

Heterogeneous photodegradation of bisphenol A with iron oxides and oxalate in aqueous solution

F. B. Li^{a, b}, X. Z. Li^{a, *}, X. M. Li^b and T. X. Liu^b, J. Dong^b

^a *Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China.*

^b *Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environment and Soil Science, Guangzhou, 510650, China.*

Abstract

To understand the degradation of endocrine disrupting chemicals (EDCs) with existence of iron oxides and polycarboxylic acids in the natural environment, the photodegradation of bisphenol A (BPA) at the interface of iron oxides under UV illumination was conducted. Four iron oxides were prepared by a hydrothermal process and then sintered at different temperatures of 65°C, 280°C, 310°C and 420°C named “IO-65”, “IO-280”, “IO-310”, and “IO-420”, respectively. The prepared iron oxides were characterized by X-ray diffraction (XRD) and Brunauer- Emmett- Teller (BET) methods. The XRD pattern of IO-65 showed a crystal structure of lepidocrocite (γ -FeOOH) and that of IO-420 demonstrated a crystal structure of hematite (α -Fe₂O₃), while IO-280 and IO-310 have the mixed crystal structures of maghemite (γ -Fe₂O₃) and hematite. The BET results revealed that the specific surface areas decreased with the increase of sintering temperature. The results demonstrated that the photodegradation of BPA depends strongly on the properties of iron oxides and oxalate, and pH. The properties of iron oxides influenced strongly the dependence of the BPA degradation on the oxalate concentration. The optimal initial concentrations of oxalate for BPA degradation under UV illumination were determined to be 2.0, 2.0, 2.4, and 2.0 mM for IO-65, IO-280, IO-310, and IO-420, respectively. The first-order kinetic constants k for BPA degradation under UV illumination in the presence of oxalate with the optimal initial concentration are ranked as IO-280 > IO-65 > IO-280 > IO-420. The experiments demonstrated that the optimal pH value should be in the range of 3-4. Furthermore, the dependence of BPA degradation should be also attributable to the formation of the dissolved Fe-oxalate in the solution and the adsorbed Fe-oxalate on the surface of iron oxides, and also the formation of hydrogen peroxide.

Keywords: Bisphenol A; Iron oxides; Oxalic acid; Photodegradation;

* *Corresponding author. Tel: (852) 2766 6016; Fax: (852) 2334 6389; E-mail address: cexzli@polyu.edu.hk or cefbli@soil.gd.cn (The first author)*

34 1. Introduction

35 Iron oxides are a kind of natural minerals and geocatalysts, widely existing in the earth's crust
36 and also suspending in aqueous streams, aerosol, clouds, and fogs as fine particles [1]. Major iron
37 oxides including hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), and lepidocrocite
38 ($\gamma\text{-FeOOH}$) show semiconductor properties with a narrow band gap of 2.0-2.3 eV and could be
39 photoactive under solar irradiation [2]. The photocatalytic degradation of organic pollutants on the
40 surface of iron oxides is very feasible and useful for removal of organic pollutants from
41 contaminated soils and waters [3].

42 It is noticeable that iron oxides and polycarboxylic acids can form a photochemical system to
43 conduct a photo-Fenton-like reaction with much higher quantum efficiency than that of the
44 $\text{Fe}(\text{OH})^{2+}$ photochemical process or photocatalytic reaction with iron oxides alone [4-6]. Since the
45 polycarboxylic acids are also abundant in natural environment [7,8], this photochemical oxidation
46 process can directly utilize natural matters such as iron oxides and polycarboxylic acids together
47 with solar energy to decompose organic pollutants economically. It is meaningful to investigate the
48 photochemical reaction in such an iron oxide-polycarboxylate complex system so as to better
49 understand the natural transformation of organic pollutants. Among the family of polycarboxylic
50 acids, oxalic acid is one of the most active members. In fact, the photochemistry of Fe(III)-oxalate
51 complexes in natural aquatic environment, fog, precipitates, tropospheric aerosols and soil solutions
52 have received considerable attention over the past three decades [9-13], because the iron
53 oxide-oxalate exhibits strong ligand-to-metal charge absorption bands in the UV and visible region.
54 A number of investigations focused on ferrioxalate/UV and ferrioxalate/ H_2O_2 /UV systems for
55 wastewater treatment [14-17]. Since they are homogeneous photochemical reactions with artificial
56 addition of H_2O_2 , these reactions do not occur in the natural environment. In fact, the photochemical
57 reaction of iron oxide-oxalate complexes involves both mechanisms of the homogeneous reaction in
58 aqueous solution and also the heterogeneous reaction on the surface of iron oxide [18-20], which
59 highly relies on the characteristics of iron oxides and oxalate content.

60 Bisphenol A (BPA) as the raw materials of epoxy and polycarbonate resins has been
61 extensively used in softeners, fungicides, and similar products at about 1,700 tons annually all over
62 the world [21]. BPA can be released into the natural environment as well as surface water during
63 manufacturing, processing and application. Since it was detected in aquatic environment, air and soil
64 from ppb to ppm levels [21], BPA as one of endocrine disrupting chemicals has been paid great
65 attention to its removal and degradation. Even though many literatures had reported the
66 photocatalytic degradation of BPA by using TiO_2 , TiO_2 -zeolite, TiO_2 pillared montmorillonite
67 [22-24] for wastewater treatment, to the best of our knowledge, the photocatalytic degradation of
68 BPA in an iron oxide-oxalate complex system has been only investigated up to a limited extent. This

69 study was aimed at investigating the photocatalytic reaction of BPA with iron oxides and oxalate
70 under UV illumination in order to determine the key factors affecting such a heterogeneous reaction.
71

72 **2. Experimental**

73 *2.1. Preparation of iron oxides*

74 Lepidocrocite (γ -FeOOH) samples were first prepared using ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$),
75 sodium nitrite (NaNO_2) and hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$) with the following procedure [25]:
76 20 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 28 g of $(\text{CH}_2)_6\text{N}_4$, and 7 g of NaNO_2 were dissolved in 400, 80, and 80 mL of
77 distilled water, respectively; the three solutions were well mixed to form a bluish green precipitate;
78 the precipitate was remained in the solution and aged at 65°C for 3 h, then centrifuged and washed
79 three times with 95% alcohol and other three times with distilled water to remove anions and
80 organic impurities; after dried at 65°C for 48 h, the precipitate became dehydrated gel and was
81 ground as γ -FeOOH; then the γ -FeOOH sample was sintered at 3 different temperatures of 280, 310,
82 and 420°C for 2 h, respectively. Eventually, one non-sintered iron oxide (IO-65) and three sintered
83 iron oxides (IO-280, IO-310, and IO-420) were obtained.
84

85 *2.2. Characterization of Iron Oxides*

86 To determine the crystal phase composition of iron oxides samples, X-ray diffraction (XRD)
87 measurement was carried out using a Rigaku D/MAX-III A diffractometer with $\text{CuK}\alpha$ radiation ($\lambda =$
88 0.15418 nm). The accelerating voltage of 35 kV and an emission current of 30 mA were applied.
89 The specific surface area, micropore surface area, and total pore volume were measured by the
90 Brunauer-Emmett-Teller (BET) method [26,27], in which the N_2 adsorption at -196°C was applied
91 and a Carlo Erba Sorptometer was used.
92

93 *2.3. Experimental setup and procedures*

94 A Pyrex cylindrical photoreactor with an effective volume of 250 mL was used to conduct all
95 photocatalytic reaction experiments, in which an 8-W UV lamp (Luzchem Research, Inc.) with the
96 main emission at 365 nm is positioned at the centre of the vessel as a UV light source. Light
97 intensity ($I = 1.2$ mW cm^{-2}) was determined using a black-ray ultraviolet meter (Model No J221).
98 This cylindrical photoreactor is surrounded by a circulating water jacket to control temperature at
99 $25 \pm 2^\circ\text{C}$ during the reaction, and is covered with aluminium foil to keep away from any indoor light
100 irradiation. The BPA chemical was purchased from Aldrich. The reaction suspension was prepared
101 by adding 0.25 g of iron oxide powder into 250 mL of BPA solution or a mixture solution of BPA
102 and oxalic acid. Prior to photoreaction, the suspension was magnetically stirred in the dark for 30
103 min to establish an adsorption/ desorption equilibrium status. During the photoreaction, the aqueous

104 suspension was irradiated by UV light with constant aeration. During each experiment, several
105 analytical samples were taken from the suspension at the given time intervals for analyses after
106 centrifuged for 20 min and filtered through a 0.45 μm Millipore filter to remove the particles.

