



Enhanced mechanism of catalytic ozonation by ultrasound with orthogonal dual frequencies for the degradation of nitrobenzene in aqueous solution

Lei Zhao^{a,b,*}, Jun Ma^{b,*}, Xuedong Zhai^a

^a School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, People's Republic of China

^b National Engineering Research Center of Urban Water Resources, State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Harbin 150090, People's Republic of China

ARTICLE INFO

Article history:

Received 20 February 2009

Received in revised form 2 July 2009

Accepted 8 July 2009

Available online 14 July 2009

Keywords:

Enhanced mechanism

Catalytic ozonation

Ultrasound

Nitrobenzene

Degradation

ABSTRACT

The experiments have been performed with a semi-continuous batch reactor to investigate the degradation efficiency of nitrobenzene in aqueous solution by ultrasound with the different orthogonal dual frequencies catalytic ozonation. The introduction of ultrasound can enhance the degradation efficiency of nitrobenzene compared to the results obtained from the processes of ozonation alone and ultrasound alone. The degradation of nitrobenzene is found to be zero-order in the two systems of ultrasound alone, and the reactions follow the pseudo-first-order kinetic model in the processes of ozone alone and ozone/ultrasound. The investigation confirms that the degradation of nitrobenzene follows the mechanism of hydroxyl radical ($\cdot\text{OH}$) oxidation, and the enhancement function is even more pronounced in the presence of ultrasound with the greater difference between the orthogonal dual frequencies due to the obvious synergetic effect between ozone and ultrasound, which increases the utilization efficiency of ozone, and accelerates the initiation of $\cdot\text{OH}$ and the formation of H_2O_2 , resulting in the rapid formation of an increasing diversity of byproducts and the advancement degree of mineralization of total organic carbon (TOC). The oxidative byproducts have been, respectively identified in the different processes selected, including *o*, *p*, *m*-nitrophenols, phenol, malonic acid, 4-nitrocatechol, nitrate ion, maleic acid, oxalic acid, hydroquinone, *p*-quinone, 1,2,3-trihydroxy-5-nitrobenzene and acetic acid.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Nitrobenzene, as a carcinogenic pollutant [1], is one of the fastest-growing end-use synthetic products of benzene [2]. Its commercial uses are reduction to aniline, solvent, metal polishes, shoe-black, perfume, dye intermediates [3,4], plastics, explosives, pharmaceuticals [5], pesticides [6] and a combustible propellant [7]. However, nitrobenzene resists to oxidation by conventional chemical oxidation due to the strong electron-withdrawing property of the nitro-group. Mineralization of nitrobenzene by microorganisms is prevented due to the effects of toxic and mutagenic deriving from nitrobenzene and its transformation on biological systems, such as nitrosobenzene, hydroxylaminobenzene and aniline [1,3]. In order to afford the inexpensive and effective processes for the water treatment, various biological treatment processes, chemical reduction methods and advanced oxidation processes (AOPs) have been studied for the degradation of nitrobenzene in aqueous solution.

In recent years, ozonation combined with ultrasound has been actively researched as a promising method of AOPs [8]. Comparing with ozonation or ultrasound alone, it appears to be more effective and uses less energy, and it has the advantages of being non-selective, leading to no secondary pollution, and being particularly effective in removing persistent and biorefractory pollutants from water [9]. Many researches have been reported on the removal of contaminants in aqueous solution by the process of ozone/ultrasound, including methyl orange, phenol, *p*-nitrotoluene, aniline, anthraquinone dye, C.I. reactive blue 19, chitosan and pentachlorophenol [10–12]. In addition, the experimental result indicates that the presence of ultrasound can enhance the ozonolysis of nitrobenzene [13]. However, there is no report on the degradation of trace nitrobenzene ($\mu\text{g L}^{-1}$ level) by ozone/ultrasound. In fact, the removal of organic micro-pollutant in water is very important to the practical operation in wastewater treatment and drinking water supply with source water of the river and the lake.

In order to further increase the degradation efficiency of ozonation and develop a convenient and clean operation for the water treatment, the comparative experiments have been performed to investigate the degradation efficiency of organic micro-pollutant in the different processes, including ultrasound alone, ozone alone and ozone/ultrasound. Nitrobenzene reacts slowly with molecular

* Corresponding authors. School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, People's Republic of China. Tel.: +86 451 82291644/86283010; fax: +86 451 82368074 (L. Zhao), tel.: +86 451 86282292/86283010; fax: +86 451 82368074 (J. Ma).

E-mail addresses: zhaolei999999@126.com (L. Zhao), majun@hit.edu.cn (J. Ma).

ozone ($0.09 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$), while reacts quickly with hydroxyl radical ($\cdot\text{OH}$) ($2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Therefore, nitrobenzene, as a special indicator of $\cdot\text{OH}$ and a major environmental pollutant, is chosen as a target organic compound due to its toxicity of the central nervous system and its refractory nature to conventional chemical oxidation. The originality of the present study is to reveal the enhanced mechanism of combined process from the aspects of the synergistic effect between ozone and ultrasound with the different orthogonal dual frequencies.

2. Experimental

2.1. Materials and reagents

The synthetic solution was prepared by spiking $50 \mu\text{g L}^{-1}$ nitrobenzene (Beijing Chemical Factory, China, purified by distillation pretreatment, 99.80%) in Milli-Q water (Millipore Q Biocel system). Other chemicals used in the experiments were analytical grade reagents. A diluted sodium thiosulphate solution was used in the experiments for quenching the reaction. Except for volumetric flasks, the other glassware was muffled overnight at 673 K. The volumetric flasks were washed by soaking them in chromic acid and then rinsing with distilled water.

2.2. Experimental procedure

The experiments were carried out in a semi-continuous ultrasonic reactor, as shown in Fig. 1, which was made entirely of stainless steel with a breadth of 11.5 cm, a depth of 11.5 cm and a height of 26.8 cm. The three flattened sides of the reactor were, respectively mounted with three series of piezoelectric transducers (3 No. each), which were arranged in series and driven at 20, 28 and 40 kHz (A, B and C field), respectively. The emitting system was connected to a frequency generator and a power supply. The ultrasonic power input of every field was 100 W. The experiment focused more attention on the enhancement function of ultra-

sound with the different orthogonal dual frequencies, namely the combined ultrasonic fields AB and AC. Therefore, typical power intensity and power density were same to AB and AC, which were 0.65 W cm^{-2} and 64.1 W L^{-1} , respectively.

