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Decolorization of orange II by catalytic oxidation using iron (III) phthalocyanine-tetrasulfonic acid

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Abstract

Orange II, C.I. Acid Orange 7 (AO7), is oxidatively decolorized via catalytic oxidation by iron(III) phthalocyanine-tetrasulfonic acid (Fe(III)-PcTS) as a biomimetic catalyst and $KHSO_5$ as an oxygen donor. The nature of the decolorization of AO7 was investigated in the catalyst concentration range of 10–50 μM, in which the initial concentration of AO7 was 417 mg l^{-1}. A 99.6% decolorization was observed at [$KHSO_5$] = 2.5 mM and [Fe(III)-PcTS] = 20 μM after a 3-h reaction period. However, the fact that only 4.9% of the TOC was removed indicated that the conversion to CO_2 was incomplete. The results of a total organic nitrogen analysis of the reaction mixture showed that the nitrogen in the azo chain was mainly converted to N_2 gas. In addition, 38.6% of the AO7 was converted to 1,2-dihydroxynaphthalene, and 21.4% to *p*-phenolsulfonic acid. These results indicate that the degradation via this catalytic system involves the conversion of AO7 to phenolic compounds, followed by N_2 production. In addition, a Microtox test showed that toxicity of the solution increased as a result of AO7 oxidation using this catalytic system.

Keywords: Azo dyestuff; Orange II; Oxidation; Decolorization; Iron(III) phthalocyanine-tetrasulfonic acid; Toxicity

1. Introduction

Colored contaminants in aquatic environments are common problems associated with the dye industry and are an issue of environmental concern. When color is fixed to a fabric or yarn, some remains in the dye bath solution, which is then released in the form of an effluent. Azo and anthraquinone dyes are both heavily used in the textile industry. In particular, azo dyes, characterized by nitrogen-to-nitrogen double bonds (–N=N–), account for up to 70% of all textile dyestuffs that are produced, and are the most common chromophore in reactive dyes [1].

Decolorization can be observed when the color disappears from the solution but this is not an indication that organic compounds have been completely degraded. In addition, a problem arises when the break down components of a dye molecule are converted to compounds that are more toxic than the parent molecule. Thus, information relative to chemical compounds produced during the decolorization process by a variety of treatments is an important issue. A number of studies on the removal of dyestuffs by photocatalytic or enzymatic oxidation have been reported [2–13] and have shown that color can be removed sufficiently. Studies have also been reported on byproducts or reaction intermediates in photocatalytic or non-photocatalytic oxidation reactions [7,9–13]. However, evaluations of the byproducts produced and their toxicities as a result of a variety of dyestuff treatments are currently incomplete. Most of studies of the oxidation of nitrogenous organic compounds have mainly focused on TOC removal. Thus, it is essential to identify byproducts that are formed during the oxidation reactions, and to evaluate their toxicity.

Catalytic systems using iron(III) phthalocyanine-tetrasulfonic acid (Fe(III)-PcTS) are particularly attractive as a biomimetic catalyst which is comparable to peroxidase,

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and it can be used in environmental applications [14]. Moreover, it is feasible to degrade pentachlorophenol by catalytic oxidation using Fe(III)-PcTS and $KHSO_5$ [15]. In the present study, the oxidative degradation of azo-dyestuffs by Fe(III)-PcTS was investigated. Orange II, C.I. Acid Orange 7 (AO7), was chosen as a model azo dye. To determine the nature of the byproducts produced, reaction solutions were analyzed by GC/MS and ion chromatography. In addition, the toxicities of the solution before and after the reaction were evaluated by means of a Microtox test.

2. Materials and methods

2.1. Reagents and materials

AO7 was purchased from Wako Pure Chemical Industries and was used without further purification. Fe(III)-PcTS was purchased from Aldrich (99.0% purity). Dihydroxynaphthalene (DHN) isomers and *p*-phenolsulfonic acid (*p*-PSA) were purchased from Tokyo Chemical Industry.

