



A systematic study of the degradation of dimethyl phthalate using a high-frequency ultrasonic process

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ABSTRACT

A comprehensive study of the sonochemical degradation of dimethyl phthalate (DMP) was carried out using high-frequency ultrasonic processes. The effects of various operating parameters were investigated, including ultrasonic frequency, power density, initial DMP concentration, solution pH and the presence of hydrogen peroxide. In general, a frequency of 400 kHz was the optimum for achieving the highest DMP degradation rate. The degradation rate was directly proportional to the power density and inversely related to the initial DMP concentration. It was interesting to find that faster removal rate was observed under weakly acidic condition, while hydrolysis effect dominated in extreme-basic condition. The addition of hydrogen peroxide can increase the radical generation to some extent. Furthermore, both hydroxylation of the aromatic ring and oxidation of the aliphatic chain appear to be the major mechanism of DMP degradation by sonolysis based on LC/ESI-MS analysis. Among the principle reaction intermediates identified, tri- and tetra-hydroxylated derivatives of DMP, as well as hydroxylated monomethyl phthalates and hydroxylated phthalic acid were reported for the first time in this study. Reaction pathways for DMP sonolysis are proposed based on the detected intermediates.

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1. Introduction

Phthalate esters (PAEs) are widely used as plasticizers in industrial processes where they impart flexibility in various resins [1]. Some phthalates are suspected to be endocrine disrupting compounds (EDCs) by mimicking estrogens, and therefore the possible leaching of phthalates from plastics into the aqueous environment may lead to negative effects on organisms [2]. Many studies have been carried out trying to degrade PAEs, although most of them were conducted using biological methods, and monomethyl phthalate (MMP) and phthalic acid (PA) were found to be the most frequent end-products [3–5].

Compared to biological methods, advanced oxidation processes (AOPs) have attracted greater interest in degrading refractory organics, by virtue of their high efficiency and the avoidance of further treatment of biological sludge. The application of ultrasonic irradiation, as an alternative to the more established AOPs (e.g. O_3/H_2O_2 , O_3/UV , H_2O_2/UV), has the advantage that it is potentially simpler, safer, cleaner, requires less chemical dosing, and has been widely investigated. The propagation of ultrasound through a liquid induces both physical and chemical processes by acoustic cavitation: the formation, growth and adiabatically implosive col-

lapse of bubbles in the liquid [6,7]. The final collapse of the bubbles produces extremely high temperatures ($>5000\text{ }^\circ\text{C}$) and pressures ($>100\text{ MPa}$), cleaving water molecules into $\cdot\text{OH}$ and $\text{H}\cdot$ radicals inside the bubble and in the liquid shell surrounding the bubble [8]. These radicals can combine mutually or with peripheral water molecules to form other radical species (e.g. $\text{HO}_2\cdot$) and H_2O_2 , which in turn can oxidize organic substrates causing their degradation or even mineralization [9,10].

Although many studies have been performed using ultrasound to degrade different organic compounds, the information concerning the sono-degradation of PAEs is scarce, especially concerning the possible intermediates and products, which is useful to evaluate the process and/or find other proper processes to combine with it. Besides, many studies have focused on improving the efficiency of organic compound degradation by incorporating other AOPs with ultrasound [11–13], which is adverse for scrutinizing the detailed mechanism of sonolysis due to the faster reaction rate of the combined processes.

In this study, dimethyl phthalate (DMP), the simplest member of the group of PAEs, was selected as the model compound to systematically examine its sono-degradation. DMP is one of the most common PAEs in the aqueous environment. It demonstrates a relatively high water solubility (ca. 4000 mg/L at $25\text{ }^\circ\text{C}$) and is more hydrophilic ($\log K_{ow} = 1.60$) compared to other PAEs. It is considered to have negligible volatility (with a Henry's law constant of

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1.22×10^{-7} atm m³/mol) [1,14]. Owing to its environmental significance, intensive efforts have been made to develop methods to remove DMP from waters and wastewaters. Many studies have reported the degradation of DMP using diverse processes, such as photocatalysis with TiO₂ suspensions [15], ozonation with high silica zeolites and UV radiation [16], photochemical degradation by Fenton reagent [17], etc. Most of these methods are viable only in the presence of catalysts or other chemical inducers, giving rise to both chemical consumption and further chemical contamination. The sonolysis of DMP utilizing solely a high frequency ultrasonic system (HFUS) has the advantage in this respect, but no information concerning DMP sonolysis has so far been reported.

In view of the above, the performance of HFUS with DMP as the selected compound was investigated in this study. The effects of several parameters on the efficiency of the system were evaluated, these being the ultrasonic frequency, ultrasonic power, DMP concentration, initial solution pH, and the effect of the presence of H₂O₂. In addition, the main intermediates of DMP sono-degradation were identified and possible degradation pathways are also proposed.

