Oxidative degradation/mineralization of dimethyl phthalate (DMP) from plastic industrial wastewater using ferrate(VI)/TiO₂ under ultraviolet irradiation

Ping Wang 1 · Yi Ding 1 · Liting Zhu 1 · Yunhao Zhang 1 · Sijie Zhou 1 · Linbei Xie 1 · Ao Li 1

Received: 19 April 2021 / Accepted: 16 September 2021 / Published online: 9 October 2021
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Abstract
A novel ferrate(VI)/titanium dioxide/ultraviolet [Fe(VI)/TiO₂/UV] system was successfully established for the photocatalytic oxidation of dimethyl phthalate (DMP). This system demonstrated a higher removal efficiency of DMP (95.2%) than the conventional TiO₂/UV and Fe(VI) alone systems (51.8% and 23.5%, respectively) and produced obvious synergistic effects. Response surface methodology (RSM), based on a three level, three independent variables design, was conducted through Design Expert 8.0.6 program, and a second-order polynomial model (R² = 0.998) was developed to quantitatively describe the photocatalysis of TiO₂ combined with Fe(VI) oxidation under ultraviolet irradiation. The fresh TiO₂ and photochemical reacted Fe(VI)/TiO₂ were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and element dispersive spectrum (EDS), which indicated that Fe(VI) was imprinted into the TiO₂, and the surface adsorbed Fe-O-(organic) materials inhibited DMP degradation. This photocatalytic oxidant showed high activity and stability after nine cycles without loss of its effectiveness (counting from the second cycle). The intermediates/products of DMP were analyzed by gas chromatography-mass spectrometry. The proposed pathway for DMP degradation involved one electron transfer of hydroxyl radical and breaking of the ester bond and benzene ring. The mineralization efficiencies of DMP in actual industrial wastewater and simulated water were 87.1% and 95.2%, respectively, suggesting practical field applications. A ecotoxicity test (17.3% inhibition on bioluminescence) in treating actual industrial wastewater containing DMP implied that the proposed Fe(VI)/TiO₂/UV had a potential for industrial water treatment.

Keywords Ferrate(VI)/TiO₂/UV · Photocatalytic oxidation · Dimethylphthalate (DMP) · Response surface methodology (RSM) · Industrial water treatment

Introduction
Phthalic acid esters (PAEs) are synthetic organic compounds used as plasticizers in a broad spectrum of industrial and commercial applications. PAEs are among the widespread environmental contaminants worldwide (Turan et al. 2021). They are nearly ubiquitous and are detected in the air (up to μg m⁻³ level), the water (up to μg L⁻¹ level), the soil and sediment (up to μg g⁻¹ dw level), the food (up to mg kg⁻¹ level), and the tissues and body fluids of humans and animals (up to μg L⁻¹ level) (Martine et al. 2013; Wang et al. 2013; Zhang et al. 2015; Li et al. 2016). Dimethyl phthalate (DMP), a representative PAEs, with a hydrolysis half-life of about 3 years is difficult to be degraded in nature (Staples et al. 1997).

Conventional techniques, including catalytic ozonation, gamma-radiation/H₂O₂ process (Şolpan and Mehrnia 2018), dielectric barrier discharge (Jia et al. 2018), ultraviolet (UV) photocatalysis (Jing et al. 2018; Lei et al. 2018) and biodegradation treatment (Hu et al. 2015; Zhou et al. 2017), have been extensively employed to remove DMP. Recently, biodegradation method was worldwide mostly adapted to the deep treatment of PAEs (Sarti et al. 2006). However, these compounds are difficult to be degraded in the conventional wastewater biochemical treatment systems. Traditional
biodegradation is not suitable for low concentrations of DMP when considering the removal efficiency and cost. In contrast, advanced oxidation technologies have a very strong application prospect by using the extremely oxidized •OH as an oxidant, which can completely mineralize or partially decompose these organic pollutants. Photocatalytic oxidation method utilizes a photoexcited catalyst to generate photogenerated electrons (ecb) and holes (hvb) (Eq. 1) and selectively degrades the low molecular weight organic pollutants completely without secondary pollution. Titanium dioxide (TiO2) has attracted researchers’ attention for years due to its non-toxicity, low cost, excellent high physicochemical, strongly oxidizable, and high availability (Hu et al., 2021).

In general, the conduction band electrons (ecb) and valence band holes (hvb) are generated when the surface of TiO2 is illuminated with UV light (Eq. 1). Ferrate [FeO4^2-, Fe(VI)], a hexavalent iron species, is a strong oxidizing agent which can be judged from the redox potential of Eq. 2 and Eq. 3 in acidic and alkaline solutions, respectively (Wood 1958). Potassium ferrate (K2FeO4) can effectively remove organic pollutants in water, such as phenol and chlorophenol, algae, and its toxins (Yuan et al., 2002; Graham et al., 2004; Sharma et al., 2010). Heterogeneous photocatalytic oxidation has been proved to be a promising water purifying method using a semiconductor material as a catalyst to generate a highly reactive electron-hole pairs that participate in and accelerate the redox reaction under ultraviolet (UV) irradiation. During the photocatalytic process, the key to improve the photocatalytic efficiency is to introduce oxidizing ions to capture electrons to reduce the chance of recombination of electrons and holes. Photoreaction of Fe(VI) may occur through three single electron steps, which results in the sequential species of Fe(V), Fe(IV), and Fe(III) (Eqs. 4–6). The reactivity of Fe(V) species is 10^3–10^5 folds higher than that of Fe(VI) (Li et al., 2005). Fe(V) ion can act as electron scavengers in the photocatalytic reactions to improve the efficiency of photoreaction (Sharma et al., 2001). The optimal combination of high-valence iron oxidation and TiO2 photocatalysis is of great significance for developing DMP removal strategy.

