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Facilitation of pentachlorophenol degradation by the addition of ascorbic acid to aqueous mixtures of tetrakis(sulfonatophenyl)porphyrin and iron(II)

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Abstract

Pentachlorophenol (PCP) was degraded in an aqueous mixture of tetrakis(sulfonatophenyl)porphyrin (TPPS) and Fe(II) at pH 6. The degradation was enhanced by the addition of ascorbic acid (ASC), and PCP was largely degraded to tetrachlorohydroquinone (TeCHQ) and tetrachlorocatechol (TeCC). Chloride ions were released during the reaction in molar amounts that were approximately 2–3 times larger than those of PCP degraded. This suggests that further oxidative products are also produced. The percentage of PCP degraded decreased with increasing concentrations of 2-propanol, a hydroxyl radical ($OH^{\bullet}$) scavenger. This supports the hypothesis that $HO^{\bullet}$ is involved in PCP degradation. When an aqueous solution, which contained only TPPS, was shaken under aerobic conditions, H_2O_2 was generated at mM level after a 24 h reaction period. Thus, TPPS appears to be involved in the reduction of dissolved oxygen to $O_2^{\bullet -}$, leading to the generation of H_2O_2. However, in the presence of both TPPS and ASC, >100 μM-levels of H_2O_2 were generated. This shows that the addition of ASC to TPPS enhances the generation of H_2O_2. These results lead to the conclusion that the degradation of PCP in the present systems can be attributed to a Fenton-like process.

Keywords: Pentachlorophenol; TPPS; Iron; Ascorbic acid; Oxidative transformation; Fenton-like reaction

1. Introduction

Highly chlorinated phenols have been listed as a priority pollutant by the US Environmental Protection Agency [1]. In particular, pentachlorophenol (PCP), which is known to be an endocrine disrupter, has been used for wood preservative and herbicide, and this use has led to extensive contamination of aquatic and soil environments. Therefore, devising new processes for PCP degradation is attractive, in terms of environmental protection and remedial technologies.

It has been suggested that a sequence involving the anaerobic and aerobic biodegradation of chlorinated organic compounds could be used in treatment processes [2–4]. Such a use of bio-functionalities represents a potentially clean environmental process. A number of bacterial-transformations have focused on the reductive dechlorination of chlorinated organic

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compounds, such as PCBs and chlorinated benzene [2,3]. To understand microbial-catalyzed remedial processes under anaerobic conditions, the reductive dechlorination of chlorinated organic compounds has been studied using biomimetic molecules, such as Vitamin B12 and metalloporphyrins, which facilitate some microbial reactions [5–7].

On the other hand, some aerobic microorganisms are able to biodegrade a limited number of chlorinated organic compounds, but frequently fail to metabolize the most heavily chlorinated compounds. However, free radical-based oxidation reactions provide an attractive alternative to conventional treatment strategies for the elimination of recalcitrant aromatic compounds [8]. In this respect, hydroxyl radicals ($HO^{\bullet}$) are among the most reactive oxidants found in aqueous environments and can readily degrade a variety of aromatic compounds [9–11]. It is well-known that $HO^{\bullet}$ can be produced by the reaction of Fe(II) with H_2O_2, i.e. the Fenton reaction. Nevertheless, only a few reports on biologically Fenton-like processes have appeared [12,13]. McKenzie et al. demonstrated the use of a microbially driven Fenton-like process using *Shewanella putrefaciens* strain 200, an anaerobe, and this process can be applied to PCP degradation [13]. In this system, the reduction of Fe(III)–(II) and the generation of H_2O_2 occur simultaneously. The advantages of this process are that the addition of H_2O_2 is not necessary and the process can be conducted at neutral pH. However, Fenton-like processes for the biomimetic systems, in which the reduction of Fe(III) and H_2O_2 generation occur simultaneously, have not been reported to date. In the present study, we report that the addition of ascorbic acid (ASC) to a mixture of Fe(II) and tetrakis(sulfonatophenyl) porphyrin (TPPS) (TPPS/ASC/Fe(II) system) results in an enhancement in PCP degradation at pH 6. Possible reaction mechanisms for the degradation of PCP in this system are discussed.

2. Experimental

2.1. Reagents

A TPPS ($C_{44}H_{30}N_4O_{12}S_4{\cdot}4H_2SO_4{\cdot}4H_2O$) was purchased from Dojindo Laboratory. A stock solution of TPPS (1 mM) was prepared by dissolving the reagent in phosphate buffer (0.02 M, pH 6). PCP was purchased from Nacalai Tesque Inc. (99% purity), and was used without further purification. A stock solution of Fe(II) (0.01 M) was prepared by dissolving $Fe(NH_4)_2{\cdot}(SO_4)_2{\cdot}6H_2O$ (99.9% purity, Nacalai Tesque Inc.) in water. Ascorbic acid (ASC) and cysteine (Cys) (99.0% purity) were purchased from Nacalai Tesque Inc. Phosphate buffer solutions (0.02 M, pH 6) were prepared by mixing aqueous solutions of NaH_2PO_4 and Na_2HPO_4. All stock solutions were freshly prepared before each experiment.

