Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO$_2$-UV reaction system

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ABSTRACT

The application of a combined ferrate-photocatalysis process for the aqueous degradation of dimethyl phthalate (DMP) has been studied. The behaviour of the Fe(VI)-TiO$_2$-UV process at pH 9 in the presence and absence of dissolved oxygen has been compared and significant differences found. In comparative tests under N$_2$ and O$_2$ bubbling, the chemical reduction rate of ferrate as conductance band electron acceptor was similar, but the resulting degradation of DMP was substantially lower in the presence of oxygen. It is speculated that the presence of oxygen leads to the formation of Fe-O-(organic) complex species that adsorb to, and deactivate, the surface of the photocatalyst. The presence of surface adsorbed complex species was indicated by FTIR spectroscopy and a reduced TiO$_2$ adsorption capacity for DMP. In the presence of typical environmental levels of dissolved oxygen (~10 mg L$^{-1}$), the Fe(VI)-TiO$_2$-UV process achieved a modest degree of DMP degradation (40% in 120 mins).

Keywords: Dimethyl phthalate; Ferrate; Photocatalysis; Oxidation; Titanium dioxide; UV irradiation
1. Introduction

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

The short-chained esters such as dimethyl phthalate (DMP) are among the most frequently identified PAEs in diverse environmental samples, including surface marine waters, freshwaters and sediments (Gledhill et al., 1980), high concentrations of about 300 mg L\(^{-1}\) of DMP have been documented in landfill leachate (Mersiowsky, 2002). DMP and its intermediates are suspected to be responsible for functional disturbances in the nervous systems and liver of animals. Known as an endocrine-disrupting chemical, it may also promote chromosome injuries in human leucocytes and also interfere with the reproductive systems and normal development of animals and humans (Jobling et al., 1995; Allsopp et al., 1997). Therefore, the US Environmental Protection Agency (USEPA) has listed it as a priority pollutant.
In addition to their potential toxicity, phthalate esters are becoming a class of pollutants of concern in environmental- and waste- waters since they are recalcitrant to both biodegradation, owing to the benzene carboxylic group, and photolytic degradation, due to the weak absorption of light at wavelengths greater than 300 nm (Staples et al., 1997; Maihot et al., 2002; Zhao et al., 2004). Therefore, it is necessary to identify appropriate treatment technologies that may be applied to remove such pollutants from waters and wastewaters. Among the range of possible treatment technologies, photocatalysis using semiconductor catalysts such as TiO$_2$, has been shown to be an effective treatment for various aqueous pollutants (Chen et al., 1999; Davis and Green, 1999).

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

$$\text{TiO}_2 + \text{hv} \rightarrow h_v^+ + e_b^-$$  \hspace{1cm} (1)

However, the recombination between electrons ($e^-$) and holes ($h^+$) is an extremely efficient process. One strategy for inhibiting the $e^-/h^+$ recombination is to add some electron acceptors to the reaction. Oxygen (as dissolved O$_2$) has been widely demonstrated to be a good acceptor for such a purpose, with a role extending beyond that of electron scavenging (Linsebigler et al., 1995), and it is always present in source waters and effluents. The use of other peroxides such as H$_2$O$_2$, S$_2$O$_8^{2-}$ and O$_3$ has been demonstrated also to enhance significantly the rate of degradation of
different organic contaminants (Malato et al., 1998; Wong and Chu, 2003), because
they can trap the photogenerated electrons more efficiently than O₂ (Plelizzetti et al.,
1991). Ideally, these additives should fulfill the criteria of dissociating into harmless
byproducts and lead to the formation of ·OH radicals or other oxidizing agents.

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

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

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

Recently, there have been a limited number of reported investigations concerning
the degradation of organic water pollutants by the combination of ferrate and
photocatalysis (Sharma et al., 2005b; Yuan et al., 2006). In our previous studies, while
the rates for organic conversion were increased in the Fe(VI)-TiO₂-UV system due to the synergistic oxidation-reduction reaction, it was also found there is a significant selectivity for different compounds, which depends on the reaction conditions. In the work reported here, DMP was selected as the target chemical, since it is refractory to ferrate oxidation alone and has a low reaction rate by TiO₂ photocatalysis under a N₂ gas flow. Various experiments were carried out using DMP solutions in the Fe(VI)-TiO₂-UV system, in which the scavenging of TiO₂ photocatalysis electrons by Fe(VI), and DMP degradation, were studied simultaneously under different reaction conditions in order to evaluate the reaction process in great detail. In particular we have investigated the application of different gases (N₂ and O₂) to the reaction solution and their effects on the deactivation of photocatalysis within the overall oxidation-reduction reaction.

