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Ultrasound/Zn^0 for aqueous 4-nitrobenzoic acid degradation

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ABSTRACT

4-Nitrobenzoic acid is stable, toxic, and non-biodegradable. Conventional methods for wastewater treatment are ineffective for the treatment of 4-nitrobenzoic acid. In this study, the degradation efficiency of 4-nitrobenzoic acid by ultrasound in the presence of zero-valence zinc (Zn) was reported. The operating parameters were optimized, and the potential mechanisms were investigated. The results showed that there was a significant synergetic effect between ultrasound and Zn, and the synergetic factor was 2.26. The optimized treatment conditions were as follows: Initial pH 7.0 and Zn dosage of 0.4 g/L, under which the 4-nitrobenzoic acid degradation efficiency reached more than 85% after 30 min. The potential mechanisms included hydroxylation and the mechanical effect of ultrasound and the reduction and particle effects of Zn, which enhanced each other. The determination of intermediate products indicated that the catalytic degradation of 4-nitrobenzoic acid started with the destruction of the nitro group.

Keywords: Ultrasonic irradiation; Zero-valence zinc; Synergetic factor; Particle effect

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1. Introduction

Due to the rapid growth of industrial applications, a large amount of nitrobenzene compounds have been discharged into water bodies. The nitrobenzene compounds are known as stable, toxic, and non-biodegradable pollutants that induce threats to the environment. Conventional methods for wastewater treatment are not efficient in eliminating nitrobenzene compounds. Advanced oxidation processes (AOPs) are the preferred solution for these refractory compounds. AOPs are based on physicochemical processes that oxidize and mineralize pollutants into CO_2, N_2, water, and mineral acids, such as sulfuric and hydrochloric acids, by means of highly oxidizing agents, mainly hydroxyl radicals [1].

Ultrasonic oxidation, as a typical AOP, has been used to treat refractory organic pollutants and has showed high efficiency [2–5]. US results in the formation, growth, and collapse of cavitation bubbles. Subsequently, millions of hotspots with extreme conditions (5,000 K and 1,000 atm) are generated in water, and hydroxyl free radicals and other oxidative species are created [6–8]. With the action of ultrasonic irradiation, contaminants can be transformed to biodegradable substances with low toxicity and can even be mineralized. However, US alone is inefficient

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for the degradation of some pollutants [9,10]. To improve the degradation efficiency, a solid catalyst was introduced into the ultrasonic system, resulting in a higher efficiency [11–13].

Zero-valence zinc (Zn) showed high catalytic activity in the degradation of pollutants. Research studies have used Zn in the treatment of nitrobenzene and chlorinated organic compounds including dichloroethylene, dichloroacetylene, and trichloroethylene [14,15]. In the treatment of trichloroethylene, the degradation efficiency of Zn was 10 times that of zero-valence iron [16]. Zn was also reported to be effective in the treatment of trichloropropane [17]. However, few studies used Zn in an ultrasonic system. Under ultrasonic irradiation, the transfer rate between Zn and pollutants could be accelerated. In addition, the high temperature and pressure might increase the reaction rates significantly. In this manner, excellent degradation efficiency of pollutants could be achieved.

In this paper, Zn was used together with ultrasound to remove 4-nitrobenzoic acid, a typical refractory pollutant. The reaction conditions were investigated in depth, including the pH value of the solution, the catalyst dose, and the initial concentration of 4-nitrobenzoic acid. The potential mechanism was clarified, and the degradation intermediates were determined. The aim was to propose a practical approach for the treatment of refractory organic pollutants.

2. Materials and methods

2.1. Chemicals

The 4-nitrobenzoic acid (Aldrich, USA), sodium hydroxide (Guoyao Inc., Beijing, China), and tert-butanol (TBA) (Guoyao Inc., Beijing, China) and $ZnSO_4$ (Huaen Inc., Tianjin, China) were of analytical grade. These chemicals were used without further purification. Zn and ZnO particles were purchased from Tianjin Guangfu Technology Development Co. Ltd. Zn used had a particle size of approximately 80–100 μm, and the purity of Zn was 98%. Solutions were prepared with water purified by a Millipore Milli-Q UV Plus system.

