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3 Influence of oxalic acid formed on the degradation of phenol by Fenton reagent

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19 ABSTRACT

20 The objective of this work is to examine the influence of oxalic acid formed
21 on the degradation of phenol by Fenton reagent. Oxalic acid formed at initial stage
22 within 30 min significantly suppresses the reduction of ferric ion, thus terminating
23 degradation reaction. The yield of oxalic acid is dependent on the amount of ferrous
24 ion dosed since the minimal amount of oxalic acid is formed after the degradation
25 reaction terminates. Mineralization of phenol by Fenton reagent stagnates after 120
26 min under the conditions used in this study. The reason why the mineralization
27 stagnated can be assumed to be following two mechanisms other than the depletion of
28 H₂O₂. In the case where a small amount of ferrous ions is dosed, the reduction of ferric
29 ions is minimal by oxalic acid formed. In the case where a large amount of ferrous ions
30 is dosed, the amount of degradable organic compounds is insufficient owing to
31 preferential conversion to oxalic acid. The mineralization can be enhanced by the
32 intermittent dosing of ferrous ions, which facilitates the suppression of oxalic acid
33 formation during the degradation by Fenton reagent.

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35 KEY WORD: Fenton reaction, Phenol degradation, Mineralization, Oxalic acid

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37 **1. Introduction**

38 Treatment of wastewater containing organic pollutants has been of great
39 concern all over the world. Advanced oxidation processes (AOPs) have great potential
40 in treating wastewater containing organic pollutants at room temperature, and a number
41 of AOPs have been proposed. Among them, Fenton oxidation, in which wastewater is
42 treated with Fenton reagent (ferrous salt + H₂O₂), is an attractive oxidative process for
43 wastewater treatment because iron is a very abundant and non-toxic element and
44 hydrogen peroxide is easy to handle and environmentally safe (Andreozzi et al., 1999).
45 Therefore, it has been adopted as the process for treating various industrial wastes
46 (Wadley and Waite, 2004; Bautista et al., 2008).

47 In Fenton oxidation, a very active hydroxyl radical formed during reactions
48 involving Fenton reagent (Reaction (1)) attacks organic compounds, enabling these
49 compounds to be degraded through oxidation (Harber and Weiss, 1934).



51 The regeneration of Fe(III) to Fe(II) through the reduction by H₂O₂ or HO₂· formed
52 from H₂O₂ also occurs in this reaction system (Barb et al., 1951a, 1951b; Walling, 1975).
53 Therefore, as long as H₂O₂ is available, the redox cycle of iron ions is basically
54 continuous between Fe(II) and Fe(III), thus forming a hydroxyl radical. It is essential to

55 promote this cycle in order to degrade organic compounds efficiently. It is well known
56 that with the Fenton process, this mineralization is very likely to stagnate before it is
57 complete. Therefore, the Fenton process has been proposed primarily as a pretreatment
58 to reduce the effluent toxicity to safe levels and to improve biodegradability for further
59 biological treatment (Chamarro et al., 2001; Lopez et al., 2004). In order to enhance the
60 degree of mineralization and thus the usefulness of the Fenton process, it is necessary to
61 analyze the intermediate products that remain in the water treated with Fenton reagent
62 and to examine the reasons why the mineralization stagnates.

63 It has been noted that the benzenediols and benzoquinones could expedite the
64 redox cycle of iron (Tamagaki et al., 1989a, 1989b; Chen and Pignatello, 1997).
65 Mijangos et al. (2006) examined the changes in solution color during treatment and
66 reported that the observed color was due to an intermediate product of the main reaction,
67 such as benzoquinones or benzene rings coordinated with ferric ions. Kang et al. (2002)
68 focused on the interaction of the organic intermediates with the Fe species. Zimbron and
69 Reardon (2009) suggested that organic intermediates formed during pentachlorophenol
70 degradation by Fenton reagent have a HO· scavenging effect from the kinetic model
71 calculation. Among these intermediate products, we focus on the relatively stable
72 organic acids, which may remain after the treatment, in order to enhance the degree of

73 mineralization. Acetic, maleic, malonic, and oxalic acids are known to be poorly
74 degradable by Fenton reagent (Bigda, 1995). In particular, oxalic acid can deactivate Fe
75 ion activity by the strong coordination with Fe(III) (Sun and Pignatello, 1992, 1993;
76 Kwon et al., 1999). Zazo et al. (2005) reported that oxalic acid reached a high relative
77 concentration among organic acids formed during phenol degradation by Fenton reagent,
78 although its formation rate was lower than that of other acids. They also reported that
79 the concentration of oxalic acid increased at increasing ferrous ion dose (Zazo et al.,
80 2007).

