Annotated Confirmation Report

Degradation of Refractory Contaminants in Water by Chemical-free Radical Generated by Ultrasound and UV Irradiation

The Hong Kong Polytechnic University

DEGRADATION OF REFRACTORY CONTAMINANTS IN WATER BY CHEMICAL-FREE RADICALS GENERATED BY ULTRASOUND AND UV IRRADIATION

The Hong Kong Polytechnic University
Department of Civil and Environmental Engineering

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

2014

Table of Content

Use the plural form for "content". The heading should be "Table of Contents".

Also include the following:

i. An abstract.

ii. Acknowledgements

iii. A list of figures.

iv. A list of abbreviations

Also include a short introduction to help guide the reader through the report.

Special Note:

The page numbers may not exactly match those in the report due to the annotations.

1. Literature review

Advanced oxidation processes (AOPs) involving the generation of hydroxyl radicals (OH·) as the primary oxidant have been shown to be successful in degrading refractory organic contaminants in waters and wastewaters.[1] Among various AOPs, high-frequency ultrasound (US) has attracted considerable interest in recent years by virtue of its particular comparative advantages, such as the avoidance of chemical dosing and catalysts, safety, a lower demand for solution clarity, etc.[2] The sonochemical effect is mainly attributed to the acoustic cavitation phenomenon, which is the process of formation, growth and sudden collapse of gas bubbles, leading to the generation of extreme conditions (e.g. 5000 K, 1000 atm) locally. The pyrolysis of water molecules under such conditions is believed to yield both H· and OH· radical species.[2]

✓Explains importance of topic using present perfect. e.g. "have been shown to"
✓Introduces key terms and abbreviations

✓Explains key terms, giving key figures to further define

Also mention how the report is organised at the start, i.e. Section 2 describes..."

✓Explains main problem with current methods
✓Gives sources

Although US can achieve the degradation of refractory compounds, one of its shortcomings is its relatively low efficiency, mostly due to the inevitable recombination of generated radicals (ca. 80%) to form more stable molecules (H_2O_2, H_2O, etc), [3] which reduces the effective contact between radicals and target contaminants. In order to counter these effects and enhance the oxidation performance by US, its combination with other AOP technologies (photocatalysis, Fenton process, ozonation, etc) has been tested in an attempt to show either an additive or a synergistic benefit. The hybrid technique of combining ultraviolet (UV) irradiation and US has been found to be beneficial in enhancing the degradation of target compounds but the majority of previous studies have been conducted under photocatalyst mediated conditions,[4-6] which has the disadvantage of incurring the additional costs of the catalysts and their final disposal. The combination of catalyst-free UV and US (henceforth US/UV), however, has the advantage of avoiding the cost of the catalyst, the additional process complexity and the potential hazard of catalyst leaching into the aqueous environment. Currently, information regarding the US/UV process is relatively limited, and a similar conjecture of the auxiliary role of photolysis of the ultrasonically generated H_2O_2 is proposed.[7] There is a need for more detailed information concerning the exact role of H_2O_2 in the treatment reactions and a mechanistic model to describe the US/UV process; these are addressed in this study.

✓Explains possible solution to problem with current methods

💡Do not overuse etc. If the list is exhaustive it is not needed, if not use “more stable such as H_2O and H_2O_2”.

✓Explains advantages and disadvantages of method.

✓Suggests alternative to overcome existing problems

✓Explains why this study is needed, e.g., “information…is relatively limited” “There is a need for” and “These are addressed in this study”

Dimethyl phthalate (DMP) was selected as the model compound for this study since it is an anthropogenic contaminant of environmental concern and relatively recalcitrant to degradation in the environment. It is one of the most common phthalate esters, which are a group of industrially important chemicals, widely employed as plasticizers and additives to improve the mechanical properties and flexibility of various products.[8, 9] However, DMP has been listed as a priority pollutant by the U.S. Environmental Protection Agency (USEPA) owing to its toxicological properties.[10] Substantial quantities of DMP are released into environmental water bodies through the disposal of manufacturing wastewater and from direct leaching from plastic products, leading to its widespread occurrence and potential risks on the health of humans and wildlife.

✓Explains choice for subject of study

✓Uses academic style to describe size, e.g. "substantial" others to use include "a large number" and "numerous"

💡Comment on the strengths and weaknesses of previous studies and how they relate to the current study.

✓Highlights research 'gap', i.e. what has not been studied before to make this study important

Various methods of treating DMP by AOPs have been investigated in recent years, such as O_3/H_2O_2,[11] O_3/UV,[8] TiO_2-UV,[12] and Fe(VI)-TiO_2-UV,[13] and a limited number of studies have considered the sonolytic degradation of DMP, proposing the dominant role of $OH\cdot$ radical oxidation. [14, 15] However, the potential enhancement of DMP degradation by the combination of US with UV (sonophotolysis) has not been reported so far.

2. Problem to be tackled

In view of the above, the main interest of this study is to ascertain the main mechanism of the hybrid process of US/UV in the absence of any catalyst with DMP as a chosen probe. The contribution of H_2O_2 is examined both qualitatively and quantitatively, and a novel inverted S-curve degradation model is proposed to describe the hybrid process.

✓Summarises question to be researched at end of Literature Review

3. Methodology

Chemicals. DMP (> 99% purity) and hydrogen peroxide (35%, w/w) were purchased from Sigma Aldrich Inc., USA. All the chemicals used in this study were of A.R. grade and all solvents were of HPLC grade and used without purification. Sulfuric acid and sodium hydroxide were used for pH adjustment. The deionized-distilled water used throughout all the experiments was obtained from a Millipore Waters Milli-Q water purification system. The initial concentration of the DMP solution was 0.05 mM in all tests, and the initial pH was 6.5 ± 0.2, unless stated otherwise.

Have an introductory paragraph outlining the contents of the methodology section.

✓Uses past simple tense and passive voice to describe methodology used, e.g. "was obtained"

✓includes clear subsections, but could also number them, i.e.
3. Methodology
3.1 Chemicals
3.2 Sonolysis

Sonolysis. The sonolysis experiments were performed in a stainless steel jacketed cubic groove reactor with an effective volume of 1.5 L (tailor-made by Ning Bo Scientz Biotechnology Co., China) (see Fig. 1). Ultrasound at a frequency of 400 kHz and 120 W (nominal output power) was applied from the bottom of the reactor through six piezoelectric ceramics (with a diameter of 2 cm each) fixed underneath the bottom plate. An initial solution volume of 250 mL was used for all the experiments in this study and the ultrasonic power density determined calorimetrically was 0.0304 W·mL^{-1}.[16] The sonolysis experiments were conducted without any sparged gas. A convolute cooling finger was submerged below the liquid surface to maintain a constant solution temperature at 28 ± 2 ℃.

