

Degradation of 2,4-dichlorophenol in aqueous solution by a hybrid oxidation process

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Abstract

A hybrid photo-electro-reaction system has been developed in this study, which consists of three functional electrodes: a TiO₂/Ti sheet as the anode, a steel (Fe) sheet as another anode in parallel, and a piece of graphite felt (GF) as the cathode. While an electrical current is applied between the Fe anode and GF cathode and UV light is irradiated on the surface of TiO₂/Ti anode, both of E-Fenton reaction and photoelectrocatalytic (PEC) reaction are involved simultaneously. The integration of E-Fenton and PEC reactions was evaluated in terms of 2,4-dichlorophenol (2,4-DCP) degradation in aqueous solution. In the meantime, the current distribution between two anodes and pH influence on the 2,4-DCP degradation were studied and optimized. Experimental results confirmed that 2,4-DCP in aqueous solution was successfully degraded by 93% and mineralized by 78% within 60 min in such a hybrid oxidation process. When a current intensity of 3.2 mA was applied, the current efficiency for H₂O₂ generation on the GF cathode was determined to be 61%. Furthermore, the experiments demonstrated that combination of E-Fenton reaction with photocatalytic reaction let the process be less pH sensitive and would be more favorable to water and wastewater treatment in practice.

Keywords: E-Fenton; H₂O₂; Photocatalysis; TiO₂; 2,4-DCP; Graphite felt

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31 1. Introduction

32
33 2,4-Dichlorophenol (2,4-DCP) is a chemical precursor for manufacture of a
34 widely used herbicide 2,4-dichlorophenoxy acetic acid (2,4-D). After the herbicide
35 have been applied on agricultural sites, 2,4-DCP is the major transformation product
36 of 2,4-D by solarphotolysis and/or microbial activities in the nearby soil [1] or in
37 natural water [2]. 2,4-DCP has also been found in disinfected water after chlorination,
38 in the flue gas of municipal waste incineration [3], or in pulp and paper wastewater
39 [4]. It has been realized that 2,4-DCP may cause some pathological symptoms and
40 changes to endocrine systems of human [5,6].

41 Photocatalysis (PC) is a promising technique of advanced oxidation processes and
42 has been proven to be successful in purification of water and wastewater [7-9].
43 However, the quick recombination between excited electrons and holes (e^-/h^+) from
44 TiO₂ catalyst results in a low quantum yield of below 5% only. Recently,
45 photoelectrocatalysis (PEC) demonstrated great attraction in research to further
46 accelerate PC reaction [10,11] by applying an external potential to drive away the
47 conduction band electrons from TiO₂ photoanode to a counter electrode as a cathode.
48 This is an efficient way to eliminate the recombination of e^-/h^+ pairs and results in the
49 extension of hole's lifetime [12,13].

50 On the other hand, Fenton reaction is also a well-proved technique to oxidize
51 organic pollutants from water and wastewater effectively, in which hydrogen peroxide
52 (H₂O₂) is catalyzed by ferrous ions (Fe²⁺) to produce hydroxyl radicals (HO•). Recent
53 development has been focused on the generation of H₂O₂/Fe²⁺ by electrochemical
54 means named the electro-Fenton (E-Fenton) process. In such a E-Fenton process,
55 while Fe²⁺ can be electrically generated on a sacrificial anode via oxidation of iron,
56 H₂O₂ is generated on a carbon cathode via the two-electron reduction of sparged
57 oxygen [14,15]. Since the efficiency of H₂O₂ generation on the cathode is a key factor
58 to affect the performance and operating cost in practical application, a variety of
59 cathode materials such as mercury pool [16], carbon felt [17], reticulated vitreous
60 carbon [18], graphite [19], activated carbon fiber [20], or carbon-PTFE [21] have been

61 studied. It should be noted that the Fenton reaction is not a universal solution and has
62 two apparent limits of pH restriction and reaction selectivity, as an efficient reaction
63 rate only occurs in a narrow pH range of 2-4 and many chemicals such as acetic acid,
64 acetone, carbon tetrachloride, methylene chloride, *n*-paraffins, maleic acid, malonic
65 acid, oxalic acid, and trichloroethane etc. are refractory towards Fenton reagent and
66 [22].

67 Due to the similarity of reaction mechanism utilizing hydroxyl radicals to destroy
68 organics in aqueous solution between the PEC reaction and E-Fenton reaction, it
69 would be a good approach to combine them together to be a more efficient process. In
70 the meantime, some of the drawbacks of each technique might be eliminated by some
71 characteristics of another technique. The research work presented in this paper has
72 developed a hybrid process by combination of PEC reaction and E-Fenton reaction in
73 a three-electrode reaction system, in which 2,4-DCP was used as a model chemical in
74 aqueous solution and its degradation under different reaction conditions was studied.
75 Furthermore, the reaction mechanism relevant to the interaction between PEC reaction
76 and E-Fenton reaction was also discussed based on the experimental results.