\[
\begin{align*}
TiO_2 + hv & \rightarrow h_{vb}^+ + e_{cb}^- \quad (1) \\
E^\circ & = 3.2 \text{ V} \\
\text{FeO}_4^{2-} + 8H^+ + 3e^- & \rightarrow \text{Fe}^{3+} + 4H_2O \quad (2) \\
E^\circ & = 2.2 \text{ V} \\
\text{FeO}_4^{2-} + 4H_2O + 3e^- & \rightarrow \text{Fe(OH)}_3^- + 5OH^- \quad (3) \\
E^\circ & = 0.7 \text{ V} \\
\text{Fe(VI)} + e_{cb}^- & \rightarrow \text{Fe(V)} \quad (4) \\
\text{Fe(V)} + e_{cb}^- & \rightarrow \text{Fe(IV)} \quad (5)
\end{align*}
\]

The demand for rapid, simple, and economical wastewater treatments to remove environmental organic pollutants has stimulated the investigation of Fe(VI)/TiO2/UV strategy. This combination of Fe(VI) oxidation and TiO2 photocatalysis is a promising technique that can exploit the high oxidative potential of highly reactive species [electrons (ecb) and holes (hvb)] to achieve either complete or partial decomposition of recalcitrant and toxic organics. Ferrate(VI) has been the most widely used metal catalyst to mediate the activation of TiO2 using UV light (Eq. 1), because it is cost-effective, low toxic, and easy to handle. In recent years, several investigations have been reported on the degradation of environmental pollutants by Fe(VI) photocatalytic combinations. Specifically, Ma et al. (2015) reported that the sulfonamides such as sulfadiazine, sulfamethoxazole, and sulfadimethylpyrimidine reduced by 89.2%, 82.0%, and 83.4%, respectively, after 10 min of Fe(VI)/TiO2/UV treatment. Yuan et al. (2008a, 2008b) observed DMP degradation/oxidation by the ferrate-enhanced TiO2-UV synergetic photocatalysis, and studied the application of combined ferrate-photocatalysis process for the aqueous degradation of DMP. Winkelmann et al. (2008) also studied the photocatalytic degradation of cyanate (NCO-) with Fe(VI)/UV/TiO2/NCO- system.

However, major challenges exist in applying homogeneous TiO2 activation by Fe(VI) under UV irradiation: the pH must be within a strict range, and the amounts of Fe(VI) and TiO2 must be optimized. In water solution, the lowest rate of reduction of Fe(VI) occurs between pH 9.4 and 9.7 (Sharma, 2002). Although oxidative ability of Fe(VI) is high under acidic conditions, Fe(VI) is highly unstable, and most Fe(VI) decomposition results in a low degradation efficiency of DMP (Fig. S3b). The Fe(VI) is much more chemically stable and can persist much longer in solution under alkaline conditions (pH 9.0–11.0), leading to an obvious degree of DMP degradation. Ferrate(VI) is an effective oxidant and disinfectant, which promotes the photocatalytic oxidation of organic pollutants. An insufficient amount of Fe(VI) provides a low treatment efficiency, while excessive Fe(VI) can consume the amount of electrons, thus affecting the removal of organic pollutants, as in Eqs. 2 and 3. Meanwhile, to control the release of soluble Fe(VI) into water solution, TiO2, a novel supporting material, with the ability to effectively immobilize soluble Fe(VI) species is expected to control the release of Fe(VI) and to enhance the activation efficiency for practical environmental remediation.

In this study, a Fe(VI)/TiO2/UV system was prepared to evaluate its photocatalytic and oxidative properties towards the removal of DMP. Herein, TiO2 was utilized as a photocatalyst, and Fe(VI) was as an oxidant. The influence of the experimental parameters (pH, initial concentrations of DMP, K2FeO4, and TiO2) on DMP removal was optimized.
using response surface methodology (RSM). The main objective of this study was to investigate the removal kinetics of DMP by the Fe(VI)/TiO₂/UV system and to assess the potential of this system for the photocatalytic oxidation of DMP in industrial water treatment. The possible removal mechanism of DMP was initially studied. Furthermore, the ecotoxicity of plastic industrial wastewater after Fe(VI)/TiO₂/UV oxidation was tested on Vibrio fischeri.

**Materials and methods**

**Materials and chemicals**

DMP (purity > 98.7%) was purchased from Aldrich Chemical Company. Sodium borate (Na₂B₄O₇·10H₂O) and sodium phosphate dibasic (Na₂HPO₄) which are used as buffer solutions were purchased from Nanjing Chemical Reagent Company. K₂FeO₄ (purity > 95%), P-25 TiO₂, tert-butanol (TBA), dimethyl sulfoxide (DMSO), ethylenediamine tetra acetic acid disodium salt (EDTA-2Na), and p-benzoquinone (TBA) were obtained from Shanghai Maclean Biochemical Technology Company. All chemicals were of analytical grade (BQ) were obtained from Shanghai Maclean Biochemical Technology Company. All chemicals were of analytical grade and were used without further purification. The stock solution of K₂FeO₄ was prepared by dissolving 2.52 mol L⁻¹ K₂FeO₄ with a pH of 9.0 and used within 10 min to minimize the self-decomposition of Fe (VI). DMP solutions were prepared by stirring 24 h at 25.0 ± 1.0°C. 0.01% HCl or 0.01% NaOH was used for pH adjustment. All the solutions were prepared with deionized water (18.0 MΩcm, Milli-Q Millipore, Waters Alliance, Milford, MA, USA).