2.2 Experimental runs

US was performed using a JY92-II ultrasonic generator (Ningbo Xinzhi Technology Co., China) with a maximum operating power of 650 W and a frequency of 24 kHz. All experiments were conducted in 150-ml glass beakers. Each time, 100 ml of 4-nitrobenzoic acid solution was tested. The ultrasonic power density was 2 W/ml, and the temperature was kept at 25 ± 2℃ using a water circulator (HX-08, Qiqian Scientific Instrument Inc., Shanghai, China). After the reaction, the mixture was centrifuged at 5,000 rpm for 15 min. Next, the supernatant was used for 4-nitrobenzoic acid concentration detection.

The concentration of 4-nitrobenzoic acid was determined using the HPLC method, which was performed on Waters e2695 HPLC equipped with a UV detector at 278 nm and a 150 mm × 4.6 μm × 5 μm C18 reversed-phase column. The mobile phase consisted of 60% methanol and 40% water. The flow rate was 1.0 ml/min, and the injection volume was 10 μL. The rate constant of 4-nitrobenzoic acid degradation was obtained by fitting the experimental data into the first-order reaction equation.

$$-\ln\,(C/C_0) = kt \tag{1}$$

where C_0 (mmol/L) and C (mmol/L) are the concentrations of 4-nitrobenzoinc acid at the initial time and at a given time t (min), respectively; k (min^{-1}) is the reaction rate constant of the pseudo-second-order model; and t (min) is the reaction time.

The 4-nitrobenzoic acid degradation products were identified through Waters xevoG2 Q-TOF UPLC/MS system (Waters Corporation) equipped with a 150 mm × 4.6 μm × 5 μm C18 reversed-phase column. The surface morphology of Zn was investigated at different scales and magnifications using Hitachi S4700 scanning electron microscope (SEM) analyzer.

3. Results and discussion

3.1. Catalytic activity in the ultrasonic degradation of 4-nitrobenzoic acid

Three processes were tested in the degradation of 4-nitrobenzoic acid, including sole ultrasonic irradiation (US), sole Zn and US combined with zero-valence zinc (US/Zn). The results of 4-nitrobenzoic acid degradation are shown in Fig. 1(a). These three processes fitted well to the pseudo-first-order reactions, as shown in Fig. 1(b).

Clearly, with US alone, less than 10% of the 4-nitrobenzoic acid was degraded. With Zn, the degradation efficiency was approximately 39%. After US combined with Zn, the degradation efficiency of 4-nitrobenzoic acid improved significantly, approaching 80%. The first-order rate constants were calculated to be 0.0516, 0.0024, and 0.0204/min for US/Zn, US, and Zn, respectively. As observed, the reaction rate constant of US/Zn was much higher than the sum of

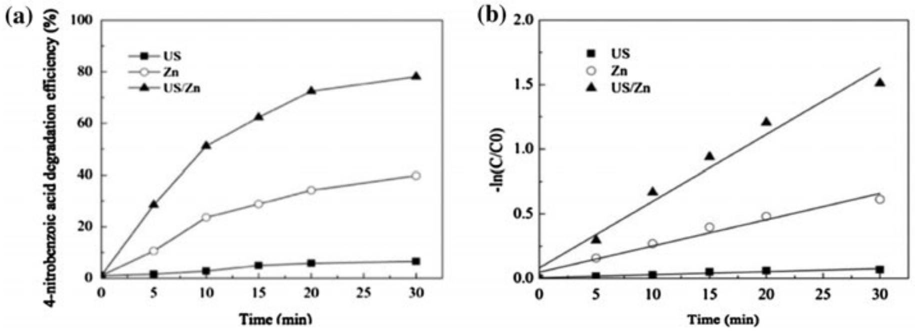

Fig. 1. Catalytic ultrasonic degradation of 4-nitrobenzoic acid with Zn, (4-nitrobenzoic acid = 1×10^{-5} mol/L, pH 7.0, Zn^0 = 0.4 g/L, 2 W/ml, 25℃).