2. Materials and methods

2.1. Chemicals

DMP (99.6%) and H₂O₂ (35% by weight) were purchased from Sigma Aldrich Inc., USA. All chemicals were of analytical standard and used without further purification. Solutions of 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used for pH adjustment. Deionized-distilled water prepared from a Millipore Waters Milli-Q water purification system was used exclusively in this study.

2.2. Analytical method

The DMP concentration was determined by high performance liquid chromatography (HPLC) (Waters), comprising a HPLC pump (Waters 515), a UV detector (Waters 2489), an auto sampler (Waters 717), and a Brava C18-BDS column (5 μm particle size, 250 × 4.6 mm). The mobile phase of acetonitrile/water (60/40, vol/vol) was employed at a flow rate of 1.0 mL/min. The injection volume was 10 μL and the concentration of DMP was detected at 230 nm. The concentration of H₂O₂ was determined by measuring the absorbance of titanium peroxide (TiO₂²⁺) using a spectrophotometer at 405 nm [18]. The ultrasonic power dissipated into the liquid was calculated using a calorimetric method [19]. In the calorimetric experiment, the temperature of the solution was measured by a digital thermometer and recorded at a 15 s interval for the initial 10 min.

The identification of intermediates was performed by a Thermo Quest Finnigan LCQ Duo LC/MS system equipped with a PDA-UV detector and a mass spectrometer with an electrospray ionization source and a quadrupole ion-trap mass analyzer. Positive mode was applied to detect DMP, while negative mode was chosen to qualitatively detect the intermediates. The mobile phase was a mixture of 100% methanol (A) and 0.1% formic acid (B) with a linearly gradient flow from 10%A:90%B to 90%A:10%B within 55 min. From 55 to 60 min, the ratio turned back to the initial composition. The [DMP]₀ for mass analysis was 0.25 mM. The intermediates without commercial standard were quantified by their nominal concentrations using the same response factor of DMP. This approximation is reasonable on the basis that most of the UV absorbance may be derived from the resonance structure of the ring [20]. The total organic carbon (TOC) was analyzed by Shimadzu TOC-5000A analyzer.

2.3. Ultrasonic system

Sonolytic experiments were conducted in a cubic stainless steel jacketed reactor with an effective volume of 1.5 L (tailor-made by Ning Bo Scientz Biotechnology Co., China) (see Fig. 1). Three different frequencies of 400, 800, and 1200 kHz were provided respectively by three independent basins with an identical reactor size. Electrical power was transduced into ultrasonic vibration by six piezoelectric ceramics stuck uniformly in two rows (i.e. in a 2 × 3 format) on the back of the basin bottom. The nominal input power was adjustable manually via the control panel. A convolute cooling finger was submerged in the tested water to keep the solution temperature constant at 28 ± 2 °C (not applicable in the calorimetric experiment). A volume of exactly 250 mL DMP solution was used throughout this study, except for the tests relating to different water volumes. The initial pH of DMP solution was maintained at 6.5 ± 0.2 unless stated otherwise (e.g. for the tests at different initial pH levels). Aliquots of DMP solution were withdrawn from the reactor at predetermined time intervals for further measurement. The total reduction in solution volume was kept below 5% of the initial volume. All the selected tests were duplicated with an observed deviation of less than 5%.

3. Results and discussion

3.1. Ultrasonic frequency optimization

The DMP degradation performance for different ultrasonic frequencies (400, 800, and 1200 kHz) and powers is shown in Fig. 2. The results suggested that the DMP sono-degradation follows pseudo first-order kinetics. The greatest degradation performance was obtained from the 400 kHz process using its maximum input power (available) of 120 W. A reaction rate constant, k_A , of $6.7 \times 10^{-3} \text{ min}^{-1}$ was observed and 87.2% of DMP was removed in 300 min. At the same frequency, the degradation rate decreased substantially when the input power reduced only moderately to 100 W, indicating that the power supplied to the ultrasound system was also a major factor affecting the compound degradation efficiency. Analogously, a similar phenomenon was observed for the 800 kHz process, in which an increase in the nominal input power from 120 W to its maximum of 160 W produced a corresponding increase in the DMP removal performance. However, the performance at 800 kHz was inferior to that of the 400 kHz/120 W situation, and the magnitude of the k_A of the 800 kHz process was less than one third of the 400 kHz process with the same input power (120 W). The worst performance was evident from the 1200 kHz process at its maximum nominal input power of 60 W, where there was no measurable DMP degradation within 30 min.

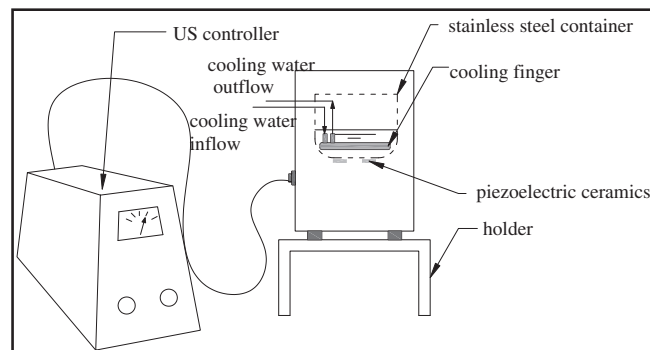


Fig. 1. Schematic diagram of the ultrasonic apparatus.