2.2. Decolorization tests

A 2.5 ml aliquot of an aqueous solution of AO7 (1000 mg l^{-1}) was placed in an L-shaped test tube and a 0.5 ml aliquot of aqueous Fe(III)-PcTS (200 μM) was then added to the solution. A 2.75 ml of aliquot of 0.02 M NaH_2PO_4/Na_2HPO_4 buffer at pH 6 was then added to the mixture. A 0.25 ml aliquot of aqueous 0.01 M $KHSO_5$ was added and the tube was allowed to shake on a thermostatic water bath at 25 ± 0.1 °C. To monitor the rates of decolorization, the absorbance at 487 nm was measured using a Jasco V-550 type UV-Vis spectrophotometer. Total organic carbon (TOC) in the test solutions was determined by means of a Shimadzu-TOC-500 analyzer. All oxidation runs were conducted in triplicate. Control experiments involved the use of only the buffer solution, Fe(III)-PcTS and $KHSO_5$ reaction mixture, AO7 only, AO7 and Fe(III)-PcTS without $KHSO_5$, and $KHSO_5$ only in buffer solution.

2.3. Byproduct analysis

2.3.1. Phenolic compounds and organic acids

After 180 min of reaction, 5 ml of the test solution was transferred to a 50 ml beaker and the solution acidified with H_2SO_4 to pH 2. A 1.0 ml aliquot of 1 M ascorbic acid was added followed by stirring for 60 min on a magnetic stirrer. A 0.6 ml aliquot of anthracene (1 mM) in hexane was added as an internal standard. The solution was then extracted three times with 15 ml portions of ethyl acetate. Na_2SO_4 (15 g) was added to the ethyl acetate phase and the solution allowed to stand for 6–12 h. The solution was filtered through 5C paper (ADVANTEC) and the filtrate dried on a rotary evaporator. The residue was dissolved in 500 μl of methanol, followed by the addition of acetic anhydrate/pyridine (1 ml, v/v = 2/3). After standing for 60 min, a 1 ml aliquot of the mixture was injected into the GC/MS system. The recovery of 1,2-DHN by this extraction procedure was 98 ± 4% (n = 3). Organic acids in the reaction mixture, such as *p*-PSA, formic and oxalic acids, were measured by means of a DX-500 type ion chromatograph (Dionex).

2.3.2. Nitrogen species

To investigate what the azo linkage (–N=N–) would be converted to after decolorization, nitrogen species in the reaction mixture, such as NO_2^-, NO_3^-, NH_4^+ and total organic nitrogen, were measured. NO_2^-, NO_3^- and NH_4^+ were analyzed by means of ion chromatography, whereas analyses of total organic nitrogen were done by the Sumica Chemical Analysis Service (Kisaradu, Japan).

2.4. Microtox test

To evaluate the toxicity of the solutions before and after the reaction, the Microtox test was carried out using a Microtox kit equipped with a model-500 type bioluminescence spectrophotometer (AZUR Environmental). The procedures used in the test have been described in a previous paper [16]. In this test, reaction mixtures were diluted with 0.02 M NaH_2PO_4/Na_2HPO_4 buffer (pH 6) up to 0.17–9.27 mg l^{-1} of TOC, and the diluted solution was then used in the tests. In this experiment, the concentration of toxic compounds in the solution was normalized to TOC, because AO7 could be converted to a variety of compounds via oxidation. According to previous reports [16,17], the EC_{50} value was employed to compare the toxicities of the solutions before and after the reaction. All Microtox tests were conducted in triplicate.

3. Results and discussion

3.1. Reaction kinetics

Fig. 1 shows the kinetics of decolorization of AO7. In this experiment, the solution might be shielded from UV

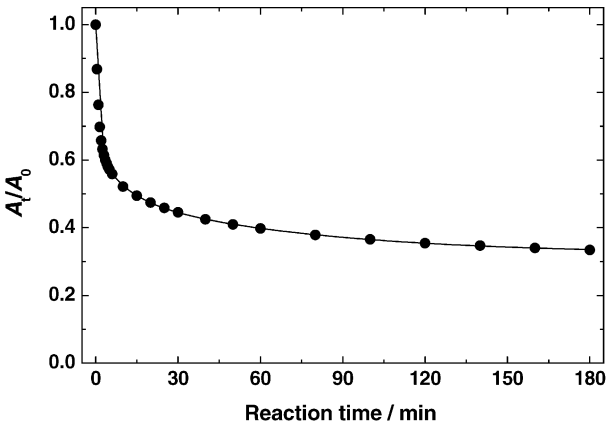

Fig. 1. Kinetics of AO7 decolorization. [AO7]: 30 mg l^{-1}, [Fe(III)-PcTS]: 2 μM, [$KHSO_5$]: 50 μM, pH 6.