**Photocatalytic experiments**

Photocatalytic experiments were conducted in a 2000-mL quartz reactor equipped with two peripheral immobilized 9 W UV lamps (PL-S 9W/10/2P, PHILIPS) at 25.0 ± 1.0°C through a thermostat circulator (THD-2015, Tianheng, China) (supporting information, Fig. S1). The emission wavelength was at 365 nm (Fig. S2). Unless otherwise stated, the experiment was started with the addition of certain amounts of Fe(VI)/TiO₂ into the aqueous solutions containing desired amounts of DMP in the dark. Initial pH was adjusted by 0.01% HCl or 0.01% NaOH and then measured by pH-meter (Mettler Toledo Five Easy Plus pH-Meter, Shanghai, China). The prepared Fe(VI)/TiO₂-DMP solutions were kept in the dark for 30 min to achieve adsorption/desorption equilibrium. Afterwards the photodegradation started, water samples were withdrawn at regular intervals and analyzed immediately after filtration through 0.45 μm membrane. Finally, the photoreaction was terminated by the addition of sodium sulfate. The photochemical reacted Fe(VI)/TiO₂ was centrifuged (7000 rpm, 5 min) to be separated from the solutions and then was prepared for the following characterization analysis.

Meanwhile, the fresh TiO₂ and photochemical reacted Fe(VI)/TiO₂ were characterized by X-ray diffraction (XRD) spectra, scanning electron microscope (SEM), and element dispersive spectrum (EDS). The XRD pattern of samples’ architectural feature was recorded by a Rigaku D/MAX II X-ray Diffractometer. The microstructure of samples’ external surface was measured with a Hitachi S-4500 SEM. The elements (C, Ti, O, and Fe) distributed on the TiO₂ surface were detected by EDS.

**Analytical quantification**

The degradation efficiency (ηDMP, %) of DMP and mineralization efficiency (ηTOC, %) of total organic carbon (TOC) were measured to evaluate the photo-degradability. The concentrations of DMP were analyzed by high performance liquid chromatography (Agilent 1100, USA) equipped with UV230 + UV-vis detector and Acclaim TM C₁₈ column (250 mm × 4.6 mm, 5 μm). The mobile phase was methanol: water (70:30, v/v), flow rate was 1.0 mL/min, and UV wavelength was 227 nm (Wang et al. 2012, 2015). Concentration of Fe(VI) was determined by UV-vis spectrophotometer (Shimadzu UV-2550, Tokyo, Japan) at a wavelength of 510 nm (ε₅₁₀nm = 1150 M⁻¹ cm⁻¹). The intermediates of DMP degradation were analyzed by gas chromatography-mass spectrometry (GC-MS) (Trace ISQ, Thermo Scientific, USA) fitted with a fused capillary column (DV-1, 15 m long, 0.25 mm diam.). The initial temperature was 100°C and rose to 300°C at 10°C/min. The injection volume was 0.5 μL. The mass spectrometer was operated at electron ionization energy of 70 eV (Wang and Fan 2014). The wastewater was collected from Changzhou Juli Plastics Co., Ltd. The inflow and effluent of wastewater in this plant were 100 m³ day⁻¹ and 96 m³ day⁻¹, respectively. The water parameter analysis for the wastewater was carried out before and after the treatment according to APHA procedures (APHA 2012). Additionally, total organic carbon (TOC) was determined by a TOC analyzer (Model 1010, O.I. Analytical, NY) equipped with nondispersive infrared (NDIR) detector, with carrier gas of N₂, oxidant of 10% sodium peroxydisulfate, and TOC standard solution of anhydrous potassium biphthalate. The simulated water containing DMP 0.32 mg L⁻¹ was prepared, based on the DMP concentration measured in the wastewater. All the experiments were performed in triplicate. The relative standard deviation of quantitative analysis with triple measurements was below 5%.

**Optimization of multivariable by RSM**

RSM was used to construct a mathematical model to quantitatively detect the interaction among TiO₂, K₂FeO₄, and pH.
Three levels of pH (7.0, 9.0, and 11.0), TiO$_2$ (20, 40, and 60 mg L$^{-1}$), and K$_2$FeO$_4$ (10, 30, and 50 mg L$^{-1}$) were selected as independent variables and designated as $X_1$, $X_2$, and $X_3$, respectively, as shown in Table 1. The interaction between variables and responses was found out by analyzing data using Design Expert 8.0.6 program.

**Ecotoxicity assessment**

The ecotoxicity assessment of wastewater was conducted with the standard Microtox® toxicity test system (Microbics Corp., Carlsbad, CA, USA). 2.0 mL of sample was taken directly from the water treatment system and supplied NaCl to reach 2% final concentration. The pH of samples was adjusted to 7.0 ± 0.1 using 0.01% HCl or 0.01% NaOH. The bioluminescence intensity of *Vibrio fischeri* exposed to the sample solutions for 15 min was measured using a Dxy2 biological toxicity analyzer (Institute of Soil Science, Academia Sinica, Nanjing, China). The inhibition of bioluminescence was used to assess the acute ecotoxicity of DMP solutions prior to and after water treatment. The results were compared to an aqueous control.

**Results and discussion**

**Optimization of DMP degradation conditions by RSM**

RSM is a multivariate statistical technique for determining the optimal conditions for multivariable system and can predict the combined effects of experimental variables. It is less laborious and time-consuming than other approaches that applied to optimize a complex process. Based on the results of single-factor tests (Fig. S3), a three-factor, three-level Box-Behnken design was utilized for the mathematical modeling of DMP degradation efficiency as a function of pH, TiO$_2$ dosage, and K$_2$FeO$_4$ dosage. The experimental design along with the maximum observed and predicted degradation efficiency were listed in Table 2. The degradation behavior of Fe(VI)/TiO$_2$/UV system was fitted to the following second-order polynomial equation using multiple regression analysis.

\[
\eta_{\text{DMP}}(\%) = +90.59 -1.76X_1 + 15.50X_2 + 1.86X_3 + 0.17X_1X_2 + 0.44X_1X_3 - 0.69X_2X_3 - 14.24X_1^2 - 14.41X_2^2 - 23.22X_3^2
\]  

(7)

The data calculated by ANOVA for Eq. 7 was listed in Table 3. The $F$-value was the ratio between mean square of factors in different groups and mean square of factors in same group. The $F$-value and $P$-value of the model were 338.83 and < 0.0001, respectively, indicating that the regression model was extremely significant. The coefficients for the pH ($X_1$), TiO$_2$ dosage ($X_2$), and K$_2$FeO$_4$ dosage ($X_3$) were significant ($P < 0.05$). And a coefficient $R^2$ value of 0.998 showed that Eq. 7 was highly reliable; the model also revealed statistically insignificant lack of fit ($P = 0.8227$), which indicated that the model was adequate for prediction within the ranges of variables.