the rate constants of US and Zn alone. An obvious synergistic effect was achieved, and the synergistic factor was calculated as follows:

$$E = \frac{k_{\text{combined}}}{k_{\text{method}-1} + k_{\text{method}-2} + \cdots + k_{\text{method}-n}} \tag{2}$$

where E is the synergistic factor, k (min^{-1}) is the reaction rate constant of pseudo-first-order model, and method_n refers to the individual method (for example, US and Zn reduction in this study). Accordingly, for this study, E was given by:

$$E = 0.0516/(0.0024 + 0.0204) = 2.26$$

US combined with Zn was very efficient and could be a potential solution for 4-nitrobenzoic acid pollution. In a catalytic ultrasonic oxidation system (ultrasound + MnO_2/CeO_2), the synergetic effect between sonication and solid catalyst was also observed [18]. Zhao et al. [18] explained that solid particles in water could act as cavitation nuclei during sonication, thus significantly enhancing the ultrasonic cavitation intensity. Such an effect should also exist in the ultrasound/Zn system. In particular, the size of Zn used in this study was 80–100 μm, which was close to the resonance size of the cavitation bubbles in a 24-kHz ultrasound field (~110 μm).

3.2. *Effects of the operational parameters*

In a catalytic ultrasonic process, the degradation efficiency is influenced by different operation parameters including pH value, catalyst dose, ultrasonic density, and pollutant concentration. In this paper, these operation parameters were studied and optimized.

3.2.1. *pH value*

The pH value plays an important role in catalytic ultrasonic processes [19,20]. The pH value might affect the states of pollutants and the activity of the catalyst. The effects of pH (ranging from 5.0 to 9.0) on the degradation of 4-nitrobenzoic acid were investigated. The results are shown in Fig. 2. Clearly, the 4-nitrobenzoic acid degradation efficiency was very stable in a wide range of pH values, which is beneficial for the practical use. Due to the slight differences in degradation efficiency under different pH values and in consideration of equipment corrosion, the optimal pH condition was chosen as 7.0.

3.2.2. *Zero-valence zinc dose*

The solid catalyst particles could act as cavitation nuclei during US [18]. Therefore, more active centers

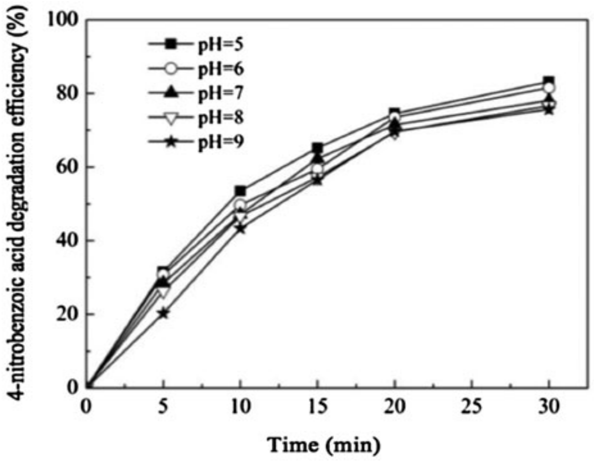

Fig. 2. Effects of pH value on 4-nitrobenzoic acid degradation (4-nitrobenzoic acid = 1×10^{-5} mol/L, Zn^0 = 1.0 g/L, 2 W/ml, 25℃).

were available in the solution with higher catalyst dose. Thus, the catalyst dose might influence the degradation efficiency of 4-nitrobenzoic acid in the catalytic ultrasonic process. The effects of Zn dose (from 0.2 to 1.0 g/L) were studied, and the results are shown in Fig. 3.

As observed in Fig. 3(a), the 4-nitrobenzoic acid degradation efficiency increased with higher catalyst dose. As the catalyst dose increased from 0.2 to 0.4 g/L, the degradation efficiency of 4-nitrobenzoic acid was improved significantly. When the catalyst dose was higher than 0.4 g/L, a slight increase was obtained. Fig. 3(b) showed that the pseudo-first-order rate constant increased from 0.023 to 0.05 1/min as the catalyst dose increased from 0.2 to 0.4 g/L and then became stable. The catalyst dose of 0.6 g/L was the best in terms of pollutant degradation, and the catalyst dose of 0.4 g/L was preferred when considering both pollutant degradation and cost.