2. Materials and Methods

2.1. Chemicals

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

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

2.3. Analyses

The DMP concentration was determined using high performance liquid
chromatography (HPLC) incorporating a high pressure pump (Spectrasystem HPLC P4000), a UV detector (UV 6000LP), and an auto sampler (AS3000). A pinnacle II C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.) was employed and a mobile phase of acetonitrile/water (80:20, v/v) was used 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 UV detection at 227 nm. The ferrate concentration was measured by means of UV-visible light absorbance spectroscopy at 510 nm. The crystal structure of the catalysts were examined by X-ray diffraction (XRD) using a diffractometer with radiation of a Cu target (Ka, λ = 0.15406 nm).

3. Results and Discussion

3.1. Ferrate reduction in the TiO₂-Ferrate reaction system

An initial set of experiments was conducted to study the reaction and chemical reduction of ferrate with DMP solution in the absence of dissolved oxygen and under different reaction conditions, as follows: (1) ferrate with DMP solution in the dark; (2) ferrate with DMP solution under UV illumination; (3) ferrate and TiO₂ with DMP solution in the dark; (4) ferrate and TiO₂ with DMP solution under UV illumination. To purge the dissolved oxygen from the reaction solution, N₂ gas was applied to the reaction solution in the above experiments. The experimental results are shown in Fig. 1a. It can be seen that Fe(VI) was reduced very slowly in the dark and only slightly faster either under UV illumination alone or with TiO₂ suspension but without UV illumination. However, in contrast, a rapid Fe(VI) reduction occurred in the presence
of TiO$_2$ suspension under UV illumination. Since DMP is refractory to ferrate oxidation, it is clear that the rapid reduction of Fe(VI) resulted from its scavenging of excited conduction band electrons from the TiO$_2$ catalyst. It is believed that the electron scavenging by Fe(VI) greatly diminishes the recombination of conduction band electrons (e$^-$) and valence band holes (h$^+$), thereby enhancing the quantum efficiency of TiO$_2$ catalyst during the photoreaction.

[Fig. 1]

3.2. DMP degradation in the TiO$_2$-Ferrate reaction system

It has been shown previously that the presence of certain metal ions or oxidizing reagents in a photocatalytic system can act as electron acceptors to prevent the rapid self-recombination of e$^-$ and h$^+$, thereby enhancing the degradation of a target compound by photocatalysis (Malato et al., 1998; Wong and Chu, 2003). This effect was demonstrated in our experiments with DMP and the results of reactions under different conditions, and in the absence of dissolved oxygen, are shown in Fig. 1b. It can be seen that DMP was not significantly degraded by ferrate alone, indicating a clear selectivity of ferrate oxidation to this particular organic substrate. Although the TiO$_2$ photocatalysis reaction has less selectivity in the reaction with organic substrates, the degradation of DMP by a typical TiO$_2$ photocatalytic oxidation was also poor, with only a 12% reduction in DMP after 120 min. However, in marked contrast, the DMP degradation by photocatalysis with ferrate (Fe(VI)-TiO$_2$-UV system) was substantial and reached approximately 65% after 120 min (Fig. 1b). These results demonstrate a clear synergistic effect from the combination of photocatalysis with...
ferrate. Due to its greater oxidizing power than other electron acceptors, such as permanganate or peroxides, and its possible reduction to highly reactive Fe(V), ferrate may play both roles of electron scavenging (thus enhancing the photo-oxidation) and direct oxidation of organic substances; the latter comprising both DMP and intermediate reaction products from the DMP degradation.

