

1 Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO₂-UV
2 reaction system

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11 **ABSTRACT**

12 The application of a combined ferrate-photocatalysis process for the aqueous
13 degradation of dimethyl phthalate (DMP) has been studied. The behaviour of the
14 Fe(VI)-TiO₂-UV process at pH 9 in the presence and absence of dissolved oxygen has
15 been compared and significant differences found. In comparative tests under N₂ and
16 O₂ bubbling, the chemical reduction rate of ferrate as conductance band electron
17 acceptor was similar, but the resulting degradation of DMP was substantially lower in
18 the presence of oxygen. It is speculated that the presence of oxygen leads to the
19 formation of Fe-O-(organic) complex species that adsorb to, and deactivate, the
20 surface of the photocatalyst. The presence of surface adsorbed complex species was
21 indicated by FTIR spectroscopy and a reduced TiO₂ adsorption capacity for DMP. In
22 the presence of typical environmental levels of dissolved oxygen (~10 mg L⁻¹), the
23 Fe(VI)-TiO₂-UV process achieved a modest degree of DMP degradation (40% in 120
24 mins).

25 **Keywords:** Dimethyl phthalate; Ferrate; Photocatalysis; Oxidation; Titanium dioxide;
26 UV irradiation

28 **1. Introduction**

29 Phthalate acid esters (PAEs) are a class of chemical compounds that are widely used
30 in various industrial production as plasticizers for the production of polyvinyl chloride
31 resins, adhesives, and cellulose film coating (about 85% of the whole production) in
32 order to improve the mechanical properties of the plastic resin, particularly its
33 flexibility and softness (Giam et al., 1984; Nilsson, 1994; Vitali et al., 1997).
34 However, to provide the required flexibility, the phthalate plasticizer is not covalently
35 bound to the resin and is therefore capable of migrating into the environment (Nilsson,
36 1994). The current worldwide production of phthalate acid esters has reached 2.7
37 million metric tons per year (Bauer and Hermann, 1997), and such large production
38 and utilization are causing a significant environmental diffusion of these compounds.

39 The short-chained esters such as dimethyl phthalate (DMP) are among the most
40 frequently identified PAEs in diverse environmental samples, including surface
41 marine waters, freshwaters and sediments (Gledhill et al., 1980), high concentrations
42 of about 300 mg L⁻¹ of DMP have been documented in landfill leachate (Mersiowsky,
43 2002). DMP and its intermediates are suspected to be responsible for functional
44 disturbances in the nervous systems and liver of animals. Known as an
45 endocrine-disrupting chemical, it may also promote chromosome injuries in human
46 leucocytes and also interfere with the reproductive systems and normal development
47 of animals and humans (Jobling et al., 1995; Allsopp et al., 1997). Therefore, the US
48 Environmental Protection Agency (USEPA) has listed it as a priority pollutant

49 (USEPA, 1992).

50 In addition to their potential toxicity, phthalate esters are becoming a class of
51 pollutants of concern in environmental- and waste- waters since they are recalcitrant
52 to both biodegradation, owing to the benzene carboxylic group, and photolytic
53 degradation, due to the weak absorption of light at wavelengths greater than 300 nm
54 (Staples et al., 1997; Maihot et al., 2002; Zhao et al., 2004). Therefore, it is necessary
55 to identify appropriate treatment technologies that may be applied to remove such
56 pollutants from waters and wastewaters. Among the range of possible treatment
57 technologies, photocatalysis using semiconductor catalysts such as TiO₂, has been
58 shown to be an effective treatment for various aqueous pollutants (Chen et al., 1999;
59 Davis and Green, 1999).

60 The photocatalytic method is based on the reactive properties of electron–hole pairs
61 generated in the semiconductor particles under illumination by light of energy greater
62 than its band gap.



64 However, the recombination between electrons (e⁻) and holes (h⁺) is an extremely
65 efficient process. One strategy for inhibiting the e⁻/h⁺ recombination is to add some
66 electron acceptors to the reaction. Oxygen (as dissolved O₂) has been widely
67 demonstrated to be a good acceptor for such a purpose, with a role extending beyond
68 that of electron scavenging (Linsebigler et al., 1995), and it is always present in
69 source waters and effluents. The use of other peroxides such as H₂O₂, S₂O₈²⁻ and O₃
70 has been demonstrated also to enhance significantly the rate of degradation of

71 different organic contaminants (Malato et al., 1998; Wong and Chu, 2003), because
72 they can trap the photogenerated electrons more efficiently than O₂ (Plelizzetti et al.,
73 1991). Ideally, these additives should fulfill the criteria of dissociating into harmless
74 byproducts and lead to the formation of ·OH radicals or other oxidizing agents.