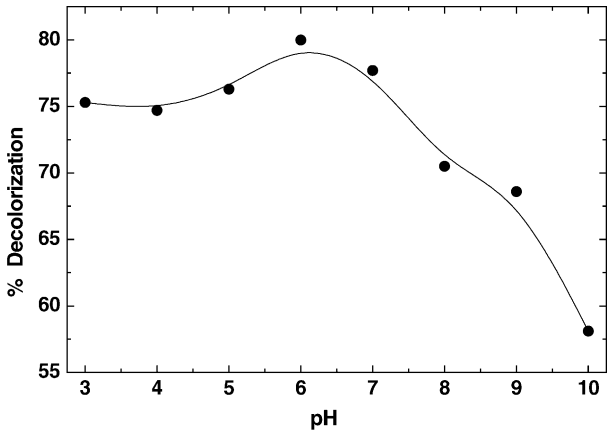

Fig. 2. Effect of pH on the decolorization of AO7. [AO7]: 417 mg l^{-1}, [Fe(III)-PcTS]: 20 μM, [$KHSO_5$]: 500 μM, reaction time: 180 min.

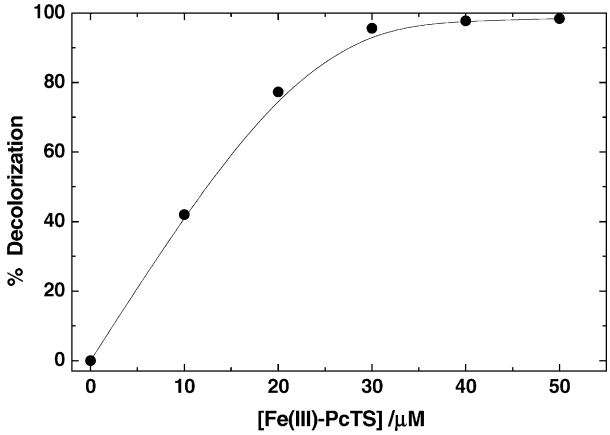

Fig. 3. Effect of Fe(III)-PcTS concentration on the decolorization of AO7. [AO7]: 417 mg l^{-1}, [$KHSO_5$]: 500 μM, reaction time: 180 min.

light between each measurement period. However, we first checked whether AO7 underwent decomposition by light at 487 nm. When a solution containing AO7 only was irradiated by light at 487 nm, no significant decrease in absorbance was observed after 180 min of irradiation. As shown in Fig. 1, the absorbance decreased rapidly up to 50% of the initial reading within 15 min and then gradually decreased by 65% after 180 min of reaction time. Henceforth, all experiments involved 180-min reaction period at 25 °C.

3.2. Effect of initial pH

Fig. 2 shows the effect of initial pH on the extent of decolorization of AO7 by Fe(III)-PcTS and $KHSO_5$. In the pH range of acid–neutral, a higher decolorization rate occurred, compared to the use of a basic solution. In a comparable oxidation in which AO7 was decolorized by an oxidative enzyme (manganese peroxidase), a pH range between 4.5 and 7 was compatible with a high decolorizing efficiency [13]. From a dyestuff point of view, AO7 is one of the acid dyes and a dyeing process using AO7 usually involves the use of acidic conditions. Therefore, the preferable pH in acid–neutral has the advantage that no pH adjustment would be needed for the dye effluent.

3.3. Effects of [Fe(III)-PcTS] and [$KHSO_5$]

Fig. 3 shows the percentages of decolorization of AO7 as a function of [Fe(III)-PcTS]. The percentage of decolorization increased with increasing concentration of catalyst. However, TOC removal was incomplete. This indicates that, at the concentrations of Fe(III)-PcTS used, the catalyst degrades only the azo linkage (–N=N–) but does not convert the reaction products completely to CO_2.

