



Oxidative degradation of dimethyl phthalate (DMP) by UV/H₂O₂ process

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ABSTRACT

The photochemical degradation of dimethyl phthalate (DMP) in UV/H₂O₂ advanced oxidation process was studied and a kinetic model based on the elementary reactions involved was developed in this paper. Relatively slow DMP degradation was observed during UV radiation, while DMP was not oxidized by H₂O₂ alone. In contrast, the combined UV/H₂O₂ process could effectively degraded DMP, which is attributed to the strong oxidation strength of hydroxyl radical produced. Results show that DMP degradation rate was affected by H₂O₂ concentration, intensity of UV radiation, initial DMP concentration, and solution pH. A kinetic model without the pseudo-steady state assumption was established according to the generally accepted elementary reactions in UV/H₂O₂ advanced oxidation process. The rate constant for the reaction between DMP and hydroxyl radical was found to be $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ through fitting the experimental data to this model. The kinetic model could adequately describe the influence of key factors on DMP degradation rate in UV/H₂O₂ advanced oxidation process, and could serve as a guide in designing treatment systems for DMP removal.

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1. Introduction

Phthalate esters (PAEs), also known as dialkyl or alkyl aryl esters of 1,2-benzenedi-carboxylic acid, are a group of compounds that have broad uses in a wide array of industrial applications such as plasticizers for plastics, nail polish, fishing lures, caulk, adhesives, dope and paint industry [1]. They are also utilized in the manufacture of perfumes, hair sprays, lubricants, children's toys and medical devices [2]. Nowadays, PAEs are controversial because many phthalates are suspected to be mutagens, hepatotoxic agents and endocrine disruptors, and can lead to adverse effects on organisms even in a low concentration [3,4]. The U.S. Environmental Protection Agency (USEPA), European Union and the China National Environmental Monitoring Center have classified some PAEs (e.g., dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di-(2-ethylhexyl) phthalate and benzylbutyl phthalate) as priority environmental pollutants [5–7].

Besides their occurrence in wastewater from the manufacturing processes, PAEs tend to leach and volatilize from the solid products during use or after disposal. They have become ubiquitous environmental pollutants and are found in food, atmosphere, natural waters, soils, plants and aquatic organisms [8,9]. An investigation in China found the presence of phthalates in drinking water samples from all the water treatment plants surveyed [10], which indicates that these compounds cannot be removed effectively by conventional water treatment processes. The most common method for PAEs removal from water is biological treatment, which is based on the metabolic degradation of phthalates by microorganisms under aerobic or anaerobic conditions [7,11]. PAEs with long alkyl-chains are poorly degraded and some of them are considered recalcitrant to biological degradation [12]. It is necessary to develop alternative treatment technologies that can effectively remove such PAEs from waters and wastewaters.

In recent years, considerable interest has been focused on the application of advanced oxidation process for the treatment of phthalate esters in water [13–17]. Among the range of possible treatment technologies, homogeneous advanced oxidation process employing hydrogen peroxide (H₂O₂) with UV radiation has been found to be very effective in the degradation of organic compounds [18–20]. In UV/H₂O₂ process, the photolysis of hydrogen peroxide generates effective oxidizing species, hydroxyl radical (OH•, $E_0 = 2.8 \text{ V}$), which can oxidize a broad range of organic pollutants quickly and nonselectively [21].

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The simplest and lowest molecular weight PAE, dimethyl phthalate (DMP), shows high water solubility (~ 4000 mg/L) and volatile (with a Henry's law constant of 1.1×10^{-5} kPa). It is relatively hydrophilic ($\log K_{ow}$: 1.60) and has low tendency to adsorb on organic carbon (K_{oc} : 44–160 L/kg) [22]. DMP is one of the most frequently occurring phthalates in diverse environmental samples, including surface water, drinking water, marine water, and sludge [23]. Recently, DMP degradation by Ru/Al₂O₃ catalytic ozonation process [12], Fenton reaction [24], and Fe(VI)–TiO₂–UV process [25] has been reported. Treatment of DMP by UV/H₂O₂ advanced oxidation process has also been studied [26–28]. These studies were mainly concerned with proposing possible catalysts and/or proving the process feasibility for pollutant degradation. Our previous work [29] was carried out mainly on DMP removal efficiency and formation kinetics of byproduct. No quantitative information on the corresponding reaction pathways and the kinetic parameters on hydroxyl radical oxidation were reported.

