Reaction pathways of dimethyl phthalate degradation in TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems

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Abstract

The photocatalytic degradation of dimethyl phthalate (DMP) in aqueous TiO_2 suspension under UV illumination has been investigated using oxygen (O_2) and ferrate (Fe(VI)) as electron acceptors. The experiments demonstrated that Fe(VI) was a more effective electron acceptor than O_2 for scavenging the conduction band electrons from the surface of the catalyst. Some major intermediate products from DMP degradation were identified by HPLC and GC/MS analyses. The analytical results identified dimethyl 3-hydroxyphthalate and dimethyl 2-hydroxyphthalate as the two main intermediate products from the DMP degradation in the TiO_2-UV-O_2 system, while in contrast phthalic acid was found to be the main intermediate product in the TiO_2-UV-Fe(VI) system. These findings indicate that DMP degradation in the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems followed different reaction pathways. An electron spin resonance analysis confirmed that hydroxyl radicals existed in the TiO_2-UV-O_2 reaction system and an unknown radical species is suspected to exist in the TiO_2-UV-Fe(VI) reaction system. Two pathway schemes of DMP degradation in the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) reaction systems are proposed. It is believed that the radicals formed in the TiO_2-UV-O_2 reaction system preferably attack the aromatic ring of the DMP, while in contrast the radicals formed in the TiO_2-UV-Fe(VI) reaction systems attack the alkyl chain of DMP.

Keywords: Dimethyl phthalate; DMP; Electron acceptor; Ferrate; Fe(VI); Photocatalysis

1. Introduction

Phthalate esters represent a large family of chemicals which are widely used as plasticizers, primarily in the production of polyvinyl chloride resins (Bemis et al., 1978). Dimethyl phthalate (DMP) is a short-chained ester with two carboxyl groups on the aromatic ring. It is typically used in cellulose-ester-based plastics, such as cellulose acetate and butyrate (Staples et al., 1997), and it is a component of paints, adhesives, printing inks and coatings. Due to its wide applications in industry and large quantities of use, DMP has been recognized as a significant environmental contaminant and is commonly detected in natural ecosystems. Health and environmental concerns about this phthalate ester have been recognized for many years, particularly in regard to its physiological and biochemical effects on organisms (Zhao et al., 1995; Wang et al., 2004). It is known as an endocrine-disrupting chemical which may promote chromosome injuries in human leucocytes and interfere with the reproductive system and normal development of animals and humans (Jobling et al., 1995; Allsopp et al., 1997).

DMP is a relatively stable compound in the natural environment. The hydrolysis half-life is estimated to be about 20 y (Staples et al., 1997). Studies of its biodegradation in fresh water, marine water, sediment, wastewater and sludge, have revealed a low degradation rate in the range of several days to a few months (Staples et al., 1997). Only a few results concerning DMP photolysis are available since phthalic acid dialkyl esters have been reported to be relatively photoresistant; for example, quantum yields of decomposition Φ (phthalate) < 0.03 (Hizal et al., 1993). In view of this, it is necessary to identify a satisfactory treatment process for the effective destruction of this compound from contaminated waters and wastewaters.

In recent years, a great deal of attention has been paid to the photocatalytic degradation of alkyl phthalate esters using titanium dioxide (TiO_2) either immobilized on films or dispersed in aqueous suspension (Taborba et al., 2001; Rahman et al., 2003). In the photocatalytic process, one strategy to enhance oxidative efficiency is to inhibit the e^-/h^+ recombination by adding other (irreversible) electron acceptors to the reaction (Malato et al., 1998; Wong and Chu, 2003). Oxygen (O_2) has been widely chosen as a good electron acceptor for such a purpose, although its role is more than just electron scavenging (Linsebigler et al., 1995).

Ferrate (Fe(VI)) as a strong oxidizing reagent has been used to trap the electrons produced during the photocatalytic process and then enhance the photocatalytic degradation of organic compounds (Sharma et al, 2006; Yuan et al., 2006). In our previous studies, it has been found that the ferrate enhanced photocatalytic degradation of alkyl phthalate ester is strongly influenced by different parameters such as, the mass ratio of ferrate to TiO_2, the pH of reaction solution and so on, but the mechanism and the reaction pathway of DMP degradation by photocatalysis alone and synergetic photocatalysis with ferrate are still not clear. Therefore, this paper presents a further investigation of DMP degradation in an attempt to gain more insight into the underlying reaction mechanisms by photocatalysis alone and synergetic photocatalysis with ferrate, respectively. This study has been particularly focused on the analysis of the intermediate products and the determination of free radicals formed during the photocatalytic reaction.

2. Methodology

2.1 Chemicals

DMP chemical was purchased from Aldrich (98.7% purity) and used as a model pollutant. Potassium ferrate (K_2FeO_4) with high purity (>90%) was synthesized in our laboratory according to an improved method (Li et al., 2005) and used as an oxidizing reagent. TiO_2 (Degussa P-25) was used as a photocatalyst in this study.