Ozone was produced from pure oxygen (Harbin Gas Co. Ltd., China, 99.999%) through an XFZ-5 ozone generator (Qinghua Tongli Co. Ltd., China) at a power setting of 40 W, and was subsequently fed into the ultrasonic reactor to contact thoroughly with water samples through a porous titanium plate at the bottom of the reactor. The total applied ozone in this experiment was controlled at 1.0 mg L^{-1} . Before the experimental operation, the reactor was pre-ozonated for 4 min to satisfy any ozone demand in the reactor, and then was washed several times with distilled water to exclude any possible side effects. During the degradation experiment, the synthetic solution (4 L) with the nitrobenzene concentration of $50 \mu\text{g L}^{-1}$ was pumped into the reactor by a MP-20R magnetic pump (Shanghai Xishan Pump Co. Ltd., China) and then circulated at a rate of 4 L min^{-1} . A cooling system was kept outside the reactor and cold water was pumped from a thermostatic bath in order to control reaction temperature constantly at 298 K. Water samples were taken from the reactor at various reaction times to analyze the residual concentration of nitrobenzene. The oxidation reaction was quenched by the addition of a small amount of sodium thiosulphate solution. In addition, compared to the scavenger effect of buffer solution (HCO_3^- , CO_3^{2-} , H_2PO_4^- , and H_2PO_2^-), the degradation of trace initial nitrobenzene concentration $50 \mu\text{g L}^{-1}$ led to a slight reduction to 6.72–6.80 from initial pH 6.87 which scarcely affect the experimental results, and could be neglected. Therefore, the experiments were carried out at initial pH 6.87 in this study without adding any buffer solution to maintain the pH at a constant value.

2.3. Analytical method

The concentration of ozone in the gas was measured by iodometric titration method [14]. The concentration of residual ozone

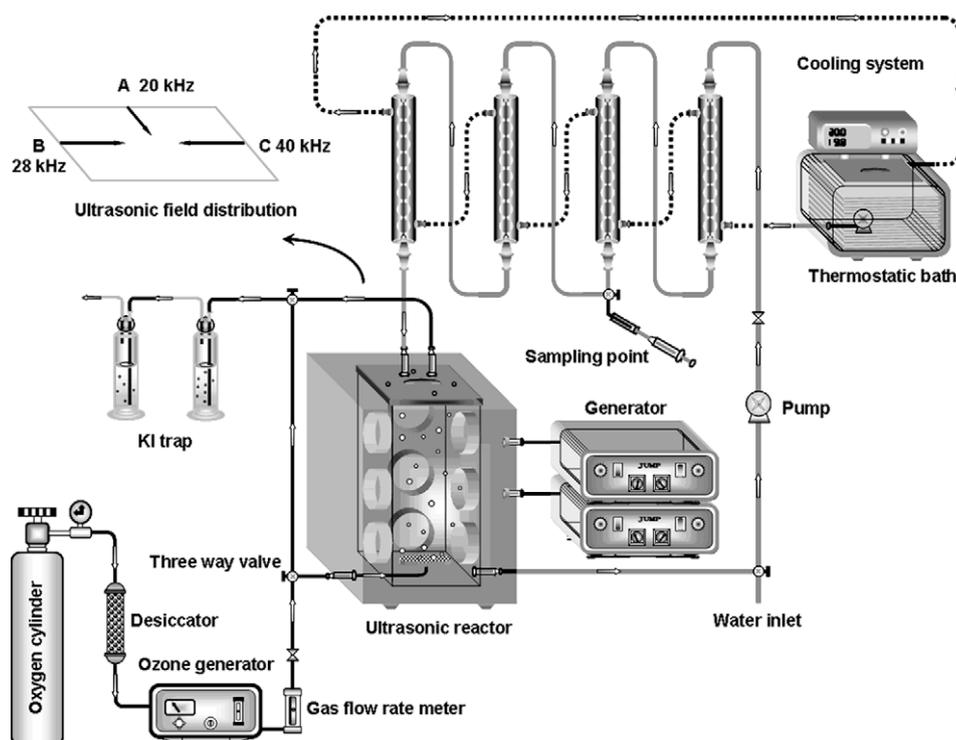


Fig. 1. Schematic of experimental apparatus.

in aqueous solution was measured by spectrophotometer using the indigo method [15]. The concentration of H_2O_2 formed in the oxidation system was determined by the photometric method [16]. The concentration of nitrobenzene was determined by a GC-14C gas chromatograph (Shimadzu, Japan) according to the previous method [17]. An electron paramagnetic resonance (EPR) experiment was conducted for the determination of $\cdot OH$ generated in the selected processes [17]. Mineralization of pollutant was monitored for total organic carbon (TOC) removal, which was determined with a TOC analyzer (Analytic Jena Multi N/C 3100). A gas chromatographic and mass spectrometric analyzes system (GC/MS, 6890GC/5973MS, Agilent, USA) and ion chromatography (IC, CDD-6A, Shimadzu Co., Japan) were used to identify the byproducts of the degradation of nitrobenzene [18].

3. Results and discussion

3.1. Degradation efficiency of nitrobenzene in the selected processes

The degradation efficiency of nitrobenzene was investigated in the selected processes, including AB, AC, ozone alone, ozone/AB and ozone/AC. The results are illustrated in Fig. 2.

As shown in Fig. 2, after the 60 min treatment of a nitrobenzene aqueous solution of $50 \mu g L^{-1}$, the degradation efficiency of nitrobenzene in the process of ozone alone is 32.5%, and ultrasonic fields with the different orthogonal dual frequencies of AB and AC only results in the degradation of 14.2% and 20.7%, respectively. The combined processes of ozone/AB and ozone/AC can enhance greatly the degradation efficiency of nitrobenzene. Comparing the result of ozone/AB with the cumulative effect of ozone alone and AB, an increment of approximately 11.9% of nitrobenzene degradation is observed. Under the same experimental conditions, ozone/AC system leads to about 83.8% nitrobenzene conversion, indicating an increment of 30.6% compared to the cumulative effect of ozone alone and AC, suggesting that the combined processes of ozone with ultrasound selected by the present study can produce the synergetic effect to improve the degradation of nitrobenzene in aqueous solution, and the process of ozone/AC can obtain the more obvious synergetic effect.