107

108 2.4. Analytical methods

109 The BPA concentration was determined by liquid chromatography (Finnigan LCQ DUO) with a
110 UV detector. While a Pinnacle II C18 column (5 μm beads, 250 \times 4.6 mm ID) and a mobile phase
111 (70% HCN: 30% water) at a flow rate of 0.8 mL min^{-1} were used for BPA separation, a maximum
112 absorption wavelength at 278 nm was used for BPA determination. The oxalic acid concentration
113 was determined by ion chromatography (Dionex DX-120), in which an ion column (IONPAC
114 ASII-AC) together with a guard column (AGII-HC 4 mm) was used and a mobile phase consisting
115 of 15 mM KOH solution was operated at a flow rate of 1.5 mL min^{-1} . Total Fe concentration was
116 analysed by atomic absorption spectrometry and ferrous ion (Fe^{2+}) concentration was analyzed by
117 the ferrozine method. In this study, the adsorbed $\text{Fe}^{3+/2+}$ species and Fe^{2+} species on the surface of
118 iron oxides were extracted by using 0.1 mol L^{-1} HCl solution under 30 min stirring prior to the
119 above analyses. The H_2O_2 concentration in the solution was determined using a H_2O_2 -photometer
120 (Lovibond ET-8600 Germany) at LED 528 nm with a detection limit of 0.03 mg L^{-1} .

121

122 3. Results and Discussion

123 3.1. Crystal structure and physical properties of iron oxides

124 The prepared 4 iron oxide samples were first examined by XRD to determine their crystal
125 structure. The XRD patterns as shown in Fig. 1 confirmed that the IO-65 sample has 8 characteristic
126 peaks of (020), (120), (031), (111), (051), (220), (151), and (231), attributable to lepidocrocite, and
127 the IO-420 sample has other 8 characteristic peaks of (012), (104), (110), (113), (024), (116), (214),
128 and (300), attributable to hematite. Furthermore, the XRD results showed that the IO-280 and
129 IO-310 samples contain some characteristic peaks, attributable to both of maghemite and hematite.
130 It can be seen that IO-280 has a broad peak at $2\theta = 35.7^\circ$ representing a maghemite peak of (311)
131 and also a hematite peak of (110); IO-310 has a less broad peak at the same position, indicating a
132 reduced fraction of maghemite; and IO-420 has a sharp peak at the similar position representing
133 hematite only. These results indicate that the thermal treatment of $\gamma\text{-FeOOH}$ samples achieved a
134 phase transfer from lepidocrocite to maghemite and further to hematite. It is obvious that the content
135 of hematite indicated by two main peaks of (104) with a d_{hkl} -value of 2.69 and (110) with a
136 d_{hkl} -value of 2.51 in the iron oxides increases with the increased sintering temperature in this study.
137 Unfortunately, the exact fraction of maghemite/hematite can not be determined from these limited

138 results. The crystal sizes of IO-65, IO-280, IO-310, and IO-420 were 13.7, 23.2, 32.6, and 54.7 nm
139 deduced from Sherrer's formula with their strongest peak of XRD based on Fig. 1

140

141 **[Fig. 1]**

142

143 To investigate the pore structure and adsorption property of iron oxides, a set of nitrogen
144 adsorption/desorption tests was carried out and their results are presented in Fig. 2. The results
145 showed that the isotherms of iron oxides had a typical shape of Type IV curves [26], and the wide
146 hysteresis loops of IO-65 exhibited a typical pattern of Type H2 at a relative pressure from about 0.4
147 to 1 while the width of hysteresis loops became narrow gradually with the increase of sintering
148 temperature a typical pattern of Type H3 at a relative pressure from about 0.70-1, 0.75-1 and 0.86-1
149 for IO-280, IO-310, and IO-420, respectively. The above results indicated that iron oxides might
150 have a porous structure [27]. The results also showed that iron oxides had mainly a
151 disordered-porous structure and their pore volume varied against the pore size in the main range of
152 2-110 nm with different maximum portions at about 5, 11, 16, and 25 nm for Io-65, IO-280, IO-310,
153 IO-420, respectively. Obviously, the pore size increased significantly with the increased temperature.
154 The specific surface area and total pore volume of iron oxide samples were measured by the BET
155 method. The specific surface areas of IO-65, IO-280, IO-310, and IO-420 were found to be 115.44,
156 75.91, 60.48 and 29.40 m² g⁻¹, respectively, while their total pore volumes were 0.2977, 0.3485,
157 0.3762 and 0.2747 m³ g⁻¹, respectively. These results show that the specific surface area of the iron
158 oxides decreases with the increased sintering temperature. However, it seems that the total pore
159 volume does not follow the same pattern of surface area, in which the IO-310 sample has the highest
160 total pore volume among all samples.

161

162 **[Fig. 2]**

163

164 *3.2 Photodegradation of BPA under different reaction conditions.*

165 Fig. 3 showed BPA degradation with an initial concentration (C_{BPA}) of 0.11 mM under the
166 different reaction conditions. Without UV light (dark) and only with 1.2 mM oxalic acid and 1.0 g
167 L⁻¹ IO-310, the BPA concentration was only slightly decreased by 2.7% because of adsorption on the
168 surface of iron oxide (curve a). Under UV illumination without iron oxide and oxalic acid, the
169 removal percentage of BPA was about 3.3% after 60 min (curve b). Under UV illumination with 1.0
170 g L⁻¹ IO-310 and without oxalic acid, the removal percentage of BPA was 23.7% after 60 min and
171 its first-order kinetic constants was determined to be $0.45 \times 10^{-2} \text{ min}^{-1}$ ($R^2=0.993$) (curve c). When
172 both 1.2 mM oxalic acid and 1.0 g L⁻¹ iron oxide were added into the BPA solution to form the