Photolysis. An aluminum photoreaction chamber (also tailor-made by Ning Bo Scientz Biotechnology Co.) was employed for the photolysis process, in which six lamps (maximum) can be installed on the ceiling of the chamber. In addition, a ventilation fan was installed in the chamber to prevent heat accumulation. The monochromatic ultraviolet light wavelength utilized in this study was 253.7 nm and different UV intensities could be obtained by varying the number of UV lamps. The intensity of incident UV light with 6 lamps was approximately 1.03 × 10^{-5} Einstein·L^{-1}·s^{-1} (as cited by the lamp manufacturer, Southern New England Ultraviolet Co., USA). The ultrasonic reactor described in the sonolysis study is the same reactor (container) used for the photolysis experiment for fair tests. The reactor was placed in the center of the photo-chamber and the liquid surface was adjusted manually so as to maintain a constant distance of 20 cm from the UV lamps (see Fig. 1). To ensure a stable UV output, the lamps were allowed to warm up for 10 min before conducting each experiment.

✓Avoids overly complex sentences to describe experiment

✓Uses strong subjects, i.e. "A ventilation fan was installed… to prevent heat accumulation." NOT "To prevent heat accumulation, a ventilation fan…"

Refer to the location of figures, i.e. "(see Fig 1 on page 8)"

Sonophotolytic reaction. The simultaneous US/UV (sonophotolytic) reaction was realized by placing the sonicator (i.e. the reactor) inside the photo-chamber, so that both the US and UV could be applied simultaneously (see Fig. 1). The sequential tests involving either UV followed by US, or vice versa, were carried out by respectively switching on/off either the sonicator or UV lamps, for given time periods.

✓Explains key terms, e.g. "sonophotolytic"

Analysis. During irradiation, 1.0-2.0 mL aliquots were withdrawn from the reactor at predetermined time intervals for further analysis. The DMP concentration was quantified by HPLC (Waters 717), consisting of a pump (Waters 515), a UV detector (Waters 2489), an auto sampler (Waters 717), and a Brava C18-BDS column (5µm, 25 × 0.46 cm). The maximum absorption wavelength (λ_{max}) selected for DMP detection was 230 nm. A mixture of acetonitrile/water (60:40, v/v) was used as the mobile phase at a flow rate of 1.0 mL·min^{-1}. The concentration of H_2O_2 was determined by measuring the absorbance of titanium peroxide (TiO_2^{2+}) complex formed from the reaction of $TiOSO_4$ with H_2O_2 using the Biochrom Libra S12 spectrophotometer at 405 nm.[17] All the experiments were conducted at room temperature (air-conditioned at 24 ± 1 ºC) in duplicate and the error is less than 5%.

✓Numbers figure (Fig. 1.) and gives figure title

💡Place the figure near to where it is described in the text, i.e. the previous section.

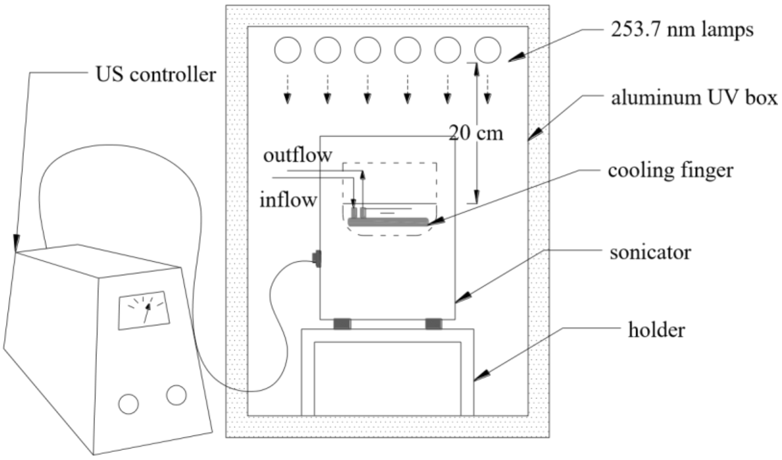


Fig. 1. The diagram of the experimental setup

4. Preliminary Results

💡 Give a short introductory paragraph outlining this section and if possible linking to the previous section.

4.1 Effect of UV light intensity. The DMP photo-decomposition with different UV light intensities (viz. different numbers of lamps) is shown in Fig. 2, where pseudo first-order kinetics was assumed. As expected, the rate of compound degradation increased systematically with light intensity, but the extent of DMP degradation by photolysis alone was relatively minor. Thus, only 21.3% of DMP was eliminated after 150 min at the greatest applied light intensity (6 lamps), most likely resulting from the poor quantum yield at 253.7 nm. The photo-degradation of DMP was found to follow closely pseudo first-order kinetics and the rate constant (*k*) was linearly related with the light intensity (inset of Fig. 2). The theoretical photo-decay rate of a specific compound can be expressed by the following relationship (Eq. 1): [18]

✓Outlines key findings, giving most important figures
✓Suggests possible reasons for findings using tentative language, e.g. "most likely"

$$k = 2.303\phi I_{\lambda}\varepsilon_{\lambda} l \qquad (1)$$

where ϕ is the quantum yield (mol·Einstein^{-1}), I_λ is the light intensity (Einstein·L^{-1}·s^{-1}), ε_λ is the compound molar absorptivity (L·mol^{-1}·cm^{-1}), and l is the light path (cm). This is consistent with the experimentally observed linear correlation between k and the light intensity. By substituting the appropriate values in Eq. 1, where ε_λ is 1.43×10^3 L·mol^{-1}·cm^{-1} (measured experimentally) and l is 1.8 cm, the quantum yield was determined to be 4.1×10^{-4} mol·Einstein^{-1}. A similarly low value for ϕ (= 8.5×10^{-4} mol·Einstein^{-1}) was reported by Chen et al.. [12]

✓Numbers formula

✓Refers to formula in text, e.g. "the following relationship"

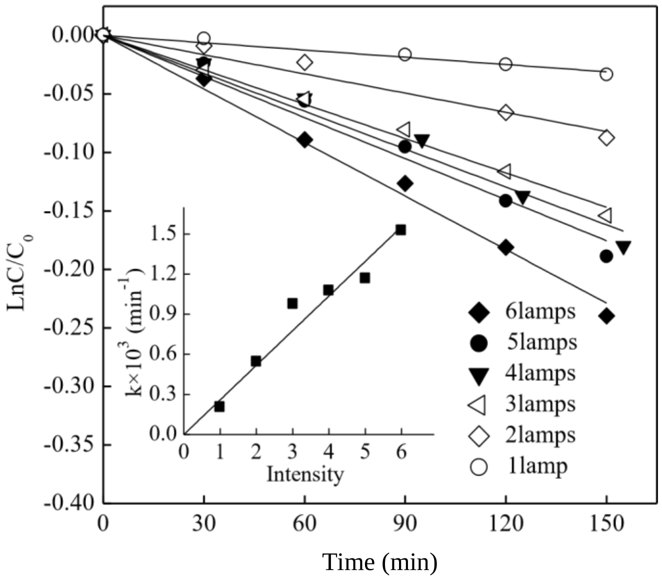


Fig. 2. Effect of UV light intensity on DMP photolytic degradation (C_0 = 0.05mM, λ = 253.7 nm).

