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# Enhanced ozonation degradation of atrazine in the presence of nano-ZnO: Performance, kinetics and effects

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## ABSTRACT

Enhanced ozonation degradation of atrazine (ATZ) with nano-ZnO (nZnO) as catalyst and the influences of the operational parameters have been investigated through semi-continuous experiments in this study. The results demonstrated that the combination of ozone (O<sub>3</sub>) and nZnO showed an obvious synergetic effect and the ATZ degradation conformed to pseudo-first-order kinetics. An improvement of ATZ degradation efficiency by 41.8% and pseudo-first-order rate constant by more than a factor of four was obtained in the O<sub>3</sub>/nZnO process after 5 min of reaction compared to O<sub>3</sub> alone. Meanwhile, the degradation efficiency of ATZ was gradually enhanced with increasing nZnO dosage and initial pH in the range from 3.0 to 8.0, and a higher amount of ATZ was degraded when the initial concentration of ATZ rose from 0.5 to 5 mg/L. Additionally, sulfate ion, chloride ion, nitrate ion and low concentrations of humic acid substances led to enhancement of the ATZ degradation. The notable decrease of ATZ removal efficiency observed in the presence of radical scavengers and the results of free radical tests indicated that  $\cdot\text{OH}$  is the dominant active radical species. The mechanism investigation demonstrated that the enhancement effect could be attributed to the introduction of nZnO, which could promote the utilization of O<sub>3</sub>, enhance the formation of superoxide radical, and further accelerate the production of hydrogen peroxide and the generation of  $\cdot\text{OH}/\text{O}_2^{\cdot-}$ .

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## Introduction

The presence of micropollutants, particularly pesticides, in surface waters is a concern not only for their adverse environmental impact on aquatic ecosystems, but also for their potential harmful effects on human health (Schwarzenbach et al., 2006). Atrazine (ATZ) is one of the most widely applied herbicides in the world, and has been associated with physiological problems in aquatic fauna and malformation of newborn babies (Hayes et al., 2010). It has been classified as a possible human carcinogen, priority hazardous substance and endocrine disrupting compound.

Ozonation is one of the most effective wastewater treatment technologies and has been widely adopted for micropollutant oxidation, natural organic matter (NOM) transformation and pathogen inactivation (Ikehata et al., 2006). However, some micropollutants, including ATZ, have a low reaction rate and only partial mineralization is achieved with ozone (O<sub>3</sub>) (Acero et al., 2000). Thus, to improve the reaction efficiency of refractory organic pollutants during ozonation processes, application of heterogeneous catalysts has received considerable attention (Kasprzyk-Hordern et al., 2003). Metal oxides, metals on supports, minerals, and activated carbons, as four main catalyst categories, have been widely used in heterogeneous

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catalytic ozonation (Nawrocki and Kasprzyk-Hordern, 2010). The main advantages of catalytic ozonation are better  $O_3$  utilization, increased contaminant removal efficiency, greater degree of organic matter mineralization, and easy separation of catalysts (Legube and Leitner, 1999; Qi et al., 2015).

Zinc oxide (ZnO) is a well-known heterogeneous catalyst material used in a large number of industrial processes, due to its advantages of high catalytic activity, nontoxicity, insolubility, and low cost (Jung and Choi, 2006). Meanwhile, ZnO, with a band gap of 3.37 eV, has become a promising photocatalyst in the past few years because of its distinctive catalytic, optoelectronic, and photochemical properties (Hayat et al., 2011). Moreover, nano-materials, which can exhibit unusual chemical and physical properties, have received much attention in the past two decades. The high surface area and good dispersivity of nano-catalysts are favorable to catalysis (Zaera, 2013). Previous studies revealed that ZnO exhibited high catalytic activity in  $O_3$  degradation of phenol in wastewater (Dong et al., 2011; Huang et al., 2005). However, the reaction efficiency and characteristics of catalytic ozonation using nano-ZnO (nZnO, 20–40 nm) remain unknown, and very little information is available on the detailed operational effects and mechanism of nZnO-catalytic ozonation of ATZ in aqueous solution.

