

1 **Effects of dissolved oxygen, pH, and anions on the 2,3-dichlorophenol degradation by**
2 **photocatalytic reaction with anodic TiO₂ nanotube films**

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10

11 **Abstract**

12 In this study, the highly-ordered TiO₂ nanotube (TNT) arrays on titanium sheets were prepared
13 by an anodic oxidation method. Under UV illumination, the TNT films demonstrated the higher
14 photocatalytic activity in terms of 2,3-dichlorophenol (2,3-DCP) degradation in aqueous solution
15 than the conventional TiO₂ thin films prepared by a sol-gel method. The effects of dissolved
16 oxygen (DO) and pH on the photocatalytic degradation of 2,3-DCP were investigated. The results
17 showed that the role of DO in the 2,3-DCP degradation with the TNT film was significant. It was
18 found that 2,3-DCP in alkaline solution was degraded and dechlorinated faster than that in acidic
19 solution whereas dissolved organic carbon removal presented an opposite order in dependence of
20 pH. In the meantime, some main intermediate products from 2,3-DCP degradation were identified
21 by a ¹H-NMR technique to explore a possible degradation pathway. A major intermediate, 2-
22 chlororesorcinol, was identified from the 2,3-DCP decomposition as a new species compared to
23 the findings in previous reports. Photocatalytic deactivation was also evaluated in the presence of
24 individual anions (NO₃⁻, Cl⁻, SO₄²⁻, and H₂PO₄⁻). The inhibition degree of photocatalytic
25 degradation of 2,3-DCP caused by these anions can be ranked from high to low as SO₄²⁻ > Cl⁻ >
26 H₂PO₄⁻ > NO₃⁻. The observed inhibition effect can be attributed to the competitive adsorption and
27 the formation of less reactive radicals during the photocatalytic reaction.

28

29 *Keywords:* Anion; Dissolved oxygen; Photodegradation; TiO₂ nanotube; 2,3-Dichlorophenol

30

31 **1. Introduction**

32 The halogenated aromatics in aquatic bodies are mainly from industrial wastewater and
33 chlorination process of water purification and have been known to cause severe pollution
34 problems (Bellar et al., 1974; Kinzell et al., 1979; Ku et al., 1996). Dichlorophenols (DCP), such
35 as 2,3-DCP, 2,4-DCP, 2,5-DCP, and 2,6-DCP, have limited degradation by most conventional
36 biological processes due to their toxicity (Zheng et al., 2004; Ye and Shen, 2004). The
37 photocatalysis with immobilized TiO₂ thin films is an alternative to using TiO₂ powder with ease
38 of separating TiO₂ catalyst from aqueous suspension (Arabatzis et al., 2002; Gracia et al., 2004).
39 However, this process has limited surface area with the declined efficiency of photocatalytic
40 reaction compared to using TiO₂ powder in aqueous suspension. Therefore, synthesis of the TiO₂
41 films with larger surface area and a better structure is a key step for its practical application.

42 Recently TiO₂ nanotube films have gained great attraction due to their large surface area, good
43 mechanical adhesion strength, and high electronic conductivity. The immobilized TiO₂ nanotube
44 films can be prepared by an anodic oxidation method through direct growth on titanium metal. As
45 a result, this not only develops a new way to engineer TiO₂ nanostructures, but also explores wide
46 applications in solar energy conversion (Hahn et al., 2007), water splitting (Mor et al., 2005), gas
47 sensors (Mor et al., 2006), and environment purification (Quan et al., 2005; Zhuang et al., 2007).
48 Quan et al. (2005) reported that the degradation of pentachlorophenol using an anodic TiO₂
49 nanotube film with large surface area was much faster than that using a traditional TiO₂ thin film
50 formed by a sol-gel method. Xie (2006) reported that an anodic TiO₂/Ti nanotubular film as a
51 photoanode exhibited a good reactivity for the photoelectrocatalytic degradation of bisphenol A in
52 aqueous solution. However, these works were mainly focused on the aspect of material science,
53 but the effects of key reaction conditions such as dissolved oxygen (DO), pH, and the anions
54 commonly contained in wastewater on the photocatalytic reaction of using the TiO₂ nanotube
55 films have not well been investigated.

56 It is well known that DO can act as an electron acceptor to eliminate the recombination of
57 photogenerated electron-hole pairs and the nanotubular TiO₂ surface with better separation of
58 electrons and holes allows more efficient channeling of the charge carriers into useful reduction
59 and oxidation reactions. On the other hand, the presence of various inorganic anions such as SO₄²⁻,
60 Cl⁻, H₂PO₄⁻, and NO₃⁻ coexisting in various industrial effluents may cause some negative effects
61 on the photocatalytic decomposition of organic compounds (Chen et al., 1997; Hu et al., 2003).

62 These anions are likely to retard the rates of organic compound oxidation by bidding for oxidizing
63 radicals or by blocking the active sites of the TiO₂ catalyst. Therefore, this study aims at
64 evaluating the influence of DO, pH, and selected inorganic anions on the photocatalytic
65 degradation of 2,3-DCP in aqueous solution using the anodic TiO₂ nanotube films under UV light
66 irradiation.

67

68 **2. Experimental**

69 *2.1. Materials*

70 Titanium foils (140 μm thickness, 99.6% purity) were purchased from Goodfellow Cambridge
71 Ltd. as a raw material to prepare TiO₂ nanotube films. 2,3-DCP chemical with analytical grade
72 was obtained from Aldrich Chemical Company and employed as a model pollutant. Deionized
73 distilled water (DDW) was used throughout the experiments.

74

75 *2.2. Anodic oxidation process*

76 A large piece of raw Ti foil was cut into small rectangle pieces of 30 mm × 10 mm each, which
77 were ultrasonically cleaned in acetone-ethanol solution and then rinsed by DDW as the prepared
78 Ti foil samples. The anodic oxidation process was performed in a two-electrode cell, in which the
79 prepared Ti foil was used as the anode and a platinum foil with the same size was employed as the
80 cathode. Both the electrodes were submerged in aqueous 0.1 M NH₄F electrolyte solution with an
81 initial pH 1.5 and were connected with a regulated DC power supply (Kikusui Electronic Corp.
82 Japan, PAC 35-5). All anodization experiments were conducted at a constant electrical potential of
83 25 V and lasted for 1 h. The freshly anodized TiO₂/Ti foil was washed by DDW and further
84 calcined at 500 °C for 1 h. The product TiO₂ nanotubular films were named “TNT” films.