2.2 Experimental

Aqueous DMP solution with an initial concentration of 7-10 mg L^{-1} was prepared at pH 9.0, containing 1 mmol sodium borate ($Na_2B_4O_7.10H_2O$)/5 mmol sodium phosphate dibasic (Na_2HPO_4). At this pH, ferrate (as de-protonated FeO_4^{2-}) is stable and its spontaneous decomposition can be ignored. In the above solution, phosphate serves as a complexing agent for Fe(III) to eliminate its interference in the ferrate analysis by spectrophotometry. The TiO_2 catalyst (40 mg L^{-1}) and ferrate were applied at different concentrations for the different experiments. All experiments were carried out in a quartz bottle and a UV lamp (Philips 8W) with its main emission at 365 nm was used as an external UVA light source. The light intensity on to the reaction solution was determined to be 0.40 mW cm^{-2} by a radiometer (Lutron UVA-365). During each experiment, a gas flow of either O_2 or N_2 was applied (bubbled) to the reaction solution continuously, to either oxygenate or de-oxygenate the solution, respectively, and which also maintained a well-mixed solution and a fully suspended TiO_2 catalyst. Samples taken at different time intervals were immediately quenched with sodium sulphite to stop any further reaction and then filtered through a Millipore (0.22 μm) membrane using a syringe prior to the analysis.

2.3 Analytical methods

DMP was analyzed by high performance liquid chromatography, using a high pressure pump (Spectra system HPLC P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). In the HPLC analysis, a pinnacle II C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.) was employed with a mobile phase of acetonitrile/water (80:20, v/v) at a flow rate of 0.8 mL $\min^{-1}$. An injection volume of 20 μL was used and the concentration of DMP was determined by the UV detector at 227 nm.

To determine the intermediate products from the DMP degradation reaction, a solid phase extraction method was applied to concentrate the compounds from the reaction solution using a Sulpeco C18 100 mg solid phase extraction cartridge, which was primed with methanol (10 mL) first and then distilled water (15 mL) as pretreatment. A solution sample was first filtered through a Millpore filter and its pH was adjusted to 1-2 with 0.1 mol hydrochloric acid. The solution sample was then passed through the pretreated Sulpeco C_{18} 100 mg solid phase extraction cartridge at a flow rate of 10 mL $\min^{-1}$ using vacuum suction. The cartridge was subsequently washed thoroughly with distilled water (10 mL), 10% methanol (10 mL) and 20% methanol (5 mL) in sequence and then dried by air blowing for 2 min. After this, the dried cartridge was eluted with 100% methanol (1 mL) at an ambient pressure to remove DMP. The residual extraction solution was passed through a Sulpeco C_{18} 100 mg solid phase extraction cartridge after the same pretreatment again. After the cartridge was dried by air blowing for 2 min, the intermediate products were eluted using 100% methanol (1 mL).

While non-polar compounds, including DMP and products, were extracted with hexane, polar compounds were extracted with chloroform. The compounds were analyzed by GC/MS using a Varian 3700 gas chromatograph with a quartz capillary column (Perranphase PVMS/54, length = 25 m, i.d. = 0.3 mm) and a Varian MAT 44 mass spectrometer employing the electron impact (EI) method. After the sample injection at 290 °C, the oven temperature was kept initially at 40 °C for 5 min and then increased at a rate of 10 °C $\min^{-1}$ up to 290 °C and kept for 5 min. The results of the GC-MS analysis were interpreted by comparison with commercial standards in the library records of the National Institute of Standards (NIST).

To identify the existence of hydroxyl radicals, the electron spin resonance (ESR) signals of radicals trapped by 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) were obtained using an electron paramagnetic resonance spectrometer (Bruker ESP 300E) equipped with a Quanta-ray Nd/YAG laser system and an irradiation light source (λ = 355 nm) at ambient temperature. The settings included the center field = 3480.00 G, microwave frequency = 9.79 GHz, and power = 5.05 mW.

3. Results and Discussion

3.1 DMP degradation in TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems

It has been demonstrated that the addition of certain metal ions or oxidizing reagents, such as oxygen, into a photocatalytic system can act as electron acceptors which prevents the immediate self-recombination of conduction band electrons (e^-) and valence band holes (h^+), thereby enhancing the degradation of target organic compounds (Malato et al., 1998; Wong and Chu, 2003). To study the degradation of DMP under different reaction conditions, four experiments (Ferrate only, TiO_2-UV, TiO_2-UV-O_2, and TiO_2-UV-Fe(VI)) were conducted and the results are shown in Fig. 1. The first experiment was carried out in aqueous DMP solution with the addition of ferrate only (in the dark) and the results showed that DMP was resistant to ferrate oxidation, indicating a significant selectivity of ferrate reactivity. The second experiment was performed in aqueous DMP+TiO_2 solution under UV illumination with a N_2 gas flow and the results showed that the DMP degradation was very limited without the addition of an electron acceptor. The third experiment was conducted in aqueous DMP+TiO_2 solution under UV illumination with an O_2 gas flow and the results showed that the DMP degradation by photocatalysis in the presence of oxygen (dissolved [O_2] ~ 35 mg L^{-1}) as an electron acceptor was substantially degraded, to the extent of 68% after 120 min. The fourth experiment was carried out in aqueous DMP+TiO_2+Fe(VI) solution under UV illumination with a N_2 gas flow and the results showed that DMP degradation by photocatalysis with ferrate as an electron acceptor was the greatest, equivalent to 83% after 120 min. These results indicate that ferrate under these conditions is a more effective electron acceptor than O_2 for scavenging the conduction band electrons from the surface of TiO_2. In addition, ferrate may be also capable of directly oxidizing particular intermediate products from the initial degradation of DMP and thereby enhancing the DMP degradation overall due to a synergistic effect from the combination of photocatalytic reactions and direct ferrate oxidation reactions.

