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**Degradation of azo dye orange G in aqueous solution
by persulfate with ferrous ion**

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Abstract

23 The oxidative degradation of azo dye, orange G (OG), in aqueous solution by the
24 persulfate/Fe²⁺ reagent has been investigated. Effects of pH, dosages of persulfate and
25 Fe²⁺, temperature, and the presence of inorganic ions (Cl⁻, NO₃⁻, HCO₃⁻ and H₂PO₄⁻)
26 on the OG degradation were examined in batch experiments. OG degradation by the
27 persulfate/Fe²⁺ reagent was found to follow the first-order kinetic model. Under an
28 optimum condition ([persulfate] = 4 mM, [Fe²⁺] = 4 mM and pH 3.5), the OG in
29 aqueous solution with an initial concentration of 0.1 mM was degraded by 99% within
30 30 min. The OG degradation increased with the increased persulfate and Fe²⁺ dosages
31 and an optimal molar ratio of persulfate to Fe²⁺ was found to be 1:1. The experimental
32 results showed that increasing the reaction temperature was beneficial to the OG
33 degradation, not as efficient as chemical activation. In the meantime, the apparent
34 activation energy for the OG degradation was determined to be 92.2 kJ mol⁻¹.
35 Furthermore, the experiments demonstrated that the OG degradation could be
36 significantly inhibited due to the existence of inorganic ions in a sequence of NO₃⁻ <
37 Cl⁻ < H₂PO₄⁻ < HCO₃⁻. The results of this study provided fundamental understanding of
38 the OG reaction with the persulfate/Fe²⁺ reagent.

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40 *Keywords:* Azo dye; Degradation; Fe²⁺; Kinetics; Orange G; Persulfate

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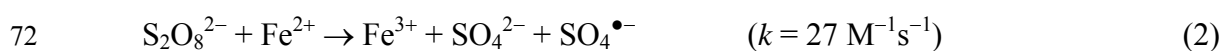
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44 **1. Introduction**

45 Azo dyes represent more than 50% of all dyes in common use because of their
46 chemical stability and versatility [1]. However, most of them are non-biodegradable,
47 toxic and potentially carcinogenic in nature [2] and at present are abated by some
48 non-destructive processes, such as coagulation, activated carbon adsorption and
49 membrane filtration [3-5]. The degradation and mineralization of dyes have not been
50 achieved in these treatment processes. Therefore, the development of destructive
51 processes for treating dyeing wastewater has significant interests currently. Several
52 advanced oxidation processes, such as TiO₂-mediated photocatalysis [6-8], Fenton or
53 photo-Fenton reaction [9-11], and other reactions using potassium permanganate
54 [12,13], oxone/Co²⁺ reagent [14,15] and persulfate [16,17], have been extensively
55 studied in the degradation of dye solutions. Actually, the persulfate technique for the
56 efficient degradation of biorefractory substances has been successfully verified for some
57 pollutants [18-23] and furthermore, it has potential to completely mineralize organic
58 compounds.

59 Persulfate (S₂O₈²⁻) is one of the strongest oxidants known in aqueous solution and
60 has the higher potential ($E^{\circ} = 2.01$ V) than H₂O₂ ($E^{\circ} = 1.76$ V). It offers some
61 advantages over other oxidants as a solid chemical at ambient temperature with ease of
62 storage and transport, high stability, high aqueous solubility and relatively low cost [20].
63 These features let it be a promising choice for clean-up applications. Reactions of
64 persulfate with organic pollutants in water, however, are generally slow at ambient
65 temperature, and activation of persulfate is necessary to accelerate the process. It has
66 been reported that persulfate anion can thermally or chemically by transition metal ions,

67 such as Fe^{2+} be activated to generate a strong oxidant sulfate free radical ($\text{SO}_4^{\bullet-}$, $E^o =$
68 2.5-3.1 V) [16]. Similar to the Fenton's reaction, the transition metal is coupled with an
69 oxidant. The overall stoichiometric reaction between persulfate and Fe^{2+} is expressed by
70 Eq (1) through two steps of Eqs (2) and (3) as follows [24]:



74 Orange G (OG), a typical azo dye in textile wastewaters, has been the subject of
75 intense investigations [11,25,26]. However, the information about OG degradation by
76 the persulfate/ Fe^{2+} reagent is still limited. In this study, the kinetics of OG degradation
77 was elucidated based on the experimental data. Furthermore, the influences of some
78 important reaction conditions such as pH of solutions, dosages of persulfate and Fe^{2+} ,
79 temperature, and presence of some inorganic ions on OG degradation in aqueous
80 solution were investigated. Furthermore the mineralization of OG by the persulfate/ Fe^{2+}
81 reagent was compared with the Fenton reagent.

82

83 **2. Experimental**

84

85 *2.1. Materials*

86 OG chemical was purchased from Hengrun dyestuff chemical Co. (Guangzhou,
87 China) and was used as received without further purification. Its physiochemical
88 characteristics are listed in Table 1. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 99%) and ferrous

89 sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were obtained from Aldrich. Sodium chloride, sodium
90 dihydrogen phosphate, sodium bicarbonate and sodium nitrate were purchased from J.T.
91 Baker. Other reagents with analytical reagent grade were obtained from International
92 Laboratory (IL, USA).

93 Aqueous solutions were prepared in the deionized water obtained from a Millipore
94 Milli-Q system. An OG stock solution was prepared at 10 mM. A $\text{Na}_2\text{S}_2\text{O}_8$ solution was
95 prepared at 200 mM freshly. A FeSO_4 solution (100 mM) was prepared in 0.01 M
96 H_2SO_4 .

97

98 *2.2. Experimental procedures*

99 Batch experiments were first performed in graduated and plugged test tubes.
100 Reaction solutions were obtained by adding FeSO_4 solution into aqueous OG solution
101 and the initial pH of the reaction solutions was adjusted with NaOH (0.1 M) or H_2SO_4
102 (0.1 M) solution. Then the reaction was initiated by adding $\text{Na}_2\text{S}_2\text{O}_8$ into the prepared
103 reaction solutions with a volume of 50 ml. At the given time intervals, the sample
104 aliquots were taken from the tubes and analyzed immediately. Before analysis, sodium
105 azide [20] was added to quench any further oxidation reactions and the water samples
106 were then filtered through a 0.45 μm membrane filter. All experiments were carried out
107 at a room temperature of 20 ± 1 °C unless otherwise stated.

108 Several sets of the experiments were conducted to determine the effects of various
109 parameters on OG degradation. In all experiments, the initial OG concentration was
110 kept at 0.1 mM. For determining the effect of pH on OG degradation, three pH values of

111 aqueous solutions at 3.5, 7.0 and 9.0 were studied, respectively. In the remaining
112 experiments, the pH values of the solutions were kept constant at 3.5. To determine the
113 effects of persulfate and Fe^{2+} dosages on the OG degradation, the ratios of
114 $[\text{persulfate}]/[\text{Fe}^{2+}]$ at 1:1, 2:1, 4:1, 8:1 and 10:1 with $[\text{Fe}^{2+}] = 1 \text{ mM}$ were conducted.
115 After the optimal dosage of persulfate was obtained, the concentration of Fe^{2+} was
116 changed with a fixed concentration of persulfate. To determine the effect of temperature
117 on OG degradation, temperature varied from 293 to 313 K in different experiments. To
118 investigate the effects of co-existing inorganic ions on OG degradation, the
119 concentrations of NaCl, NaNO_3 , NaHCO_3 and NaH_2PO_4 ranged from 1 to 100 mM were
120 studied, respectively.