77

78 **2. Experimental**

79 *2.1. Preparation of three electrodes*

80 Titanium sheet (purity: 99.6%; thickness: 0.14 mm) from Goodfellow Cambridge
81 Ltd. was used as a raw material to prepare a TiO₂/Ti film electrode. A piece of Ti
82 sheet (10 mm × 50 mm) was ultrasonically cleaned in alcohol and acetone solutions,
83 respectively and then washed with distilled water. The cleaned Ti sheet was
84 submerged in 2 M HF solution for 2 min to polish its surface chemically. An anodic
85 oxidation process at low voltage was conducted in a dual-electrode reaction chamber,
86 in which the cleaned Ti sheet was used as the anode and a Pt foil with the same size
87 was applied as the cathode. Two electrodes were submerged in aqueous electrolyte
88 solution (1.5 M H₃PO₄ and 0.3 M HF) and an electrophoresis power supply (EPS
89 600 Pharmacia Biotech) was used to provide electrical potentials/currents between
90 two electrodes. The anodic oxidation process was conducted in two stages for about

91 30 min. In the first stage, a constant current density of 10 mA cm^{-2} was fixed, until
92 voltage gradually increased up to 30 V (galvanostatic anodization). In the second
93 stage, the constant voltage of 30 V was kept to allow the current density was gradually
94 reduced (potentiostatic anodization) until the oxidation reaction was complete. Then
95 the anodized TiO_2/Ti sheet was calcinated at 723 K for 2 h for further phase
96 transformation and crystallization. A piece of rectangle stainless steel sheet ($10 \text{ mm} \times$
97 $50 \text{ mm} \times 1 \text{ mm}$) after surface passivation pretreatment was simply used as an iron (Fe)
98 electrode. A piece of graphite fiber (GF) about 2 mm thick supplied by US National
99 Electrical Carbon Products Inc. was cut into the same size ($10 \text{ mm} \times 50 \text{ mm}$) as a GF
100 electrode without any further treatment.

101

102 *2.2. A three-electrode photoreactor and experimental procedure*

103 A novel three-electrode ($\text{TiO}_2\text{-Fe-GF}$) photoreactor system used in this study
104 consists of a cylindrical quartz glass reactor with a three-electrode configuration and
105 an 8-W medium-pressure mercury lamp (LZC-UVA-365, Canada) with a main
106 emission at 365 nm as an external UV-A light source. In this reactor, while the GF
107 electrode was used as the cathode to generate H_2O_2 , the TiO_2/Ti electrode was
108 employed as the first anode to conduct PEC reaction under UV-A illumination and the
109 Fe electrode was used as the second anode in parallel to release ferrous ion (Fe^{2+})
110 continuously for E-Fenton reaction. In addition, a saturated calomel electrode (SCE)
111 was also placed in a separate chamber for potential control. In such a $\text{TiO}_2\text{-Fe-GF}$
112 photoreactor, the working current and potential on the GF cathode were controlled by
113 a potentiostat (ZF-9, Shanghai, China) and the current distribution between two
114 anodes (TiO_2/Ti and Fe) was controlled by an external variable resistor.

115

116 [Fig. 1]

117

118 2,4-DCP chemical was purchased from Aldrich with analytical grade. Aqueous
119 2,4-DCP solution was prepared by dissolving 2,4-DCP into aqueous electrolyte
120 solution ($0.02 \text{ M Na}_2\text{SO}_4$). During each reaction, 50 mL of the 2,4-DCP solution was
121 continuously aerated by oxygen and an electrical current was applied between the

122 anodes and cathode. Samples were taken from the reaction solution at different time
123 intervals for analyses. Prior to HPLC analysis, all samples were filtered by a 0.45 μm
124 Millipore filter to remove any particulates including the fiber desquamation from GF
125 electrode. During the reaction, 50 mL reaction solution was continuously aerated by
126 an oxygen gas flow at 40 mL min^{-1} , which was sufficient for oxygen supply and
127 mixing.