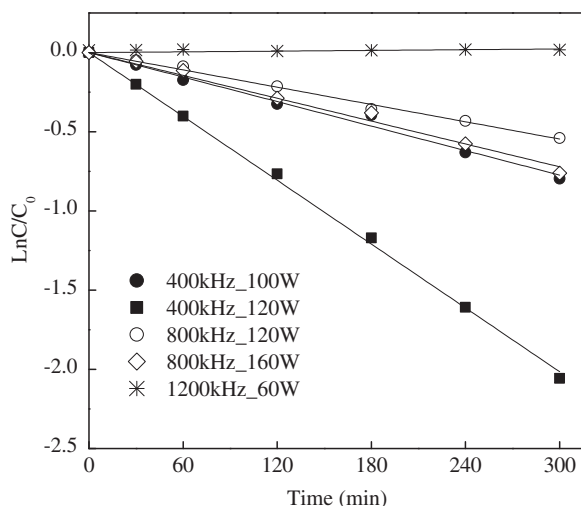


Fig. 2. Temporal variation of DMP concentration with ultrasonic frequency and power ($[DMP]_0 = 0.1$ mM; 250 mL solution volume).

The observation from these tests that the most effective frequency for degrading DMP was 400 kHz, agrees with the results reported in other studies [9]. The ultrasonic frequency plays an essential role in determining the efficacy of the process by influencing the cavitation performance. The number of acoustic cycles and bubble collapses increases as the frequency increases, whereas the bubbles formed at high-frequency with a correspondingly smaller explosion diameter, release less energy than the low-frequency bubbles for one single pulsation [21,22]. Thus, a higher frequency may compensate for the lower energy release per single bubble explosion by occurring more frequently. However, an above optimal frequency only leads to a small energy release for a single bubble, which could not be accumulated sufficiently by the repeating frequency. The optimal frequency is determined by the comprehensive performance of energy release (bubble sizes and repeating frequency) and is likely to vary for different target compounds. From the results of these initial tests, the most effective frequency was found to be 400 kHz and this was used in all further tests in this study.

3.2. Effect of power density

In order to clarify the power effect on sonolysis efficiency, the DMP degradation performance was investigated by varying the solution volume with a constant nominal input power of 120 W. From Fig. 3(a), a significant decrease of the degradation rate was observed with the increase of solution volume, indicating the importance of power density (the power applied per unit volume of irradiated liquid [23]) on DMP sonolysis.

The actual power dissipated into the water can influence the amplitude of the ultrasonic wave, causing the bubbles to oscillate more violently, and thereby giving rise to an increased production of radicals and a greater pyrolysis performance [24]. The ultrasonic power actually entering the solution can be determined approximately by measuring the initial rate of solution temperature rise, dT/dt , and by Eq. (1):

$$\text{Power (W)} = (dT/dt) \cdot C_p \cdot M \quad (1)$$

where C_p is the specific heat of water (4200 J/kg °C), and M is the mass of water (kg). It was observed that the initial rate of solution temperature rise was inversely related to the solution volume, but the total power absorbed was almost the same for different volumes, accounting for 6.3–8.2% of the nominal input power. Kimura

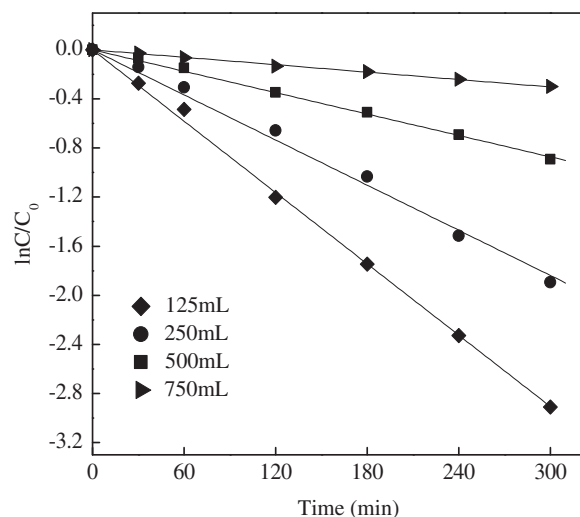


Fig. 3a. Temporal variation of DMP concentration with solution volume ($[DMP]_0 = 0.1$ mM; 400 kHz; 120 W).

et al. also reported that the calorimetrically determined ultrasonic power measurements were independent of the water volume [25]. Hence, it was concluded that the variation in solution volume only changed the power density; the power density can be deduced from Eq. (1) by incorporating the water density, as follows:

$$\text{Power density (W/mL)} = C_p \cdot \rho \cdot dT/dt. \quad (2)$$

Since C_p and density ρ (mass/volume) are constants, a higher power density (via less solution volume) leads to a more rapid temperature rise, as observed experimentally.