75 Ferrate (FeO₄²⁻), the salt of the Fe(VI) oxyanion, is a powerful oxidant over a wide
76 pH range and during aqueous oxidation it is chemically reduced to iron(III) species,
77 such as Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺, depending on the conditions, and molecular
78 oxygen. The reduction potential of Fe(VI) in basic solution is more positive than V_{cb}
79 (-0.7 V), and the thermodynamic driving force for the formation of OH⁻ ions is
80 significantly higher than that of the photocorrosion pathway of TiO₂ in basic media
81 (Chenthamarakshan et al., 2000). The combination of ferrate and photocatalysis has
82 been speculated as offering an important oxidation synergy arising from the
83 (conductance band) electron scavenging by ferrate, with the combined process
84 summarised as:

85 (a) One electron reduction of Fe(VI) to Fe(V) (FeO₄²⁻ + e_{cb}⁻ → FeO₄³⁻); Fe(V) has
86 been reported to be substantially more reactive than Fe(VI) with certain pollutants
87 (Sharma et al., 2005a);

88 (b) More efficient photocatalytic oxidation by reduced electron/hole recombination
89 due to electron scavenging by ferrate (via process (a)).

90 Recently, there have been a limited number of reported investigations concerning
91 the degradation of organic water pollutants by the combination of ferrate and
92 photocatalysis (Sharma et al., 2005b; Yuan et al., 2006). In our previous studies, while

93 the rates for organic conversion were increased in the Fe(VI)-TiO₂-UV system due to
94 the synergistic oxidation-reduction reaction, it was also found there is a significant
95 selectivity for different compounds, which depends on the reaction conditions. In the
96 work reported here, DMP was selected as the target chemical, since it is refractory to
97 ferrate oxidation alone and has a low reaction rate by TiO₂ photocatalysis under a N₂
98 gas flow. Various experiments were carried out using DMP solutions in the
99 Fe(VI)-TiO₂-UV system, in which the scavenging of TiO₂ photocatalysis electrons by
100 Fe(VI), and DMP degradation, were studied simultaneously under different reaction
101 conditions in order to evaluate the reaction process in great detail. In particular we
102 have investigated the application of different gases (N₂ and O₂) to the reaction
103 solution and their effects on the deactivation of photocatalysis within the overall
104 oxidation-reduction reaction.

105

106 **2. Materials and Methods**

107 *2.1. Chemicals*

108 Dimethyl phthalate (DMP) chemical with 98.7% purity was obtained from Aldrich
109 Chemical Company. Potassium ferrate (K₂FeO₄) with a purity of >90% was
110 synthesized in our lab according to a preparation procedure used in previous work (Li
111 et al., 2005). A 0.001M sodium borate (Na₂B₄O₇·10H₂O)/0.005M sodium phosphate
112 dibasic (Na₂HPO₄) solution at pH 9.0 was prepared and used with the dual aims of
113 maintaining the aqueous stability of ferrate and to eliminate the interference of Fe³⁺ in
114 the ferrate analysis. TiO₂ powder (Degussa P-25) was used as a model photocatalyst.

115 2.2. *Experimental method*

116 All reactions were carried out in a quartz reactor and an 8-W medium-pressure
117 mercury lamp (LZC-UVA-365) was used as a UVA light source. The light intensity
118 was 0.40 mW cm^{-2} , as determined by a radiometer (Lutron UV light meter, Model
119 UVA-365). Aqueous DMP solution with an initial concentration of $7\text{-}10 \text{ mg L}^{-1}$ was
120 prepared at pH 9 with $0.005\text{M Na}_2\text{HPO}_4$ and $0.001\text{M Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Ferrate
121 chemical was added just before each reaction at different molar ratios as required.
122 During the reaction it was assumed that the chemical reduction of Fe(VI) leads to
123 Fe(III) species which preferentially react with the phosphate in solution to form a
124 soluble complex, thereby preventing $\text{Fe}(\text{OH})_3$ precipitation; separate tests by the
125 authors and other studies have confirmed this. In the experiments involving
126 photocatalysis, the TiO_2 catalyst was added at a dosage of 40 mg L^{-1} and initially
127 mixed with the DMP solution in the dark for 30 min to achieve an
128 adsorption/desorption equilibrium before the photoreaction. In particular experiments
129 either oxygen or nitrogen gas was applied (bubbled) to the reaction solution in
130 sufficient quantities and continuously. During the reactions, samples for analysis were
131 taken at different time intervals and the reaction terminated by adding sodium sulphite,
132 followed by filtration (by syringe through a $0.22 \mu\text{m}$ Millipore membrane) to remove
133 any particulates prior to analysis. All experiments were carried out at room
134 temperature.