128

129 2.3. Analytical methods

130 2,4-DCP concentration was determined by high performance liquid
131 chromatograph (HPLC Finnigan P4000 Model) equipped with a UV detector
132 (UV6000LP). The separation column is a reverse-phase column (RESTEK Pinnacle
133 II, d-C18 4.6 mm \times 250 mm, 5 μm) and a mobile phase consists of
134 acetonitrile:water:acetic acid (69:30:1). H_2O_2 concentration was measured by a
135 spectrophotometer (GENESYS 2 UV-VIS) at 400 nm wavelength, using $\text{K}_2\text{Ti}(\text{C}_2\text{O}_4)_3$
136 (analytical grade) as a colored indicator. Dissolved organic carbon (DOC)
137 concentration was measured by a TOC analyzer (Shimadzu TOC-5000A) after sample
138 filtration using the 0.45 (m Millipore filter.

139

140 3. Results and discussion

141

142 3.1. Effect of current intensity on H_2O_2 generation

143 The GF cathode used in this study is a carbon material with a microporous
144 structure and high reduction potential, which can generate H_2O_2 on its surface with
145 the following reaction:

146



148

149 The rate of H_2O_2 generation on the GF cathode depends on several factors
150 including electrolyte properties, applied current intensity, and dissolved oxygen
151 concentration in the reaction solution. To study the rate of H_2O_2 generation affected
152 by current intensity as a main parameter, a set of experiments in aqueous 0.02 M

153 Na₂SO₄ solution (without 2,4-DCP) was conducted by applying different current
154 intensity from 0.5 mA to 5.0 mA between the Pt anode and the GF cathode. Each
155 experiment lasted for 150 min and samples were taken at different time intervals to
156 determine the accumulative H₂O₂ concentration in the solution. The experimental
157 results are shown in Fig. 2.

158

159 [Fig. 2]

160

161 It can be seen that H₂O₂ concentration in the Na₂SO₄ solution gradually built up
162 along with reaction time and eventually approached to its maximum levels. The
163 experimental results showed that the higher current intensity was applied, the higher
164 H₂O₂ concentration was achieved. For example, the accumulative H₂O₂ concentration
165 at 60 min was increased from 0.125 mM at 0.5 mA to 0.728 mM at 3.2 mA
166 significantly and was further increased up to 0.836 at 5.0 mA. To evaluate the current
167 efficiency of H₂O₂ generation on the cathode, it is assumed that H₂O₂ is electrically
168 generated from oxygen in aqueous solution with a theoretical amount determined by
169 the following equation:

170

$$171 \quad Q = I \times t = 2n \times N_A \times e = 2n \times (6.02 \times 10^{23}) \times (1.60 \times 10^{-19})$$

172

173 where Q is total quantity of electricity in coulombs (C); t is reaction time (s) and I is
174 current intensity (A); n is the moles of electrogenerated H₂O₂ (M); N_A is Avogadro's
175 constant (6.02×10^{23} molecules/mole); and e is electron charge (1.60×10^{-19} C).

176 According the above equation, the theoretical amount of H₂O₂ at different current
177 intensity for the reaction time at 60 min was calculated and the current efficiency of
178 H₂O₂ generation is evaluated as listed in Table 1. It can be seen that the efficiency of
179 H₂O₂ generation on the GF cathode is decreased from 67% to 45% with the increased
180 current intensity from 0.5 mA to 5.0 mA. Since the efficiency was quickly declined
181 from 61% to 45% at the current intensity higher than 3.2 mA, the current intensity of
182 3.2 mA was employed in the following experiments as a cost-effective condition.

183

184 [Table 1]

185

186 3.2. Current distribution between two anodes

187 In this three-electrode photoreactor, two anodes (TiO₂/Ti and Fe) were applied in
188 parallel. While a total current intensity of 3.2 mA was applied on the GF cathode to
189 generate H₂O₂ sufficiently, the division of the current between two anodes was
190 controlled by the external variable resistor. A set of experiments at different ratios of
191 Fe:TiO₂/Ti (3.2:0, 3.1:0.1, 3.0:0.2, 2.6:0.6, and 1.8:1.4) was conducted in aqueous
192 2,4-DCP solution with an initial concentration of 15 mg L⁻¹ under UV-A illumination
193 for 60 min and the experimental results are shown in Fig. 3. The experiments
194 demonstrated that the 2,4-DCP degradation reaction was affected by current
195 distribution between two anodes significantly and the fastest degradation was
196 achieved by nearly 90% at the ratio of 3.1:1.0 (3.1 mA on the Fe anode and 0.1 mA on
197 the TiO₂/Ti anode). These results indicate that a small current on the TiO₂/Ti anode is
198 sufficient to enhance the photocatalytic reaction and also avoid any electro-corrosion
199 of the TiO₂/Ti electrode. On the other hand, a higher current on the Fe anode can
200 release more ferrous ions into the reaction solution to enhance the E-Fenton reaction.