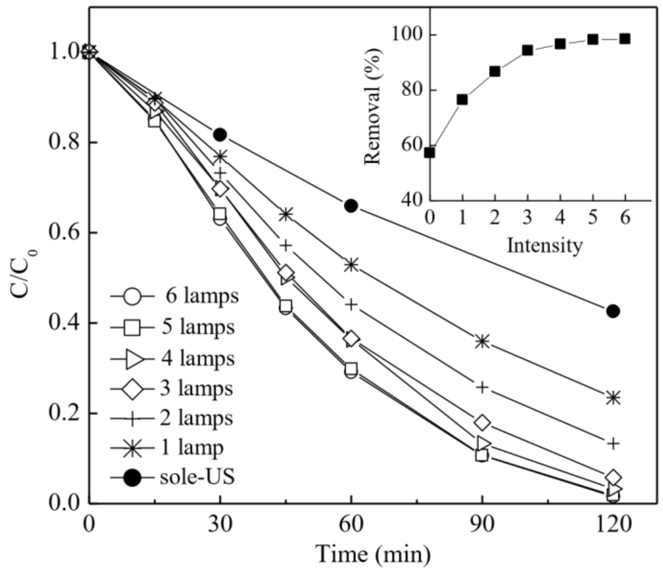


Fig. 3. Effect of UV light intensity on DMP sonophotolytic degradation (C_0 = 0.05mM, λ = 253.7 nm, US: 400 kHz-120 W).

The effect of UV light intensity was also investigated for the combined US/UV process (see Fig. 3). As with UV alone, the DMP degradation increased with UV light intensity, but the increase diminished at higher light intensities (more than 3 lamps) with the DMP degradation reaching a maximum, indicating that the UV irradiation was not a rate-limiting factor in the process (i.e. the system turns into a highly optical dilute condition, and the rate becomes less-dependent on light intensity). It was clear that the combined US/UV process significantly improved the DMP degradation (98.4% in 120 min with 6 lamps) compared to that of solely US (57.4% in 120min) or solely UV (16.6% in 120min with 6 lamps) processes. Thus, the effectiveness of the three processes could be summarized as: UV (6 lamps) < US < UV (6 lamps)/US. It was evident that the nature of the DMP degradation kinetics by the

✓Uses range of language to compare and contrast different variables and results, e.g. "also". "as with UV alone", "but" "higher" "significantly improved" "solely" "different from that alone"

✓Refers to later sections e.g. "This will be discussed in more detail later"

Give section numbers, i.e. "discussed in Section 4.4".

combined US/UV process was different from that of US and UV alone. A distinct, and repeatable, lag phase (slower kinetics) appeared in the initial period (< 30 min), which was more obvious with higher light intensities. This indicated a departure from quasi-first order kinetics in which the decay curve had the form of an inverted S-curve; this will be discussed in more detail later. In all subsequent tests the maximum UV light intensity was applied (6 lamps) in order maximize the reactions and enable the fundamental mechanisms to be investigated.

4.2 Formation of H_2O_2 during sonication. As has been established previously, H_2O_2 is produced during sonication by the interaction of US-generated radical species, either directly ($2{\cdot}OH \rightarrow H_2O_2$, $2HO_2{\cdot} \rightarrow H_2O_2$) or with water molecules ($O{\cdot} + H_2O \rightarrow H_2O_2$).[19, 20] In this study, the formation of H_2O_2 during sonication was evaluated qualitatively and quantitatively both in pure water and 0.05 mM DMP solution, and the results are presented in Fig. 4. The results showed that the concentration of H_2O_2 increased linearly with sonication time, and that the concentration increase in the 0.05 mM DMP solution was less than that in pure water, owing to the higher consumption of hydroxyl radicals (the main precursor in forming H_2O_2) by DMP and its intermediates. Based on this result, the kinetics of H_2O_2 formation during sonolysis can be formulated as Eq. 2.

✓Uses present simple tense to refer to general processes, e.g. "is produced" and uses past simple tense to refer to current study.

✓Uses text to explain main findings in words and in figures, e.g. "The results showed that..."

$$\frac{d[H_2O_2]}{dt} = k_1 \qquad (2)$$

where k_1 was determined to be 6.97×10^{-4} and 9.75×10^{-4} mM·min^{-1} for 0.05 mM DMP solution ($R^2 = 0.9980$) and pure water ($R^2 = 0.9951$), respectively.

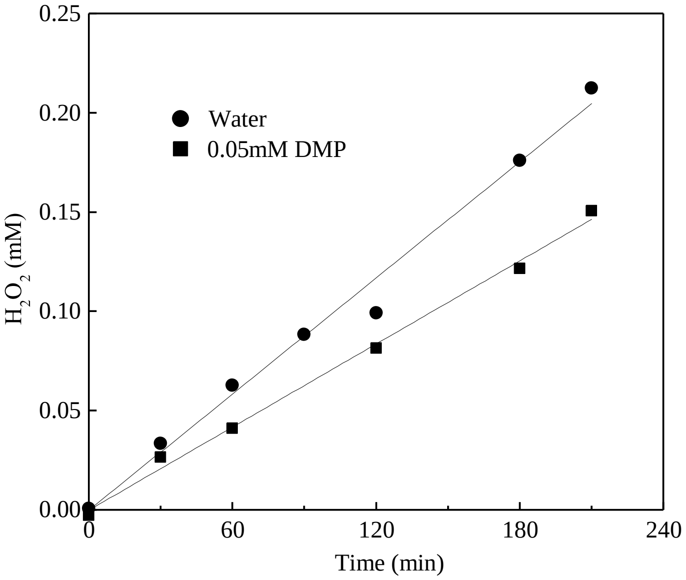


Fig. 4. Variation of H_2O_2 concentration over sonication time (US: 400 kHz - 120 W)

4.3 DMP degradation by UV/H_2O_2 process. Since the presence of H_2O_2 in the sonolysis process was confirmed, the combined process of US/UV also incorporates the advanced oxidation process of UV/H_2O_2. In order to ascertain the features of the UV/H_2O_2 process, the degradation of DMP directly by the UV/H_2O_2 process was investigated with various initial H_2O_2 concentrations, ranging from 0.05 to 0.50 mM (concentrations selected based on the results of the sonolytic experiment). The possible contribution of direct oxidation by H_2O_2 was found to be negligible from the results of control tests