173 photo-Fenton-like system under UV illumination (curve d, e, f, g), the removal percentage of BPA
174 was significantly increased up to 68.1%, 84.0%, 67.4%, and 60.8% after 40 min reaction, and the
175 first-order kinetic constants k were determined to be 3.08×10^{-2} , 5.06×10^{-2} , 2.93×10^{-2} , and $2.58 \times$
176 10^{-2} min^{-1} for IO-65, IO-280, IO-310, and IO-420, respectively. Obviously, the k value was ranked
177 in an order of IO-280 > IO-65 > IO-310 > IO-420. The results showed that iron oxides, oxalate, and
178 UV light all play most important roles in the BPA degradation reaction. The BPA photodegradation
179 should be greatly enhanced in the cooperation of iron oxide and oxalate, and also strongly depended
180 on the properties of iron oxides. The photochemical process in the presence of iron oxide and
181 oxalate together has been described in detail [5, 6, 10, 13]. In this suspension, oxalic acid is first
182 adsorbed on the surface of iron oxide to form iron oxide-oxalate complexes of $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$,
183 which can be excited to form a series of radicals including oxalate radical $(\text{C}_2\text{O}_4)^{\bullet-}$, carbon-centered
184 radical $(\text{CO}_2)^{\bullet-}$, superoxide ion $(\text{O}_2^{\bullet-})$, $\bullet\text{OOH}$ and hydroxyl radical $(\bullet\text{OH})$, and form H_2O_2 . And
185 Fe-oxalate complexes of $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$ can form in the solution. It must be noted that this
186 photochemical process happened both on the surface of iron oxide as a heterogeneous reaction and
187 in the solution as a homogeneous reaction. To compare the efficiency in iron oxide-oxalate system
188 with that in Fe(III)-oxalate homogeneous system, a homogeneous system was set up by adding 0.75
189 mM Fe^{3+} (the same amount in IO-310 suspension) and 1.2 mM oxalate to degrade BPA under UV
190 illumination ($I = 1.2 \text{ mW cm}^{-2}$) and the results are shown as curve h in Fig. 3. The results showed
191 that the BPA removal was only 58.8%, much lower than that in curve f, indicating that the
192 degradation of BPA in aqueous iron oxide-oxalate suspension was achieved by both of reaction in
193 the solution and also the reaction on the surface of iron oxides.

194

195 **[Fig. 3]**

196

197 3.3. Photodegradation of BPA with iron oxides and oxalate

198 As an alternative technique to the photo-Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UVC}$), ferric ion (Fe^{3+}) can
199 also catalyze the H_2O_2 decomposition in acidic solution under UVA illumination to form
200 hydroperoxyl radicals ($\text{HO}_2\bullet$) and hydroxyl radicals ($\bullet\text{OH}$) known as the photo-Fenton-like reaction
201 ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UVA}$). Since iron oxide and oxalate can form an iron oxide-oxalate complex to enhance
202 the photo-Fenton-like reaction [4-6], the effect of oxalic acid on BPA photodegradation becomes
203 very interesting. Four sets of experiments under UV illumination with an initial BPA concentration
204 of 0.11 mM and an iron oxide dosage of 1.0 g L^{-1} were carried out using IO-65, IO-280, IO-310, and
205 IO-420, respectively. In each set of experiments, the different initial concentrations of oxalic acid
206 (C_{ox}) up to 4.4 mM were applied. The experiments demonstrated that IO-280 achieved the best
207 performance of BPA degradation and the results with different C_{ox} are shown in Fig. 4. The

208 experimental data were also fitted using the first-order kinetic model to determine its kinetic
209 constant (k) at different C_{ox} , as showed in Fig. 5. It can be seen clearly that the BPA degradation
210 strongly depended on C_{ox} in the 4 sets of experiments. The reaction rate was significantly increased
211 with the increase of oxalate concentration at its low dosage, but was slightly inhibited with an
212 excessive amount of oxalate. These results indicate that an optimal dosage of oxalate between 2.0
213 and 3.0 mM achieved the fastest rate of BPA degradation under these experimental conditions.

214

215 **[Fig. 4]**

216 **[Fig. 5]**

217

218 These experiments demonstrated clearly that the presence of iron oxides and oxalate in
219 cooperation can greatly accelerate the BPA degradation reaction under UV illumination. The
220 first-order kinetic constant (k) was increased 22.6 times from $2.0 \times 10^{-3} \text{ min}^{-1}$ without oxalate to 4.52
221 $\times 10^{-2} \text{ min}^{-1}$ with oxalate for IO-65, 19.6 times for IO-280, 12.1 times for IO-310, and 11.4 times for
222 IO-420 under UV illumination with the optimal C_{ox} . These results provide very useful information
223 to better understand the reaction mechanism of BPA degradation in such an iron oxide-oxalate
224 complex system. If we compare the kinetic k values under the optimized reaction conditions, the rate
225 of BPA degradation under UV illumination can be ranked as IO-280 > IO-310 > IO-65 > IO-420.

226

227 Actually our experiments demonstrated that oxalate itself can also be degraded in such a
228 photo-Fenton-like reaction significantly. To better understand this photocatalytic reaction, the
229 degradation of oxalate as a side reaction was also investigated. In the above experiments, oxalate
230 concentration was analyzed at different time intervals, and two sets of results are shown in Fig. 6. It
231 can be seen that after 40 min reaction, oxalate was significantly degraded by nearly 80% under UV
232 illumination. The first-order kinetic constant (k) for oxalate degradation under UV illumination was
233 determined to be 3.73×10^{-2} , 4.18×10^{-2} , 3.62×10^{-2} , and $3.05 \times 10^{-2} \text{ min}^{-1}$ for IO-65, IO-280,
234 IO-310, and IO-420, respectively. These results indicate that the degradation of oxalate depends
235 strongly on characters of iron oxides. IO-280 achieved the highest activity for degrading oxalate
236 under UV illumination. The kinetic constant k values for oxalate degradation under UV illumination
237 follows the orders of IO-280 > IO-65 > IO-310 > IO-420. It should be noted that the orders of
238 reaction rate for oxalate degradation are same as that of BPA degradation under UV illumination in
239 such a photo-Fenton like reaction system.

240

241 **[Fig. 6]**

242

243 3.4 The effect of pH value on BPA photodegradation.

244 The pH value is also an important factor to affect such a photo-Fenton-like reaction. Two sets
245 of experiments were conducted under UV illumination, respectively. The initial concentrations of
246 oxalic acid and BPA were 2.4 mM and 0.11 mM, respectively. The variations of pH vs. reaction
247 time are plotted in Fig. 7. All experiments demonstrated a rapid increase of pH especially at the
248 early stage of reaction. It can be seen that the pH increased significantly from the initial values of
249 2.90, 2.90, 2.85, and 2.71 to 5.01, 5.23, 4.92, and 4.00 after 40 min reaction under UV illumination
250 for IO-65, IO-280, IO-310, and IO-420, respectively. It is believed that the pH increase mainly
251 resulted from the loss of oxalic acid. While IO-280 achieved the most oxalate reduction under UV
252 illumination, they pH raised to the highest levels. A slight pH increase just prior photoreaction
253 was also found due to the strong adsorption of oxalate onto the surface of iron oxides in the dark. It
254 was also noted that the order of the increased amount of pH value from high to low was in
255 agreement with the order of the k value for oxalate degradation with 4 iron oxides.

256

257 **[Fig. 7]**

258

259 To investigate the effect of pH on the BPA photodegradation, a set of experiments was carried
260 out with 1.0 g L⁻¹ iron oxides in the presence of BPA ($C_{\text{BPA}} = 0.11$ mM) and oxalate ($C_{\text{ox}} = 1.2$ mM)
261 under UV illumination. Before the reactions, pH in the solution was adjusted by adding NaOH or
262 HClO₄. The experimental data at different pH values were fitted by using the first-order model and
263 the dependence of the first-order kinetic constant k values on pH value was presented in Fig. 8. The
264 results showed that BPA photodegradation should depend strongly on pH in the iron oxide-oxalate
265 system. Obviously, there was an optimal pH value for BPA photodegradation. The maximal k values
266 for different iron oxides were determined to be 3.48×10^{-2} min⁻¹ at pH 3.95 for IO-65, 5.73×10^{-2}
267 min⁻¹ at pH 3.93 IO-280, 3.32×10^{-2} min⁻¹ 3.93 for IO-310, and 2.73×10^{-2} at pH 3.69 for IO-420,
268 respectively. The BPA degradation would be inhibited significantly when pH was beyond the range
269 of about 3-4. Obviously, the pH value should be a very important factor affecting this
270 photo-Fenton-like reaction.