121

122 *2.3. Chemical analysis*

123 The concentration of OG in aqueous solution was analyzed by UV-vis
124 spectrophotometry (PerkinElmer, Lambda 20) at a maximum absorption wavelength of
125 478 nm. Total organic carbon (TOC) concentration was measured by a TOC analyzer
126 (Shimadzu TOC-5000A) after filtering the samples by the 0.45 μm filter. The
127 concentration of Fe^{2+} was determined colorimetrically using a UV-vis
128 spectrophotometer at 510 nm after adding 1,10-phenanthroline to form a colored
129 complex of Fe^{2+} -phenanthroline [27]. Persulfate ion was determined by iodometric
130 titration with sodium thiosulfate [28]. The data presented in this work were obtained
131 from duplicate experiments and the errors of measurement were estimated to be within
132 5%.

133

134 **3. Results and discussion**

135

136 *3.1. Kinetics of OG degradation*

137 The reaction of OG degradation with the persulfate/Fe²⁺ reagent versus reaction
138 time is presented in Fig. 1. It can be seen that the spectrum of light absorption by OG
139 solution before reaction consists of three main peaks at 259, 328, and 478 nm plus a
140 shoulder peak at 421 nm. While the peaks at 259 and 328 nm are assigned to its
141 aromatic rings, the peaks at 478 nm and the shoulder at 421 nm are assigned to the
142 conjugated structure formed by the azo bond [29]. As the reaction proceeded, the two
143 characteristic absorption peaks at 328 and 478 nm decreased dramatically and almost
144 disappeared after 30 min, showing that the chromophore and conjugated π^* system
145 were completely destroyed. On the other hand, the peak at 259 nm declined slowly,
146 indicating that the aromatic rings were still present. In this study, the variation of
147 absorption peak at 478 nm was applied to evaluate the extent of OG degradation. The
148 plot of $\ln(C_0/C)$ versus time (inset of Fig. 1) shows a linear relationship, indicating that
149 the OG degradation follows the first-order kinetic model below:

$$150 \quad C = C_0 \exp(k_{\text{obs}}t) \quad (4)$$

151 where C is the concentration of OG at time t ; C_0 is the initial concentration of OG and
152 k_{obs} is the observed reaction rate constant.

153 In the inset of Fig. 1, the rate constant of OG degradation was found to be 0.12
154 min^{-1} under a suitable condition ($[\text{OG}] = 0.1 \text{ mM}$, $[\text{persulfate}] = 4 \text{ mM}$, $[\text{Fe}^{2+}] = 4 \text{ mM}$,

155 pH 3.5).

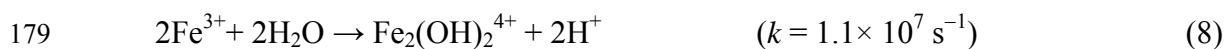
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157 3.2. Effect of pH

158 The pH value of aqueous solution plays a significant role in the degradation of
159 organic compounds. Three experiments of OG degradation with the persulfate/Fe²⁺
160 reagent were carried out at initial pH 3.5, 7.0 and 9.0, respectively. The first-order
161 kinetic rate constants for the OG degradation with different pH values were obtained
162 and are shown in Table 2. With the increase of pH, the efficiency of OG degradation
163 decreased (Fig. 2), indicating that the acidic pH is more favorable to the OG degradation
164 than neutral and alkaline pH. The decreased OG degradation in the neutral and alkaline
165 media might result from the precipitation of iron (Fe²⁺ and Fe³⁺). This result agreed with
166 our earlier reports on the Fenton's reagents [9,30]. The soluble Fe²⁺ species is stable
167 between a wide pH range of 2.0 to 9.0, while Fe³⁺ precipitation occurs at pH > 4.0 [30].
168 It has been known that when the pH value of the aqueous solution is higher than 4.0, the
169 amount of soluble Fe²⁺ could be decreased due to the formation of Fe²⁺ complexes
170 which hinder the further reaction of Fe²⁺ with persulfate. The reaction can be described
171 by the Eq. (5) [31]:



173 On the other hand, the precipitated Fe³⁺ oxyhydroxides, such as FeOH²⁺,
174 Fe₂(OH)₂⁴⁺, Fe(OH)₂⁺, Fe(OH)₃⁰ and Fe(OH)₄⁻ [31], have low efficiency to activate
175 persulfate and to produce the sulfate radicals. The formations of Fe³⁺ oxyhydroxides are
176 shown in Eqs. ((6)-(8)) below:



180 Both aspects are favored at high pH, and this precipitation could be experimentally
181 confirmed by the production of turbidity at pH 7.0. Therefore, at high pH, the low
182 activity of the catalyst leads to decrease the amounts of radicals, and then decreased
183 efficiency of OG degradation. In addition, the self-dissociation of the oxidant through
184 non-radical pathways at high pH might be another reason causing the decreased
185 efficiency of OG degradation. The feature of optimal pH ranged from 2.0 to 4.0 is a
186 characteristic of the Fenton reagent. A recent study by Rastogi et al. [32] on the
187 degradation of polychlorinated biphenyls by Fe^{2+} -peroxymonosulfate oxidative system
188 also confirmed that the higher degradation efficiency achieved at acidic pH value.
189 Therefore in this study the best pH value for the following experiments of OG oxidation
190 was chosen to be 3.5.

191

192 *3.3. Effects of persulfate and Fe^{2+} dosages*

193 Persulfate plays an important role as a source of $\text{SO}_4^{\bullet-}$ generation in the
194 persulfate/ Fe^{2+} reagent. The effect of persulfate dosage on OG degradation was
195 examined by varying the ratios of persulfate to Fe^{2+} from 1:1 to 10:1. The experimental
196 results are shown in Fig. 3 and Table 2. It can be observed that at $[\text{Fe}^{2+}] = 1 \text{ mM}$,
197 increasing the dosage of persulfate from 1 to 4 mM, equivalent to a $[\text{persulfate}]/[\text{Fe}^{2+}]$
198 ratio from 1:1 to 4:1, resulted in an increase in OG degradation from 53% to 81% within

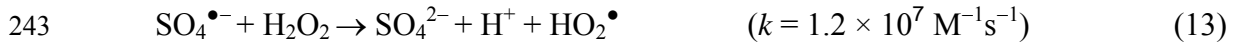
199 30 min reaction. However, further increase of the persulfate dosage beyond a
200 [persulfate]/[Fe²⁺] ratio of 4:1 resulted in only a slight increase in the OG removal. For
201 example, the efficiency of OG degradation at 30 min reaction was achieved by 81% to
202 82% while the ratio of [persulfate]/[Fe²⁺] was increased from 4:1 to 10:1. This is in
203 agreement with the observations by other researchers [19,33] who applied Fe²⁺ to
204 activate persulfate to degrade other pollutants. This phenomenon can also be observed
205 in the Fenton reagent where the excessive amount of hydrogen peroxide had a
206 detrimental effect on the degradation efficiency [9,30]. Therefore, in the following
207 experiments, while the concentration of persulfate was kept at 4 mM and the ratio of
208 [persulfate] to [OG] was 40:1, effect of Fe²⁺ dosage on the OG degradation was studied.

