

Degradation of 2,4-dinitrophenol by combining sonolysis and different additives

Zhaobing Guo^{a,*}, Ruo Feng^b, Jiu hai Li^a, Zheng Zheng^c, Youfei Zheng^a

^a School of Environmental Science & Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, PR China

^b Institute of Acoustics, Nanjing University, Nanjing 210093, PR China

^c State Key Laboratory of Pollution Control and Resource Reuse, School of Environment, Nanjing University, Nanjing 210093, PR China

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Abstract

Based on the effects of various additives on ultrasonic degradation of 2,4-dinitrophenol (DNP) in aqueous solution, the degradation mechanisms and reaction kinetics of DNP in different processes were proposed. The results showed that some additives, such as CuO, CCl₄, O₃, NaCl and KI, were favorable for DNP sonochemical degradation. On the contrary, DNP degradation efficiency was restrained by Na₂CO₃, indicating that •OH radicals oxidation played an important role in DNP ultrasonic removal. The significant increases in DNP degradation in US/CuO/H₂O₂, US/CCl₄ and US/O₃ systems were also related to the intermediates formed during the reactions, such as HO₂•/•O₂⁻ radicals, chlorine-containing radicals and HClO. In addition, DNP ultrasonic removal was observed to behave as pseudo-first-order kinetics under different experimental conditions tested in the present work.

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1. Introduction

The pollution resulting from 2,4-dinitrophenol (DNP) discharge into the water environment is considered as one of the general problems in the dye industry in China. High toxicity and stability of DNP make it hard to be removed from aqueous solution by conventional biological treatment processes [1]. DNP has been placed on US Environmental Protection Agency's (USEPA's) "Priority Pollutants List". The USEPA recommends restricting its concentration in natural water below 10 ng/L [2].

Recently, the technique of ultrasound (US) has received great attentions for treating hazardous organic pollutants in the wastewater, and has made many excellent achievements at the laboratory scale [3–6]. Ultrasonic irradiation has been demonstrated as a promising method for the destruction of aqueous pollutants due to its advantages of being non-selective and

without secondary pollution. However, it is found that the degradation rate is rather slow by merely using ultrasonic wave. Therefore, some efforts have been devoted to increase the sonodegradation efficiency by hybrid techniques [7]. Gültekin and Ince [8] revealed that ozone substantially increased the sonodegradation efficiency of aryl-azo-naphthol dyes. Neppolian et al. [9] found that the coupled US/Fe²⁺/H₂O₂ technique was very effective in the mineralization of methyl-*tert*-butyl ether. On the other hand, addition of CuO/H₂O₂ in trichloroethylene sonodegradation did not present a positive synergic effect [10], indicating that the additives might have different influences on the ultrasonic removal of the organic pollutants. In our previous study, it was observed that H₂O₂ little facilitated the ultrasonic degradation of DNP. In addition, US had different effects on the DNP degradation in Fe²⁺/H₂O₂ system compared to that in Cu²⁺/H₂O₂ system [11]. In order to effectively increase the removal efficiency and further elucidate the sonodegradation mechanisms of aqueous DNP, ultrasonic treatments of aqueous DNP were studied by adding some additives, such as CuO, O₃, salts and organic compounds. Meanwhile, degradation kinetics of DNP in different processes was also conducted.

* Corresponding author. Tel.: +86 25 82029166; fax: +86 25 58731090.
E-mail addresses: guozbnuist@163.com, guocumt@nuist.edu.cn (Z. Guo).

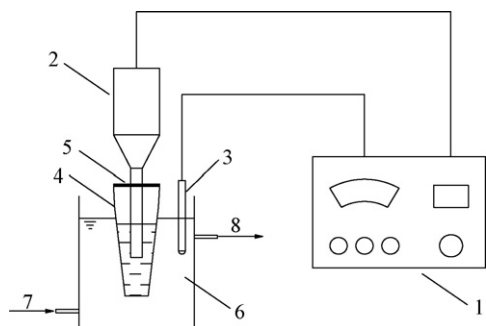


Fig. 1. Experimental device of ultrasonic irradiation. (1) Ultrasonicator; (2) titanium alloy rod; (3) temperature detector; (4) reactor; (5) sealed membrane; (6) water-jacketed; (7) water input; (8) water out.

