



Photocatalytic degradation of dimethyl phthalate in an aqueous solution with Pt-doped TiO₂-coated magnetic PMMA microspheres

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ARTICLE INFO

Article history:

Received 29 March 2009

Received in revised form 23 June 2009

Accepted 23 June 2009

Available online 30 June 2009

Keywords:

Dimethyl phthalate

Photocatalytic degradation

Platinum-doped

UV radiation

Titanium dioxide

Magnetic poly(methyl methacrylate) microspheres

ABSTRACT

This study investigates the photocatalytic degradation of dimethyl phthalate (DMP) with both the titanium dioxide-coated magnetic poly(methyl methacrylate) (TiO₂/mPMMA) and platinum-doped TiO₂/mPMMA (Pt–TiO₂/mPMMA) microspheres. The TiO₂/mPMMA and Pt–TiO₂/mPMMA microspheres are employed as novel photocatalysts that offer high photocatalytic activity, magnetic separability and good durability. The photocatalytic experiments of DMP under various conditions are conducted to examine the effects of the initial DMP concentration, photocatalyst dosage, UV radiation intensity and Pt doping content on the degradation of DMP. In addition, the correlations of the photocatalytic kinetics and quantum yield for DMP removal are proposed associated with the system parameters. According to the experimental results, there exists a distinct relationship between the reduction percentages of total organic carbons and DMP. Furthermore, the photodegradation mechanism of DMP in the photocatalytic process is established based on the identification of the intermediates. Moreover, the good repeatability of the photocatalytic performance with the use of the Pt–TiO₂/mPMMA microspheres has also been demonstrated in the multi-run experiments. Therefore the Pt–TiO₂/mPMMA microspheres are considered as a practical and promising photocatalyst in a suspension reaction system and they can be effectively recovered after use. This study provides useful information about the applications of the TiO₂/mPMMA and Pt–TiO₂/mPMMA microspheres for the photodegradation of DMP.

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1. Introduction

Many environmental hormones such as phthalic acid esters have been found in the wastewater that comes from urban sewage and factories and is accelerated by rapid economic development in the recent decades [1]. Large amounts of phthalic acid esters are often leached from the plastics dumped at municipal landfills. These pollutants are refractory to environmental microorganisms and accumulate in natural bodies of water, ultimately becoming widely distributed within the aqueous system, e.g., rivers, lakes and groundwater, and exerting a noticeable influence on the ecological environment [2]. The endocrine system of the human body may be disturbed when phthalic acid esters are ingested or inspired.

Dimethyl phthalate (DMP) is one of the most common phthalic acid esters. The chemical structure of DMP is composed of a benzene ring with methyl ester groups attached at the ortho-positions. DMP has been used as a plasticizer in tools, automotive parts, toothbrushes, food packaging, cosmetics, insecticide, etc. DMP has

been frequently detected in wastewater effluents and river water because of its high mobility in the aquatic system [3]. DMP has endocrine disrupting effects on aquatic species by altering the action of endogenous steroid hormones. Thus DMP is an aqueous pollutant of concern in water and wastewater systems. The common method for DMP removal in the wastewater is biological treatment, which is based on the metabolic degradation of DMP by microorganisms under aerobic or anaerobic conditions. However, several studies have found that some phthalates with long alkyl-chains may be refractory to biological treatment.

Titanium dioxide (TiO₂) nanoparticles are known to be an excellent photocatalyst in the removal of organic pollutants [4,5]. However, commercial products of TiO₂ photocatalysts usually have a small particle size that makes them difficult to recover after use. The TiO₂ photocatalysts tend to accumulate, causing blockage of the instruments and limiting its practical use. According to previous studies [6,7], the evidence of the practicality of using TiO₂ photocatalysis for the removal of DMP was presented. However, the investigations into the photocatalytic parameters such as the initial DMP concentration, photocatalyst dosage, UV radiation intensity, Pt doping amount, and related photocatalytic kinetics are still lacking in the literature. This information would be essential for the rational

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Nomenclature

A_q	outer area of quartz tubes submerged in solution (cm^2)
C_{BLb}	concentration of DMP in solution (mg/L or mM)
C_{BLb0}	initial concentration of DMP in solution (mg/L or mM)
C_{TOC}	concentration of TOC in solution (mg/L)
C_{TOC0}	initial concentration of TOC in solution (mg/L)
$d_{\text{Pt-TiO}_2}$	Pt doping content based on TiO_2 weight (%)
DMP	dimethyl phthalate
F_s	fraction of emitted light absorbed by solution
$[I_{254}]$	UV radiation intensity at 254 nm (W/L)
$[I_{\text{UV}}]$	light intensity measured on outer surface of quartz tubes (W/cm^2)
k_B	photocatalytic reaction rate constant in Eq. (1) ($\text{mg}/(\text{L min})$)
k_B'	modified k_B in Eq. (2), $k_B' = k_B K_B$ (min^{-1})
K_B	equilibrium adsorption constant of Langmuir's isotherm in Eq. (1) (L/mg)
mPMMA	magnetic poly(methyl methacrylate)
Pt-TiO ₂ /mPMMA	platinum-doped TiO ₂ /mPMMA
r	photocatalytic reaction rate ($\text{mg}/(\text{L min})$)
R^2	determination coefficient
t	time (min)
$t_{f,\text{DMP}}$	time required for the concentration reduction of DMP greater than 99% (min)
TiO ₂	titanium dioxide
TiO ₂ /mPMMA	titanium dioxide-coated magnetic poly(methyl methacrylate)
TOC	total organic carbons (mg/L)
UV	ultraviolet
V_l	volume of solution (L)
W_{cat}	photocatalyst dosage (g/L)
Greek letters	
η_{BLb}	reduction percentage of DMP (%) = $1 - C_{\text{BLb}}/C_{\text{BLb0}}$
η_{TOC}	reduction percentage of TOC (%) = $1 - C_{\text{TOC}}/C_{\text{TOC0}}$
θ_B	fraction of TiO ₂ surface covered by DMP = $K_B C_{\text{BLb}} / (1 + K_B C_{\text{BLb}})$
Φ	quantum yield (%)

design and optimal control of photocatalytic degradation of DMP in an aqueous solution.

In addition, several studies have attempted to prepare the photocatalysts regard to a combination of the photoactive and magnetic properties [8–10]. However, the direct coating of TiO₂ on a magnetite core may impair photocatalytic activity because the generated electrons and holes in TiO₂ particles can be transferred to the neighboring magnetite rather than to the TiO₂ surface [11]. An insulating silica layer is adopted to avoid the interactions between the magnetite core and titania coating [8,10–13]. In our previous work [14], we synthesized the titanium dioxide-coated magnetic poly(methyl methacrylate) (TiO₂/mPMMA) microspheres that offered good insulating properties, a simple titania-coating process, low density and controllable polymer characteristics. Good magnetic and photocatalytic characteristics of the TiO₂/mPMMA microspheres were derived from their abundant magnetite and photocatalyst contents. These TiO₂/mPMMA microspheres have potential for application in a slurry photocatalytic reactor and recovery in a magnetic separation process.