2.2. Monitoring of PCP degradation

A 25 μl aliquot of 0.01 M PCP in acetonitrile was placed in an L-shaped test tube (Taitec Co., Ltd.), and the acetonitrile was then removed at room temperature by evaporation. A 5 ml aliquot of buffer solution was then added, and the PCP was dissolved by mixing gently. After the addition of aqueous solutions of TPPS and ASC, the test tube was shaken in a T-22S type thermostatic shaking water bath (Thomas Kagaku Co., Ltd.) at 25 °C. After the reaction period, 2.5 ml of methanol was added and the solution was vigorously mixed. To analyze PCP, tetrachlorohydroquinone (TeCHQ) and tetrachlorocatechol (TeCC), a 20 μl aliquot of the solution was injected into a Jasco PU-980 type HPLC pumping system, which was connected to an SPD-6D UV–VIS detector (Shimadzu). The detection wavelength was set at 220 nm. The mobile phase was a mixture of an aqueous solution of 0.8% H_3PO_4 and methanol. The following methanol gradient was used: 50% for 3 min, 50–85% for 22 min and 85% for 10 min. The flow rate of eluent was set at 1.0 ml min^{-1}. A 5C18-MS Cosmosil Packed Column (4.6 ∅ × 250 mm; MetaChem Technologies) was used as the solid phase, and the column temperature was maintained at 50 °C. It was confirmed that the addition of methanol prevented any further degradation of PCP for periods of up to 2 days. HPLC analyses for a series of samples were carried out within 2 days. The concentration of Cl^- in the solutions was measured by means of a DX-120 type ion chromatograph (Dionex).

2.3. Determination of H_2O_2

The H_2O_2 concentrations in the test solutions were determined by a colorimetric method as described

in a previous paper [14]. Before the addition of the chromogen, TPPS and ASC in the test solutions, which interfere with the H_2O_2 measurements, were eliminated by passing the solution through an anion-exchange column packed with DEAE Sephadex A-25 (Pharmacia).

2.4. UV–VIS absorption spectra

The stability of TPPS during the reaction was monitored by UV–VIS absorption spectroscopy of TPPS. An aqueous solution, which contained TPPS (50 μM), Fe(II) (50 μM) and ASC (1 mM) at pH 6, was shaken in a thermostatic shaking water bath. Periodically (0, 8, 20 and 30 h), a 300 μl aliquot of the test solution was added to 2.7 ml of 0.02 M phosphate buffer (pH 6) in a quartz cell (1 cm × 1 cm). The spectrum was then measured by a Jasco V-550 type spectrophotometer (Japan Spectroscopic Co., Ltd.). Test solutions in the absence of Fe(II) were used as controls.

3. Results and discussion

3.1. Degradation kinetics of PCP

Fig. 1a shows the degradation kinetics of PCP in the presence of TPPS and Fe(II) (TPPS/Fe(II) system). It has been reported that, in the oxidative and reductive dechlorination by metalloporphyrins, the addition of reducing agents or axial ligands is effective [5–7,15]. Therefore, a variety of additives were examined to accelerate the PCP degradation at pH 6 and included: catechol, *p*-hydroquinone, sodium phosphite, gallic acid, protocatechuic acid, 2-propanol, EDTA, caffeic acid, cysteine (Cys) and ascorbic acid (ASC). Except for Cys and ASC, the percentages of PCP degradation in the presence of additives were smaller than that in their absence. Figs. 1b and c show the degradation kinetics of PCP in the presence of Cys and ASC. Pseudo-first-order rate constants (k_{obs}) were evaluated from the kinetic curves (figure caption of Fig. 1). Because the k_{obs} value in the presence of Cys was about the same as that in the absence of additives, the addition of Cys was deemed not to be effective in enhancing PCP degradation. However, the k_{obs} value in the presence of ASC was 4-times larger than that in the absence of additives, indicating a significant enhancement in the degradation of PCP in the TPPS/Fe(II) system.

3.2. Reaction products

Although PCP was degraded to a significant extent in the TPPS/ASC/Fe(II) system, the mechanism of this

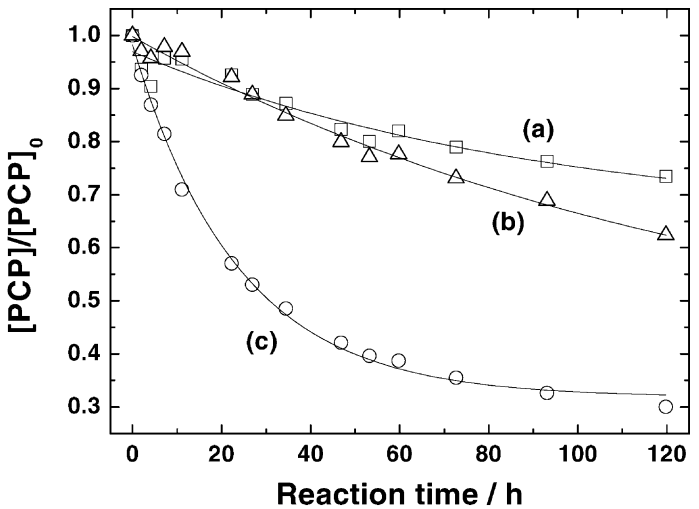

Fig. 1. Effects of ASC and Cys on the reaction kinetics of PCP degradation. None (a), Cys (b), ASC (c). [ASC] and [Cys]: 1.0 mM, pH 6.0 (0.02 M phosphate buffer), $[PCP]_0$, [TPPS] and [Fe(II)]: 50 μM. The pseudo-first-order rate constants were calculated by curve-fitting (solid lines): none; $(3.1 \pm 1.6) \times 10^6\ s^{-1}$, Cys; $(2.1 \pm 0.6) \times 10^6\ s^{-1}$, ASC; $(1.2 \pm 0.1) \times 10^5\ s^{-1}$.