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

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

With N₂ gas bubbling, the results showed that ferrate rapidly disappeared within the first 20 min, while DMP also decreased rapidly initially and then more gradually, with an overall loss of DMP equivalent to 64% at 120 min (Fig. 2a). These results indicate that the DMP degradation by TiO₂ photocatalysis during the first 20 min was significantly enhanced due to the participation of ferrate. In contrast, the experiments with O₂ gas bubbling showed a very different behaviour with a very similar loss of ferrate but almost no degradation of DMP during the 120 min reaction time (Fig. 2b); this phenomenon was confirmed by undertaking several replications of the tests. From these results it is evident that the existence of dissolved oxygen in the reaction
solution did not reduce the rate of ferrate reduction, as ferrate is a more favorable electron acceptor ($E^0 = 0.72$ V for Fe(VI) reduction) than oxygen ($E^0 = -0.13$ V for O$_2$ reduction) (Wang and Hong, 1999). However, the existence of dissolved oxygen (DO) in the Fe(VI)-TiO$_2$-UV reaction system clearly inhibited the DMP degradation to a major extent. The influence of DO concentration on the DMP degradation was studied further by gas bubbling with N$_2$, air and O$_2$, respectively, and the results are shown in Fig. 3. It can be seen clearly that the rate of DMP degradation decreased systematically with increased DO concentration in the range of 0-35 mg L$^{-1}$.

From previous studies, it has been reported that carboxylic acids can react with certain metal ions in an aqueous photocatalytic reaction to form metal-oxygen complexes such as Cr-O-complexes or Hg-O-complexes. These metal-complexes can attach at the surface of TiO$_2$ to block the photocatalysis. It has also been reported that the formation of metal complexes that deactivate the surface photocatalysts could be aided by the presence of oxygen. Furthermore, the surface and structural features of the photocatalyst are very important in the extent to which the deactivation process takes place. These studies suggest that the existence of dissolved oxygen in the metal-TiO$_2$-UV system can play a double role of scavenging the excited electrons on the TiO$_2$ surface and forming certain metal-O-complex species, thereby inhibiting organic substrate degradation (Colón, 2001; Botta, 2002). Thus, this study has shown that DMP degradation in the Fe(VI)-TiO$_2$-UV reaction can be substantially diminished by the presence of oxygen in the reaction solution. It is believed that DO
in the Fe(VI)-TiO₂-UV system causes the formation of a Fe-O-complex from the reduced Fe species, such as Fe(IV) or Fe(III), and with DMP and/or its reaction products, either on the surface of TiO₂ catalyst or in the bulk solution, thereby preventing the DMP oxidation reaction. However, the mechanism of photocatalytic degradation of DMP with a benzenecarboxylic group is complicated and there have been many studies concerning the mechanism followed by organic compounds containing this group during their photocatalytic oxidation (Colón, 2001; Botta, 2002). Benzenecarboxylic compounds tend to form quinone/hydroquinone and polyhydroxy derivative (mainly dihydroxyl) species in the first stages of photodegradation. Therefore, it might be proposed that the formation of derivative species from the aromatic ring leads to the formation of metal-O-complexes in the presence of dissolved oxygen, probably at the surface of the photocatalyst, which thereby deactivates the catalyst. In contrast, it seems that the absence of DO (ie. under a nitrogen flow) avoids the formation of the Fe-O-complex that causes the deactivation of the photocatalysis observed for the DMP degradation in the Fe(VI)-TiO₂-UV reaction system.

3.4. Further study of the deactivation of the photocatalysis

In order to study further the deactivation of the photocatalysis in the Fe(VI)-TiO₂-UV reaction system in the presence of oxygen, an experiment was performed involving the DMP solution with TiO₂ catalyst (40 mg L⁻¹) at pH 9 under UV illumination for 120 min, during which ferrate chemical was systematically dosed four times (0.16 mM × 4 = 0.64 mM) at 0, 30, 60 and 90 min to observe the corresponding ferrate
reduction and DMP degradation; the results are shown in Fig. 4. It can be seen in Fig. 4a that the ferrate was rapidly reduced in the presence of TiO₂ and UV illumination, with the majority of the ferrate disappearing within 10 min. After each subsequent addition of ferrate, its chemical reduction followed a similar pattern, but the rate of reduction gradually decreased. These results indicate that the proposed formation of a Fe-O-(organic) complex on the surface of the TiO₂ only diminished the ferrate reduction to a minor degree. However, the corresponding DMP degradation (Fig. 4b) appeared insensitive to the dosing of ferrate and displayed a steady and gradual trend throughout the first 120 min reaction; the overall degradation was approximately 15%.