The photocatalytic activity of TiO₂ can be significantly improved by doping with noble metals such as platinum (Pt), which acts as the photogenerated electron acceptor [15–17]. Thus, under UV illumi-

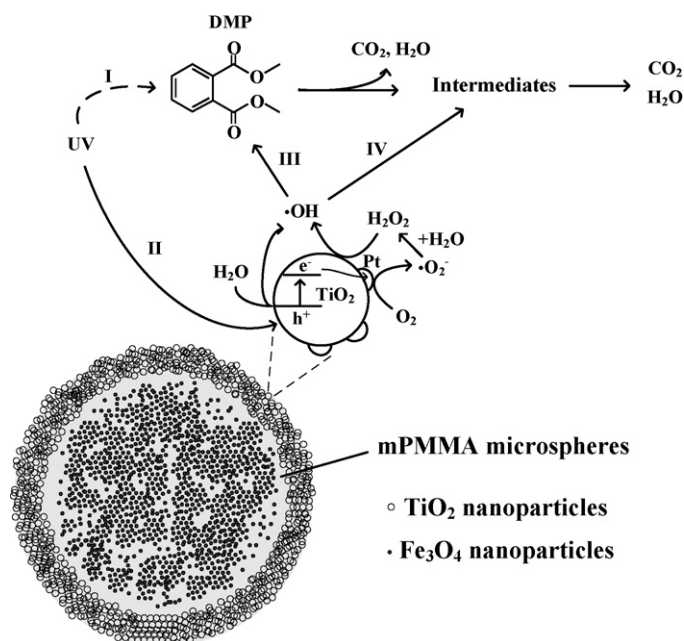


Fig. 1. Simplified DMP photocatalytic scheme under UV illumination with Pt-TiO₂/mPMMA microspheres.

nation, the photogenerated electrons effectively transfer from the TiO₂ surface to the doped Pt particles to suppress the recombination of electrons and holes and promote the transfer of holes on the TiO₂ surface. This produces a longer electron–hole pair separation lifetime, resulting in improved quantum yield (Φ) and photocatalytic efficiency.

In this study, we investigate the photocatalytic degradation of DMP in an aqueous solution with novel photocatalysts including TiO₂/mPMMA and platinum-doped TiO₂/mPMMA (Pt-TiO₂/mPMMA) microspheres. The photocatalytic experiments of DMP take place in a completely stirred tank reactor under various initial DMP concentrations (C_{BLb0}), photocatalyst dosages (W_{cat}), UV radiation intensities ($[I_{254}]$) and Pt doping contents based on TiO₂ weight ($d_{\text{Pt-TiO}_2}$). The concentration variations of DMP and total organic carbons (TOC) in the solution are analyzed at specified time intervals. TOC is a convenient and direct expression of total organic content as an index of mineralization. Moreover, we present the photocatalytic kinetics and Φ for the DMP reduction in the context of a set of given system parameters. The intermediates that appear in the course of the photocatalysis are identified in conjunction with the DMP degradation mechanism. In addition, the durability of the Pt-TiO₂/mPMMA microspheres in the photocatalytic process is demonstrated by using multi-run experiments.

2. Materials and methods

2.1. Chemicals

DMP, with a chemical formula of $\text{C}_{10}\text{H}_{10}\text{O}_4$, purchased from Merck (Darmstadt, Germany), has a molecular weight of 194.19 Da, a boiling point of 282 °C, and a CAS registry number of 84-66-2. The molecular structure of DMP is shown in Fig. 1. Dihydrogen hexachloroplatinate hexahydrate (IV) ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) with a purity of 99.9% was purchased from W. C. Heraeus GmbH (Hanau, Germany). All experimental solutions were prepared with deionized water without other buffers.

2.2. Preparation of Pt–TiO₂/mPMMA microspheres

Details of the synthesis of the TiO₂/mPMMA microspheres may be found elsewhere [14,18]. For the preparation of Pt–TiO₂/mPMMA microspheres, 3.7 L of aqueous solution consisting of three different weights of TiO₂/mPMMA microspheres (6, 10, or 15 g) and 150 mL of methanol was held in a reactor, and then purged with nitrogen to remove dissolved oxygen while stirred by a mechanical stirrer at 300 rpm. 15 mL of H₂PtCl₆·6H₂O solution with a Pt concentration of 1 g/L was added into the solution. The pH value of the solution was controlled at 3 ± 0.5 by using 0.1 M HNO₃ solution and continuously purged with nitrogen. Afterwards the mixed solution was irradiated by low-pressure mercury lamps (model PL-S 9W, Philips, Eindhoven, Netherlands) at 365 nm for 24 h. The Pt–TiO₂/mPMMA microspheres were subsequently separated using a magnet and washed with deionized water three times. The Pt–TiO₂/mPMMA microspheres were dried and stored for the following applications. As a result, the Pt–TiO₂/mPMMA microspheres were synthesized with three $d_{\text{Pt-TiO}_2}$ values of 0.6, 0.9, and 1.5 wt% which were denoted as 0.6, 0.9, and 1.5 wt% Pt–TiO₂/mPMMA microspheres, respectively. The $d_{\text{Pt-TiO}_2}$ value was calculated assuming the complete photoreduction of Pt ions on the surface of the TiO₂/mPMMA microspheres. The Pt–TiO₂/mPMMA microspheres have a narrow particle size distribution of 5–11 μm. The recovery efficiency of such micro-sized Pt–TiO₂/mPMMA microspheres was found to be significantly enhanced by the magnetic separation instead of gravity separation.

2.3. Experimental apparatus

An airtight reactor with a 17.2 cm inner diameter was made of Pyrex glass with an effective volume of 5.5 L and equipped with a water jacket to maintain a constant solution temperature of 25 °C for all photocatalytic experiments. The design of the reactor was based on the criteria for the shape factors of a standard six-blade turbine [19]. Two quartz tubes of 3.8 cm outer diameter symmetrically installed inside the reactor were used to house the UV lamps. About 3.75 L of the DMP-containing solution (V_L) was used in each experiment, and the total sampling volume was within 5% of the solution. The stirring speed was 800 rpm to ensure the complete mixing of the system in accordance with previous studies [14,20]. All fittings, tubing and bottles were made of stainless steel, Teflon or glass.

The low-pressure mercury lamps (model PL-S 9W, Philips, Eindhoven, Netherlands) generated UV radiation at 254 nm. The radiation intensity [I_{254}] was measured by a digital radiometer (Ultra-Violet Products, Upland, CA, USA) with radiation sensor model DIX-254A. The [I_{254}], in the unit of W/L, was defined as the average applied power of UV radiation per unit volume in the well-mixed system, proportional to the number of photons absorbed by the solution per unit volume and time. The [I_{254}] value can be calculated from the product of [I_{UV}](A_q/V_L) F_s , where [I_{UV}] is the light intensity measured on the outer surface of the quartz tubes by the sensor in the unit of W/cm², A_q is the outer area (cm²) of the quartz tubes submerged in the solution, and F_s is the fraction of the emitting UV light absorbed by the solution [21]. The value of F_s was determined close to the unit by measuring the transmittance of UV radiation through the solution.