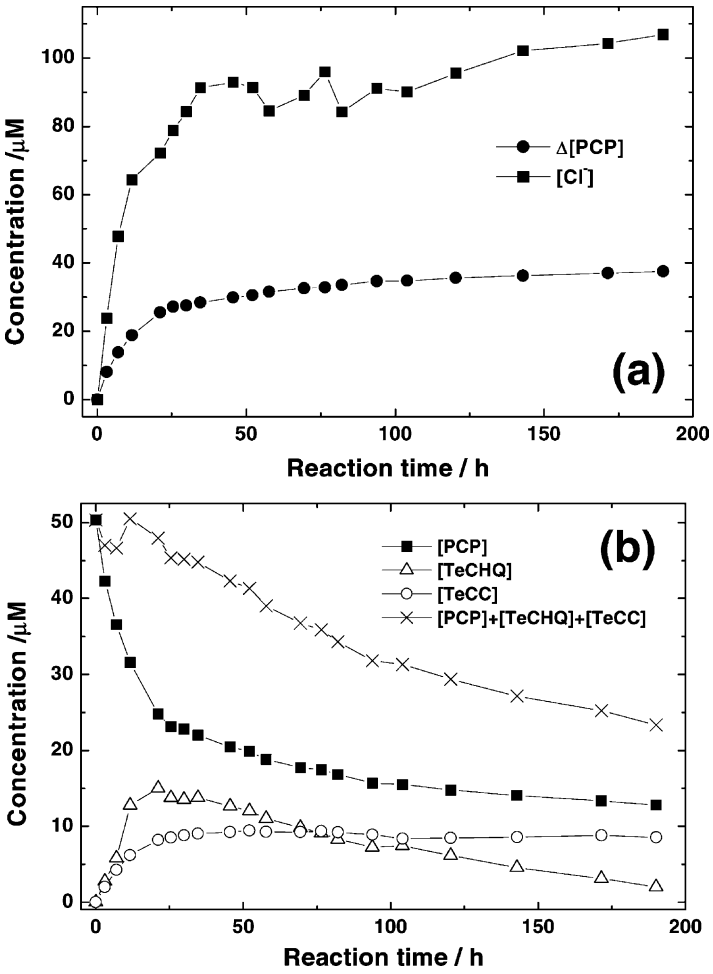

Fig. 2. Reaction kinetics of the release of Cl^- (a), and of the production of TeCHQ and TeCC (b). $[PCP]_0$, [TPPS] and [Fe(II)]: 50 μM, pH 6.0 (0.02 M phosphate buffer), [ASC]: 1.0 mM.

reaction is unclear. To better understand this, we determined the nature of the reaction products. Fig. 2a shows the release of Cl^- during PCP degradation, in which Δ[PCP] represents the concentration of PCP degraded, as calculated by subtraction of the [PCP] at an arbitrary reaction period from the [PCP] initially added. The concentrations of Cl^- were 2–3 times larger than the concentrations of PCP degraded. This indicates that 2–3 chlorine atoms are released from PCP during its degradation in the TPPS/ASC/Fe(II) system.

Fig. 2b shows the production of TeCHQ and TeCC during PCP degradation. In the oxidative transformation of phenols with $HO^•$ attack, further hydroxylated compounds, such as catechol, hydroquinone and/or resorcinol, may be produced. In particular, in the case of an $HO^•$ related oxidation, *iso*-attacks of $HO^•$ to phenolic rings can yield *o*- and *p*-substituted hydroxylation products [16,17]. Therefore, the formation of TeCHQ and TeCC suggests that the PCP degradation observed in the present system is due to an oxidative process accompanied by $HO^•$ attack, i.e. a Fenton-like process.

As shown in Fig. 2b, the sum of the reaction products in the reaction mixture ([PCP] + [TeCHQ] + [TeCC]) was smaller than the initial concentra-

tion of PCP, and the concentrations of unknown species increased with reaction time. In photo-Fenton process [18], dimerization compounds, such as 2-hydroxy-nonachlorodiphenyl ether (2H-NCDE) and octachlorodibenzo-*p*-dioxin (OCDD), can be formed as a result of PCP degradation. To identify these compounds, the reaction mixture from a TPPS/ASC/Fe(II) system (reaction time: 48 h) was extracted with hexane and this extract was then analyzed by GC/MS, as described previously [18]. Although PCP, TeCHQ and TeCC were identified, the formation of 2H-NCDE and OCDD were not observed (data not shown). Therefore, the unknown species were not dimerization compounds derived from PCP. If TeCC and TeCHQ represent all of the reaction products in the present system, the Δ[PCP] values in Fig. 2a are equal to the [Cl^-] released. It is known that, in the degradation of chlorinated phenols via the Fenton processes, chlorohydroquinones and chlorocatechols were further oxidized to organic acids, such as chlorinated maleic and muconic acids, and then to CO_2 [19]. Therefore, the larger amount of Cl^- release shown in Fig. 2a may be attributed to the formation of further oxidized products, such as maleic and muconic acids.

3.3. Effects of the ASC, Fe(II) and TPPS concentrations on the PCP degradation

To confirm the enhancement of PCP degradation more precisely, the percentages of PCP degradation and the concentrations of byproducts were investigated in a variety of ASC, Fe(II) and TPPS concentrations. Fig. 3 shows the effect of ASC concentration on PCP degradation in the TPPS/Fe(II) system. In the absence of ASC, approximately 25% of the PCP was degraded. However, the percentage of PCP degradation increased with the concentration of ASC up to 1 mM and then reached a plateau. Fig. 4a shows the effect of Fe(II) concentration on the percentage of PCP degradation. In the absence of Fe(II), PCP was not degraded even in the presence of ASC. Moreover, the percentage of PCP degradation increased with increasing Fe(II) concentration up to 10 μM in the presence of TPPS only and up to 25 μM in the presence of both TPPS and ASC. Fig. 5a shows the effect of TPPS concentration on the percentage of PCP degradation. In the absence of TPPS and ASC (symbol ○ in Fig. 5a), no degradation of PCP was detected, but approximately 25% of the PCP was degraded in the presence of ASC and Fe(II) (ASC/Fe(II) system) (symbol ● in Fig. 5a). The