The relationship between DMP decay rate and power density is more evident in Fig. 3(b), where the power density and k_A were inversely related to solution volume. An approximately linear relationship of k_A as a function of power density was indicated from the results (inset of Fig. 3(b)), confirming the positive role of power density on DMP degradation. Hwang et al. also investigated the dependence of the reaction rate constant on the power density by varying the input power to obtain different power densities, and the linear relationship was also proposed [26]. This positive role of power density can be explained by the extent of the cavi-

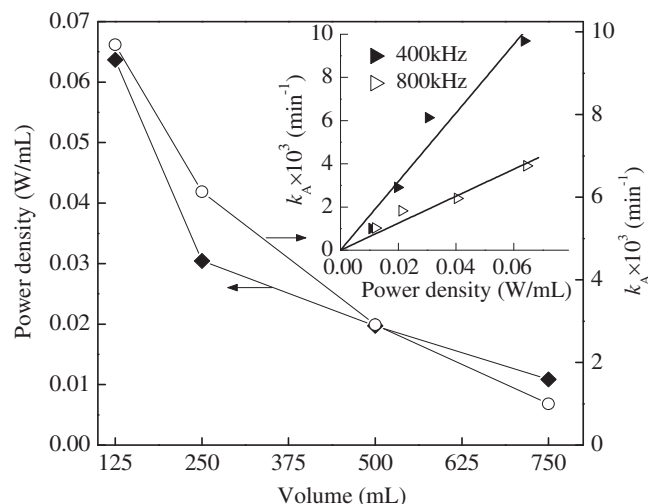


Fig. 3b. Variation of DMP degradation rate and power density with solution volume ($[DMP]_0 = 0.1$ mM; 400 kHz; 120 W).

tion activity, whereby the number and/or density of the cavitating bubbles increases with increasing power density [27].

Comparative tests were conducted with the 800 kHz process and a similar linear trend was observed but with a much lower gradient (inset of Fig. 3(b)). Thus, the 400 kHz process with a higher gradient displayed a better DMP degradation capability compared to that of the 800 kHz system with the same input power. Hence, in general, the slope can well characterize the sonochemical property among different ultrasonic systems and the linear correlation between k_A and power density potentially might become a useful tool in predicting the sonochemical process performance if the characterization constant (slope) is predetermined.

3.3. Effect of initial DMP concentration

Previous studies have shown that the first-order degradation rate of organic compounds by ultrasound is inversely related to the initial compound concentration (e.g. [11]) and similar results were found in this study where the initial DMP concentration was varied from 0.01 to 0.15 mM (Fig. 4). The reason for this behavior has not been fully explained in previous studies, and one hypothesis is proposed here.

In view of the low volatility and hydrophilic nature of DMP, the principal mechanism of DMP degradation in the HFUS is most likely its oxidation by free radicals both at the cavitation bubble interface and in the aqueous phase, rather than by pyrolysis inside the bubble. This was confirmed by conducting tests in the presence of 1.0 M MeOH, an effective radical ($\cdot\text{OH}$) scavenger ($k_{\text{OH}} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [28]), in the DMP solution, and no measurable reduction in the DMP concentration was evident for 300 min. Thus, the degradation of DMP by hydroxyl radicals can be written as follows:

$$-d[\text{DMP}]/dt = k_{\text{DMP}}[\cdot\text{OH}]^x[\text{DMP}] \quad (3)$$

The rate constant k_{DMP} has been reported to be second-order ($x = 1$) with a value of $2.67 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [29]. During sonication at a constant power input, it can be assumed that the rate of $\cdot\text{OH}$ generation is constant, and that the $\cdot\text{OH}$ concentration in solution during the reaction maintains a steady state, whereby the generation of $\cdot\text{OH}$ radicals equals their consumption by reaction with the target compound and scavengers [9]. The main reactions in pure water induced by ultrasonic irradiation are summarized as follows (R1–R11) [9,10]. A prominent product of sonication is hydrogen per-

oxide (reactions R4, R6 and R10), which accumulates linearly in solution during the period of ultrasound irradiation (data not shown) and which also acts as a hydroxyl radical scavenger (R11; $k_{\text{OH}} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [28]):