2. Materials and methods

2.1. Materials

DNP was purchased from Shanghai Chemicals Factory. All chemicals, used as received, were of reagent grade with purity higher than 99%.

2.2. Ultrasonic device

The experimental device is shown in Fig. 1, which is made up of a water-jacketed glass vessel (75 mL) and an ultrasonicator (JY92-2D, Inc. Scientz, China), and is connected with an immersible horn via a titanium alloy rod (6 mm in diameter). The reactor is double-walled-type with recirculating water flowing between the walls in order to keep the temperature at 288 ± 0.5 K.

2.3. Sonolysis and analysis

50 mL DNP solution (20 mg/L) was placed in a sealed glass vessel and titanium alloy rod was immersed beneath the surface of aqueous solution (2 cm). According to experimental plan, different additives with a known amount were added to the solution, respectively. Ultrasonic pulses (on/off = 1 s/1 s) were used to initiate DNP degradation at the frequency of 20 kHz and the power dissipation into the system of 44 W, which was measured using calorimetry. Samples were removed at various time intervals and DNP concentrations were determined by a high-pressure liquid chromatograph (HPLC, Aligent1100), which was equipped with a multiple wavelength UV diode array detector. The determination wavelength was set at 360 nm. The eluent used consisted of 70% methanol and 30% water and the column temperature was maintained at 298 K. CCl_4 was analyzed by gas chromatograph (GC, Aligent 6890), Nitrite and nitrate ions, resulting from DNP degradation, were detected using ion chromatograph (Waters model ILC-1) [12].

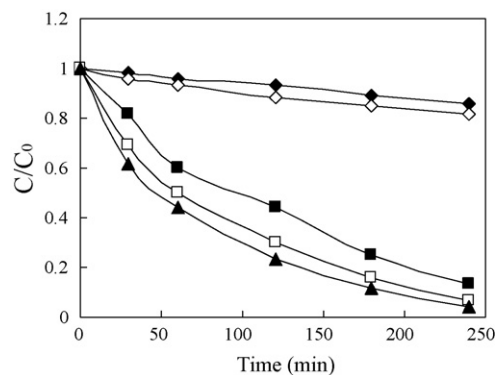


Fig. 2. DNP sonodegradation in different systems. Power dissipation: 44 W; (◆) US; (◇) US/H₂O₂; (■) CuO/H₂O₂; (□) US/CuO/H₂O₂; (▲) US/CuO/H₂O₂/air.

3. Results and discussion

3.1. Degradation of DNP by US/CuO/H₂O₂

The experiments have been conducted to investigate DNP degradation in different systems at solution pH of 4.0, CuO addition amount of 0.2 mg/mL and H₂O₂ concentration of 100 mg/L (Fig. 2). It can be obtained from Fig. 2 that approximately 14, 18, 87, 93 and 96% of DNP were removed after 4 h treatment in US, US/H₂O₂, CuO/H₂O₂, US/CuO/H₂O₂ and US/CuO/H₂O₂/air system, respectively. Fig. 2 also shows that DNP concentration decreased exponentially with sonication time, indicating that DNP degradation followed a pseudo-first-order kinetic model, which is described by Eq. (1). The corresponding rate constants in different processes were listed in Table 1.

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_0 is the initial concentration; C_t the concentration at sonication time (t) and k the rate constant.

It can be observed from Fig. 2 and Table 1 that DNP removal efficiency and degradation rate constant in US/CuO/H₂O₂ process were larger than the sum of both in CuO/H₂O₂ process and in US process, which was mainly ascribed to the promotion of ultrasound on CuO-catalysed decomposition of H₂O₂ to form more active free radicals, such as $\cdot\text{OH}$ radicals and $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ radicals. Drijvers et al. [10] came to a similar conclusion in removing aqueous phenol by US/CuO/H₂O₂.