✓Uses reduced passive voice to more effectively refer to figures, e.g. "The results summarised in Fig 5 indicated that…" rather than "The results which are summarised in Fig 5 indicated that…"

which showed there was no detectible change in DMP concentration in the presence of 30 mM H_2O_2 solution during 180 min. The results summarised in Fig. 5 indicated that the DMP degradation followed pseudo first-order kinetics ($R^2 > 0.9950$) for each of the applied H_2O_2 concentrations. Thus, the DMP degradation by UV/H_2O_2 process can be expressed as:

$$-\frac{d[\mathrm{DMP}]}{dt} = k_2[\mathrm{DMP}] \qquad (3)$$

where k_2 was 0.0265 min^{-1} in the presence of only 0.05 mM initial H_2O_2, which is 18 times greater than that observed with UV alone (0.0015 min^{-1}). Thus, it can be concluded that DMP photo-degradation is accelerated substantially by the presence of H_2O_2, attributed mainly to the generation of hydroxyl radicals from the photo-decomposition of H_2O_2.[21, 22]

✓Uses tentative language to refer to conclusions, e.g. "attributed mainly to..."
✓Uses present simple tense to discuss conclusions

The pseudo first-order rate constant (k_2) was found to increase linearly with the initial concentration of H_2O_2 (inset of Fig. 5). The value of k_2 therefore can be further expanded to a more general rate expression including two reaction mechanisms as follows:

$$k_2 = k_3[\mathrm{H_2O_2}]_0 + k_{\mathrm{UV}} \qquad (4)$$

where k_3 was determined to be 0.5060 $\text{min}^{-1}\cdot\text{mM}^{-1}$ and the intercept (k_{UV}) is the direct photolysis rate constant ($[H_2O_2]_0 = 0$ mM), with the value of 0.0015 min^{-1}.

Hence, Eq. 3 can be re-written by substituting Eq. 4 as:

$$-\frac{d[\text{DMP}]}{dt} = \{k_3[\text{H}_2\text{O}_2]_0 + k_{\text{UV}}\}[\text{DMP}] \qquad (5).$$

However, it should be noted that the concentration of H_2O_2 is replenished continuously in the US/UV process (Fig. 4) rather than one-off feed. In order to clarify the kinetic property of DMP photolysis under the condition of a continuous supplement with H_2O_2, stepwise-UV/H_2O_2 was examined by stepwise dosing H_2O_2 (thrice in total), during the reaction (cross points in Fig. 5). The reaction was initiated with 0.05 mM H_2O_2, and then additional concentrations of 0.05 and 0.10 mM H_2O_2 were added at 20 and 40 min, respectively. For each resulting total H_2O_2 concentration (i.e. 0.05, 0.10 and 0.20 mM), the overall DMP degradation demonstrated first order kinetics and a stepwise increase in rate constant which was identical to the rate constant obtained when the same overall H_2O_2 concentration was added at the beginning of the reaction. From this it was evident that the reaction rate was only dependent on the prevailing H_2O_2 concentration and was not sensitive to H_2O_2 consumption during the reaction.

✓ Uses range of structures to describe ordering of process, e.g. "initiated", "then, additional", "respectively", "at the beginning of", "during the reaction"

In short, irrespective of the dosing pattern, the DMP decay rate in UV/H_2O_2 process is mainly determined by the total dosage of H_2O_2 and pseudo first-order kinetics

Be more specific with linking words, rather than "In short" use "in fact", "To sum up".

is applicable for the reaction span without any supplement with H_2O_2. Thus, Eq. 4 could be restated as the rate constant of both one-off and stepwise UV/H_2O_2 (at a certain moment t), where the $[H_2O_2]_0$ should be re-defined as the total dosage up to the moment t.

The consistent agreement with first-order kinetics in the DMP reactions with UV/H_2O_2 (Fig. 5) over periods up to 60 min indicated that the concentration of H_2O_2 during the reactions was not limiting. Thus, although being consumed during the reaction, the H_2O_2 concentration, and thus the ·OH radical concentration, was always in excess relative to the DMP concentration. From Eq. 1 the photolytic consumption of H_2O_2 can be estimated by assuming values for the quantum yield (ϕ = 0.98 mol·Einstein^{-1} [23]) and molar absorptivity (ε_λ = 19.0 L·mol^{-1}·cm^{-1} [24]), giving a rate, k, of 8.0×10^{-4} s^{-1}. This low value for the photolysis rate corresponds to a reduction of only 38% in H_2O_2 concentration over 10 min from an initial concentration of 0.5 mM, and hence supports the assumption that the concentration of H_2O_2 was not rate-limiting in the experiments.

✓Develops paragraph with clear topic sentence
✓Develops argument using logical connectives, "Thus", "Hence"
✓Restates main point in final sentence

By comparing the calculated initial rate of H_2O_2 consumption, where theoretically one mole of H_2O_2 produces two moles of ·OH radicals ($k_{OH\cdot} = 2 \times 8.0 \times 10^{-4} \times [H_2O_2]_0$, mM· s^{-1}), and the experimentally measured initial rate of DMP degradation according to Eq. 5 (ignoring direct photolysis) under the corresponding conditions ($[DMP]_0$ = 0.05 mM, $k_{DMP} = 0.5060/60 \times [H_2O_2]_0 \times 0.05$, mM· s^{-1}), the theoretical reaction stoichiometry (·OH: DMP) was estimated to be 3.8:1.

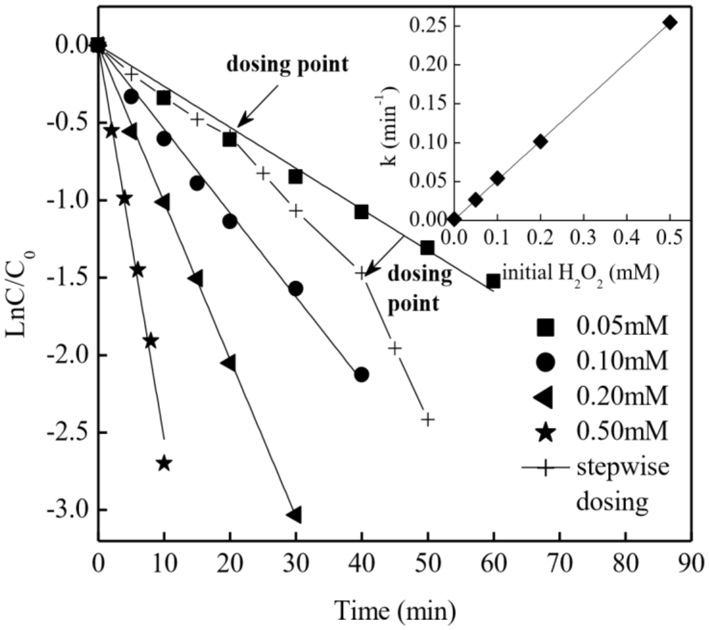


Fig. 5. Degradation of DMP by UV/H_2O_2 process with different initial H_2O_2 concentrations and degradation of DMP by stepwise UV/ H_2O_2 process (UV: λ = 253.7 nm, 6 lamps, $[DMP]_0 = 0.05$ mM).

