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Enhanced degradation of nitrobenzene by combined ultrasonic irradiation and a zero-valent zinc catalyst

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ABSTRACT

Enhanced ultrasonic catalytic activity in nitrobenzene degradation was found by combining ultrasonic irradiation and a zero-valent zinc (Zn^0) catalyst. In this system, the influence of the reaction parameters, reaction kinetics, intermediates, and mechanism was investigated. Under the optimum conditions (initial nitrobenzene concentration of 0.01 mmol/L, Zn^0 dosage of 0.4 g/L, initial pH 7, ultrasonic intensity 4.0 W/cm^2), approximately 91.2% of nitrobenzene could be removed within 30 min. The degradation process followed the pseudo-first-order kinetics model, and the reaction rate constant was 0.0670 min^{-1}. The mechanism of the synergetic effect of ultrasound and Zn^0 was proposed. Three intermediates of nitrophenol, phenylhydroxylamine, and aniline were identified by liquid chromatography–mass spectrometry (LC-MS). The degradation pathways of hydroxyl radical oxidation and Zn^0 reduction were deduced. This combined system is promising for the removal of nitrobenzene pollutants from water.

Keywords: Catalytic; Ultrasonic; Zero-valent zinc; Degradation; Nitrobenzene

1. Introduction

Persistent organic pollutants (POPs) have caused wide concern due to their toxicity and persistence in ecological systems [1]. Many of these compounds have demonstrated biomagnification within an aquatic system, resulting in greater concentrations in aquatic organisms [2]. Nitrobenzene is a common POP and is widely used in the dye, pharmaceutical, aniline, and explosives industries [3]. Nitrobenzene can be released into surface and groundwater due to improper wastewater treatment. The photo-oxidation half-life of nitrobenzene is 3,009–1.90×10^5 h in water. Thus, nitrobenzene poses a potential threat to human health as a result of drinking water or eating contaminated fish [4]. Nitrobenzene has been listed as a priority pollutant by the United States Environmental Protection Agency, and the maximum permissible concentration for wastewater is 1 mg/L [5]. Therefore, it is necessary to remove nitrobenzene from water. However, nitrobenzene (NB) is resistant to conventional chemical oxidation due to the strong electro-withdrawing effect of the nitro group [6]. Biodegradation of nitrobenzene is also difficult to achieve because of the toxic and mutagenic effect on biological systems [7]. In the adsorption process, enrichment of nitrobenzene was achieved rather than degradation, which may cause secondary pollution. Therefore, there is a need

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to search for an effective technology to remove nitrobenzene in aqueous systems.

Advanced oxidation processes (AOPs) have been developed in the past to degrade pollutants in water by generating highly reactive species, such as hydroxyl radicals ($OH^{\cdot}$) [8–13]. Ultrasonic irradiation has been investigated as an effective AOP for treating refractory organics in the field of wastewater treatment [14–17]. The phenomenon of acoustic cavitation plays the dominate role in the ultrasonic process, which involves the formation and collapse of microbubbles from acoustic wave-induced compression/rarefaction [18,19]. The sudden collapse of these cavitation bubbles generates high temperatures (up to 5,000 K) and high pressures (above 1,000 atm). Such "hot spots" dissociate the water vapor present in the cavities into highly reactive species, including hydroxyl ($^{\cdot}OH$), hydrogen ($^{\cdot}H$), and hydroperoxyl ($HO_2^{\cdot}$) radicals [18]. These free radicals play an important role in ultrasonic process for organic pollutants degradation.

However, ultrasound alone is highly energy intensive and is therefore not economically attractive as an alternative for industrial wastewater treatment [18]. To increase the treatment efficiency and reduce the energy consumption, catalysts have been introduced to enhance ultrasonic processes [20–22]. Zero-valent iron (Fe^0) has been investigated to enhance the rate of nitrobenzene reduction under ultrasonic irradiation, and the mechanism involves continuous activation of the Fe^0 surface by acoustic cavitation and accelerated mass transport rate between the solution phase and Fe^0 surface [23,24]. Moreover, zero-valent zinc (Zn^0), which is a stronger reductant than Fe^0, can result in a more rapid and complete degradation of organic pollutants [25]. In addition, Zn^0 is relatively free from potential precipitation problems because the solubility of zinc compounds is greater than iron(III) precipitates, such as goethite, hematite, lepidocrocite, maghemite, and magnetite [26]. Therefore, it is meaningful to develop a highly effective process combining ultrasonic irradiation and Zn^0 as a catalyst for refractory wastewater treatment.