In particular, DNP removal by US/CuO/H₂O₂/air after 4 h irradiation extended to 96%. There is a general consensus that the dissolved gas can be used as cavitation nucleus and lowered the cavitation threshold, which was favorable for the intensification of cavitation effect. Consequently, the addition of air in

Table 1
Pseudo-first-order degradation rate constants of DNP in different systems

Reaction system	Rate constant, k (min ⁻¹)	Correlation coefficient, R^2
US	0.0006	0.9983
US/H ₂ O ₂	0.0009	0.9568
CuO/H ₂ O ₂	0.008	0.9868
US/CuO/H ₂ O ₂	0.0107	0.9941
US/CuO/H ₂ O ₂ /air	0.0128	0.9897

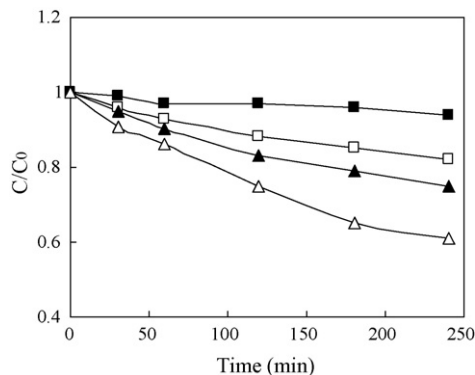


Fig. 3. Degradation of DNP by US/H₂O₂ and different salts. Power dissipation: 44 W; (■) US/H₂O₂/Na₂CO₃; (□) US/H₂O₂; (▲) US/H₂O₂/NaCl; (△) US/H₂O₂/KI.

US/CuO/H₂O₂ process was of major importance in the enhanced formation of •OH radicals, and then facilitated DNP degradation.

3.2. Degradation of DNP by US/H₂O₂/salts

The effects of NaCl on ultrasonic degradation of aqueous organic pollutants were inconsistent. Mahamuni and Pandit [13] found that phenol sonodegradation was accelerated by the addition of NaCl. However, Shimizu et al. [14] arrived at an opposite conclusion that NaCl suppressed the ultrasonic degradation of methylene blue. To further determine the influences of different salts on DNP degradation in US/H₂O₂ process, Na₂CO₃, NaCl and KI (0.1 mol/L) were, respectively, used in this study. The removal efficiencies of DNP in the presence of three salts were described in Fig. 3, and the corresponding rate constants were compared in Table 2.

As indicated in Fig. 3, the additions of Na₂CO₃, NaCl and KI led to DNP removal efficiencies in US/H₂O₂ process changed from 18 to 6, 24 and 39%, and the rate constants varied from 9×10^{-4} to 3×10^{-4} , 1.3×10^{-3} and $2.2 \times 10^{-3} \text{ min}^{-1}$, respectively. The results showed that DNP degradation was restrained by Na₂CO₃, but was promoted by NaCl and KI in US/H₂O₂ process.

HCO₃⁻ and CO₃²⁻ will be produced shortly after the addition of Na₂CO₃ to aqueous solution. HCO₃⁻ and CO₃²⁻ can easily react with •OH radicals. As a result, the concentration of •OH radicals will inevitably decrease in the presence of Na₂CO₃. Considering the synchronous decrease in DNP removal efficiency, it can be primarily concluded that DNP degradation in US/H₂O₂ process was mainly controlled by the oxidation of •OH radicals.