4.4 Effect of initial solution pH. Solution pH is an important parameter influencing the efficiency of numerous AOPs. However, information regarding the effect of pH on the performance of the combined US/UV process is scarce. Fig. 6 summarises the results of the sonophotolytic degradation of DMP at different initial pH values, in the range from 2.44 to 10.89. The solid data points in the inset of Fig. 6 depict the overall removal of DMP after 60 min under various initial pH. The results show a systematic reduction in DMP degradation with increasing pH, except at pH 10.89. An investigation of the hydrolysis of DMP over the same pH range showed no hydrolysis effects except under the strong basic conditions at pH 10.89, where 31.8% of DMP was hydrolyzed in 60 min. By excluding the hydrolysis effect,

✓ Uses academic language to describe quantities, e.g. "numerous", "scarce"

Place the background in a short introductory paragraph with a statement of the main idea of this section.

the hollow data point shown in the inset of Fig. 6 is the net DMP removal by sonophotolysis which was consistent with the trend of decreasing DMP removal with increasing initial pH. Since DMP is a non-dissociating compound, the possible reasons for the decrease in DMP degradation with increasing pH are: (a) the decreasing oxidation potential of OH· with increasing pH;[25] (b) the rapid consumption of OH· in alkaline solution according to reaction R1, where $k_{\text{forward}} = 1.2 \times 10^{10}\ M^{-1}\cdot s^{-1}$ and $k_{\text{back}} = 9.3 \times 10^{7}\ s^{-1}$,[5] and reaction R2, owing to the presence of the conjugate base of H_2O_2, HO_2^-, in alkaline conditions ($pK_a = 11.6$), where the rate constant, k_{HO2-} is $7.5 \times 10^{9}\ M^{-1}\cdot s^{-1}$ (cf. $k_{H2O2} = 2.7 \times 10^{7}\ M^{-1}\cdot s^{-1}$): [25]

$$\cdot OH + OH^- \leftrightarrow H_2O + O\cdot^- \qquad (R1)$$

$$\cdot OH + HO_2^- \rightarrow O_2\cdot^- + H^+ \qquad (R2)$$

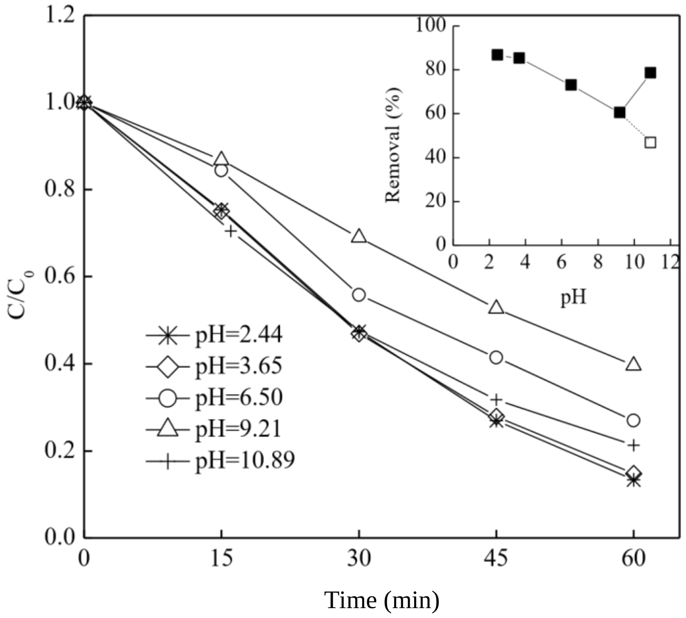


Fig. 6. Effect of initial solution pH on DMP sonophotolytic ($[DMP]_0$ = 0.05 mM, λ = 253.7 nm, 6 lamps, 400 kHz - 120 W).

4.5 Sequential and simultaneous tests of US and UV. In order to examine the US/UV process in more detail and to confirm synergistic effects, DMP reactivity tests were conducted with the US and UV in series (in alternative order) and together. Thus, DMP solutions were first irradiated with UV (or US) for 120 min, and then transferred to undergo US (or UV) irradiation for a further 120 min. The results were compared with those of the combined US/UV process and can be seen in Fig. 7. A rapid DMP degradation was achieved by the combined US/UV process with an almost complete elimination of DMP (> 98%) in 120 min, while the corresponding removal values for the individual US and UV processes were only 53.9% and 15.4%, respectively. These results suggest a synergistic, rather than additive, behavior in the combined US/UV process. For simplification, an approximate pseudo first-order rate constant of the combined process, k_{USUV}, was calculated from the data and found to be 0.0238 min^{-1}. Consequently, a synergy index could be determined as follows:

✓Develops paragraph:
- a. Reason for procedure
- b. General procedure
- c. Specific details of procedure
- d. How the results were analysed
- e. Findings
- f. Conclusions

✓Uses tentative language to refer to conclusions, e.g. "suggest" when explaining possible conclusions

$$\text{Synergy Index} = \frac{k_{\mathrm{USUV}}}{k_{\mathrm{UV}} + k_{\mathrm{US}}} = \frac{0.0238}{0.0076 + 0.0015} = 2.6154 > 1$$

For the cases where the US and UV processes are applied in series, the residual DMP in the US pre-treated solution was totally removed by subsequent exposure to UV light for an additional 120 min, whereas for the UV pre-treated solution 36.7% DMP still remained after 120 min of sonication. The greater degradation of DMP in the US→UV process indicates that photolysis of US generated products, particularly H_2O_2, accelerates the DMP degradation. The concentration of H_2O_2 in solution was monitored during the sequential and combined US/UV tests (Fig. 7b). In the case of the sequential US UV arrangement it is evident that H_2O_2 accumulates continuously during the US phase and then is rapidly consumed in the following UV phase, via direct photolysis. In contrast, the build-up of H_2O_2 in the combined US/UV sonophotolytic process was much slower than the US alone, representing the balance between H_2O_2 generation (by US) and consumption (by UV).

While the experimental results indicated pseudo first-order kinetics for the degradation of DMP by sonolysis and photolysis separately, with respective rate constants of k_{US} = 0.0076 min^{-1} and k_{UV} = 0.0015 min^{-1}, the degradation by sonophotolysis did not appear to obey first-order kinetics; this contrasts with the study by Rong et al. [26] which found that *p*-chlorophenol degradation by US, catalyst-free UV and their combination, all obeyed first-order kinetics. From the DMP degradation results shown in Fig. 7(a), a slight lag phase was evident in the initial 30 min period, followed by a more rapid degradation until the DMP was nearly completely consumed. In order to explain this behavior a phenomenological model was developed which is described below.