In this study, the enhanced degradation of nitrobenzene by combined ultrasonic irradiation and zero-valent zinc catalyst was investigated. The effects of the initial pH, initial nitrobenzene concentration, Zn^0 dosage, and ultrasonic intensity were studied in detail. The reaction kinetics and degradation mechanism were discussed. The degradation products were analyzed by liquid chromatography–mass spectrometry (LC-MS), and degradation pathways were proposed.

2. Experimental

2.1. Reagents and materials

All chemicals in this work were analytical grade reagents. Nitrobenzene, tertiary butanol, and zero-valent zinc were purchased from Sigma–Aldrich Inc., Tianjin Bodi Chemical Co., and Tianjin Basifu Chemical Co., respectively. Solutions were prepared with deionized water purified by a Millipore Milli Q UV Plus system.

2.2. Batch experiments

Ultrasonic irradiation was performed with a JY92-II ultrasonic generator (Ningbo Xinzhi Technology Co., China) with a maximum power of 250 W and frequency of 20 kHz. All of the batch experiments for nitrobenzene degradation were conducted in 150 mL beakers. The solution was adjusted with diluted NaOH and H_2SO_4 to the desired initial pH, and the final volume was 100 mL. The desired dosage of Zn^0 was introduced into the reaction solution immediately. The ultrasonic probe was inserted into the beaker with the tail end approximately 1.5 cm below the liquid level. Then, the beaker was sealed with parafilm and placed in a water bath at 25℃ with magnetic stirring. At set intervals, 1.5 mL of sample was analyzed after immediately filtering through a 0.45-μm membrane filter. Control experiments were also performed under the same conditions. The scope of the influencing factors of the reaction was studied as follows: initial concentration (0.01, 0.04, 0.07, and 1.0 mmol/L), pH value (5, 6, 7, 8, and 9), ultrasonic intensity (1, 2, 4, and 6 W/cm^2), Zn^0 dosage (0.2, 0.4, 0.6, and 1.0 g/L), and reaction time (5, 10, 15, 20, and 30 min). The ultrasonic intensity was controlled by changing the ultrasonic power. The ultrasound intensity was calculated as follows: ultrasonic power/emitting surface area of the ultrasound generator, and the unit was W/cm^2.

2.3. Analytical techniques

The surface morphology of the samples was investigated using a Hitachi S 4,700 scanning electron microscope (SEM) analyzer with secondary electron detector at different scales and magnifications. The maximum absorption wavelength of nitrobenzene was characterized by a Shimadzu UV2500 spectrometer, and the $\lambda_{\max}$ remained unchanged in a pH range of 5–9. Determination of nitrobenzene was performed with a Waters e2695 high-performance liquid chromatography instrument (HPLC) equipped with a C18 reversed phase column (4.6 × 150 mm I.D.). Elution conditions: mobile phase was composed of 55/45 v/v methanol and deionized water; flow rate: 1 ml/min; injection volume: 10 μL; column temperature: 30℃. The degradation products were identified by a Finnigan TSQ7000 instrument with a diode-array detector, an ESI interface, and an ODS-C18 column (4.6 × 150 mm I.D.). Elution conditions: mobile phase with gradient elution composed of acetonitrile and formic acid; flow rate: 0.3 mL/min; injection volume: 20 μL; column temperature: 20℃. Mass spectrum conditions: voltage of ESI: 55 kV, source temperature: 350℃, and gas: nitrogen.

3. Results and discussion

3.1. Catalytic properties

The catalytic activity of Zn^0 was evaluated in terms of the degradation efficiency of nitrobenzene (Fig. 1). The nitrobenzene removal efficiency with ultrasonic irradiation alone was very low, only 8.1% after 30-min reaction. The low removal efficiency is due to the relatively small amount of reactive species generated. The removal efficiency with Zn^0 alone was only 36.6% due to the aggregation of Zn^0, which decreased the reduction ability significantly. Zn^0 had excellent catalytic properties in the combined system, and the removal efficiency of nitrobenzene was improved to 86.3% after 30 min. The combined system of ultrasonic irradiation and Zn^0 enhanced the degradation ability significantly compared to the ultrasonic irradiation and Zn^0 systems.