271

272 Balmer and Sulzberger [13] had reported that when the pH was at around 4, the main
273 Fe(III)-oxalate species were $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^-$ and $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$, which are highly photoactive. In our
274 experiment, the iron oxide-oxalate complex system at pH value of about 3-4 might have a higher
275 concentration of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^-$ and $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$ in the solution, and $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^-$ and
276 $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$ on the surface. When the pH value increased to about 4-5, Fe(III)-oxalate species
277 were mainly $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^+$ and $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)]^+$, which are low photoactive. When pH was up to 6, the

278 Fe^{3+} and Fe^{2+} almost can not exist in the solution and the predominant Fe(III) and Fe(II) species
279 were Fe(II)-OH and Fe(III)-OH as the precipitate, which might hardly be photoactive.

280

281 **[Fig. 8]**

282

283 3.5. Formation of hydrogen peroxide and Fe-oxalate species

284 Hydrogen peroxide (H_2O_2) is an important intermediate in the aqueous iron oxides and oxalate
285 suspension by irradiating with UV light. During the photoreaction, H_2O_2 could be formed and then
286 decomposed by reacting with Fe^{2+} species, simultaneously. It was found in the experiments that its
287 concentration was at a low level of below 0.3 mg L^{-1} as shown in Fig. 9. In the reaction using
288 IO-420, the highest H_2O_2 concentration was determined to be 0.13 mg L^{-1} at 5 min reaction and then
289 H_2O_2 concentration decreased quickly below the detection limit of 0.03 mg L^{-1} afterwards. In the
290 other three reactions using IO-65, IO-280, IO310, and IO-420, H_2O_2 concentration varied in the
291 range of $0.05\text{-}0.3 \text{ mg L}^{-1}$. These results confirmed that the H_2O_2 formation is really involved in such
292 a photo-Fenton-like reaction, but its accumulated concentration was at a low level of blow 0.3 mg
293 L^{-1} .

294

295 **[Fig. 9]**

296

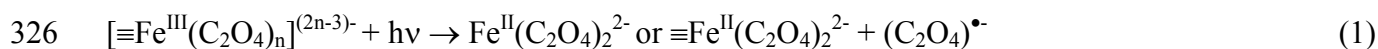
297 During the photochemical reactions, some Fe-oxalate complexes of $[\equiv\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$ and
298 $[\equiv\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_n]^{2-2n}$ on the surface of iron oxide and $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_n]^{3-2n}$ and $[\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_n]^{2-2n}$ in the
299 solution can also be formed. The formation of Fe-oxalate species will be indispensable to the
300 formation of hydrogen peroxide. To study the formation of Fe-oxalate species, the experiments
301 using different catalysts (IO-65, IO-280, IO-310, and IO-420) were conducted under UV
302 illumination with $C_{\text{ox}}=1.2 \text{ mM}$ and $C_{\text{BPA}}=0.11 \text{ mM}$, in which dissolved Fe^{3+} and Fe^{2+} species were
303 monitored during the BPA degradation reaction, as showed in Fig. 10A, while adsorbed $\text{Fe}^{3+/2+}$
304 species were showed in Fig. 10B. Fig. 10A showed that the concentration of dissolved Fe^{3+} species
305 was much higher than that of dissolved Fe^{2+} species, and was the highest at the beginning of
306 photoreaction and then decreased gradually along with reaction time for IO-65, IO-280 and IO-310.
307 To be contrast, the concentration of dissolved Fe^{3+} species for IO-420 increased gradually from 0 to
308 30 min, and then decreased slightly. Obviously, IO-310 was dissolved at the fastest rate and IO-420
309 was dissolved at the slowest rate. The concentration of dissolved Fe^{2+} species increased sharply at
310 the first few minutes of the reaction, and then either gradually reduced after a peak time for IO-65,
311 IO-280 and IO-310, while that increased gradually along time for IO-420. It is well known that
312 ferric ion (Fe^{3+}) can form ferric hydroxide ($\text{Fe}(\text{OH})_3$) and well precipitate from aqueous solution in a

313 pH range of 5-9. It is believed that the reduction of dissolved Fe^{2+/3+} species at the later stage of the
 314 reaction resulted from the precipitation of some insoluble Fe-containing compounds such as
 315 Fe(OH)₃ because pH jumped quickly from the initial pH below 3 up to almost 5 within the first 5
 316 min, as shown in Fig. 7. However, the variation of adsorbed Fe^{3+/2+} species was significantly
 317 different with that of dissolved Fe^{3+/2+} species. Fig. 10B showed that the amount of adsorbed Fe³⁺
 318 species on the catalyst surface had a declined trend with the increased reaction time in general, that
 319 increased at the first 5 min for IO-65 and at the first 10 min for IO-420, and then gradually
 320 decreased at the peaks, while that decreased consistently along the reaction for IO-280 and IO-310.
 321 In contrast, the amount of adsorbed Fe²⁺ species had an increased trend throughout the reaction and
 322 reached the higher levels at the later stage of reaction.

323

324 **[Fig. 10]**

325



330

331 The experimental results showed that the formation of adsorbed Fe^{3+/2+}-oxalate species on the
 332 surface of IO-420 was difficult and also resulted in a low concentration of dissolved Fe^{3+/2+}-oxalate
 333 in the bulk solution, because of its pure composition of α-Fe₂O₃ with more stable thermodynamics
 334 than other iron oxides, which means that, the less amount of Fe^{3+/2+}-oxalate species led to the lower
 335 photochemical activity. It is interesting that the *k* values for oxalate degradation followed an order of
 336 IO-280 > IO-65 > IO-310 > IO-420, and the *k* values for BPA degradation in the presence of 2.4
 337 mM oxalate followed the same order. The equations 1-3 indicate that the reaction of oxalate
 338 degradation can form oxalate radical (C₂O₄)^{•-}, carbon-centered radical (CO₂)^{•-}, and superoxide ion
 339 (O₂^{•-}). Therefore, the faster oxalate degradation, implying a more effective electron transfer, may
 340 lead to the more rapid BPA degradation. In addition, the experiments in this study confirmed that the
 341 amount of adsorbed Fe²⁺-oxalate species on the surfaces of different iron oxides in the order of
 342 IO-280 > IO-65 > IO-310 > IO-420. If it is believed that the formation of adsorbed Fe²⁺-oxalate
 343 species on the surface of iron oxides were attributable to the electron transfer between the adsorbed
 344 Fe³⁺-oxalate species and oxalate, the higher amount of adsorbed Fe²⁺-oxalate species on the surface
 345 of iron oxides would imply the higher efficiency of electron transfer from oxalate. In summary, it
 346 can be seen that both the formation of adsorbed Fe²⁺-oxalate species on the iron oxides and oxalate

347 degradation reaction could affect the BPA degradation reaction in an interactive way. The exact
348 mechanism needs to be further explored in the future studies.

349

350 **4. Conclusions**

351 The experiments in this study confirmed that the iron oxides sintered at different temperatures
352 have different crystal structures and their specific surface areas decreased with the increased
353 sintering temperature. The BPA degradation is primarily affected by the properties of iron oxides.
354 The existence of oxalate together with iron oxides can enhance much faster degradation of BPA in
355 aqueous solution than iron oxides alone. It was found that the concentration of oxalate (C_{ox}) was a
356 critical factor affecting the BPA degradation. In the meantime, oxalate degradation, pH, and the
357 formation of hydrogen peroxide and Fe-oxalate species also play the important roles in the reaction.