209 Fe²⁺ is one of the main species that can catalyze persulfate to produce SO₄^{•-}
210 radicals [34] and its existence can influence the efficiency of OG degradation
211 significantly. It should be noted that OG cannot be effectively oxidized by persulfate
212 alone. Fig. 4a showed the effect of Fe²⁺ dosage on OG degradation with different molar
213 ratios of [persulfate]/[Fe²⁺]. When the Fe²⁺ concentration varied from 0.5 to 4 mM
214 ([persulfate]/[Fe²⁺] = 8:1, 4:1, 2:1 and 1:1), the efficiency of OG degradation within 30
215 min reaction was achieved by 54%, 80%, 94% and 99%, respectively. The higher
216 efficiency of OG degradation at the higher Fe²⁺ dosage might result from the higher
217 production of SO₄^{•-} in the reaction. However, with a further increase of Fe²⁺
218 concentration up to 8 mM ([persulfate]/[Fe²⁺] = 1:2), the efficiency of OG degradation
219 was slightly reduced to 98%. It indicates that Fe²⁺ can also act as a sulfate radical
220 scavenger at its high concentration as expressed by Eq. (3) [31,35].

221 Similar results have been found in other reports [19,33,36]. Therefore, it may be
 222 concluded that while an essential amount of Fe^{2+} is required to effectively activate
 223 persulfate and to generate a sufficient amount of sulfate radicals in the reaction solution,
 224 an excess amount of Fe^{2+} would be detrimental to the OG degradation. Furthermore, the
 225 detection of Fe^{2+} (Fig. 4b) indicated that they were consumed quickly and their
 226 concentrations decreased sharply once the reaction was initiated. Under the conditions
 227 that different amounts of Fe^{2+} were added, most of Fe^{2+} were transformed to Fe^{3+} after
 228 several minutes. Therefore, how to maintain a certain amount of Fe^{2+} in the reaction
 229 solution during a long reaction time is a key technique for its practical application. By
 230 employing a suitable complexing agent in conjugation with Fe^{2+} , the amount of soluble
 231 Fe^{2+} in the reaction solution can be well controlled even the pH in bulk solution is
 232 neutral. For example, Liang et al. found an enhanced degradation efficiency of
 233 trichloroethylene by the persulfate/ Fe^{2+} reagent using ferrous citrate as a catalyst [37].

234 At the same time, the results shown in Fig. 4c indicated that an increase of Fe^{2+}
 235 concentration did result in an increase of persulfate decomposition proportionally, but
 236 no proportional increase of OG removal was achieved. This phenomenon suggests that
 237 sulfate radicals were consumed by some reactions other than with OG, as indicated in
 238 Eqs ((9)-(15)) [35,38,39]:





246

247 3.4. Effect of temperature

248 The effect of temperature on OG degradation was investigated in a rang of 293-313
 249 K. It can be seen from Fig. 5 that increasing temperature had a positive effect on the OG
 250 degradation. The efficiency of OG degradation within 5 min reaction time was
 251 increased from 76% to 100%, when the temperature increased from 293 to 313 K. Since
 252 persulfate can also be thermally activated to produce $\text{SO}_4^{\bullet-}$ [18,22], another set of
 253 experiments without Fe^{2+} at different temperatures was conducted and the results are
 254 presented in Table 2. The data showed that the rate constant, k , of OG degradation by
 255 persulfate without the activation of ferrous ions increased with the enhanced
 256 temperature, but the k values were still much lower than those activated by Fe^{2+} . These
 257 results indicate that raising temperature (lower than 323 K) is not an efficient way to
 258 activate persulfate compared to chemical activation.

259 Furthermore, according to the apparent kinetic rate constant at different
 260 temperatures, the apparent activation energy for OG degradation by the persulfate/ Fe^{2+}
 261 reagent was computed using Arrhenius equation (Eq. (16)).

262
$$k = A \exp\left(-\frac{E}{RT}\right)$$
 (16)

263 where A is the preexponential (or frequency) factor; E is the apparent activation energy
 264 (J mol^{-1}); R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the reaction absolute

265 temperature (K).

266 A good linear relationship was obtained in the Arrhenius plot of $\ln k$ versus $1/T$
267 (inset of Fig. 5). The apparent activation energy was calculated to be 92.2 kJ mol^{-1} . This
268 value may indicate that the OG degradation in aqueous solution by the persulfate/ Fe^{2+}
269 reagent requires moderate activation energy, as the thermal reaction energy has a
270 normal range of $60\text{-}250 \text{ kJ mol}^{-1}$ [40]. Liang et al. [19,21] suggested that it requires a
271 relatively high activation energy of around $108\text{-}130 \text{ kJ mol}^{-1}$ to degrade
272 trichloroethylene and 1,1,1-trichloroethane. The activation energy of the thermal crack
273 of the O–O bond of persulfate anion was also reported to be $140.2 \text{ kJ mol}^{-1}$ by Kolthoff
274 and Miller [41]. Huang et al. [42] reported the activation energy of 26 kJ mol^{-1} for the
275 degradation of bisphenol A by UV-activated persulfate. The different values may be due
276 to the structure of different target compounds. Compared to all the activation energy
277 mentioned above, the relative lower value of the OG degradation in aqueous solution by
278 the persulfate/ Fe^{2+} reagent implies that such reaction can be easily achieved.

279

280 *3.5. Effect of co-existing inorganic ions*

281 Usually, a great amount of salts are employed in various dyeing processes and the
282 strength of dissolved inorganic ions in dyeing wastewater may affect the efficiency of
283 dye degradation reaction. In this study, the effects of several inorganic ions (NO_3^- , Cl^- ,
284 HCO_3^- and H_2PO_4^-) that commonly occur in real dye-containing wastewater on the OG
285 degradation were examined in a concentration range of 1 to 100 mM, and the
286 experimental results are given in Table 3.

287 It can obviously be found from Table 3 that the concentration of inorganic ions had
288 negative effects on the OG degradation with the persulfate/Fe²⁺ reagent. The higher
289 ionic concentration in the solutions, the lower reaction rate of OG degradation occurred.
290 It might result from a decreased amount of sulfate radicals due to the high ionic
291 concentration. The result is in agreement with other studies [18,43]. It is known that
292 phosphate and bicarbonate are efficient scavengers of hydroxyl radicals and the
293 bicarbonate anions quenched the hydroxyl radicals more efficiently than phosphate [44].
294 Furthermore, it can also be found that all anions could inhibit the reaction rate of OG
295 degradation and the degree of their inhibiting effects can be ranked from low to high in
296 an order of NO₃⁻ < Cl⁻ < H₂PO₄⁻ < HCO₃⁻.

297

298 *3.6. Mineralization of OG*

299 Although the OG degradation with the persulfate/Fe²⁺ reagent occurred quickly
300 within a few minutes, the reduction of TOC was much more slowly than the OG
301 degradation, which took a few hours. Fig. 6 showed the TOC removals in the OG
302 solution with different dosages of persulfate. The rate of TOC removal was positively
303 related to the persulfate concentration in the range of 1 to 4 mM. A further increase in
304 persulfate dosage did not lead to further increase in TOC removal due to the two-edged
305 effects of per sulfate on the yields of reactive species. On one hand, more persulfate in a
306 certain range could enhance the OG degradation by supplying more sulfate radicals
307 though reaction (1). On the other hand, excessive persulfate would compete with OG for
308 sulfate radicals through reaction (15) [34].

309 Furthermore, the same dosage of hydrogen peroxide instead of persulfate was used
310 for comparison. It was found that the TOC reductions in the OG solutions with
311 hydrogen peroxide/ Fe^{2+} as the Fenton's reagent and the persulfate/ Fe^{2+} reagent were
312 achieved by 53% and 96% in 24 h, respectively. These results may suggest that the
313 persulfate/ Fe^{2+} reagent can degrade OG in aqueous solutions more completely than the
314 Fenton's reagent after an extended duration. It has been reported that the sulfate radical
315 can completely oxidize the insecticide lindane [36] and even mineralize PCBs [32].
316 Sulfate radicals have a longer half life than hydroxyl radicals mainly due to their
317 preference for electron transfer reactions while hydroxyl radicals can participate in a
318 variety of reactions with equal preference [37,45]. The high oxidation efficiency of the
319 sulfate radicals, in combination with the slow rate of consumption of precursor oxidants,
320 makes sulfate radical-based processes very effective for the degradation of recalcitrant
321 organic compounds. Sulfate radicals normally react with electron transfer process while
322 hydroxyl radicals can also react via electron-atom abstraction along with electron
323 transfer process which is less prominent in their cases [45]. As argued by Thendral et al.
324 [46], the high reactivity of the sulfate radical anion can be attributed to its redox partner
325 bisulfate/sulfate ion's ability as a leaving group. Therefore, such a feature of sulfate
326 radicals may be beneficial to the application of dyeing wastewater treatment where a
327 higher degree of mineralization is required.