Thus, the net rate of change of $\cdot\text{OH}$ radicals in solution can be expressed as follows:

$$-d[\cdot\text{OH}]/dt = k_g - k_{\text{OH}}[\cdot\text{OH}]^y[\text{DMP}] - k_{\text{per}}[\cdot\text{OH}]^w[\text{H}_2\text{O}_2] - k_{\text{int}}[\cdot\text{OH}]^z[\text{Int}] \quad (4)$$

where k_g is the zero-order rate constant for $\cdot\text{OH}$ radical generation; $[\text{DMP}]$, $[\text{H}_2\text{O}_2]$ and $[\text{Int}]$ are respectively the time-dependent concentrations of DMP, hydrogen peroxide, and DMP reaction intermediates; and k_{OH} , k_{per} and k_{int} are the corresponding reaction rate constants. Since under steady state conditions, $d[\cdot\text{OH}]/dt = 0$, and initially ($t \approx 0 \text{ s}$) $[\text{H}_2\text{O}_2]$ and $[\text{Int}]$ can be assumed to be zero, and $[\text{DMP}] = [\text{DMP}]_0$ (initial DMP concentration), Eq. (4) can be simplified to give the $[\cdot\text{OH}]$ concentration as follows:

$$[\cdot\text{OH}] = (k_g/k_{\text{OH}}[\text{DMP}]_0)^{1/y} \quad (5)$$

Combining Eq. (3) (assuming $x = 1$) and Eq. (5), gives the following expression for the degradation of DMP:

$$-d[\text{DMP}]/dt = k_{\text{DMP}}(k_g/k_{\text{OH}}[\text{DMP}]_0)^{1/y}[\text{DMP}] \quad (6)$$

Eq. (6) represents the first order degradation kinetics for DMP where the pseudo first-order rate constant (k_A) is equal to $k_{\text{DMP}}(k_g/k_{\text{OH}}[\text{DMP}]_0)^{1/y}$. The results shown in Fig. 4 are consistent with the inverse dependency of k_A on $[\text{DMP}]_0$ as indicated by Eq. (6), which in general terms can be written as:

$$k_A = A[\text{DMP}]_0^{-B} \quad (7)$$

where $A = k_{\text{DMP}}(k_g/k_{\text{OH}})^{1/y}$, and $B = 1/y$.

The results obtained experimentally (Fig. 4) were in close agreement with Eq. (7) ($r^2 = 0.98$), with the value of B determined to be 0.39 ($y = 2.6$).

For the subsequent tests, unless otherwise stated, an initial DMP concentration of 0.05 mM was selected in order to shorten the reaction time.

3.4. Effects of initial solution pH on DMP sono-degradation

The solution pH is generally an important factor influencing the efficiency of the oxidation processes, and the influence of initial pH on the sono-degradation of DMP was studied in the range of pH

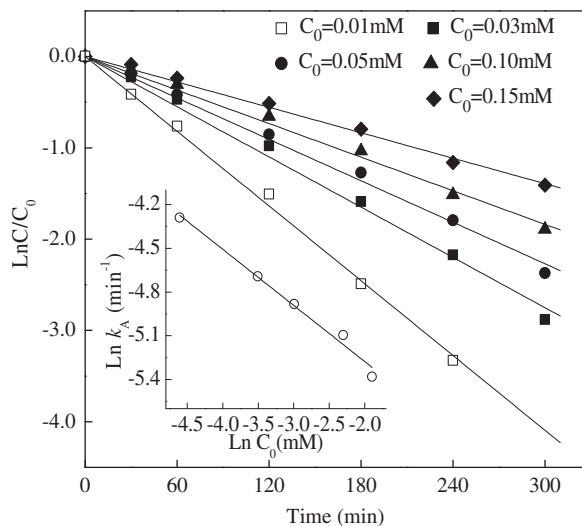


Fig. 4. Effect of initial DMP concentration on DMP degradation (400 kHz; 120 W).

2–11; the results are presented in Fig. 5. It can be seen that the rate constant was not substantially affected by pH, but generally decreased (by 15%) with increasing pH for the pH range of 4–9.

Complementary tests were carried out without ultrasound (only stirring) to determine the direct effect of hydrolysis of DMP at the different pH conditions. No significant hydrolysis was detected for all the pH conditions except for pH 11. Hydrolysis was evident at pH 11 corresponding to a DMP degradation of 49.4% in 240 min, which when compared to the overall degradation of 85.3% in 240 min with ultrasonic irradiation, indicated the extensive role of DMP hydrolysis in strongly alkaline conditions. Yim et al. have also reported the significant hydrolysis at pH 12 when they examined the sonolysis of another PAEs member, diethyl phthalate (DEP). In addition, the monoalkyl phthalate, which was regarded as the hydrolysis product of DEP, also showed a faster ultrasonic degradation efficiency under alkaline conditions [30]. Since the hydrolysis of DMP also followed pseudo first-order kinetics (data not shown), the net degradation rate excluding hydrolysis is also shown in Fig. 5. By excluding hydrolysis effects, it is clear that the rate of DMP degradation by sonication decreased systematically, and to an increasingly greater extent, between pH 5 and 11. Since DMP is a non-dissociating compound, the most likely reason for this degradation with increasing pH is the effect of increasing hydroxyl radical scavenging by hydroxide ions ($k_{OH} = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [28]), and the decreasing oxidation potential of $\cdot\text{OH}$ with increasing pH [17].