2.4. Photocatalytic experiments

The experiments were conducted under various conditions of C_{BLb0} , W_{cat} , [I_{254}], and $d_{\text{Pt-TiO}_2}$ to examine the photocatalytic degradation of DMP. Five C_{BLb0} of 0.05, 0.1, 0.15, 0.2, and 0.4 mM were adopted for the experiments. The initial TOC concentration (C_{TOC0}) is measured about 18 mg/L in the case of $C_{\text{BLb0}} = 0.15$ mM, while the

C_{TOC0} of the solution is proportional to C_{BLb0} . The effect of W_{cat} on the photocatalytic degradation of DMP was evaluated at three different levels of 0.4, 1 and 2.5 g/L. The contribution of UV radiation at 254 nm was tested with two intensities ([I_{254}]) of 0.259 and 0.499 W/L. The initial pH value of the solution was about 6.58. The initial concentration of the dissolved oxygen in the solution was in the range of 5.4–7.9 mg/L.

A solution with a preset C_{BLb0} and W_{cat} was prepared for the experiments. Before the experiments commenced, the UV lamps were activated and shielded by aluminum foil for 30 min to ensure the stability of the UV intensity and solution temperature. Then the UV radiation was introduced into the reactor to begin the photocatalytic degradation of DMP. Samples were drawn out from the reactor at desired time intervals over the course of the experiments. The Pt–TiO₂/mPMMA microspheres in the samples were immediately recovered by a magnet, and the samples were stored at 4 °C for subsequent analyses. The multi-run experiments involved five successive runs to test the durability of the Pt–TiO₂/mPMMA microspheres.

2.5. Analytic instrumentation

The concentration of DMP (C_{BLb}) was analyzed using a high-performance liquid chromatography system, with a 250 × 4.6 mm column (model ODS-2, GL Sciences Inc., Tokyo, Japan) and a diode array detector (model L-2455, Hitachi, Tokyo, Japan) at 230 nm. The HPLC solvent, at a flow rate of 1.0 mL/min, was composed of methanol/water at a 50:50 ratio. The injection volume of the analytical solution was 40 μL, and the DMP concentration detection limit was 0.01 mg/L. The concentration of TOC (C_{TOC}) was analyzed by the TOC analyzer (model 1030W, OI Corporation, College Station, TX, USA). The TOC instrument used the UV-persulfate technique to convert the organic carbon compounds into carbon dioxide for subsequent quantification by an infrared carbon dioxide analyzer calibrated with a potassium hydrogen phthalate standard. The intermediates in the samples were further identified by high-performance liquid chromatography coupled with a triple quadrupole mass spectrometer with highly selective reaction monitoring (Thermo Fisher Scientific Inc., Waltham, MA, USA). A pH meter (model 300T, Suntex, Taipei, Taiwan) was used to measure the pH of the solution.

3. Results and discussion

3.1. Photocatalytic degradation of DMP

To illustrate the possible roles of UV radiation and Pt–TiO₂/mPMMA microspheres on attacking the DMP and its intermediates, a simplified scheme for the photocatalytic degradation of DMP with the Pt–TiO₂/mPMMA microspheres is shown in Fig. 1. The photocatalytic mechanism consists of the generation of oxidative species such as hydroxyl radicals ($\bullet\text{OH}$) and successive oxidation reactions. The direct photolysis of DMP by UV radiation was slow [22,23], suggesting the poor oxidative ability of reaction I. The major contribution of UV radiation is to generate $\bullet\text{OH}$ through the initiation of reaction II. The photo-induced electronic excitation creates a TiO₂ vacancy while a generated electron is transferred to the doped Pt. The surrounding dissolved oxygen acquires the electron to form the $\bullet\text{O}_2^-$ radical. The $\bullet\text{OH}$ radical can be further produced by a water molecule reacting with the $\bullet\text{O}_2^-$ or the vacancy. This leads to the vigorous oxidations of DMP and its intermediates, denoted reactions III and IV, respectively.

Fig. 2 shows the time variations of the dimensionless DMP concentration ($C_{\text{BLb}}/C_{\text{BLb0}}$) in the photocatalytic experiments with the TiO₂/mPMMA and Pt–TiO₂/mPMMA microspheres of various