85

86 *2.3. Experimental*

87 One piece of TNT films with an area of 3 cm² was placed in a single-compartment reactor filled
88 with 25 mL of aqueous 2,3-DCP solution (20 mg L⁻¹) and an 8-W medium-pressure mercury lamp
89 with a main emission at 365 nm (Institute of Electrical Light Source, Beijing, China) was applied
90 as an external UV light source. A distance between the lamp and the top surface of the solution is
91 6 cm. Prior to photoreaction, the 2,3-DCP solution was magnetically stirred in the dark for 60 min
92 in order to achieve adsorption/desorption equilibrium. The reaction systems were aerated

93 continuously with an air flow, unless otherwise mentioned. During the photoreaction, samples
94 were collected from the solution at different intervals for analyses.

95

96 *2.4. Characterization and chemical analysis*

97 The surface morphology and element composition of the anodic TNT films were first examined
98 by the field-emission scanning electron microscopy (FESEM) and X-ray diffraction measurement
99 (XRD, with a Bruker D8 Discover X-ray diffractometer). To investigate the surface charges of
100 photocatalysts in aqueous solution, zeta potential measurements were carried out using a Malvern
101 Zetasizer 3000 (Malvern, UK). TiO₂ nanotubes were peeled off from TNT films to obtain TNT
102 powder and then the TNT powder was used to prepare its suspension with a concentration of 0.1 g
103 L⁻¹ in aqueous solution and dispersed ultrasonically for 2 h. Degussa P25 was also used to prepare
104 its suspension with the same concentration for comparison. The 2 M HCl and 2 M NaOH solutions
105 were used to adjust pH to the desired values. As a result, the isoelectric point of the catalysts was
106 obtained by the measurement of the zeta-potential. 2,3-DCP concentration was analyzed by HPLC
107 (Finnigan SpectraSYSTEM P4000) consisting of a Pinnacle II C18 reverse-phase column (5 μm,
108 4.6 mm × 250 mm) and a UV detector (UV 6000LP). The mobile phase of acetonitrile/water (v:v
109 = 3:2) was flowed at 1.0 mL min⁻¹. The concentration of dissolved organic carbon (DOC) was
110 determined by a total organic carbon analyzer (Shimadzu TOC-5000A). Chloride ions released
111 from the 2,3-DCP degradation were determined by spectrophotometry at 460 nm after the reaction
112 with mercury thiocyanate.

113 In order to unambiguously identify the intermediate products of 2,3-DCP degradation, ¹H-NMR
114 analysis, a special feature of this study versus previous contributions (D'Oliveira et al., 1993), was
115 employed, in which 2,3-DCP solutions of 300 mg L⁻¹ were used in photocatalytic experiments and
116 1 mL of each sample was taken in a NMR tube at different time intervals.

117

118 **3. Results and discussion**

119

120 *3.1. Morphology and structure of TNT film*

121 The morphology of TNT film was first examined by FESEM and its image is shown in Fig. 1a.
122 It can be seen that the TNT film has a tubular porous structure, on which TiO₂ nanotubes were
123 well-aligned as uniform arrays with high density. While the inner diameter of the nanotubes was

124 about 100 nm, the tube length was about 0.31 μm and the wall thickness was 28 nm on average.
125 The XRD pattern of the TNT film calcined at 500 $^{\circ}\text{C}$ was analyzed and compared with that of Ti
126 foil, as shown in Fig. 1b. The TNT film had characteristic peaks at 25.35 $^{\circ}$ (101), 27.5 $^{\circ}$ (110), 36.1 $^{\circ}$
127 (101), 48.1 $^{\circ}$ (200), 54.3 $^{\circ}$ (211), and 69.8 $^{\circ}$ (220), respectively. According to the XRD indexation,
128 the crystal form of TNT is a mixture of rutile and anatase phases in good agreement with previous
129 reports (Uchikoshi et al., 2004; Eder et al., 2006). From the FESEM and XRD results, it can be
130 confirmed that the well-aligned TiO_2 nanotubular arrays well grew on the Ti substrate successfully
131 in aqueous NH_4F electrolyte solution during such a low-voltage anodization process.

132

133 [Fig. 1]

134

135 3.2. Photocatalytic activity of TNT film

136

137 The photocatalytic activity of the TNT film was evaluated in terms of 2,3-DCP degradation in
138 aqueous solution under UV illumination. A TiO_2 thin film with the same size was also prepared by
139 the sol-gel method reported by Yu et al. (2001) and was heated at the same temperature of 500 $^{\circ}\text{C}$
140 for comparison, which had a nonporous structure and a film thickness of $\sim 1.0 \mu\text{m}$ (not shown
141 here). Two experiments were conducted under same experimental condition with an initial 2,3-
142 DCP concentration of 20 mg L^{-1} and initial pH 5.3. The results are presented in Fig. 2. It can
143 clearly be observed that after 300 min reaction while the TiO_2 film degraded 2,3-DCP by less than
144 40%, the TNT film achieved the much higher removal by 93% with a factor of about 2.6 times.
145 Such higher reaction activity of TNT film might result from several factors of larger surface area,
146 hollow interior walls, and a nanoscale-dimensional feature. It can be understood that when TiO_2
147 semiconductor is irradiated, electrons and holes are generated, but could recombine immediately.
148 If the electrons and holes created do not recombine rapidly, they need to be either trapped in some
149 metal-stable states or migrate to the semiconductor surface separately. The nanotube array
150 architecture of the TNT film with a wall thickness of 28 nm ensures that the holes are never
151 generated far from the semiconductor–electrolyte interface because the wall thickness is much less
152 than the minority carrier diffusion length of $L_p \approx 100 \text{ nm}$ in TiO_2 (Hamnett, 1980), thus charge
153 carrier separation takes place efficiently. In addition, the hollow feature of nanotubes enables the
154 electrolyte species to permeate the entire internal and external surfaces. Paulose et al. (2006)

155 suggested that this could cause the holes to reach the electrolyte surface through diffusion, which
156 takes place on a scale of picoseconds, and finally also reduce the bulk recombination. Besides
157 these, the tube-to-tube contact points (~5 nm) presented in Fig. 1 may become another role
158 responsible for the higher photoactivity for TNT film due to their quantum size effect and creation
159 of a contact network between the nanotubes. This network let the charge carrier-transfer become
160 easier and distance-longer. This hypothesis has been confirmed by Varghese and co-workers
161 (2003). They stated that the nanoscale geometry of the nanotubes, in particular the tube-to-tube
162 contact points, is believed to be responsible for the outstanding hydrogen gas sensitivity (Varghese
163 et al., 2004). On the other hand, Lubberhuizen et al. (2000) also claimed that strong scattering
164 inside the nanoporous network leads to a long effective path-length of photons and finally to very
165 effective light absorption. Hence, complete light absorption is achieved in nanoporous films with a
166 thickness considerably smaller than the light absorption depth in bulk material.