81 In this study, we focus on the formation of organic acids, especially oxalic acid,
82 and discuss its influence on the degradation of phenol by Fenton reagent. We examine
83 the effect of the reaction conditions on the formation behavior of oxalic acid. We
84 discuss the influence of oxalic acid on the consumption of H_2O_2 and the mineralization
85 behavior under the conditions used in this study for the view point of iron cycle. Finally,
86 we propose a method for enhancing the degree of mineralization using the same amount
87 of Fenton reagent.

88

89 **2. Experimental methods**

90 *2.1. Chemicals*

91 All chemicals were purchased from WAKO Pure Chemical Industries. Phenol
92 (> 99%) was used as the organic pollutant in this study. It was used without any other
93 purification. A 1000 mg L⁻¹ phenol solution was prepared using distilled water and was
94 stored in a glass bottle. Solutions of FeSO₄·6H₂O and Fe₂(SO₄)₃·9H₂O (0.25 M each)
95 were prepared and used as ferrous and ferric ion sources, respectively.

96 2.2. Procedure

97 The reactor was a 300 mL glass beaker with a magnetic stirrer. We prepared
98 250 mL of a 100 mg L⁻¹ phenol solution, adjusted the pH to 3.0 using 0.1 M H₂SO₄, and
99 dosed a designated amount of H₂O₂ solution (15 wt%). We then dosed a designated
100 amount of 0.25 M FeSO₄ to initiate the reaction. The experiment was carried out at
101 room temperature (23 ± 2 °C) in a dark room to avoid the effect of light. The initial
102 concentrations of ferrous ion, C_{Fe(II),0}, and H₂O₂, C_{H₂O₂,0}, in a reactor were varied from
103 0.1 to 1.5 mM and from 5 to 80 mM, respectively.

104 2.3. Analysis

105 The treated water was analyzed immediately after the treatment. The
106 concentrations of phenol and H₂O₂ were determined by colorimetric methods with a
107 UV-Vis spectrometer (UVmini-1240, Shimadzu). The 4-aminoantipyrine and iodide
108 methods (Allen et al., 1952; Kormann et al., 1988) were utilized for the analysis of

109 phenol and H₂O₂ at $\lambda = 507$ and 350 nm, respectively. The total organic carbon (TOC)
110 concentration was measured using a TOC analyzer (TOC-V_{CSH}, Shimadzu). The
111 quantitative measurement of organic acids was carried out by using a
112 non-suppressor-type ion chromatograph system equipped with a Shim-pack IC-A1
113 column (100 mm long). An aqueous solution of phthalic acid (2.5 mM) and
114 tris(hydroxymethyl)aminomethane (2.4 mM) was used as the mobile phase at a flow
115 rate of 1.5 mL min⁻¹ under isocratic conditions. Prior to analysis, treatment using a
116 solid-phase extraction cartridge was performed in order to remove ferric ions from
117 organic acid because ferric ions interfere with the quantitative analysis of oxalic acids,
118 as is examined in Supplementary Material (SM).

119

120 **3. Results and discussion**

121 *3.1. Mineralization behavior of phenol during the degradation by Fenton reagent*

122 Phenol was degraded by more than 95% within a few minutes under the
123 conditions performed in this study. Therefore, the TOC concentration, which is directly
124 correlated to the degree of mineralization, is examined. Figure 1 shows the change of
125 the TOC yield, Y_{TOC} , against treatment time when $C_{\text{Fe(II),0}}$ or $C_{\text{H}_2\text{O}_2,0}$ was varied. $C_{\text{Fe(II),0}}$
126 and $C_{\text{H}_2\text{O}_2,0}$ were 1.0 and 20 mM, respectively. Under the reaction conditions examined,

127 the Y_{TOC} significantly decreased just after the reaction was initiated, and then decreased
128 more gradually. Mineralization appeared to stagnate after 120 min in all cases. $C_{\text{Fe(II)},0}$
129 affects the mineralization rate in the initial stage, however, it has little effect on the
130 mineralization rate after 120 min. About 60% of the carbon contained in the phenol
131 remained in the water at 240 min. $C_{\text{H}_2\text{O}_2,0}$ had a similar effect on the mineralization
132 behavior of phenol as $C_{\text{Fe(II)},0}$ although the effect was more significant.