[Fig. 1]

3.2 The identification of intermediate products by HPLC analysis

The formation of intermediate products was studied in two experiments, in which DMP in aqueous solution was degraded in the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems, respectively. The samples from the above two experiments were taken after 60 min of reaction and analyzed by HPLC; their spectra are shown in Fig. 2. Fig. 2a shows that some peaks were well detected by the UV detector, representing DMP and its intermediate products in the TiO_2-UV-O_2 photacatalysis reaction. Fig. 2b shows some peaks in the TiO_2-UV-Fe(VI) photocatalysis reaction. In both reactions, all products with shorter retention times than that of DMP (5.85 min) correspond to compounds of greater polarity than DMP. Two primary photoproduct peaks were prominent at 4.28 min (IP1) and 4.62 min (IP2) in the TiO_2-UV-O_2 reaction system, while only one intermediate product (IP) peak at 3.98 min was obtained in the TiO_2-UV-Fe(VI) photocatalysis with N_2 flow system.

[Fig. 2]

The UV/VIS absorption spectra of DMP and the intermediate products after TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) reactions are presented in Fig. 3. The UV–VIS spectrum of DMP comprises two maxima, a weak peak at 277 nm and a strong peak at 227 nm. After the TiO_2-UV-O_2 photocatalysis, two intermediate products are formed: IP1 presents an absorption band at λ_{max} = 255 nm and IP2 presents an absorption band at λ_{max} = 302 nm with a shoulder peak at λ_{max} = 233 nm (Fig. 3a). The absorption shifting to the longer means that an organic group is added to the aromatic ring of DMP. After the TiO_2-UV-Fe(VI) photocatalysis, the spectrum of IP comprises two maxima, a weak peak at 227 nm and a more intense peak at 277 nm (Fig. 3b), which is very different to that of IP1 and IP2 in the TiO_2-UV-O_2 photocatalysis, but similar to the spectrum of DMP. From this, it is believed that the aromatic ring of DMP has not been modified or destroyed by oxidation and the reaction principally involves the oxidation of the alkyl chain.

[Fig. 3]

3.3 Identification of intermediate products by GC/MS analysis

From the GC/MS analysis, the two primary products evident from the HPLC analysis (IP1 and IP2) had corresponding peaks with retention times at 18.28 and 21.54 min; these were determined to be the two main intermediate products from the DMP degradation in the TiO_2-UV-O_2 system after extraction with chloroform. These two compounds, IP1 and IP2, were identified by the MS spectra to be dimethyl 3-hydroxyphthalate (3-DMHP) and dimethyl 2-hydroxyphthalate (2-DMHP), respectively.

When ferrate (as an electron acceptor) was added to enhance the efficiency of DMP degradation by photocatalysis, the principal intermediate product, IP, was detected by HPLC analysis (RT = 3.98 min), as described previously, but it could not be extracted by hexane or chloroform. However, after acidification, it could be separated and accumulated by the solid phase extraction (SPE) method and eluted using 100% methanol (1 mL) from the solid phase extraction cartridge. The GC/MS analysis confirmed that the product IP (RT = 15.82 min) was in agreement with phthalic acid.

After identification of the above reaction products, the DMP degradation and temporal formation of intermediate products in both the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) reaction systems were further studied and the experimental results are shown in Fig. 4. The results in the TiO_2-UV-O_2 system demonstrated that the DMP was gradually degraded, the two main photoproducts, 3-DMHP and 2-DMHP, were formed accordingly. During the reaction, concentrations of these two intermediates reached their maximum values at around 60 min, and then gradually decreased due to further degradation. The kinetics of formation and degradation for both intermediate products followed a similar pattern. After the degradation of the two intermediate products, more product compounds with shorter retention times were detected by HPLC analysis. In the UV-TiO_2-Fe(VI) photocatalysis system under N_2 flow, ferrate was added batchwise with five equal additions at 30min intervals, each equivalent to 0.16 mmol, giving a total concentration of ferrate equivalent to 0.80 mmol. In the first 10 min (approximately) after ferrate was added, the DMP decreased rapidly and phthalic acid (PA) is formed; in the following 20 min, ferrate is photo-reduced completely and PA is degraded by UV-TiO_2 photo-oxidation. However the DMP showed no significant degradation under photocatalysis alone. This behaviour was repeated each time ferrate was added into the reaction solution. Thus, in summary, it is evident that ferrate (under N_2) enhances the UV-TiO_2 photocatalytic degradation of DMP, forming PA as a major product, and that UV-TiO_2 photocatalysis alone (in the absence of ferrate) is able to degrade the PA in contrast to the non-reactivity of DMP.

[Fig. 4]

3.4 ESR study on the reactions in the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems

The electron spin resonance (ESR) technique allows the monitoring of chemical reaction processes involving extremely small changes; thus, it provides a useful tool to disentangle the complex processes involved in photocatalytic experiments (Grela et al., 1996; Brezová et al., 1994a; Brezová et al., 1994b). The compound, 5, 5-dimethyl-1-pyrroline-1-oxide (DMPO), was used as a spin-trapping reagent in the reaction solution.