167

168 [Fig. 2]

169

170 3.3. Effect of DO

171 The effect of DO concentration on 2,3-DCP degradation with the initial concentration of 20 mg
172 L⁻¹ at initial pH 5.3 was investigated in two sets of experiments using the TiO₂ film and TNT film
173 by purging N₂, air, or O₂ gas, respectively and the results are shown in Fig. 3. Figure 3 shows that
174 after 300 min reaction under UV illumination, 2,3-DCP was degraded with the TiO₂ film by 49%
175 at a high DO level of 33 mg L⁻¹ (O₂), by 37% at a medium level of 8.1 mg L⁻¹ (air), and by 29% at
176 a low level of 0.3 mg L⁻¹ (N₂), respectively. It is evident that for the TiO₂ film, increasing the DO
177 concentration in the solution significantly increases the extent of 2,3-DCP degradation. Meanwhile,
178 even at the very low DO concentration (N₂) the reaction rate was still significant. The similar
179 result about the photocatalytic degradation of 4-chlorobenzoic acid using a TiO₂ thin film in a
180 rotating disk photocatalytic reactor was also observed (Dionysiou et al., 2002). It has been
181 reported that when molecular oxygen is used as an electron acceptor to trap and remove electrons
182 from the surface of the titania particles for minimizing the build-up of free electrons, the reaction
183 of adsorbed oxygen with photo-generated electrons at the surface of the titania catalyst is
184 relatively slow and may be the rate-controlling step in photocatalytic oxidation reactions
185 (Gerischer and Heller, 1991). Therefore, increasing the charge transfer rate from titania to

186 molecular oxygen will increase the efficiency of photocatalysis for organic substrate photo-
187 oxidation. If the adsorbed oxygen is in excess of the photo-generated electrons at the surface, the
188 rate of electron transfer to molecular oxygen will be maximized. However, they are affected by the
189 types and characteristics of titania through the efficiency of electron-hole generation,
190 recombination, and also charge transfer reaction rates (Almquist and Biswas, 2001).

191 For the TNT film, it can be seen from Fig. 3 that, at the very low DO concentration (N_2), the
192 removal of 2,3-DCP was achieved by as high as 81% after 300 min reaction. The large decay of
193 2,3-DCP should be due to the unique nanotubular structure of TNT film, which owns a better
194 separation of electron-hole and allows more efficient channeling of the charge carriers into the
195 photochemical reactions, in spite of the absence of electron acceptor. Furthermore, the
196 decomposition of 2,3-DCP increases to 93% in the presence of air and rises to 95% in the presence
197 of oxygen, respectively. Only a slight enhancement of 2% from air to O_2 gas indicates that an air
198 saturated water system can provide sufficient electron scavengers to accelerate the photocatalytic
199 reaction using the TNT film under UV illumination.

200

201 [Fig. 3]

202

203 3.4. Effect of pH

204 Solution pH is one of the most important parameters that influence the photocatalytic reactions.
205 To study the effect of pH on the photocatalytic degradation of 2,3-DCP, one set of experiments
206 was carried out under same experimental conditions, but different initial pH in the range of 3.4-
207 10.9. The experimental results are shown in Table 1. It is evident that at initial pH 3.4, the pseudo-
208 first-order rate constant (k) of 2,3-DCP degradation was only $7 \times 10^{-3} \text{ min}^{-1}$ and the solution pH
209 varied from 3.4 to 3.0 after 300 min UV irradiation. Instead, at initial pH 10.9 the k value reached
210 $24 \times 10^{-3} \text{ min}^{-1}$ (3.4 times higher than that at pH 3.4) and the corresponding pH of the solution
211 dropped from 10.9 to 7.1. The results in Table 1 demonstrated that 2,3-DCP was degraded faster at
212 the higher pH and some acidic products were formed from the 2,3-DCP degradation.

213

214 [Table1]

215

216 In general, medium pH has a complex effect on the photodegradation rates of chlorophenols
217 depending on different molecular structures of chlorophenols as well as the semiconductors used
218 in the oxidation process. Several researches showed that the removal efficiency of chlorophenols
219 decreased with increasing pH values (Ku et al., 1996; Leyva et al., 1998; Quan et al., 2007). It is
220 suggested that TiO₂ surface carries a net positive charge (pH_{zpc} 6.25) at low pH value, while the
221 chlorophenols and intermediates are negatively charged naturally. Because of this, low pH value
222 can facilitate the adsorption of the organic compounds and promote better photocatalytic
223 degradation. In contrast, better removal efficiency of chlorophenols in alkaline condition has also
224 been reported (Stafford et al., 1994; Serpone et al., 1995; Doong et al., 2001), which is consistent
225 with our results. It is explained that the higher pH value can provide more hydroxide ions (OH⁻) to
226 react with holes to form hydroxyl radicals, subsequently enhancing the degradation rate of
227 substituted phenols. The photocatalytic transformation of chlorophenols does not involve the •OH
228 oxidation exclusively and direct electron transfer and surface adsorption reactions also contribute
229 the disappearance of chlorophenols in TiO₂ (Stafford et al., 1994). Since the effect of pH can not
230 be generalized, Gogate and Pandit (2004) recommended that laboratory scale studies are required
231 for establishing the optimum pH conditions unless data are available in the literatures with exactly
232 similar operating conditions. In our case, the faster 2,3-DCP degradation occurring at the higher
233 pH may be attributed to two reasons: (1) more hydroxyl radicals are formed in alkaline solution
234 with more OH⁻ ions; and (2) it is easier for 2,3-DCP to absorb UV light energy at high pH, when
235 the functional group of phenol is dissociated to the phenate ion due to its pK_a = 7.7 (Tehan et al.,
236 2002) and the kinetic reaction constant has been found to be greater by several orders of
237 magnitude (Langlais et al., 1991). The much higher reactivity of the dissociated compounds at the
238 higher pH is believed to be via the attack of electrophilic species such as •OH radicals on the
239 phenate ion, which should be faster with a greater electron density on the aromatic ring. In contrast,
240 at low pH the undissociated species (C₆H₃Cl₂OH) is predominant. The hydrogen atom in polar O–
241 H bond and the electronegative chlorine atom on o-chlorophenol may form intramolecular
242 hydrogen bonding (O–H ··· Cl) and develop a stable 5-membered ring. This hypothesis has been
243 supported by a number of literature precedents (Brune et al., 1999; Kolla et al., 2004). By taking
244 into account these, a possible coordination can be found in Scheme 1. In this way, there is an
245 increase of the o-chlorophenol resonance structure in the ground electronic state and at the same
246 time, an increase of the surroundings rigidity occurs due to formation of the chelate ring. Both