328

329 **4. Conclusions**

330

331 In this work, OG as a model azo dye in aqueous solution was successfully degraded
332 by the persulfate/Fe²⁺ reagent and it was found that the reaction of OG degradation
333 follows the first-order kinetic model. Under the optimum condition ([OG] = 0.1 mM,
334 [persulfate] = 4 mM, [Fe²⁺] = 4 mM and pH 3.5), 99% of OG degradation was achieved
335 in 30 min. The apparent activation energy for OG degradation with the persulfate/Fe²⁺
336 reagent was determined to be 92.2 kJ mol⁻¹. The presence of inorganic ions had
337 inhibitory effects on the OG degradation in the sequence of NO₃⁻ < Cl⁻ < H₂PO₄⁻ <
338 HCO₃⁻. The experiments also demonstrated that the persulfate/Fe²⁺ reagent can degrade
339 OG in aqueous solution to a higher degree than the Fenton's reagent, which is beneficial
340 for mineralization of azo dyes.

341

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343

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352 **References**

- 353 [1] M. Neamtu, I. Siminiceanu, A. Yediler, A. Kettrup, Kinetics of decolorization and
354 mineralization of reactive azo dyes in aqueous solution by the UV/H₂O₂ oxidation,
355 *Dyes Pigments* 53 (2002) 93–99.
- 356 [2] M. Styliidi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic
357 degradation of Acid Orange 7 in aqueous TiO₂ suspensions, *Appl. Catal. B:*
358 *Environ.* 47 (2004) 1892–1901.
- 359 [3] A. Szygula, E. Guibal, M.A. Palacin, M. Ruiza, A.M. Sastre, Removal of an
360 anionic dye (Acid Blue 92) by coagulation-flocculation using chitosan, *J. Environ.*
361 *Manage.* 90 (2009) 2979–2986.
- 362 [4] A. Khaled, A. El Nemr, A. El-Sikaily, O. Abdelwahab, Removal of Direct N
363 Blue-106 from artificial textile dye effluent using activated carbon from orange
364 peel: Adsorption isotherm and kinetic studies, *J. Hazard. Mater.* 165 (2009)
365 100–110.
- 366 [5] G. Capar, U. Yetis, L. Yilmaz, Membrane based strategies for the pre-treatment of
367 acid dye bath wastewaters, *J. Hazard. Mater.* 135 (2006) 423–430.
- 368 [6] K. Vinodgopal, D.E. Wynkoop, P.V. Kamat, Environmental photochemistry on
369 semiconductor surfaces: photosensitized degradation of a textile azo dye, Acid
370 Orange 7, on TiO₂ particles using visible light, *Environ. Sci. Technol.* 30 (1996)
371 1660–1666.
- 372 [7] Y.B. Xie, X.Z. Li, Interactive oxidation of photoelectrocatalysis and electro-Fenton
373 for azo dye degradation using TiO₂-Ti mesh and reticulated vitreous carbon
374 electrodes, *Mater. Chem. Phys.* 95 (2006) 39–50.

- 375 [8] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.M.
376 Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein
377 Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated
378 titania, *Appl. Catal. B: Environ.* 39 (2002) 75–90.
- 379 [9] X.R. Xu, H.B. Li, W.H. Wang, J.D. Gu, Degradation of dyes in aqueous solutions
380 by the Fenton process, *Chemosphere* 57 (2004) 595–600.
- 381 [10] J. Fernandez, J. Bandara, A. Lopez, P. Buffat, J. Kiwi, Photoassisted Fenton
382 degradation of nonbiodegradable azo dye in Fe-free solutions mediated by cation
383 transfer membranes, *Langmuir* 15 (1999) 185–192.
- 384 [11] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using
385 low iron concentration of Fenton and Fenton-like system, *Chemosphere* 58 (2005)
386 1409–1414.
- 387 [12] X.R. Xu, H.B. Li, W.H. Wang, J.D. Gu, Decolorization of dyes and textile
388 wastewater by potassium permanganate, *Chemosphere* 59 (2005) 893–898.
- 389 [13] A. Aleboyeh, M.E. Olya, H. Aleboyeh, Oxidative treatment of azo dyes in aqueous
390 solution by potassium permanganate, *J. Hazard. Mater.* 162 (2009) 1530–1535.
- 391 [14] J. Fernandez, P. Maruthamuthu, A. Renken, J. Kiwi, Bleaching and photobleaching
392 of Orange II within seconds by the oxone/Co²⁺ reagent in Fenton-like process, *Appl.*
393 *Catal. B: Environ.* 49 (2004) 207–215.
- 394 [15] Z.Y. Yu, L. Kiwi-Minsker, A. Renken, J. Kiwi, Detoxification of diluted azo-dyes
395 at biocompatible pH with the oxone/Co²⁺ reagent in dark and light processes, *J.*
396 *Mol. Catal. A: Chem.* 252 (2006) 113–119.

- 397 [16] J.E.B. McCallum, S.A. Madison, S. Alkan, R.L. Depinto, R.U.R. Wahl, Analytical
398 studies on the oxidative degradation of the reactive textile dye Uniblue A, *Environ.*
399 *Sci. Technol.* 34 (2000) 5157–5164.
- 400 [17] A.H. Gemeay, A.F.M. Habib, M.A.B. El-Din, Kinetics and mechanism of the
401 uncatalyzed and Ag(I)-catalyzed oxidative decolorization of Sunset Yellow and
402 Ponceau 4R with peroxydisulfate, *Dyes Pigments* 74 (2007) 458–463.
- 403 [18] K.C. Huang, R.A. Couttenye, G.E. Hoag, Kinetics of heat-assisted persulfate
404 oxidation of methyl *tert*-butyl ether (MTBE), *Chemosphere* 49 (2002) 413–420.
- 405 [19] C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ
406 remediation of TCE. I. Activated by ferrous ion with and without a
407 persulfate–thiosulfate redox couple, *Chemosphere* 55 (2004) 1213–1223.
- 408 [20] T.K. Lau, W. Chu, N.J.D. Graham, The aqueous degradation of butylated
409 hydroxyanisole by UV/S₂O₈²⁻: study of reaction mechanisms via dimerization and
410 mineralization, *Environ. Sci. Technol.* 41 (2007) 613–619.
- 411 [21] C.J. Liang, Z.S. Wang, C.J. Bruell, Influence of pH on persulfate oxidation of TCE
412 at ambient temperatures, *Chemosphere* 66 (2007) 106–113.
- 413 [22] R.H. Waldemer, P.G. Tratnyek, R.L. Johnson, J.T. Nurmi, Oxidation of chlorinated
414 ethenes by heat-activated persulfate: kinetics and products, *Environ. Sci. Technol.*
415 41 (2007) 1010–1015.
- 416 [23] S.X. Li, D. Wei, N.K. Mak, Z.W. Cai, X.R. Xu, H.B. Li, Y. Jiang, Degradation of
417 diphenylamine by persulfate: performance optimization, kinetics and mechanism, *J.*
418 *Hazard. Mater.* 164 (2009) 26–31.