Table 2
Pseudo-first-order degradation rate constants of DNP by US/H₂O₂ and different salts

Reaction system	Rate constant, k (min ⁻¹)	Correlation coefficient, R^2
US/H ₂ O ₂	0.0009	0.9568
US/H ₂ O ₂ /Na ₂ CO ₃	0.0003	0.8922
US/H ₂ O ₂ /NaCl	0.0013	0.9609
US/H ₂ O ₂ /KI	0.0022	0.9791

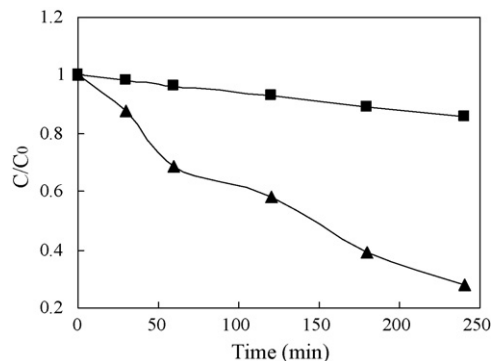


Fig. 4. DNP Sonodegradation in the presence and absence of CCl₄. Power dissipation: 44 W; (■) US; (▲) US/CCl₄.

The majority of oxidation reactions take place in the interface of cavitation bubbles produced by ultrasonic irradiation. Pollutants in that region undergo degradation due to exposure to free radicals and high temperature and pressure. The addition of NaCl to aqueous solution increased the hydrophobicity of DNP, which pushed DNP molecules from the bulk solution towards the interface. This increased the possibility of •OH radicals attack and promoted the pyrolytic decomposition on DNP, which was confirmed by our experimental results. The degradation efficiency of DNP in US/H₂O₂/NaCl process was 1.3 higher times compared to that without NaCl. Similar results for sonolytic degradation of phenol and chlorobenzene were reported [15]. Mahamuni and Pandit [13] concluded that NaCl was responsible for physically pushing phenol towards the interface and increasing the interface phenol concentration, but NaCl was not observed to take part in any chemical reactions in phenol degradation. Similarly to NaCl, KI effectively facilitated DNP degradation in US/H₂O₂ process, about 144% increase in degradation rate constant was observed compared to that in the absence of KI, indicating that KI was possibly favorable for H₂O₂ decomposition to form more •OH radicals.

3.3. Degradation of DNP by US/CCl₄

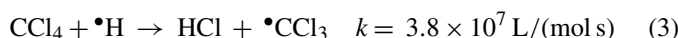
CCl₄ was found to remarkably facilitate the sonolysis of phenol [16]. However, the increasing degradation efficiencies of CCl₄ for various pollutants usually presented a distinct difference. In particular, the enhanced removal mechanism of CCl₄ for the pollutants is not very clear. Consequently, ultrasonic degradation of DNP was conducted in the presence and absence of CCl₄ (100 mg/L), and C/C_0 of DNP was plotted against sonication time in Fig. 4, where C_0 represents the initial concentration of DNP. The rate constants of DNP in the presence and absence of CCl₄ were compared in Table 3.

Table 3
Pseudo-first-order sonodegradation rate constants of DNP in the presence and absence of CCl₄

Reaction system	Rate constant, k (min ⁻¹)	Correlation coefficient, R^2
US	0.0006	0.9983
US/CCl ₄	0.0052	0.9906

As described in Fig. 4 and in Table 3, the removal efficiency and rate constant of DNP in US/CCl₄ process were remarkably increased compared to those in US process after 4 h irradiation at the power dissipation of 44 W.

When adding CCl₄ to DNP solution in US process, the following reactions exist.



It can be noted that CCl₄ was a hydrogen atom scavenger according to the high rate constant (Eq. (3)). Consequently, CCl₄ inevitably restrained the recombination reaction between hydrogen atom and $\bullet\text{OH}$ radicals in sonochemical degradation process. Considering that there was no reaction between CCl₄ and $\bullet\text{OH}$ radicals [17], an increase in $\bullet\text{OH}$ radicals concentration and an enhancing effect in DNP degradation were achieved in the presence of CCl₄. Zheng et al. [16] drew a similar conclusion when they studied the effect of CCl₄ on the ultrasonic degradation of phenol.