At lower catalyst doses, fewer active centers were available in the solution, so the cavitation effects were weak. Thus, the degradation efficiency of 4-nitrobenzoic acid was much lower. At higher doses, more active centers were present in the solution and the cavitation effects became stronger; the degradation efficiency was obviously improved. Once the catalyst dose was beyond the optimal condition, excessive amount of catalyst particles can scatter the ultrasonic energy transfer [21,22], thereby weakening the cavitation effects.

3.2.3. Initial 4-nitrobenzoic acid concentration

Sometimes the initial concentration has strong effects on the pollutant degradation efficiency. In this paper, the effects of the initial 4-nitrobenzoic acid concentration on its degradation efficiency were studied in the range from 1×10^{-5} to 10×10^{-5} mol/L. As observed in Fig. 4(a), the degradation efficiency was slightly increased by increasing the initial pollutant concentration from 1×10^{-5} mol/L to 4×10^{-5} mol/L. For 4-nitrobenzoic acid concentrations greater than 7×10^{-5} mol/L, the degradation efficiency decreased obviously. The calculated pseudo-first-order rate constants, shown in Fig. 4(b), reached the highest level at 4×10^{-5} mol/L of 4-nitrobenzoic acid concentration. With further increases in the 4-nitrobenzoic acid concentration, the rate constant decreased rapidly by almost 90%.

Such a phenomenon might be explained as follows. When the initial concentration of 4-nitrobenzoic acid was 1×10^{-5} mol/L, the amount of 4-nitrobenzoic acid molecules around the cavitation bubble and in contact with the catalyst was low. Therefore, the chance for the pollutant to react inside the cavitation bubble or on the surface of the catalyst was low. An increase in initial concentration was beneficial for pollutant reaction. Such a beneficial effect of higher initial concentration was previously reported [23]. However, when the 4-nitrobenzoic acid concentration was higher than 4×10^{-5} mol/L, an excessive number of pollutant molecules can compete for the cavitation bubbles and the catalyst particles for reaction. In addition, many intermediate products were generated around the cavitation bubbles/catalyst particles. Moreover, the spreading of the hydroxyl free radical and other active compounds was blocked leading to a smaller reaction zone for 4-nitrobenzoic acid and active compounds [24,25]. Thus, the degradation efficiency of 4-nitrobenzoic acid decreased significantly.

3.3. Potential mechanisms

In the catalytic ultrasonic process, many researchers have proved that hydroxyl free radical oxidation is an important mechanism in the degradation of pollutants [26,27]. However, other mechanisms

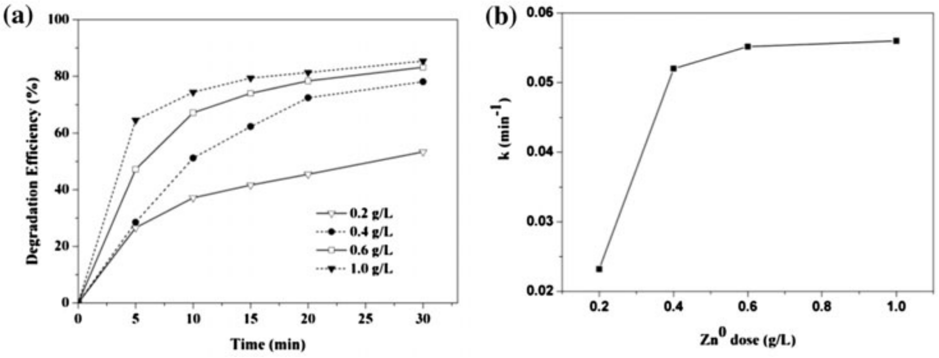

Fig. 3. Effects of catalyst dose on 4-nitrobenzoic acid degradation: (a) degradation efficiency and (b) reaction rate (4-nitrobenzoic acid = 1×10^{-5} mol/L, pH 7.0, 2 W/ml, 25℃).