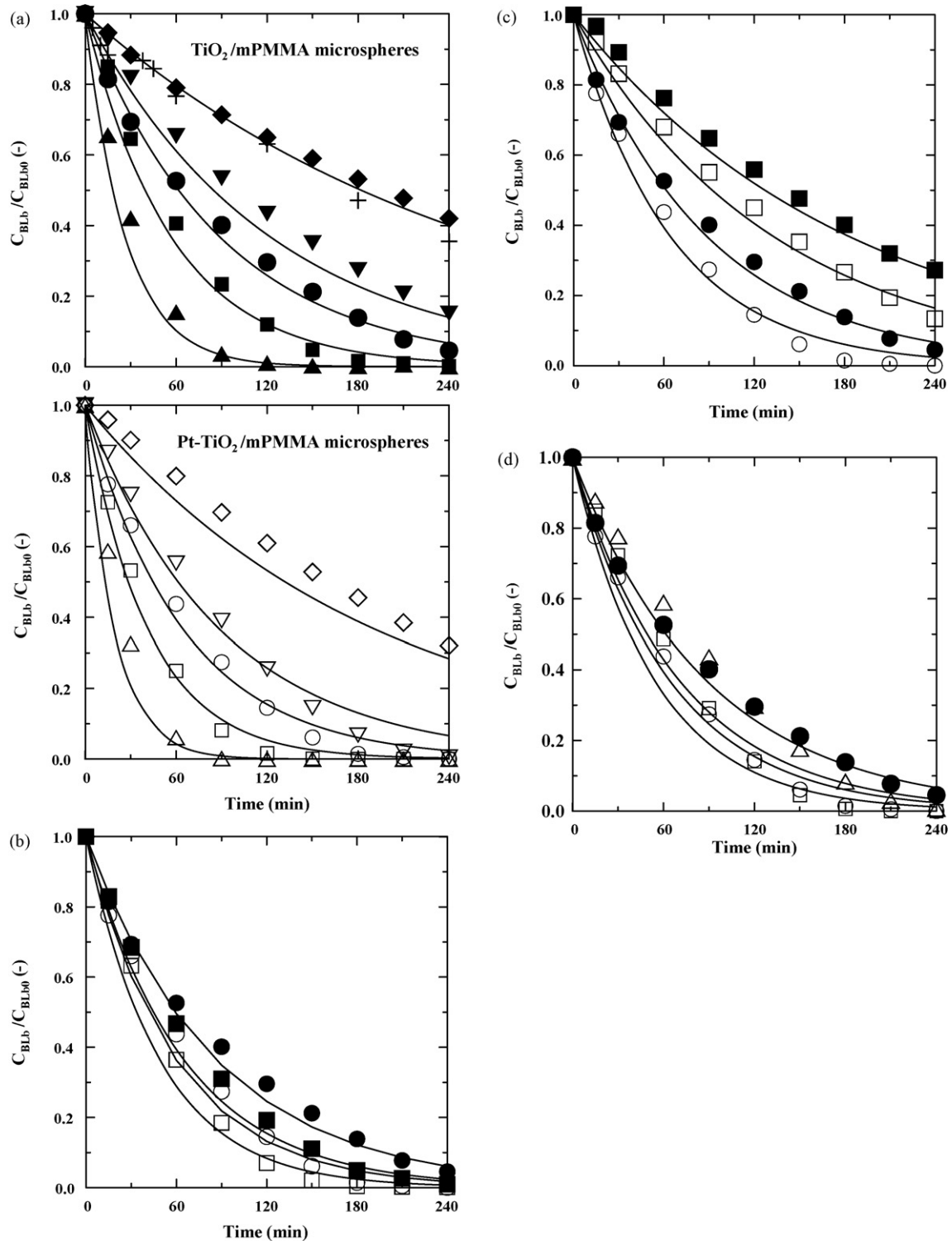


Fig. 2. Time variations of $C_{\text{B}lb}/C_{\text{B}lb0}$ for DMP photocatalytic degradation with $\text{TiO}_2/\text{mPMMA}$ and $\text{Pt-TiO}_2/\text{mPMMA}$ microspheres under various experimental conditions. (a) \blacktriangle , \blacksquare , \bullet , \blacktriangledown , and \blacklozenge : $C_{\text{B}lb0} = 0.05, 0.1, 0.15, 0.2,$ and 0.4 mM (with $\text{TiO}_2/\text{mPMMA}$ microspheres); \triangle , \square , \circ , \triangledown , and \diamond : $C_{\text{B}lb0} = 0.05, 0.1, 0.15, 0.2,$ and 0.4 mM (with 0.9 wt% $\text{Pt-TiO}_2/\text{mPMMA}$ microspheres). $+$: $C_{\text{B}lb0} = 0.4$ mM (with Degussa P25 TiO_2). $W_{\text{cat}} = 1$ g/L. $[I_{254}] = 0.499$ W/L. (b) $C_{\text{B}lb0} = 0.15$ mM. \bullet and \blacksquare : $W_{\text{cat}} = 1$ and 2.5 g/L (with $\text{TiO}_2/\text{mPMMA}$ microspheres). \circ and \square : $W_{\text{cat}} = 1$ and 2.5 g/L (with 0.9 wt% $\text{Pt-TiO}_2/\text{mPMMA}$ microspheres). $[I_{254}] = 0.499$ W/L. (c) $C_{\text{B}lb0} = 0.15$ mM. $W_{\text{cat}} = 1$ g/L. \blacksquare and \bullet : $[I_{254}] = 0.259$ and 0.499 W/L (with $\text{TiO}_2/\text{mPMMA}$ microspheres). \square and \circ : $[I_{254}] = 0.259$ and 0.499 W/L (with 0.9 wt% $\text{Pt-TiO}_2/\text{mPMMA}$ microspheres). (d) $C_{\text{B}lb0} = 0.15$ mM. $W_{\text{cat}} = 1$ g/L. $[I_{254}] = 0.499$ W/L. \bullet : $\text{TiO}_2/\text{mPMMA}$ microspheres. \triangle , \square , \circ , and \square : $0.60, 0.90,$ and 1.50 wt% $\text{Pt-TiO}_2/\text{mPMMA}$ microspheres.

$C_{\text{B}lb0}$, W_{cat} , $[I_{254}]$, and $d_{\text{Pt-TiO}_2}$ individually. DMP would be immediately decomposed in the early period of the photocatalysis. As shown in Fig. 2a, the effect of $C_{\text{B}lb0}$ on the photodegradation rate of DMP is remarkable. Although the elimination rate at higher $C_{\text{B}lb0}$ seems slower in terms of the $C_{\text{B}lb}/C_{\text{B}lb0}$,

rate of DMP ($dC_{\text{B}lb}/dt$, mg/(L min)) is evidently higher. It is worth noting that the photocatalytic performance of the $\text{TiO}_2/\text{mPMMA}$ microspheres is similar to that of the Degussa P25 TiO_2 particles. However, one should notice that the photocatalytic activity of the $\text{TiO}_2/\text{mPMMA}$ microspheres is considered higher because of its

Table 1
Values of k_B' and Φ under different experimental conditions for DMP photodecomposition.

Photocatalyst	C_{BLb0} (mM)	W_{cat} (g/L)	$[I_{254}]$ (W/L)	$d_{\text{Pt-TiO}_2}$ (wt%)	$t_{f,\text{DMP}}^a$ (min)	k_B' (min^{-1})	Φ^b (mol/Einstein, %)
No catalyst	0.15	0	0.499	–	>240	0.0003	0.0850
	0.05	1	0.499	0	120	0.0366	0.650
	0.1	1	0.499	0	210	0.0202	0.862
	0.15	0.4	0.499	0	>240	0.0066	0.817
TiO ₂ /mPMMA microspheres	0.15	1	0.259	0	>240	0.0052	1.38
	0.15	1	0.499	0	>240	0.0117	0.940
	0.15	2.5	0.499	0	240	0.0169	1.10
	0.2	1	0.499	0	>240	0.0074	1.11
	0.4	1	0.499	0	>240	0.0036	1.52
	0.05	1	0.499	0.90	90	0.0443	0.875
	0.1	1	0.499	0.90	150	0.0304	1.05
	0.15	0.4	0.499	0.90	240	0.0129	1.08
	0.15	1	0.259	0.90	>240	0.0076	1.64
Pt-TiO ₂ /mPMMA microspheres	0.15	1	0.499	0.60	240	0.0135	1.09
	0.15	1	0.499	0.90	210	0.0194	1.29
	0.15	1	0.499	1.50	180	0.0174	1.50
	0.15	2.5	0.499	0.90	180	0.0228	1.54
	0.2	1	0.499	0.90	240	0.0149	1.47
	0.4	1	0.499	0.90	>240	0.0045	1.78

^a $t_{f,\text{DMP}}$ = time required for concentration reduction of DMP greater than 99%.