- 419 [24] R. Woods, I.M. Kolthoff, E.J. Meehan, Arsenic(IV) as an intermediate in the
420 induced oxidation of Arsenic(III) by the Iron(II)-persulfate reaction and the
421 photoreduction of Iron(III). I. Absence of oxygen. *J. Am. Chem. Soc.* 85 (1963)
422 2385–2390.
- 423 [25] J.H. Sun, X.L. Wang, J.Y. Sun, R.X. Sun, S.P. Sun, L.P. Qiao, Photocatalytic
424 degradation and kinetics of Orange G using nano-sized Sn(IV)/TiO₂/AC
425 photocatalyst, *J. Mol. Catal. A: Chem.* 260 (2006) 241–246.
- 426 [26] S.P. Sun, C.J. Li, J.H. Sun, S.H. Shi, M.H. Fan, Q. Zhou, Decolorization of an azo
427 dye Orange G in aqueous solution by Fenton oxidation process: Effect of system
428 parameters and kinetic study, *J. Hazard Mater.* 161 (2009) 1052–1057.
- 429 [27] APHA, AWWA, WEF, Standards Methods for the Examination of Water and
430 Wastewater, APHA, Washington, DC, 1998.
- 431 [28] I.M. Kolthoff, V.A. Stenger, Volumetric analysis, In: Titration Methods:
432 Acid-Base, Precipitation, and Complex Reactions, vol. II, Second Revised Edition.
433 Interscience Publishers, Inc., New York, 1947.
- 434 [29] J. Deng, J. Jiang, Y. Zhang, X. Lin, C. Du, Y. Xiong, FeVO₄ as a highly active
435 heterogeneous Fenton-like catalyst towards the degradation of Orange II, *Appl.*
436 *Catal. B: Environ.* 84 (2008) 468–473.
- 437 [30] X.R. Xu, Z.Y. Zhao, X.Y. Li, J.D. Gu, Chemical oxidative degradation of methyl
438 *tert*-butyl ether in aqueous solution by Fenton's reagent, *Chemosphere* 55 (2004)
439 73–79.
- 440 [31] A. Stefánsson, Iron(III) hydrolysis and solubility at 25 °C, *Environ. Sci. Technol.*

- 441 41 (2007) 6117–6123.
- 442 [32] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Sulfate radical-based ferrous-
443 peroxymonosulfate oxidative system for PCBs degradation in aqueous and
444 sediment systems, *Appl. Catal. B: Environ.* 85 (2009) 171–179.
- 445 [33] S.Y. Oh, H.W. Kim, J.M. Park, H.S. Park, C. Yoon, Oxidation of polyvinyl alcohol
446 by persulfate activated with heat, Fe^{2+} , and zero-valent iron, *J. Hazard Mater.* 168
447 (2009) 346–351.
- 448 [34] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition
449 metals with common oxidants, *Environ. Sci. Technol.* 38 (2004) 3705–3712.
- 450 [35] W.J. Mcelroy, S.J. Waygood, kinetics of the reactions of the SO_4^- radical with SO_4^- ,
451 $\text{S}_2\text{O}_8^{2-}$, H_2O and Fe^{2+} , *J. Chem. Soc. Faraday Trans.* 86 (1990) 2557–2564.
- 452 [36] J.S. Cao, W.X. Zhang, D.G. Brown, D. Sethi, Oxidation of lindane with Fe(II)
453 activated sodium per sulfate, *Environ. Eng. Sci.* 25 (2008) 221–228.
- 454 [37] C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ
455 remediation of TCE. II. Activated by chelated ferrous ion, *Chemosphere* 55 (2004)
456 1225–1233.
- 457 [38] J.D. Laat, T.G. Le, Kinetics and modeling of the Fe(III)/ H_2O_2 system in the
458 presence of sulfate in acidic aqueous solutions, *Environ. Sci. Technol.* 39 (2005)
459 1811–1818.
- 460 [39] M.S. Tsao, W.K. Wilmarth, The aqueous chemistry of inorganic free radicals. I. the
461 mechanism of the photolytic decomposition of aqueous persulfate ion and evidence
462 regarding the sulfatehydroxyl radical interconversion equilibrium, *J. Phys. Chem.*

463 63 (1959) 346–353.

464 [40] R.G. Mortimer, Physical Chemistry, Burlington, M.A. Elsevier Academic Press,
465 2008.

466 [41] I.M. Kolthoff, J.K. Miller, The chemistry of persulfate: I. The kinetics and
467 mechanism of the decomposition of the persulfate ion in aqueous medium, *J. Am.*
468 *Chem. Soc.* 73 (1951) 3055–3059.

469 [43] Y.F. Huang, Y.H. Huang, Identification of produced powerful radicals involved in
470 the mineralization of bisphenol A using a novel UV- $\text{Na}_2\text{S}_2\text{O}_8/\text{H}_2\text{O}_2\text{-Fe(II,III)}$
471 two-stage oxidation process, *J. Hazard. Mater.* 162 (2009) 1211–1216.

472 [43] A. Burbano, D.D. Dionysiou, M. Suidan, Oxidation kinetics and effect of pH on the
473 degradation of MTBE with Fenton reagent, *Water Res.* 39 (2005) 107–118.

474 [44] J. Kochany, E. Lipczynskakochany, Application of the EPR Spin-trapping
475 technique for the investigation of the reactions of carbonate, bicarbonate, and
476 phosphate anions with hydroxyl radicals generated by the photolysis of H_2O_2 ,
477 *Chemosphere* 25 (1992) 1769–1782.

478 [45] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, Rate constants and mechanism
479 of reaction of $\text{SO}_4^{\bullet-}$ with aromatic-compounds, *J. Am. Chem. Soc.* 99 (1977)
480 163–164.

481 [46] P. Thendral, S. Shailaja, M.S. Ramachandran, Nickel peroxide: A more probable
482 intermediate in the Ni(II)-catalyzed decomposition of peroxomonosulfate, *Int. J.*
483 *Chem. Kinet.* 39 (2007) 320–327.

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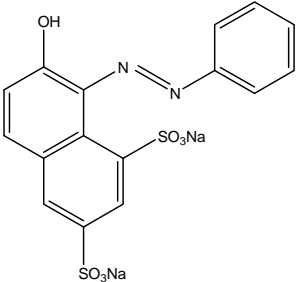
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504 Table 1

505 Physiochemical characteristics of Orange G.

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Dye	Chemical structure	Molecular formula	MW (g mol ⁻¹)	λ_{\max} (nm)
Orange G		C ₁₆ H ₁₀ N ₂ Na ₂ O ₇ S ₂	452	478

507

509 Table 2

510 The first-order rate constants for OG degradation by persulfate/Fe²⁺ reagent at different
 511 reaction conditions. [OG] = 0.1 mM.

pH	[S ₂ O ₈ ²⁻]/[Fe ²⁺]/[OG] molar ratios	[S ₂ O ₈ ²⁻] (mM)	[Fe ²⁺] (mM)	Temp. (K)	Rate constant (min ⁻¹)	
					<i>k</i>	<i>R</i> ²
					3.5	40:10:1
7.0	40:10:1	4	1	293	0.0085	0.915
9.0	40:10:1	4	1	293	0.0037	0.908
3.5	10:10:1	1	1	293	0.014	0.910
3.5	20:10:1	2	1	293	0.027	0.960
3.5	80:10:1	8	1	293	0.042	0.964
3.5	100:10:1	10	1	293	0.043	0.963
3.5	40:5:1	4	0.5	293	0.020	0.972
3.5	40:20:1	4	2	293	0.076	0.938
3.5	40:40:1	4	4	293	0.12	0.951
3.5	40:80:1	4	8	293	0.11	0.942
3.5	40:40:1	4	4	303	0.38	0.987
3.5	40:40:1	4	4	313	1.32	0.980
3.5	40:0:1	4	0	293	0.0005	0.960
3.5	40:0:1	4	0	303	0.0009	0.987
3.5	40:0:1	4	0	313	0.0059	0.979

513 Table 3

514 The pseudo-first order rate constants, k_{obs} (min^{-1}), for OG degradation with co-existing
515 substances. $[\text{OG}] = 0.1 \text{ mM}$, $[\text{Fe}^{2+}] = 4 \text{ mM}$, $[\text{persulfate}] = 4 \text{ mM}$, $\text{pH} = 3.5$.