This study aimed to investigate the enhancement of activity by nZnO in the degradation of ATZ by  $O_3$ . The effects of operating variables, such as nZnO dosage, ATZ initial concentration, initial pH, temperature, inorganic anions, NOM, and free radical scavengers on ATZ degradation in the  $O_3$ /nZnO process were also assessed. Free radicals were determined by the electron paramagnetic resonance (EPR) technique. A possible mechanism for nZnO-catalyzed  $O_3$  for ATZ degradation was proposed.

## 1. Materials and methods

### 1.1. Materials and reagents

The nZnO (size:  $30 \pm 10$  nm, specific surface area:  $32.236 \text{ m}^2/\text{g}$ , purity: >99.9%) and 5,5-dimethyl-1-pyrrolin-N-oxide (DMPO, purity >97%) were purchased from Aladdin Industrial Corporation (Shanghai, China). ATZ with the highest purity available (>97%) was provided by Tokyo Chemical Industry (Tokyo, Japan). High performance liquid chromatography (HPLC)-grade methanol and acetonitrile (ACN) were purchased from Fisher Scientific (Geel, Belgium), and humic acid (HA) sodium salt (Product No. H16752, Lot No. STBF3718V) was obtained from Sigma-Aldrich (St. Louis, MO, USA). ZnO, *tert*-butyl-alcohol (TBA), benzoquinone (BQ), indigo carmine, sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) and all other reagents were of analytical grade and supplied by Sinopharm Chemical Reagent Company, China.

All the solutions were prepared using ultrapure water (Milli-Q Advantage A10, Millipore, USA). All glassware used in this study was soaked in 1 mol/L  $\text{HNO}_3$  for 12 hr and rinsed thoroughly with tap water and then ultrapure water. Due to the low water solubility of ATZ, its stock solution (20 mg/L) was magnetically stirred for 48 hr in the dark to achieve complete dissolution.

### 1.2. Experimental procedures

Catalytic ozonation experiments were performed in a semi-continuous glass reactor (500 mL) equipped with a thermostatic bath and magnetic stirring. The designed dosage of nZnO was added into the reactor and then a certain amount of ATZ stock solution was introduced. Diluted NaOH or HCl solution was employed to adjust the initial pH to the desired values. The change in solution volume was negligible since the amount of NaOH or HCl solution added was very small.  $O_3$  gas was produced from pure oxygen using a laboratory ozone generator (3S-A3, Tongling Technology, China). The  $O_3$  gas stream was injected into the reactor through two stainless steel diffusers. The flow rate of  $O_3$  and  $O_2$  gas was constantly controlled at 0.5 L/min. An  $O_3$  analyzer (IDEAL-2000, Zibo IDEAL Company, China) was installed at the inlet of the reactor with ultraviolet light detection at 254 nm. The concentration of  $O_3$  gas displayed digitally by the analyzer was automatically corrected to normal temperature and pressure conditions. To prevent any  $O_3$  discharge to the environment, the off-gas of non-dissolved  $O_3$  was absorbed using potassium iodide solution. A schematic diagram of the ozonation experimental system is shown in Fig. 1. Samples were collected at different time intervals, quenched with 0.1 mol/L  $\text{Na}_2\text{S}_2\text{O}_3$  and centrifuged at 10,000 r/min for 10 min (Centrifuge 5418, Eppendorf, Germany), and the supernatant was separated and filtered through a  $0.45 \mu\text{m}$  cellulose nitrate membrane for further analysis. ATZ adsorption experiments (in the absence of  $O_3$ ) were carried out using the same experimental setup. Municipal secondary effluent was collected from Tangxun Lake WWTP in Wuhan city. The characteristics of the filtered municipal secondary effluent were as follows: total organic carbon (TOC) 10.75 mg/L, pH 7.82, chemical oxygen demand (COD) 36.92 mg/L. All the experiments were performed at least in duplicate.

### 1.3. Analytical methods

The dissolved  $O_3$  concentration was analyzed by the indigo method (Bader and Hoigné, 1981). The concentration of  $O_3$  in the gas phase was measured by an IDEAL-2000 ozone analyzer (IDEAL-2000, Zibo IDEAL Company, China). The concentration of ATZ in water was determined by a Waters e2695 HPLC (Waters e2695, Waters, USA) equipped with a Waters Sunfire C18 column (150 mm  $\times$  4.6 mm,  $5 \mu\text{m}$  particle size). ACN/water (70:30, v/v) was used as the mobile phase at a constant flow rate of 1.0 mL/min. The sample was detected by an ultraviolet/visible (UV/Vis) detector (Waters 2489, Waters, USA) at 225 nm and the injected volume was 50  $\mu\text{L}$ . The method detection limit of ATZ was determined to be 0.01 mg/L by using a signal-to-noise (S/N) ratio approach.