247 effects may resist the attack of •OH radicals on the protonated phenol ring at low pH condition,
248 evidently mirroring a corresponding decrease of the 2,3-DCP degradation.

249

250 [Scheme 1]

251

252 Table 1 also illustrates the pH dependency of the dechlorination of 2,3-DCP and DOC reduction
253 using the TNT film. Similar to its degradation, the photocatalytic dechlorination of 2,3-DCP was
254 observed to be faster at alkaline pH than that at acidic pH (pH 10.9 > 7.8 > 5.3 > 3.4). However,
255 DOC reduction demonstrated an opposite result on the pH dependency, in which the
256 photocatalytic reaction at initial pH 10.9 after 300 min UV irradiation lead to a significant release
257 of chloride by 99% , whereas the loss of DOC was only 20%. In the case of acidic pH (pH 3.4 and
258 5.3), the dechlorination of 2,3-DCP was only 52% and 57% after 300 min, whereas the reduction
259 of DOC reached 47% and 40%, respectively. These results indicate that acidic condition is more
260 favorable for the 2,3-DCP mineralization (further degradation) rather than its decomposition
261 (initial degradation). This may be mainly attributed to the formation of organic intermediates in
262 the photocatalytic reaction. Information on the intermediate concentrations at different pH and the
263 pathway of 2,3-DCP degradation has been studied through the ¹H-NMR analysis as shown in
264 Table 2.

265 Table 2 shows the ¹H-NMR spectral data of residual aromatic compounds and their corresponding
266 concentrations at 12 h irradiation time for the photodegradation of 2,3-DCP with an initial
267 concentration of 300 mg L⁻¹ with different initial pH. It was clearly observed that the distribution of
268 intermediates of 2,3-DCP was pH-dependent. Compound like 2-chlororesorcinol is the major
269 intermediate from the decomposition of 2,3-DCP under three pH conditions (pH 3.4, 5.3, and 10.9).
270 For example, the concentration of 2-chlororesorcinol at pH 10.9 reached 90 mg L⁻¹, which was
271 critically higher than those at pH 3.4 (12.6 mg L⁻¹) and 5.3 (18.9 mg L⁻¹). Furthermore, at pH 10.9
272 the total concentration of residual compounds in the irradiated solution (including the residual 2,3-
273 DCP and compounds 1-7) is obviously higher than those at pH 3.4 and 5.3. This accumulated
274 amount of 2-chlororesorcinol indicated its degradation more slowly under an alkaline condition
275 rather than that under an acidic condition, resulting in a lower DOC reduction under the alkaline
276 condition. Furthermore, the different concentration distribution of intermediates detected at different
277 pH values indicates that the solution media is susceptible to OH attack on the aromatic moiety.

278 Based on the organic intermediates identified by the $^1\text{H-NMR}$ analysis, a possible pathway of
279 2,3-DCP degradation in this reaction system can be proposed as shown in Fig. 4. The reactions
280 may mainly involve the addition of hydroxyl radicals to the organic substrate by three approaches
281 of (a) hydroxylation of the aromatic ring, (b) substitution of chlorine by OH, and (c) oxidation of
282 hydroxylated hydroquinone to the corresponding quinone (Antonarakis et al., 2002). The routes (a)
283 and (b) in Fig. 4 was based on the dechlorination process, where the $\bullet\text{OH}$ substitution removes the
284 chlorine in the ring, leading to form the hydroxyl derivatives (compounds **1**, **2**, and **5**). Due to the
285 stereochemical inhibition of *ortho*-chlorosubstituents, compound **1** is the major intermediate from
286 the 2,3-DCP decomposition under three pH conditions.

287 In general, the OH groups in the chlorophenol ring are *ortho* and *para* directing with activation,
288 whereas Cl substituents are *ortho* and *para* directing with deactivation. When the OH radical, an
289 electrophilic reagent, is attacking 2,3-DCP, it is expected to attack the electron rich positions and
290 cause to generate major *para*- or *ortho*-substituted intermediates (i.e. 3-chlorocatechol, 3,4-
291 dichlorocatechol, and 2,3-dichloroquinol). This seems to be the case of this study. Besides the
292 *para*- or *ortho*-substituted intermediates in present paper, however, a new intermediate, 2-
293 chlororesorcinol, with the highest concentration was observed as *meta*-substituted intermediate
294 under three pH conditions, which is different from the previous report (D'Oliveira et al., 1993).
295 This indicates that this ring position is attacked by $\bullet\text{OH}$ radical preferentially. This can be
296 attributed to the strong stereochemical inhibition of *ortho*-chlorosubstituents to $\bullet\text{OH}$ radical attack,
297 due to the close proximity of OH and Cl groups on the aromatic ring (Tang and Huang, 1995)
298 and/or to the formation of intramolecular hydrogen bonding between the OH and Cl groups in the
299 aromatic ring (mentioned above). As a result, compound corresponding to a primary OH
300 substitution at the *meta*-position was detected.