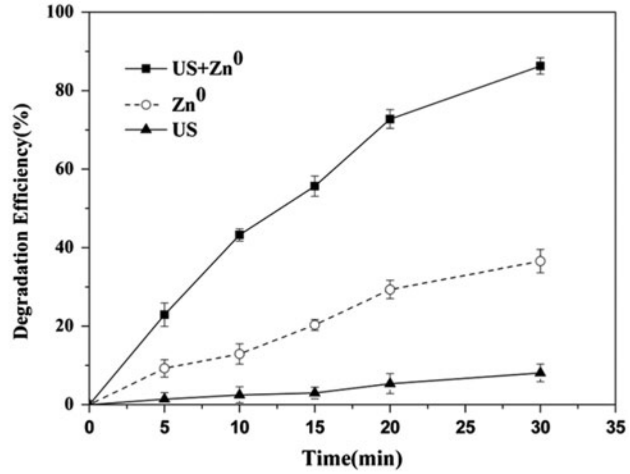

Fig. 1. Enhanced degradation properties of ultrasonic irradiation and Zn^0 on nitrobenzene degradation. Experimental conditions: [NB] = 0.01 mmol/L, pH 7, Zn^0 = 0.4 g/L, Intensity = 2.0 W/cm^2, T = 25℃.

Because Zn^0 particles enhance the ultrasonic cavitation effect by acting as a cavitation nucleus during reaction process, more highly reactive species were produced in the combined system of ultrasonic irradiation and Zn^0. The high oxidation ability of the reactive species and the reduction effect of Zn^0 played important roles in nitrobenzene degradation. Furthermore, the fast degradation of nitrobenzene suggested a strong synergy effect between ultrasonic irradiation and the catalytic activity of Zn^0.

3.2. Effect of pH

The solution pH can significantly influence catalytic ultrasound activity [27,28]. The influence of different initial pH values was investigated in the presence of Zn^0 catalyst under ultrasonic irradiation (Fig. 2). There was no significant difference in the degradation efficiency at 30 min when the initial pH was 5, 6, 7, 8, and 9 because the structure of nitrobenzene in aqueous solution did not change with pH; therefore, its degradation was not affected. The natural pH of the nitrobenzene solution was nearly 7.0. Considering both the removal efficiency and minimum equipment corrosion, the initial pH value of 7 was chosen as the optimum condition.

3.3. Effect of Zn^0 dosage

The effect of Zn^0 catalyst dosage on nitrobenzene degradation was investigated (Fig. 3). The removal efficiency rapidly increased from 59.3 to 86.3% at 30 min when the Zn^0 dosage increased from 0.2 to

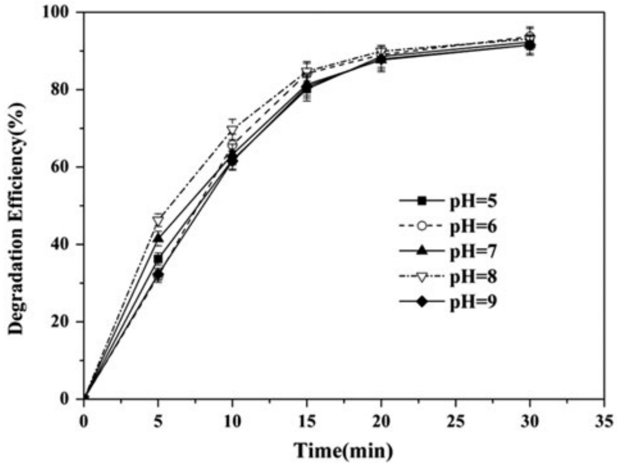

Fig. 2. Effect of pH on nitrobenzene degradation. Experimental conditions: [NB] = 0.01 mmol/L, Zn^0 = 1.0 g/L, Intensity = 2.0 W/cm^2, T = 25℃.