516

Substances	1 mM	10 mM	100 mM
No		0.12	
Cl^-	0.067	0.022	0.0075
NO_3^-	0.11	0.084	0.029
HCO_3^-	0.0008	0.0002	0
H_2PO_4^-	0.0025	0.0009	0

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Figure captions

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531 Fig. 1 UV-Vis spectral changes of OG in aqueous solutions by persulfate/ Fe^{2+} reagent
532 over reaction time (inset: the first-order linear relationship; $[\text{OG}] = 0.1 \text{ mM}$, $[\text{Fe}^{2+}] = 4$
533 mM , $[\text{persulfate}] = 4 \text{ mM}$, $\text{pH } 3.5$).

534

535 Fig. 2 Effect of pH on OG degradation by persulfate/ Fe^{2+} reagent. $[\text{OG}] = 0.1 \text{ mM}$,
536 $[\text{Fe}^{2+}] = 1 \text{ mM}$, $[\text{persulfate}] = 4 \text{ mM}$.

537

538 Fig. 3 Effect of initial concentration of persulfate on OG degradation by persulfate/ Fe^{2+}
539 reagent. $[\text{OG}] = 0.1 \text{ mM}$, $[\text{Fe}^{2+}] = 1 \text{ mM}$, $\text{pH } 3.5$.

540

541 Fig. 4 (a) Effect of ferrous ion on OG degradation by persulfate/ Fe^{2+} reagent; (b)
542 Change in the remaining Fe(II) concentration over time; (c) Change in the remaining
543 persulfate concentration over time. ($[\text{OG}] = 0.1 \text{ mM}$, $[\text{persulfate}] = 4 \text{ mM}$, $\text{pH } 3.5$)

544

545 Fig. 5 Effect of temperature on OG degradation by persulfate/ Fe^{2+} reagent. $[\text{OG}] = 0.1$
546 mM , $[\text{Fe}^{2+}] = 4 \text{ mM}$, $[\text{persulfate}] = 4 \text{ mM}$, $\text{pH } 3.5$.

547

548 Fig. 6 Effect of persulfate dosage on OG mineralization and comparison with peroxide.
549 $[\text{OG}] = 0.1 \text{ mM}$, $[\text{Fe}^{2+}] = 4 \text{ mM}$, $\text{pH } 3.5$; (...): $4 \text{ mM H}_2\text{O}_2$.

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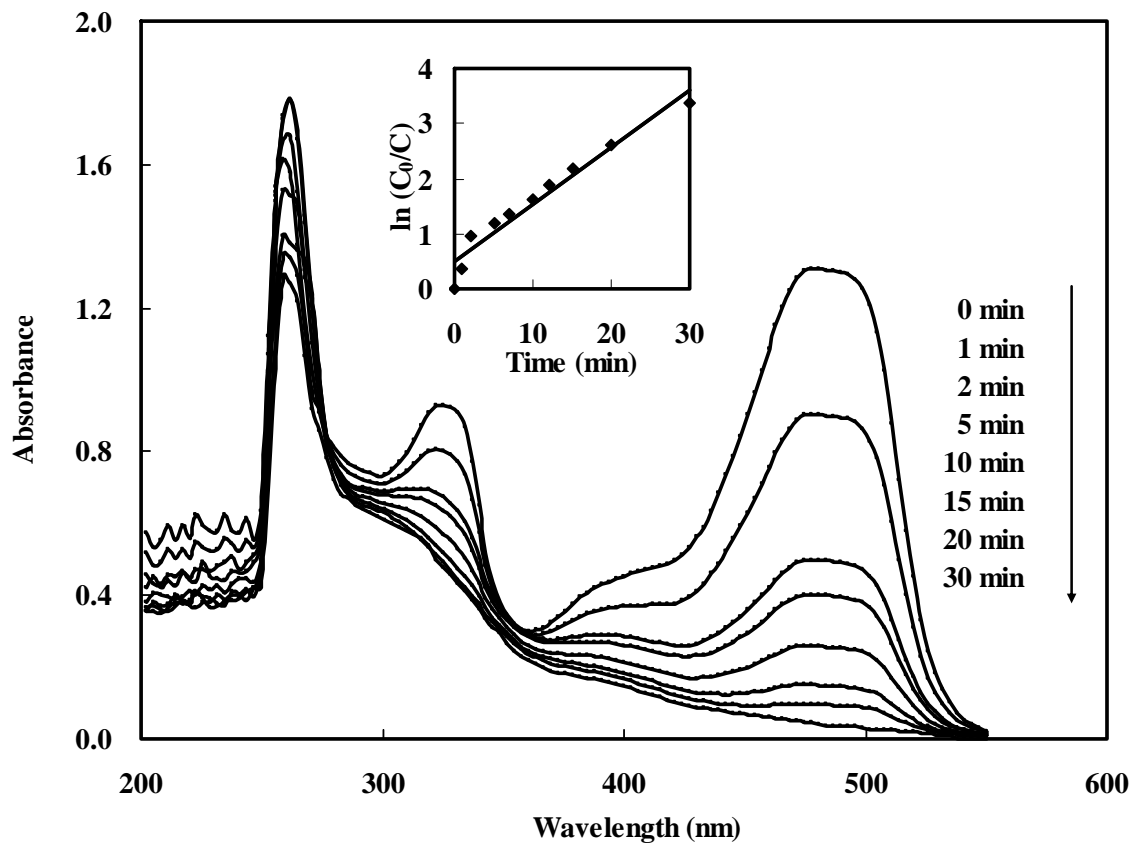