^b Calculated for photocatalytic period from $t=0$ through $t_{f,\text{DMP}}$ or through 240 min if $t_{f,\text{DMP}} > 240$ min.

smaller TiO₂ content. The use of higher W_{cat} value is advantageous to the utilization of UV radiation, resulting in an increase of the decomposition rate of DMP (Fig. 2b). The $[I_{254}]$ value also plays an important role in the photocatalytic degradation of DMP as depicted in Fig. 2c. The elimination rate of DMP is significantly enhanced by higher $[I_{254}]$ in the photocatalysis involving the TiO₂/mPMMA or Pt-TiO₂/mPMMA microspheres. As depicted in Fig. 2d, the case with the 0.60 wt% Pt-TiO₂/mPMMA microspheres presents an insignificant difference in terms of DMP removal in comparison with the TiO₂/mPMMA microspheres. Comparatively, the 0.90 and 1.50 wt% Pt-TiO₂/mPMMA microspheres show better performance for the elimination of DMP.

The time required for the concentration reduction of DMP greater than 99% is taken as a characteristic time (denoted as $t_{f,\text{DMP}}$) in the DMP photodecomposition. The $t_{f,\text{DMP}}$ values under various experimental conditions are summarized in Table 1. The $t_{f,\text{DMP}}$ values are in the following order: direct photocatalysis > TiO₂/mPMMA microspheres > Pt-TiO₂/mPMMA microspheres. Moreover, the $t_{f,\text{DMP}}$ value also increases with higher C_{BLb0} as well as with smaller W_{cat} , $[I_{254}]$, or $d_{\text{Pt-TiO}_2}$.

3.2. Photocatalytic kinetics of DMP removal

The Langmuir-Hinshelwood model is often applied to quantify the photocatalytic reaction rate (r) [24–30]. The r is supposed to relate to the fraction of TiO₂ surface covered by DMP (θ_B) and is then derived as Eq. (1) by combining with the Langmuir isotherm.

$$r = -\frac{dC_{\text{BLb}}}{dt} = k_B\theta_B = \frac{k_B K_B C_{\text{BLb}}}{1 + K_B C_{\text{BLb}}} \quad (1)$$

where k_B and K_B are the photocatalytic reaction rate constant and equilibrium adsorption constant of the Langmuir isotherm, respectively.

The adsorption of DMP on the Degussa P25 TiO₂ particles at 25 °C in darkness over 48 h is found to be small, and may be attributed to the steric repulsions between the methyl groups of DMP [7]. Accordingly, Eq. (1) can be simplified to a pseudo-first-order reaction as Eq. (2) because the term $K_B C_{\text{BLb}}$ is much smaller than 1.

$$r = -\frac{dC_{\text{BLb}}}{dt} = k_B K_B C_{\text{BLb}} = k_B' C_{\text{BLb}} \quad (2)$$

The modified k_B , notated k_B' , can be obtained from the regression of the experimental data of DMP reduction in Fig. 2. Table 1 sum-

marizes the values of k_B' under various experimental conditions, where higher k_B' value represents higher photodecomposition rate of DMP. Further, all the k_B' values in Table 1 are employed to derive the correlation of k_B' associated with the system parameters as Eq. (3) using a multifactor regression.

$$k_B' (\text{min}^{-1}) = 0.00298(1 + 0.422d_{\text{Pt-TiO}_2}) \left(\frac{[I_{254}]}{C_{\text{BLb0}}} \right)^{1.107} W_{\text{cat}}^{0.311}; \quad (3)$$

$$R^2 = 0.939$$

Note that the $[I_{254}]/C_{\text{BLb0}}$ ratio ($\text{W L}^{-1} \text{m M}^{-1}$) is the most important factor impacting the k_B' value. The increased W_{cat} and $[d_{\text{Pt-TiO}_2}]$ are also advantageous to the enhancement of k_B' . As shown in Fig. 2, the prediction for the time variations of the $C_{\text{BLb}}/C_{\text{BLb0}}$, based on Eqs. (2) and (3), suggests good agreement with the experimental data.

The Φ is defined as the numeric ratio of the eliminated molecules of DMP to the supplied photons and represents the utilization efficiency of the applied UV radiation. The Φ value as indicated in Table 1 is calculated from the experimental data in Fig. 2 based on the photocatalytic period from the initial time to $t_{f,\text{DMP}}$. The entire quantity of incident light is assumed to be absorbed by the photocatalysts and the consumption of the oxidative species for the intermediates is neglected in this calculation. The obtained Φ values, in the range of 0.650–1.78%, are further employed to derive the corresponding regression equation as Eq. (4). Obviously, the Φ would increase with W_{cat} and $d_{\text{Pt-TiO}_2}$ while noticeably decrease with $[I_{254}]/C_{\text{BLb0}}$.

$$\Phi = 1.567(1 + 0.30d_{\text{Pt-TiO}_2}) \left(\frac{[I_{254}]}{C_{\text{BLb0}}} \right)^{-0.369} W_{\text{cat}}^{0.194}; \quad (4)$$

$$R^2 = 0.968$$

3.3. TOC removal and degradation mechanism for the photocatalysis of DMP

To investigate the mineralization of DMP in the photocatalytic processes, the time variations of the dimensionless TOC concentration ($C_{\text{TOC}}/C_{\text{TOC0}}$) are studied under different levels of the C_{BLb0} , W_{cat} , $[I_{254}]$, and $d_{\text{Pt-TiO}_2}$ as shown in Fig. 3. It is apparent that the $C_{\text{TOC}}/C_{\text{TOC0}}$ value varies slightly in the initial photocatalytic stage, implying that the initial intermediates from the decomposition of DMP still contribute high TOCs relative