358

359 **Acknowledgements**

360 The authors would thank the Research Grant Committee of Hong Kong Government for
361 financial support to this work (RGC No: PolyU 5170/04E) and also thank China National Natural
362 Science Foundation (Project No. 20377011) and Guangdong Natural Science Foundation (Key
363 Project No.036533).

364

365 **References**

- 366 [1] U. Schwertmann, R.M. Cornell, Iron oxides in the laboratory: preparation and characterization.
367 Second ed., WILEY-VCH, 2000.
- 368 [2] J.K. Leland, A.J. Bard, *J. Phys. Chem.* 91 (1981) 5076.
- 369 [3] M.A.A. Schoonen, Y. Xu, D.R. Strongin, *J. Geochem. Explor.* 62 (1998) 201.
- 370 [4] Y.G. Zuo, Y.W. Deng, *Chemosphere* 35 (1997) 2051.
- 371 [5] C. Siffert, B. Sulzberger, *Langmuir* 7 (1991) 1627.
- 372 [6] B.C. Faust, J. Allen, *Environ. Sci. Technol.* 27 (1993) 2517.
- 373 [7] B.W. Strobel, *Geoderma* 99 (2001) 169.
- 374 [8] J.F. Ma, S.J. Zheng, H. Matsumoto, S. Hiradate, *Nature* 390 (1997) 569.
- 375 [9] A. Bozzi, T. Yuranova, J. Mielczarski, A. Lopez, J. Kiwi, *Chem. Commun.* 19 (2002) 2202.
- 376 [10] P. Mazellier, B. Sulzberger, *Environ. Sci. Technol.* 35 (2001) 3314.
- 377 [11] V. Nadtochenko, J. Kiwi, *J. Chem. Soc. Faraday Trans.* 93 (1997) 2373.
- 378 [12] Y.G. Zuo, J. Holgné, *Environ. Sci. Technol.* 26 (1992) 1014.
- 379 [13] M.E. Balmer, B. Sulzberger, *Environ. Sci. Technol.* 33 (1999) 2418.
- 380 [14] P. Huston, J.J. Pignatello, *Environ. Sci. Technol.* 30 (1996) 3457.
- 381 [15] J. Jeong, J. Yoon, *Water Res.* 38 (2004) 3531.
- 382 [16] Y. Lee, J. Jeong, C. Lee, S. Kim, J. Yoon, *Chemosphere* 51 (2003) 901.
- 383 [17] X.Z. Li, M. Zhang, H. Chua, *Water Sci. Technol.* 33 (1996) 111-118.

- 384 [18] R.M. Smith, A.E. Martell, *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 2
385 and 3 *Inorganic Complexes/Other Organic Ligands*.
- 386 [19] B. Sulzberger, H. Laubscher, *Mar. Chem.* 50 (1995) 103.
- 387 [20] Q.G. Mulazzani, *J. Phys. Chem.* 90 (1986) 5347.
- 388 [21] I.T. Cousins, C.A. Staples, G.M. Klecka, D. Mackay, *Hum. Ecol. Risk Assess.* 8 (2002) 1107.
- 389 [22] K. Chiang, T.M Lim, L. Tsen, C.C. Lee, *Appl. Catal. A: Gen.* 261 (2004) 225.
- 390 [23] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, *Environ. Sci. Technol.* 37 (2003) 1048.
- 391 [24] N. Watanabe, S. Horikoshi, H. Kawabe, Y. Sugie, J.C. Zhao, H. Hidaka, *Chemosphere* 52
392 (2003) 851.
- 393 [25] P.G. Hall, N. S. Clarke, S.C.P. Maynard, *J. Phys. Chem.* 99 (1995) 5666.
- 394 [26] S.L. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London,
395 1982.
- 396 [27] J.G. Yu, J.C. Yu, M.K.P. Leung, W.K. Ho, B. Cheng, X.J. Zhao, J.C. Zhao, *J. Catal.* 217 (2003)
397 69.
- 398

399 **List of Figure Captions**

400

401 FIG. 1 XRD patterns of the iron oxides

402

403 FIG. 2 Pore volume distribution of iron oxides and the nitrogen adsorption-desorption isothermal
404 curves of iron oxides at -196°C

405

406 FIG. 3 Photodegradation of 0.11 mM BPA under different conditions: (a) 1.2 mM oxalic acid + 1.0
407 g L⁻¹ IO-310, (b) UV, (c) UV + 1.0 g L⁻¹ IO-310, (d) 1.0 g L⁻¹ IO-65 + UV + 1.2 mM oxalic
408 acid, (e) 1.0 g L⁻¹ IO-280 + UV + 1.2 mM oxalic acid, (f) 1.0 g L⁻¹ IO-310 + UV + 1.2 mM
409 oxalic acid, (g) 1.0 g L⁻¹ IO-420 + UV + 1.2 mM oxalic acid, (h) 0.75 mM Fe³⁺ + UV + 1.2
410 mM oxalic acid

411

412 FIG. 4 Effect of the initial concentration of oxalic acid on the BPA degradation with the initial
413 concentration of 0.11 mM under UV illumination by using IO-65 (A), IO-280 (B), IO-310 (C),
414 and IO-420 (D)

415

416 FIG. 5 Dependence of the first-order kinetic constants of the BPA degradation on the initial
417 concentration of oxalic acid under UV light illumination

418

419 FIG. 6 Dependence of the first-order kinetic constant k value on the pH value in the solution by
420 using 1.0 g L⁻¹ iron oxides in the presence of BPA with the initial concentration of 0.11 mM
421 and oxalate with the initial concentration of 1.2 mM under UV light

422

423 FIG. 7 Effect of iron oxides with the dosage of 1 g L⁻¹ on the photodegradation of oxalate under UV
424 light illumination in the presence of $C_{ox} = 2.4$ mM and $C_{BPA} = 0.11$ mM

425

426 FIG. 8 Effect of iron oxides with the dosage of 1 g L⁻¹ on the variation of pH under UV light
427 illumination in the presence of $C_{ox} = 2.4$ mM and $C_{BPA} = 0.11$ mM

428

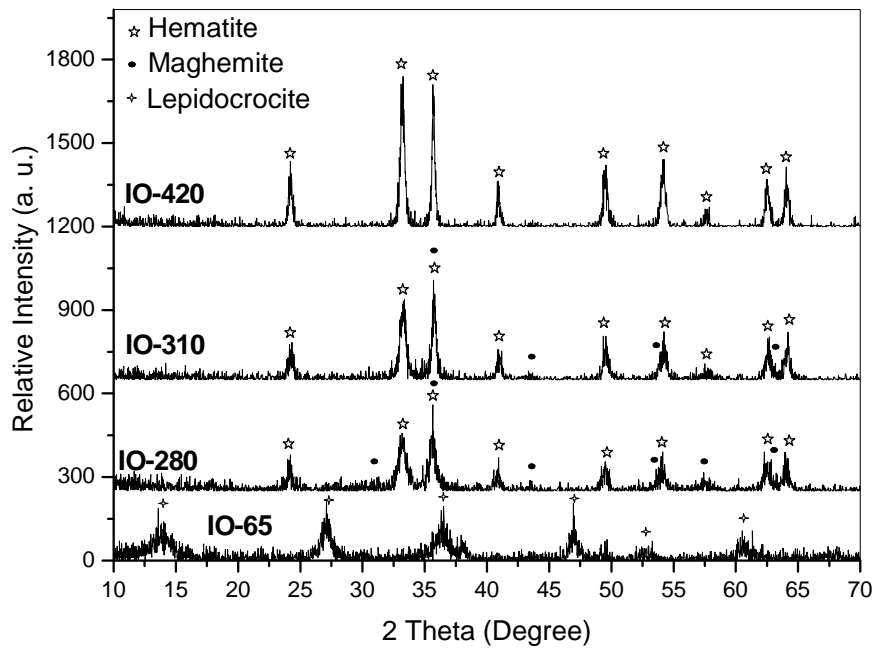
429 FIG. 9 Effect of iron oxides with the dosage of 1 g L⁻¹ on the formation of peroxide hydrogen under
430 UV light illumination in the presence of $C_{ox} = 2.4$ mM and $C_{BPA} = 0.11$ mM