✓Uses tentative language to refer to conclusions, e.g. "did not "
✓Uses names for key study, e.g. "Rong et al."
✓Compares findings from different studies

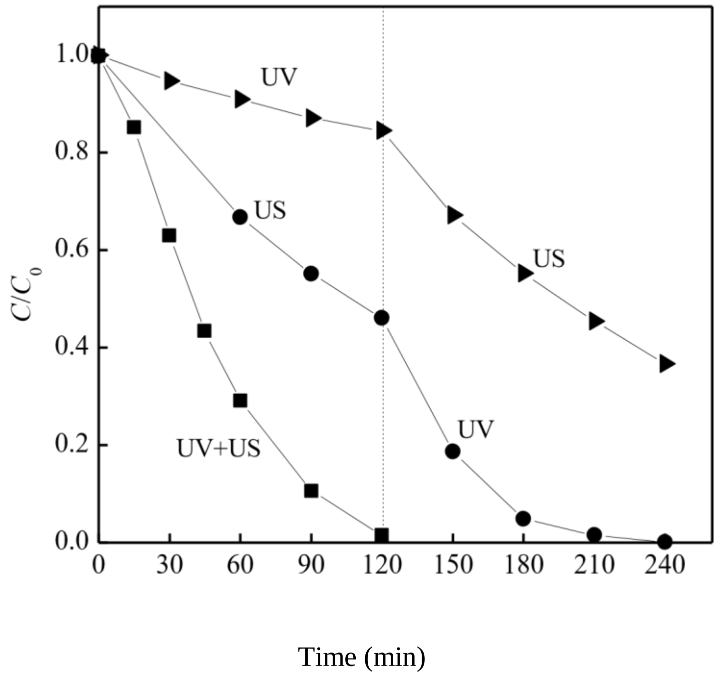


Fig. 7 (a). DMP degradation performance of sequential and simultaneous experiments using US (400 kHz - 120 W) and UV (253.7 nm, 6 lamps), $[DMP]_0$ = 0.05 mM.

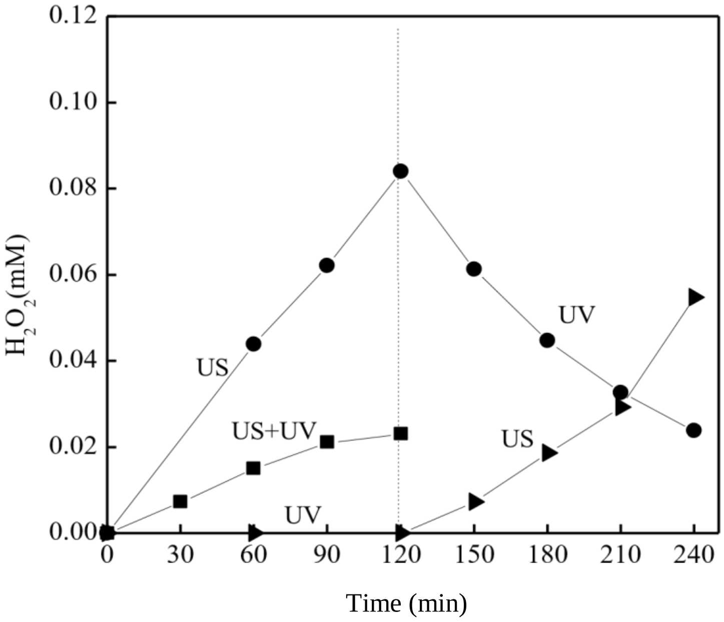


Fig. 7 (b). The variation of H_2O_2 concentration during the sequential and simultaneous tests using US (400 kHz – 120 W) and UV (253.7 nm, 6 lamps), $[DMP]_0$ = 0.05 mM.

4.6 Modeling the sonophotolytic degradation of DMP. The main reactions involved in the sonophotolytic degradation of DMP are summarized as follows (R3 – R8):

$$H_2O \xrightarrow{)))} \cdot OH_{)))} + \cdot H_{)))} \qquad (\mathrm{R3})$$

$$\mathrm{DMP} + \cdot OH_{)))} \xrightarrow{k_{US}} \mathrm{Products} + H_2O \qquad (\mathrm{R4})$$

$$\mathrm{DMP} + h\nu \xrightarrow{k_{UV}} \mathrm{Products} \qquad (\mathrm{R5})$$

$$2 \cdot OH_{)))} \xrightarrow{k_1} H_2O_2 \qquad (\mathrm{R6})$$

$$H_2O_2 + h\nu \longrightarrow 2 \cdot OH \qquad (\mathrm{R7})$$

$$\mathrm{DMP} + \cdot OH \longrightarrow \mathrm{Products} + H_2O \qquad (\mathrm{R8})$$

Where))) denotes the ultrasonic wave and the subscript $_{)))}$ means the products generated by ultrasonic irradiation.

To facilitate the modeling procedure, the US/UV process is divided into two dependent processes based on the above analysis, a US part and a UV/H_2O_2 part, and the ultrasonically produced H_2O_2 linking the two parts. In this way, the above reactions can be simplified to:

✓Uses present simple tense to discuss theoretical content of study, i.e. "process is divided into…"

$$\mathrm{DMP} + \cdot\mathrm{OH}_{)))} \xrightarrow{k_{\mathrm{US}}} \mathrm{Products} + \mathrm{H_2O} \qquad \text{(R4)}$$

$$2 \cdot \mathrm{OH}_{)))} \xrightarrow{k_1} \mathrm{H_2O_2} \qquad \text{(R6)}$$

$$\mathrm{DMP} + \mathrm{H_2O_2} \xrightarrow[h\nu]{k_4} \mathrm{Products} + \mathrm{H_2O} \qquad \text{(R9)}$$

where k_4 represents the rate constant of the UV/H_2O_2 part in the US/UV process, and R9 combines reaction R5, R7 and R8.

In deriving the model the following assumptions were made: (a) both the sonolytic and photolytic degradation of DMP follow pseudo first-order kinetics; (b) DMP degradation is principally by reactions R4 and R9 (i.e. DMP is oxidized by OH radicals generated via either R3 or R7, in which the other minor oxidants, if any, contributing for DMP elimination are ignored); (c) the sonolytic degradation of DMP in the combined US/UV process (R4) is not influenced by the UV process; (d) Eq. 4 is applicable to represent the DMP degradation via the UV/H_2O_2 process where the $[H_2O_2]_0$ term is defined as the total dosage up to moment *t*.

Present list of four or more elements in a vertical list with each point on a new line.