It is speculated that the formation of a Fe-O-(organic) complex on the surface of the TiO₂ was able to substantially inhibit or block the photocatalysis of DMP.

To further investigate the deactivation of the photocatalysis resulting from the Fe-O-(organic) complex formation on the surface of TiO₂ catalyst or in the bulk reaction solution, the TiO₂ catalyst used in the above reaction was removed from the reaction solution by centrifuging and then washed with either distilled water only or 1% HCl solution, respectively; the recovered TiO₂ catalysts were then available for subsequent testing. A set of four experiments using fresh TiO₂, the water-washed TiO₂, or the HCl-washed TiO₂, at the same dosage of 40 mg L⁻¹ was performed in either the residual DMP solution after the previously described 120 min reaction, or a fresh DMP solution, for 120 min. The results of these tests are shown in Fig. 5.
The first experiment using fresh TiO₂ in the residual DMP solution demonstrated that the DMP degradation was not significantly improved by replacing the catalyst with fresh TiO₂, indicating the inhibition of further DMP degradation by the presence of Fe-O-(organic) complexes in the bulk solution. The other three experiments involved using fresh DMP solutions with the different TiO₂ catalysts. These demonstrated that the water-washed TiO₂ still retained a certain amount of the Fe-O-(organic) complex on its surface since there was a low photocatalytic activity for DMP degradation, but the HCl-washed TiO₂ achieved a good DMP degradation (55% after 120 min) similar to that of fresh TiO₂. These results provided evidence that the DMP degradation was diminished by the formation of the Fe-O-(organic) complex on the surface of the catalyst and that the deactivated TiO₂ catalyst can be reactivated by washing with 1%HCl solution. In summary, the experimental results in Figs. 5 and 6 indicate that DMP degradation by photocatalytic oxidation is adversely affected by the formation of Fe-O-(organic) complexes from the presence of dissolved oxygen and reduced iron species in the reaction; the reduced oxidation appears to occur where the Fe-O-(organic) complexes are in the bulk solution or coated on the surface of TiO₂ the catalyst.

3.5. Adsorption of DMP on fresh and used TiO₂ catalysts

It is generally believed that the photocatalysis of DMP in aqueous solution is a heterogeneous reaction that mainly occurs on the surface of TiO₂ catalysts and the rate of DMP adsorption onto the TiO₂ surface can play a key role in the Fe(VI)-TiO₂-UV(O₂) system. A set of adsorption experiments involving aqueous
DMP solution with TiO$_2$ catalyst (0.5 g L$^{-1}$) was performed at pH 9 in the dark for 24 h to determine and study the DMP adsorption isotherms. Specifically, three conditions were considered: (1) fresh TiO$_2$ catalyst in fresh DMP solutions; (2) used TiO$_2$ catalyst in fresh DMP solutions; (3) fresh TiO$_2$ catalyst in the residual DMP solution after 2 h reaction. The results of this set of experiments are shown in Fig. 6.

From Fig. 6, it can be seen that the fresh TiO$_2$ in the fresh DMP solution exhibited the greatest DMP adsorption, while the used TiO$_2$ in the fresh DMP solution, and the fresh TiO$_2$ in the residual DMP solution, showed a much lower DMP adsorption. These results indicated that the formation of a Fe-O-(organic) complex either on the surface of the TiO$_2$ catalyst or in the bulk solution inhibited the DMP adsorption onto the TiO$_2$ catalyst, which might be one of the important reasons for a low DMP degradation in the reaction system.