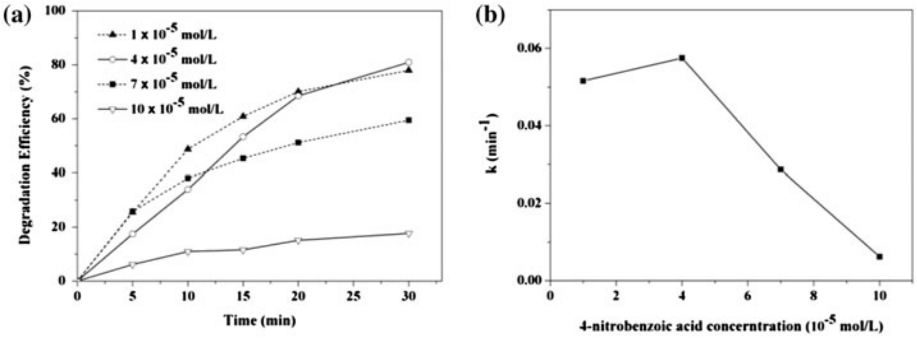

Fig. 4. Effects of 4-nitrobenzoic acid concentration on the degradation efficiency, (a) degradation efficiency and (b) reaction rate (pH 7.0, Zn^0 = 0.4 g/L, 2 W/ml, 25℃).

were unclear. In this paper, we studied the role of hydroxyl free radical oxidation, the effects of ultrasonic irradiation, and the role of Zn to reveal the mechanisms in the catalytic ultrasonic degradation of 4-nitrobenzoic acid.

3.3.1. *Impact of hydroxyl free radical scavenger*

To determine the role of hydroxyl free radical in 4-nitrobenzoic acid degradation, a hydroxyl free radical scavenger was added into the catalytic ultrasonic system. Due to the high reaction rate between TBA and the hydroxyl free radical (6×10^8/M s) [28], TBA was chosen as the free radical scavenger.

Fig. 5 shows the results of TBA addition. Clearly, TBA weakened the degradation of 4-nitrobenzoic acid in the US/Zn^0 system. The 4-nitrobenzoic acid degradation efficiency decreased with increasing TBA concentration. When the concentration of TBA was increased to 50×10^{-3} mol/L, the degradation efficiency of 4-nitrobenzoic acid decreased by more than 15%. If hydroxyl free radical oxidation was the dominant mechanism in this system, then a higher concentration of TBA would successfully compete with 4-nitrobenzoic acid for hydroxyl free radical, resulting in a dramatic decrease in pollutant degradation. Li et al. reported that the 1,1,1-trichloroethane removal efficiency was decreased by 24.49% after addition of 187.4 mmol/L TBA [29]. The results in Fig. 5 illustrated that hydroxyl free radicals did contribute to 4-nitrobenzoic acid degradation, although it was not the key parameter.

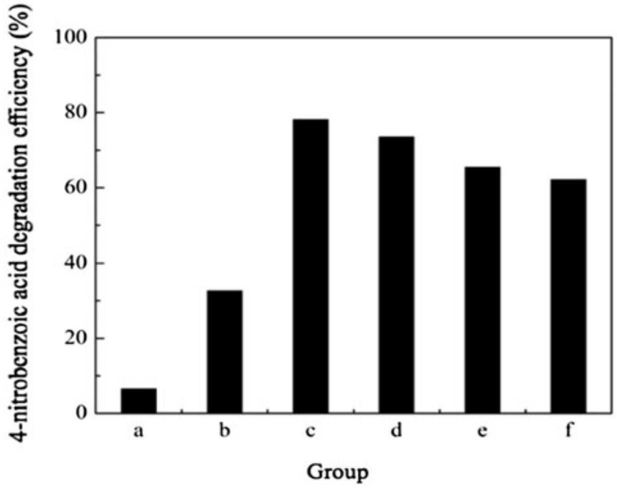

Fig. 5. Effects of TBA addition on 4-nitrobenzoic acid degradation: a-US, b-Zn, c-US/Zn, d-US/Zn + 1×10^{-3} mol/L TBA, e-US/Zn + 10×10^{-3} mol/L TBA, f-US/Zn + 50×10^{-3} mol/L TBA (4-nitrobenzene acid = 1×10^{-5} mol/L, pH 7.0, Zn^0 = 0.4 g/L, 2 W/ml, 25℃, 30 min).

3.3.2. *Effects of US on the catalyst particles*

During the ultrasonic irradiation, microjets with high speed are generated; such microjets strongly attack the catalyst particles. The active sites can then be constantly explored to pollutants due to the sweeping of the catalyst surface by microjets. The SEM images of fresh and used catalyst are shown in Fig. 6.