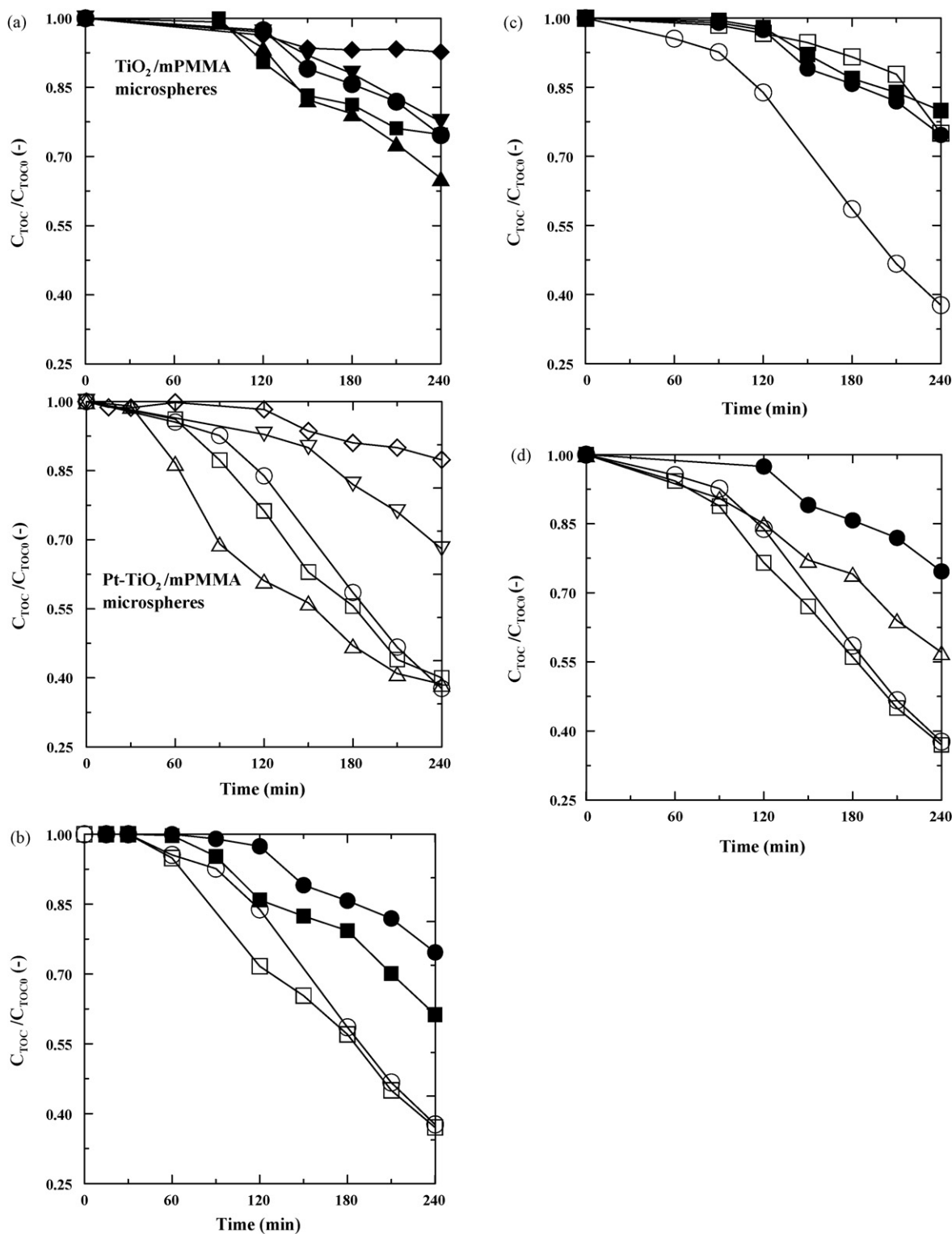


Fig. 3. Time variations of C_{TOC}/C_{TOC0} for DMP photocatalytic degradation with $TiO_2/mPMMA$ and $Pt-TiO_2/mPMMA$ microspheres under various experimental conditions. Notations and experimental conditions are the same as specified in Fig. 2.

to the initial value. The C_{TOC}/C_{TOC0} would start to significantly decrease with time after the inactive stage. Furthermore, the C_{TOC}/C_{TOC0} decreases faster with smaller C_{BLb0} as well as with higher W_{cat} , [1254], or d_{Pt-TiO_2} that is similar to that associated with DMP reduction. Note that the experiments with the $Pt-TiO_2/mPMMA$ microspheres show a remarkable improvement in terms of TOC removal compared to those with the $TiO_2/mPMMA$ microspheres. Therefore, the use of $Pt-TiO_2/mPMMA$

microspheres is recommended for the photodecomposition of DMP in an aqueous solution, although the $TiO_2/mPMMA$ microspheres may be sufficient for the removal of DMP. On the whole, the removal efficiencies of DMP and TOC with the use of the $Pt-TiO_2/mPMMA$ microspheres can be improved about 20–60% compared with those using the $TiO_2/mPMMA$ microspheres. Compared with the ozonation of DMP [22], the present photocatalytic process shows comparatively slow DMP removal and

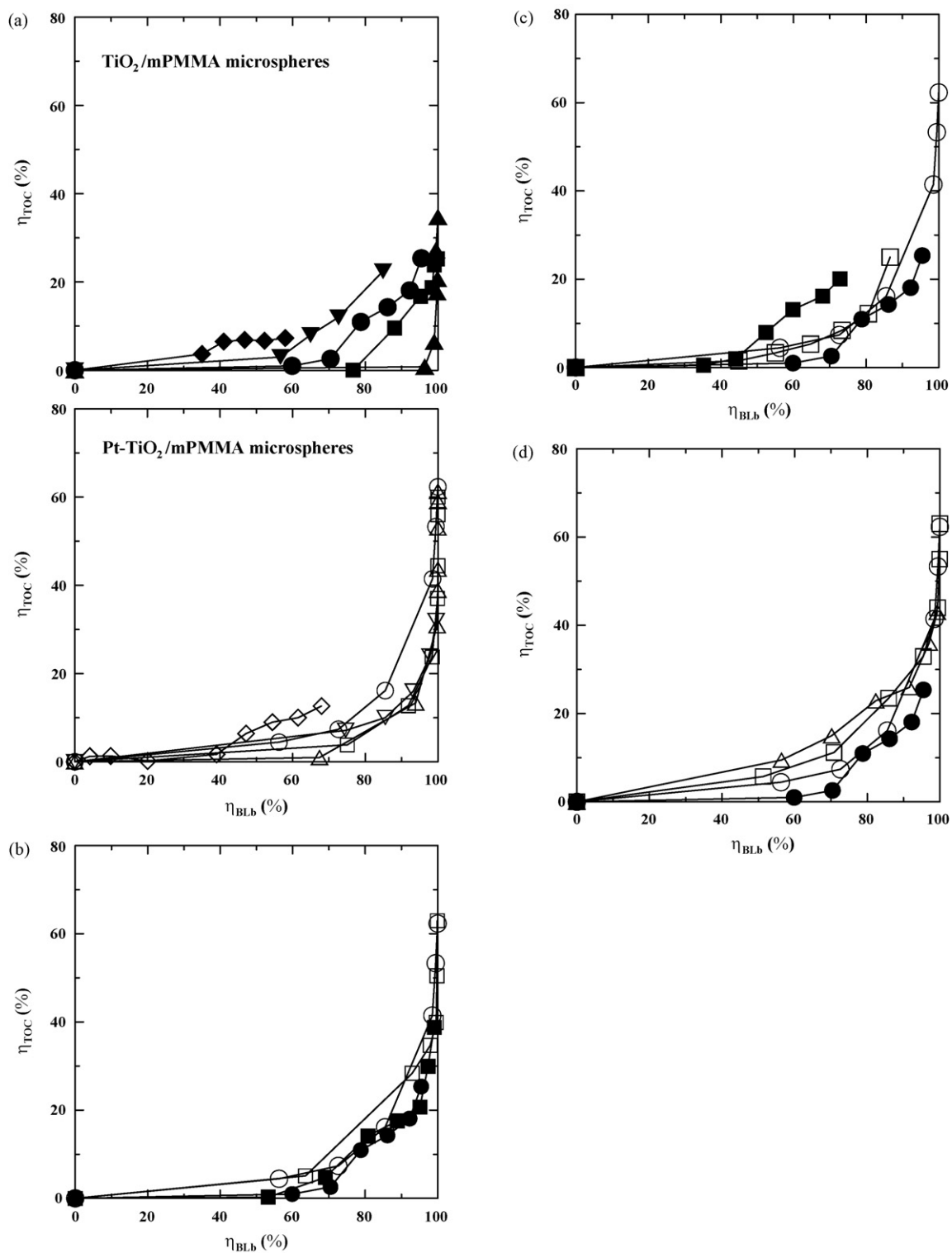


Fig. 4. η_{TOC} vs. η_{BLb} for DMP photocatalytic degradation with $TiO_2/mPMMA$ and $Pt-TiO_2/mPMMA$ microspheres under various experimental conditions. Notations and experimental conditions are the same as specified in Fig. 2.

high mineralization rates because of the non-selective oxidation of $\bullet OH$.