135 2.3. *Analyses*

136 The DMP concentration was determined using high performance liquid

137 chromatography (HPLC) incorporating a high pressure pump (Spectrasystem HPLC
138 P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). A pinnacle II
139 C18 column (5 μm particle size, 250 mm \times 4.6 mm i.d.) was employed and a mobile
140 phase of acetonitrile/water (80:20, v/v) was used at a flow rate of 0.8 ml min⁻¹. An
141 injection volume of 20 μL was used and the concentration of DMP was determined by
142 UV detection at 227 nm. The ferrate concentration was measured by means of
143 UV-visible light absorbance spectroscopy at 510 nm. The crystal structure of the
144 catalysts were examined by X-ray diffraction (XRD) using a diffractometer with
145 radiation of a Cu target (K α , λ = 0.15406 nm).

146

147 **3. Results and Discussion**

148 *3.1. Ferrate reduction in the TiO₂-Ferrate reaction system*

149 An initial set of experiments was conducted to study the reaction and chemical
150 reduction of ferrate with DMP solution in the absence of dissolved oxygen and under
151 different reaction conditions, as follows: (1) ferrate with DMP solution in the dark; (2)
152 ferrate with DMP solution under UV illumination; (3) ferrate and TiO₂ with DMP
153 solution in the dark; (4) ferrate and TiO₂ with DMP solution under UV illumination.
154 To purge the dissolved oxygen from the reaction solution, N₂ gas was applied to the
155 reaction solution in the above experiments. The experimental results are shown in Fig.
156 1a. It can be seen that Fe(VI) was reduced very slowly in the dark and only slightly
157 faster either under UV illumination alone or with TiO₂ suspension but without UV
158 illumination. However, in contrast, a rapid Fe(VI) reduction occurred in the presence

159 of TiO₂ suspension under UV illumination. Since DMP is refractory to ferrate
160 oxidation, it is clear that the rapid reduction of Fe(VI) resulted from its scavenging of
161 excited conduction band electrons from the TiO₂ catalyst. It is believed that the
162 electron scavenging by Fe(VI) greatly diminishes the recombination of conduction
163 band electrons (e⁻) and valence band holes (h⁺), thereby enhancing the quantum
164 efficiency of TiO₂ catalyst during the photoreaction.

165 **[Fig. 1]**

166 *3.2. DMP degradation in the TiO₂-Ferrate reaction system*

167 It has been shown previously that the presence of certain metal ions or oxidizing
168 reagents in a photocatalytic system can act as electron acceptors to prevent the rapid
169 self-recombination of e⁻ and h⁺, thereby enhancing the degradation of a target
170 compound by photocatalysis (Malato et al., 1998; Wong and Chu, 2003). This effect
171 was demonstrated in our experiments with DMP and the results of reactions under
172 different conditions, and in the absence of dissolved oxygen, are shown in Fig. 1b. It
173 can be seen that DMP was not significantly degraded by ferrate alone, indicating a
174 clear selectivity of ferrate oxidation to this particular organic substrate. Although the
175 TiO₂ photocatalysis reaction has less selectivity in the reaction with organic substrates,
176 the degradation of DMP by a typical TiO₂ photocatalytic oxidation was also poor,
177 with only a 12% reduction in DMP after 120 min. However, in marked contrast, the
178 DMP degradation by photocatalysis with ferrate (Fe(VI)-TiO₂-UV system) was
179 substantial and reached approximately 65% after 120 min (Fig. 1b). These results
180 demonstrate a clear synergistic effect from the combination of photocatalysis with

181 ferrate. Due to its greater oxidizing power than other electron acceptors, such as
182 permanganate or peroxides, and its possible reduction to highly reactive Fe(V), ferrate
183 may play both roles of electron scavenging (thus enhancing the photo-oxidation) and
184 direct oxidation of organic substances; the latter comprising both DMP and
185 intermediate reaction products from the DMP degradation.

186 *3.3. Photocatalytic reduction of ferrate and degradation of DMP in the presence of*
187 *dissolved oxygen.*

188 In this further study of the DMP degradation in the Fe(VI)-TiO₂-UV reaction system,
189 comparative experiments were carried out under identical conditions but with a
190 continuous gas flow of either N₂ or O₂. In both cases the change in ferrate and DMP
191 concentrations with time were carefully monitored and the experimental results are
192 shown in Fig. 2.

193 **[Fig. 2]**

194 With N₂ gas bubbling, the results showed that ferrate rapidly disappeared within the
195 first 20 min, while DMP also decreased rapidly initially and then more gradually, with
196 an overall loss of DMP equivalent to 64% at 120 min (Fig. 2a). These results indicate
197 that the DMP degradation by TiO₂ photocatalysis during the first 20 min was
198 significantly enhanced due to the participation of ferrate. In contrast, the experiments
199 with O₂ gas bubbling showed a very different behaviour with a very similar loss of
200 ferrate but almost no degradation of DMP during the 120 min reaction time (Fig. 2b);
201 this phenomenon was confirmed by undertaking several replications of the tests. From
202 these results it is evident that the existence of dissolved oxygen in the reaction

203 solution did not reduce the rate of ferrate reduction, as ferrate is a more favorable
204 electron acceptor ($E^0 = 0.72$ V for Fe(VI) reduction) than oxygen ($E^0 = -0.13$ V for O₂
205 reduction) (Wang and Hong, 1999). However, the existence of dissolved oxygen (DO)
206 in the Fe(VI)-TiO₂-UV reaction system clearly inhibited the DMP degradation to a
207 major extent. The influence of DO concentration on the DMP degradation was studied
208 further by gas bubbling with N₂, air and O₂, respectively, and the results are shown in
209 Fig. 3. It can be seen clearly that the rate of DMP degradation decreased
210 systematically with increased DO concentration in the range of 0-35 mg L⁻¹.