The objectives of the present study were to investigate the degradation of DMP by UV–H₂O₂ advanced oxidation process and the factors influence the reaction rate, and to develop a mechanistic kinetic model to describe the degradation rate of DMP. The results show that UV–H₂O₂ advanced oxidation process is a promising treatment technology for removing DMP in water treatment.

2. Experimental

2.1. Material and analysis

DMP (>99%) was obtained from Sigma–Aldrich (St. Louis, MO, USA) and used as received. H₂O₂ (30%, w/w) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Distilled water was used to prepare all experimental solutions. pH of the DMP solutions in this study was around 6.8, and solutions of NaOH or HCl were used for pH adjustment when studying the effect of solution pH.

A Shimadzu 2010 AHT high performance liquid chromatogram (HPLC) system (Kyoto, Japan) with an autosampler and a Shimadzu VP-ODS column (150 mm \times 4.6 mm) was used to analyze DMP. The mobile phase consisted of 50%/50% (v/v) methanol (Fisher, Pittsburgh, PA, USA) and Milli-Q water (Millipore, Molsheim, France) at a flow rate of 1.00 mL min⁻¹. The sample injection volume was 10 μ L and DMP was detected by an UV detector at the wavelength of 224 nm. At least two replications of each measurement were carried out and more replications were executed in cases where the variation between each measurement exceeded 5%.

2.2. Photoreactor

The UV irradiation set-up was a completely mixed batch reactor (CMBR). The schematic diagram of experiment system and the detailed physical parameters can be found in a previous paper [30]. Ten 30 W commercial low pressure–Hg UV lamps (emitting wavelength: 253.7 nm) with quartz sleeves were fixed symmetrically in the reactor. The intensity of UV light in the reactor was controlled by turning on or off the lamps and was monitored by a luxometer (Model UV-A, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China). All experiments were carried out at a constant temperature of 25 ± 1 °C controlled by a thermostat in controlled temperature room.

3. Kinetic modeling

The widely accepted major photochemical and chemical reactions and the rate constants in UV/H₂O₂ advanced oxidation process

Table 1

Key elementary reactions and kinetic parameters in UV/H₂O₂ advanced oxidation process

Reactions step		Rate constant (M ⁻¹ s ⁻¹)	Literature
Initiation			
H ₂ O ₂ $\xrightarrow{k_1, h\nu}$ 2OH•	(1)	System dependent	[32]
Hydroxyl radical propagation			
H ₂ O ₂ + OH• $\xrightarrow{k_2}$ HO ₂ • + H ₂ O	(2)	2.7×10^7	[33]
H ₂ O ₂ + HO ₂ • $\xrightarrow{k_3}$ OH• + H ₂ O + O ₂	(3)	3.0	[34]
Hydroxyl radical termination			
2OH• $\xrightarrow{k_4}$ H ₂ O ₂	(4)	5.5×10^9	[33]
2HO ₂ • $\xrightarrow{k_5}$ H ₂ O ₂ + O ₂	(5)	6.6×10^9	[35]
OH• + HO ₂ • $\xrightarrow{k_6}$ H ₂ O + O ₂	(6)	8.3×10^5	[36]
Decomposition			
DMP + OH• $\xrightarrow{k_7}$ products + CO ₂ + H ₂ O	(7)	To be determined	

are summarized in Table 1 [31]. All rate constants were obtained from literatures [32–36], with the exception of k_1 , which depends on the specific system and should be experimentally determined [31], and k_7 , which is unknown.