301 In the routes (c) and (d), the detected intermediates are all rationalized as being formed by
302 hydrogen abstraction, followed by *para*- and *ortho*-hydroxylation of the ring, respectively.
303 Hydroxyl radicals attack preferentially the aromatic moiety due to their electrophilic character to
304 form the hydroxylated compounds **3** and **4**. The two products are then followed to dechlorinate
305 through the $\bullet\text{OH}$ attack (compound **6**) and finally oxidized to corresponding quinone (compound **7**).
306

307 [Table 2]

308 [Fig. 4]

309

310 3.5. Effect of anions

311 The existence of inorganic anions such as chloride, sulfate, carbonate, nitrate, and phosphate is
312 considerably common in wastewaters and also in natural water. The importance of anions effect
313 on the photodegradation of pollutants has been remarkably recognized due to the occurrence of the
314 competitive adsorption, resulting in the inhibitive effect on the photoreaction of organic pollutants.
315 In this study, the initial pH 5.3 was employed and the effect of Cl^- on the photocatalytic
316 degradation of 2,3-DCP in the TNT/UV system was first studied by adding NaCl into the reaction
317 solution at different concentrations of 0.005, 0.05 and 0.1 M, The results are shown in Fig. 5a. It
318 can be seen that while the removal of 2,3-DCP without any anion was achieved by 93% after 300
319 min UV irradiation, it was achieved by 77% only at $[\text{Cl}^-] = 0.005 \text{ M}$, and further down to 64% at
320 $[\text{Cl}^-] = 0.1 \text{ M}$. This indicates that the rate of 2,3-DCP degradation decreased with an increased Cl^-
321 concentration significantly. The observed inhibition effect is often explained by competitive
322 adsorption (Chen et al., 1997). To understand the adsorption behavior of the TNT catalyst in
323 aqueous solution, the TiO_2 nanotubes were peeled off from the TNT films and a powdery
324 suspension was prepared to measure its point of zero charge (pzc) in the pH range of 3.3–10.7 as
325 shown in Fig. 6, where P25 powder with the same concentration was also used as the reference. It
326 can be seen that the pzc of P25 and TNT samples were at pH 6.21 and 5.23, respectively. The
327 results demonstrated that the isoelectric point of TNT catalyst was very close to the reported value
328 of pH 5.3 (Wang et al., 2006) and lower than that of P25 powder. In fact, the photocatalytic
329 process mainly occurs on the photocatalyst surface, but not in the bulk solution. It is suggested that
330 the isoelectric point would greatly influence the adsorption of organic substrates and its
331 intermediates on the surface of photocatalyst during photoreaction (Hu et al., 2001). Therefore, the
332 TiO_2 nanotube surface is positively charged at $\text{pH} < 5.2$, and Cl^- can be easily adsorbed onto the
333 positively charged surface of the catalyst by electrostatic attraction, leading to the competitive
334 adsorption.

335

336 [Fig. 5]

337 [Fig. 6]

338

339 The other probability is that chloride ions can act as scavengers of positive holes (h^+) and/or
340 hydroxyl radical ($\bullet OH$) through the following reactions:

341



344

345 Meanwhile, the dichloride radical anion $Cl_2\bullet^-$ from the further reaction of $Cl\bullet$ with Cl^- (Eq. 3) is
346 reactive with organic substances and the recombination of two chloride radicals $Cl\bullet/Cl_2\bullet^-$ (Eqs. 4
347 and 5) (Rincón and Pulgarin, 2004) are the source of molecular chlorine, thus ending the radicals
348 transfer.

349



353

354 Since $Cl\bullet$ is less reactive than $\bullet OH$, the excess Cl^- may have the inhibition effect on the
355 photodegradation of 2,3-DCP in aqueous solution.

356 Figure 5b shows the effects of different anions (i.e. Cl^- , NO_3^- , $H_2PO_4^-$, and SO_4^{2-}) at the same
357 concentration of 0.05 M. Compared to the control test in the aqueous 2,3-DCP solutions without
358 anion, the existence of all anions reduced the 2,3-DCP degradation to a certain degree. Among
359 them, the strongest inhibition of 2,3-DCP degradation resulted from SO_4^{2-} due to its ionic
360 properties. At $pH < 5.3$, like Cl^- , SO_4^{2-} can inhibit the photodegradation of the chlorophenol
361 through two ways of: (1) competitive adsorption with the 2,3-DCP on the TNT film surface due to
362 the higher ionic strength and (2) trapping positive holes and/or hydroxyl radical, where SO_4^{2-} can
363 be led to the generation of less reactive radical $SO_4\bullet^-$. Actually, the divalence charge for SO_4^{2-} can
364 lead to the stronger binding of the SO_4^{2-} with the catalyst, as compared with the single valence
365 ions such as NO_3^- , Cl^- , and $H_2PO_4^-$, thus resulting in the stronger competitive adsorption. For the
366 addition of $H_2PO_4^-$, the behavior of $H_2PO_4^-$ ions is similar to SO_4^{2-} ions, in that the $H_2PO_4^-$
367 reacted with h^+ and $\bullet OH$ to form $H_2PO_4\bullet^-$, less reactive than that of h^+ and $\bullet OH$. Formation of
368 inorganic radical anions under these circumstances was also reported in some literatures (Abdullah
369 et al., 1990; Bekbölet et al., 1998; Hu et al., 2003). The addition of NO_3^- to the solution in this

370 study showed a minor effect on the photocatalytic degradation of 2,3-DCP only. Abdullah et al.
371 (1990) also reported that the presence of NaNO_3 had negligible effect on the photodegradation of
372 ethanol and 2-propanol under UV light irradiation. On the basis of above discussion, the observed
373 inhibition effect may be therefore explained by combination of the competitive adsorption and the
374 formation of less reactive radicals during the photocatalytic reaction.

375

376 **4. Conclusions**

377 The highly-ordered TiO_2 nanotube arrays were successfully formed on Ti foil by an anodic
378 oxidation method. The experimental results showed that the anodic TNT film had the higher
379 photocatalytic activity than the conventional TiO_2 thin film prepared by a sol-gel method with a
380 factor of about 2.6 times. DO acts as an effective electron acceptor to extend the hole's lifetime
381 and to form the oxidizing species of $\bullet\text{OH}$ radicals, affecting the photoactivity of the TNT film.
382 Effect of solution pH demonstrated that an alkaline condition is favorable to 2,3-DCP degradation
383 and dechlorination, but an acidic condition is more beneficial to further mineralization. The
384 presence of NO_3^- had a weak inhibition effect on the degradation of 2,3-DCP, while SO_4^{2-} had the
385 strongest inhibition.

386

387 **Acknowledgements**

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389 Polytechnic University in providing a PhD scholarship for H. C. Liang.

390

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512

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514 **List of figure captions**

515

516 Fig. 1. (a) FESEM images of TNT film; (b) XRD patterns of Ti foil and TNT film calcined at 500
517 °C for 1 h.

518

519 Fig. 2. 2,3-DCP degradation with TiO₂ film and TNT film under UV illumination (Initial pH 5.3
520 and [C₀] = 20 mg L⁻¹).