431 Fig. 10 Concentration of dissolved Fe³⁺ and Fe²⁺ species in the solution (A) and adsorbed Fe³⁺ and
432 Fe²⁺ species on the surface (B) plots on reaction time with $C_{ox}^0 = 2.4$ mM and $C_{BPA} = 0.11$ mM
433 under UV illumination

434

435
436
437

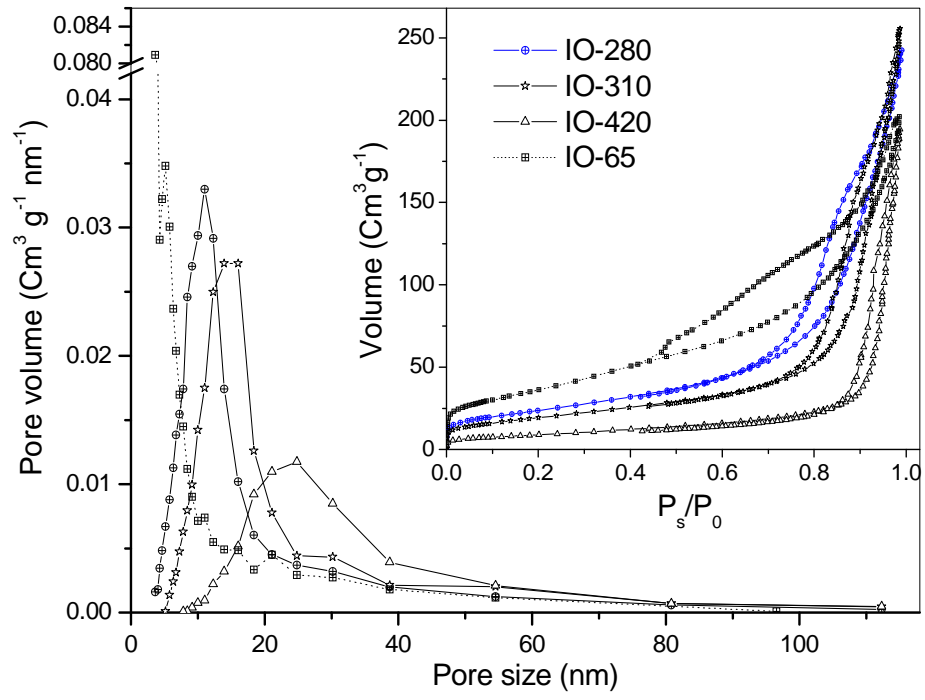
FIG. 1



438
439
440
441

442
443
444

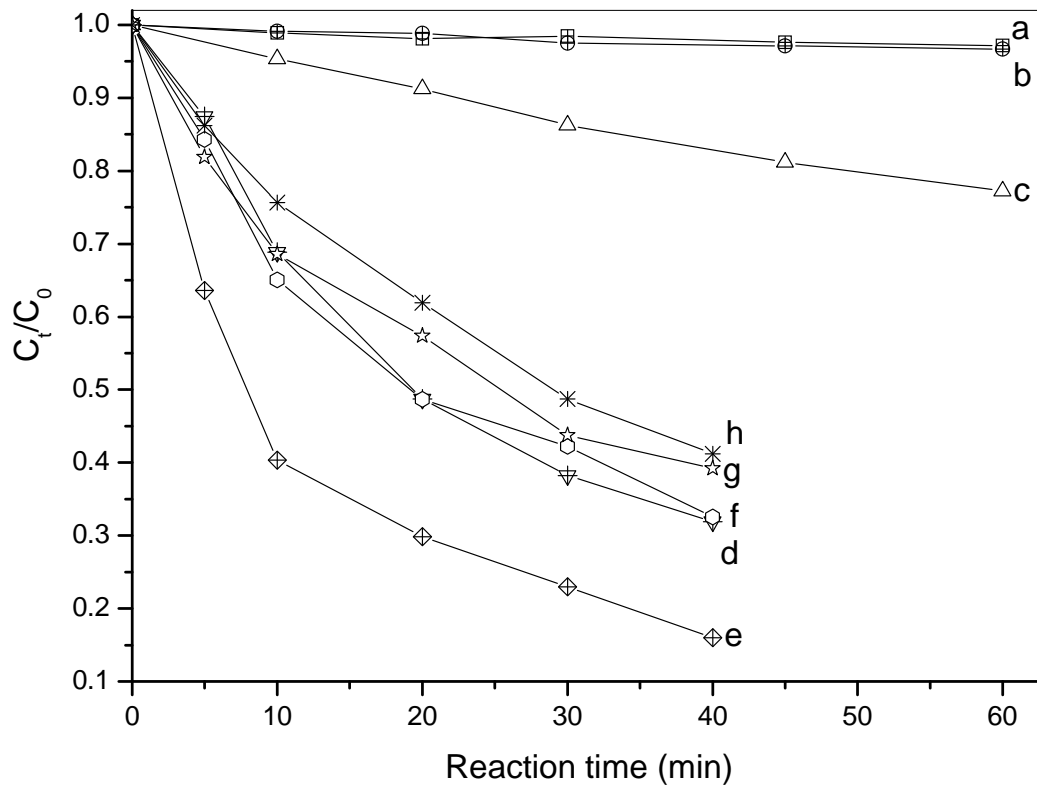