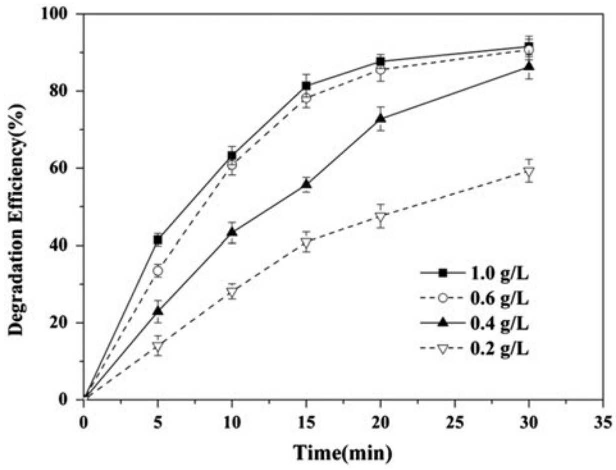

Fig. 3. Effect of the Zn^0 dose on nitrobenzene degradation. Experimental conditions: [NB] = 0.01 mmol/L, pH 7, Intensity = 2.0 W/cm^2, T = 25℃.

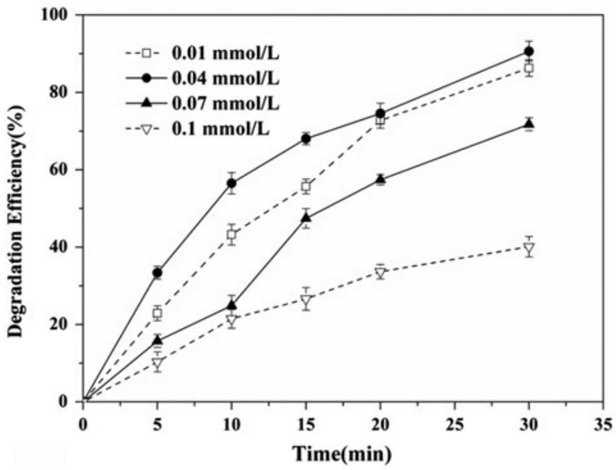

Fig. 4. Effect of the initial concentration on nitrobenzene degradation. Experimental conditions: pH 7, Zn^0 = 0.4 g/L, Intensity = 2.0 W/cm^2, T = 25℃.

0.4 g/L. More active sites were provided to enhance the reduction of nitrobenzene as the Zn^0 dosage increased. More cavitation bubbles were formed as the Zn^0 dosage increased, leading to more highly reactive species generated. When the Zn^0 dosage exceeded 0.4 g/L, the removal efficiency slightly increased approximately 5.3% at 30 min. Excess Zn^0 agglomerated and deposited to some extent, leading to limited mass transfer rate on the solid–liquid interface. In addition, the attenuation of ultrasound occurred due to the scattering effect of Zn^0 particles [29]. Thus, the optimum Zn^0 dosage of 0.4 g/L would be technically and economically feasible.

3.4. Effect of the initial concentration of nitrobenzene

The effect of different initial concentrations of nitrobenzene was investigated (Fig. 4). The removal efficiency increased with initial concentration from 0.01 to 0.04 mmol/L. More molecules were enriched in the cavitation bubbles and the surface layer, which enhanced the degradation of nitrobenzene. Furthermore, the removal efficiency decreased rapidly from 90.6 to 40.1% as the initial concentration of nitrobenzene increased from 0.04 to 0.1 mmol/L. When an excessive amount of nitrobenzene molecules and intermediates adsorbed on the surface of the cavitation bubbles or existed in the aqueous phase, the diffusion of reactive species generated by ultrasonic cavitation was blocked, decreasing the chance of reaction between reactive species and nitrobenzene. In addition, the reduction ability of Zn^0 was limited with a given dosage in the combined system. Hence, an initial concentration of 0.04 mmol/L was sufficient for high degradation efficiency.