Before the reaction, the surface of the catalyst was very rough and then became comparably smooth after the reaction (Fig. 6). In addition, some impact craters were observed on the used catalyst. Those observations showed that during the catalytic ultrasonic process, the surface of Zn was continuously attacked by microjets, leading to obvious changes in morphology. The particle size of Zn was also affected by ultrasonic irradiation. As shown in Fig. 7, the particle size distribution became narrower after reaction. For the fresh and used Zn, the average particle sizes were 18.40 and 15.80 μm, respectively.

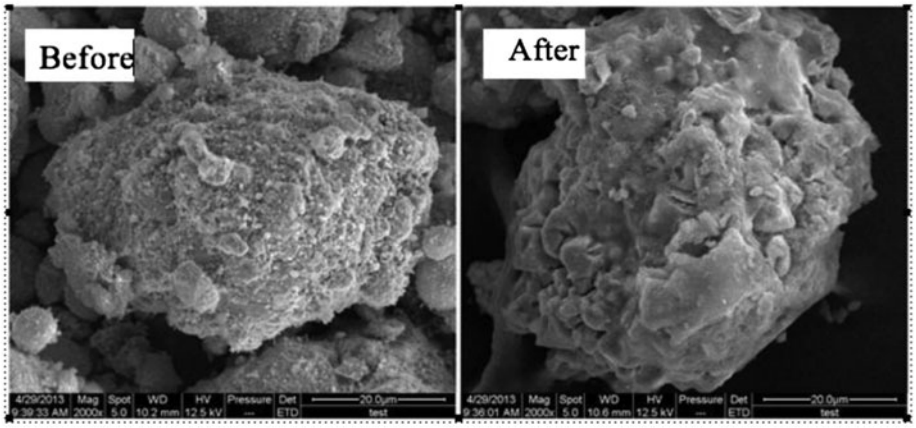

Fig. 6. SEM images of Zn before and after reactions (2,000 times).

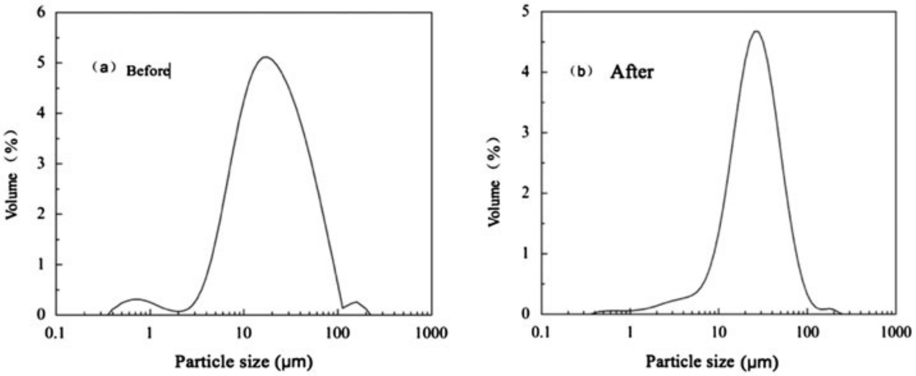

Fig. 7. Change of Zn size in the catalytic ultrasonic process (4-nitrobenzoic acid = 1×10^{-5} mol/L, pH 7.0, Zn^0 = 0.4 g/L, 2 W/ml, 25℃, 30 min).

With ultrasonic irradiation, the generated microjets could sweep intermediate products on the active sites. Therefore, more active sites were available for 4-nitrobenzoic acid degradation. With smaller particles, the catalyst could be dispersed much better. Thus, catalyst particles could come into contact with the 4-nitrobenzoic acid more easily. In addition, US could enhance the mass transfer, thereby accelerating the reaction rate.