521

522 Fig. 3. Effect of DO concentration on 2,3-DCP degradation with TiO₂ film and TNT film by
523 blowing different gases (N₂, air or O₂), respectively (Initial pH 5.3 and [C₀] = 20 mg L⁻¹).

524

525 Fig. 4. Pathway of the 2,3-DCP degradation in the TNT/UV system.

526

527 Fig. 5. (a) Influence of Cl⁻ concentrations on the photocatalytic deactivation of TNT/UV system
528 (Initial pH 5.3 and [C₀] = 20 mg L⁻¹); (b) Photocatalytic deactivation in the presence of
529 different anions at 0.05 M (Initial pH 5.3 and [C₀] = 20 mg L⁻¹): (●) no anion; (■) NO₃⁻; (▲)
530 H₂PO₄⁻; (▼) Cl⁻; (◆) SO₄²⁻.

531

532 Fig. 6. Zeta potential analysis of P25 and TNT samples as a function of pH.

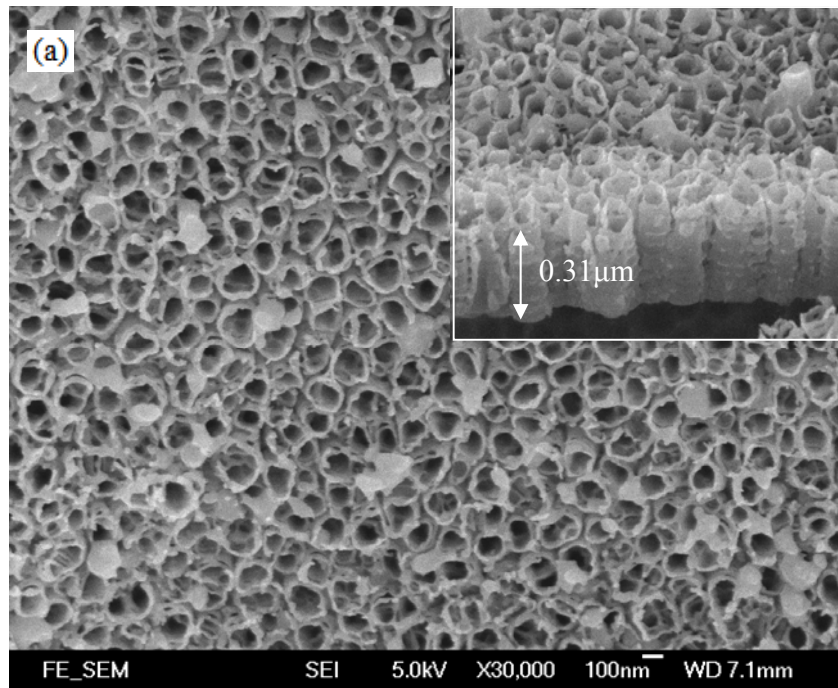
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534 Scheme 1. Formation of intramolecular hydrogen bonding in 2,3-DCP molecular structure.

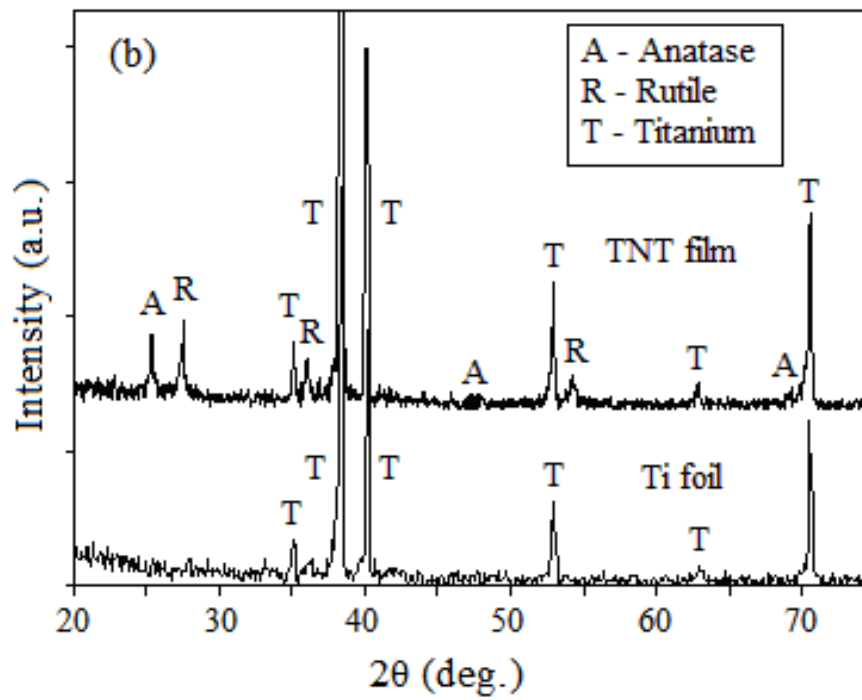
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537 Fig. 1.



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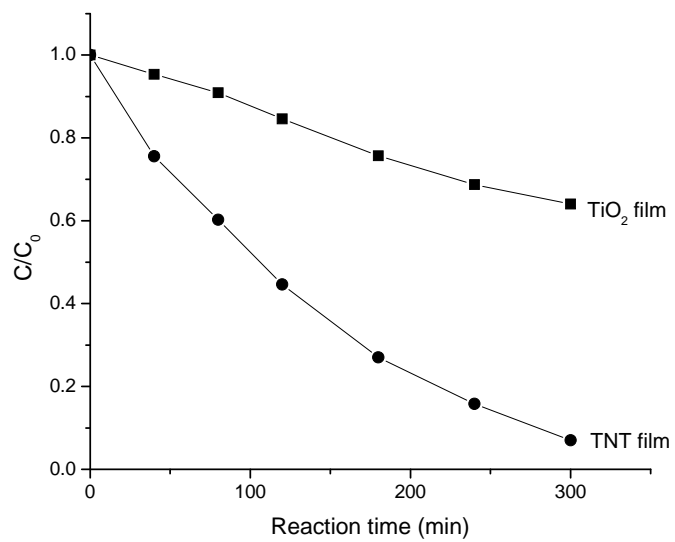
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542 Fig. 2