3.5. Effect of ultrasonic intensity

The effect of ultrasonic intensity on the degradation of nitrobenzene was investigated (Fig. 5). The degradation efficiency increased gradually with increasing output power of ultrasound. A similar phenomenon was found in the sonocatalytic degradation of methyl parathion in the presence of TiO_2 [30]. The cavitation effect became stronger as the output power

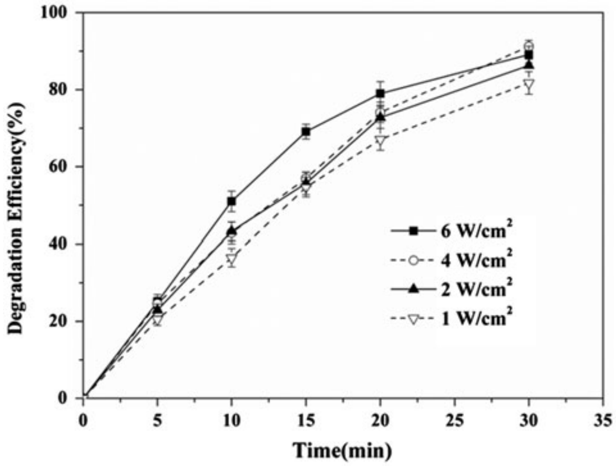

Fig. 5. Effect of the ultrasonic intensity on nitrobenzene degradation. Experimental conditions: [NB] = 0.01 mmol/L, pH 7, Zn^0 = 0.4 g/L, T = 25℃.

of the ultrasound increased, leading to more reactive species being generated [28]. However, excessive ultrasound power led to the formation of more gas bubbles, which scattered the energy [31]. Thus, less ultrasound energy was used to initiate the cavitation effect, leading to slightly decreased degradation efficiency. Therefore, the ultrasonic intensity of 4 W/cm^2 was chosen as the optimum condition. Because 2 W/cm^2 was much more energy efficient and resulted in good nitrobenzene removal, it was also a good choice in terms of both cost and efficiency.

3.6. Reaction kinetics

Kinetic studies were conducted for the three reaction systems: ultrasonic alone, Zn^0 alone, and ultrasonic irradiation and Zn^0 combined. The correlation between $-\ln(C/C_0)$ vs. irradiation time was established (Fig. 6). All three systems followed pseudo-first-order kinetics with correlation coefficients (R^2) higher than 0.97. The values of the rate constants were 0.00277, 0.02128, and 0.06702 min^{-1}, respectively, in the ultrasound, Zn^0, and combined systems. The highest constant rate recorded on the combined system is attributed to the synergic effect of ultrasound and Zn^0. The mutually promoted effects included enhanced ultrasonic cavitation by Zn^0 and reproducing of reduction active sites by ultrasonic micro-jet ejection. Thus, the degradation rate of nitrobenzene in the combined system was far greater than the sum of the two systems alone.

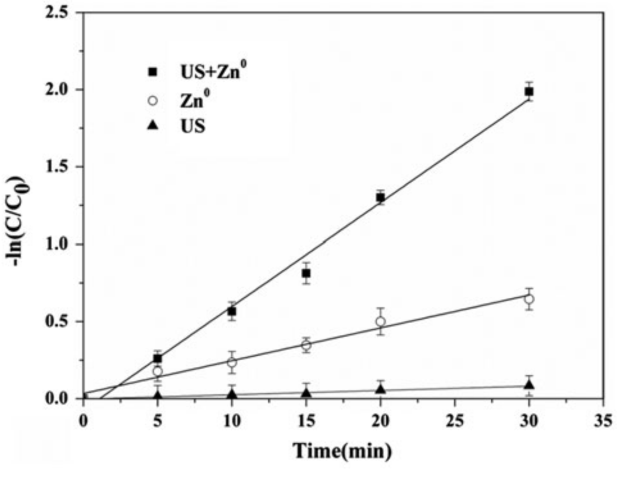

Fig. 6. Pseudo-first-order kinetics of nitrobenzene degradation by combined ultrasound and Zn^0 catalyst. Experimental conditions: [NB] = 0.01 mmol/L, pH 7, Zn^0 = 0.4 g/L, Intensity = 4 W/cm^2, T = 25℃.

3.7. Proposed mechanism

The degradation mechanism of the combined system consists of two parts: hydroxyl radical oxidation and reduction of Zn^0.