The lower DMP degradation rate at pH 2 compared to the rates at pH 4 and 5 is believed to be the effect of hydroxyl radical scavenging by hydrogen sulphate ions ($k_{OH} \approx 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [28]), arising from the use of sulphuric acid to lower the pH in these tests ($\text{p}K_a$ of $\text{HSO}_4 \approx 1.9$). At pH 4 and 5 the concentration of added sulphate is very low and therefore the extent of scavenging will be considerably less than at pH 2.

3.5. Effect of addition of hydrogen peroxide on DMP decomposition

As discussed previously, hydrogen peroxide is generated during ultrasound irradiation via reactions R4, R6 and R10. The influence of H_2O_2 on the sonochemical degradation of a target compound is expected to be determined by its impact on the concentration of $\cdot\text{OH}$ in solution, and the direct, or synergistic (with $\cdot\text{OH}$), reaction between H_2O_2 and the compound. In the former case, the presence of H_2O_2 can have both a positive and negative effect on $[\cdot\text{OH}]$ in

solution, in which $\cdot\text{OH}$ are generated directly from H_2O_2 sonolysis [10,31]:



and where $\cdot\text{OH}$ radicals are scavenged by H_2O_2 , as described previously. Given the complexity of these related mechanisms, it is expected that the net effect of the presence of H_2O_2 on DMP degradation will depend on the prevailing reaction conditions. A previous study by the authors with a group of iodinated compounds [23] showed that the extent of compound degradation by ultrasound was significantly enhanced by the addition of H_2O_2 to the solution, but that the enhancement was significantly dependent on the compound concentration (i.e. much less at higher concentration).

In this study, the impact of H_2O_2 on DMP degradation was considered by the application of different H_2O_2 concentrations (0–10 mM) at the start of a sonication reaction lasting 180 min. Prior to these tests it was established that direct oxidation of DMP by H_2O_2 alone was not significant (data not shown). The results of addition of hydrogen peroxide in the presence of ultrasound are shown in Fig. 6, where in general H_2O_2 had a promoting effect on DMP degradation, which increased with the initial H_2O_2 concentration. As observed in the previous study mentioned above [23], the promoting effect of H_2O_2 was dependent on $[\text{DMP}]_0$, where the presence of moderate concentrations of H_2O_2 (<5 mM) significantly enhanced the compound degradation rate of the 0.02 mM DMP solution, but gave very little enhancement in the case of the 0.05 mM DMP solution. However, at the greatest H_2O_2 concentration (10 mM) the degradation rates for the two DMP concentrations were relatively close. It is believed that these effects reflect the relative concentrations (molar ratio) of $\cdot\text{OH}$ radicals and DMP in the solutions, and the relative contribution that H_2O_2 makes to $\cdot\text{OH}$ radical generation or scavenging. The accumulation of H_2O_2 during the sonolysis process within 3 h was less than 0.2 mM in a 0.05 mM DMP solution (data not shown). Based on the result of Fig. 5, under this low range of $[\text{H}_2\text{O}_2]$, the role of H_2O_2 is mainly a radical source rather than a radical scavenger.

3.6. Identification of reaction intermediates from DMP sonolysis

The ultrasonic degradation of DMP is mainly attributed to hydroxyl radical oxidation (see Section 3.3). However, the sonolytic process is slower compared to other $\cdot\text{OH}$ generating AOPs (e.g. Fen-

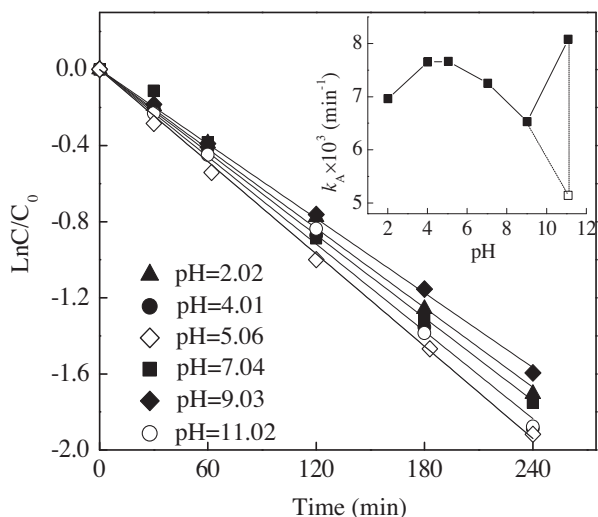


Fig. 5. Effect of initial solution pH on DMP degradation ($[\text{DMP}]_0 = 0.05 \text{ mM}$; 400 kHz; 120 W).