The following assumptions were made to establish the kinetic model of DMP degradation in UV/H₂O₂ advanced oxidation: (1) DMP decomposition only occurred through reaction with hydroxyl radical, and (2) the change of solution pH during the advanced oxidation process was negligible. The rate expressions for H₂O₂, OH, HO₂⁻ and DMP concentrations can be written as

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k_1[\text{H}_2\text{O}_2] - k_2[\text{H}_2\text{O}_2][\text{OH}\cdot] - k_3[\text{H}_2\text{O}_2][\text{HO}_2\cdot] + k_4[\text{OH}\cdot][\text{OH}\cdot] + k_5[\text{HO}_2\cdot][\text{HO}_2\cdot] \quad (8)$$

$$\frac{d[\text{OH}\cdot]}{dt} = 2k_1[\text{H}_2\text{O}_2] - k_2[\text{H}_2\text{O}_2][\text{OH}\cdot] + k_3[\text{H}_2\text{O}_2][\text{HO}_2\cdot] - k_4[\text{OH}\cdot][\text{OH}\cdot] - k_6[\text{OH}\cdot][\text{HO}_2\cdot] - k_7[\text{OH}\cdot][\text{DMP}] \quad (9)$$

$$\frac{d[\text{HO}_2\cdot]}{dt} = k_2[\text{H}_2\text{O}_2][\text{OH}\cdot] - k_3[\text{H}_2\text{O}_2][\text{HO}_2\cdot] - k_5[\text{HO}_2\cdot][\text{HO}_2\cdot] - k_6[\text{OH}\cdot][\text{HO}_2\cdot] \quad (10)$$

$$\frac{d[\text{DMP}]}{dt} = -k_7[\text{OH}\cdot][\text{DMP}] \quad (11)$$

In this model, no pseudo-steady state assumption was made for the concentrations of OH• and HO₂• during the oxidation, which is different from most kinetic models described in the literature [37–39]. Despite the fact that the previous kinetic models for the UV/H₂O₂ advanced oxidation process have been applied with different levels of success, invoking the pseudo-steady state assumption can result in significant errors in some cases [31]. The simultaneous ordinary differential equations that result from the substitution of the rate equations were solved using Matlab 7.4.0 (R2007a) function *ode23s*. Values of k_1 and k_7 were obtained through non-linear least squares fitting of the data using the function *lsqnonlin*.

4. Results and discussion

4.1. UV direct photolysis and H₂O₂ oxidation of DMP

To investigate the direct photolysis of DMP by UV irradiation, four sets of experiments were carried out with varying initial DMP concentrations at an UV radiation intensity of 133.9 μ W/cm². DMP

concentrations decreased slowly during the UV radiation under all conditions studied (data not shown). After 90 min reaction, only 19.0%, 13.4%, 10.8% and 10.6% of the DMP degraded in the solutions with the initial DMP concentrations of 0.31, 0.61, 1.10 and 1.60 mg/L, respectively. These results suggest that DMP is resistant to direct UV-photolysis, and it is more recalcitrant to UV-photolysis than diethyl phthalate (DEP) [30]. Previous studies also showed that DMP could be degraded by UV photolysis, but the process was not very efficient [27,28].

Experiments were also conducted to study the direct oxidation of DMP (1.0 mg/L) by H_2O_2 (40 mg/L), but the DMP concentration remained unchanged after 3 h. This observation indicates that DMP cannot be oxidized by hydrogen peroxide alone, which is similar to the case of DEP [30].

The above results demonstrated that neither UV irradiation nor H_2O_2 oxidation could cause significant DMP degradation. Consequently, UV/ H_2O_2 advanced oxidation, a process with high oxidation potential due to the production of OH^\bullet radicals, was studied for oxidative degradation of DMP in aqueous phase.