The concentration of zinc ion released in the reaction process was measured with the dithizone-spectrophotometric method according to the Water Quality Determination Standard in China (GB 7472-87). Solution pH was determined with a pH meter (PB-10, Sartorius, Germany) after three-point calibration. The TOC was monitored with an TOC analyzer (vario TOC select, Elementar, Germany) using the non-purgeable organic carbon method. The concentration of  $\text{H}_2\text{O}_2$  generated during the ozonation process was measured using a photometric method (Sellers, 1980).

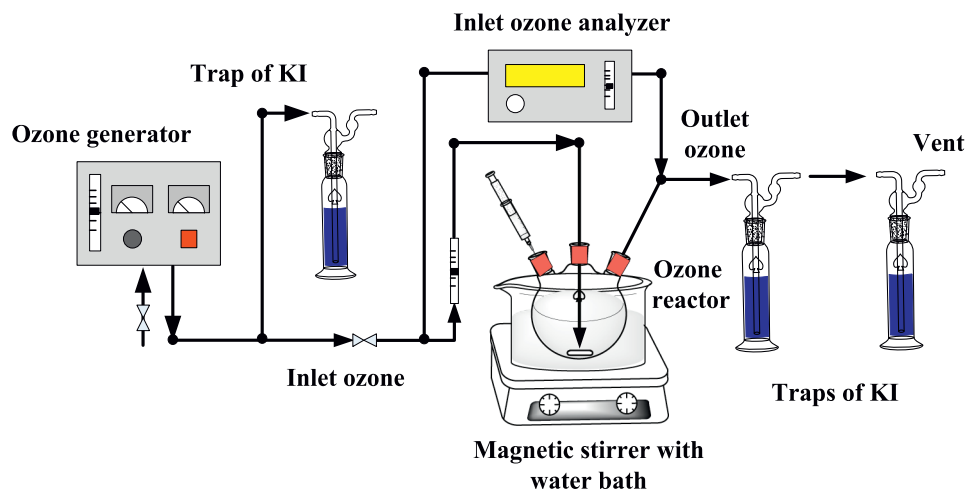


Fig. 1 – Schematic diagram of the ozonation system.

DMPO, 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 a predetermined time and placed in a capillary tube, which was fixed at the cavity of the EPR spectrometer. The trapped radical species were measured using an EPR spectrometer (Bruker A300, Bruker, Germany). The EPR parameters were: microwave frequency 9.862 GHz; microwave power 20.004 mW; modulation amplitude 1.25 G; and modulation frequency 100 kHz.

Intermediates from ATZ oxidation were separated using an ultra-high performance liquid chromatography (UPLC) system (Agilent 1290, Agilent, USA) equipped with a Zorbax SB-C18 column (100 mm × 2.1 mm, 1.8 μm) (Zorbax SB-C18, Agilent, USA), then detected by tandem mass spectrometry (MS/MS) (Agilent 6420, Agilent, USA). Milli-Q water containing 0.2% formic acid (v/v) (A) and ACN (B) were used as the mobile phases at a flow rate of 0.25 mL/min. The injected volume was 20 μL. The gradient elution program (time in min, percentage of mobile phase B) was set as follows: (0, 10%), (2, 10%), (5, 30%), (8, 50%), (13, 80%), (18, 100%), (20, 100%), (20.1, 10%), and (23, 10%). The mass spectrometry equipped with an electrospray ionization (ESI) source and operated in the positive ion mode, was employed to analyze the ATZ intermediates. The MS system was operated under the following conditions: capillary voltage 3.5 kV, drying gas temperature 350°C, drying gas flow rate 10 L/min, nebulizing gas pressure 35 psi, and fragmentor voltage 100 V. Product ions ( $m/z$ ) were acquired from 50.0 to 220.0 under MS2 scan mode. The quantitative analysis software (B.04.00, Agilent, USA) was employed for the data analysis.