FIG. 2



445
446
447
448
449

450
451
452
453
454

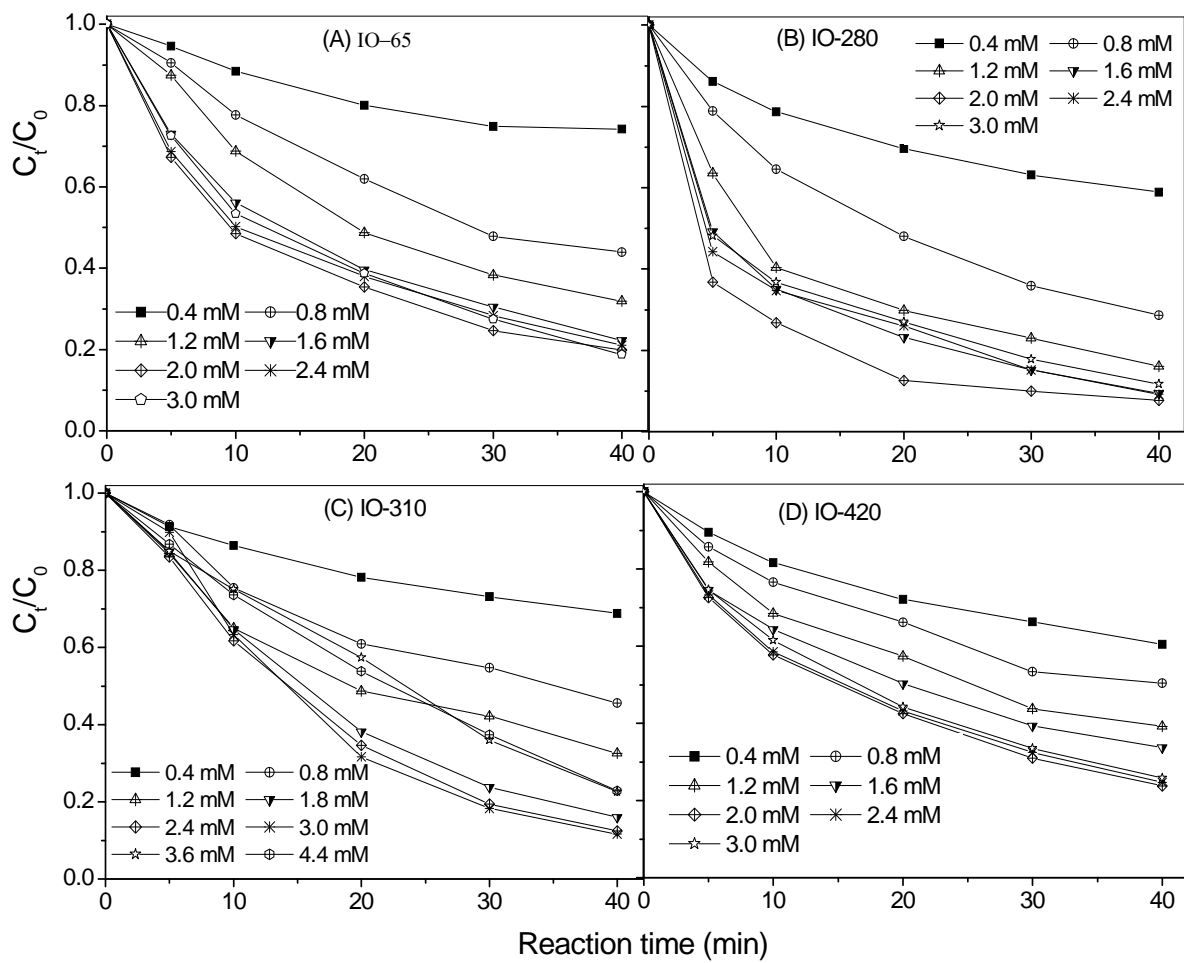
FIG. 3



455
456
457
458

459
460
461
462

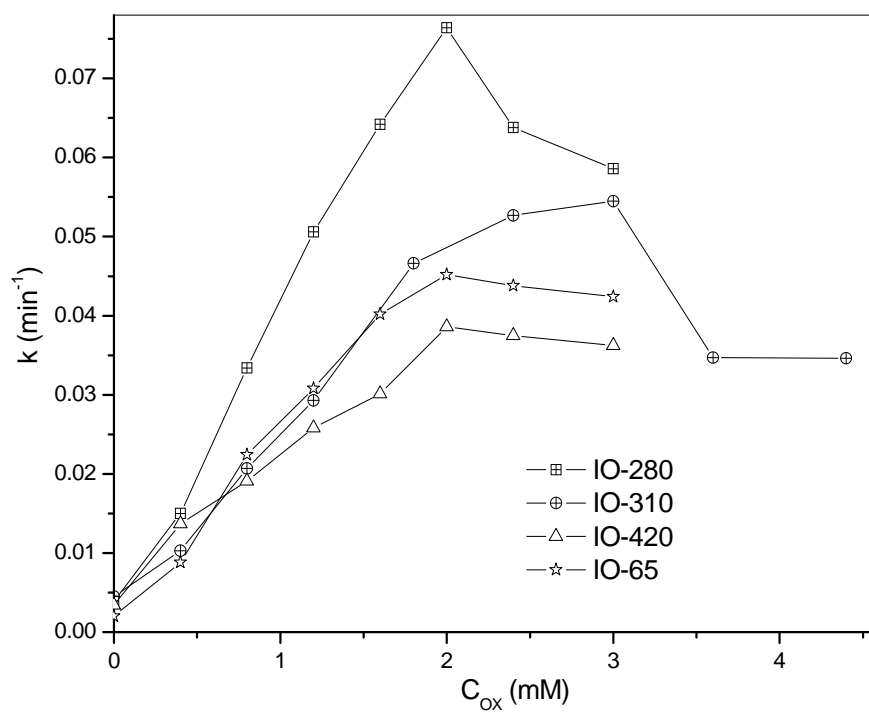
FIG. 4



463
464
465

466
467
468

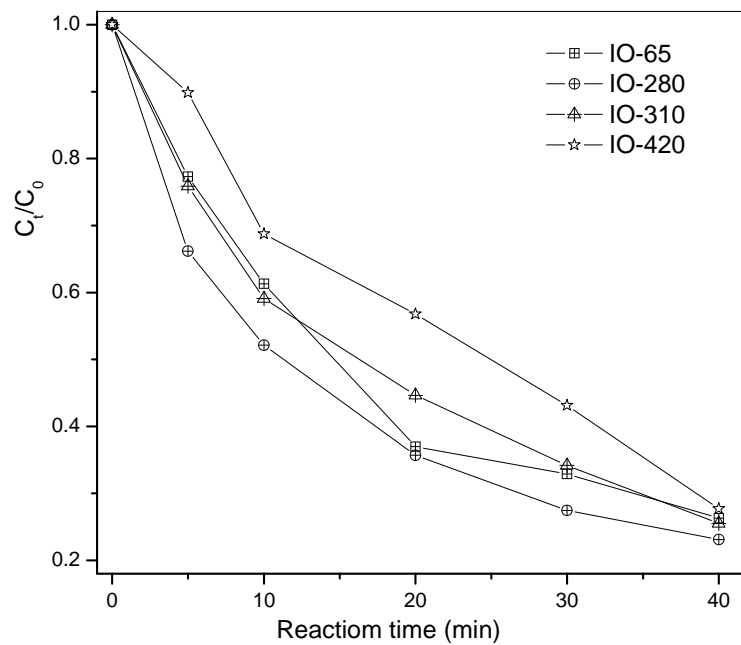
FIG. 5



469
470
471
472
473

474
475
476
477
478
479

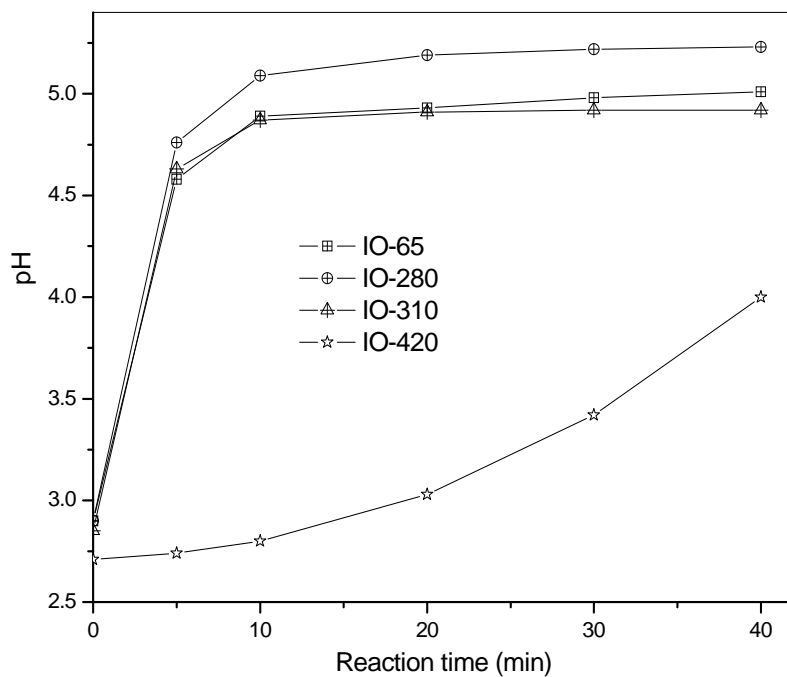