Response surfaces were plotted by Design-Expert 8.0.6 software to investigate the effects of the three independent variables and their interactions on DMP degradation. As shown in Fig. 1a, the interaction between pH and TiO$_2$ dosage was not significant, which was in agreement with the results of the variance. The degradation efficiency of DMP increased with TiO$_2$ dosage in the pH range of 7.0–11.0. Figure 1a and b presented that pH played an important role in the photocatalytic process. In fact, the effect of pH could be wide-ranging. The relationship between pH and K$_2$FeO$_4$ dosage was significant, as shown in Fig. 1b. When the pH was between 7.0 and 11.0, K$_2$FeO$_4$ dosage was between 10.0 and 50.0 mg L$^{-1}$, the degradation efficiency of DMP increased with the K$_2$FeO$_4$ dosage increasing from 10.0 to 30.0 mg L$^{-1}$, but it decreased while K$_2$FeO$_4$ dosage increased further. The degradation efficiency increased with increasing pH until around 9, and then it decreased when pH > 9.0. The maximum degradation efficiency of DMP was 93.48% at pH 9.0.

As shown in Fig. 1c, the combined effect of TiO$_2$ dosage and K$_2$FeO$_4$ dosage was highly significant. Under the condition of the same dosage of TiO$_2$, the degradation efficiency increased firstly and then decreased with the increase of K$_2$FeO$_4$ dosage. When the dosage of K$_2$FeO$_4$ was between 10.0 and 50.0 mg L$^{-1}$, the degradation efficiency of DMP increased with the increase of TiO$_2$ dosage. Results indicated that the maximum degradation efficiency was observed when the K$_2$FeO$_4$ dosage was 30.0 mg L$^{-1}$

As shown in Table 4, the predicted optimal conditions based on the RSM were initial TiO$_2$ concentration of 50.73 mg L$^{-1}$, pH 8.89, and initial K$_2$FeO$_4$ concentration of 30.64 mg L$^{-1}$. To verify the accuracy and reliability of
the prediction model, three parallel verification tests were performed under the optimal conditions. The degradation efficiency of DMP was 91.36 ± 2.12%. The experimental value closely agreed with the result obtained from RSM, which validated the findings of response surface optimization.

An optimal condition could be therefore obtained as 50.73 mg L\(^{-1}\) TiO\(_2\), 30.64 mg L\(^{-1}\) K\(_2\)FeO\(_4\), and pH 8.89.

### Performance of the Fe(VI)/TiO\(_2\)

#### Stability of ferrate(VI)

The initial concentration of K\(_2\)FeO\(_4\) solution was 30.0 mg L\(^{-1}\), and the variation of the stability (self-decomposition) of Fe(VI) with time \(t\) (min) was observed at pH values of 7.0, 8.0, 9.0, and 10.0 in the absence of catalyst TiO\(_2\) and UV light.

### Table 2  Response surface Box-Behnken design and the experimental and predicted removal of DMP

| Run | \(\chi_1\)/pH | \(\chi_2\)/TiO\(_2\) dosage (mg L\(^{-1}\)) | \(\chi_3\)/K\(_2\)FeO\(_4\) dosage (mg L\(^{-1}\)) | \(\eta_{\text{DMP}}\) (%) |
|-----|-------------|---------------------------------|---------------------------------|----------------|
| 1   | 7.0         | 40                              | 10                              | 53.93          |
| 2   | 9.0         | 40                              | 30                              | 89.25          |
| 3   | 9.0         | 40                              | 30                              | 89.24          |
| 4   | 9.0         | 60                              | 10                              | 67.14          |
| 5   | 7.0         | 60                              | 30                              | 78.74          |
| 6   | 11.0        | 40                              | 50                              | 53.22          |
| 7   | 7.0         | 40                              | 50                              | 56.91          |
| 8   | 9.0         | 40                              | 30                              | 93.48          |
| 9   | 11.0        | 60                              | 30                              | 76.62          |
| 10  | 9.0         | 20                              | 50                              | 40.16          |
| 11  | 9.0         | 60                              | 50                              | 69.32          |
| 12  | 9.0         | 20                              | 10                              | 35.22          |
| 13  | 11.0        | 40                              | 10                              | 48.46          |
| 14  | 11.0        | 20                              | 30                              | 44.81          |
| 15  | 7.0         | 20                              | 30                              | 47.61          |
| 16  | 9.0         | 40                              | 30                              | 90.51          |
| 17  | 9.0         | 40                              | 30                              | 90.49          |