4.2. Effect of H_2O_2 concentration in UV/ H_2O_2 advanced oxidation

Hydrogen peroxide concentration is an important parameter in UV/ H_2O_2 advanced oxidation process. The effect of initial H_2O_2 concentration on the degradation of DMP was investigated with H_2O_2 concentration varying from 2.5 to 40 mg/L at an UV radiation intensity of $133.9 \mu\text{W}/\text{cm}^2$. Fig. 1 shows the semi-logarithmic graphs of $[\text{DMP}]_0/[\text{DMP}]$ in the presence of H_2O_2 at different concentrations as a function of reaction time. The good linear fits ($R^2 > 0.99$) of experimental data are indicative of pseudo-first order reaction kinetics of DMP degradation:

$$\ln \left(\frac{[\text{DMP}]_0}{[\text{DMP}]} \right) = -k_{\text{app}} t \quad (12)$$

where $[\text{DMP}]$ and $[\text{DMP}]_0$ are the concentration of DMP at time t and 0, respectively, and k_{app} is the pseudo-first order rate constant for overall degradation rate of DMP. In Fig. 1, the slopes of the fitted straight lines represent the $-k_{\text{app}}$; it is obvious that the pseudo-first order rate constant increases with H_2O_2 concentration under the experimental conditions studied. Borup and Middlebrooks [26] also observed that DMP degradation in UV/ H_2O_2 advanced oxidation is of first order with respect to hydrogen peroxide concentration,

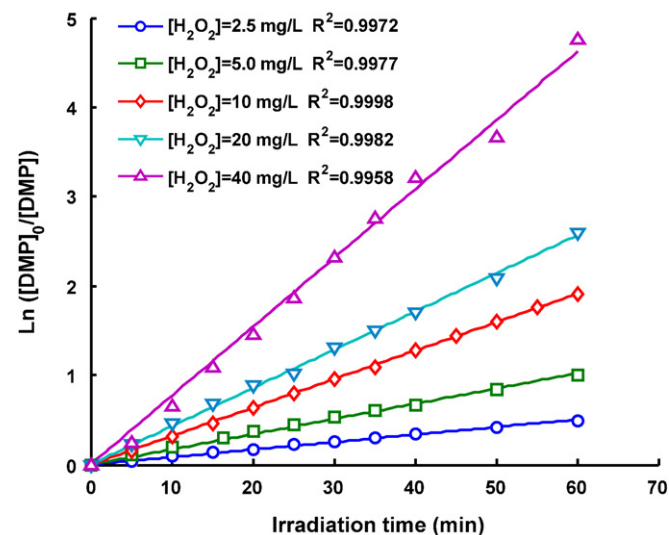


Fig. 1. Effect of initial H_2O_2 concentration on DMP degradation, where $I_0 = 133.9 \mu\text{W}/\text{cm}^2$, pH 6.8 and $[\text{DMP}]_0 = 1.1 \text{ mg/L}$.

and Tawabini and Al-Suwaiyan [28] reported that DMP removal rate increased with the concentration of hydrogen peroxide. The linear dependence of k_{app} on hydrogen peroxide concentration is attributed to the increased hydroxyl radical production from the photolysis of H_2O_2 at increasing concentrations (Eq. (1)). These results also suggest that DMP degradation in the experimental system is probably controlled by the amount of hydroxyl radicals available. Many studies have shown that excess hydrogen peroxide would inhibit the oxidation rate [40–42]. The optimum value for the molar ratio of H_2O_2 concentration to that of target compounds is on the order of several thousands [43]. When H_2O_2 is used in excess, it acts as a scavenger of hydroxyl radical (Eqs. (2) and (6)) and consequently reduce the oxidation rate. This was not observed in this study because the H_2O_2 dosages used were far below the inhibiting point.

