; $[KHSO_5]$, 500 µM and reaction time, 90 min. Peak assignments in the mass spectra [mass fragment, relative intensity]: (1) PCP 270 [M+4, 32.3], 268 [M+2, 85.3], 266 [M, 100], 264 [M−2, 85.1], 308 [M+$CH_3$CO, 13.4]; (2) TeCHQ 252 [M+4, 48.7], 250 [M+2, 86.2], 248 [M, 100], 246 [M−2, 97.3], 290 [M+$CH_3$CO, 51.2], 332 [M+2$CH_3$CO, 14.5]; (3) 2H-NCDE 500 [M+4, 16.5], 498 [M+2, 63.4], 496 [M, 100], 494 [M−2, 74.4], 492 [M−4, 34.9]; (4) 4H-NCDE 502 [M+6, 12.8], 500 [M+4, 37.9], 498 [M+2, 87.9], 496 [M, 100], 494 [M−2, 83.2], 492 [M−4, 31.7], 426 [M-2Cl, 47.7]; (5) OCDD 464 [M+4, 24.4], 462 [M+2, 55.2], 460 [M, 100], 458 [M−2, 97.9], 456 [M−4, 33.5].

the other catalysts. However, resols 1 and 2, which enhanced PCP disappearance and dechlorination, were less effective in $CO_2$ conversion than FeTPPSOH and resol 3.

### 3.4.2. Chlorinated organic compounds

To identify byproducts derived from PCP, the reaction mixture was extracted with *n*-hexane, and the extract was then injected into a GC/MS. Fig. 7 shows the GC/MS chromatograms for FeTPPSOH and resol 2. For the FeTPPSOH system, peaks corresponding to *p*-tetrachlorohydroquinone (TeCHQ, 2), 2-hydroxy-nonachlorodiphenyl ether (2H-NCDE, 3), 4-hydroxy-nonachlorodiphenyl ether (4H-NCDE, 4) and octachlorodibenzo-*p*-dioxin (OCDD, 5) were evident and these compounds were identified by their mass spectra, as described in the legend for Fig. 7. Only TeCHQ was detected in resol 2 (Fig. 7b)—2H-, 4H-NCDEs and OCDD were not observed. Similar byproduct patterns were observed for the other resol catalysts. These results suggest that an advantage of resol catalysts is that they do not form more harmful byproducts, such as OCDD.

The mechanisms by which the resol catalysts suppress the formation of harmful dimers may be related to the uptake of PCP intermediates by HA during oxidative coupling, as described in previous studies [11,24–26]. To confirm this hypothesis, the fraction including resol was isolated and the chlorine in this fraction was analyzed. In this experiment, resol 2 was examined. Chlorine was not found in a control sample that was prepared without PCP. However, in the presence of PCP, 0.47 mg of chlorine was found in the fraction after the reaction, corresponding to 37% of chlorine in the disappeared PCP. This result supports the assumption that the intermediates derived from PCP as a

result of catalytic oxidation can bind to the HA moieties in the resol catalyst.

### 4. Conclusions

FeTPPSOH was introduced into HA via formaldehyde polycondensation. The prepared resol catalysts exhibited retarded self-degradation, compared with degradation in FeTPPSOH alone. Percent PCP disappearance, an index of catalytic activity, was 5–10% greater with the resol catalysts. Thus, resol catalysts effectively enhanced catalytic activity because of the reduced self-degradation. In addition, the resol catalysts prepared using larger HA/FeTPPSOH ratios, gave rise to catalysts with higher catalytic activity. This result indicates that the ratio of HA to FeTPPSOH is more important than the amount of formaldehyde in the polycondensation reaction. Analysis of the reaction byproducts demonstrated that another advantage of resol catalysts is that they prevent the formation of more harmful dimers, such as OCDD. The introduction of functional groups into HA is a novel and, apparently, effective trend in current humic technology. Recently, a quinonoid-enriched HA was examined for its ability to reduce neptunium(V), which is radio-toxic [27]. The catalytic functionality introduced into HA examined in the present study may be applied to the remediation of PCP-contaminated soil.