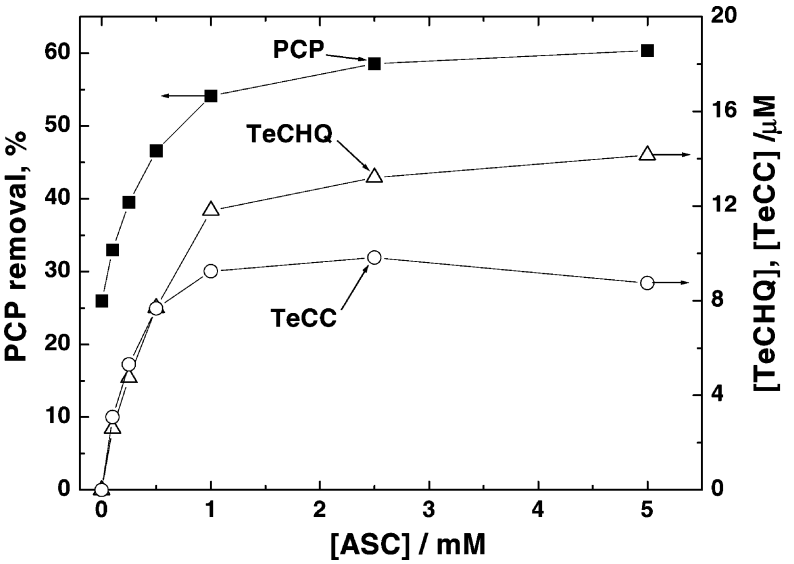

Fig. 3. Effects of the ASC concentration on PCP degradation and byproducts formations. $[PCP]_0$, [TPPS] and [Fe(II)]: 50 μM, pH 6.0 (0.02 M phosphate buffer), reaction time: 48 h.

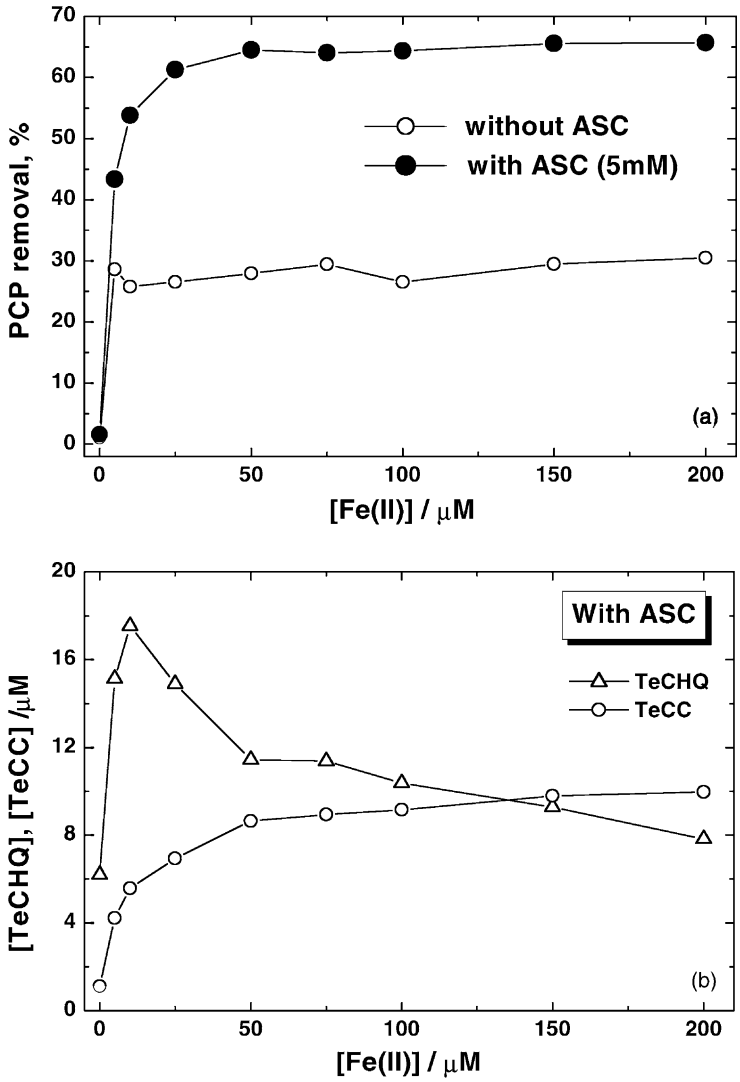

Fig. 4. Effect of the Fe(II) concentration on PCP degradation (a) and byproducts formations (b). $[PCP]_0$, and [TPPS]: 50 μM, pH 6.0 (0.02 M phosphate buffer), [ASC]: 5 mM, reaction time: 48 h.

percentage of PCP degradation increased with increasing TPPS concentration. However, in the presence of ASC, the percentage of PCP degradation reached a plateau for concentrations above [TPPS] = 25 μM.

Fig. 3 also shows the effect of ASC concentration on the formation of TeCHQ and TeCC, which represent the main byproducts. The trends of TeCHQ and TeCC formation were similar to that of the percentage of PCP degraded. Although the concentrations of TeCHQ and TeCC were nearly equal up to [ASC] = 0.5 mM, the concentration of TeCHQ was higher than that of TeCC above [ASC] = 1 mM. It has been reported that, when $HO^{\bullet}$ adds to PCP, the ratio of TeCHQ to TeCC is approximately 15/8 [17]. Above [ASC] = 1 mM, the average ratio of [TeCHQ]/[TeCC] was calculated to be 14/9. This supports the hypothesis that $HO^{\bullet}$ is associated with oxidative transformations of PCP. Fig. 4b shows the effect of Fe(II) concentration on the formation of byproducts. TeCC increased up to 50 μM and then increased gradually. TeCHQ increased up to