4.3. Effect of UV radiation intensity in UV/ H_2O_2 advanced oxidation

UV radiation intensity is another important parameter in UV/ H_2O_2 advanced oxidation process. The effect of the UV radiation intensity on DMP degradation was studied at five radiation levels: 21.2, 50.1, 77.2, 107.6 and $133.9 \mu\text{W}/\text{cm}^2$. Fig. 2 shows the semi-logarithmic graphs of $[\text{DMP}]_0/[\text{DMP}]$ under different UV radiation intensities as a function of reaction time. As expected, increasing UV radiation intensity significantly increased the degradation rate of DMP. UV light intensity plays a key role in the formation of hydroxyl radical (Eq. (1)), and thus affects DMP oxidation rate. The k_{app} values under the UV radiation intensities of 21.2, 50.1, 77.2, 107.6 and $133.9 \mu\text{W}/\text{cm}^2$ are 0.0205, 0.0354, 0.0553, 0.0761 and 0.0907 min^{-1} , respectively. Previous studies showed that DMP removal rate increased with the UV radiation [26,29]. Results of this study indicate that the pseudo-first order degradation rate follows a linear relationship with UV radiation intensity ($k_{\text{app}} = 6.98 \times 10^{-4} I_0$, $R^2 = 0.987$).

4.4. Effect of initial DMP concentration in UV/ H_2O_2 advanced oxidation

The concentrations of DMP occurring in water and wastewater vary over a wide range. Consequently, it is necessary to study the effect of DMP concentration on the degradation rate in UV/ H_2O_2

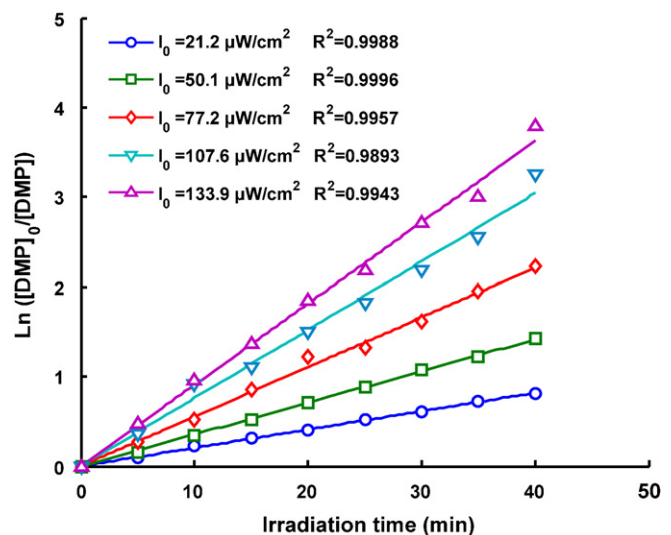


Fig. 2. Effect of UV radiation intensity on DMP degradation, where $[\text{H}_2\text{O}_2]_0 = 40 \text{ mg/L}$, pH 6.8 and $[\text{DMP}]_0 = 0.80 \text{ mg/L}$.

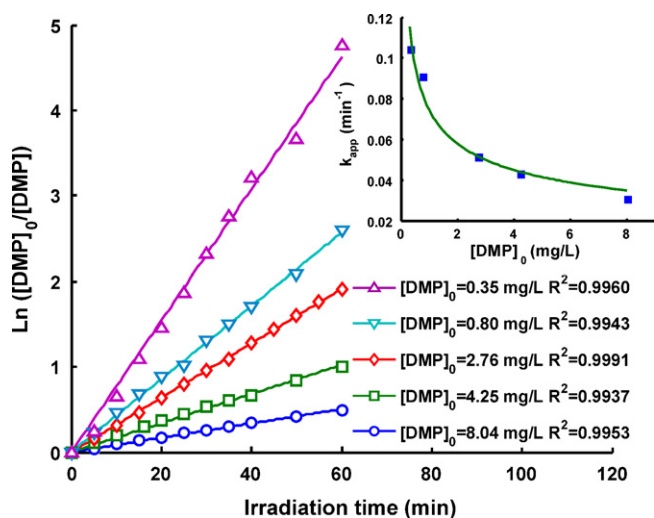


Fig. 3. Effect of initial DMP concentration on DMP degradation, where $I_0 = 133.9 \mu\text{W}/\text{cm}^2$, pH 6.8 and $[\text{H}_2\text{O}_2]_0 = 40 \text{ mg/L}$.