201

202 [Fig. 3]

203

204 3.3. Interaction of individual reactions

205 In such a hybrid reaction system, several reactions could contribute to the
206 2,4-DCP degradation in aqueous solution, including (1) direct photolysis by UV-A
207 illumination, (2) direct electro-chemical oxidation on the TiO₂/Ti anode or Fe anode,
208 (3) PEC reaction and H₂O₂-assisted PEC reaction on the TiO₂/Ti electrode, and (4)
209 E-Fenton reaction and photo-assisted E-Fenton reaction in the solution. Since the
210 photolysis of 2,4-DCP under UV-A irradiation is insignificant due to low adsorption
211 band of below 286 nm by 2,4-DCP [23] and the direct electro-chemical oxidation on
212 both anodes is also weak due to a low current intensity of 3.2 mA only. Comparatively
213 both the H₂O₂-assisted PEC reaction and photo-assisted E-Fenton reaction may play

214 more important roles. To study the interaction of individual reactions, three
215 experiments were conducted. The first experiment was carried out using two
216 electrodes only (TiO₂/Ti anode and GF cathode). The experiment was performed in
217 the 2,4-DCP solution (initial concentration = 15 mg L⁻¹) under UV-A illumination by
218 applying a weak current at 0.1 mA as a H₂O₂-assisted PEC oxidation reaction. The
219 second experiment was conducted using two electrodes (Fe anode and GF cathode)
220 and a high current at 3.1 mA was applied with and without UV-A illumination as
221 photo-assisted E-Fenton and E-Fenton reactions. The third experiment was conducted
222 using three electrodes together (TiO₂/Ti anode, Fe anode and GF cathode) and a total
223 current intensity of 3.2 mA with a distribution ratio of 3.1:0.1 was applied. The
224 experiment was performed under UV-A illumination to represent an integrative
225 oxidation reaction. All the above experiments with an initial pH 5.8 lasted for 60 min.
226 and the experimental results are compared in Fig. 4.

227

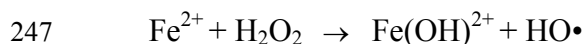
228 [Fig. 4]

229

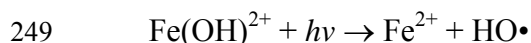
230 The experimental results showed that the 32% of 2,4-DCP reduction was achieved
231 by the E-Fenton reaction after 60 min; 45% by the photo-assisted E-Fenton reaction;
232 and 46% by the H₂O₂-assisted TiO₂ PEC reaction. These results confirmed that both
233 the TiO₂ PEC reaction and E-Fenton reaction played significant roles in the 2,4-DCP
234 degradation. These results also confirmed that the 2,4-DCP degradation by E-Fenton
235 reaction was really enhanced by UV-A illumination. Furthermore, much higher
236 percent of 2,4-DCP reduction up to 93% was achieved by the integrative reaction, in
237 which the proper current distribution with the ratio of 3.1:0.1 can well balance both
238 reactions in such a three-electrode reaction system. In such a reaction system, while
239 the existence of H₂O₂ in the solution could enhance the TiO₂ PEC reaction as the
240 H₂O₂-assisted TiO₂ PEC reaction and UV-A illumination could also enhance the
241 E-Fenton reaction as the photo-assisted E-Fenton reaction, where some interactive
242 reactions may occur as well. It has been reported that Fe(OH)²⁺ has an absorption
243 band between 290 and 400 nm and can produce hydroxyl radicals and Fe(II) ions. The

244 primary reactions in the case of photo-Fenton reaction using the near-UV and even
245 visible light can be given as follows [24]:

246



248



250

251 To further compare the rates of 2,4-DCP reduction in the above experiments, all
252 experimental data were fitted by the simple first-order kinetic model, the values of
253 kinetic constant, k , for all reactions were calculated and are presented in Table 2. It
254 can be noted that both constants of H_2O_2 -assisted PEC reaction and photo-assisted
255 E-Fenton reaction are 1.01 and 1.11, respectively, while the constant of the integrative
256 reaction is 4.23. These results demonstrated that the H_2O_2 -assisted PEC reaction and
257 photo-assisted E-Fenton reaction were two main reactions dominating in such a
258 three-electrode reaction system. However, the rate of integrative reaction was even
259 higher than the sum of H_2O_2 -assisted PEC reaction and photo-assisted E-Fenton
260 reaction. It should be indicated that any extra benefits obtained from the combination
261 of photochemical reaction and electrochemical reaction would be more attractive
262 rather than the simple summation only. However, the exact mechanism of individual
263 reactions involved in such a three-electrode reaction system is quite sophisticated and
264 needs to be further explored in the following studies.