3.6. Comparison of fresh and used TiO$_2$ catalysts

The fresh and used TiO$_2$ catalysts were examined by an XRD method to study the characteristics of their structure and their XRD patterns are shown in Fig. 7. The results demonstrated there is no significant difference between the fresh (a) and used (b) TiO$_2$ catalysts and two types of peaks representing anatase and rutile phases can be seen in both the patterns. These XRD patterns confirmed that there is no significant change found in the crystal structure of TiO$_2$ catalyst after the reaction although some deposits with a dark yellow colour were visually observed on the used TiO$_2$ catalyst. These deposits could be Fe(OH)$_3$ or an Fe-O-(organic) complex which needs to be
The TiO$_2$ catalysts used in three different reaction conditions were further examined by FTIR to study their chemical composition; these were: (a) TiO$_2$-UV under a N$_2$ gas flow; (b) Fe(VI)-TiO$_2$-UV under a N$_2$ gas flow; (c) Fe(VI)-TiO$_2$-UV under a O$_2$ gas flow. The FTIR spectra of the three catalysts are shown in Fig. 8. It can be seen that all of them have the same peaks near the 3434 and 1634 cm$^{-1}$ wave numbers corresponding to the stretching vibrations of O-H linkage on the TiO$_2$ surface. However spectrum “c” is very different from the spectra “a” and “b” although the same dosage of ferrate was used in the reaction conditions of “b” and “c”. Four new peaks were observed at wave numbers, 1407, 1083, 984 and 515 cm$^{-1}$, which can be assigned to C-O, C-H, C-H and Fe-O vibrations, respectively (Pretsch et al., 2000). These results provide further evidence that the presence of oxygen in the photocatalytic reaction leads to the formation of a surface-bound chemical complex on the TiO$_2$ catalyst.

4. Conclusions

This study has investigated the photoreduction of ferrate and photocatalytic degradation of DMP in an aqueous Fe(VI)-TiO$_2$-UV reaction system, at pH 9, under different gas flow conditions. It was found that when the reaction was conducted under a N$_2$ gas flow, ferrate was highly effective in scavenging the excited, conductance band electrons from the surface of TiO$_2$ catalyst which contributed to a
substantial oxidation of DMP by the synergistic effects of ferrate, and photocatalytic, oxidation mechanisms. However, when the reaction was performed under an air or O₂ gas flow, the DMP degradation was greatly inhibited even though the ferrate was rapidly reduced. It is believed that the presence of oxygen leads to the formation of Fe-O-(organic) complexes from the reduced Fe(III) or Fe(IV) species, the dissolved oxygen and low concentrations of DMP reaction products. While there is experimental evidence that suggests that the complexes are present both in the bulk solution and adsorbed on the surface of the TiO₂ catalyst, it believed that the presence of surface-adsorbed Fe-O-(organic) complexes has a greater inhibiting effect on DMP degradation. Thus, the adsorbed complexes block the adsorption of DMP on the TiO₂ and prevent interactions between the DMP and valence band holes; however, the adsorbed complexes do not appear to significantly diminish the UV activation of TiO₂. Although the results of this study indicate that the presence of dissolved oxygen in environmental waters decreases the oxidation performance of the Fe(VI)-TiO₂-UV process, the performance may still exceed that of alternative chemical treatment methods and be capable of achieving a satisfactory degradation of recalcitrant contaminants such as phthalate acid esters.

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REFERENCES


Jobling, S., Reynolds, T., White, R., Parker, M.G., Sumpter, J.P., 1995. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environ. Health Persp. 103, 582-587.


Figure Captions

Fig. 1. Ferrate reduction and DMP degradation under different reaction conditions. ([DMP]₀ = 10.3 mg L⁻¹, [Fe(VI)]₀ = 0.16 mM, Light Intensity = 0.40 mW cm⁻², pH 9, [TiO₂] = 40 mg L⁻¹, with N₂ flow)

Fig. 2. Photocatalytic conversions for Ferrate reduction and DMP oxidation using:
(a) N₂ flow; (b) O₂ flow.

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

Fig. 4. Photocatalytic conversions for Ferrate photoreduction and DMP photooxidation using O₂ flow: (a) Ferrate reduction; (b) DMP degradation.

Fig. 5. Photocatalytic degradation of DMP with different TiO₂ and DMP solutions.

Fig. 6. The variation of DMP adsorption with different TiO₂ and DMP solutions.

Fig. 7. XRD patterns for the TiO₂ catalyst: (a) before use; (b) after use.

Fig. 8. FTIR spectra for the TiO₂ catalyst: (a) N₂ flow only; (b) 0.16 mM ferrate and N₂ flow; (c) 0.16 mM ferrate and O₂ flow.
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