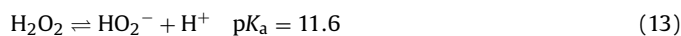
advanced oxidation process. Experiments were conducted at an UV radiation intensity of $133.9 \mu\text{W}/\text{cm}^2$ and 40 mg/L H_2O_2 , with the initial DMP concentration ranged from 0.35 to 8.04 mg/L . Fig. 3 shows the semi-logarithmic graphs of $[\text{DMP}]_0/[\text{DMP}]$ under different initial DMP concentrations as a function of reaction time. The degradation rate of DMP decreased with increasing DMP concentration without exhibiting a linear trend but an exponential relationship (see the inset in Fig. 3, $k_{\text{app}} = 0.0745[\text{DMP}]_0^{-0.3637}$, $R^2 = 0.964$). Borup and Middlebrooks [26] observed that DMP degradation in UV/ H_2O_2 advanced oxidation is of zero order with respect to organic concentration, while Tawabini and Al-Suwaiyan [28] found that DMP removal rate decreased with the initial DMP concentration. The effect of DMP concentration on the transformation rate is mainly due to the absorption of UV radiation by DMP molecules [44]. Increases in DMP concentration induce an inner filter effect and the solution becomes less permeable to UV radiation [18]. This decreases the UV radiation available for absorption by hydrogen peroxide, and reduces hydroxyl radical formation and thus the DMP degradation rate [43].

4.5. Effect of initial solution pH in UV/ H_2O_2 advanced oxidation

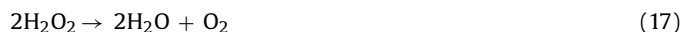
The impact of solution pH on target compounds oxidation and hydroxyl radical formation in UV/ H_2O_2 advanced oxidation process has been investigated in many studies [19,23,45]. The reactivity of hydrogen peroxide and the reaction rates of target compounds were found to depend highly on the solution pH. The effect of solution pH on DMP degradation was studied in the pH range of 2.5–11 in this study. Fig. 4 plots the pseudo-first order degradation rate of DMP as a function of solution pH. k_{app} increased with increasing pH in the range of pH 2.5–4, but started to decrease at higher solution pH. Tawabini and Al-Suwaiyan [28] observed that DMP removal UV/ H_2O_2 advanced oxidation was better at pH range of 3–6 than at pH 9. Results here suggest an optimum solution pH of around 4.0 for DMP degradation in UV/ H_2O_2 advanced oxidation process, which is similar to those of azo dye and acid Blue 74 degradation in UV/ H_2O_2 treatment [42,43]. A nonlinear empirical expression ($k_{\text{app}} = 0.3438 - 1.5082/\ln(\text{pH}) + 3.3498/\text{pH}$) could fit the k_{app} data reasonably well ($R^2 = 0.9791$), which can be used to guide the selection of pH conditions in treating DMP by UV/ H_2O_2 advanced oxidation process.

The effect of solution pH on DMP degradation rate in UV/ H_2O_2 advanced oxidation is caused by two competing processes:

hydroxyl radical production and scavenging. Hydroperoxide anion (HO_2^- , the ionic form of H_2O_2) is more reactive than hydrogen peroxide, and hydroxyl radical formation is enhanced under alkaline conditions [46]. This process can be described by the following reactions:



On the other hand, the hydroperoxide anion is also a scavenger of the hydroxyl radical (Eq. (15)) and can cause decomposition of H_2O_2 (Eq. (16)). It is reported that reaction rate of hydroxyl radical with hydroperoxide anion is about 100 times faster than that with H_2O_2 [43]. Furthermore, the rate of hydrogen peroxide self-decomposition (Eq. (17)) also increases strongly with increasing solution pH [19,43].



Together, these competing processes control the hydroxyl radical concentration in UV/ H_2O_2 advanced oxidation process, which causes k_{app} to increase initially with solution pH and then decrease after reaching a peak value.