Fig. 4 shows the percentages of decolorization of AO7 as a function of [$KHSO_5$]. The rate of decolorization of AO7 increased with increasing [$KHSO_5$]. At a [$KHSO_5$] = 2.5 mM and [Fe(III)-PcTS] = 20 μM, the decolorization reached up to 99.6% at 180 min. However, TOC removal was only 4.9% at [$KHSO_5$] = 2.5 mM. This suggests that at higher concentration of $KHSO_5$, the azo linkage (–N=N–) is degraded, followed by the break down of small amounts of the aromatic portion of AO7. Oxalic (3.3 mg l^{-1}) and formic acids (6.25 mg l^{-1}) were detected when higher concentration of $KHSO_5$ (2.5 mM) was used. These results indicate that the catalytic system does not lead to complete mineralization to CO_2.

3.4. Byproduct patterns

As described previously, the initial pH has no obvious effect on the decolorization of AO7 when the Fe(III)-PcTS catalytic system is used. However, in the present experiment, the pH of the solutions decreased from pH 6.0 to 3.4–2.8 after the reaction. In an alternate experiment, the addition of aqueous $KHSO_5$ (500 μM) to the reaction without any catalyst present had no effect on the buffer function. Thus, the decrease in pH is not due to the addition of $KHSO_5$. Although oxalic and formic acids were produced in small amounts, other types of strong acids might also be pro-

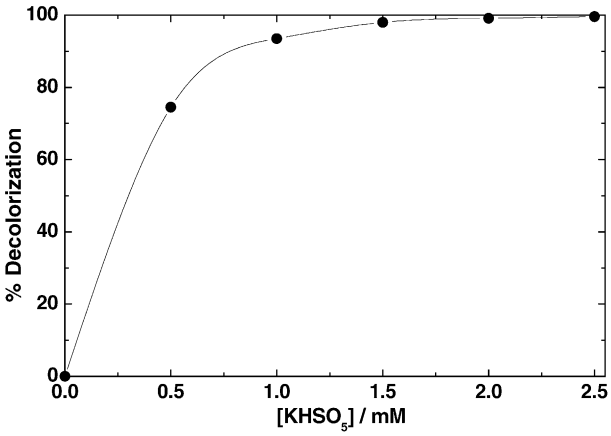

Fig. 4. Effect of $KHSO_5$ concentration on the decolorization of AO7. [AO7]: 417 mg l^{-1}, [Fe(III)-PcTS]: 20 μM, reaction time: 180 min.