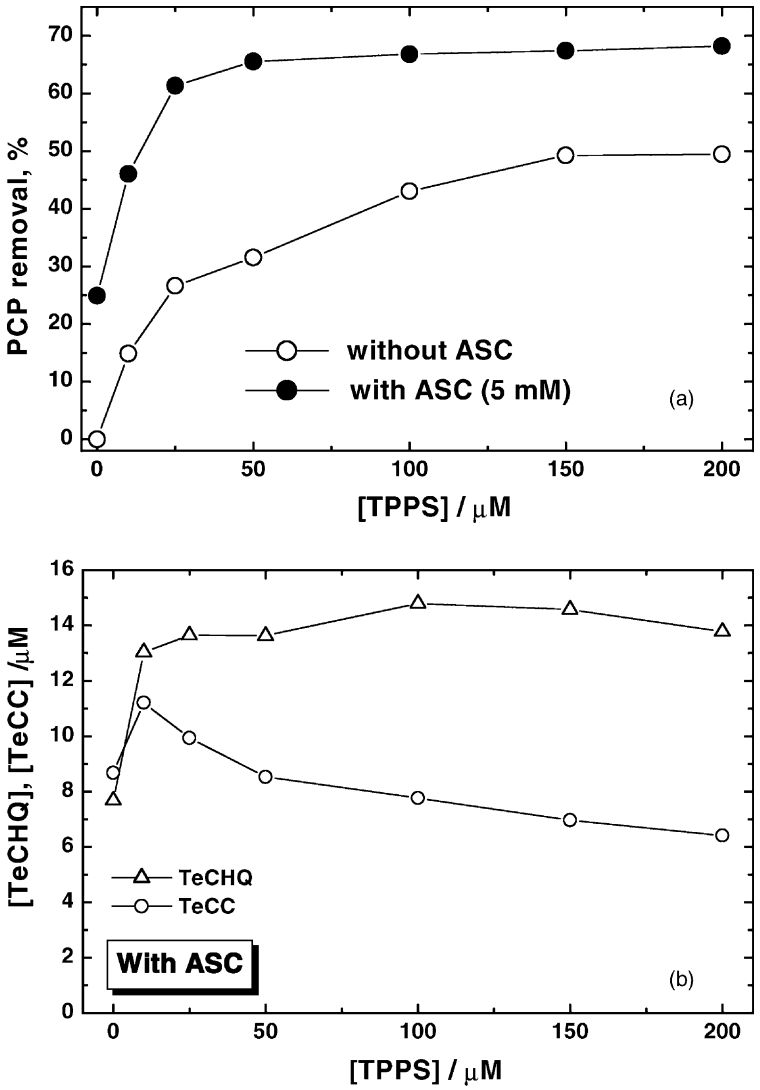

Fig. 5. Effect of the TPPS concentration on PCP degradation (a) and byproducts formations (b). $[PCP]_0$, and [Fe(II)]: 50 μM, pH 6.0 (0.02 M phosphate buffer), [ASC]: 5 mM, reaction time: 48 h.

[Fe(II)] = 10 μM and then decreased gradually. At [Fe(II)] = 200 μM, the concentration of TeCC was larger than that of TeCHQ. In the absence of Fe(II), no byproducts were observed. Fig. 5b shows the effect of TPPS concentration on the formation of byproducts. In the absence of TPPS, a small amount of TeCHQ and TeCC was observed. This supports the hypothesis that oxidative transformation can occur even in the ASC/Fe(II) system. Above [TPPS] = 10 μM, TeCC levels gradually decreased, and the concentrations of TeCHQ were higher than those of TeCC, in which the ratio of [TeCHQ]/[TeCC] was approximately 15/8. Such a trend also suggests the participation of $HO^{\bullet}$ in the reaction.

In the TPPS/Fe(II) and ASC/Fe(II) systems, very small HPLC peaks corresponding to TeCHQ and TeCC were detected, but these are below the quantitative determination limit of the HPLC system used

here. To confirm the presence of TeCHQ and TeCC in these systems, reaction mixtures were extracted with hexane and these extracts were then examined by GC/MS. TeCHQ and TeCC were also detected in these systems. Therefore, the main byproducts in the TPPS/Fe(II) and ASC/Fe(II) systems are TeCHQ and TeCC, similar to the TPPS/ASC/Fe(II) system.

In the presence of only Fe(II) or TPPS, PCP cannot be degraded and converted to TeCHQ and TeCC. In addition, even in the absence of TPPS, PCP degradation was observed in the presence of both ASC and Fe(II). However, in the presence of only ASC or of ASC and TPPS, the degradation of PCP and the production of TeCHQ and TeCC was clearly observed. Therefore, the TPPS/Fe(II), ASC/Fe(II) and TPPS/ASC/Fe(II) systems both supported PCP degradation. Moreover, for a variety of Fe(II) and TPPS concentrations, the presence of ASC resulted in an increase in the percentage of PCP degraded. We conclude that the addition of ASC to the TPPS/Fe(II) system is effective in enhancing PCP degradation.

3.4. Inhibition of PCP degradation by the addition of 2-propanol

If the degradation of PCP in the TPPS/ASC/Fe(II) system is the result of a Fenton-like process, the addition of an $HO^{\bullet}$ scavenger, such as 2-propanol (2-PrOH), would be expected to inhibit the degradation of PCP [18]. Fig. 6 shows the effect of 2-PrOH concentration on the percentage of PCP degradation in the TPPS/ASC/Fe(II) system. As expected, the percentages of PCP degradation decreased with increasing 2-PrOH concentrations. Moreover, phenolic acids are also attacked by $HO^{\bullet}$ [20], and this may compete with the amount of $HO^{\bullet}$ available for attacking PCP. Thus, it can be expected that the addition of phenolic acids may result in a reduction in the percentage of PCP degradation. Although the percentage of PCP degradation was 72% in the absence of phenolic acids, the addition of 125 μM of gallic, protocatechuic and caffeic acids resulted in a decrease in the percentage of PCP degraded up to 43, 36 and 38%, respectively. These results support the conclusion that $HO^{\bullet}$ is involved in the degradation of PCP.