211 **[Fig. 3]**

212 From previous studies, it has been reported that carboxylic acids can react with
213 certain metal ions in an aqueous photocatalytic reaction to form metal-oxygen
214 complexes such as Cr-O-complexes or Hg-O-complexes. These metal-complexes can
215 attach at the surface of TiO₂ to block the photocatalysis. It has also been reported that
216 the formation of metal complexes that deactivate the surface photocatalysts could be
217 aided by the presence of oxygen. Furthermore, the surface and structural features of
218 the photocatalyst are very important in the extent to which the deactivation process
219 takes place. These studies suggest that the existence of dissolved oxygen in the
220 metal-TiO₂-UV system can play a double role of scavenging the excited electrons on
221 the TiO₂ surface and forming certain metal-O-complex species, thereby inhibiting
222 organic substrate degradation (Colón, 2001; Botta, 2002). Thus, this study has shown
223 that DMP degradation in the Fe(VI)-TiO₂-UV reaction can be substantially
224 diminished by the presence of oxygen in the reaction solution. It is believed that DO

225 in the Fe(VI)-TiO₂-UV system causes the formation of a Fe-O-complex from the
226 reduced Fe species, such as Fe(IV) or Fe(III), and with DMP and/or its reaction
227 products, either on the surface of TiO₂ catalyst or in the bulk solution, thereby
228 preventing the DMP oxidation reaction. However, the mechanism of photocatalytic
229 degradation of DMP with a benzenecarboxylic group is complicated and there have
230 been many studies concerning the mechanism followed by organic compounds
231 containing this group during their photocatalytic oxidation (Colón, 2001; Botta, 2002).
232 Benzenecarboxylic compounds tend to form quinone/hydroquinone and polyhydroxy
233 derivative (mainly dihydroxyl) species in the first stages of photodegradation.
234 Therefore, it might be proposed that the formation of derivative species from the
235 aromatic ring leads to the formation of metal-O-complexes in the presence of
236 dissolved oxygen, probably at the surface of the photocatalyst, which thereby
237 deactivates the catalyst. In contrast, it seems that the absence of DO (ie. under a
238 nitrogen flow) avoids the formation of the Fe-O-complex that causes the deactivation
239 of the photocatalysis observed for the DMP degradation in the Fe(VI)-TiO₂-UV
240 reaction system.

241 *3.4. Further study of the deactivation of the photocatalysis*

242 In order to study further the deactivation of the photocatalysis in the Fe(VI)-TiO₂-UV
243 reaction system in the presence of oxygen, an experiment was performed involving
244 the DMP solution with TiO₂ catalyst (40 mg L⁻¹) at pH 9 under UV illumination for
245 120 min, during which ferrate chemical was systematically dosed four times (0.16
246 mM × 4 = 0.64 mM) at 0, 30, 60 and 90 min to observe the corresponding ferrate

247 reduction and DMP degradation; the results are shown in Fig. 4. It can be seen in Fig.
248 4a that the ferrate was rapidly reduced in the presence of TiO₂ and UV illumination,
249 with the majority of the ferrate disappearing within 10 min. After each subsequent
250 addition of ferrate, its chemical reduction followed a similar pattern, but the rate of
251 reduction gradually decreased. These results indicate that the proposed formation of a
252 Fe-O-(organic) complex on the surface of the TiO₂ only diminished the ferrate
253 reduction to a minor degree. However, the corresponding DMP degradation (Fig. 4b)
254 appeared insensitive to the dosing of ferrate and displayed a steady and gradual trend
255 throughout the first 120 min reaction; the overall degradation was approximately 15%.
256 It is speculated that the formation of a Fe-O-(organic) complex on the surface of the
257 TiO₂ was able to substantially inhibit or block the photocatalysis of DMP.

258 **[Fig. 4]**

259 To further investigate the deactivation of the photocatalysis resulting from the
260 Fe-O-(organic) complex formation on the surface of TiO₂ catalyst or in the bulk
261 reaction solution, the TiO₂ catalyst used in the above reaction was removed from the
262 reaction solution by centrifuging and then washed with either distilled water only or
263 1% HCl solution, respectively; the recovered TiO₂ catalysts were then available for
264 subsequent testing. A set of four experiments using fresh TiO₂, the water-washed
265 TiO₂, or the HCl-washed TiO₂, at the same dosage of 40 mg L⁻¹ was performed in
266 either the residual DMP solution after the previously described 120 min reaction, or a
267 fresh DMP solution, for 120 min. The results of these tests are shown in Fig. 5.