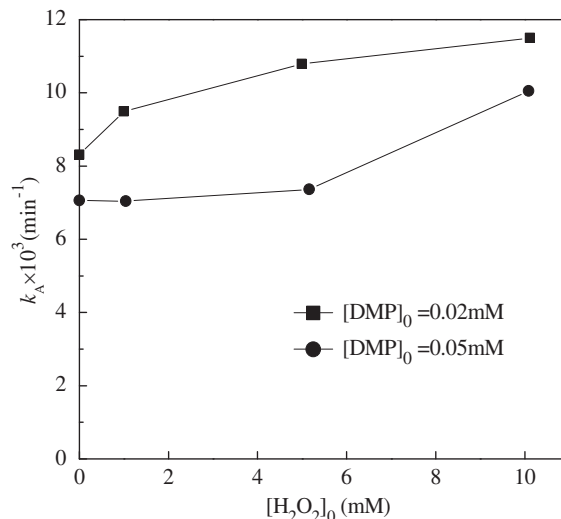


Fig. 6. Influence of hydrogen peroxide dose on the DMP degradation rate (400 kHz; 120 W).

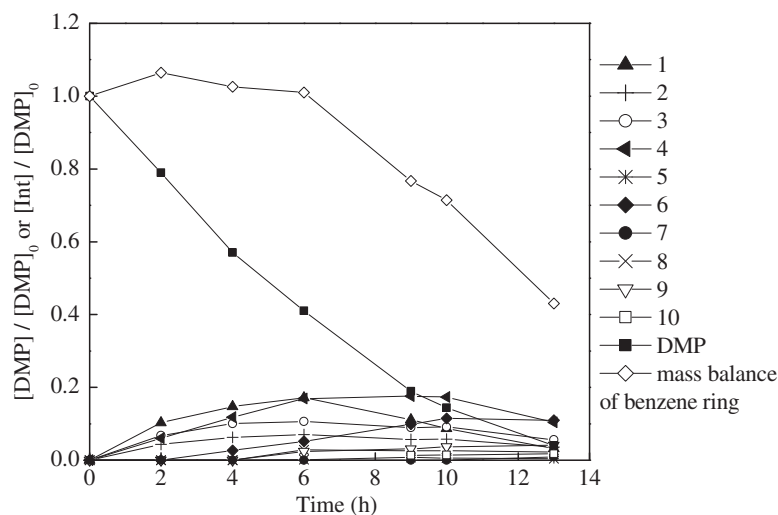


Fig. 7. The concentration evolution of DMP and the detected sonolysis intermediates of DMP (400 kHz; 120 W; $C_0 = 0.25$ mM).

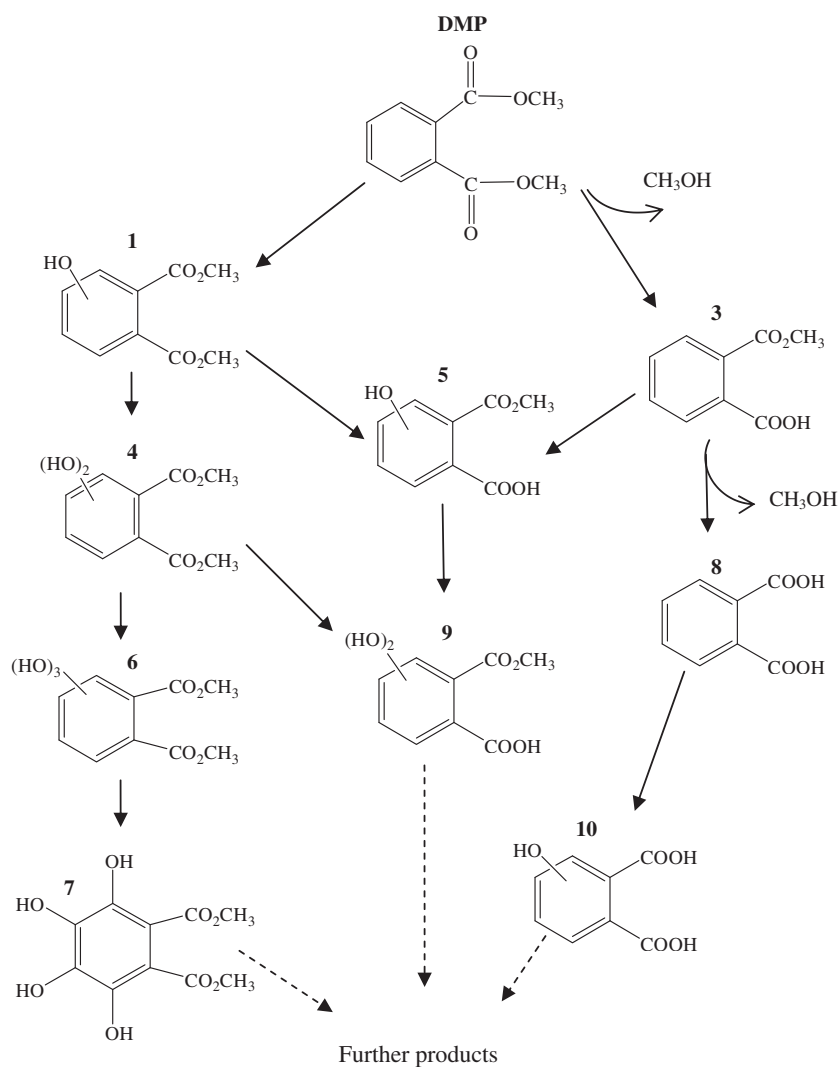


Fig. 8. Degradation pathways of sonochemical degradation of DMP (Dashed arrows indicate reactions that require more than one step).