The overall DMP degradation rate by the US/UV process is therefore assumed to be the sum of reactions R4 and R9:

$$-\frac{d[\mathrm{DMP}]}{dt} = k_{\mathrm{US}}[\mathrm{DMP}] + k_4[\mathrm{DMP}] \qquad (6)$$

It should be noted that the UV/H_2O_2 part in this process (the second term on the right-hand side of Eq. 6) is distinct from the traditional UV/H_2O_2 process as the supplementation of H_2O_2 is in a continuous mode by sonication rather than an one-off dosing at the beginning. From the observation of the stepwise UV/H_2O_2, DMP removal rate constants in UV/H_2O_2 process linearly depends on the total dosage of H_2O_2 regardless of the dosing manner (Fig. 5). Additionally, the UV/H_2O_2 pathway in the US/UV process could be deemed as consisting of numerous tiny stepwise-UV/H_2O_2 processes and the instantaneous degradation rate (k_4) at moment t is assumed to be linearly related with the total provision of H_2O_2 up to moment t based on Eq. 4, so the following equation could be obtained:

✓Uses "note with subject, e.g. "It should be noted that…" this is better than, "Note that…"

$$k_4 = k_3 \cdot (k_1 \cdot t) + k_{\mathrm{UV}} \qquad (7)$$

where $k_1 \cdot t$ is the H_2O_2 concentration generated by the US system up to time t (Eq. 2).

Combining Eq. 6 and Eq. 7 gives the following expression:

$$-\frac{d[\mathrm{DMP}]}{dt} = k_{\mathrm{US}}[\mathrm{DMP}] + \{k_3 \cdot (k_1 \cdot t) + k_{\mathrm{UV}}\}[\mathrm{DMP}] \qquad (8).$$

Using a definite integral of Eq. 8 to solve for the DMP concentration, C, gives:

$$\int_{C_0}^{C} -\frac{dC}{C} = \int_0^t \{(k_{\mathrm{US}} + k_{\mathrm{UV}}) + k_3 \cdot k_1 \cdot t\} dt \qquad (9).$$

Finally, the following solution (empirical model) is obtained:

$$C = \exp\left[\ln C_0 - (k_{US} + k_{UV}) \cdot t - \frac{k_3 k_1 t^2}{2}\right] \quad \text{, or}$$

$$\frac{C}{C_0} = \exp\left[-(k_{US} + k_{UV}) \cdot t - \frac{k_3 k_1 t^2}{2}\right] \qquad (10)$$

where C is the DMP concentration at time t (mM); C_0 is the initial concentration of DMP (mM); k_{US} and k_{UV} are the pseudo first-order rate constants for the solely US and solely UV processes, respectively (min^{-1}); k_3 is the gradient shown in Fig. 5 (inset) ($min^{-1} \cdot mM^{-1}$); k_1 is the gradient of the ultrasonically generated H_2O_2 ($mM \cdot min^{-1}$) (Eq. 2). By inspection the form of Eq. 10 satisfies the following limiting conditions: $t \rightarrow 0, {}_0C \rightarrow C$; and $t \rightarrow \infty, C \rightarrow 0$.

A comparison between the model and experimental data is given in Fig. 8, which demonstrated a good agreement, thereby supporting the assumptions that were made in developing the model. It is believed that the model provides a useful representation of the interacting US/UV processes and reveals the synergetic role of H_2O_2 via the two characteristic constants, k_1 and k_3. The derivative of Eq. 10, dC/dt, gives the rate of DMP degradation at any given reaction time, and this is shown graphically in the inset of Fig. 8. The two phases of increasing and decreasing reaction rate are evident, where the first phase corresponds to the beneficial increase in H_2O_2 concentration, and the second phase corresponds to the declining DMP concentration; the value of dC/dt at time zero represents the term $C_0 \times (k_{US}+k_{UV})$, or the rate without the participation of H_2O_2.

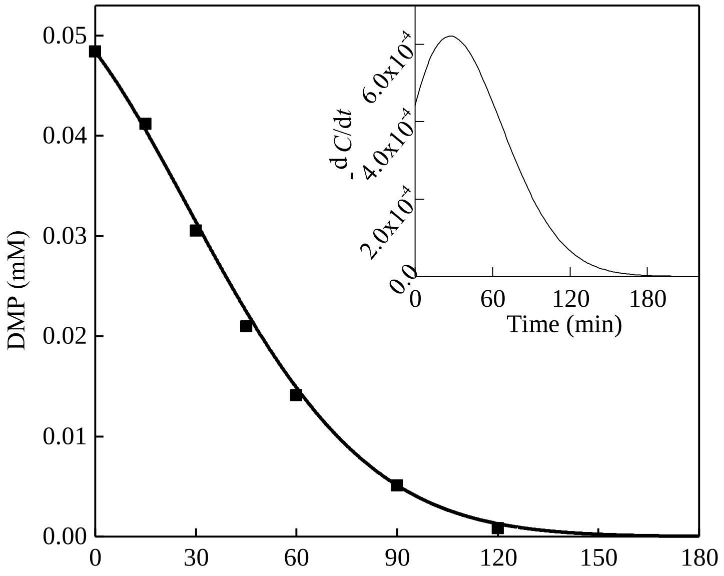
✓Uses passive voice to appear more objective, e.g. "It is believed…"

The maximum of the dC/d*t* curve, the inflection point on the *C*-*t* curve, indicates the maximum degradation rate and the time at which this occurs. This critical point can be determined by the second derivative of Eq. 10, and the corresponding $t_{\max}$ (critical time) and d*C*/d*t* $_{\max}$ (critical rate) are given below:

$$t_{\max} = \frac{\sqrt{k_3 k_1} - (k_{\mathrm{US}} + k_{\mathrm{UV}})}{k_3 k_1} \qquad (11)$$

$$\frac{\mathrm{d}C}{dt}_{\max} = \sqrt{k_3 k_1} \times \exp\left[(\mathrm{Ln}C_0 - \frac{1}{2}) + \frac{(k_{\mathrm{US}} + k_{\mathrm{UV}})^2}{2 k_3 k_1} \right] \qquad (12)$$

Using the experimental data and the above equations, the values for the critical time and maximum degradation rate were calculated to be 27.4 min and 6.21×10^{-4} mM·min^{-1}, respectively. It is evident that the position of the critical point and the shape of the degradation curve are determined by the efficiency of the two dominant mechanisms and the properties of the target compound.



Time(min)

Fig. 8. Modeling the process of US/UV and comparison with the experimental data. (UV: 253.7 nm, 6 lamps; US: 400 kHz – 120 W; k_{US} = 0.0076 min^{-1}, k_{UV} = 0.0015 min^{-1}, k_3 = 0.5060 min^{-1}·mM^{-1}, k_1 = $6.97\times10^{-}4$ mM·min^{-1}, C_0 = 0.0484 mM).

End the results section with a short summary of the main findings and brief statement of why these findings are important/different/interesting and how they compare to previous studies.

5. Areas to be addressed in the next period:

Include a short introductory paragraph at the start of the section. The title is not enough, i.e. "The following five areas will be addressed during the next stage of this study.".

Give a timeline in possible suggesting when work will be finished.

1. The degradation mechanism of the sonolysis, photolysis and sonophotolysis of the previously investigated compounds, DMP and atrazine, needs to be further identified in order to assess the treatment processes in eliminating the toxicity and estrogenic property of the recalcitrant compounds.

2. The potential treatment performance of the HFUS/UV process will be further investigated using other model EDC compounds, namely, nonylphenol and di-butyl phthalate under the optimal conditions to quantify the reaction kinetics and degradation mechanisms.