In addition, the results of kinetics investigation are shown in Fig. 3. Based on normalized concentration (C/C_0) versus reaction time, the linearity of the plots in Fig. 3a depicts that the degrada-

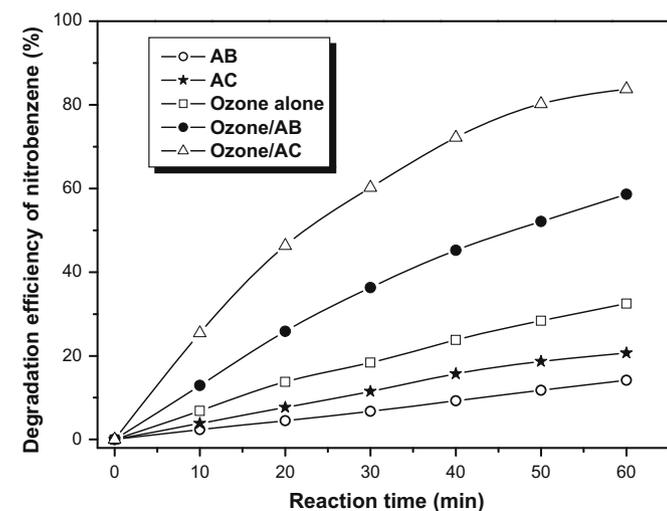


Fig. 2. Comparison of the degradation efficiency of nitrobenzene in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu g L^{-1}$; total applied ozone: $1.0 mg L^{-1}$).

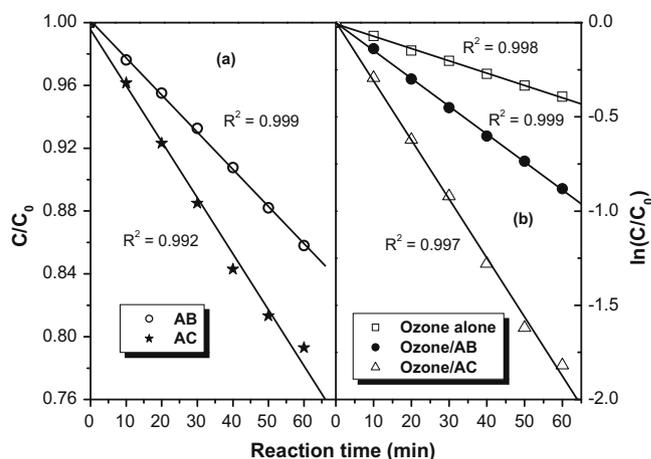


Fig. 3. Kinetic plots for the degradation efficiency of nitrobenzene in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu g L^{-1}$; total applied ozone: $1.0 mg L^{-1}$; C: the instantaneous concentration of nitrobenzene; C_0 : the initial concentration of nitrobenzene; (a) kinetic plots of the processes of AB and AC; (b) pseudo-first-order plots of the processes of ozone alone, ozone/AB and ozone/AC).

tion reactions are the zero-order with respect to nitrobenzene in the processes of AB and AC. The plots of $\ln(C/C_0)$ versus reaction time for representative kinetic runs are presented in Fig. 3b, and it is interesting to emphasize that the three reactions follow the pseudo-first-order kinetic model in the processes of ozone alone, ozone/AB and ozone/AC. These phenomena in Fig. 3 indicate that, as an effectively assistant enhanced method, the introduction of ultrasound with the different orthogonal dual frequencies does not cause the conversion of kinetic order during the ozonation for the degradation of nitrobenzene.

Generally, it is now widely believed that ozone reacts in aqueous solution on various organic and inorganic compounds, either by direct, selective reactions of molecular ozone or through a radical type reaction involving $\cdot OH$ [19,20]. Since the oxidizing potential of $\cdot OH$ is much higher than that of molecular ozone, $\cdot OH$ is a less selective and more powerful oxidant than molecular ozone, and it is one of the most reactive free radicals and one of the strongest oxidants [21]. Furthermore, the reaction rate constant of nitrobenzene with ozone alone is only $0.09 \pm 0.02 M^{-1}s^{-1}$ [22], while the rate constants for reaction of nitrobenzene with $\cdot OH$ is $2.2 \times 10^8 M^{-1}s^{-1}$ [23]. In fact, the initiation of $\cdot OH$ also can be, respectively observed in the processes of ultrasound alone and ultrasound/ozone [24]. Therefore, for the experimental phenomena in Fig. 2, it may be assumed that nitrobenzene is degraded mainly by $\cdot OH$ oxidation in the selected processes.

3.2. Initiation of $\cdot OH$ in the selected processes

In order to further identify the reaction mechanism of the degradation of nitrobenzene in the selected processes, the experiments were carried out to determine the initiation of $\cdot OH$ by means of the spin trapping/EPR technique, which can detect unstable radicals by measuring the intensity of DMPO- $\cdot OH$ adduct signal. The experimental results are summarized in Fig. 4.

Firstly, Fig. 4a presents the profile of the DMPO- $\cdot OH$ adduct signal in the process of ozone alone without addition of nitrobenzene. Like the profile in Fig. 4a, the spectra of the DMPO- $\cdot OH$ adduct signal in the other processes selected by the present experiment are all composed of quartet lines having a peak height ratio of 1:2:2:1, and the parameters are hyperfine constants $\alpha_N = 1.49 mT$, $\alpha_H = 1.49 mT$ and g -value = 2.0055, which coincide with those of the DMPO- $\cdot OH$ adduct as demonstrated previously [25]. These