### Table 3  ANOVA for response surface quadratic model

| Source           | Sum of squares | Degree of freedom | Mean square | \(F\)-value | \(P\)-value |
|------------------|----------------|-------------------|-------------|-------------|-------------|
| Model            | 16410.06       | 9                 | 712.23      | 338.83      | <0.0001     |
| \(\chi_1\)      | 24.78          | 1                 | 24.78       | 11.79       | 0.0109      |
| \(\chi_2\)      | 1922.62        | 1                 | 1922.62     | 914.65      | <0.0001     |
| \(\chi_3\)      | 27.60          | 1                 | 27.60       | 13.13       | 0.0085      |
| \(\chi_1\chi_2\) | 0.12           | 1                 | 0.12        | 0.055       | 0.8213      |
| \(\chi_1\chi_3\) | 0.79           | 1                 | 0.79        | 0.38        | 0.5587      |
| \(\chi_2\chi_3\) | 1.90           | 1                 | 1.90        | 0.91        | 0.3729      |
| \(\chi_1^2\)    | 853.74         | 1                 | 853.74      | 406.15      | <0.0001     |
| \(\chi_2^2\)    | 874.25         | 1                 | 874.25      | 415.91      | <0.0001     |
| \(\chi_3^2\)    | 2271.06        | 1                 | 2271.06     | 1080.41     | <0.0001     |
| Residual         | 14.71          | 7                 | 2.10        |             |             |
| Lack of fit      | 2.73           | 3                 | 0.91        | 0.30        | 0.8227      |
| Pure error       | 11.99          | 4                 | 3.00        |             |             |
| Total            | 6424.77        | 16                |             |             |             |

Note: \(R^2 = 99.77\%; \ R^2 \ (\text{adj}) = 99.74\%\)
The Fe(VI) concentration was determined by UV-vis spectroscopy every 1 min. Figure 2a showed that there was an insignificant decrease in the amount of Fe(VI) at pH 9.0 or 10.0. The decomposition of Fe(VI) could be described with the pseudo-first-order kinetic model \( \ln([\text{Fe}]_t/[\text{Fe}]_0) = -kt \) (Eq. 8). Herein, \([\text{Fe}]_0, [\text{Fe}]_t, \) and \( k \) stand for the initial concentration (mg L\(^{-1}\)), the concentration of K\(_2\)FeO\(_4\) (mg L\(^{-1}\)) at time \( t \) (min), and the pseudo-first-order rate constant (min\(^{-1}\)), respectively. The \( R^2 \) values for all pH values were over 0.99 (supporting information, Table S1). As illustrated in Fig. 2b, the decomposition kinetic constant at pH 9.0 was calculated as 0.00319 min\(^{-1}\), which was about 84.9-, 25.0-, and 2.1-fold higher than that at pH 7.0, 8.0, and 10.0, respectively. The stability of Fe(VI) was highly pH dependent. Fe(VI) was extremely unstable when pH value was lower than 9.0, and there was a maximum stability in pH range of 9.0–10.0.

### Deactivation of the TiO\(_2\)

The TiO\(_2\) used in DMP removal was extracted by suction filtration and then dried under vacuum. Four experimental conditions were employed with the same dose of TiO\(_2\) (50.0 mg L\(^{-1}\)) in the presence of Fe(VI): (1) degradation of DMP solution with fresh TiO\(_2\); (2) degradation of DMP solution with water-washed TiO\(_2\); (3) degradation of DMP solution with 1% HCl-washed TiO\(_2\); and (4) after 120 min of solution reaction, degradation of residual DMP solution with fresh TiO\(_2\). As shown in Fig. 2c, the degradation of residual DMP solution with fresh TiO\(_2\) and the degradation of DMP solution with water-washed TiO\(_2\) achieved low efficiency in degrading 18.3 and 24.2%, respectively. However, the degradation of DMP by 1%HCl-washed TiO\(_2\) was more than 90% within 120 min, which was similar to that of fresh TiO\(_2\). These results disclosed that the degradation of DMP might be inhibited by forming a Fe-O-(organic) complex on the surface of the catalyst and in bulk solution during the reaction process, but the deactivated TiO\(_2\) catalyst could be reactivated by washing with 1% HCl solution.

### Adsorption of the TiO\(_2\)

The photocatalytic degradation of DMP in aqueous solution mainly occurred on the surface of TiO\(_2\) catalyst, and the adsorption rate of DMP on the surface of TiO\(_2\) played a key role in the Fe(VI)/TiO\(_2\)/UV system (EL-Mekkawi et al. 2020). A number of adsorption tests were carried out in the darkness at pH 9.0 for 48 h to determine the adsorption equilibrium. The amount of TiO\(_2\) added in each test was 0.5 g L\(^{-1}\). The adsorption isotherm test was carried out under the three conditions: (1) adsorption with fresh TiO\(_2\) in fresh DMP solution; (2) adsorption with used TiO\(_2\) in fresh DMP solution; and (3) adsorption with fresh TiO\(_2\) in reacted DMP solution. The adsorption of DMP was described with Langmuir model.

\[
\frac{1}{Qe} = \frac{1}{B_L Q_m} + \frac{1}{C_e Q_m} \quad (8)
\]

\(Q_e\) is the adsorption capacity of TiO\(_2\) at equilibrium (mg g\(^{-1}\)), \(B_L\) is the Langmuir constant related to the affinity of the adsorption sites (L mg\(^{-1}\)), \(Q_m\) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)), and \(C_e\) is the equilibrium concentration of DMP (mg L\(^{-1}\)).
where $Q_m$ (mg g$^{-1}$) is the maximum adsorption amount of DMP adsorbed by TiO$_2$, $C_e$ (mg L$^{-1}$) is the concentration of DMP under equilibrium conditions, $Q_e$ (mg g$^{-1}$) is the amount of DMP adsorbed by TiO$_2$ under adsorption equilibrium, and $B_L$ is the Langmuir adsorption constant of DMP on TiO$_2$ surface without UV light.

As represented in Fig. 2d, the fresh TiO$_2$ in the fresh DMP solution exhibited the maximum DMP adsorption, while the used TiO$_2$ in the fresh DMP solution and the fresh TiO$_2$ in the reacted DMP solution showed much lower adsorption (Priyanka et al. 2019). These results indicated that the formation of Fe-O-(organic) complexes on the surface of TiO$_2$ catalyst or in the bulk solution inhibited the adsorption of DMP on the surface of TiO$_2$.

