



Rapid degradation of aniline in aqueous solution by ozone in the presence of zero-valent zinc



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HIGHLIGHTS

- The combination of ozone with Zn(0) is an effective approach to the degradation of aniline.
- The degradation efficiency of aniline markedly increased with an increase of Zn(0) dosage.
- O_2^- is dominant active species responsible for the degradation of aniline by ozone induced with Zn(0).

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ABSTRACT

The effects of Zn(0) dosage from 0.1 to 1.3 g L⁻¹, pH from 2 to 12 and temperature from 288 to 318 K on the degradation of aniline in aqueous solution by ozone in the presence of Zn(0) were investigated through batch experiments. The results demonstrated that Zn(0) had a significantly synergistic role in the degradation of aniline by ozone. A complete decomposition of the initial aniline (10 mg L⁻¹) was achieved by ozone together with Zn(0) within 25 min, and meanwhile nearly 70% of the total organic carbon in the solution was removed. The decomposition efficiency of aniline markedly increased with an increase of Zn(0) dosage. However, temperature exerted a slight impact on the degradation of aniline and the optimum removal efficiency of aniline was realized at 298 K. Aniline was efficiently degraded at all the tested pHs except for 12. Free radicals were investigated by electron paramagnetic resonance technique and free radical scavengers. H₂O₂ concentration generated during the reactions was analyzed using a photometric method. Based on the results obtained in this study, it is proposed that O_2^- instead of $\cdot OH$ is the dominant active species responsible for the degradation of aniline. It is concluded that ozone combined with Zn(0) is an effective and promising approach to the degradation of organic pollutants.

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1. Introduction

Aniline is an important intermediate widely used in the production of polyurethanes, rubber additives, dyes, pharmaceuticals, pesticides and herbicides (Tang et al., 2010; Zhu et al., 2012). On the other hand, aniline is recognized as a major environmental pollutant since it is bio-refractory and hazardous to the human health, and reacts in blood to convert hemoglobin into methaemoglobin by preventing oxygen uptake (Brillas and Casado, 2002). Aniline has been frequently detected in the environment in the recent decades due to the improper discharge from industries (Hu et al., 2015). Therefore, it is necessary to develop a novel and efficient approach to decompose aniline in wastewater.

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Ozone due to its high oxidation potential has been widely adopted for the degradation of organic pollutants in wastewater and for the disinfection of drinking water (Sauleda and Brillas, 2001; Rodríguez et al., 2013). Nevertheless, ozone alone is not an effective oxidant owing to its selective reactions. In general, only a partial mineralization of organic contaminants is achieved with ozone (Zhao et al., 2009; Lee and von Gunten, 2010; Rodríguez et al., 2013). Thus, how to improve the oxidative ability of ozone has received considerable attention. Ozone activated by a heterogeneous catalyst has exhibited a high potential for enhancing the degradation efficiency of refractory organic pollutants. Heterogeneous catalysts include carbons (Faria et al., 2007; Guzman-Perez et al., 2011), metal oxides (Zhang and Ma, 2008; Wang et al., 2011) or metal oxides on supports (Ma et al., 2004; Maddila et al., 2013) and ceramic honeycomb (Zhao et al., 2008). In addition, zero-valent iron (Fe(0)) has been also used as a catalyst to enhance the oxidation degradation of organic contaminants by

ozone (Pan et al., 2012; Zhang et al., 2013). It has been reported that an introduction of Fe(0) in the ozonation process can significantly reduce COD, color and turbidity of wastewater (Quiroz et al., 2011).

As compared with Fe(0), zero-valent zinc (Zn(0)) shows a higher reduction activity and has been applied as a strong reductant for dechlorination of chlorinated organic pollutants (Choi and Kim, 2009; Gao et al., 2011). Therefore, Zn(0) is expected to be a more efficient catalyst for ozonation. Up to now, ozone combined with Zn(0) in treating organic pollutants has been rarely reported. The aim of the present study was to investigate Zn(0) synergistic role in the degradation of aniline by ozone. The effects of Zn(0) dosage, pH and temperature on aniline degradation were also assessed. Free radicals were investigated by electron paramagnetic resonance (EPR) technique and free radical scavengers. H₂O₂ concentration generated from the reactions was analyzed using a photometric method. A possible Zn(0) catalytic mechanism of aniline degradation by ozone was proposed. The results from the present study are helpful to explore Zn(0) as a heterogeneous catalyst to efficiently degrade aniline by ozone.