3.7.1. Hydroxyl radical oxidation

Ultrasonic irradiation results in cavitation bubbles, and the collapse of these bubbles generates extremely high temperatures and pressures. These “hot spots” can covert water into highly reactive species, including hydroxyl (·OH), hydrogen (·H), and hydroperoxyl ($HO_2^{\cdot}$) radicals. The hydroxyl radical, which has a high redox potential of 2.8 eV, can initiate a complex chain of oxidative degradation of organics [32]. To investigate the dependence of nitrobenzene degradation on hydroxyl radicals, ultrasonic catalytic degradation was conducted in the presence of tert-butanol, which is a common hydroxyl radical scavenger. Fig. 7 shows the nitrobenzene degradation in the absence and presence of different concentrations of tert-butanol. The degradation efficiency can reach 91.2% without tert-butanol addition, and the degradation decreased with increasing concentration of tert-butanol. Moreover, the degradation efficiency reduced to 63.3% at 50 mmol/L tert-butanol due to the decreased amount of hydroxyl radicals in the aqueous solution. Hydroxyl radicals played an important role in the degradation process.

3.7.2. Reduction of Zn^0

As mentioned in Fig. 1, the degradation efficiency reached 36.6% due to reduction in the sole Zn^0 system. Zn^0 has a standard reduction potential of –0.763 eV, and this makes Zn^0 a reducing agent for

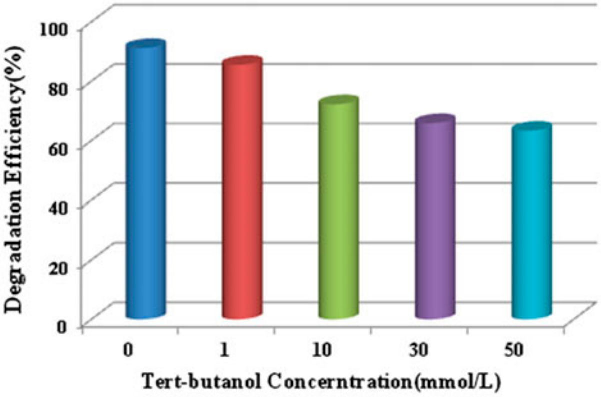

Fig. 7. Effect of tert-butanol addition on nitrobenzene degradation. Experimental conditions: [NB]=0.01 mmol/L, pH 7, Zn^0 = 0.4 g/L, Intensity = 4 W/cm^2, T = 25℃.

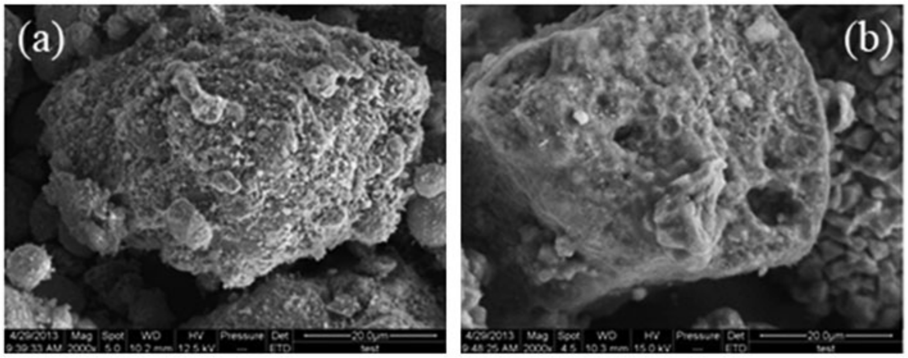

Fig. 8. SEM images of Zn^0: (a) Fresh and (b) Used.

redox-labile substances. Nitrobenzene, which has a nitro group, is mostly reduced to the corresponding amine. Generally, this process consists of two-electron additions, proceeding through nitroso and hydroxylamino intermediates [6]. The high degradation rate in the combined system is attributed to the fast mass transfer rate between the solid–liquid interface, which was enhanced by the chemical effects of continuous ultrasonic cleaning and activation of the Zn^0 surface [23]. Moreover, the superficial cleaning actions were achieved by shock waves and micro-jets formed during cavitation bubbles collapse in the form of corrosion (Fig. 8). The morphology of the Zn^0 catalyst changed significantly after being used. The surface of the used catalyst became flat and small pores disappeared. Therefore, the reduction of Zn^0 was enhanced by ultrasonic cavitation in the combined system.