DMP degraded very slowly in the dark in the presence of Fe(VI)/TiO$_2$. The results depicted in Fig. S4 could be described with Langmuir–Hinshelwood model, which was expressed as follows (Eq. 9):

$$\frac{1}{k_{app}} = \frac{1}{kk_p} + \frac{C_0}{k}$$

where $k_{app}$ is the first-order rate constant (min$^{-1}$), $k$ is the intrinsic reaction rate constant (mg L$^{-1}$ min$^{-1}$), and $K_p$ is the light adsorption equilibrium constant (L mg$^{-1}$). Figure S4 (a) (pH 9.0, TiO$_2$ dosage 0.5 g L$^{-1}$) elucidated that $C_0$ and 1/$k_{app}$ in TiO$_2$/Fe(VI)/UV system had a good linear relationship ($R^2 = 0.960$), and the slope of the line $k$ was 0.464 mg L$^{-1}$ min$^{-1}$, and $K_p$ was 0.155 L mg$^{-1}$ calculated by the intercept. As seen in Fig. S4(b) (pH 9.0, [TiO$_2$]$_0$ = 0.5 g L$^{-1}$, [K$_2$FeO$_4$]$_0$ = 30.0 mg L$^{-1}$), 1/Q$_e$ and 1/C$_e$ had a good linear relationship ($R^2 = 0.996$), and $B_L$ can be calculated from intercept and slope of the line. $B_L$ (0.0238 L mg$^{-1}$) was far smaller than $K_p$ (0.155 L mg$^{-1}$), demonstrated that TiO$_2$ surface adsorption was obviously enhanced in the presence of Fe(VI) under UV irradiation.

### Comparative studies of DMP degradation

To assess the contribution of the mechanism to the efficacy of DMP degradation, the removal rates of the six processes, i.e., Fe(VI) alone in the dark, Fe(VI)/UV, TiO$_2$ alone in the dark, TiO$_2$/UV, Fe(VI)/TiO$_2$ in the dark, and Fe(VI)/TiO$_2$/UV, were evaluated under the optimal operating conditions. As shown in Fig. 3a, the Fe(VI) or TiO$_2$ alone in the dark had no significant effect on DMP degradation (23.4% and 20.1%, respectively), indicating that the specific organic matrix of Fe(VI) oxidation and TiO$_2$ catalysis had a clear selectivity. The degradation efficiency of DMP in TiO$_2$/UV treatment was only 51.8% within 120 min. In stark contrast, the degradation efficiency of DMP by the Fe(VI)/TiO$_2$/UV system reached approximately 95.2% after 120 min. As seen from Fig. 3b, the pseudo-first-order kinetic ln([DMP]$_t$/[DMP]$_0$) = $-k_{obs}$[Fe(VI)]dt could be applied for the DMP degradation in the Fe(VI)/TiO$_2$/UV system with a calculated $k_{obs}$ of 2.53 × 10$^{-1}$ min$^{-1}$.
This value was about 11- and 4-fold higher than that obtained in the Fe(VI) alone in the dark ($2.23 \times 10^{-3}$ min$^{-1}$) and TiO$_2$/UV ($6.08 \times 10^{-3}$ min$^{-1}$) systems, respectively. Comparative analysis of Fig. 3 a and c demonstrated a distinct synergistic effect achieved in the combined Fe(VI)/TiO$_2$/UV system. Since Fe(VI) has higher oxidizing power than other electron acceptors, such as permanganate or peroxyde, Fe(VI) may be reduced to Fe(V) with high activity. Therefore, Fe(VI) can act as an electron scavenger to enhance photo-oxidation and organic oxidation. Meanwhile, the electron scavenging of the catalyst by Fe(VI) reduction greatly reduces the recombination of the conduction band electron ($e^-$) and the valence band hole ($h^+$) in photocatalytic systems, thereby improving the quantum efficiency in the photocatalytic reaction of TiO$_2$ and then enhancing photocatalytic degradation of the target compound, DMP (Wong and Chu 2003).

Recyclability of the Fe(VI)/TiO$_2$

The lifetime and reusability of the catalyst are important issues for its continuous treatment of wastewater. Cycling experiments were carried out to examine the stability and reusability of Fe(VI)/TiO$_2$ photocatalyst via the degradation of DMP over nine cycles. After complete degradation of each cycle, the catalyst was centrifuged from the simulated water and carefully washed with deionized water and 0.1% HCl to remove contaminants on the catalyst surface. Then, the solid catalyst was dried under vacuum and reused for the next run. Figure 3 d displayed the results of DMP degradation for nine cycling runs. In the light of cycling experimental results, $\eta_{TOC}$ was 99.1% in the first run and decreased to 91.3% in the ninth cycle. It could be acquired that the catalyst was stable and reusable for nine runs with a high recycling performance. The reduction in photocatalytic oxidation efficiency from 99.1 to 91.3% was acceptable because of DMP loss through separation and recovery and pore clogging of the catalysts caused by DMP and its by-products. These effects reduced the specific surface area of the catalysts and surface catalytic activity. Moreover, the SEM and XRD analyses of the catalyst were verified before and after application to ascertain the durability of catalysts, as shown in Fig. 4a–c. The obtained results also revealed that the catalysts were not corroded under UV irradiation and maintained durable after nine cycles of DMP degradation. This was consistent with the results of SEM and XRD.