268 **[Fig. 5]**

269 The first experiment using fresh TiO_2 in the residual DMP solution demonstrated
270 that the DMP degradation was not significantly improved by replacing the catalyst
271 with fresh TiO_2 , indicating the inhibition of further DMP degradation by the presence
272 of Fe-O-(organic) complexes in the bulk solution. The other three experiments
273 involved using fresh DMP solutions with the different TiO_2 catalysts. These
274 demonstrated that the water-washed TiO_2 still retained a certain amount of the
275 Fe-O-(organic) complex on its surface since there was a low photocatalytic activity
276 for DMP degradation, but the HCl-washed TiO_2 achieved a good DMP degradation
277 (55% after 120 min) similar to that of fresh TiO_2 . These results provided evidence that
278 the DMP degradation was diminished by the formation of the Fe-O-(organic) complex
279 on the surface of the catalyst and that the deactivated TiO_2 catalyst can be reactivated
280 by washing with 1% HCl solution. In summary, the experimental results in Figs. 5 and
281 6 indicate that DMP degradation by photocatalytic oxidation is adversely affected by
282 the formation of Fe-O-(organic) complexes from the presence of dissolved oxygen
283 and reduced iron species in the reaction; the reduced oxidation appears to occur where
284 the Fe-O-(organic) complexes are in the bulk solution or coated on the surface of TiO_2
285 the catalyst.

286 *3.5. Adsorption of DMP on fresh and used TiO_2 catalysts*

287 It is generally believed that the photocatalysis of DMP in aqueous solution is a
288 heterogeneous reaction that mainly occurs on the surface of TiO_2 catalysts and the rate
289 of DMP adsorption onto the TiO_2 surface can play a key role in the
290 Fe(VI)- TiO_2 -UV(O_2) system. A set of adsorption experiments involving aqueous

291 DMP solution with TiO₂ catalyst (0.5 g L⁻¹) was performed at pH 9 in the dark for 24
292 h to determine and study the DMP adsorption isotherms. Specifically, three conditions
293 were considered: (1) fresh TiO₂ catalyst in fresh DMP solutions; (2) used TiO₂
294 catalyst in fresh DMP solutions; (3) fresh TiO₂ catalyst in the residual DMP solution
295 after 2 h reaction. The results of this set of experiments are shown in Fig. 6.

296 **[Fig. 6]**

297 From Fig. 6, it can be seen that the fresh TiO₂ in the fresh DMP solution exhibited
298 the greatest DMP adsorption, while the used TiO₂ in the fresh DMP solution, and the
299 fresh TiO₂ in the residual DMP solution, showed a much lower DMP adsorption.
300 These results indicated that the formation of a Fe-O-(organic) complex either on the
301 surface of the TiO₂ catalyst or in the bulk solution inhibited the DMP adsorption onto
302 the TiO₂ catalyst, which might be one of the important reasons for a low DMP
303 degradation in the reaction system.

304 *3.6. Comparison of fresh and used TiO₂ catalysts*

305 The fresh and used TiO₂ catalysts were examined by an XRD method to study the
306 characteristics of their structure and their XRD patterns are shown in Fig. 7. The
307 results demonstrated there is no significant difference between the fresh (a) and used
308 (b) TiO₂ catalysts and two types of peaks representing anatase and rutile phases can
309 be seen in both the patterns. These XRD patterns confirmed that there is no significant
310 change found in the crystal structure of TiO₂ catalyst after the reaction although some
311 deposits with a dark yellow colour were visually observed on the used TiO₂ catalyst.
312 These deposits could be Fe(OH)₃ or an Fe-O-(organic) complex which needs to be

313 studied further.

314 **[Fig. 7]**

315 The TiO₂ catalysts used in three different reaction conditions were further
316 examined by FTIR to study their chemical composition; these were: (a) TiO₂-UV
317 under a N₂ gas flow; (b) Fe(VI)-TiO₂-UV under a N₂ gas flow; (c) Fe(VI)-TiO₂-UV
318 under a O₂ gas flow. The FTIR spectra of the three catalysts are shown in Fig. 8. It
319 can be seen that all of them have the same peaks near the 3434 and 1634 cm⁻¹ wave
320 numbers corresponding to the stretching vibrations of O-H linkage on the TiO₂
321 surface. However spectrum “c” is very different from the spectra “a” and “b” although
322 the same dosage of ferrate was used in the reaction conditions of “b” and “c”. Four
323 new peaks were observed at wave numbers, 1407, 1083, 984 and 515 cm⁻¹, which can
324 be assigned to C-O, C-H, C-H and Fe-O vibrations, respectively (Pretsch et al., 2000).
325 These results provide further evidence that the presence of oxygen in the
326 photocatalytic reaction leads to the formation of a surface-bound chemical complex
327 on the TiO₂ catalyst.