In the TiO_2-UV-O_2 system, the existence of ·OH radicals was confirmed by the ESR spectroscopy upon irradiation at $\lambda = 355$ nm; a 1:2:2:1 quartet spectrum ($a_N = a_H = 1.49$ mT) was observed upon irradiation. This signal is a characteristic of a relatively stable nitroxide (DMPO-OH) upon reaction with photogenerated OH radicals on the surface of TiO_2 (see Fig. 5a). In the TiO_2-Fe(VI) system in the dark, a septet spectrum was found, as shown in Fig. 5b, which means a different radical might be formed between ferrate and DMPO.

[Fig. 5]

From temporal measurements, see Fig. 5c, it was evident that the new radical species produced in the TiO_2-UV-Fe(VI) system, was very unstable and decreased within a short period of irradiation. Thus, in the early stages of irradiation, the radical species quickly appeared and was able to attack the DMP. Subsequently, with the disappearance of the new radical after approximately 10 min irradiation, the ·OH radical became the main active species in the reaction and continued the DMP degradation.

3.5 Pathway of DMP degradation in the TiO_2-UV-O_2 and TiO_2-UV-Fe(VI) systems

From the ESR analysis, the DMP degradation induced by excitation of photocatalysis occurred clearly due to the attack by ·OH radicals. The attack is mainly located on the aromatic ring of DMP, if we consider that 3-DMHP and 2-DMHP are two major products from the initial degradation of DMP in the solution. A plausible mechanism for the formation of these products involving electron transfer reactions and reactions with hydroxyl radicals formed in the TiO_2-UV-O_2 photocatalytic system is proposed as shown in Scheme A.

[Scheme A]

In this scheme the model compound 1 is reduced upon the addition of an electron to form the radical anion 2, which may undergo addition of a hydroxyl radical followed by loss of a proton to give a hydroxyl added product 4. Alternatively, the formation of 4 could also be explained by the direct addition of a hydroxyl radical to form product 3 and then followed by the loss of a hydrogen atom. Compound 4 has the two dismutation hydroxylated derivatives (5 and 6) of DMP (Stanford et al., 1994; Mailhot et al., 2002)

Previous studies have indicated that the attack of hydroxyl radicals leads to the formation of hydroxy photoproducts (hydroxylated on the aromatic ring) for phthalates with shorter alkyl chains (dimethyl and diethyl) (Bajt et al., 2001; Rahman, 2003), while in the case of longer dialkyl phthalates (dibutyl and di(2-ethylhexyl)) only very low concentrations of hydroxylated compounds were observed (Hustert and Moza, 1988). Our results are in agreement with these studies about the importance of the chemical structure of the pollutant for the site of ·OH radicals attack. When the alkyl chain is shorter than three carbon atoms, the attack of ·OH radicals on the aromatic ring becomes important compared to the attack on the alkyl chain. This observation can be explained by the increase of sites of ·OH attack when the alkyl chain is longer.

In contrast, for the TiO_2-UV-Fe(VI) system, we found the principal location for the DMP attack to be on the alkyl chain. The addition of the ferrate as electron acceptor to the photocatalytic reaction produces the new, presently unknown radical species, which prefers to attack the alkyl chain rather than the aromatic ring. A plausible mechanism for the formation of these products involving electron transfer reactions and Fe(VI) oxidation is proposed as shown in Scheme B.

$TiO_2 + h\nu \rightarrow h_{vb}^{+} + \quad e_{cb}^{-}$;

$H_2O + h_{vb}^{+} \rightarrow OH\cdot + H^{+}$

$\mathrm{Fe(VI)} + e_{cb}^{-} \rightarrow \mathrm{Fe(V)} \qquad \text{or} \qquad \mathrm{Fe(VI)} + 2e_{cb}^{-} \rightarrow \mathrm{Fe(IV)}$

In the TiO_2-UV-Fe(VI) system, the photocatalytic degradation of DMP has been found to yield one main intermediate product, resulting from electron transfer reactions and reactions with hydroxyl radicals. The model compound 1 upon the loss of one electron or two electrons with Fe(V) reaction can form the organic cation 2 and 3, respectively, which may undergo further reaction via the addition of one or two hydroxyl radicals forming the organic species 4 or 5, respectively. Organic species 4 will, upon loss of a methoxyl group, form the observed product 6 (monomethyl phthalate, MMP), which may then undergo a further loss of electron after Fe(V) oxidation involving the formation of the organic cation 7, upon the addition of one hydroxyl radical and then loss of an methoxyl group forming the observed final product 8 (phthalic acid, PA). Alternatively, species 5, which on subsequent removal of two methoxyl groups will lead to the formation of the final product 8 (phthalic acid) directly, as shown in Scheme B.

[Scheme B]

These results show the importance of different radicals formed in the oxidative system for attacking different site of model compound. In the TiO_2-UV-O_2 photocatalysis, the attack of ·OH radicals on the aromatic ring becomes important in comparison of the attack on the alkyl chain. However, in the TiO_2-UV-Fe(V) system (ferrate-enhanced TiO_2 photocatalysis), owing to the generation of new radical species, an attack on the alkyl chain appeared to be preferred to an attack on the aromatic ring. Also, it was observed with interest, that after the ferrate was exhausted, the ·OH radicals that continued to be formed by the TiO_2-UV photocatalysis maintained the attack on the alkyl chain rather than the aromatic ring.