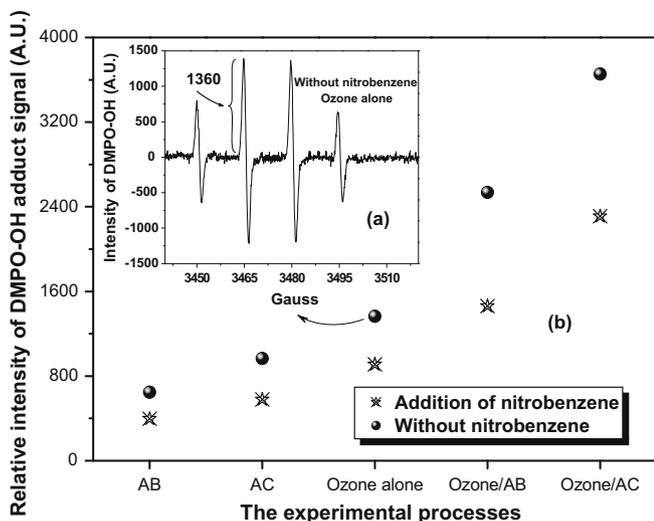


Fig. 4. Comparison of the relative intensity of DMPO–OH adduct signal in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu\text{g L}^{-1}$; total applied ozone: 1.0 mg L^{-1} ; initial DMPO concentration 100 mmol L^{-1} ; (a) the intensity of DMPO–OH adduct signal in the process of ozone alone without addition of nitrobenzene; (b) the relative intensity of DMPO–OH adduct signal in the different processes).

experimental results indicate that the initiation of $\cdot\text{OH}$ exists in the every reaction system mentioned above.

Secondly, Fig. 4b displays the relative intensity of DMPO–OH adduct signal in the different selected processes. From the results in Fig. 4b, it can be found that the relative intensity of DMPO–OH adduct signal increases according to the order of AB, AC, ozone alone, ozone/AB and ozone/AC, which is consistent with the evolution trend of degradation efficiency of nitrobenzene in these processes, confirming directly the expectation mentioned above that the degradation of nitrobenzene is mainly attributed to $\cdot\text{OH}$ oxidation.

Otherwise, comparing the relative intensity of DMPO–OH adduct signal in the every selected process, it is also observed that the process without nitrobenzene always has a stronger relative intensity than that with addition of nitrobenzene, suggesting that the former can obtain a higher concentration of $\cdot\text{OH}$ because there is no nitrobenzene, an $\cdot\text{OH}$ scavenger, to react competitively with $\cdot\text{OH}$. Based on the reaction rate constant of nitrobenzene with $\cdot\text{OH}$, this phenomenon is an auxiliary exemplification of $\cdot\text{OH}$ oxidation mechanism.

Moreover, as an intermediate species production, the initiation of $\cdot\text{OH}$ maybe influences the generation of other highly oxidative species, for example, H_2O_2 also should be formed in the selected processes.

3.3. Formation of H_2O_2 in the selected processes

As another significant new intermediate species generated from ozone decomposition, the evolution of accumulated concentration of H_2O_2 formation was investigated in the processes of AB, AC, ozone alone, ozone/AB and ozone/AC. The results are shown in Fig. 5.

From Fig. 5, it can be found that certain concentrations of H_2O_2 are formed in all the selected processes. At first, the concentration of H_2O_2 in the processes of AB and AC reaches the maximum of 0.0146 and 0.0225 mg L^{-1} at reaction time 30 and 40 min, respectively, and then decreases to 0.0059 and 0.0143 mg L^{-1} at 60 min treatment. However, in the ozone alone system, H_2O_2 forms with a rapid rate within the initial 40 min, and then the formation slows

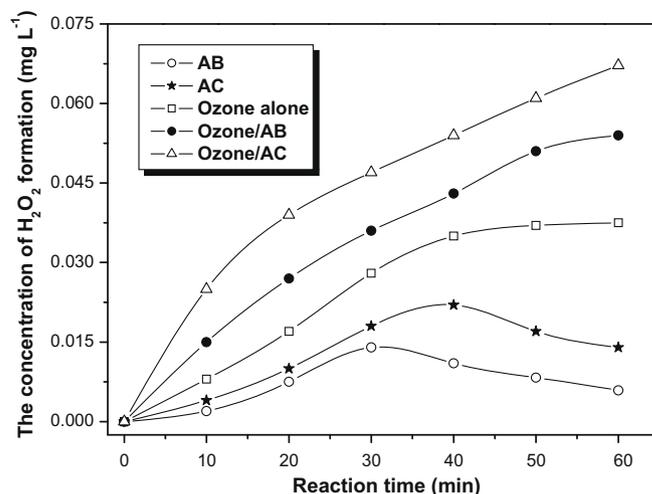


Fig. 5. Evolution of the concentration of H_2O_2 formation in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu\text{g L}^{-1}$; total applied ozone: 1.0 mg L^{-1}).

down until the concentration of H_2O_2 eventually reaches a plateau of 0.0375 mg L^{-1} at reaction time 60 min. Otherwise, the concentration of H_2O_2 formation in the processes of ozone/AB and ozone/AC increases continuously to 0.0543 and 0.0672 mg L^{-1} with the increasing reaction time to 60 min, respectively.

Comparing the results in Fig. 5, it is seen that the process of ozone alone, ozone/AB or ozone/AC can, respectively obtain a higher concentration of H_2O_2 formation than that of AB or AC system at the same reaction time point. As a consequence, the processes of AB and AC present the positive effect during the beginning 30 and 40 min, respectively, and the negative effect after this time point, resulting in an appearance of extremum. This may be attributed to the lower level of H_2O_2 formation, and the decrease in accumulated concentration of H_2O_2 is mainly due to the scavenger effect derived from the those species in the presence of reaction system and the thermal decomposition of H_2O_2 at the “hot spots” shell region formed during the ultrasonic irradiation of aqueous solution [26]. However, a plateau situation is presented in the process of ozone alone, meaning that the equilibrium is established between the positive effect and the negative effect due to the relatively higher concentration of H_2O_2 formation compared to the either case of ultrasound alone. Under the same experimental conditions, the ozone/AB and ozone/AC systems is, respectively provided with the synergistic effect for the formation of H_2O_2 to overcome the negative effect leading to a persistent increase trend of H_2O_2 formation within reaction time investigated, and the increasing trend is even more pronounced in the process of ozone/AC.

The initiation of $\cdot\text{OH}$, an active oxidative species, is the most important characteristic of AOPs. A common objective of enhanced process is to produce $\cdot\text{OH}$ in sufficient quantity to improve the degree of mineralization of the target organic compound.

3.4. Removal efficiency of TOC in the selected processes

Due to the significance of mineralization of organic compounds, the experiments were performed to detect the removal efficiency of TOC in the selected processes. The results are illustrated in Fig. 6.