328 **[Fig. 8]**

329

330 **4. Conclusions**

331 This study has investigated the photoreduction of ferrate and photocatalytic
332 degradation of DMP in an aqueous Fe(VI)-TiO₂-UV reaction system, at pH 9, under
333 different gas flow conditions. It was found that when the reaction was conducted
334 under a N₂ gas flow, ferrate was highly effective in scavenging the excited,
335 conductance band electrons from the surface of TiO₂ catalyst which contributed to a

336 substantial oxidation of DMP by the synergistic effects of ferrate, and photocatalytic,
337 oxidation mechanisms. However, when the reaction was performed under an air or O₂
338 gas flow, the DMP degradation was greatly inhibited even though the ferrate was
339 rapidly reduced. It is believed that the presence of oxygen leads to the formation of
340 Fe-O-(organic) complexes from the reduced Fe(III) or Fe(IV) species, the dissolved
341 oxygen and low concentrations of DMP reaction products. While there is
342 experimental evidence that suggests that the complexes are present both in the bulk
343 solution and adsorbed on the surface of the TiO₂ catalyst, it believed that the presence
344 of surface-adsorbed Fe-O-(organic) complexes has a greater inhibiting effect on DMP
345 degradation. Thus, the adsorbed complexes block the adsorption of DMP on the TiO₂
346 and prevent interactions between the DMP and valence band holes; however, the
347 adsorbed complexes do not appear to significantly diminish the UV activation of TiO₂.
348 Although the results of this study indicate that the presence of dissolved oxygen in
349 environmental waters decreases the oxidation performance of the Fe(VI)-TiO₂-UV
350 process, the performance may still exceed that of alternative chemical treatment
351 methods and be capable of achieving a satisfactory degradation of recalcitrant
352 contaminants such as phthalate acid esters.

353

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431 **Figure Captions**

432 **Fig. 1.** Ferrate reduction and DMP degradation under different reaction conditions.

433 ($[\text{DMP}]_0 = 10.3 \text{ mg L}^{-1}$, $[\text{Fe(VI)}]_0 = 0.16 \text{ mM}$, Light Intensity = 0.40 mW cm^{-2} , pH 9, $[\text{TiO}_2] = 40$

434 mg L^{-1} , with N_2 flow)

435 **Fig. 2.** Photocatalytic conversions for Ferrate reduction and DMP oxidation using:

436 (a) N_2 flow; (b) O_2 flow.

437 **Fig. 3.** The effect of dissolved oxygen concentration on DMP degradation.

438 **Fig. 4.** Photocatalytic conversions for Ferrate photoreduction and DMP

439 photooxidation using O_2 flow: (a) Ferrate reduction; (b) DMP degradation.

440 **Fig. 5.** Photocatalytic degradation of DMP with different TiO_2 and DMP solutions.

441 **Fig. 6.** The variation of DMP adsorption with different TiO_2 and DMP solutions.

442 **Fig. 7.** XRD patterns for the TiO_2 catalyst: (a) before use; (b) after use.

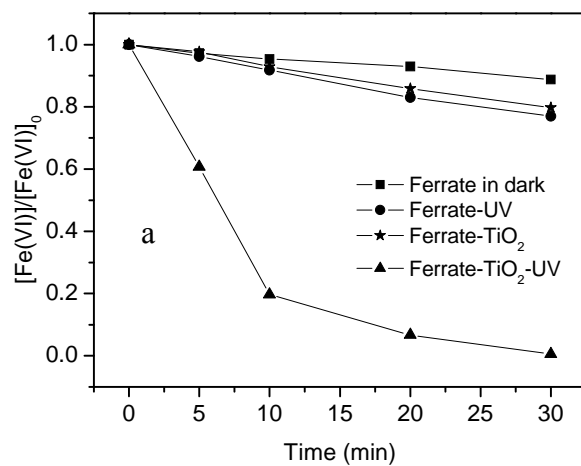
443 **Fig. 8.** FTIR spectra for the TiO_2 catalyst: (a) N_2 flow only; (b) 0.16 mM ferrate and