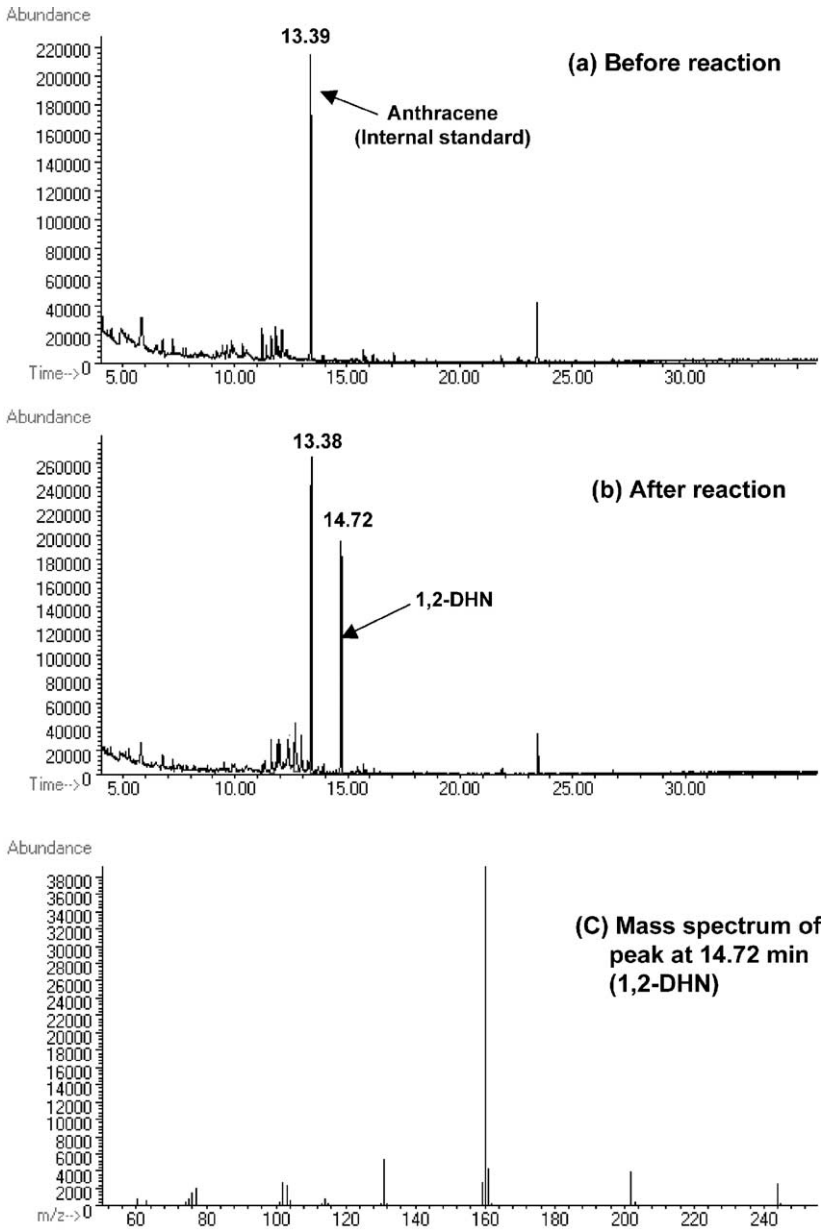

Fig. 5. GC/MS chromatogram of AO7 before (a) and after (b) the reaction, and the mass spectrum of the byproduct (1,2-DHN) (c).

duced during the decolorization reaction. A similar decrease in pH after the oxidative reaction was also found during a typical non-catalytic wet oxidation of AO7 [13]. In this oxidation system, benzenesulfonic acid, naphthol, *p*-PSA, 1,3-isobenzofurandione, 2-hydroxymethylbenzoic acid, 1,2-benzenedicarboxylic acid, acetic acid, formic acid, oxalic acid and glycolic acid were detected, as the result of the non-catalytic wet oxidation of AO7. Thus, we attempted to determine the specific byproducts produced in the reaction mixtures.

3.4.1. Phenolic compounds

To identify the byproducts produced from AO7 during the catalytic reaction, a GC/MS analysis was performed on an ethyl acetate extract of the reaction mixture. The GC/MS chromatogram shows a large peak identified as DHNs (the peak at 14.72 min in Fig. 5b). However, the specific isomer of DHN produced could not be determined. To identify the type of DHN from AO7 in Fe(III)-PcTS catalytic reaction, some standard solutions of isomers (1,2-DHN, 2,7-DHN, 2,3-DHN, 2,6-DHN and 1,5-DHN) in methanol were examined by GC/MS analysis. The retention time of standard 1,2-DHN (14.71 min) was in good agreement with that of the sample extract after the reaction (14.72 min). Moreover, the mass spectral pattern of the peak at 14.72 min in Fig. 5b (Fig. 5c) was similar to the spectrum of the 1,2-DHN standard. These results lead to the conclusion that 1,2-DHN is produced as a result of the oxidation of AO7.

On the other hand, the detection of 1,2-DHN as a byproduct suggests the production of other phenolic compounds that might be break down products of the benzenesulfonate molecule. The possibility that a phenolic compound could also be produced from a benzenesulfonate molecule and then converted to *p*-PSA cannot be excluded. Such a type of compound could not be detected by GC/MS analysis due to the SO_3^- functional group in *p*-PSA, which renders it non-volatile and undetectable by GC/MS. To identify and determine *p*-PSA, the reaction mixture was injected into an ion chromatograph. In this chromatogram, a peak corresponding to *p*-PSA was found (data not shown). However, no *p*-PSA production was detected in the presence of AO7 only, before the reaction (AO7 and Fe(III)-PcTS only) and in the other controls (Fe(III)-PcTS only and Fe(III)-PcTS + $KHSO_5$). The pH decrease observed during the catalytic reaction is also consistent with the production of *p*-PSA. These results indicate that phenolic compounds are the main byproducts of AO7 oxidation, when this catalytic system is used.