3.3.3. Comparison of various Zn-containing catalysts

In the ultrasonic system, the intensity of cavitation effects corresponds to the quantity of cavitation bubbles. To form more cavitation bubbles, more nuclei are required. The added catalyst particles could act as nuclei, thereby increasing the quantity of cavitation bubbles, leading to stronger cavitation effects. Thus, more hydroxyl free radicals were generated, and

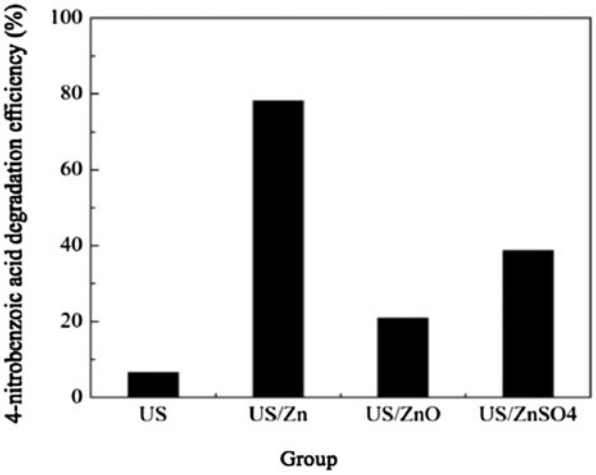

Fig. 8. Comparison of various catalysts for 4-nitrobenzoic acid (4-nitrobenzoic acid = 1×10^{-5} mol/L, pH 7.0, catalyst dose = 0.4 g/L, 2 W/ml, 25℃).