Fig. 1

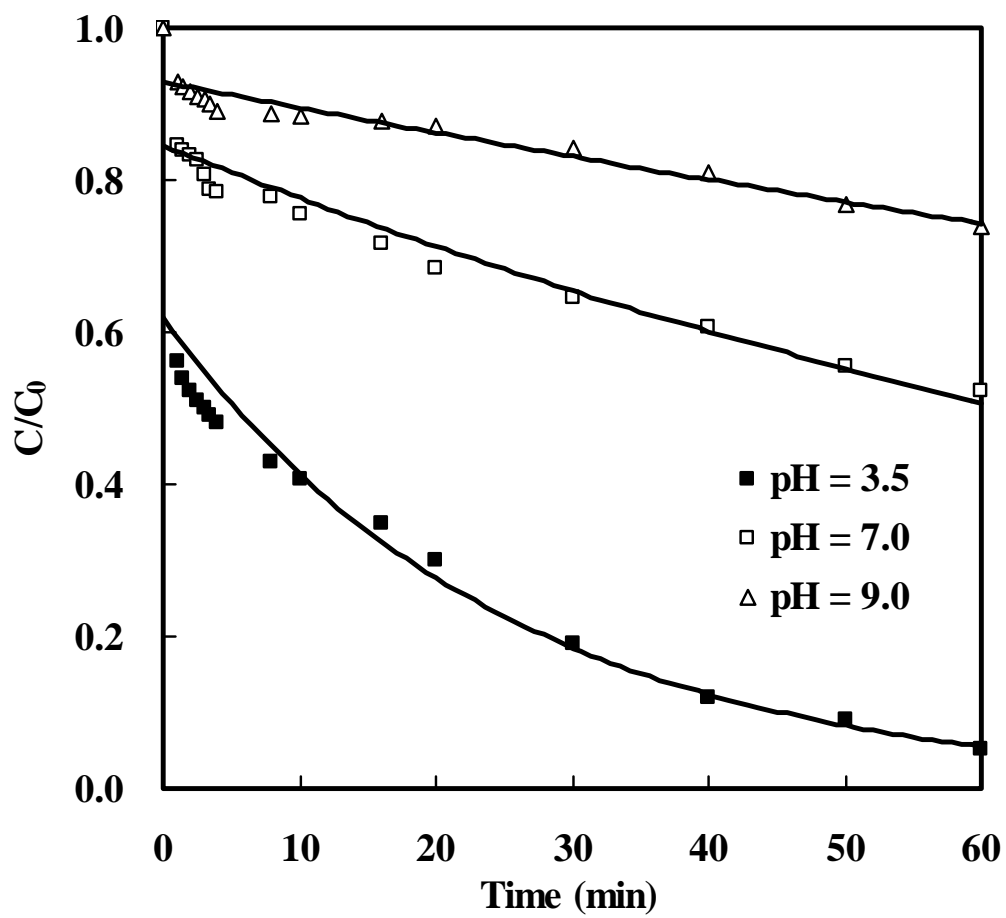
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Fig. 2

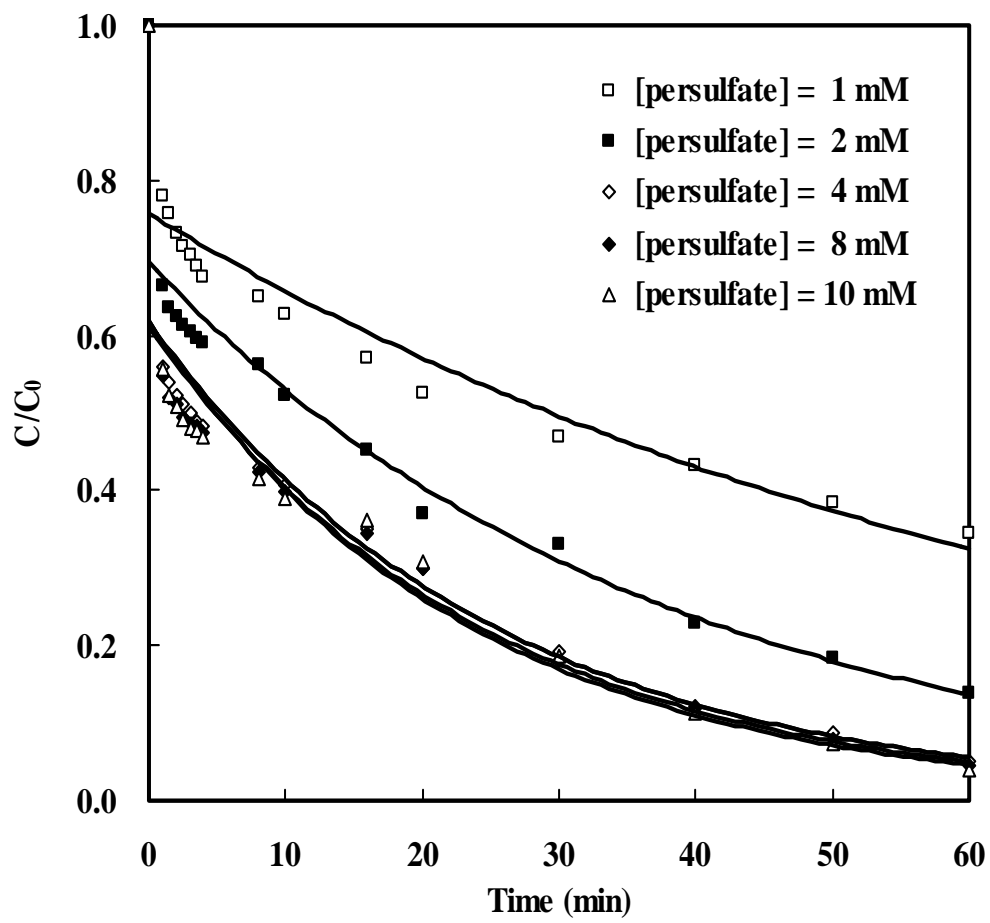
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Fig. 3

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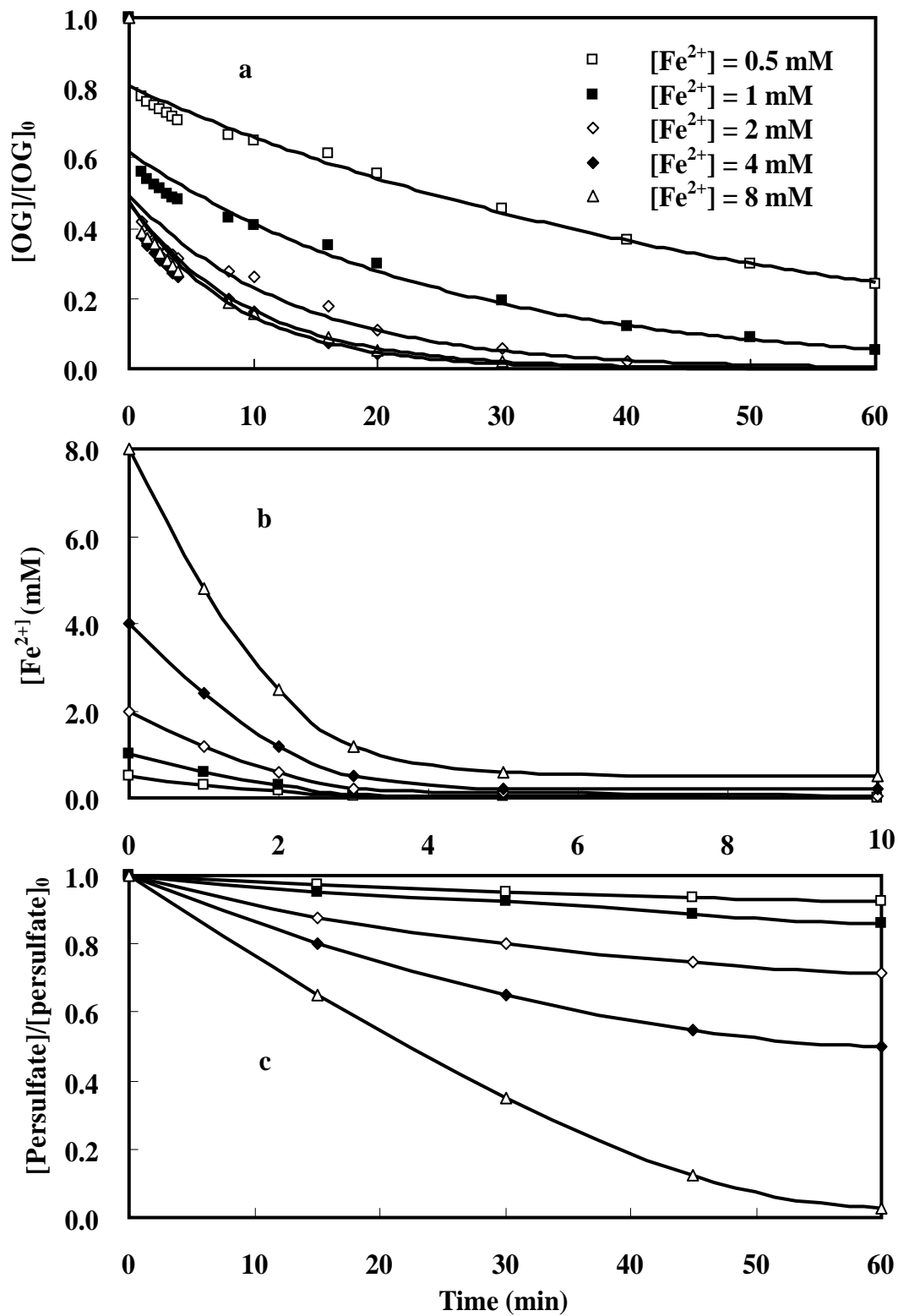