3.4.2. Nitrogen species

When the azo chain in AO7 is degraded by the catalytic system, it is possible that the nitrogen can be converted into inorganic nitrogen such as NO_2^-, NO_3^-, NH_4^+ and N_2 gas. However, the formation of NO_2^- and NO_3^- was not observed in the reaction mixtures, whereas NH_4^+ was detected at a level of 0.9 mg l^{-1}. Alternatively, the oxidized azo chain could be converted into other organic nitrogen compounds. Thus, the concentrations of total organic nitrogen before and after the reaction were measured as well as a solution containing Fe(III)-PcTS and $KHSO_5$ without AO7. If nitrogen from the azo chain in AO7 were to be converted into inorganic nitrogen species such as NO_3^-, NH_4^+ and N_2 gas, the concentration of total organic nitrogen after the reaction would be decreased considerably, compared to that before the reaction. The concentration of total organic nitrogen in the solution before the reaction (21 mg l^{-1}) was much larger than that after the reaction (8.4 mg l^{-1}). This strongly indicates that the majority of the nitrogen in AO7 is converted to N_2 gas.

3.5. Possible reaction pathway

The results of the quantitative analyses of 1,2-DHN, *p*-PSA, N_2 gas and NH_4^+ are summarized in Table 1. If the oxidation of AO7 was only the result of the cleavage of the azo group, 100% yields of 1,2-DHN and *p*-PSA would be observed. However, only 2.16 μmol of 1,2-DHN was produced, compared to 5.6 μmol of degraded AO7 (38.6% conversion). Moreover, a 21.4% *p*-PSA conversion and 38.1% N_2 gas conversion were observed. Based on these results, the possible reaction pathways for the oxidation of AO7 are summarized in Fig. 6.

Table 1
Quantitative analyses of byproducts produced from AO7

Compounds	Amounts (μmol)	Percentages
Degraded AO7 (79%)	5.60	100
1,2-DHN	2.16	38.6
p-PSA	1.20	21.4
N_2	2.13	38.0
NH_4^+-N	0.25	2.2

Volume of test solution: 5 ml, [AO7]: 500 mg l^{-1}, [Fe(III)-PcTS]: 20 μM, [$KHSO_5$]: 500 μM, pH 6, reaction time: 180 min.

The production of *p*-PSA observed in this study amounted to almost half of the 1,2-DHN production, whereas 2.13 μmol of N_2 gas, almost half the amount of the degraded AO7, was produced. This indicates that, when decolorization occurred, some of the nitrogen in the azo chain is converted to N_2 gas. The presence of small amounts of NH_4^+ (<1 mg l^{-1}) and the complete absence of NO_3^- and NO_2^- formation after the reaction also support this hypothesis. It has been reported that the splitting of the –N=N– bond during the oxidation of AO7 by sunlight induced reactions via Fenton type reagents, to give *p*-PSA, 1,2-DHN, NO_3^-, NH_4^+ and N_2 [18]. Another study reported the production of N_2 gas, in addition to NO_3^-, NH_4^+ formation in the oxidation of some azo dyes by UV-irradiated TiO_2 [8]. The evolution of N_2 in azo dyes during degradation by the Fe(III)-PcTS catalytic system can be considered to be more benign compared to the production of NO_3^- or NH_4^+. The missing nitrogen in the mass balance for the products reported in Table 1 suggests that some nitrogen species are included in as yet unidentified products. It had been reported that imine and amide derivatives were produced as a result of azo dyestuff oxidation, e.g., phthalimine in the case of TiO_2 photooxidation [9] and acetamidephenildiazine in enzymatic oxidation [7]. In addition, it is known that phenolic compounds are polymerized via oxidative reactions [19], and such polymerized compounds cannot be detected by GC/MS.