4. Conclusions

The following conclusions may be drawn from this study:

- DMP can be degraded by either TiO_2-UV-O_2 photocatalysis or TiO_2-UV-Fe(VI) photocatalysis effectively, in which the ferrate-enhanced TiO_2-UV photocatalysis is more efficient than the TiO_2-UV-O_2 photocatalyis.
- In the TiO_2-UV-O_2 system, the existence of ·OH radicals was confirmed by ESR spectroscopy upon irradiation at λ = 355 nm. A 1:2:2:1 quartet ($a_N = a_H =$ 1.49 mT) was observed upon irradiation. In the TiO_2-Fe(VI) system without UV, a new but unknown radical was believed to be formed and a septet spectrum was observed by ESR spectroscopy.
- The identification of different reaction products suggested that there are different reaction mechanisms/pathways for the two photocatalytic systems. While the radicals formed in the TiO_2-UV-O_2 reaction system appeared to attack mainly the aromatic ring of DMP, the radicals formed in the TiO_2-UV-Fe(VI) reaction system preferred to attack the alkyl chain of DMP. The compounds, 3-DMHP and 2-DMHP, were found to be the main intermediate products from DMP in the TiO_2-UV-O_2 system, while phthalic acid was the main intermediate product from DMP in the TiO_2-UV-Fe(VI) system.

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Figure Captions

Fig. 1. The degradation of DMP under different reaction conditions.
($[DMP]_0$ = 11.6 mg L^{-1}, $[Fe(VI)]_0$ = 8.96 mg L^{-1}, Light Intensity = 0.40 mW cm^{-2}, pH 9, $[TiO_2]$ = 40 mg L^{-1})

Fig. 2. HPLC chromatograms of DMP degradation after 60 min irradiation in the, (A) TiO_2-UV-O_2, and (B) TiO_2-UV-Fe(VI), reaction systems.

Fig. 3. UV absorption spectra of DMP and the principal intermediate products formed in the, (A) TiO_2-UV-O_2, and (B) TiO_2-UV-Fe(VI), reaction systems.

Fig. 4. DMP degradation and intermediate product formation in the, (A) TiO_2-UV-O_2 and (B) TiO_2-UV-Fe(VI) reaction systems.

Fig. 5. DMPO spin-trapping ESR spectra recorded in, (A) TiO_2-UV system (λ = 355nm), and (B) TiO_2 –Fe(VI) system in dark. ($[DMP]_0$ = 13.2 mg L^{-1}, $[Fe(VI)]_0$ = 8.96 mg L^{-1}, $[TiO_2]$ = 40 mg L^{-1}) , DMPO 30 μl, pH 9), and (C) DMPO spin-trapping ESR spectra recorded in aqueous ferrate-TiO_2 suspension under irradiation (λ = 355nm) (1) 10 min irradiation; (2) 20 min irradiation; (3) 30 min irradiation.