3.8. Degradation pathways and products

The degradation products in the ultrasonic catalytic process were identified by LC-MS. The intermediates of nitrobenzene degradation were determined based on their mass-to-charge ratios (m/z). Three major fragment ions at m/z 139, 109, and 93 were detected accordingly. Based on the mechanism of the ultrasonic catalytic system, the main products of nitrobenzene degradation were identified as nitrophenol (m/z139), phenylhydroxylamine (m/z109), and aniline (m/z109). Furthermore, the main degradation pathways were proposed as follows (Fig. 9) [23]. Hydroxylation is one pathway for nitrobenzene degradation by hydroxyl radicals produced by ultrasound. The formation of isomeric nitrophenols was observed during the degradation process. p-Nitrophenol and m-nitrophenol can be converted to 4-nitrocatechol through reaction with hydroxyl radicals. Reduction is another pathway for nitrobenzene conversion to aniline. The nitro group was first reduced to a nitroso group; then, Zn^0 was oxidized to Zn^{2+}. The nitroso group was reduced to hydroxyamino group and finally an amino group. With continuous ultrasonic irradiation, the ring structures of these intermediates are opened and further degraded to inorganic products, e.g. HNO_3, CO_2, and H_2O.

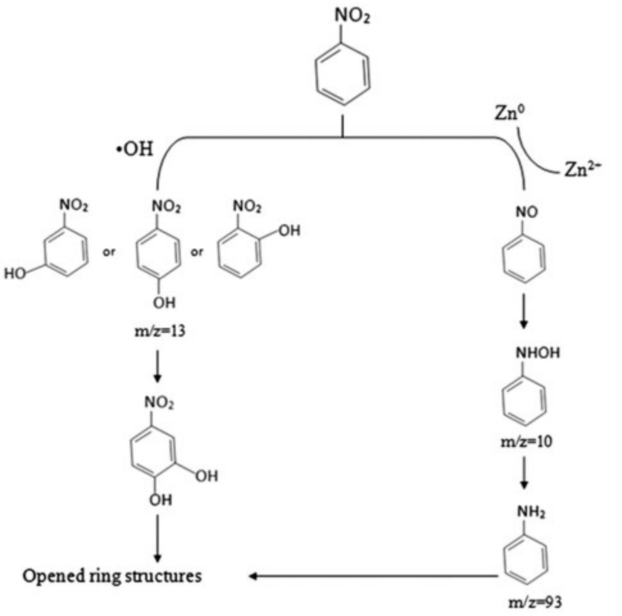

Fig. 9. Degradation pathways and products of nitrobenzene by combined ultrasound and Zn^0 catalyst.

4. Conclusions

Nitrobenzene in aqueous solution can be decomposed effectively by combined ultrasonic irradiation and a Zn^0 catalyst system. The degradation efficiency reached 91.2% within 30 min under optimal conditions. The degradation efficiency of nitrobenzene increased with the Zn^0 dosage and ultrasonic intensity but was nearly independent of the initial pH over the investigated range. The ultrasonic catalytic degradation followed pseudo-first-order kinetics. The rate constant of $0.067\,min^{-1}$ was three times greater than the combined rate constants of the sole ultrasound and sole Zn^0 systems, indicating a synergic effect of ultrasound and Zn^0. Hydroxyl radicals played an important role in the degradation process, which was confirmed by the addition of a hydroxyl scavenger. The reduction of Zn^0 was enhanced by ultrasonic cavitation; thus, the hydroxyl radical oxidation and reduction of Zn^0 were the main mechanisms of degradation in the combined system. Three intermediates of nitrophenol, phenylhydroxylamine, and aniline were identified. Two degradation pathways of hydroxylation and amination were deduced. In summary, the combined ultrasonic irradiation and Zn^0 system has great potential for the treatment of nitrobenzene-containing wastewaters, such as the dye, pharmaceutical, aniline, and explosive industrial wastewaters.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2016.1138887.

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