265

266 [Table 2]

267

268 *3.4. Effect of pH on 2,4-DCP degradation*

269 Since E-Fenton reaction is a pH-sensitive approach, the effect of pH on 2,4-DCP
270 degradation is studied by conducting three experiments for the H_2O_2 -assisted TiO_2
271 PEC reaction, the E-Fenton reaction, and the integrative reaction, respectively in a
272 wide pH range of 1-9. The reaction at pH 1 was controlled with H_2SO_4 - H_3PO_4 buffer
273 solution and the reactions at pH 3-9 are controlled with H_3PO_4 - NaH_2PO_4 - Na_2HPO_4

274 buffer solution. The experimental results are shown in Fig. 5.

275

276 [Fig. 5]

277

278 The first experiment demonstrated that pH had a moderate influence on the
279 H_2O_2 -assisted TiO_2 PEC reaction, in which 2,4-DCP degradation was increased with
280 increased pH from 1 to 7 gradually and then decreased beyond pH 7 slightly. The
281 second experiment confirmed that pH had a sharp influence on the E-Fenton reaction
282 with a maximum reaction rate at pH 2.5-3 as a common nature of most Fenton
283 reactions. Furthermore, the third experiment showed that the 2,4-DCP degradation in
284 the integrative reaction was increased quickly at the lower pH range from 1 to 3 and
285 then gradually decreased at the higher pH range from pH 3 to 9. However, the
286 reduction of 2,4-DCP degradation from its maximum value at pH 3 to the lowest
287 value at pH 9 was only 10% difference. From these results, it is believed that the
288 combination of E-Fenton reaction with photocatalytic reaction may gain a benefit to
289 overcome its pH-sensitive character and it becomes less necessary to adjust pH of
290 water and wastewater with a neutral pH condition prior to the treatment.

291 To further study the pH change during the integrative reaction, one more
292 experiment was conducted without pH control under UV-A illumination for 60 min
293 with an initial 2,4-DCP concentration of 15 mg l^{-1} and initial pH 5.8. The 2,4-DCP
294 concentration and pH were monitored simultaneously during the reaction. The
295 experimental results in Fig. 6 demonstrated that when 2,4-DCP degradation was
296 achieved by more than 90% at 60 min, pH of reaction solution was only slightly
297 decreased from 5.8 to 4.8. Although several factors may affect the pH in the reaction
298 solution, it was confirmed in our previous work that the H_2O_2 generation on the
299 cathode can increase pH by consuming H^+ , while the degradation of some organics
300 such as 2,4,6-TCP can decrease pH due to release of acidic intermediate products such
301 as organic acids [25]. Some researchers also reported that degradation of 2,4-DCP
302 produced weak acids by photo-Fenton-like oxidation [26]. This pH neutralization
303 function in the $\text{TiO}_2/\text{Ti-Fe-GF}$ reaction system might have one more benefit to

304 maintain pH for any acid-releasing reactions in practical water and wastewater
305 treatment.

306

307 [Fig. 6]

308

309 *3.5. Accumulation of H₂O₂ concentration*

310 The H₂O₂ concentration in the reaction solution plays a critical role, depending on
311 both rates of its generation and consumption. To study the H₂O₂ accumulation in the
312 integrative reaction system, 4 experiments were carried out by applying the same
313 current intensity of 3.2 mA on the GF cathode under different reaction conditions,
314 which included two experiments in aqueous 0.02 M Na₂SO₄ only solution with and
315 without UV-A illumination and other two experiments in aqueous 2,4-DCP + 0.02 M
316 Na₂SO₄ solution with and without UV-A illumination. The experimental results are
317 summarized in Fig. 7. The results demonstrated that the accumulative H₂O₂
318 concentration in the aqueous 0.02 M Na₂SO₄ only solution were significantly higher
319 than those in the 2,4-DCP+0.02 M Na₂SO₄ solution, due to no H₂O₂ consumption
320 resulted from the reaction with 2,4-DCP. On the other hand, the accumulative H₂O₂
321 concentration under UV-A illumination built up slightly slower than those without
322 UV-A illumination, due to more H₂O₂ consumption under UV-A illumination.