4.6. Intermediates during DMP degradation by UV/ H_2O_2

Chromatograms obtained from HPLC analysis (not shown) show at least two peaks of degradation intermediates/products before elution of DMP, which indicates that intermediates/products have more hydrophilic structures than DMP. Yuan et al. [47] reported that in the photocatalytic degradation of DMP in aqueous TiO_2 -UV- O_2 system, dimethyl 3-hydroxyphthalate (3-DMHP) and dimethyl 2-hydroxyphthalate (2-DMHP) were detected as main intermediate products. These results indicated that the photocatalysed degradation of DMP mainly occurred via aromatic ring decomposition rather than the aliphatic chain cracked, which is different from di-*n*-butyl phthalate (DBP) and DEP decomposition attacked by hydroxyl radicals [17,30].

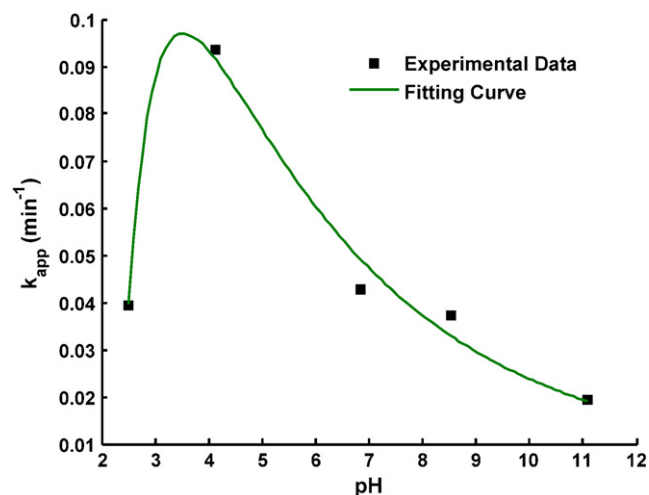


Fig. 4. Pseudo-first order rate constant (k_{app}) of DMP degradation as a function of initial solution pH.

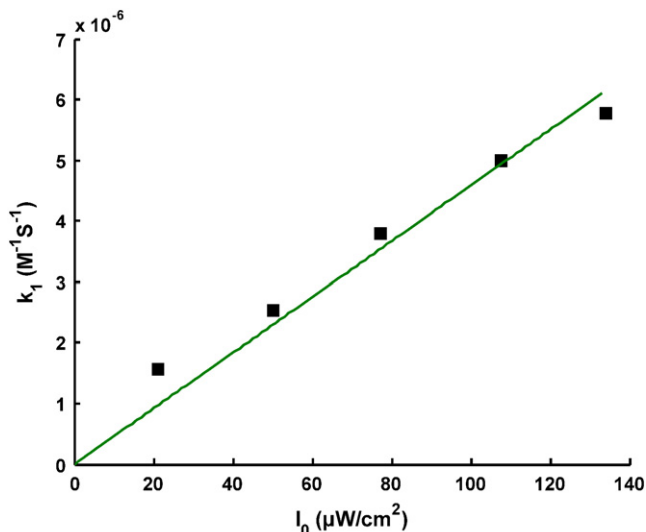


Fig. 5. Model fitted k_1 as a function of UV radiation intensity.

5. Evaluation and application of kinetic model

The unknown rate constants in the kinetic model, k_1 and k_7 , were obtained through fitting the experimental data (except for those with solution pH adjustment and with UV radiation intensity lower than $133.9 \mu\text{W}/\text{cm}^2$) to the kinetic model (Eqs. (8)–(11)) and minimizing the sum of the squares of the differences between experimental and calculated k_{app} . The best-fit values for k_1 and k_7 are 5.77×10^{-6} and $4.0 \times 10^9 \text{M}^{-1} \text{s}^{-1}$, respectively. The k_1 values under different UV radiation intensities were also obtained by fitting the corresponding experimental data to the kinetic model, with the results shown in Fig. 5. A linear dependence of k_1 on I_0 ($k_1 = 4.59 \times 10^{-8} I_0$, $R^2 = 0.9957$) is observed, which is similar to the case of azo dye degradation in UV/ H_2O_2 advanced oxidation [39].