133 Next, the consumption of H_2O_2 during the treatment is examined. Figure 2
134 shows the change of the concentration of H_2O_2 , $C_{\text{H}_2\text{O}_2}$, as a function of time at various
135 values of $C_{\text{Fe(II)},0}$ and at $C_{\text{H}_2\text{O}_2,0} = 20$ mM. H_2O_2 was rapidly consumed in the initial
136 stage within 30 min. This rapid consumption indicated that severe degradation occurred
137 and terminated within 30 min. After 30 min, minimal H_2O_2 was consumed when $C_{\text{Fe(II)},0}$
138 was less than 0.5 mM. On the other hand, $C_{\text{H}_2\text{O}_2}$ gradually decreased when $C_{\text{Fe(II)},0}$ was
139 1.0 mM. $C_{\text{H}_2\text{O}_2}$ values at 240 min were 0.2, 6.6, and 10.4 mM in the case of 1.0, 0.5, and
140 0.25 mM of $C_{\text{Fe(II)},0}$, respectively, whereas a significant difference was not observed in
141 Y_{TOC} values among the three cases. Stagnation of the mineralization after 120 min in the
142 case of $C_{\text{Fe(II)},0} \leq 0.5$ mM was not due to the depletion of H_2O_2 because sufficient H_2O_2
143 remained in the treated water. Therefore, the organic products, which are supposed to be
144 organic acids, were analyzed to examine the influence of organic acids on the

145 degradation by Fenton reagent.

146

147 *3.2. Formation behavior of oxalic acid*

148 Oxalic acid and formic acid could be quantified in the treated water in this
149 study. Other organic acids such as acetic acid, glycolic acid, malonic acid, malic acid,
150 and tartaric acid were also detected in the case of low $C_{\text{Fe(II),0}}$, however, their yields,
151 which were all less than $0.025 \text{ g-C g-C}^{-1}$, were too low to be quantified. Figure 3 shows
152 the yields of oxalic acid (Y_{oxalic}), formic acid (Y_{formic}), Y_{TOC} , and $C_{\text{H}_2\text{O}_2}$ as a function of
153 $C_{\text{Fe(II),0}}$ value in the degradation of phenol by Fenton reagent for 150 min. The yield of
154 organic acid was represented on a carbon basis, so that it could be compared with Y_{TOC}
155 directly. Y_{oxalic} was significantly dependent on $C_{\text{Fe(II),0}}$. At $0.12 \text{ g-C g-C}^{-1}$, the Y_{oxalic}
156 corresponded to just 16% of the carbon remaining in the treated water when phenol was
157 treated with 0.1 mM of $C_{\text{Fe(II),0}}$. It increased with the increase of $C_{\text{Fe(II),0}}$, and reached as
158 high as $0.55 \text{ g-C g-C}^{-1}$ when phenol was treated with 1.5 mM of $C_{\text{Fe(II),0}}$. The ratio of
159 Y_{oxalic} to Y_{TOC} exceeded 0.8, indicating that carbon remaining in the treated water almost
160 existed as oxalic acid. It can be said that oxalic acid was preferentially formed at high
161 $C_{\text{Fe(II),0}}$ because Y_{TOC} of the degradation with 1.5 mM of $C_{\text{Fe(II),0}}$ was almost the same as
162 that of the degradation with 0.3 mM of $C_{\text{Fe(II),0}}$ at 150 min. The formation of formic acid

163 was insignificant compared with oxalic acid and could not be quantified in the case of
164 $C_{\text{Fe(II)},0} \geq 1.0$ mM.

165 As for the formation profile of oxalic acid, a significant amount of oxalic acid
166 was formed at the initial stage within 30 min and its yield appeared to be almost
167 unchanged after 60 min under various values of $C_{\text{Fe(II)},0}$ and $C_{\text{H}_2\text{O}_2,0}$ (Fig. SM-1). These
168 results related to the formation behavior of oxalic acid are consistent with the report of
169 Zazo et al. (2007). Since the oxalic acid is not degraded by Fenton reagent solely,
170 degradation proceeded slowly to decrease TOC concentration after 60 min, as shown in
171 Fig. 1. 89% of the carbon contained in the phenol was converted to CO_2 or oxalic acid
172 at 150 min in the case of $C_{\text{Fe(II)},0} = 1.0$ mM. It can be said that the degradation of organic
173 compounds in the treated water almost went to completion in the case of $C_{\text{Fe(II)},0} = 1.0$
174 mM because oxalic acid is the final product of the degradation by Fenton reagent as
175 well as CO_2 . On the other hand, the degradation seemed not to go to completion in the
176 case of $C_{\text{Fe(II)},0} = 0.2$ mM because the sum of the yields of oxalic acid and CO_2 is 0.47
177 g-C g-C⁻¹ at 150 min.

178 3.3. Effect of oxalic acid on the iron cycle in the water

179 Degradation mainly proceeds by the formation of an active radical through the
180 iron cycle between Fe(II) and Fe(III). The rate of the iron cycle is determined by the

181 reduction rate of Fe(III) because the oxidation rate of Fe(II), Reaction (1), is very rapid.