323

324 [Fig. 7]

325

326 *3.6. Mineralization of 2,4-DCP*

327 To study the 2,4-DCP mineralization in the integrative reaction, DOC at different time
328 intervals was also determined and the experimental results are shown in Fig. 8. The
329 results showed that the degree of 2,4-DCP mineralization in the integrative reaction
330 was higher than both the H₂O₂-assisted-TiO₂ PEC and photo-assisted E-Fenton
331 reactions, significantly. It should be noted that 78% of 2,4-DCP mineralization was
332 achieved by the integrative reaction, which was even higher than 57% as the sum of
333 H₂O₂-assisted-TiO₂ PEC and photo-assisted E-Fenton reactions. Sabhi and Kiwi [23]

334 carried out a similar photo-assisted E-Fenton reaction and found that mineralization of
335 2,4-DCP was only 21% after 60 min reaction time when added H₂O₂ concentration
336 was 1.25mM. Similar to the pattern of 2,4-DCP degradation, the experiments further
337 confrimed that some interactive reactions might occur in such a TiO₂/Ti-Fe-GF
338 reaction system beyond the PEC reaction and E-Fenton reaction, which provided extra
339 benefits to develop an efficiency treatment process.

340

341 [Fig. 8]

342

343 **4. Conclusion**

344 In this study, it has been confirmed that 2,4-DCP in aqueous solution is
345 successfully degraded by 93% and mineralized by 78% within 60 min in a hybrid
346 oxidation process by integrating the E-Fenton and photocatalytic reactions. When a
347 current intensity of 3.2 mA was applied on the GF cathode, the current efficiency for
348 H₂O₂ generation was determined to be 61%. Although the E-Fenton reaction is a
349 pH-sensitive process, the experiments demonstrated that combination of E-Fenton
350 reaction with photocatalytic reaction let the process become less pH sensitive and can
351 be applied under a more neutralized pH condition, which would be favorable to water
352 and wastewater treatment in practice.

353

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435 Table 1. Accumulative Amount of H₂O₂ (C_{H2O2}) in Experiments and Theoretical
 436 Values at 60 min.

| Applied current intensity (mA) | C _{H2O2} (mM) | Theoretical value (mM) | Generation efficiency (%) |
|-----------------------------------|---------------------------|---------------------------|------------------------------|
| 0.5 | 0.125 | 0.187 | 67 |
| 1.5 | 0.349 | 0.56 | 62 |
| 3.2 | 0.728 | 1.19 | 61 |
| 5.0 | 0.836 | 1.87 | 45 |

437

438 Table 2. Kinetic Constant (k_R) for 2,4-DCP Degradation in Aqueous Solution

| Reaction system | k _R (×100 / min ⁻¹) | R ² | Degradation (%) |
|---|---|----------------|--------------------|
| Anodic oxidation on TiO ₂ electrode | 0.04 | 0.9982 | 2.9 |
| Anodic oxidation on Fe electrode | 0.12 | 0.9929 | 6.2 |
| Photolysis under UV-A illumination | 0.07 | 0.9971 | 3.6 |
| E-Fenton reaction | 0.62 | 0.9378 | 32 |
| TiO ₂ PEC reaction | 0.81 | 0.9825 | 36 |
| H ₂ O ₂ -assisted TiO ₂ PEC reaction | 1.01 | 0.9783 | 45 |
| Photo-assisted E-Fenton reaction | 1.11 | 0.9779 | 46 |
| Integrative reaction | 4.23 | 0.9956 | 93 |

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453 **List of figure captions**

454

455 Fig.1. Sketch of the photo-electro-reaction system.

456

457 Fig. 2. Effect of current on H₂O₂ generation (O₂ flow rate = 40 ml min⁻¹ nearby GF cathode).

458

459 Fig. 3. Effect of current distribution on 2,4-DCP degradation (Anodes: TiO₂/Ti and Fe; cathode:

460 GF; total current intensity = 3.2 mA; O₂ flow rate = 40 ml min⁻¹; initial 2,4-DCP

461 concentration = 15mg l⁻¹ under UV-A irradiation).

462

463 Fig. 4. 2,4-DCP degradation in aqueous solution by different reactions without pH control

464

465 Fig. 5. Effect of pH on 2,4-DCP degradation by different reactions with pH control.

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467 Fig. 6. pH change during 2,4-DCP degradation in aqueous solution by integrative reaction without

468 pH control.