The results of Fig. 6 indicate that the two combined ozone/ultrasound processes are more effective than each single one to remove TOC from aqueous solution containing nitrobenzene. The processes of AB and AC result in the removal efficiency of 7.7% and 12.4%, respectively. 37.6% of initial TOC is removed by ozone/AB

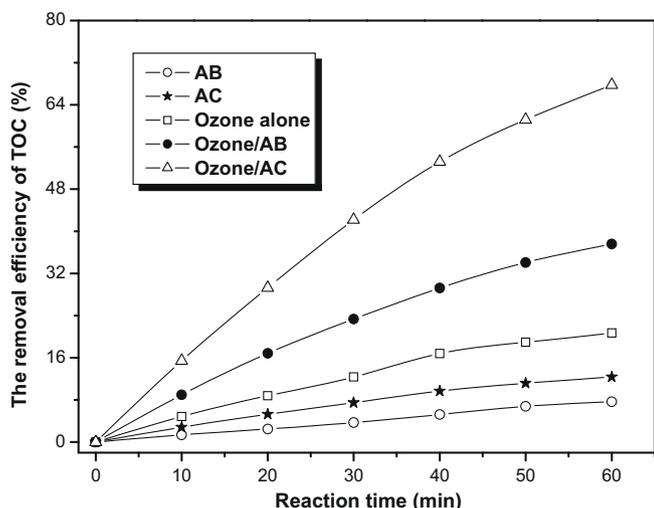


Fig. 6. Comparison of removal efficiency of TOC in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu\text{g L}^{-1}$; total applied ozone: 1.0 mg L^{-1}).

compared to 20.8% by ozone alone with the same total applied ozone of 1.0 mg L^{-1} . Simultaneously, the improvement of removal efficiency of TOC is even more pronounced in the process of ozone/AC, approximately 67.8% of initial TOC is removed after 60 min treatment.

Moreover, comparing the removal efficiency of TOC in Fig. 6 with the degradation efficiency of nitrobenzene in Fig. 2 by the same process, it is found that the removal of TOC is always lower than the disappearance of nitrobenzene, indicating that nitrobenzene has been mineralized partly into carbon dioxide and water, and the byproducts are formed via the degradation of initial compound in the every selected processes.

3.5. Formation and evolution of byproducts in the selected processes

Based on the analysis by GC/MS and IC, the formation and evolution of byproducts were identified and compared in the selected processes, and the results are shown in Fig. 7.

Combining with the determination results of initiation of $\cdot\text{OH}$ in Fig. 4, the formation and evolution of byproducts can be explained reasonably in the every selected process. At first, the results in Fig. 7 illustrate that in the process of AB, only four byproducts are detected: *p*-nitrophenol, *m*-nitrophenol, phenol and malonic acid. On the one hand, *p*-nitrophenol and *m*-nitrophenol can be formed if the attacks of $\cdot\text{OH}$ occur, respectively at γ - or β -carbons of the benzene ring of nitrobenzene via electrophilic addition [27]. On the other hand, $\cdot\text{OH}$ also can attack the nitrobenzene molecule, resulting in the occurrence of electron transfer and denitration, and the formation of phenyl radicals [28]. Phenyl radicals can be transformed into phenol through the further attack of $\cdot\text{OH}$ [29]. Otherwise, reactions of the intermediates mentioned above and nitrobenzene with $\cdot\text{OH}$ lead to the cleavage of benzene ring and the formation of oxygenated aliphatic compounds, which can be degraded to carboxylic acids via alcohols, aldehydes or ketones (from quinones), for example, malonic acid [29].

Secondly, as two new byproducts, nitrate ion and 4-nitrocatechol are found in the AC system. Nitrate ion is a result of the mineralization of organically bound nitrogen during the degradation of nitrobenzene, and the formation of 4-nitrocatechol may be explained by the electrophilic attack of $\cdot\text{OH}$ on the *ortho* position of *p*-nitrophenol and *m*-nitrophenol [30]. In fact, nitrate ion can be

measured when the concentrations of *p*-nitrophenol and *m*-nitrophenol all reach the maximum value.

As also can be observed from Fig. 7, there are three new byproducts to be measured in the process of ozone alone: maleic acid, oxalic acid and hydroquinone. The possible contribution of oxidative cleavage of a hydroxylated aromatic compound, derived from the interaction of $\cdot\text{OH}$ with nitrophenols, leads to the formation of maleic acid and oxalic acid [31]. The addition of $\cdot\text{OH}$ to *p*-nitrophenol results in the formation of hydroquinone, and hydroquinone also can be formed via a simultaneous cleavage of the nitro-group during aromatic nuclear hydroxylation. Otherwise, oxidation of phenol by $\cdot\text{OH}$ also can result in hydroquinone formation [32].

Furthermore, it should be noted that 1,2,3-trihydroxy-5-nitrobenzene and acetic acid, as the novel kinds of byproducts compared to those of the process of ozone alone, appear in the ozone/AB system. The additional formations of 1,2,3-trihydroxy-5-nitrobenzene and acetic acid are the results of aromatic nuclear hydroxylation of 4-nitrocatechol and the further $\cdot\text{OH}$ oxidation of malonic acid, respectively [33,34].

Notice from Fig. 7 that the degradation of nitrobenzene in the process of ozone/AC leads to the appearance of other byproducts: *p*-quinone and *o*-nitrophenol. The formation of *p*-quinone is derived from the further degradation of hydroquinone through the abstraction of two hydrogens [32], and *o*-nitrophenol comes from the $\cdot\text{OH}$ attack of nitrobenzene at the α -carbon via electrophilic addition [27].

Comparing the results of Fig. 7, it is obvious that the combined process of ozone/AB or ozone/AC increases, respectively the concentrations and diversities of byproducts, and the appearance time of byproducts also becomes shorter correspondingly, and the improvement of them is even more pronounced in the ozone/AC system. Also, it should be remembered that most byproducts achieve nearly the complete conversion in process of ozone/AC. Though byproducts are rapidly produced from the beginning period of the treatment, they can not be removed absolutely from aqueous solution to yield other intermediates and/or carbon dioxide and water in the process of ozone/AB. Combining with the results of Figs. 4 and 6, the phenomenon of Fig. 7 suggests that a higher concentration of $\cdot\text{OH}$ can lead to the rapid formation of an increasing diversity of byproducts, and enhance the total removal of byproducts and the degree of mineralization of target organic compound.