Fig. 6 shows model predicted pseudo-first order rate constant of DMP degradation as a function of initial hydrogen peroxide concentration and DMP concentration. DMP degradation rate constant k_{app} increases approximately linearly with the initial concentrations of hydrogen peroxide up to a threshold value in all case. k_{app} increases very slowly with further increases in H_2O_2 concentration

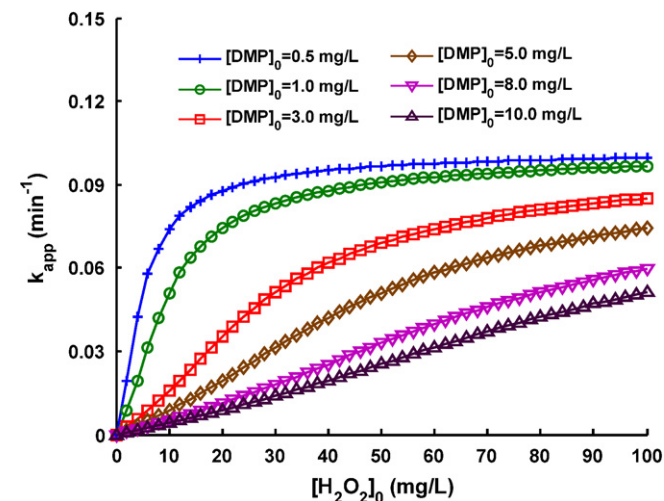


Fig. 6. Model predicted pseudo-first order rate (k_{app}) of DMP degradation in UV- H_2O_2 advanced oxidation process under varying initial hydrogen peroxide and DMP concentration at pH 6.8, $I_0 = 133.9 \mu\text{W}/\text{cm}^2$.

up to 100 mg/L. The reason has been explained in Section 4.2. Since initial concentration of DMP shows great effect on oxidation rate (see Fig. 6), the applied dosage of hydrogen peroxide also relies on the initial DMP concentration. As far as our system is concerned, hydrogen peroxide at 20 mg/L is optimum for treating aqueous streams containing less than 1 mg/L DMP. When DMP concentration is higher than 8 mg/L, there is not enough hydrogen peroxide to produce hydroxyl radicals to attack DMP and the degradation rate constant becomes dependent on hydrogen peroxide concentration. Consequently, k_{app} appears to be of first order with respect to hydrogen peroxide concentration. The model provides a comprehensive understanding of the effects of operational variables including initial hydrogen peroxide concentration, initial DMP concentration and UV light intensity on oxidation performance. Based on DMP concentration in the aqueous stream to be treated and reactor conditions, the required k_{app} and optimum hydrogen peroxide can be determined for designing an advanced oxidation treatment system.

6. Conclusions

- (1) Compared with direct UV photolysis and H_2O_2 oxidation processes, UV/ H_2O_2 advanced oxidation process is effective at degrading DMP in aqueous solution. The results obtained in this study clearly indicate the UV/ H_2O_2 process is a promising technology for removal of DMP from contaminated water.
- (2) DMP degradation in UV/ H_2O_2 advanced oxidation process follows pseudo-first order kinetics and the pseudo-first order rate constant (k_{app}) is affected by the UV radiation intensity, H_2O_2 concentration, solution pH and initial concentration of DMP.
- (3) A kinetic model for DMP degradation in UV/ H_2O_2 advanced oxidation process was developed based on experimental results and known elementary chemical reactions without employing pseudo-steady state assumption. A rate constant of $4.0 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ was determined for the reaction between DMP and hydroxyl radical.
- (4) The key factors for DMP oxidation are described in a kinetic model. This model can be used to optimize the operational parameters and provide practical guidance in designing photochemical treatment systems for treating DMP in aqueous stream.

Acknowledgments

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