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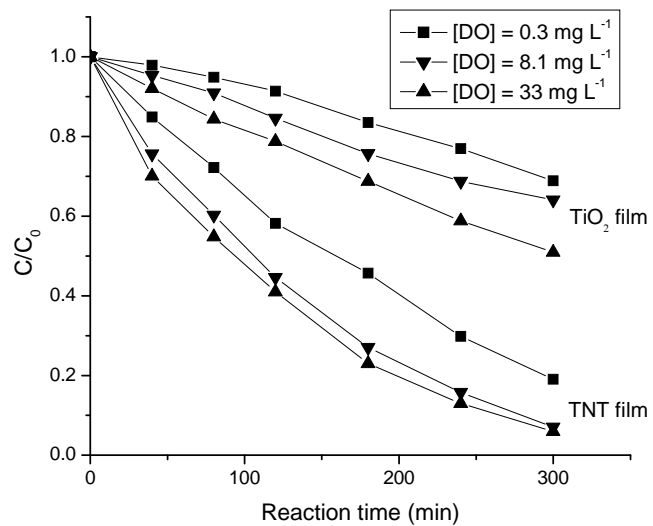
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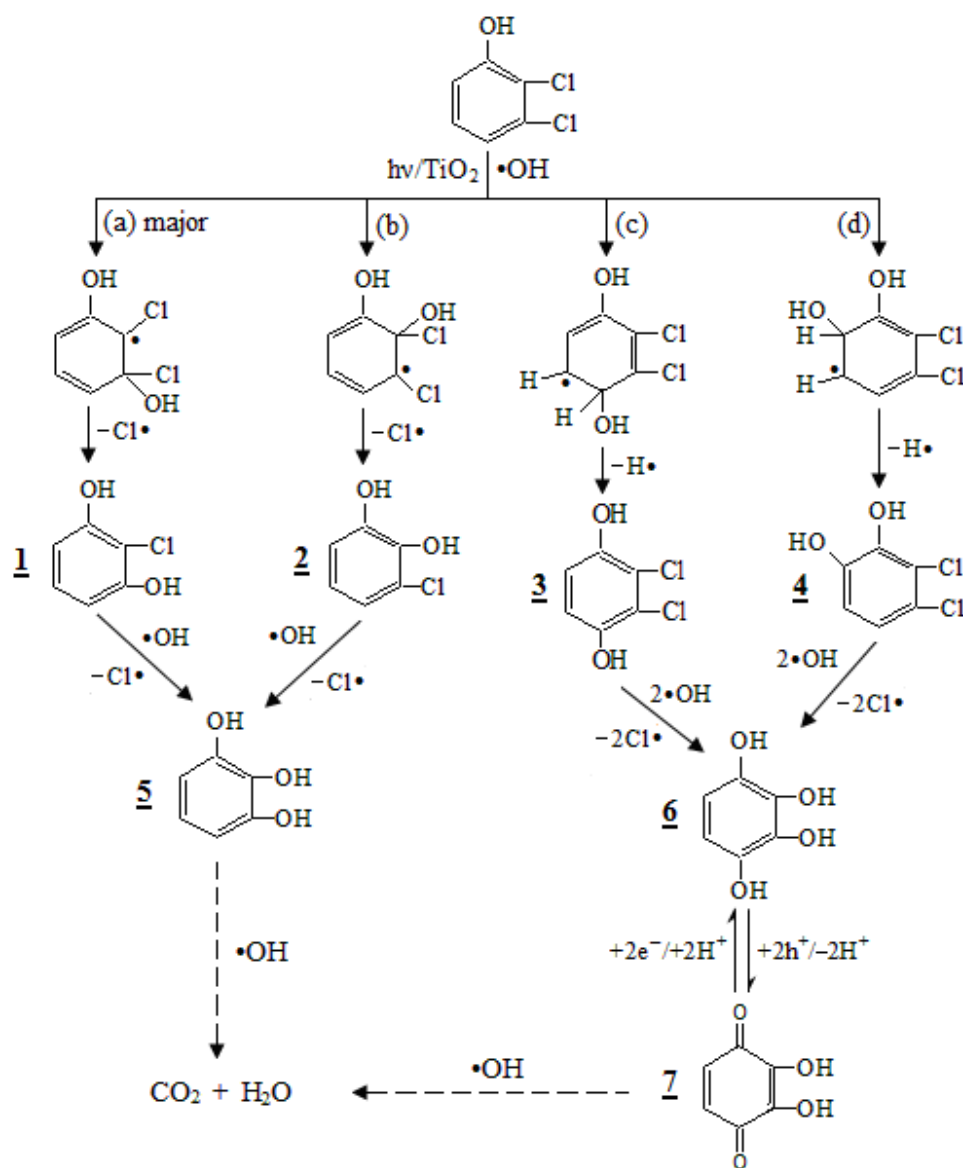
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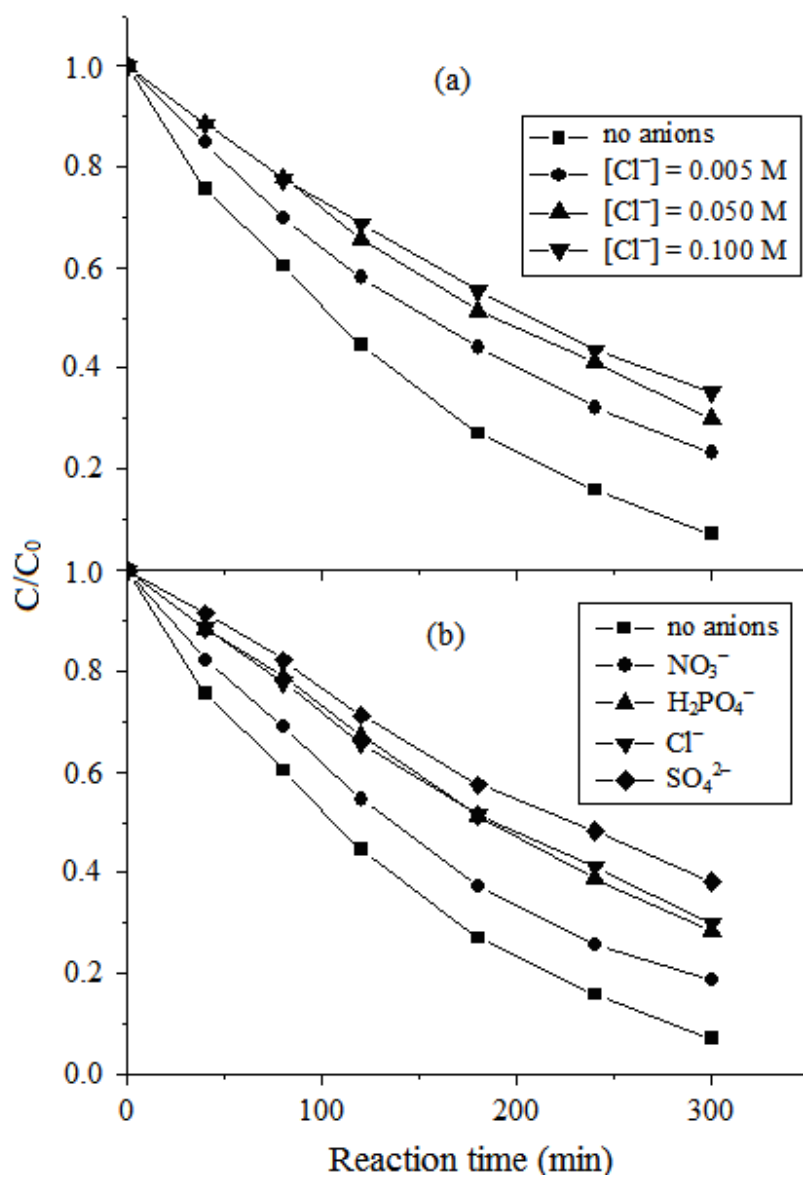
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586 Fig. 5