2. Materials and methods

2.1. Materials

The zero-valent zinc powder was purchased from Xilong Chemical Reagent (Shantou, China). To remove the oil film and oxides of zinc surface, the zinc powder was rinsed with 0.1 M NaOH and 0.1 M HNO₃, respectively. Then, the zinc powder was thoroughly washed with deionized water. The cleaned zinc powder was finally dried at 333 K in a vacuum drying oven. The specific surface area of Zn(0) particles, measured using Brunauer–Emmett–Teller gas adsorption isotherm with N₂ gas on V-Sorb 2800P surface area and porosity analyzer (Beijing Gold App instrument corporation, China), was 17.74 m² g⁻¹. Aniline was obtained from Kelong Chemical Regent (Chengdu, China) and dissolved in deionized water to the required concentration. The stock solution of N-(1-naphthyl) ethylenediamine dihydrochloride, purchased from Sinopharm Chemical Reagent, China, was prepared with deionized water and stored in the brown bottle at 277 K prior to use. Tert-butyl alcohol (TBA) and *p*-benzoquinone (BQ), the scavengers of free radicals, were obtained from Nanjing Chemical Reagent, China and Aladdin Inc. China, respectively. 5,5-dimethyl-1-pyrrolin -N-oxide (DMPO) was purchased from Adamas Reagent, Switzerland. All the other chemical reagents employed in this study were at least of analytic reagent grade and used without further purification.

All glassware used in this work was soaked with 1 M HNO₃ for 12 h and rinsed thoroughly with tap water and then deionized water.

2.2. Ozonation process

The degradation of aniline was conducted in a flask (150 mL) placed at an apparatus with thermostatic bath and magnetic stirring. The given dosage of Zn(0) was added into the flask and then 50 mL aniline solution (10 mg L⁻¹) was introduced. Diluted NaOH or H₂SO₄ solution were adopted to adjust the initial pH to the desired values. The change in solution volume was negligible since the amount of NaOH or H₂SO₄ solution added was very little. Ozone, produced from an ordinary grade air using an WH-H-Y ozone generator (Nanjing Wohuan, China) by silent electric discharge, was immediately bubbled into the flask. At predetermined time intervals, approximately 3 mL of the sample was taken with 5 mL plastic syringe and then filtrated through 0.45 μm membrane

filter to a clean and dried glass tube for the further analysis. All experiments in the section were performed in triplicate.

2.3. Analytic methods

The concentration of aniline was determined by a colorimetric method using N-(1-naphthyl) ethylenediamine as a chromogenic agent. The absorbance was measured in a 1 cm cell at 545 nm on a Alpha-1502 UV-VIS spectrometer (Shanghai Puyuan, China). The method detection limit was determined to be 0.008 mg L⁻¹. The repeatability was excellent with an average R.S.D. = 1.51% and the recovery was 93.72% with an average R.S.D = 2.88% (see Tables S1 and S2). The concentration of ozone in the gas phase was measured by the iodometric titration method (Rakness et al., 1996). The concentration of Zn(II) produced in the reaction process was measured with a flame atomic adsorption spectroscopy (HITACHI Z-2000, Japan). Solution pH was determined with a CyberScan pH2100 Bench Meter (Eutech Instruments, USA) after three-point calibration. The total organic carbon (TOC) of aniline solution was monitored with Shimadzu TOC-L analyzer (Shimadzu, Japan) using the non-purgeable organic carbon method. The concentration of H₂O₂ generated from the ozonation process was measured using a photometric method in which N, N-diethyl-*p*-phenylenediamine was oxidized by a peroxidase catalyzed reaction (Bader et al., 1988).

Intermediates from aniline oxidation were identified using Agilent 1200 series LC equipped with Agilent 6410 Triple Quad mass spectrometer with a ZORBAX Eclipse Plus C18 column (2.1 × 150 mm) (Agilent, USA). The mobile phase was a mixture of 85% methanol and 15% water and the flow rate was 0.2 mL min⁻¹.

5,5-dimethyl-1-pyrrolin-N-oxide, a commonly used spin trapping agent for various types of free radicals, was utilized to generate stable paramagnetic adducts for EPR characterization (Shi et al., 2005) to determine free radicals produced in the catalytic ozonation process. The solution was taken at the given time and placed in capillary tube, which was fixed at the cavity of the EPR spectrometer. The trapped radical species were measured using a Bruker EMX10/12 EPR spectrometer (Bruker Instruments, Inc., Germany). The EPR parameters were: microwave frequency = 9.852 GHz; microwave power = 19.540 mW; modulation amplitude = 2.00 G; and modulation frequency = 100 kHz. EPR spectra were simulated using WIN-EPR SimFonia (Bruker Instruments, Inc., Germany).

3. Results and discussion

3.1. Degradation of aniline in different systems

Comparative experiments in three different reaction systems including aniline/ozone, aniline/ozone/Zn(0) and aniline/Zn(0) bubbled with air instead of ozone were performed. Although ozone is a strong oxidant, it is difficult for ozone alone to oxidize aniline; the removal of aniline by ozone alone was negligible (Fig. 1a). Nevertheless, in the case the solution pH rapidly decreased from 6 in the beginning to 2.76 at the end of the reaction, which is attributed to the transformation of ozone from gas to liquid phase. It is also noted that Zn(0) bubbled with air hardly removed aniline from the aqueous solution. Furthermore, the result suggests that the adsorption of aniline by Zn(0) powder was negligible under the experimental condition. In the presence of ozone and Zn(0), however, 98% of the initial aniline was degraded within 20 min, demonstrating that Zn(0) had a significantly synergistic role in the degradation of aniline by ozone. Meanwhile, the solution pH decreased from 6 in the beginning to 5.28 at the end of the

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