Fig. 1

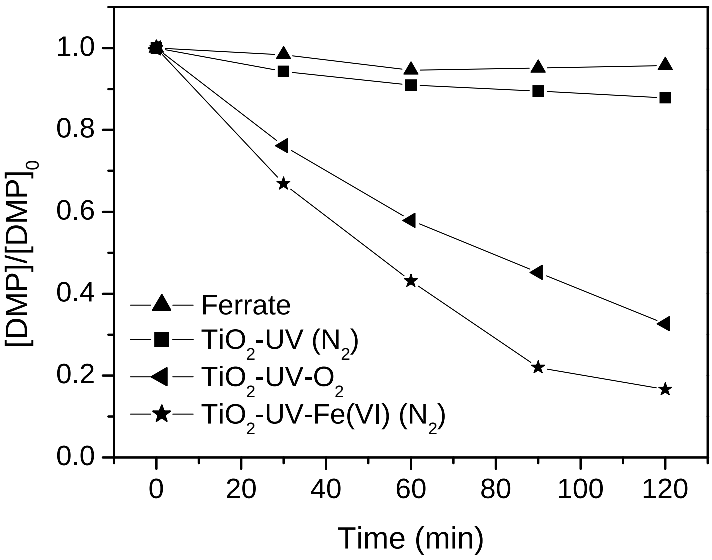
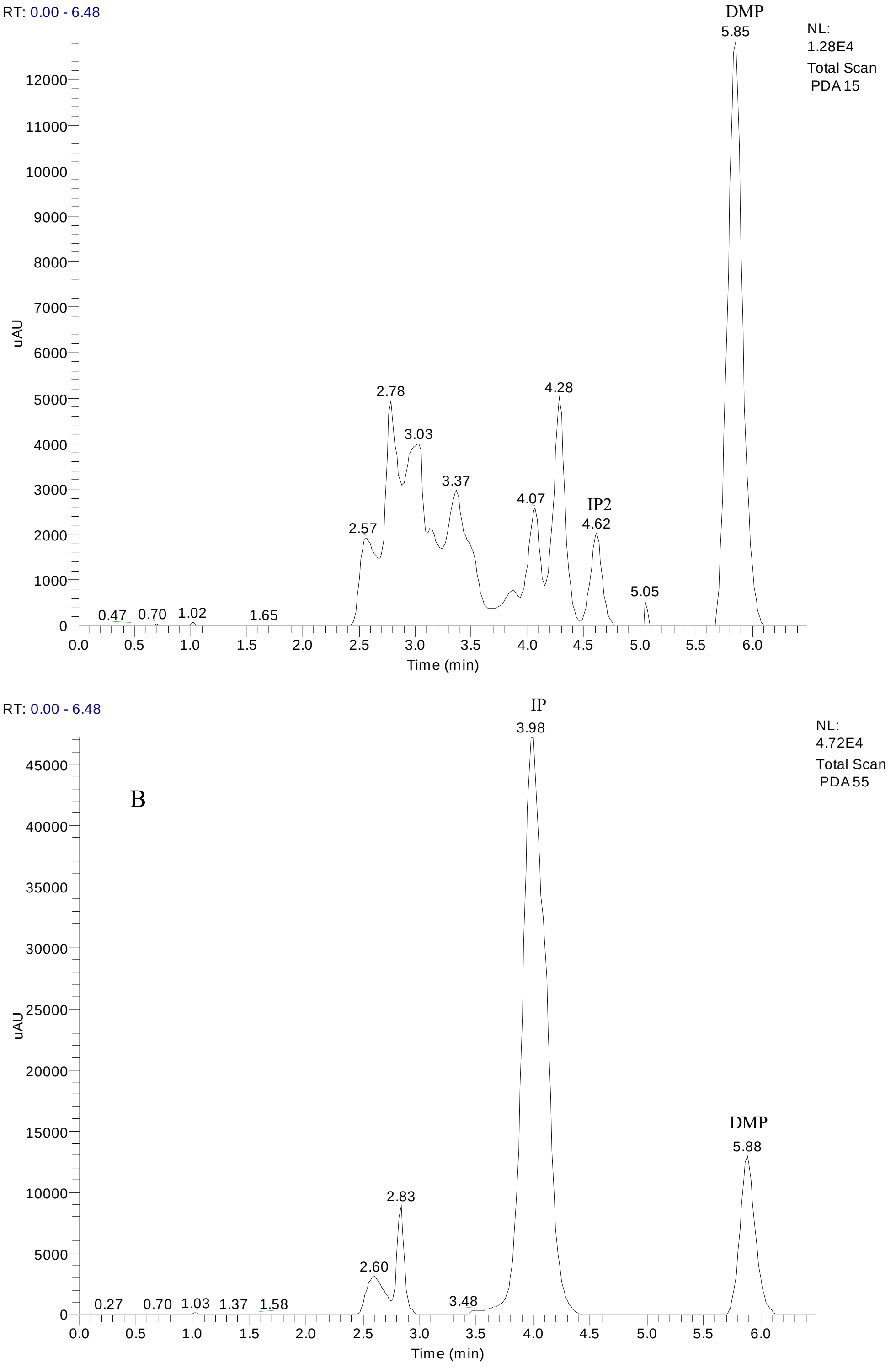

[DMP]/[DMP]$_0$
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
Time (min)
Ferrate
TiO$_2$-UV (N$_2$)
TiO$_2$-UV-O$_2$
TiO$_2$-UV-Fe(VI) (N$_2$)

Fig. 2


RT: 0.00 - 6.48
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2.78
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4.07
IP2
4.62
5.05
0.47
0.70
1.02
1.65
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
Time (min)
RT: 0.00 - 6.48
IP
3.98
NL:
4.72E4
Total Scan
PDA 55
B
uAU
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
DMP
5.88
2.83
2.60
3.48
0.27
0.70
1.03
1.37
1.58
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
Time (min)