444 N_2 flow; (c) 0.16 mM ferrate and O_2 flow.

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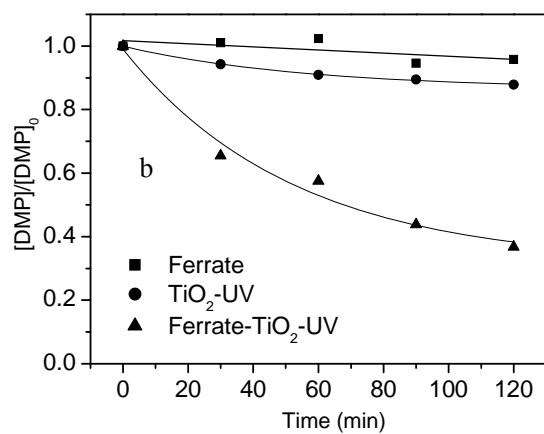
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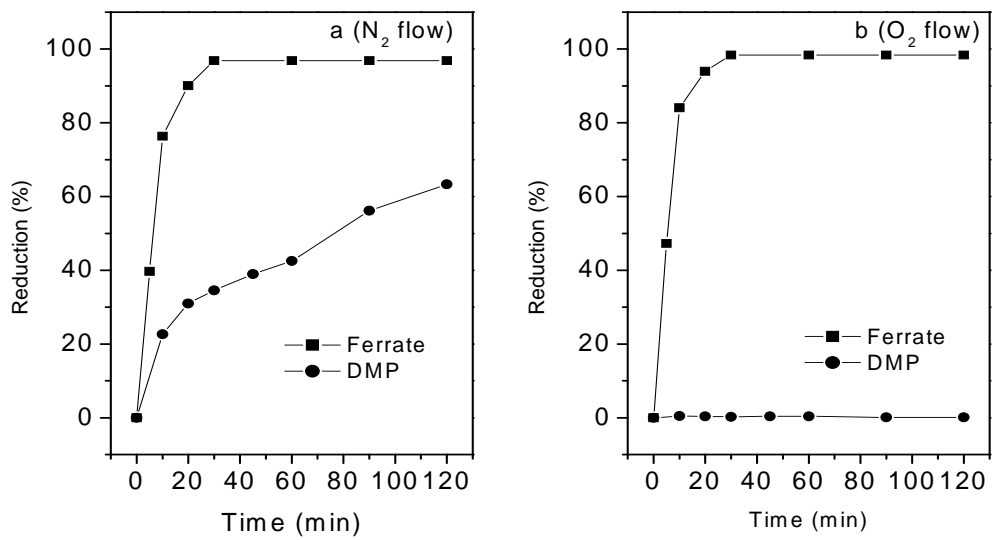
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454 Fig. 1.

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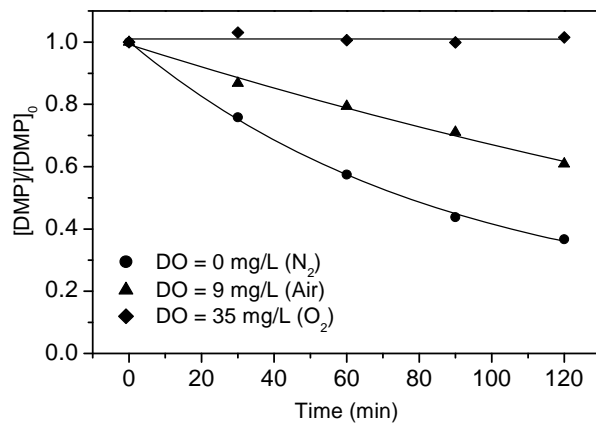
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Fig. 2.

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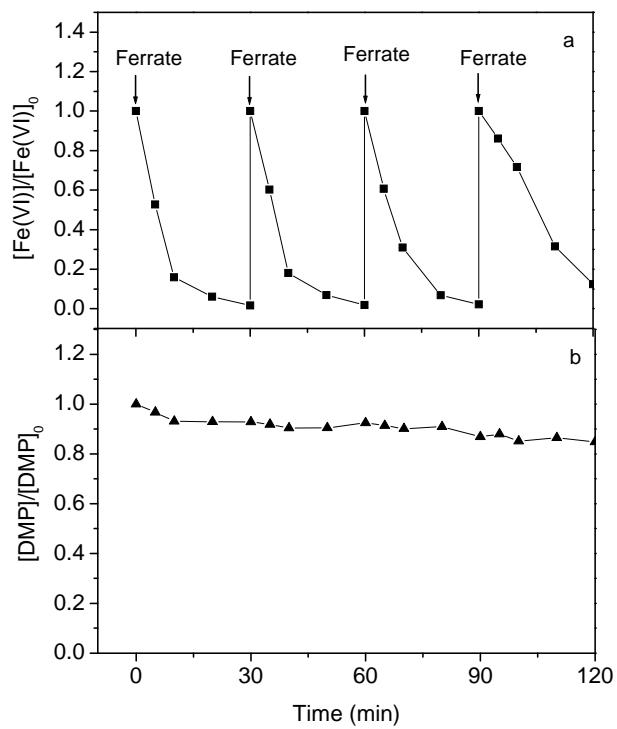
Fig. 3.