182 Therefore, the reducing behavior of Fe(III) is examined here.

183 Considering that enough H_2O_2 remains at 150 min as shown in Fig. 2, it is
184 possible that the degradation rate is extremely slow; therefore, prolonged treatment is
185 required for oxalic acid formation when $C_{Fe(II),0}$ is low. Thus, the degradation was
186 performed for 24 h at various values of $C_{Fe(II),0}$ and at $C_{H_2O_2,0} = 20$ mM. Y_{TOC} , Y_{oxalic} , and
187 $C_{H_2O_2}$ at 24 h are shown in Fig. 4.. H_2O_2 was additionally dosed to be 20 mM at 240 min
188 only in the case of $C_{Fe(II),0} = 1.0$ mM because H_2O_2 was almost consumed. Y_{oxalic} in the
189 cases of $C_{Fe(II),0} = 0.2$ and 0.5 mM showed minimal increase by extending the treatment
190 time, and it was much lower than that for $C_{Fe(II),0} = 1.0$ mM at 150 min, although a
191 considerable amount of H_2O_2 remained in the treated water. These results clearly show
192 that oxalic acid cannot be produced in the case of low $C_{Fe(II),0}$ as much as it can in the
193 case of high $C_{Fe(II),0}$. Therefore, it is considered that Fe(III) is minimally reduced, in
194 other word, the activity of Fe(III) is significantly lowered, during the degradation. It has
195 been reported that the strong coordination of oxalic acids to ferric ions deactivates the
196 degradation activity of ferric ions, as stated in the introduction. There is another
197 possibility that the unidentified products are difficult to degrade by Fenton reagent,
198 although Zazo et al. (2007) reported that they were the precursors of oxalic acid.

199 To examine the deactivation effects of oxalic acid under the conditions
200 performed here, two experiments were employed. One was the addition of ferric ions to
201 the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ and the other was the comparison of H_2O_2
202 consumption rates in the water containing oxalic acid. In the former experiment, ferric
203 ion was additionally dosed in the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ for 24 h so that
204 the concentration of total iron ions was 1.0 mM. Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ were measured
205 60 min after additional dosing at 24 h, and the results are shown in Fig. 4. Y_{TOC}
206 decreased significantly from 0.53 to 0.45 g-C g-C⁻¹ and Y_{oxalic} reached 0.32 g-C g-C⁻¹.
207 Degradation was found to proceed significantly by the addition of ferric irons. This
208 result clearly indicates that the remaining organic compounds were degradable by
209 Fenton reagent and that the stagnation of the mineralization was due to the deactivation
210 of Fe(III). It was also confirmed that some of the unidentified products were the
211 precursors of oxalic acid. As for the comparison of H_2O_2 consumption rate, Fig. 5
212 compares the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing 1.0 mM of
213 $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid, C_{oxalic} . 80% of H_2O_2 was consumed in
214 120 min when no oxalic acid was present in the water. In the case of $C_{\text{oxalic}} = 0.5$ mM,
215 H_2O_2 was consumed as is the case with no oxalic acid whereas only 25% of H_2O_2 was
216 consumed in the case of $C_{\text{oxalic}} = 1$ mM. When C_{oxalic} was 1.5 mM, minimal H_2O_2 was

217 consumed. Thus, the activity of Fe(III) is almost lost if the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$
218 exceed 1.5 in the absence of reducing agent.

219 The consumption behavior of H_2O_2 shown in Fig. 2 is examined here. H_2O_2
220 was more rapidly consumed in the initial stage within 30 min compared with the case in
221 which there was no oxalic acid, as shown in Fig. 5. This is because the reduction of
222 Fe(III) occurred not only by H_2O_2 but also by the degradation products. In this initial
223 stage, a considerable amount of oxalic acid is produced to deactivate Fe(III). The
224 consumption rate of H_2O_2 was significantly reduced after 30 min in the case of $C_{\text{Fe(II),0}} \leq$
225 0.5 mM because the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$ had already exceeded 2. Therefore,
226 the yield of oxalic acid is dependent on the $C_{\text{Fe(II),0}}$. On the other hand, in the case of
227 $C_{\text{Fe(II),0}} = 1.0$ mM, H_2O_2 was gradually consumed. Organic intermediates in the water
228 may act as reducing agents for Fe(III), because the molar ratio of C_{oxalic} to $C_{\text{Fe(III)}}$ was
229 1.5. Stagnation of mineralization was observed after 120 min in both cases, as shown in
230 Fig. 1, but the situation was different in those cases. In the former case, Fe(III) was
231 minimally reduced by the coordination of oxalic acid although a fairly large amount of
232 H_2O_2 and degradable organic compounds remained in the water. In the latter case, the
233 amount of degradable organic compounds is insufficient because of preferential
234 conversion to oxalic acid, although reduction of Fe(III) occurred slowly.