Characterization of the Fe(VI)/TiO$_2$

The crystal structures of fresh and photochemical reacted Fe(VI)/TiO$_2$ catalysts were characterized by XRD, as seen in Fig. 4c. The peaks of Fe(VI)/TiO$_2$ were observed at 25.32°, 27.34°, 37.03°, 37.76°, 38.61°, 48.06°, 53.84°, 55.08°, and

$10^{-2}$ min$^{-1}$. This value was about 11- and 4-fold higher than that obtained in the Fe(VI) alone in the dark ($2.23 \times 10^{-3}$ min$^{-1}$) and TiO$_2$/UV ($6.08 \times 10^{-3}$ min$^{-1}$) systems, respectively. Comparative analysis of Fig. 3 a and c demonstrated a distinct synergistic effect achieved in the combined Fe(VI)/TiO$_2$/UV system. Since Fe(VI) has higher oxidizing power than other electron acceptors, such as permanganate or peroxyde, Fe(VI) may be reduced to Fe(V) with high activity. Therefore, Fe(VI) can act as an electron scavenger to enhance photo-oxidation and organic oxidation. Meanwhile, the electron scavenging of the catalyst by Fe(VI) reduction greatly reduces the recombination of the conduction band electron ($e^-$) and the valence band hole ($h^+$) in photocatalytic systems, thereby improving the quantum efficiency in the photocatalytic reaction of TiO$_2$ and then enhancing photocatalytic degradation of the target compound, DMP (Wong and Chu 2003).

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62.68°, respectively, which represented Fe(VI)/TiO₂ catalyst containing anatase mine and rutile. The mixed-phase of anatase and rutile in the Degussa P25 TiO₂ had shown better photocatalytic performance than pure-phase materials (Linsebigler et al. 1995; Maness et al. 1999). These XRD patterns confirmed that no significant change was observed in the crystal structure of the Fe(VI)/TiO₂ catalyst after photocatalysis, though some dark yellow deposits were observed on the photochemical reacted Fe(VI)/TiO₂ catalyst. These deposits may be Fe(OH)₃ or Fe-O-(organic) complexes, which require further investigation. Also, SEM was used to investigate the morphology of the catalyst surface. The fresh Fe(VI)/TiO₂ was round and uniform particles with diameter of 25 nm, and the surface structures showed a slight agglomeration, as shown in Fig. 4a. Compared Fig. 4a with Fig. 4b, the morphology and particle size of fresh Fe(VI)/TiO₂ and photochemical reacted TiO₂ were almost unchanged, which was consistent with XRD results. EDS analysis confirmed the presence of Fe on the catalyst surface (see Fig. 4d), and the Fe content was relatively small, which was consistent with the results that the degradation reaction by DMP may form a Fe-O-(organic) complex on the surface of the catalyst in bulk solution, thus inhibiting the degradation of DMP.

Figure 5 is the EDS images of C, Ti, O, and Fe attached on the surface of the photochemical reacted Fe(VI)/TiO₂, and the element Fe on the surface of Fe(VI)/TiO₂ increased obviously. Simultaneously, the high content of Ti and the relatively low content of O were observed on the surface. This was consistent with the results that the sediments attached on the surface of the photochemical reacted Fe(VI)/TiO₂ may be Fe-O-(organic) complexes.

Degradation pathway

The intermediates of DMP degraded by Fe(VI)/TiO₂/UV system were analyzed by GC-MS (Fig. S5). Based on the identified intermediates, a degradation pathway of DMP by Fe(VI)/TiO₂/UV system was proposed as shown in Fig. 6. The main intermediate for DMP degradation was phthalic acid (PA), which was produced by electron transfer and the reactions with hydroxyl radicals. In view of the Figs. S5 and 6, the model compound ① DMP was first lost one or two electrons to be oxidized to organic cations ② or ③, respectively. The oxidation continuing, ② or ③ were gradually oxidized to organic substances ④ or ⑤ by adding hydroxyl radicals •OH. When the organic substance ④ lost a methoxy group, the observed product ⑥ (monomethyl phthalate, MMP) was formed. Product ⑥ undergone further electron loss after Fe(V) oxidation to form organic cation ⑦, organic cation ⑦ was added to a hydroxyl group, and then a methoxy group was lost to form the observed final product ⑧ (phthalic acid, PA). Alternatively, when the substance ⑤ lost two methoxy groups, it formed the final product ⑧ (phthalic acid, PA). Finally, under the action of ultraviolet light and •OH, DMP
and its benzene ring intermediates were further oxidized, and then the benzene ring would be opened to generate small molecule organic acids and further mineralized into CO₂ and H₂O.

In the proposed degradation pathway, the major pathway involved a single electron transfer that led to Fe(Ⅴ) and a radical cationic intermediate resulting in CO₂ extrusion.

Mineralization of DMP in the plastic production wastewater

In order to study the water treatment applications of Fe(Ⅵ)/TiO₂/UV system for the mineralization of DMP from complex water matrix, a secondary production wastewater was collected from Changzhou Juli Plastics Co., Ltd in Jiangsu Province, China. The inflow and effluent of secondary wastewater effluents in this plant are 100 m³ day⁻¹ and 96 m³ day⁻¹, respectively. The characteristics of secondary wastewater effluents were summarized in Table S2. Comparatively, the mineralization efficiency of DMP in actual wastewater (87.1%) was slightly lower than that in simulated water (95.2%), as presented in Fig. 7a. This inhibition effect was rationalized by considering that the natural organic matter and some ions (such as CO₃²⁻) in actual wastewater could compete for Fe(Ⅵ) with DMP. Meanwhile, the results of simulated water demonstrated that almost 100% DMP could be effectively photodegraded by Fe(Ⅵ)/TiO₂/UV process within 100 min, and the reaction rate constant was as high as 0.271 min⁻¹. The above results illustrated that the Fe(Ⅵ)/TiO₂/UV process was a feasible approach for degrading DMP in production wastewater.