Fig. 3

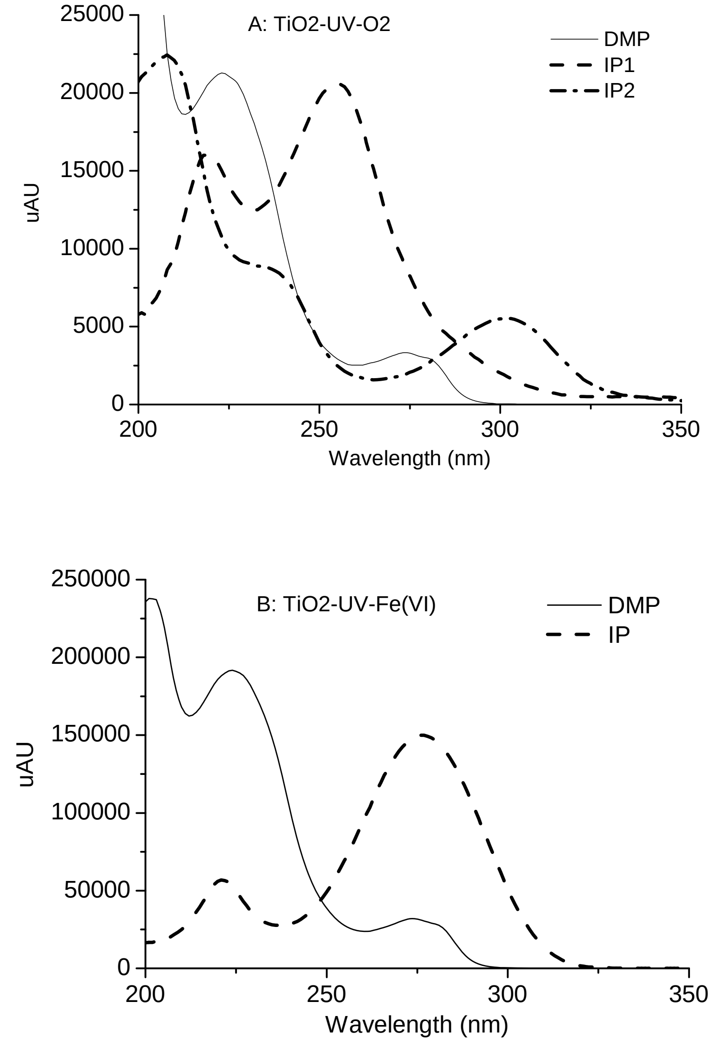

A: TiO2-UV-O2
DMP
IP1
IP2
uAU
25000
20000
15000
10000
5000
0
200
250
300
350
Wavelength (nm)
B: TiO2-UV-Fe(VI)
DMP
IP
uAU
250000
200000
150000
100000
50000
0
200
250
300
350
Wavelength (nm)

Fig. 4.