The correlations between the removal percentages of TOC ($\eta_{TOC} = (C_{TOC0} - C_{TOC})/C_{TOC0}$) and DMP ($\eta_{BLb} = (C_{BLb0} - C_{BLb})/C_{BLb0}$) during the photocatalytic degradation of DMP are illustrated in Fig. 4 by integrating the results in Figs. 2 and 3. The TOC removal from the photodecomposition of DMP can be divided into two

stages. For the regime of small η_{BLb} (generally less than 70%), the low diminution of TOC primarily comes from the oxidation of original DMP or initial intermediates that can also be explained by the photodegradation mechanism of DMP as shown in Fig. 5. In the later photocatalytic stage ($\eta_{BLb} \geq 70\%$), the η_{TOC} remarkably increases with η_{BLb} , which is characterized by the generation of the intermediates with smaller TOCs. These intermediates are

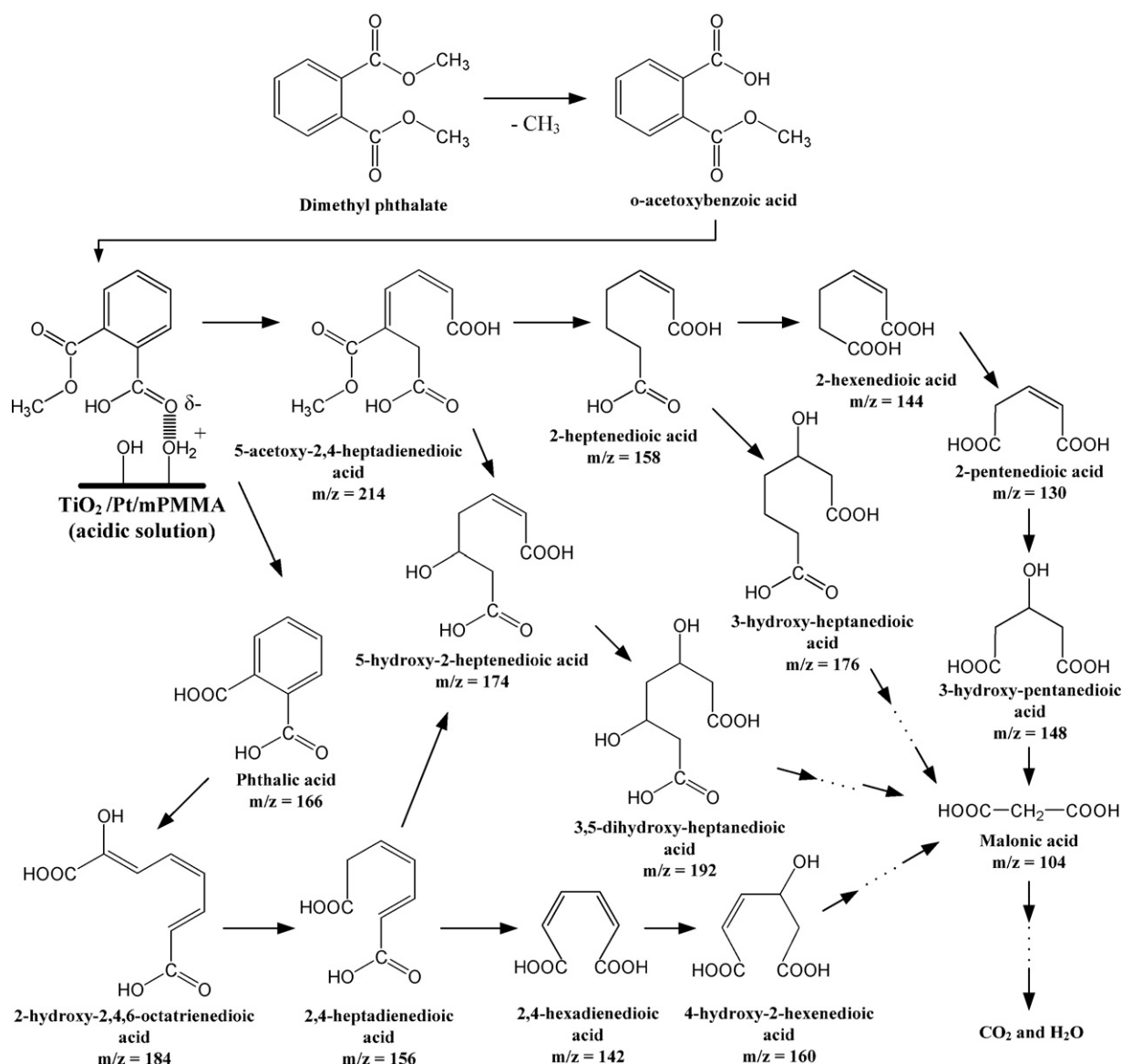


Fig. 5. DMP photodegradation mechanism under UV illumination with photocatalysts.

supposedly generated from DMP through successive oxidation reactions. Accordingly, the η_{BLb} value can be used as a supplementary index to the η_{TOC} for the photocatalytic degradation of DMP.

Referring to the demethylation mechanism of DMP near the TiO₂ surface [7] and the identified intermediates from the molecular peaks (M+H) in the triple quadrupole mass spectra. In Fig. 5, a photodegradation mechanism of DMP under the illumination of UV radiation with the photocatalysts is proposed. The intermediates include 2-hexenedioic acid, 2-pentenedioic acid, phthalic acid, 2,4-hexadienedioic acid, etc. The activity of the oxidative species on the DMP structure is depicted with the considered occurrence of possible reactions at the preferred positions around the benzene ring. The existence of these intermediates, which are also competitors for oxidation that may impair the decomposition rate of DMP, results in reduced values of k_B' and Φ . As illustrated in Fig. 5, the initial degradation of DMP is mainly associated with the generation of carboxylic groups. It is consistent with the pH variation of the solution, which rapidly decreases during the early phase before gradually reaching a steady state of about 4.50.