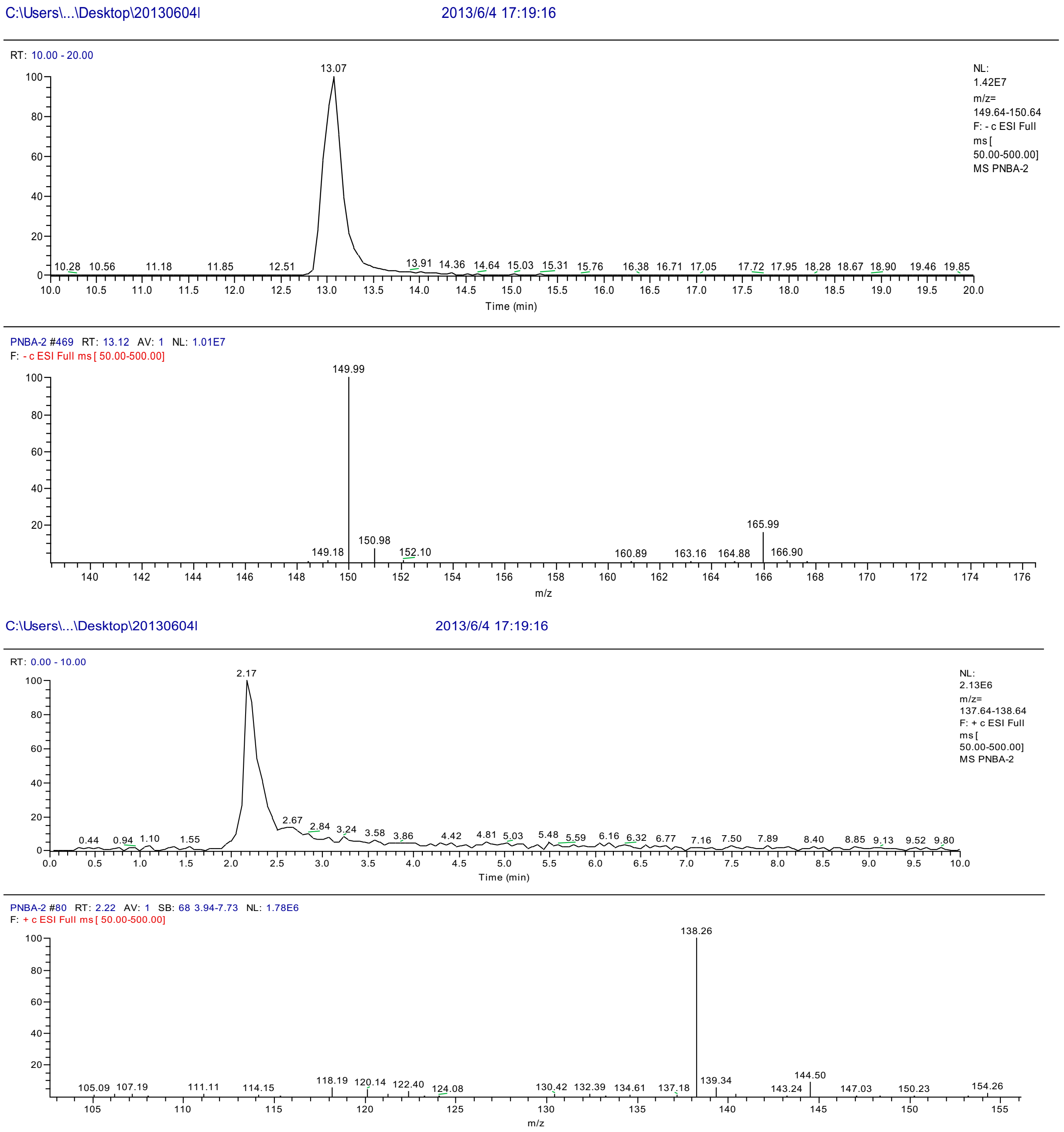

Fig. 9. MS spectra of the 4-nitrobenzoic acid intermediates in the catalytic ultrasonic process.

higher degradation efficiency of 4-nitrobenzoic acid was achieved because of the addition of zinc particles into the ultrasound field.

In addition, the reduction ability of Zn also contributed to the degradation of 4-nitrobenzoic acid. In the catalytic ultrasonic process, the Zn^{2+} concentration in the solution was found to be 0.8 mg/L, which was higher than that of the control (0.3 mg/L). Thus, more Zn was turned into Zn^{2+} in the degradation of 4-nitrobenzoic acid. To further clarify the role of Zn in 4-nitrobenzoic acid degradation, various Zn-containing chemicals were added to the ultrasonic system, and the results are shown in Fig. 8. As observed, the process of US/Zn^0 was the most efficient in the degradation of 4-nitrobenzoic acid. When the US was combined with ZnO or $ZnSO_4$, where zinc was in the state of Zn^{2+}, the degradation efficiency was much lower. Thus, the reduction ability of Zn contributed greatly to the degradation of 4-nitrobenzoic acid in the catalytic ultrasonic process.

3.4. Determination of intermediate products

After the reaction, the solution was investigated by LC/MS to determine intermediate products. Fig. 9 shows the results of the presence of two intermediate products at m/z 150 $[M-H]^-$ and 138 $[M+H]^+$. In the catalytic ultrasonic process, the nitro group and carboxyl group on the benzene ring of 4-nitrobenzoic acid were attacked. Because the nitro group on the benzene ring was easier to degrade, intermediate products at m/z 150 and 138 correspond to 4-nitrosobenzoic acid and 4-aminobenzoic acid, respectively. Thus, in the catalytic process, the nitro group of 4-nitrobenzoic acid was first oxidized to the nitroso group, and then was reduced to the amino group. The degradation scheme of 4-nitrobenzoic acid in catalytic ultrasonic process could be described as follows: 4-nitrobenzoic acid was first reduced to 4-nitrosobenzoic acid by Zn^0, then Zn^0 was oxidized to Zn^{2+}. The nitroso group of 4-nitrosobenzoic acid was subsequently reduced to hydroxyamino group and finally 4-aminobenzoic acid was generated. With continuous ultrasonic irradiation, the ring structures of these intermediates are attacked by active radicals and further decomposed into inorganic products, e.g. HNO_3, CO_2, and H_2O.

4. Conclusions

In this paper, US/Zn^0 was found to degrade more than 85% of 4-nitrobenzoic acid in 30 min. There was an obvious synergistic effect between ultrasound and Zn. The optimal conditions for the degradation of 4-nitrobenzoic acid were found to be a pH of 7.0 and a Zn^0 dose of 0.4 g/L. Excellent degradation efficiency could be achieved when the concentration of 4-nitrobenzoic acid was in the range from 1×10^{-5} to 4×10^{-5} mol/L. Hydroxyl free radical oxidation was proved to be an important mechanism in the US/Zn^0 system. The addition of Zn particles enhanced the sonication effects, and the US could maintain the activity of Zn and improve the mass transfer. Two intermediate products, 4-nitrosobenzoic and 4-aminobenzoic acid, were detected, illustrating that the nitro group of 4-nitrobenzoic acid was destroyed first in 4-nitrobenzoic acid degradation. The US/Zn^0 process showed great potential in treating refractory organic pollutants.

Acknowledgments

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