To further investigate the role of CCl₄ in DNP sonodegradation, the ultrasonic removals of CCl₄ were conducted in the presence and absence of DNP, respectively, which were compared in Fig. 5. It can be found from Fig. 5 that CCl₄ was basically removed after 2 h ultrasonic irradiation, and DNP had no great influence on CCl₄ degradation. In addition, it can be observed from Fig. 4 that DNP concentration significantly decreased after CCl₄ had been removed completely. It reveals that DNP degradation was related to the intermediates formed during the ultrasonic irradiation of CCl₄.

CCl₄, as a hydrophobic organic compound, is prone to enter the cavitation bubbles and undergoes degradation by pyrolytic cleavage. The C–Cl bond in CCl₄ was preferentially broken at high temperature to produce large amount of $\bullet\text{Cl}$ radicals compared to the H–OH bond in H₂O due to the fact that the C–Cl bond energy in CCl₄ is 73 kcal/mol and the H–OH bond energy in H₂O is 119 kcal/mol. The formation of $\bullet\text{Cl}$ radicals will lead to a series of reactions [18].

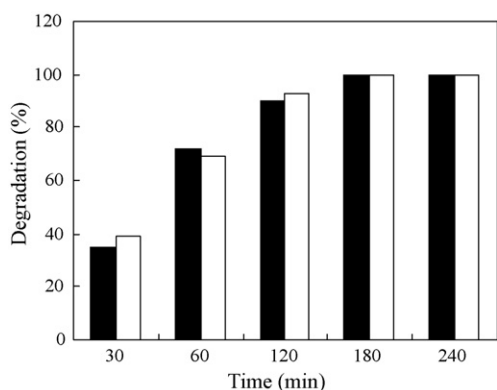


Fig. 5. Ultrasonic degradation of CCl₄ in the presence and absence of DNP. Power dissipation: 44 W; black bars: with DNP; white bars: without DNP.

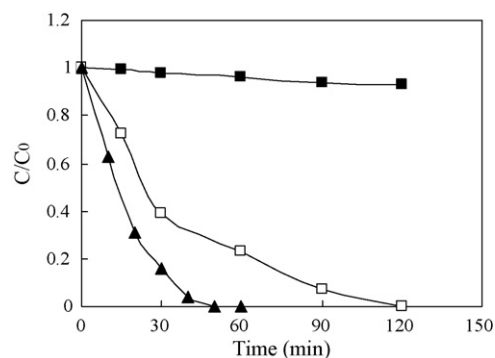
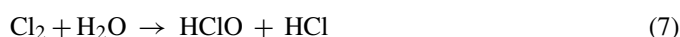


Fig. 6. Degradation of DNP in US, O₃ and US/O₃ systems. Power dissipation: 44 W; (■) US; (□) O₃; (▲) US/O₃.



HClO and chlorine-containing radicals, such as $\bullet\text{Cl}$, $\bullet\text{CCl}_3$ and :CCl_2 , have strong oxidizing property, which will distinctly accelerate the oxidation of DNP in aqueous solution. In our study, the pH of DNP solution dropped from the initial value of 4.0 to a final of 2.9 after 4 h ultrasonic irradiation in the presence of CCl₄, which was partially attributed to the formation of HClO and HCl during the degradation process.

3.4. Degradation of DNP by US/O₃

O₃ is usually used to remove persistent and biorefractory pollutants in water by combining with ultrasonic irradiation [19]. In our experiments, 50 mL DNP solution was irradiated at the power dissipation of 44 W, O₃/O₂ flow rate of 1 mL/s and the initial pH value of 4. The removals of DNP in US, O₃ and US/O₃ systems were described in Fig. 6, respectively.