3.6. Discussion on the enhanced mechanism

The chemistry of ozone in aqueous solution is complex. Molecular ozone can oxidize water impurities via direct, selective reactions or can undergo decomposition via a chain reaction mechanism resulting in the generation of $\cdot\text{OH}$ [20]. Firstly, ozone is very unstable in aqueous solution due to its high active resonance structures of molecule. The half-life time of ozone molecular varies from a few seconds up to few minutes and depends on pH, water temperature and concentration of organic and inorganic compounds in aqueous solution [20]. Furthermore, the major secondary oxidant formed from ozone decomposition in aqueous solution is the $\cdot\text{OH}$ [35], the reaction rate of which with organic molecules is usually in the order of 10^6 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [36]. Therefore, it is deduced from the results of Fig. 4 that in the ozone alone system, $\cdot\text{OH}$ is initiated from the self-decomposition of ozone in aqueous solution under this experimental conditions. However, ozone alone and ultrasound alone have been shown to achieve a very limited mineralization of organic compounds in micro-pollutant removal in aqueous solution, as shown in Figs. 2 and 6. Therefore, the combined process of ozone/ultrasound is selected in the present study, and the emphasis is located on the mechanism

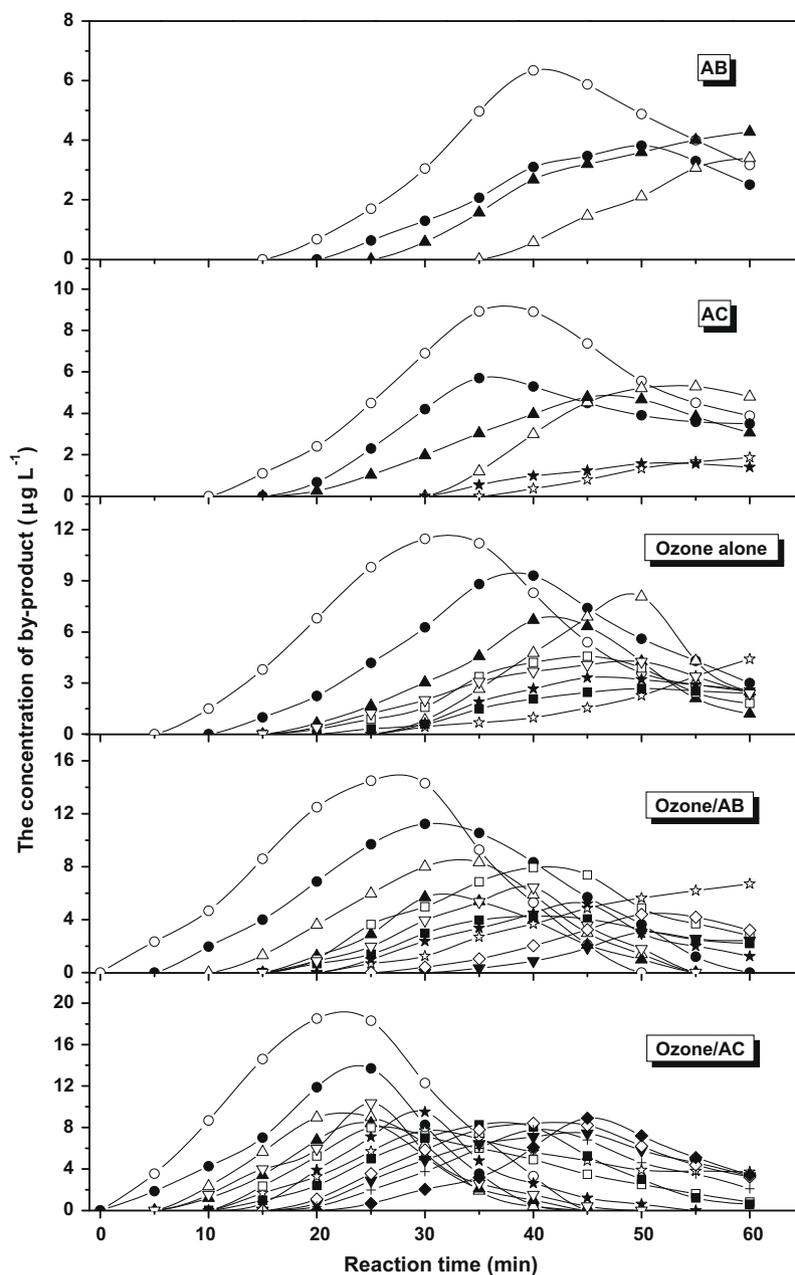


Fig. 7. Formation and evolution of byproducts in the different processes (reaction conditions – temperature: 298 K; initial pH: 6.87; initial nitrobenzene concentration: $50 \mu\text{g L}^{-1}$; total applied ozone: 1.0 mg L^{-1} ; (○) *p*-nitrophenol; (●) *m*-nitrophenol; (△) phenol; (▲) malonic acid; (☆) nitrate ion; (★) 4-nitrocatechol; (□) maleic acid; (■) oxalic acid; (▽) hydroquinone; (▼) 1,2,3-trihydroxy-5-nitrobenzene; (◇) acetic acid; (◆) *p*-quinone; (+) *o*-nitrophenol).

investigation of ultrasound with the different orthogonal dual frequencies for the enhancement efficiency of ozonation.

The present study illuminates that, due to the lower power intensity and the lower power density (0.65 W cm^{-2} and 64.1 W L^{-1}), the single ultrasonic field (A, B or C) scarcely causes the degradation of nitrobenzene, and also no enhancement efficiency of ozonation is presented at the lower total applied ozone of 1.0 mg L^{-1} (not shown). However, ultrasound with the dual frequencies catalytic ozonation can enhance the degradation efficiency of nitrobenzene compared to the both case of ozone alone and ultrasound alone under the same conditions (Fig. 2). This may be mainly attributed to the difference in the nature of the acoustic field generated, and the reactions are listed as follows.