3. Other process parameters (e.g. ionic strength, types of solvents, solution surface tension, etc) will be investigated using an appropriate probe based on the above tests results to examine the mechanism of the heterogeneous microenvironment of the liquid-gas bubble condition.

Avoid using both "e.g." and "etc." in the same clause. Only e.g. is needed here.

4. The performance of the HFUS/UV process will be bench-marked by comparison with parallel tests using UV alone, and ozone, in order to comfirm the relative superiority of the AOT.

5. The potential general treatment benefits of the HFUS/UV process for upgrading secondary wastewater effluents will be investigated in experiments using real wastewater samples, with and without spiked reference compounds. The assessment will be based on quantifying changes in general physic-chemical parameters (eg. DOC, colour), toxicity and estrogenic activity.

List more fully i.e. "in general physic-chemical parameters, such as DOC and colour, toxicity and estrogenic activity…"

References

[1] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods, Advances in Environmental Research, 8 (2004) 553-597.

[2] W.H. Song, T. Teshiba, K. Rein, K.E. O'Shea, Ultrasonically induced degradation and detoxification of microcystin-LR (cyanobacterial toxin), Environmental Science & Technology, 39 (2005) 6300-6305.

[3] N.L. Stock, J. Peller, K. Vinodgopal, P.V. Kamat, Combinative sonolysis and photocatalysis for textile dye degradation, Environmental Science & Technology, 34 (2000) 1747-1750.

[4] P.R. Gogate, S. Mujumdar, A.B. Pandit, A sonophotochemical reactor for the removal of formic acid from wastewater, Industrial & Engineering Chemistry Research, 41 (2002) 3370-3378.

[5] O. Hamdaoui, E. Naffrechoux, Sonochemical and photosonochemical degradation of 4-chlorophenol in aqueous media, Ultrasonics Sonochemistry, 15 (2008) 981-987.

[6] A.J. Johnston, P. Hocking, ULTRASONICALLY ACCELERATED PHOTOCATALYTIC WASTE TREATMENT, Acs Symposium Series, 518 (1993) 106-118.

[7] R.A. Torres, C. Petrier, E. Combet, F. Moulet, C. Pulgarin, Bisphenol A mineralization by integrated ultrasound-UV-iron (II) treatment, Environmental Science & Technology, 41 (2007) 297-302.

[8] Y.H. Chen, N.C. Shang, D.C. Hsieh, Decomposition of dimethyl phthalate in an aqueous solution by ozonation with high silica zeolites and UV radiation, Journal of Hazardous Materials, 157 (2008) 260-268.

[9] J.K.H. Cheung, R.K.W. Lam, M.Y. Shi, J.D. Gu, Environmental fate of endocrine-disrupting dimethyl phthalate esters (DMPE) under sulfate-reducing condition, Science of the Total Environment, 381 (2007) 126-133.

[10] Z.W. Xu, W.M. Zhang, L. Lv, B.C. Pan, P. Lan, Q.X. Zhang, A New Approach to Catalytic Degradation of Dimethyl Phthlate by a Macroporous OH-Type Strongly Basic Anion Exchange Resin, Environmental Science & Technology, 44 (2010) 3130-3135.

[11] B. Xu, N.Y. Gao, H.F. Cheng, S.J. Xia, M. Rui, D.D. Zhao, Oxidative degradation of dimethyl phthalate (DMP) by UV/H2O2 process, Journal of Hazardous Materials, 162 (2009) 954-959.

[12] Y.H. Chen, L.L. Chen, N.C. Shang, Photocatalytic degradation of dimethyl phthalate in an aqueous solution with Pt-doped TiO(2)-coated magnetic PMMA microspheres, Journal of Hazardous Materials, 172 (2009) 20-29.

[13] B.L. Yuan, X.Z. Li, N. Graham, Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO2-UV reaction system, Water Research, 42 (2008) 1413-1420.

[14] B. Yim, Y. Nagata, Y. Maeda, Sonolytic degradation of phthalic acid esters in aqueous solutions. Acceleration of hydrolysis by sonochemical action, Journal of Physical Chemistry A, 106 (2002) 104-107.

[15] E. Psillakis, D. Mantzavinos, N. Kalogerakis, Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction, Chemosphere, 54 (2004) 849-857. [16]

T.J. Mason, J.P. Lorimer, D.M. Bates, QUANTIFYING SONOCHEMISTRY - CASTING SOME LIGHT ON A BLACK ART, Ultrasonics, 30 (1992) 40-42.

[17] D.W. O'Sullivan, M. Tyree, The kinetics of complex formation between Ti(IV) and hydrogen peroxide, International Journal of Chemical Kinetics, 39 (2007) 457-461.

[18] T.W. Chan, N.J.D. Graham, W. Chu, Degradation of iopromide by combined UV irradiation and peroxydisulfate, Journal of Hazardous Materials, 181 (2010) 508-513.

[19] Y.G. Adewuyi, Sonochemistry: Environmental science and engineering applications, Ind. Eng. Chem. Res., 40 (2001) 4681-4715.

[20] M. Inoue, F. Okada, A. Sakurai, M. Sakakibara, A new development of dyestuffs degradation system using ultrasound, Ultrasonics Sonochemistry, 13 (2006) 313-320.

[21] W. Chu, Modeling the quantum yields of herbicide 2,4-D decay in UV/H2O2 process, Chemosphere, 44 (2001) 935-941.

[22] B. Xu, N.Y. Gao, H.F. Cheng, S.J. Xia, M. Rui, D.D. Zhao, Oxidative degradation of dimethyl phthalate (DMP) by UV/H(2)O(2) process, Journal of Hazardous Materials, 162 (2009) 954-959.

[23] J.P. Hunt, H. Taube, THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE. QUANTUM YIELDS, TRACER AND FRACTIONATION EFFECTS, Journal of the American Chemical Society (U.S.), 74 5999-6002.

[24] M.S. Morgan, P.F. Vantrieste, S.M. Garlick, M.J. Mahon, A.L. Smith, ULTRAVIOLET MOLAR ABSORPTIVITIES OF AQUEOUS HYDROGEN-PEROXIDE AND HYDROPEROXYL ION, Analytica Chimica Acta, 215 (1988) 325-329.

[25] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, CRITICAL-REVIEW OF RATE CONSTANTS FOR REACTIONS OF HYDRATED ELECTRONS, HYDROGEN-ATOMS AND HYDROXYL RADICALS (.OH/.O-) IN AQUEOUS-SOLUTION, Journal of Physical and Chemical Reference Data, 17 (1988) 513-886.

[26] L. Rong, K. Yasuda, M. Nakamura, N. Kato, K. Kawakami, Y. Kitaide, Decomposition of p-chlorophenol in aqueous solution by combination of ultrasound and ultraviolet light, Journal of Chemical Engineering of Japan, 36 (2003) 1045-1049.