It can be observed from Fig. 6 that DNP was completely removed after 1 h treatment in US/O₃ process. In contrast, only 4 and 77% of DNP were, respectively, decomposed in US and O₃ process. Meanwhile, it is noted from Table 4 that the rate constants of DNP in US/O₃, US and O₃ systems were 0.0706, 0.0006 and 0.0281 min⁻¹, respectively. The results show that DNP degradation in US/O₃ process presented a significantly synergistic effect. In US/O₃ system, the mass transfer and decomposition of O₃ can be enhanced by ultrasound. As a result, O₃ concentration in liquid phase and the production of active free radicals, such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and $\bullet\text{O}_2\text{H}$, were increased [20], which resulted in the higher degradation efficiency of DNP in US/O₃ process.

Table 4
Pseudo-first-order degradation rate constants of DNP in US, O₃ and US/O₃ systems

Reaction system	Rate constant, k (min ⁻¹)	Correlation coefficient, R^2
US	0.0006	0.9983
O ₃	0.0281	0.9818
US/O ₃	0.0706	0.9443

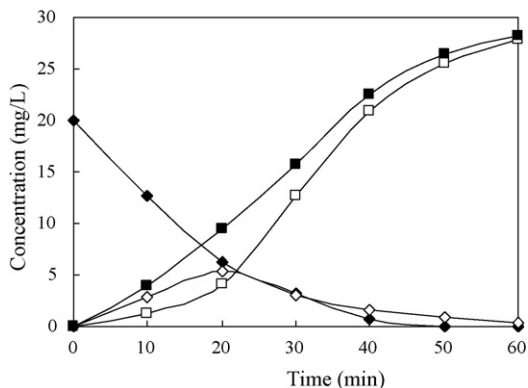


Fig. 7. Dependences of the concentrations of DNP, NO_2^- and NO_3^- on sonication time. Power dissipation: 44 W; (◆) DNP; (◇) NO_2^- ; (■) $\text{NO}_2^- + \text{NO}_3^-$; (□) NO_3^- .

The dependences of the concentrations of DNP, NO_2^- and NO_3^- on sonication time in US/ O_3 system were, respectively, detected and the results were depicted in Fig. 7. It can be seen that the concentration of NO_2^- was first increased, and then decreased due to the oxidation to form NO_3^- . The concentration of NO_3^- kept increasing with the sonication time. Almost 100% of DNP was removed after 40 min irradiation in US/ O_3 process. In principle, the concentration of NO_2^- and NO_3^- ions should be close to 40 mg/L at this time, however, the measured concentration of NO_2^- and NO_3^- ions was approximately 23.9 mg/L, only 60% of calculated value was observed.

In general, two different pathways are ascribed to the degradation of organic compounds under the circumstance of high temperature and pressure induced by the ultrasonic irradiation: (1) homolytic breaking of the bonds by pyrolysis reactions and (2) reactions with reactive free radicals. Based on the heat instability between C–N bond in DNP, it can be speculated that $\bullet\text{NO}$ and $\bullet\text{NO}_2$ radicals may be preferentially produced via the pyrolysis reactions under ultrasonic irradiation, which will be further converted into HNO_2 and HNO_3 in aqueous solution. The concentration of formed NO_2^- and NO_3^- ion would be equivalent to the calculated value if DNP degradation in US/ O_3 process was controlled by pyrolysis reactions. However, the experimental results that only 60% of calculated value was determined further demonstrated the importance of the oxidation by active free radicals on DNP degradation in US/ O_3 process. More detailed investigations into the DNP degradation intermediates are now being processed.

4. Conclusions

Ultrasonic degradation of DNP was proved to be mainly ascribed to the oxidation of $\bullet\text{OH}$ radicals. The influences of various additives on the DNP degradation efficiencies were different. CuO , CCl_4 , O_3 , KI and NaCl facilitated DNP sonochemical degradation process. However, DNP ultrasonic removal was inhibited by Na_2CO_3 . This was not only attributed to the change of $\bullet\text{OH}$ radicals concentration induced by different additives, but also related to the intermediates formed during

DNP degradation in US/ $\text{CuO}/\text{H}_2\text{O}_2$, US/ CCl_4 and US/ O_3 systems. Besides, DNP sonodegradations were found to follow a pseudo-first-order kinetic model in different treatment processes.

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