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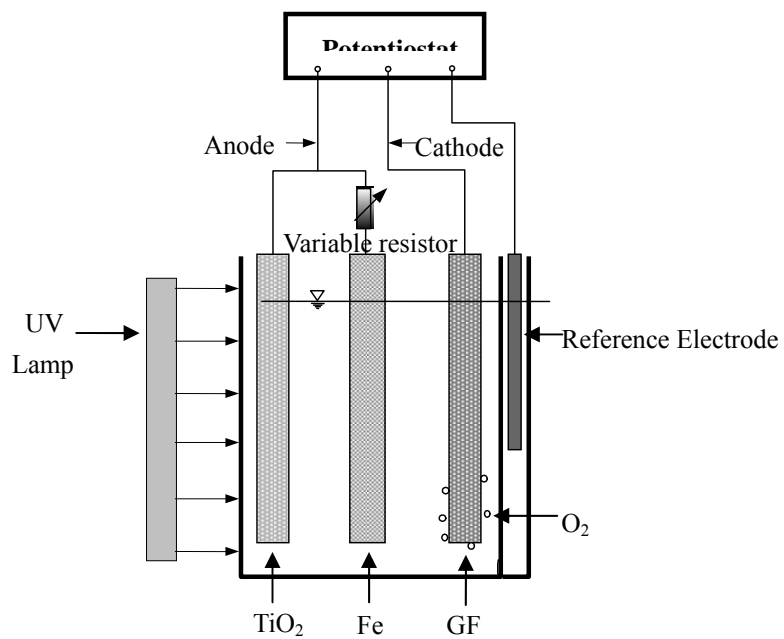
470 Fig. 7. H₂O₂ accumulation under different experimental conditions without pH control.

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472 Fig. 8. Mineralization of 2,4-DCP in aqueous solution in different reactions.

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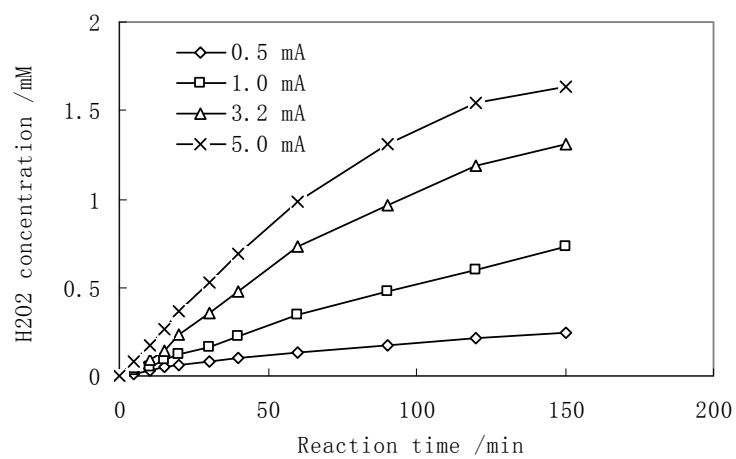
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482 Fig. 1.

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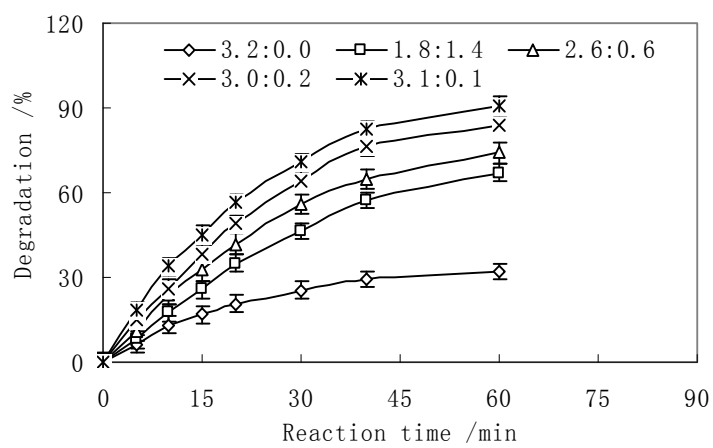
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489 Fig. 2.

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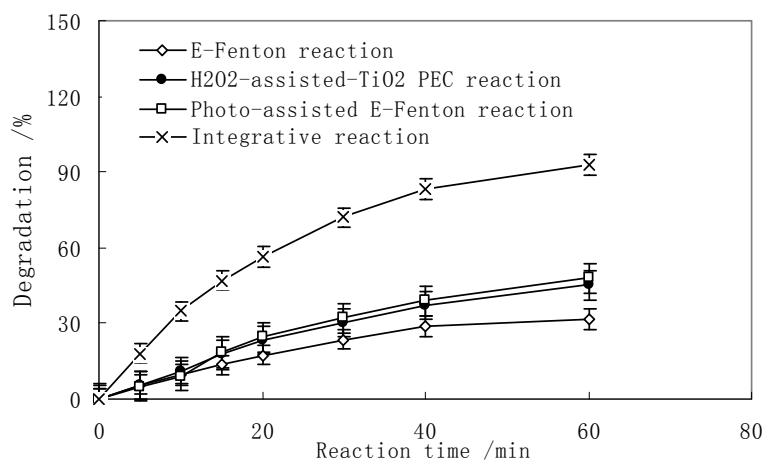
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495 Fig. 3.