Fig. 4

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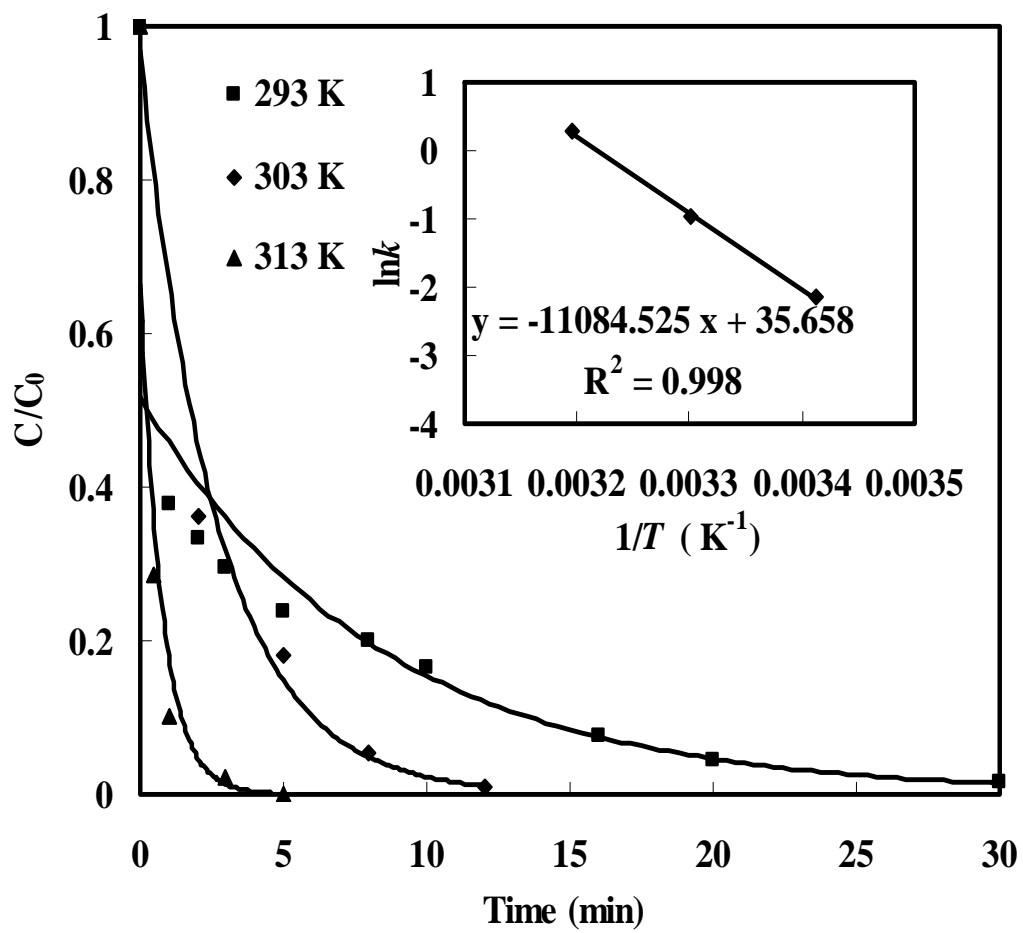


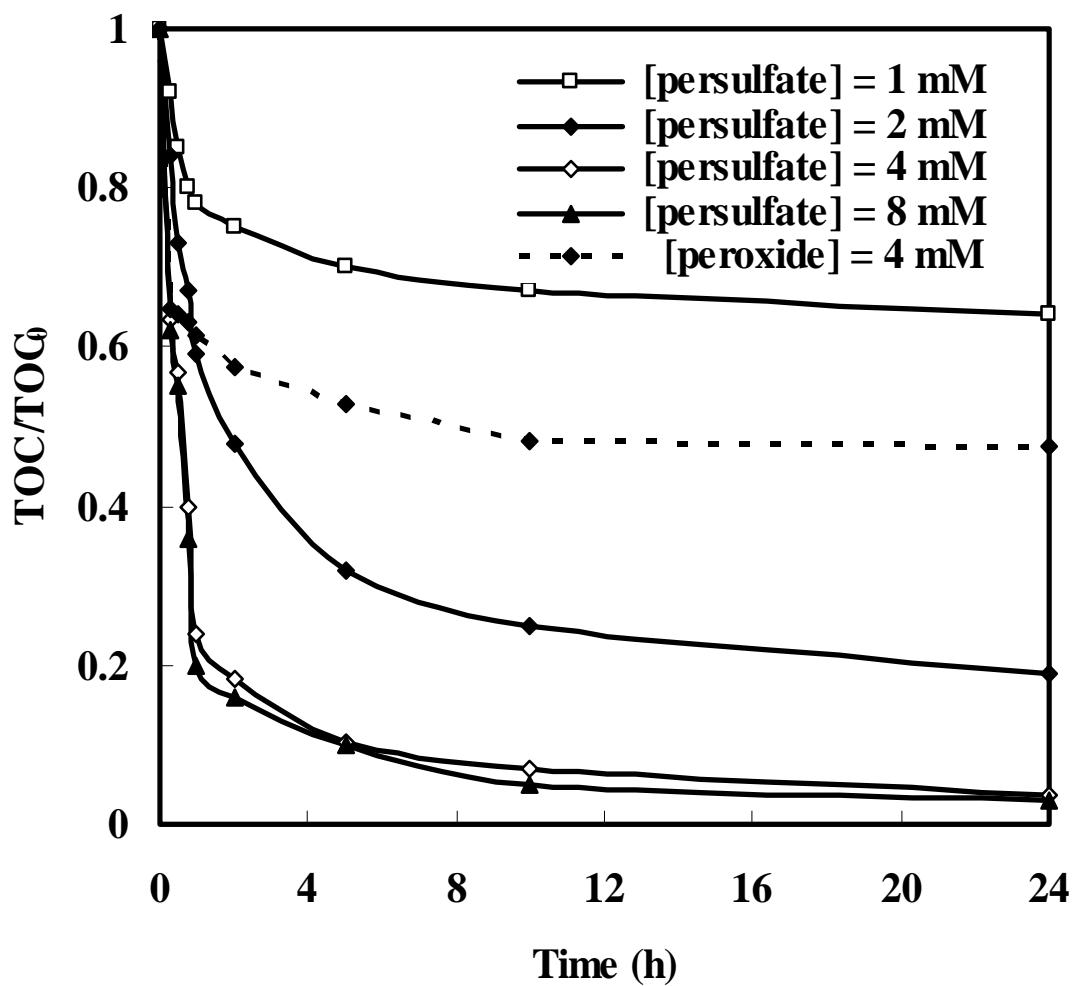
Fig. 5

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Fig. 6