ton, UV/H_2O_2 , etc.) due to its distinct heterogeneous water–bubble interface which can repel hydrophilic compounds from the $\cdot OH$ concentrated area. It has been reported that the efficiency of $\cdot OH$

scavenging in sonication process is correlated to the hydrophobicity of the solutes rather than the specific reactivity towards $\cdot OH$ in homogeneous solution [32]. Psillakis et al. have proved that the

PAEs with higher hydrophobicity demonstrated greater sonolytic degradation efficiency [33]. Therefore, reaction intermediates with more hydrophilic characteristics might have difficulties in competing $\cdot\text{OH}$ with their mother compound, DMP. The accumulation of these intermediates not only confirm this hypothesis, but makes them easier to be detected. This explains why many new intermediates were reported in this study for the first time, because they were easily escaped from the detection in other AOPs.

The information of the identified intermediates is summarized (see Table 1 in Supporting information), and the evolution profile of the main intermediates is shown in Fig. 7. For some intermediates the addition of one formate anion, $[\text{M}+45]^-$, was observed due to the use of 0.1% formic acid as the mobile phase [34]. All the intermediates detected in this study had shorter retention times than DMP, implying a higher polarity than their mother compound. The hydroxyl groups attached to the benzene ring readily participate in the $p-\pi$ conjugation effect, and therefore the electron density was increased. In addition, the carboxylic group was also beneficial for electron withdrawing, all resulting in a higher polarity of these intermediates. Many studies have reported hydroxylation in different AOPs involving the mechanism of $\cdot\text{OH}$ radicals [35–37], and hydroxylated intermediates were also found in sonochemical reactions [8]. However, in the case of DMP, only mono- and bi-hydroxylated phthalates were reported by using other AOPs [35,36]. The tri- and tetra-hydroxylated derivatives of DMP, the hydroxy-MMP, and hydroxy-PA are the reported for the first time in this study. This is partly because LC/MS is more capable of detecting hydrophilic intermediates than that of GC/MS. Another reason, as mentioned above, is the slower generation of hydroxal radicals on the hydrophobic surface of bubbles resulting in the accumulation of the more hydrophilic intermediates in the solution.

As can be seen from Fig. 7, compounds 1–4 were more abundant during the early period, but declined later after reaching a peak at 6–8 h. Compound 2 with evident LC signal hardly responded to MS detection (see Fig. 1 in SI). With further degradation of these primary intermediates, secondary derivatives appeared and accumulated gradually (compounds 5–10). In addition, the dimethyl hydroxy-phthalate with more hydroxylated groups increased slower during the reaction, indicating that the hydroxylation potentially proceeded step by step. Hence, the degradation pathway of DMP sonolysis was proposed in Fig. 8. The degradation of DMP involved the hydroxylation of the aromatic ring, the oxidation of the aliphatic chain, or both. It should be noted that the intermediates of MMP and PA have been reported to be much less toxic than DMP [38].

According to the mass balance as shown in Fig. 7 and 57% of detectable benzene ring structures were opened when 96% DMP was removed. However, no evident TOC removal was observed during this period (data not shown). This suggests the likely formation and accumulation of many aliphatic organics with higher hydrophilicity, accounting for the intact of TOC. If mineralization is one of the treatment objectives, other proper AOPs should be combined with ultrasound, such as UV irradiation (although DMP is inert toward direct photolysis [39]) to improve the decomposition of the more hydrophilic intermediates. Na et al. have proved that the mineralization of DEP was improved significantly when ultrasound was combined with UV irradiation, which might be also applicable for DMP degradation [40,41].

4. Conclusions

In this study, DMP can be degraded by HFUS via reacting with $\cdot\text{OH}$ radicals, and the degradation follows pseudo first-order kinetics. The optimal performance corresponded to a frequency of 400 kHz. The degradation rate increased directly with the ultra-

sound power density, and decreased moderately with increasing pH in the range typically found in the environment (pH 5–9). Higher initial concentration results in a lower degradation rate. Both the hydroxylation of the benzene ring and the oxidation the aliphatic chain were found to be the dominating mechanisms of DMP sonolysis. In addition, the HFUS was found to be effective in degrading more hydrophobic DMP, but less efficient in degrading its more hydrophilic intermediates. All these findings may cast some light on understanding the mechanism of the sonolytic processes and finding proper process to enhance the efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ultsonch.2012.11.005>.

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