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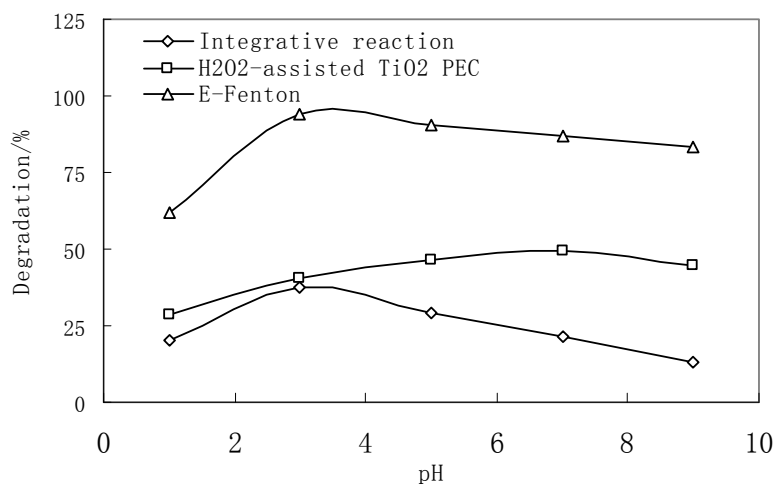
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500 Fig. 4.

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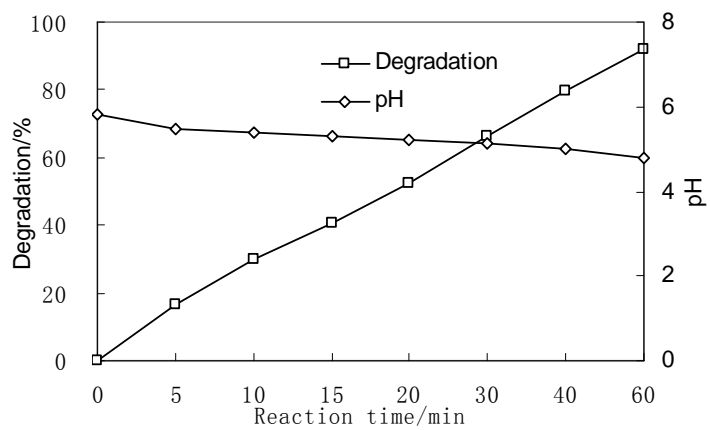
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506 Fig. 5.

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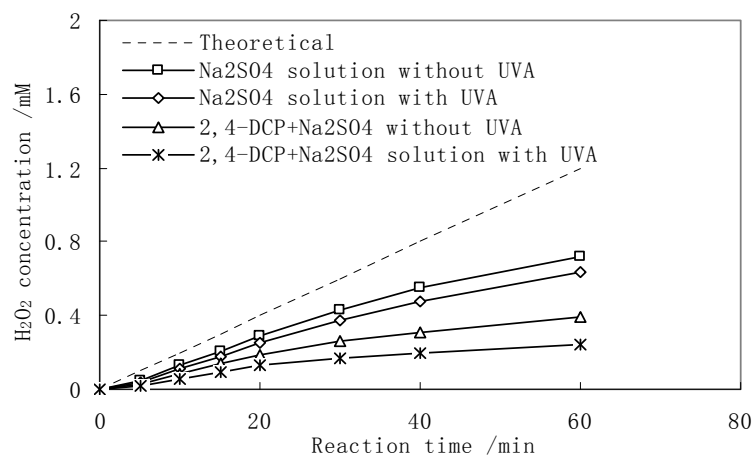
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512 Fig. 6.

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517 Fig. 7.

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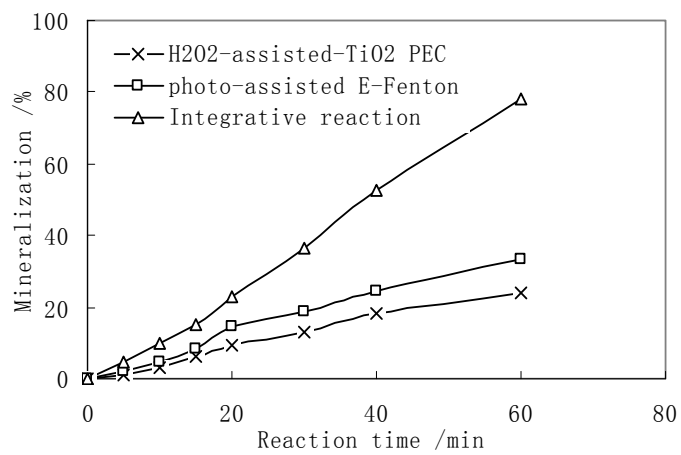
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529 Fig. 8.

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