3.5. H_2O_2 generation

In the present system, H_2O_2, a source of $HO^{\bullet}$, was not added to the test solutions. Hence, H_2O_2 may be generated and then catalytically degraded to $HO^{\bullet}$ by Fe(II). To verify that the generation of H_2O_2 occurred in the absence of Fe(II), aqueous solutions of TPPS, ASC and TPPS + ASC were shaken under aerobic

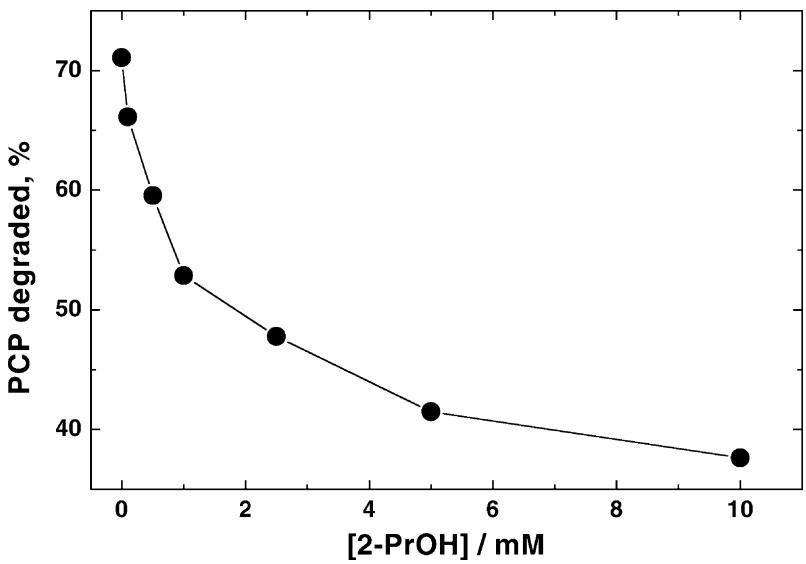

Fig. 6. Effect of 2-propanol concentration on PCP degradation. $[PCP]_0$, [TPPS] and [Fe(II)]: 50 μM, pH 6.0 (0.02 M phosphate buffer), [ASC]: 5 mM, reaction time: 48 h.

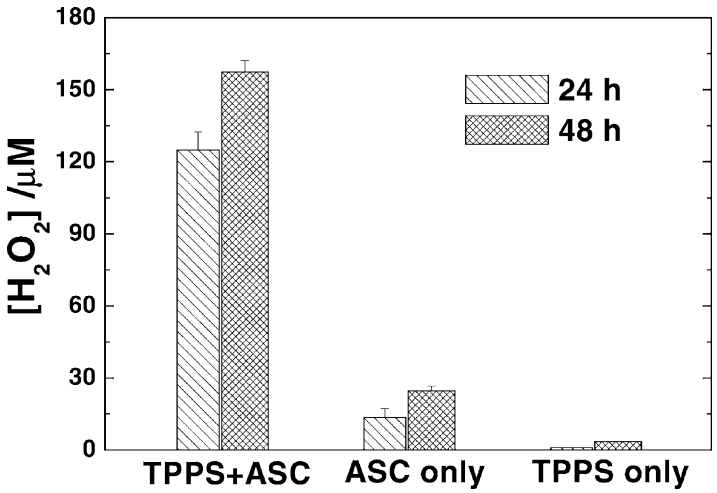

Fig. 7. H_2O_2 generation in the presence of TPPS, ASC and TPPS + ASC. [TPPS]: 50 μM, [ASC]: 1 mM, pH 6.0 (0.02 M phosphate buffer).

conditions, and the H_2O_2 concentrations determined. These results are shown in Fig. 7. In the presence of TPPS only, several μM-levels of H_2O_2 were generated during 48 h of reaction. In the presence of ASC only, several-10 μM-levels of H_2O_2 were generated. H_2O_2 generation in the presence of ASC only may be due to the auto-oxidation of ASC [21]. However, in the case of TPPS + ASC, the generation of H_2O_2 was much larger than that in the presence of TPPS or ASC only. The generation of H_2O_2 in these systems also supports the hypothesis that the degradation of PCP in the present systems is the result of Fenton-like processes. Moreover, the increased H_2O_2 generation in the case of TPPS + ASC is consistent with the enhancement of PCP degradation as a result of the addition of ASC to the TPPS/Fe(II) system.

3.6. PCP degradation under aerobic and anaerobic conditions

If the generation of H_2O_2 is a key process in the present system, it would be expected that PCP degradation would be decelerated under anaerobic conditions. Hence, the percentages of PCP degradation under aerobic conditions were compared with those under anaerobic conditions (Fig. 8). In a nitrogen atmosphere (anaerobic conditions), only 10% of the starting PCP was degraded. However, in the presence of oxygen and air (aerobic conditions), 60–70% of PCP was found to be degraded. These results are consistent with the hypothesis that H_2O_2, generated from dissolved oxygen, plays a key role in the TPPS/ASC/Fe(II) system.

3.7. Stability of TPPS during the reaction

To observe the stability of TPPS during the reaction, changes in the absorbance of the soret band peak of TPPS ($\lambda_{max} = 414$ nm) were investigated (Fig. 9). In the absence of ASC, the absorbance peak slightly decreased in the presence of added Fe(II). In the presence of ASC, the absorbance clearly decreased with increasing reaction time. When Fe(II) was not added (TPPS only and TPPS+ASC in Fig. 9), the absorbance and the shape of the peak remained unchanged. These results indicate that TPPS may be degraded during the reaction, and degree of this degradation in the presence of ASC is higher than that in the absence of ASC. This supports the view that the reactivity of the TPPS/Fe(II) system can be enhanced by the presence of ASC.