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## References

[1] T. Vartiainen, P. Lampi, J.T. Tuomisto, J. Tuomisto, Chemosphere 30 (1995) 1429–1438.

[2] R.-M. Liou, S.-H. Chen, M.-Y. Hung, C.-H. Hsu, Chemosphere 55 (2004) 1271–1280.

[3] C.N. Mulligan, F. Eftekhari, Eng. Geol. 70 (2003) 269–279.

[4] J. Marcial, J. Barrios-González, A. Tomasini, Proc. Biochem. 41 (2006) 496–500.

[5] G. Labat, J.-L. Seris, B. Meunier, Angew. Chem. Int. Ed. Engl. 29 (1990) 1471–1473.

[6] R.S. Shukla, A. Robert, B. Meunier, J. Mol. Catal. A: Chem. 113 (1996) 45–49.

[7] M.J. Nappa, C.A. Tolman, Inorg. Chem. 24 (1985) 4711–4719.

[8] S. Nakagaki, F.L. Benedio, F. Wypych, J. Mol. Catal. A: Chem. 217 (2004) 121–131.

[9] H. Nur, H. Hamid, S. Endud, H. Hamdan, Z. Ramli, Mater. Chem. Phys. 96 (2006) 337–342.

[10] M. Fukushima, A. Sawada, M. Kawasaki, H. Ichikawa, K. Morimoto, K. Tatsumi, M. Aoyama, Environ. Sci. Technol. 37 (2003) 1031–1036.

[11] M. Fukushima, H. Ichikawa, M. Kawasaki, A. Sawada, K. Morimoto, K. Tatsumi, Environ. Sci. Technol. 37 (2003) 386–394.

[12] S. Rismayani, M. Fukushima, A. Sawada, H. Ichikawa, K. Tatsumi, J. Mol. Catal. A: Chem. 217 (2004) 13–19.

[13] M. Fukushima, K. Tatsumi, Environ. Sci. Technol. 39 (2005) 9337–9342.

[14] M. Fukushima, K. Tatsumi, J. Mol. Catal. A: Chem. 245 (2006) 178–184.

[15] M. Fukushima, Y. Tanabe, K. Morimoto, K. Tatsumi, Biomacromolecules 8 (2007) 386–391.

[16] I.V. Perminova, A.N. Kovalenko, P. Schmitt-Kopplin, K. Hatfield, N. Hertkorn, E.Y. Belyaeva, V.S. Petrosyan, Environ. Sci. Technol. 39 (2005) 8518–8524.

[17] H. Uno, K. Takata, Y. Mizutani, Reac. Polym. 15 (1991) 121–129.

[18] D.W. Dixon, A.F. Gill, L. Giribabu, A.N. Vzorov, A.B. Alam, R.W. Compas, J. Inorg. Biochem. 99 (2005) 813–821.

[19] M. Kawasaki, A. Kuriss, M. Fukushima, A. Sawada, K. Tatsumi, J. Porp. Phthal. 7 (2003) 645–650.

[20] 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.

[21] R. Rego, P.J. Adriaensens, R.A. Carleer, J.M. Gelan, Polymer 45 (2004) 33–38.

[22] R. Yadav, D. Srivastava, Mater. Chem. Phys. 106 (2007) 74–81.

[23] M. Fukushima, K. Tatsumi, Environ. Sci. Technol. 35 (2001) 1771–1778.

[24] P.G. Hatcher, J.M. Bortiatynski, R.D. Minard, J. Dec, J.-M. Bollag, Environ. Sci. Technol. 27 (1993) 2098–2103.

[25] J. Dec, J.-M. Bollag, Environ. Sci. Technol. 28 (1994) 484–490.

[26] K. Morimoto, K. Tatsumi, K.I. Kuroda, Soil Biol. Biochem. 32 (2000) 1071–1077.

[27] N.S. Shcherbina, I.V. Perminova, S.N. Kalmykov, A.N. Kovalenko, R.G. Haire, A.P. Novikov, Environ. Sci. Technol. 41 (2007) 7010–7015.