235 3.4. Enhancement of the mineralization degree using same amount of Fenton reagent

236 It is, of course, desirable to enhance the degree of mineralization, in other
237 words, to reduce Y_{TOC} . Figure 4 helps us to examine the conditions that reduce Y_{TOC} . At
238 24 h, the degradation with 0.5 mM of $C_{\text{Fe(II),0}}$ gave lower Y_{TOC} compared to that with 1.0
239 mM of $C_{\text{Fe(II),0}}$. In the case of $C_{\text{Fe(II),0}} = 1.0$ mM, Y_{TOC} was reduced only slightly with the
240 prolonged treatment because a large part of organic compounds is oxalic acid even at
241 150 min. As a result, 97% of the remaining carbon was oxalic acid at 24 h because
242 $Y_{\text{oxalic}}/Y_{\text{TOC}} = 0.97$. On the other hand, the organic compounds that can be mineralized
243 remained in the degradation with 0.5 mM of $C_{\text{Fe(II),0}}$ at 150 min. Therefore, Y_{TOC} could
244 be reduced from 0.63 to 0.47 g-C g-C⁻¹ by prolonged treatment, although the
245 mineralization rate was very slow. From these results, Y_{TOC} can be reduced if the
246 degradation is allowed to proceed with a lower concentration of oxalic acid. To achieve
247 this situation, ferrous ion was supplied in intermittent doses. The same amount of
248 ferrous ion was dosed every 120 min a total of four times so that the total concentration
249 of iron ions was 1.0 mM. $C_{\text{H}_2\text{O}_2,0}$ was 40 mM. Figure 6 shows the Y_{TOC} , Y_{oxalic} , and
250 $C_{\text{H}_2\text{O}_2}$ at 480 min. Four intermittent doses were effective in enhancing the degree of
251 mineralization. Y_{TOC} in the case of four intermittent dosing was significantly reduced to
252 0.39 g-C g-C⁻¹, whereas that in the case of all-at-once dosing was 0.53 g-C g-C⁻¹,

253 although the consumption of H₂O₂ was almost the same in both cases. The formation of
254 oxalic acid was also suppressed by four intermittent dosing as expected. Phenol was
255 eventually converted to CO₂ or oxalic acid through the unidentified products during the
256 degradation by Fenton reagent. It was found that intermittent dosing was effective for
257 converting the unidentified products to CO₂ preferentially. Thus, the mineralization
258 degree could be enhanced by employing intermittent dosing using same amount of
259 Fenton reagent.

260

261 **4. Conclusions**

262 In this study, the influence of oxalic acid on the degradation of phenol by
263 Fenton reagent was examined. Oxalic acid formed during the degradation was found to
264 suppress the reduction of ferric ions by coordination, terminating the degradation
265 reaction in the initial stage within 30 min. Since the minimal amount of oxalic acid was
266 formed after the degradation reaction terminated, the yield of oxalic acid was dependent
267 on the amount of ferrous ion dosed. Mineralization of phenol by Fenton reagent
268 stagnated after 120 min under the conditions used in this study. The reason why the
269 mineralization stagnated was assumed as follows: In the case where a small amount of
270 ferrous ions was dosed, the reduction of ferric ions was minimal by oxalic acid formed,

271 although a fairly large amount of H_2O_2 and degradable organic compounds remained in
272 the water. The fact that the degradation proceeded significantly by dosing additional
273 ferric ions to the treated water supports this result. In the case where a large amount of
274 ferrous ions was dosed, the amount of degradable organic compounds was insufficient
275 owing to preferential conversion to oxalic acid, although H_2O_2 was gradually consumed.

276 Phenol was eventually converted to CO_2 or oxalic acid through the unidentified
277 products during the degradation by Fenton reagent. Therefore, it was inferred that TOC
278 can be reduced significantly if the degradation is allowed to proceed with a lower
279 concentration of oxalic acid. A same amount of ferrous ion was supplied in four
280 intermittent doses for this purpose. TOC yield could be reduced by 26% compared to
281 the degradation with all-at-once dose when the same amounts of ferrous ion and H_2O_2
282 were used. The yield of oxalic acid was also suppressed by intermittent dosing as
283 expected. These results indicated that intermittent dosing of ferrous ion was effective for
284 converting phenol to CO_2 rather than oxalic acid through the unidentified degradation
285 products.

286

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349

350 Figure Captions

351 Fig. 1. The change of the TOC concentration against treatment time during the
352 degradation of phenol by Fenton reagent when (a) $C_{\text{Fe(II)},0}$ was varied. (b) $C_{\text{H}_2\text{O}_2}$
353 was varied.