3.8. Possible reaction mechanisms

Why larger amounts of H_2O_2 are generated in the case of TPPS + ASC is an issue. H_2O_2 generation by the reduction of dissolved oxygen to superoxide radicals can be expressed as follows [22]:

$$O_2 + e \rightarrow O_2^{\bullet -} \quad (1)$$

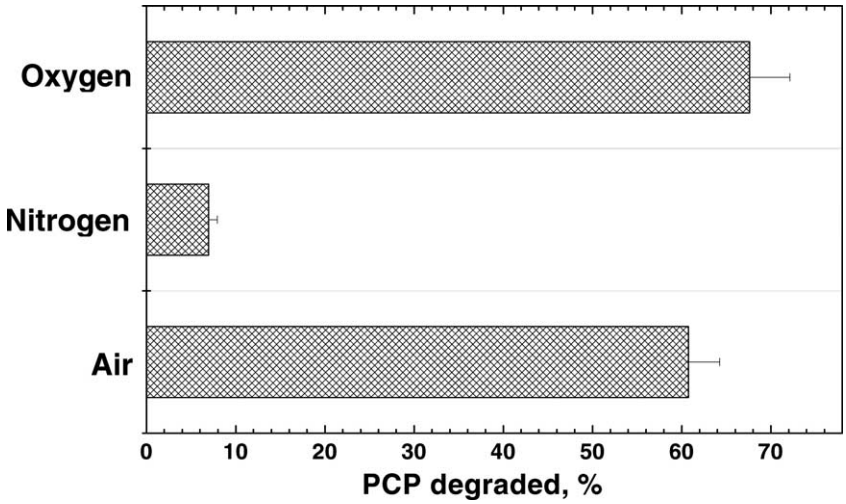

Fig. 8. PCP degradation under aerobic and anaerobic conditions. $[PCP]_0$, [TPPS] and [Fe(II)]: 50 μM, pH 6.0 (0.02 M phosphate buffer), [ASC]: 1 mM, reaction time: 48 h.

$$HO_2^{\bullet} \rightleftharpoons H^+ + O_2^{\bullet -} \quad (2)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (3)$$

Since the acid-dissociation constants of ASC (pK_{a1} and pK_{a2}) are reported to be 4.04 and 11.34 [21], monohydrogen ascorbate anions ($ASCH^-$) would be the dominant species at pH 6. Therefore, a redox couple of ascorbyl radicals ($ASC^{\bullet}$)/$ASCH^-$ is possible in the present system. The standard redox potential of the $O_2/O_2^{\bullet -}$ couple is reported to be around −0.3 V [22]. Although the $ASC^{\bullet}/ASCH^-$ couple (+0.282 V) would be expected to be a poorer reductant than the $O_2/O_2^{\bullet -}$ couple, the auto-oxidation of ASC can lead to the generation of H_2O_2 because of the lower shift of redox potentials at the physical concentrations employed [21]. That is, if the $[ASCH^-]/[ASC^{\bullet}]$ ratio would increase, the smaller apparent redox potential could be estimated by the Nernst equation. This can be supported by the results in Fig. 3 that the amounts of PCP degradation and the formation of byproduct increase with increasing ASC concentration.

On the other hand, as shown in Fig. 7, H_2O_2 was generated in the presence of TPPS only. The antioxidative abilities of pheophytin for organic molecules, such as lipids, [23] suggest that the uncomplexed species of porphyrin has the ability to reduce dissolved oxygen. In addition, studies on the reduction of quinone and cytochrome c by uncomplexed species of porphyrin showed the production of oxidized species of porphyrin, such as porphyrin cation radicals [24,25]. These results and reports suggest that TPPS has the ability to serve as electron donor, and the reduction of O_2 to $O_2^{\bullet -}$ by TPPS may give rise to TPPS cation radicals ($TPPS^{\bullet +}$). Although the redox potential of $TPPS^{\bullet +}$/TPPS is not known, both TPPS and ASC are able to reduce dissolved oxygen to $O_2^{\bullet -}$. Thus, the $[TPPS]/[TPPS^{\bullet +}]$ ratio under the experimental conditions used here may be high, and the redox potential of this couple should be lower than that of $O_2^{\bullet -}/O_2$ (−0.33 V). This can be supported by the trend shown in Fig. 5, in which the oxidation of PCP proceeds with increasing concentrations of TPPS. If $TPPS^{\bullet +}$ would be reduced by the $ASC^{\bullet}/ASCH^-$ couple, larger amounts of ASC should be required to increase the $[ASCH^-]/[ASC^{\bullet}]$ ratio. In Figs. 3–5, PCP oxidation proceeded in much higher concentrations of ASC as compared to TPPS. Therefore, dissolved O_2 can be reduced to $O_2^{\bullet -}$ by TPPS as:

$$TPPS + O_2 \rightarrow TPPS^{\bullet +} + O_2^{\bullet -}, \quad (4)$$

and the resulting $TPPS^{\bullet +}$ can be recycled to TPPS by ASC as:

$$TPPS^{\bullet +} + ASCH^- \rightarrow TPPS + ASC^{\bullet} \quad (5)$$

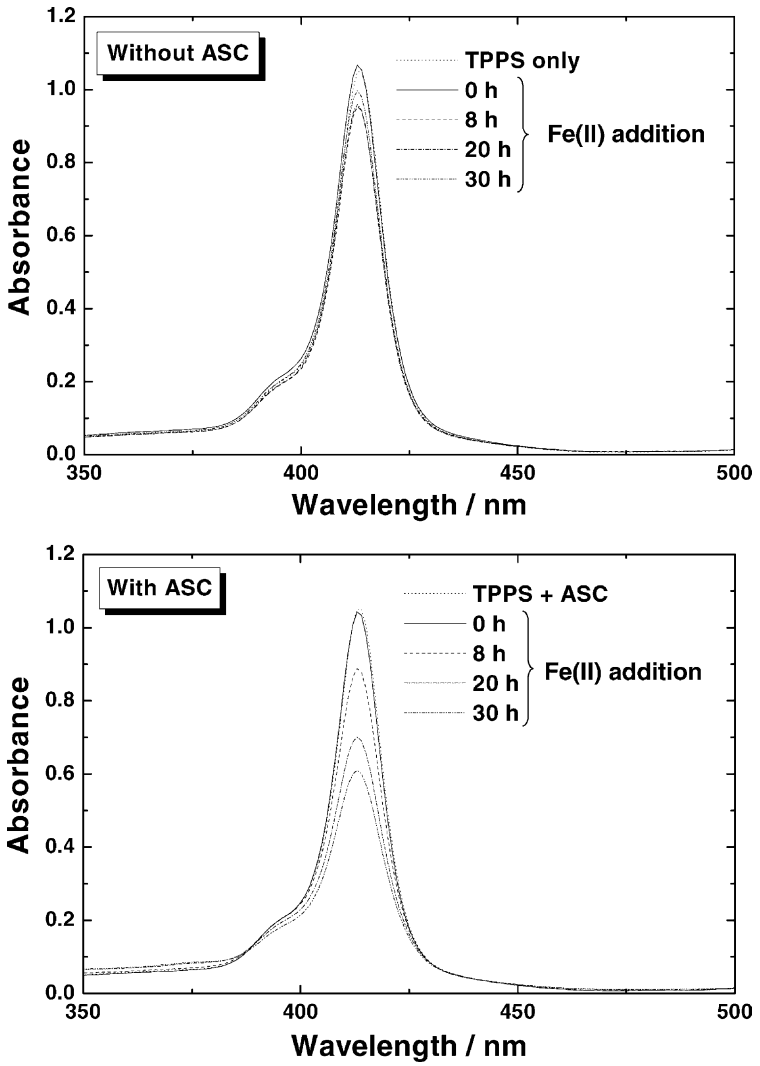

Fig. 9. Variations in the UV–VIS absorption spectra of TPPS during the reaction. [TPPS]: 5 μM, [Fe(II)]: 5 μM, [ASC]: 0.1 mM, pH 6 (0.02 M phosphate buffer).

The occurrence of these reactions can be supported by the fact that H_2O_2 generation is dramatically enhanced in the presence of both TPPS and ASC, as shown in Fig. 7.

As shown in Fig. 5, the oxidation of PCP could not be observed in the absence of Fe(II). This indicates that Fe(II) is required for the oxidation of PCP. In the TPPS/ASC/Fe(II) and TPPS/Fe(II) systems, H_2O_2 is generated by the reduction of O_2 to $O_2^{\bullet -}$ with the $TPPS^{\bullet +}$/TPPS couple, and H_2O_2 is then degraded to $HO^{\bullet}$ by Fe(II) via the Haber–Weiss process as:

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + HO^{\bullet} + OH^{-} \quad (6)$$

The *iso*-attack of $HO^{\bullet}$ to PCP can yield *o*- and *p*-substituted hydroxylated products, such as TeCHQ and TeCC. The formation of such byproducts is shown in Figs. 2–5. Several reports on ASC-derived Fenton processes emphasize that the main role of ASC is to serve as a reducing agent of Fe(III) [21,26–29]. Therefore, Fe(III), which is oxidized in reaction 6, can

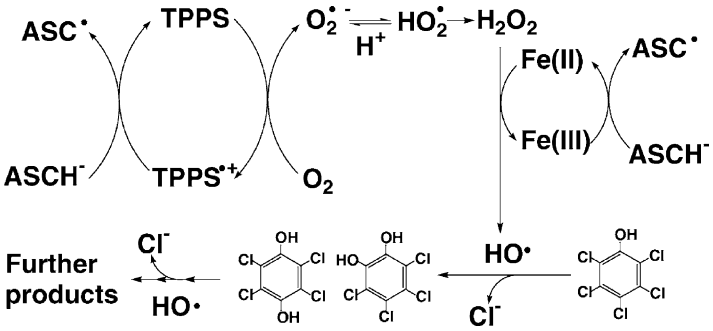

Fig. 10. Possible reaction mechanisms involved in the TPPS/ASC/Fe(II) system.

be reduced to Fe(II) by ASC, and ASC in the present system plays important roles in the assistance of the redox cycle of iron. Possible reaction mechanisms in the TPPS/ASC/Fe(II) system are illustrated in Fig. 10.

A calculation using the solubility products of $Fe(OH)_2$ ($K_{sp} = 2 \times 10^{-14}$) and $Fe(OH)_3$ ($K_{sp} = 1 \times 10^{-36}$) showed that Fe(II) was not precipitated at pH 6.0 and at [Fe(II)] = 50 μM but that Fe(III) was precipitated in the form of the hydroxide under these conditions. Hence, at pH 6, iron species would be stabilized by complexation with TPPS and/or ASC. It has been reported that complex formation between TPPS and Fe(II) occurs at higher temperatures (around 100 °C) [30]. The complexation between TPPS and Fe(II) was investigated at 25 °C for 48 h by means of absorption spectra. If a complex is formed, the Soret band of TPPS (413 nm) is shifted to 395 nm [30]. However, the absorbance at 395 nm decreased slightly with reaction time. This shows that complexation between Fe(II) and TPPS does not occur in the present system. However, it has been reported that ASC does, in fact, have the ability to complex with iron [31]. Therefore, in the present system, ASC plays an important role in stabilizing the iron species as well as providing assistance in the iron redox cycle.

4. Conclusions

The addition of ASC to a TPPS/Fe(II) system resulted in an enhancement in PCP degradation and the formation of byproducts via a Fenton-like process. Many ASC-derived Fenton processes, which have been reported, involved the addition of H_2O_2 [21,26–29]. Because large amounts of H_2O_2 can be generated from dissolved oxygen by the redox couple of $TPPS^{\bullet +}$/TPPS, the addition of H_2O_2 is not necessary in the present system. Therefore, the TPPS/ASC/Fe(II) system represents a new type of Fenton-like process, that may have applications in environmental clean-up processes.

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