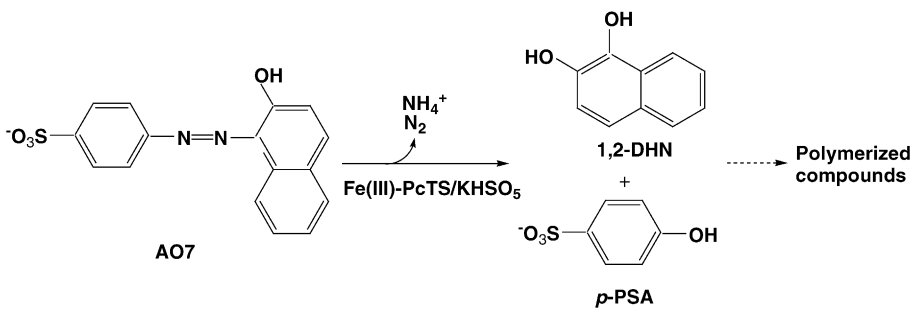

Fig. 6. Possible degradation pathways of AO7 by the catalytic system with Fe(III)-PcTS and $KHSO_5$.

Table 2
The EC_{50} values by the Microtox test before and after the reaction

Incubation time (min)	EC_{50}/mg l^{-1} of TOC	
	Before	After
15	1.63 ± 0.31	0.36 ± 0.06
30	2.12 ± 0.47	0.40 ± 0.04

[AO7]: 428 mg l^{-1}, [Fe(III)-PcTS]: 17 μM, [$KHSO_5$]: 417 μM, pH 6, reaction time: 180 min, percentage of decolorization: 73%, TOC of the solutions before and after reaction: 138 mg l^{-1}.

Thus, unidentified products, probably polymeric compounds derived from phenols and nitrogen species such as imines and amides, may be included in the polymeric compounds.

3.6. Evaluation of toxicity

To evaluate the toxicities of the solutions before and after the reaction, Microtox tests were performed. In this test, the EC_{50} values that were normalized to TOC in the solutions were employed as an index of toxicity. In general, the toxicity of a sample solution increases with decreasing EC_{50} [16,17]. The EC_{50} values of the solutions before and after reaction are summarized in Table 2. In both 15 min and 30 min of incubation periods, the EC_{50} values before the reaction were much higher than those after the reaction. These results indicate that the toxicity of the solution containing AO7 is increased as a result of oxidation with Fe(III)-PcTS and $KHSO_5$.

Although the acute toxicities of azo compounds such as AO7 have been reported [20], the EC_{50} value of AO7 has not been reported. Thus, we measured this value by means of a Microtox test. The EC_{50} values obtained were 5.04 ± 0.45 mg l^{-1} for 15 min and 6.57 ± 1.58 mg l^{-1} for 30 min, and these values were in the same order as other azo compounds such as azobenzene (1.29 mg l^{-1}) and 4-aminoazobenzene (2.66 mg l^{-1}) [17]. We discussed a possible reason for why the EC_{50} values were lower after the reaction. In the present study, the main byproducts were *p*-PSA and 1,2-DHN. The EC_{50} value for *p*-PSA is reported to be 381 mg l^{-1} [17], and this indicates that *p*-PSA is less toxic than AO7. Because the EC_{50} value for 1,2-DHN has not been reported, it was determined (0.12 ± 0.01 mg l^{-1} for 15 min and 0.09 ± 0.02 mg l^{-1} for 30 min). These values were much smaller than those of AO7. Thus, the increase of toxicity as a result of oxidation of AO7 solution is mainly due to the production of 1,2-DHN.

4. Conclusions

Considering treatment systems designed to decolorize dyestuffs in wastewater, the problem of a lack of information concerning smaller fragments produced as result of the break down of the original chromophore still exists. Information on the degradation products of dyestuffs becomes important since they are capable of affecting overall toxicity.

The use of Fe(III)-PcTS/$KHSO_5$ catalytic system for decolorizing AO7, a representative azo dyestuff, was examined. It was found that azo chain in the dye could be cleaved by this catalytic system, but the resulting organic compounds were not mineralized. The byproduct pattern showed that this type of catalytic system converted the dyes to phenolic compounds. However, the degradation of dyes to phenolic compounds via Fe(III)-PcTS/$KHSO_5$ catalytic system may lead to an increase in the toxicity of the solution.

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