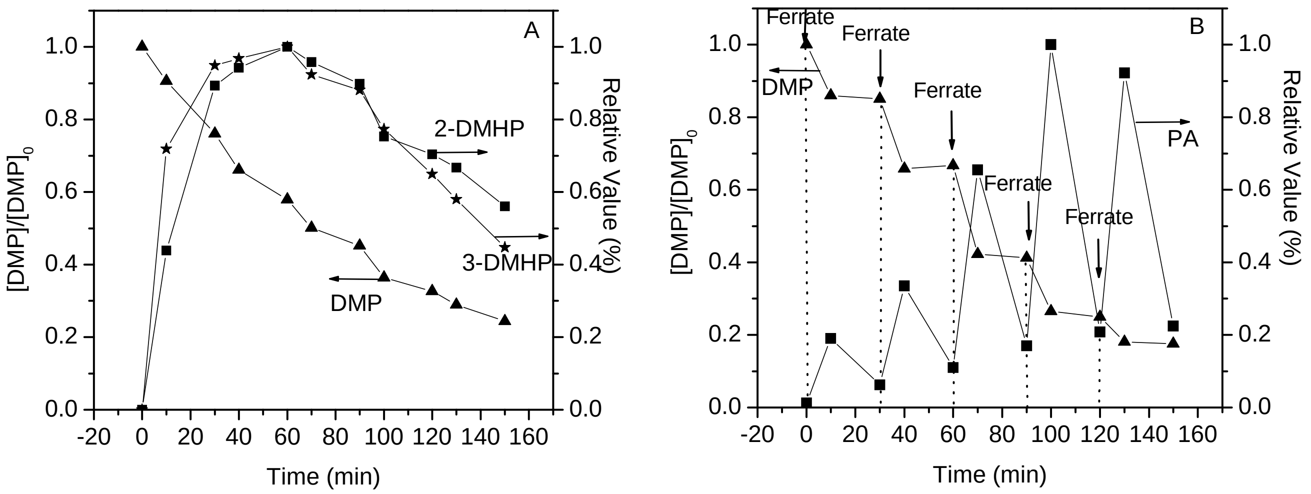
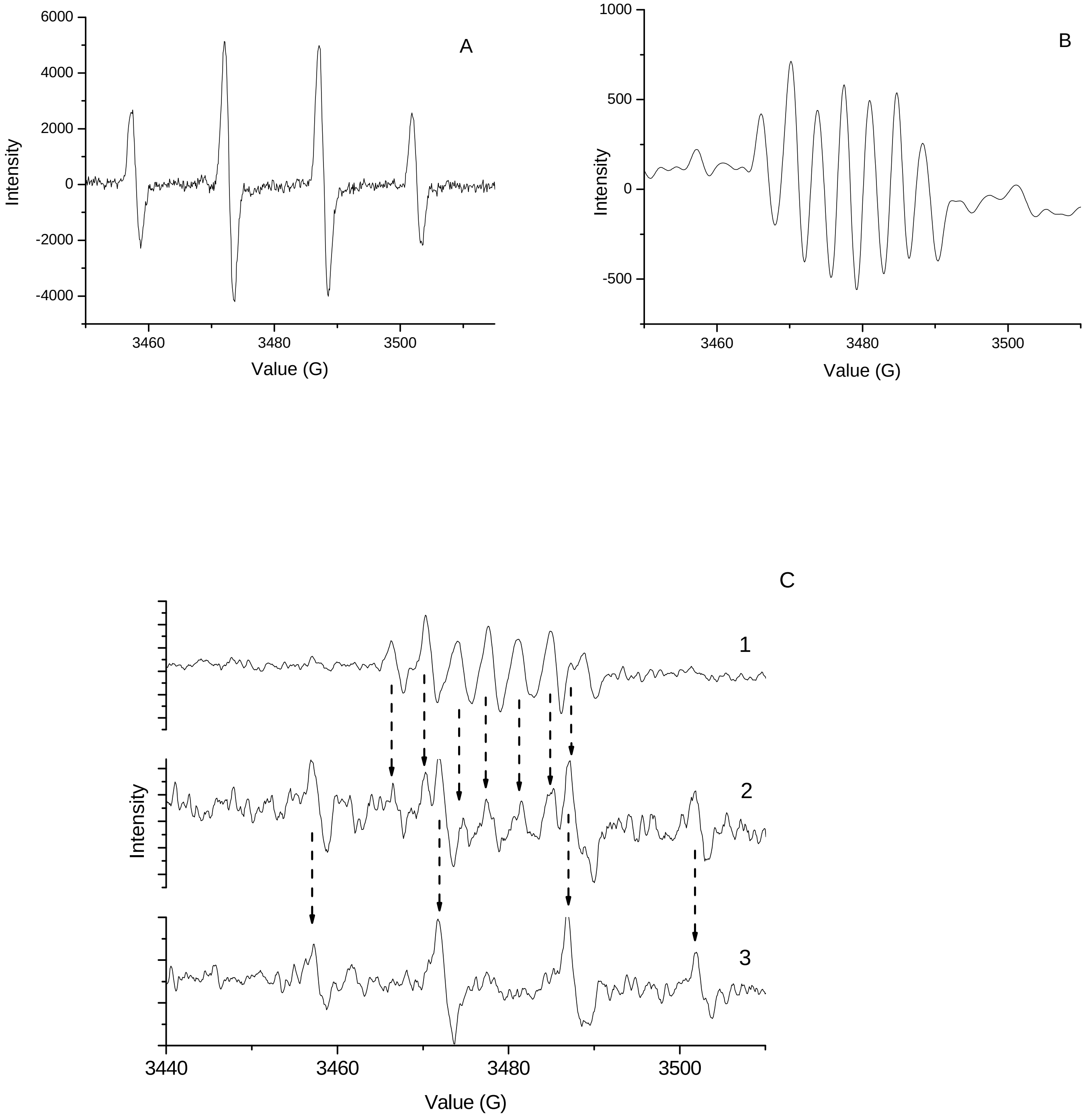
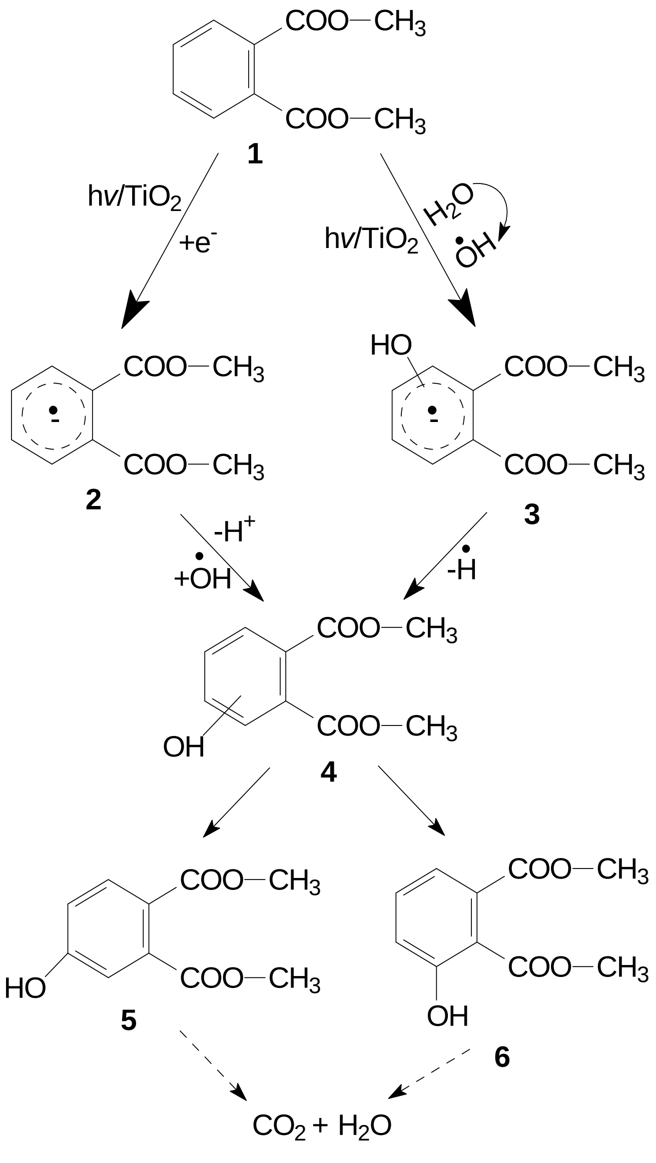

A
[DMP]/[DMP]$_0$
Relative Value (%)
Time (min)
2-DMHP
3-DMHP
DMP
B
Ferrate
Ferrate
Ferrate
Ferrate
Ferrate
DMP
PA
[DMP]/[DMP]$_0$
Relative Value (%)
Time (min)
-20
0
20
40
60
80
100
120
140
160
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 5


A
6000
4000
2000
0
-2000
-4000
Intensity
3460
3480
3500
Value (G)
B
1000
500
0
-500
Intensity
3460
3480
3500
Value (G)
C
1
2
3
Intensity
3440
3460
3480
3500
Value (G)

Scheme A: Proposed degradation pathway of DMP with TiO_2+UV



Scheme B: Proposed degradation pathway of DMP with Fe(VI)+TiO_2+UV