354

355 Fig. 2. The change of the concentration of H_2O_2 as a function of time during the
356 degradation of phenol by Fenton reagent when $C_{\text{Fe(II)},0}$ was varied.

357

358 Fig. 3. The yields of oxalic acid, formic acid, Y_{TOC} , and $C_{\text{H}_2\text{O}_2}$ as a function of $C_{\text{Fe(II)},0}$
359 value during the degradation of phenol by Fenton reagent for 150 min.

360

361 Fig. 4. Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ in the prolonged degradation when $C_{\text{Fe(II)},0}$ was 0.2, 0.5,
362 and 1.0 mM.

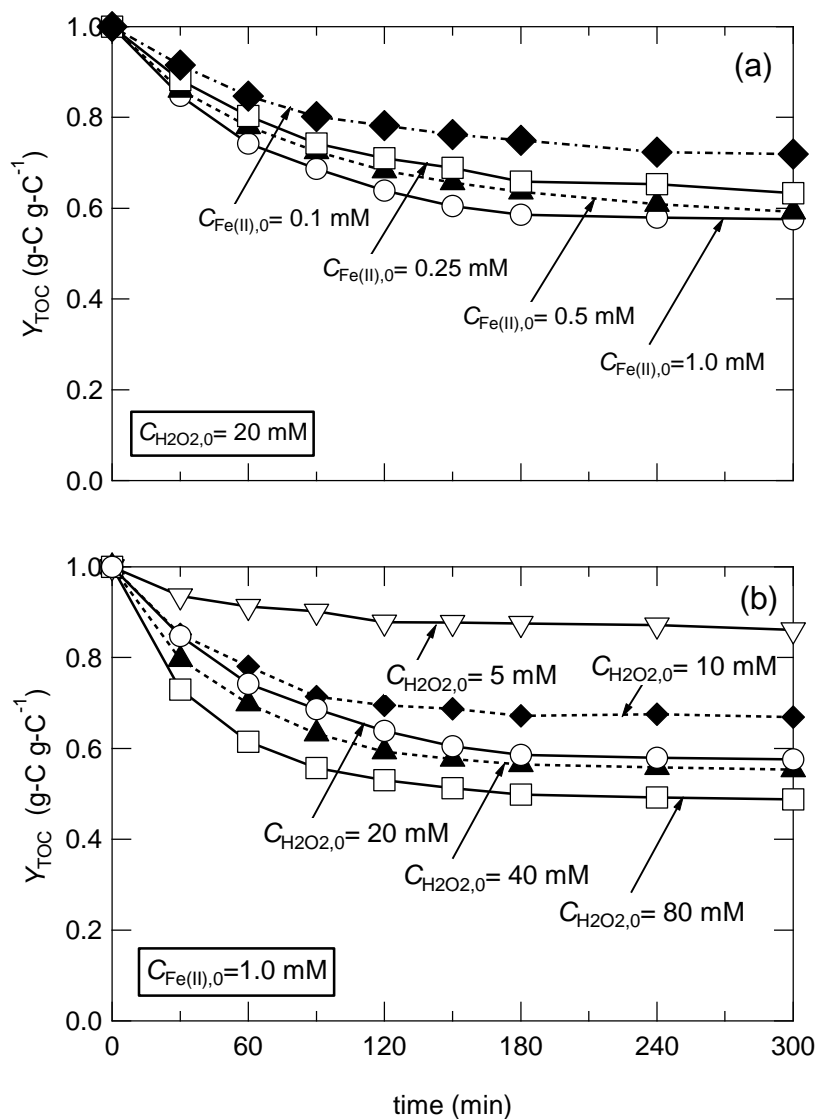
363

364 Fig. 5. Comparison of the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing
365 1.0 mM of $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid.

366

367 Fig. 6. Comparison of the Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ at 480 min between four intermittent
368 doses and all-at-once dose of Fe^{2+} when the same amounts of Fe^{2+} and H_2O_2
369 were dosed.