On the one hand, it is generally believed that the chemical effects of ultrasound arise from acoustic cavitations of liquids: this

rapid formation, growth and implosive collapse of gas vacuoles generate short-lived (-ns), localized “hot spots” whose peak temperatures and pressures have been measured at 5000 K and 1000 atm [24]. The combining irradiation of dual-frequency ultrasound can significantly increase the ultrasonic cavitation yield compared with that coming from two individual ultrasonic irradiations [37]. This enhancement effect can essentially be ascribed to the following factors. When two sound waves encounter in solution, not only the original waves but also waves with the sum frequency, difference frequency and multiple frequencies may be produced in the focal acoustic field and the larger amplitudes are created [38]. Furthermore, the simultaneous combined multi-frequency ultrasound can disturb the sample solution more strongly than the single-frequency ultrasound and may even break the surface continuity of the sample solution, thus resulting in more

cavitation nuclei in the solution. This increased disturbance leads to the enhancement of bubble–bubble and bubble–sound interactions by Bjerkness forces. The simultaneous combined ultrasonic irradiation causes more efficient mass transfer, leading to an increased cavitation activity [39]. On the other hand, this combined dual-frequency ultrasound also can produce the interference pattern of superposition waves to disturb the standing wave pattern leading to the higher energy efficiencies [40].

Except for the reasons mentioned above, it is especially important that the orthogonal dual-frequency can significantly increase the inertial cavitation activity, leading to the improvement of cavitation yield compared to the algebraic sum of the individual ultrasound irradiations [39,41]. As a result, the synergistic effect is presented obviously between ozone and ultrasound with the orthogonal dual frequencies, and the greater the difference between the orthogonal dual frequencies, the stronger enhancement efficiency is obtained in the present study. Furthermore, the experimental results (not shown) demonstrate that the utilization efficiency of ozone is 52.4%, 74.6% and 97.5%, respectively, in the processes of ozone alone, ozone/AB and ozone/AC, namely the introduction of ultrasound can increase the utilization efficiency of ozone. In other words, the synergistic effect appears to transfer ozone into aqueous solution more efficiently and also accelerate the initiation of novel oxidative intermediate species from the decomposition of ozone, such as $\cdot\text{OH}$ and H_2O_2 , which produces a higher removal efficiency of TOC, resulting in a higher degree of mineralization (Figs. 4–6).

Based on the initiation of $\cdot\text{OH}$ detected, it is revealed that the degradation of nitrobenzene occurs via several significant steps in the present selected processes, including the hydroxylation of aromatic ring, the mineralization of organic nitrogen, the transformation of aromatics to aliphatics by destruction of ring structures, the oxidation of the aliphatic chains, and the formation of organic acids (Fig. 7). This phenomenon is consistent with the primary objective of AOP, which can entail complete mineralization, implying that the final products of degradation reactions are carbon dioxide, short-chain organic acids, and inorganic ions, typically less toxic and amenable to biodegradation [24].

Otherwise, the introduction of ultrasound accelerates the degradation rate of nitrobenzene, and the reactions of the ozone/AB and ozone/AC systems all follow the pseudo-first-order kinetic model, the same to that of ozone alone (Fig. 3b), meaning that ultrasound is an effectively subordinate enhanced approach to ozonation, a dominating oxidation technique. Or else, when ozone alone is the subordinate enhanced approach, the degradation efficiency of nitrobenzene in the process of ultrasound alone will be higher than that of ozone alone, and the reaction kinetics of ozone/ultrasound may be same to that of ultrasound alone. This phenomenon is reasonable. On the one hand, the degradation byproducts will contribute to the degradation of target organic compound until the carbon species are oxidized completely to CO_2 [13]. It is observed that the ultrasonic degradation of nitrobenzene or *p*-nitrophenol follows, respectively the first-order kinetics [13,42,43], while the formation of 4-nitrocatechol from *p*-nitrophenol follows zero-order kinetics during the course of ultrasonic irradiation [42]. As another important byproduct, the sonolysis of phenol in aqueous solution is zero-order [44]. Therefore, when degradation byproducts with zero-order kinetics contribute dominantly to the removal, the degradation of target organic compound unquestionably follows zero-order kinetics. Strictly speaking, the ultrasonic reaction does not follow intrinsically a single kinetics order, which is dependent on the species and the concentrations of reactants and byproducts. Due to the lower initiation efficiency of $\cdot\text{OH}$, the apparent removal of target organic compound should approach zero-order as the rate becomes limited by the concentration of $\cdot\text{OH}$ initiated in the processes of ultrasound alone (AB or AC). How-

ever, under relatively higher initiation efficiency of $\cdot\text{OH}$, the overall disappearance of target organic compound can follow first-order kinetics because the reaction rate is not limited by the concentration of $\cdot\text{OH}$ initiated in the processes of ozone alone, ozone/AB and ozone/AC [45].

Therefore, the enhancement degradation of nitrobenzene in the present combined process is derived from the synergetic effect between ozone and ultrasound, resulting in the acceleration initiation of $\cdot\text{OH}$ which determines the improvement removal of target organic compound.

4. Conclusions

Ultrasound with the different orthogonal dual frequencies has been used to enhance ozonation for the degradation efficiency of nitrobenzene in aqueous solution. The experimental results indicate the process of ultrasound alone is lower than ozone alone for the degradation of nitrobenzene, but ozone/ultrasound combination is found more efficient than the additive effects of single operations. The kinetics in the two processes of ultrasound alone exhibit the zero-order with respect to nitrobenzene, while the degradation reactions all follow the pseudo-first-order kinetic model in the three processes of ozone alone and ozone/ultrasound. The degradation of nitrobenzene is mainly attributed to the $\cdot\text{OH}$ oxidation in the every selected process.

Comparing to the ozone alone and ultrasound alone systems, the combination process of ozone/ultrasound can increase the initiation of $\cdot\text{OH}$, the formation of H_2O_2 and the removal efficiency of TOC. The phenomena are derived from the obvious synergetic effect between ozone and ultrasound with the different orthogonal dual frequencies, and the greater the difference between the orthogonal dual frequencies, the stronger enhancement efficiency is obtained.

The byproducts analysis illustrates the degradation of nitrobenzene occurs via the hydroxylation of aromatic ring, the mineralization of organic nitrogen, the transformation of aromatics to aliphatics by destruction of ring structures, the oxidation of the aliphatic chains, and the formation of organic acids. Observed byproducts include the following: *o*, *p*, *m*-nitrophenols, phenol, 4-nitrocatechol, hydroquinone, *p*-quinone, 1,2,3-trihydroxy-5-nitrobenzene, maleic acid, malonic acid, oxalic acid, acetic acid, and nitrate ion.