3.4. Durability of Pt-TiO₂/mPMMA microspheres

The durability of the Pt-TiO₂/mPMMA microspheres is demonstrated by slight change in terms of appearance or photocatalytic activity after multi-run experiments. Fig. 6 shows satisfactory stability of the photocatalytic performance for the Pt-TiO₂/mPMMA microspheres in the repetitive cycles of DMP photodegradation. The reliability of the relationship between the η_{TOC} and η_{BLb} is reproducible, as depicted in Fig. 7. The good durability of the Pt-TiO₂/mPMMA microspheres is due to the cross-linked polymer, which usually presents adequate resistance to the TiO₂ photocatalysis [31]. Furthermore, the photo-induced reaction mainly occurs on the multilayer surface of the Pt-doped TiO₂ coating resulting in only indirect contact with the mPMMA matrix. Although the Pt-TiO₂/mPMMA microspheres may lose some TiO₂ coating with long-term use, it is possible to restore the used Pt-TiO₂/mPMMA microspheres by repeating the titania-coating and Pt-doping processes to recover the original photocatalytic activity. In addition, the application of the Pt-TiO₂/mPMMA microspheres can be combined with other advanced oxidation processes like ozonation and ozone/UV based on the catalytic activity of the Pt-TiO₂ particles.

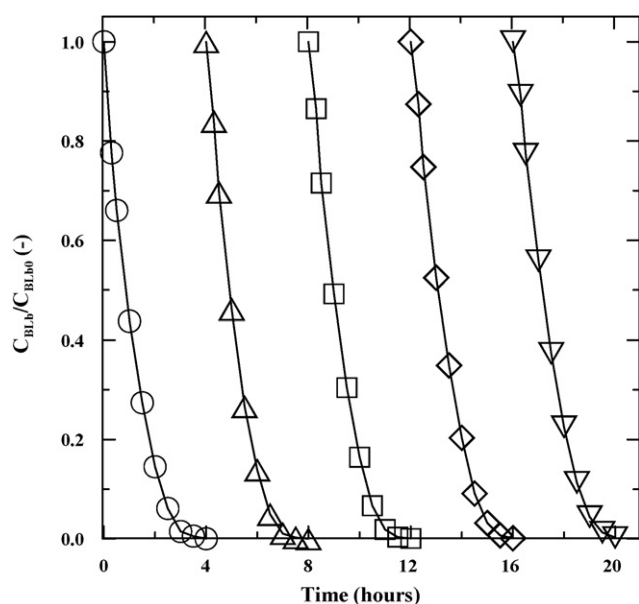


Fig. 6. Time variations of $C_{\text{B}lb}/C_{\text{B}lb0}$ for photodecomposition of DMP with 0.90 wt% Pt-TiO₂/mPMMA microspheres in multi-run experiments. ○, △, □, ◇, and ▽: 1st, 2nd, 3rd, 4th, and 5th run. $C_{\text{B}lb0} = 0.15$ mM, $W_{\text{cat}} = 1$ g/L, and $[I_{254}] = 0.499$ W/L.

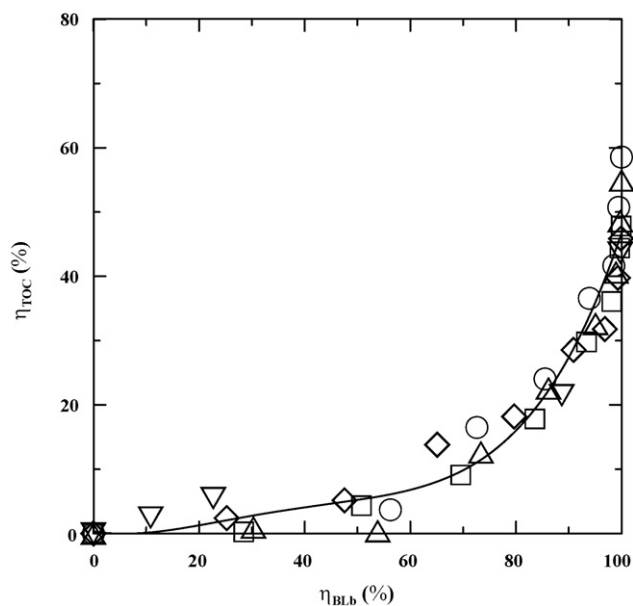


Fig. 7. η_{TOC} vs. $\eta_{\text{B}lb}$ for photodecomposition of DMP with 0.90 wt% Pt-TiO₂/mPMMA microspheres in multi-run experiments. Notations and experimental conditions are the same as specified in Fig. 6. Line: average and smooth curve of experimental data with $R^2 = 0.959$.

One should also notice that the Pt nanoparticles have the risk to be released to the environment and become a potential hazardous substance.

4. Conclusions

Titanium dioxide-coated magnetic poly(methyl methacrylate) (TiO₂/mPMMA) microspheres and platinum-doped TiO₂/mPMMA (Pt-TiO₂/mPMMA) microspheres were employed for the photocatalytic degradation of dimethyl phthalate (DMP). The efficient DMP photodecomposition using these novel photocatalysts was demonstrated. The elimination rate of the dimensionless DMP

concentration ($C_{\text{B}lb}/C_{\text{B}lb0}$) significantly increased with increasing photocatalyst dosage (W_{cat} , g/L), UV radiation intensity at 254 nm ($[I_{254}]$, W/L) and Pt doping content ($d_{\text{Pt-TiO}_2}$, wt%) while decreased with increasing initial DMP concentration ($C_{\text{B}lb0}$, mg/L). A pseudo-first-order reaction rate equation as $-dC_{\text{B}lb}/dt = k_B' C_{\text{B}lb}$ is proposed to describe the photocatalytic degradation of DMP where the modified photocatalytic reaction rate constant (k_B') is regressed as $0.00298(1 + 0.422d_{\text{Pt-TiO}_2})([I_{254}]/C_{\text{B}lb0})^{1.107} W_{\text{cat}}^{0.311}$. The quantum yield (Φ) in the range of 0.650–1.78% has the correlation of $\Phi = 1.567(1 + 0.30d_{\text{Pt-TiO}_2})([I_{254}]/C_{\text{B}lb0})^{-0.369} W_{\text{cat}}^{0.194}$. The effects of the system parameters on the removal rate of the dimensionless total organic carbons (TOC) concentration ($C_{\text{TOC}}/C_{\text{TOC0}}$) are similar to those associated with the elimination rate of $C_{\text{B}lb}/C_{\text{B}lb0}$. In addition, the Pt-TiO₂/mPMMA microspheres offer better photocatalytic performance than the TiO₂/mPMMA microspheres, especially with respect to mineralization efficiency. The clear relationship between the reduction percentages of TOC and DMP in the photocatalytic decomposition of DMP is also presented. The photodegradation mechanism of DMP, including numerous successive oxidation reactions, has been established based on the identification of the intermediates. Using multi-run experiments, the good durability of the Pt-TiO₂/mPMMA microspheres is confirmed as shown by the stability of photocatalytic performance. As a result, this study provides useful information about the photodegradation of DMP using these magnetic recoverable photocatalysts.

Acknowledgment

This study was supported by the National Science Council of Taiwan under Grant NSC 96-2221-E-027-140-MY2.

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