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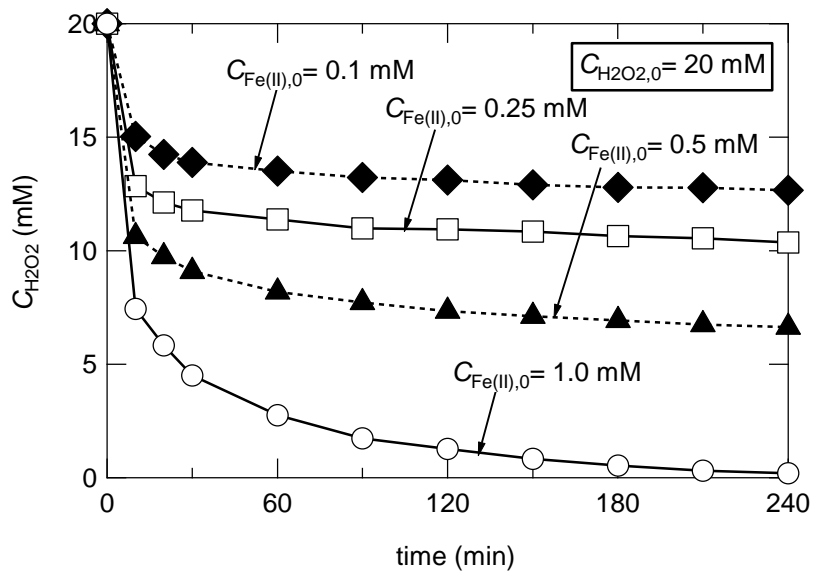
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375 Fig. 1 The change of the TOC concentration against treatment time during the
 376 degradation of phenol by Fenton reagent when (a) $C_{Fe(II),0}$ was varied. (b) $C_{H_2O_2}$
 377 was varied.

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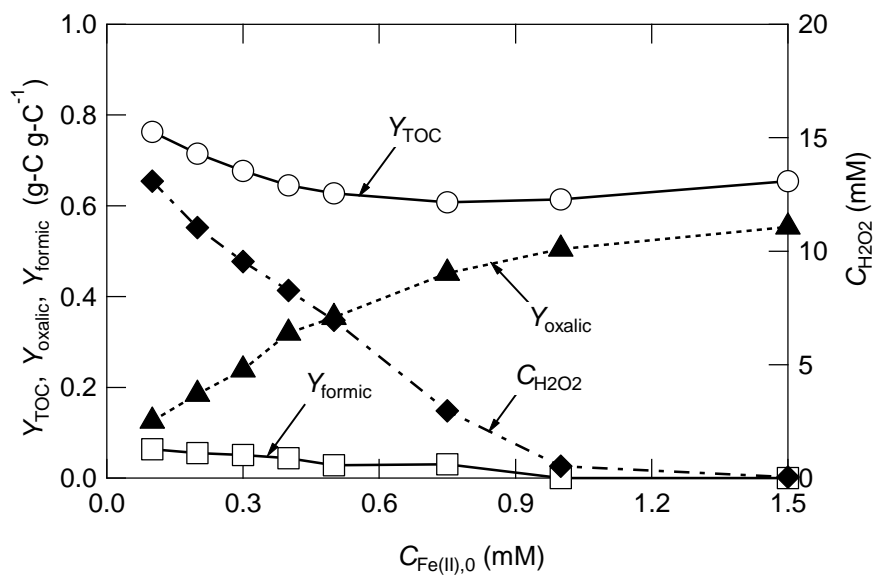


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381 Fig. 2 The change of the concentration of H_2O_2 as a function of time during the
 382 degradation of phenol by Fenton reagent when $C_{\text{Fe(II)},0}$ was varied.

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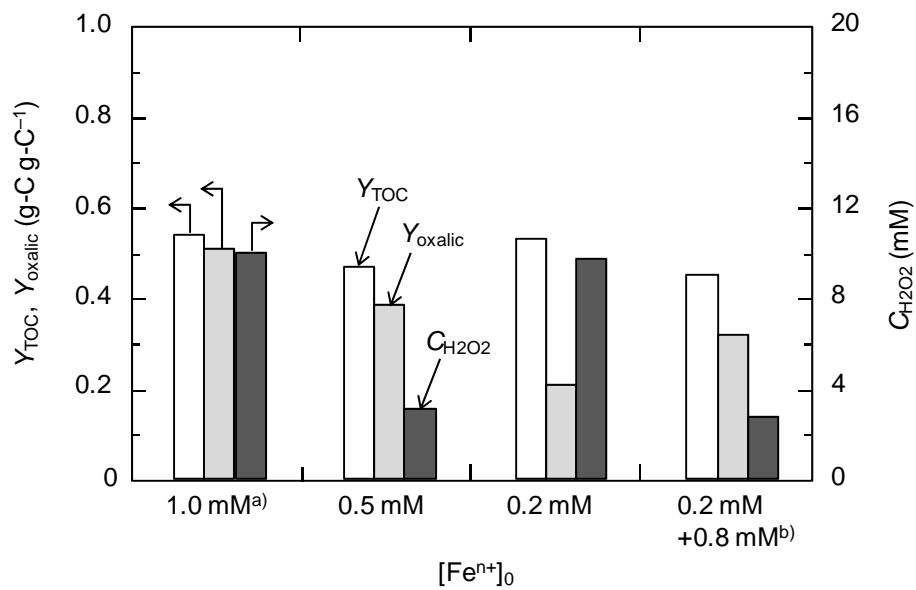
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386 Fig. 3 The yields of oxalic acid, formic acid, Y_{TOC} , and $C_{H_2O_2}$ as a function of $C_{Fe(II),0}$

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value during the degradation of phenol by Fenton reagent for 150 min.