Acknowledgements

Authors gratefully acknowledge the China Postdoctoral Science Foundation (Grant No. 20080440130), the Scheme of 863 High Technology Research and Development Program of China (Grant No. 2006AA06Z306) and the National Natural Science Foundation of China under the Scheme of National Creative Research Groups (Grant No. 50821002) for the financial support of this study.

References

- [1] Y. Mu, H.-Q. Yu, J.-C. Zheng, S.-J. Zhang, G.-P. Sheng, *Chemosphere* 54 (2004) 789–794.
- [2] J.-S. Zhao, O.P. Ward, P. Lubicki, J.D. Cross, P. Huck, *Biotechnol. Bioeng.* 73 (2001) 306–312.
- [3] S. Contreras, M. Rodríguez, E. Chamorro, S. Esplugas, *J. Photochem. Photobiol. A* 142 (2001) 79–83.
- [4] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, *Water Res.* 32 (1998) 2721–2727.
- [5] L.S. Bell, J.F. Devlin, R.W. Gillham, P.J. Binning, *J. Contam. Hydrol.* 66 (2003) 201–217.
- [6] M. Rodríguez, V. Timokhin, F. Michl, S. Contreras, J. Gimenez, S. Esplugas, *Catal. Today* 76 (2002) 291–300.
- [7] R. Mantha, K.E. Taylor, N. Biswas, J.K. Bewter, *Environ. Sci. Technol.* 35 (2001) 3231–3236.

- [8] Z. He, L. Lin, S. Song, M. Xia, L. Xu, H. Ying, J. Chen, *Sep. Purif. Technol.* 62 (2008) 376–381.
- [9] S. Song, Z.Q. He, J.M. Chen, *Ultrason. Sonochem.* 14 (2007) 84–88.
- [10] Y.G. Adewuyi, *Ind. Eng. Chem. Res.* 40 (2001) 4681–4715.
- [11] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 501–551.
- [12] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 553–597.
- [13] L.K. Weavers, F.H. Ling, M.R. Hoffmann, *Environ. Sci. Technol.* 32 (1998) 2727–2733.
- [14] K.L. Rakness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somiya, *Ozone Sci. Eng.* 18 (1996) 209–229.
- [15] H. Bader, J. Hoigné, *Water Res.* 15 (1981) 449–456.
- [16] H. Bader, V. Sturzenegger, J. Hoigné, *Water Res.* 22 (1988) 1109–1115.
- [17] L. Zhao, J. Ma, Z.Z. Sun, X.D. Zhai, *Appl. Catal. B: Environ.* 83 (2008) 256–264.
- [18] L. Zhao, Z.Z. Sun, J. Ma, H.L. Liu, *Appl. Catal. B: Environ.* 89 (2009) 326–334.
- [19] B. Legube, V.L.N. Karpel, *Catal. Today* 53 (1999) 61–72.
- [20] B. Kasprzyk-Hordern, M. Ziótek, J. Nawrocki, *Appl. Catal. B: Environ.* 46 (2003) 639–669.
- [21] C.P. Huang, C. Dong, Z. Tang, *Waste Manage.* 13 (1993) 361–377.
- [22] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 173–183.
- [23] J. Hoigné, H. Bader, *Water Res.* 10 (1976) 377–386.
- [24] Y.G. Adewuyi, *Environ. Sci. Technol.* 39 (2005) 3409–3420.
- [25] H. Utsumi, M. Hakoda, S. Shimbara, H. Nagaoka, Y. Chung, A. Hamada, *Water Sci. Technol.* 30 (1994) 91–99.
- [26] S.-N. Nam, S.-K. Han, J.-W. Kang, H. Choi, *Ultrason. Sonochem.* 10 (2003) 139–147.
- [27] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *Water Res.* 37 (2003) 1223–1230.
- [28] Q.-R. Li, C.-Z. Gu, Y. Di, H. Yin, J.-Y. Zhang, *J. Hazard Mater. B* 133 (2006) 68–74.
- [29] L. Zhao, J. Ma, Z.Z. Sun, *Appl. Catal. B: Environ.* 79 (2008) 244–253.
- [30] A. Di Paola, V. Augugliaro, L. Palmisano, G. Pantaleo, E. Savinov, J. Photochem. Photobiol. A 155 (2003) 207–214.
- [31] A. Goi, M. Trapido, T. Tuhkanen, *Adv. Environ. Res.* 8 (2004) 303–311.
- [32] E. Brillas, E. Mur, R. Saulea, L. Sánchez, J. Peral, X. Domènech, J. Casado, *Appl. Catal. B: Environ.* 16 (1998) 31–42.
- [33] M.A. Oturan, J. Peiroten, P. Chartrin, A.J. Acher, *Environ. Sci. Technol.* 34 (2000) 3474–3479.
- [34] J. Kiwi, C. Pulgarin, P. Peringer, *Appl. Catal. B: Environ.* 3 (1994) 335–350.
- [35] U. von Gunten, *Water Res.* 37 (2003) 1443–1467.
- [36] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51–59.
- [37] A.V. Prabhu, P.R. Gogate, A.B. Pandit, *Chem. Eng. Sci.* 59 (2004) 4991–4998.
- [38] S. Wang, B. Huang, Y. Wang, L. Liao, *Ultrason. Sonochem.* 13 (2006) 506–510.
- [39] A.H. Barati, M. Mokhtari-Dizaji, H. Mozdarani, Z. Bathaie, Z.M. Hassan, *Ultrason. Sonochem.* 14 (2007) 783–789.
- [40] M. Sivakumar, P.A. Tatake, A.B. Pandit, *Chem. Eng. J.* 85 (2002) 327–338.
- [41] P.M. Kanthale, P.R. Gogate, A.B. Pandit, *Chem. Eng. J.* 127 (2007) 71–79.
- [42] A. Kotronarou, G. Mills, M.R. Hoffmann, *J. Phys. Chem.* 95 (1991) 3630–3638.
- [43] I. Hua, R.H. Hochemer, M.R. Hoffmann, *J. Phys. Chem.* 99 (1995) 2335–2342.
- [44] C. Pétrier, M.-F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, N. Gondrexon, *J. Phys. Chem.* 98 (1994) 10514–10520.
- [45] G. Thoma, M. Gleason, V. Popov, *Environ. Prog.* 17 (1998) 154–160.