FIG. 6



480
481
482
483

484
485
486
487
488

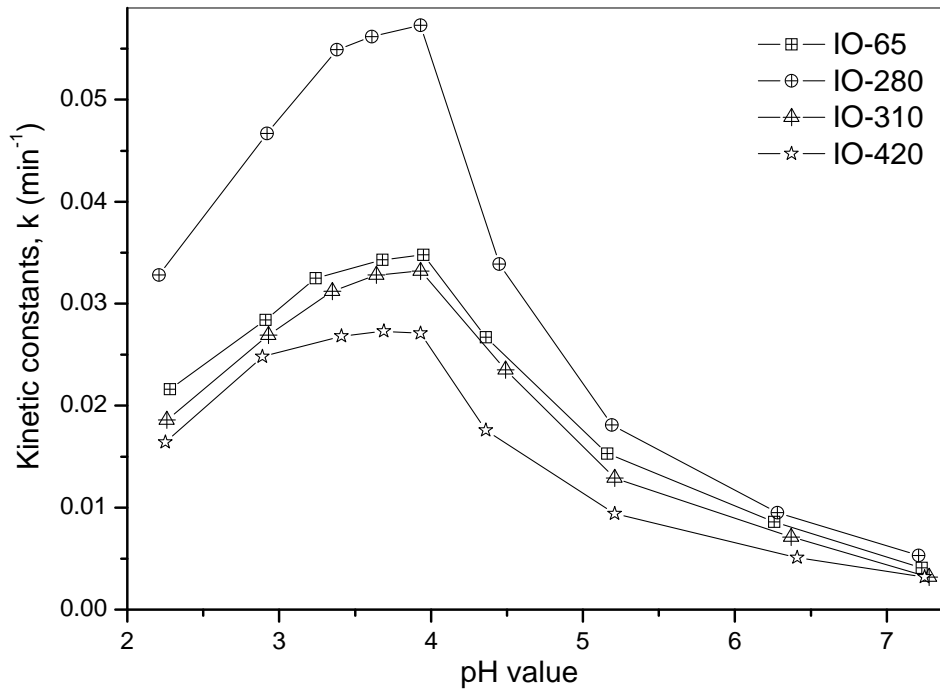
FIG.7



489
490
491
492

493
494
495
496
497
498

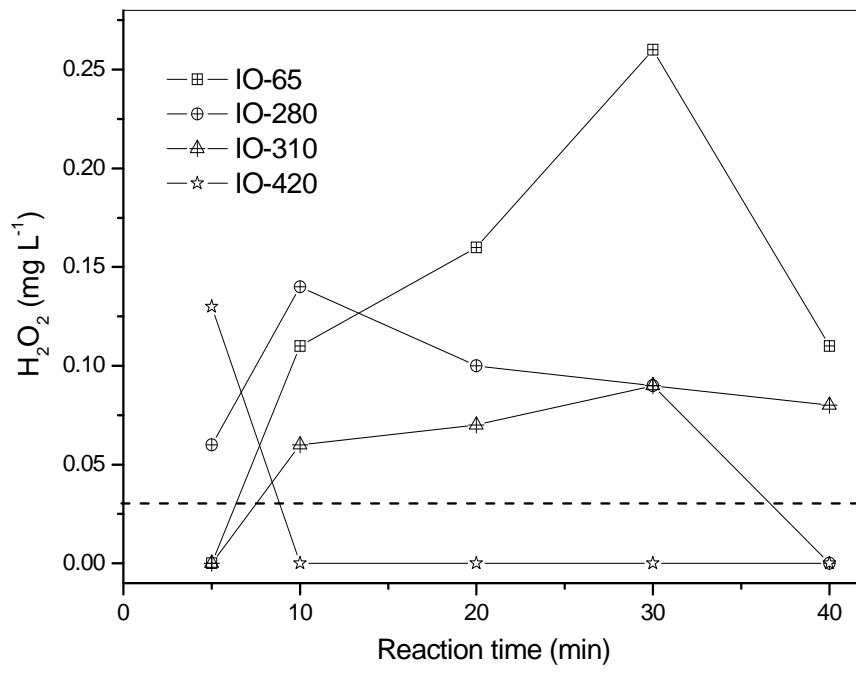
Fig. 8



499
500
501
502
503
504

505
506
507
508
509

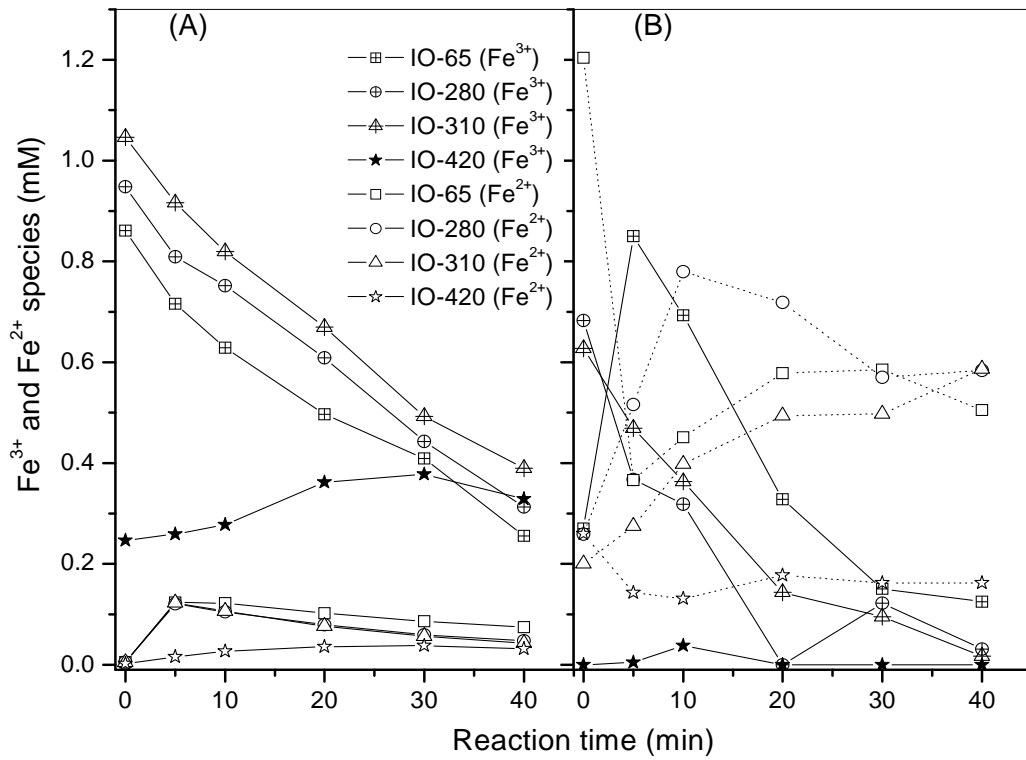
FIG. 9



510
511
512
513
514

515
516
517
518

FIG. 10



519
520
521