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a) H_2O_2 was additionally dosed at 240 min to be 20 mM because H_2O_2 was almost consumed.

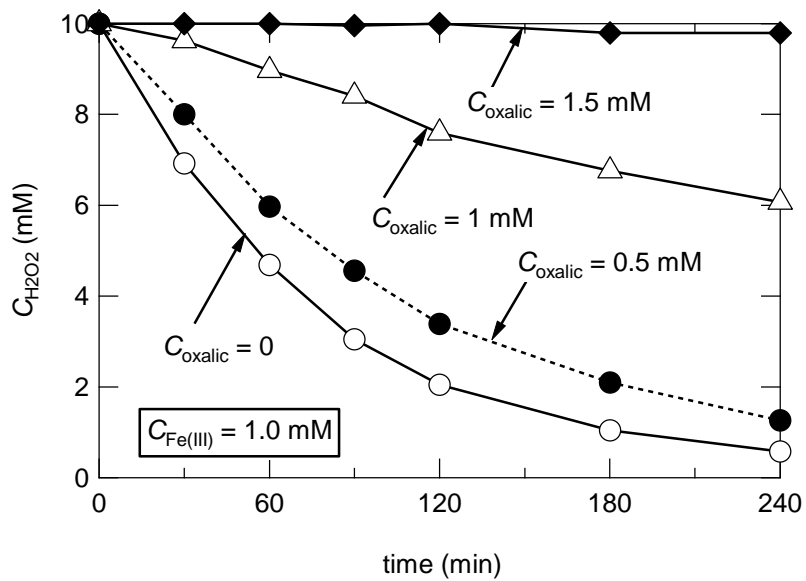
b) Fe^{3+} was dosed to the water treated with 0.2 mM of $C_{\text{Fe(II)},0}$ at 24 h so that the total amount of iron ions dosed was same as that of treated with 1.0 mM of $C_{\text{Fe(II)},0}$.

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391 Fig. 4 Y_{TOC} , Y_{oxalic} , and $C_{\text{H}_2\text{O}_2}$ in the prolonged degradation when $C_{\text{Fe(II)},0}$ was 0.2, 0.5,
 392 and 1.0 mM.

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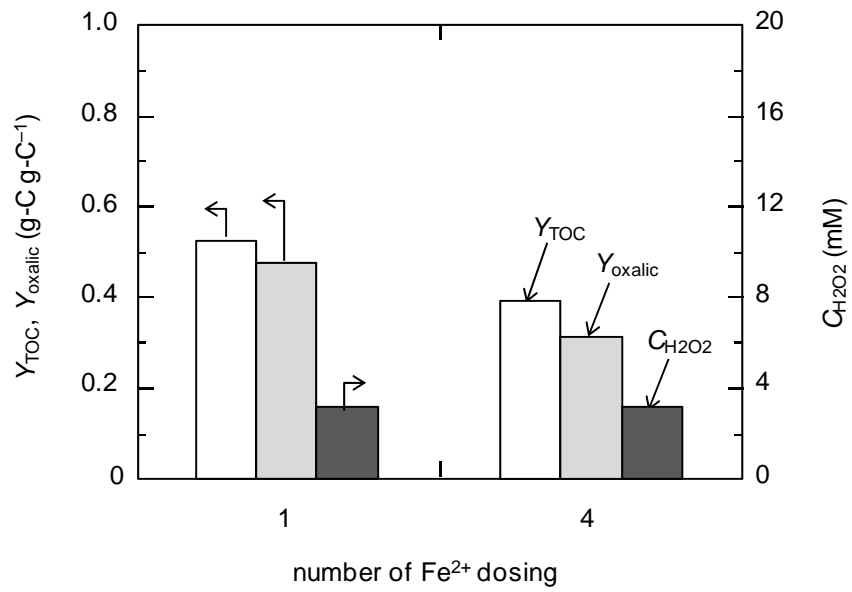
395

396 Fig. 5 Comparison of the change of $C_{\text{H}_2\text{O}_2}$ as a function of time in the water containing

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1.0 mM of $C_{\text{Fe(III)}}$ with various concentrations of oxalic acid.

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Fig. 6 Comparison of the Y_{TOC} , Y_{oxalic} , and $C_{H_2O_2}$ at 480 min between four intermittent doses and all-at-once dose of Fe^{2+} when the same amounts of Fe^{2+} and H_2O_2 were dosed.