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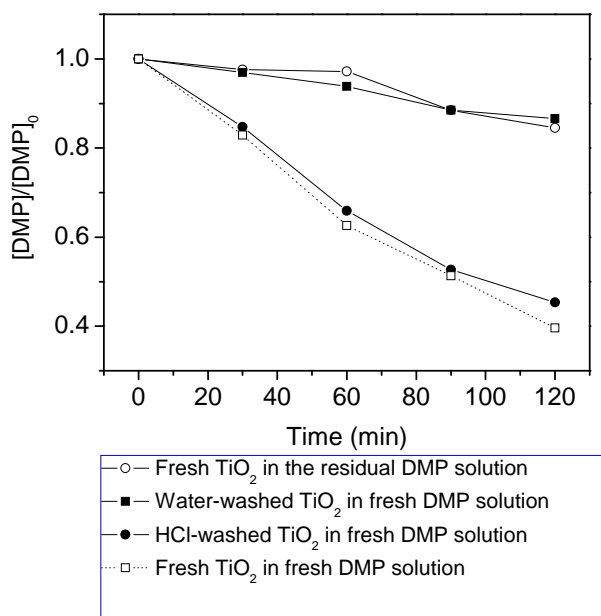
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Fig. 4.

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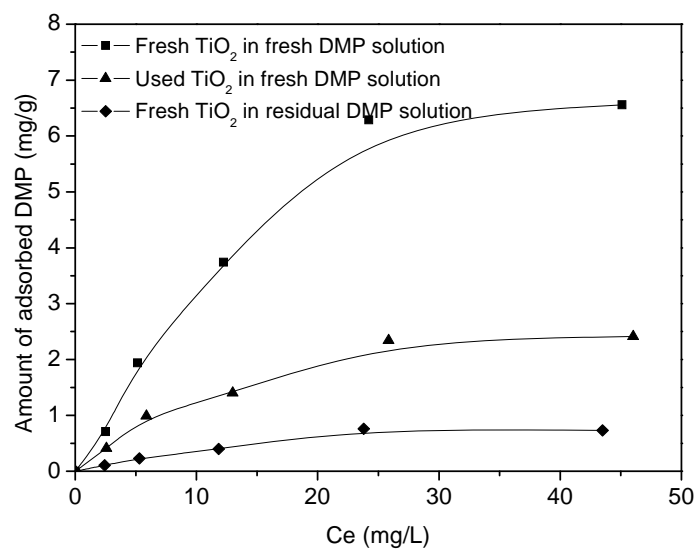
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Fig. 5.

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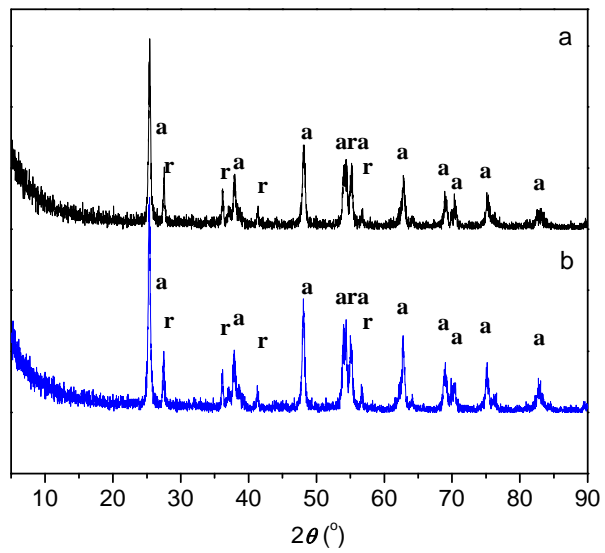
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Fig. 6.

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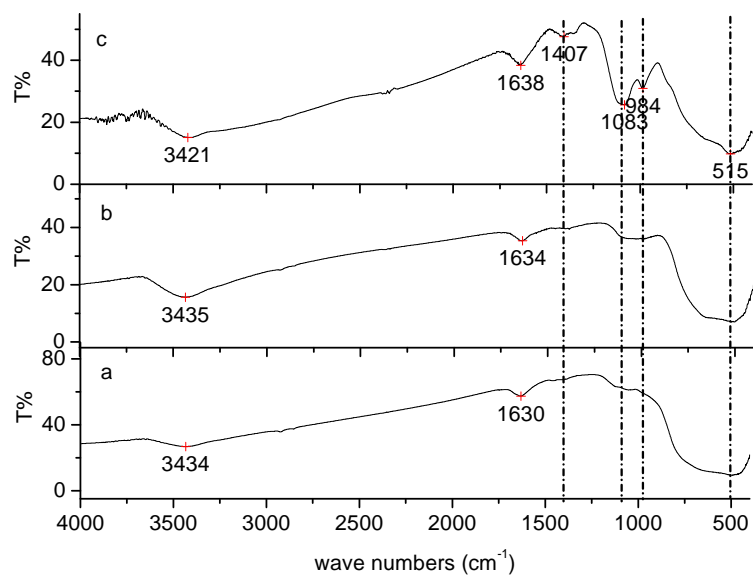
Fig. 7.

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Fig. 8.

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