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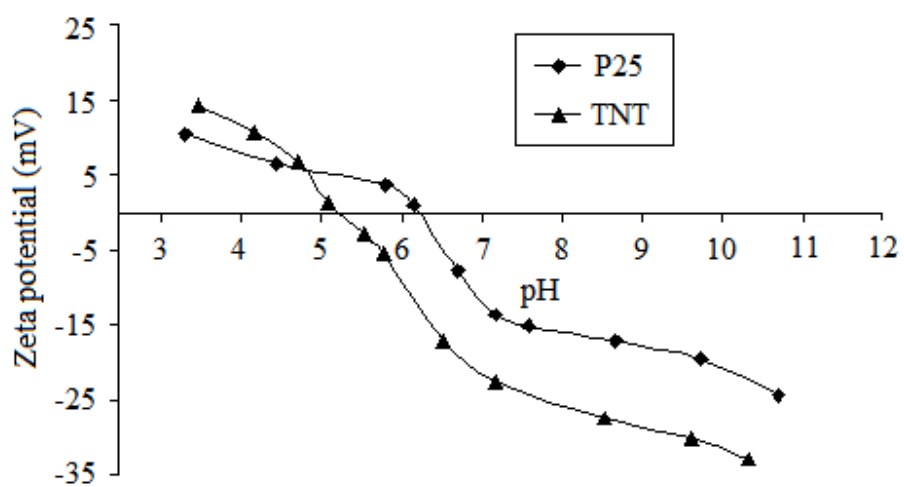
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594 Fig. 6

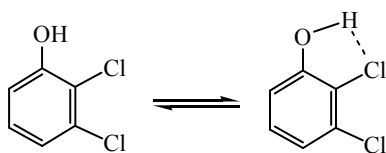


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602 Scheme 1.

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Table 1

Effect of solution pH on the 2,3-DCP degradation, dechlorination, and DOC removal after 300 min reaction

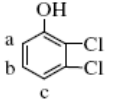
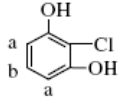
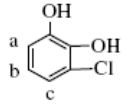
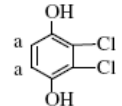
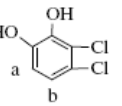
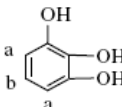
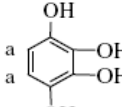
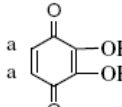
Test No.	pH		2,3-DCP degradation ^a		Dechlorination ^b (%, Cl ⁻ /Cl _{total})	DOC reduction (%)
	Initial	Final	<i>k</i> (min ⁻¹)	(%)		
1	3.4	3.0	0.007	90	52	47
2	5.3	3.4	0.008	93	57	40
3	7.8	3.8	0.011	96	74	37
4	10.9	7.1	0.024	100	99	20

^a Photocatalytic degradation of 2,3-DCP was thought to be a pseudo-first-order reaction; *k* is the kinetic constant.

^b Dechlorination was calculated on the basis of the total chlorine (Cl⁻/Cl_{total}) in 2,3-DCP of 20 mg L⁻¹.

641 Table 2

642 Identification of intermediates from 2,3-DCP degradation by ¹H-NMR analysis

Compound ^a No.	Proton	Chemical shifts (ppm)	Description ^b	Concentrations (mg L ⁻¹)		
				pH 3.4	pH 5.3	pH 10.9
	a b c	6.97 7.18 7.13	1H, d, $J_{ab} = 9.85$ 1H, m, 1H, d, $J_{cb} = 8.34$	47.2	47.2	26.0
(2,3-dichlorophenol)						
	a b	6.62 7.09	2H, d, $J_{ab} = 9.1$ 1H, t, $J_{ba} = 9.1$	12.6	18.9	90.1
(2-chlororesorcinol)						
	a b c	6.52 6.82 6.86	1H, d, $J_{ab} = 8.9$ 1H, m, 1H, d, $J_{bc} = 8.9$	8.4	12.6	2.1
(3-chlorocatechol)						
	a a	6.75	1H, s	2.3	2.3	2.3
(2,3-dichloroquinol)						
	a b	6.46 6.95	1H, d, $J_{ab} = 8.7$ 1H, d, $J_{ba} = 8.8$	trace	trace	6.9
(5,6-dichlorocatechol)						
	a b a	6.40 6.61	2H, d, $J_{ab} = 8.3$ 1H, t, $J_{ba} = 8.1$	2.7	1.8	2.7
(Pyrogallol)						
	a a	6.08	2H, s	4.2	2.1	10.5
(1,2,3,4-benzenetetrol)						
	a a	6.89	2H, s	1.7	1.7	1.6
(2,3-dihydroxy-p-benzoquinone)						

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644 ^a Different protons linked on benzene ring are marked as a, b, and c, respectively.645 ^b Singlet, doublet, triplet, and multilet are abbreviated as s, d, t, and m, respectively; coupling
646 constants (J) are given hertz.