Figure 7c demonstrates the ultraviolet light photocatalytic pictorial representation for DMP degradation, using Fe(Ⅵ)/TiO₂ as a photocatalyst. First, the conduction band electrons (eᶜᵇ⁻⁻) and valence band holes (hʳᵇ⁺⁺) are generated when TiO₂ surface absorbs photons (UV radiation) with UV light energy larger than its band gap (Eq. 10). Then, the photogenerated electron-hole pairs (excitons) separate apart, the free electrons transfer towards the conduction band and the holes to the valence band at the interface of Fe(Ⅵ)/TiO₂, where the photogenerated holes can oxidize DMP molecules (Eq. 14), or react with water and OH⁻ to form hydroxyl radicals, •OH, the main oxidizing species (Eqs. 12 and 13). The heterogeneous photocatalytic degradation of DMP was illustrated by the following equations.

\[
\text{TiO}_2 + h\nu \rightarrow h_{rb}^+ + e_{cb}^- \quad (10)
\]

\[
E^0 = 3.2 \text{ V}
\]

\[
\text{FeO}_4^{2-} + 8H^+ + 3e^- \rightarrow \text{Fe}^{3+} + 4H_2O \quad (11)
\]
In order to quench the reactive species during photocatalytic process, four types of scavengers, TBA (an \( \cdot \)OH scavenger), DMSO (an electron scavenger), EDTA-2Na (a \( h^+ \) scavenger), and BQ (an \( O_2^- \) scavenger), were used as scavengers for quenching experiments. As shown in Table S3, the presence of 1 mmol/L tert-butanol and 1 mmol/L DMSO in the photo-catalytic system showed a notable inhibitory effect on the degradation of DMP with Fe(VI)/TiO\(_2\)/UV system. These phenomena indicate that the photogenerated electrons and \( \cdot \)OH radical play an important role in DMP degradation. Finally, the reusability of the modified TiO\(_2\) was investigated, as shown in Fig. 3d. The catalyst after one reaction for 120 min was washed with methanol, dried under vacuum, and then
reused for the same test. The results indicated that there was almost no obvious reduction of photocatalytic efficiency after nine cycles.

**Ecotoxicity evaluation**

The acute ecotoxicity of the treated effluent from the reactor was evaluated via the change in luminescence intensity of *Vibrio fischeri* after exposure for 15 min (Fig. 7b). When the initial concentration of DMP was 0.33 mg/L and treatment time was 120 min, the inhibition changed with time because of the evolution of different byproducts. During the photocatalytic period, the inhibition on luminescence decreased significantly and the samples after treating for 60 min exhibited toxicity below 20%. Thereafter, 16.3% inhibition on the bioluminescence was tested after treating for 120 min. Different from our observation, a significant increment of inhibition (rose to over 40%) during wastewater treatment by Ti/TiO$_2$ films was discovered, which could be due to the higher concentration employed (Olvera-Vargas et al. 2016). Notably, the inhibition on *Vibrio fischeri* might also ascribe to the residual iron and hydroxyl radical involved in samples; therefore the removal of these compounds could further reduce adverse effects on aquatic beings (Tufail et al. 2021). In total, the minor inhibition of 16.3% on the luminescence of *Vibrio fischeri* indicated that the Fe(VI)/TiO$_2$/UV treated effluent would not significantly affect the microorganisms in aquatic environments.

**Conclusion**

The photocatalytic oxidation of DMP has been investigated by means of UV irradiation over Fe(VI)/TiO$_2$ catalysts. The major conclusions drawn from this work are summarized as follows:

1. RSM was used to optimize the experimental variables. The 3-D response surface plots indicated that the correlations between pH and K$_2$FeO$_4$ dosage and TiO$_2$ dosage and K$_2$FeO$_4$ dosage were highly significant. A maximum DMP removal of 95.2% was achieved under these optimum conditions.

2. The degradation efficiency of DMP in Fe(VI)/TiO$_2$/UV system was better than that of K$_2$FeO$_4$ and TiO$_2$ alone, indicating that there was a synergistic effect on K$_2$FeO$_4$/TiO$_2$ under UV illumination. Experiments shown that the Fe-O-(organic) complex on the surface of Fe(VI)/TiO$_2$ could inhibited DMP degradation, and the deactivated TiO$_2$ catalyst could be reactivated by being washed with 1% HCl solution.

3. The intermediates of DMP were identified as MMP and PA by GC-MS. A plausible degradation pathway was proposed based on the detected intermediates. The free radicals generated by the Fe(VI)/TiO$_2$/UV system firstly attacked the side chain of DMP, in which MMP as the first metabolite was generated through de-esterification, sequentially followed by the generation of phthalic acid (PA) after further de-esterification of MMP. Eventually, the PA and other low molecular weight organics were mineralized all the way to CO$_2$ and H$_2$O.

4. Combined Fe(VI)/TiO$_2$ could mineralize 87.1% and 95.2% of DMP from the actual wastewater and simulated water samples under UV illumination. Recycling performance of Fe(VI)/TiO$_2$/UV system exhibited high activity and stability after nine consecutive cycles and could be used repeatedly in the decontamination of plastic industrial wastewater.

5. The ecotoxicity values of wastewater decreased after the Fe(VI)/TiO$_2$/UV treatment. The treated water samples were non-toxic (the decrease in the luminescence of the *Vibrio fischeri* < 20%).

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-16636-x.

**Author contribution** Ping Wang: Funding acquisition, methodology, supervision, validation, and writing (review and editing)

Liting Zhu and Yunhao Zhang: Performed the catalytic tests, analyzed, and interpreted the results of the catalytic activity of the Fe(VI)/TiO$_2$/UV system

Yi Ding and Sijie Zhou: Investigation, data analysis, and RSM software

Linbei Xie and Ao Li: Formal analysis and validation

The first draft of the manuscript was written by Liting Zhu. All authors read and approved the final manuscript.

**Funding** This research was financially supported by the National Natural Science Foundation of China (grant numbers: 30771696, 31270680) and Jiangsu University Advantages Construction Project Funding Project.

**Data availability** All data generated or analyzed during this study are included in this published article (and its supplementary data files).

**Declarations**

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

**Competing interests** The authors declare no competing interests.
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