## 2. Results and discussion

### 2.1. Degradation of ATZ in different processes

The degradation of ATZ in aqueous solution was evaluated and compared in different processes including nZnO alone, O<sub>3</sub> alone, O<sub>2</sub>/nZnO, O<sub>3</sub>/ZnO and O<sub>3</sub>/nZnO, and the variation of ATZ

concentration versus reaction time is shown in Fig. 2. As depicted in Fig. 2, the degradation efficiency of ATZ with O<sub>3</sub> alone, O<sub>3</sub>/ZnO and O<sub>3</sub>/nZnO was 57.1%, 89.5% and 98.9%, respectively, after 5 min reaction at pH 6.0. Meanwhile, the removal of ATZ by nZnO adsorption and the O<sub>2</sub>/nZnO process was negligible (<3%). It can be seen that the presence of ZnO and nZnO enhances the degradation efficiency of ATZ, while the best result is obtained for the O<sub>3</sub>/nZnO process. The pseudo-first-order rate constant ( $k$ ) of ATZ was 0.4234 min<sup>-1</sup> ( $R^2 = 0.9946$ ) for O<sub>3</sub>/ZnO and 0.9255 min<sup>-1</sup> ( $R^2 = 0.9957$ ) for O<sub>3</sub>/nZnO, which clearly indicated that nZnO showed strong performance in enhancing O<sub>3</sub> removal of ATZ, and the combination of O<sub>3</sub> and nZnO showed an obvious synergetic effect.

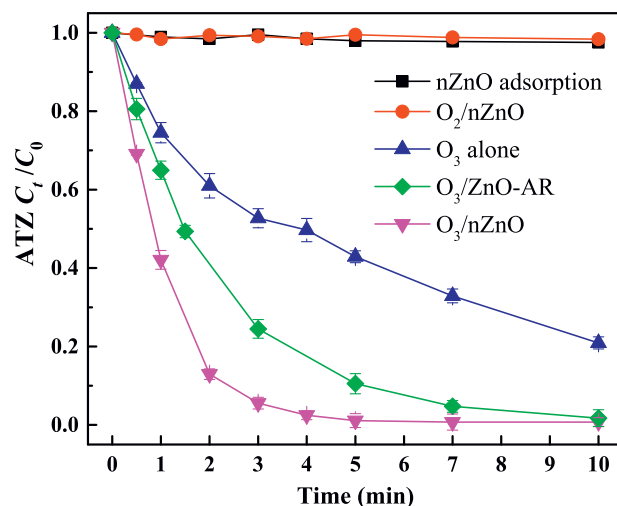


Fig. 2 – Atrazine (ATZ) degradation efficiency in the selected processes. Experimental conditions: initial ATZ concentration ([ATZ]<sub>0</sub>) 2 mg/L, nZnO dosage ([nZnO]) 250 mg/L, O<sub>3</sub> concentration ([O<sub>3</sub>]) 10 mg/L, pH<sub>0</sub> 6.0 ± 0.1, temperature (T) 20°C. C<sub>t</sub>: ATZ concentration along with the reaction time; C<sub>0</sub>: initial ATZ concentration; AR: analytical grade; nZnO: nano-ZnO.

As reported previously (Acero et al., 2000), the reaction rate constants between ATZ with molecular  $O_3$  and  $\cdot OH$  are  $6.0$  and  $3.0 \times 10^9$  mol/(L·sec), which means that ATZ reacts rapidly with  $\cdot OH$ . It was deduced that lower ATZ degradation efficiency was obtained in the process of  $O_3$  alone due to both direct oxidation by molecular ozone and indirect oxidation by  $\cdot OH$  generated from ozone self-decomposition. Accordingly, the synergetic effect of  $O_3$ /nZnO was probably attributable to the formation of more  $\cdot OH$ .

## 2.2. Influences of operational factors in $O_3$ /nZnO process

Proper operational parameters are crucial to the oxidation of micropollutants in drinking water or reclaimed water treatment plants. The following section describes experiments performed to investigate the influence of operational parameters on ATZ degradation efficiency, including nZnO dosage, initial ATZ concentration, initial pH, temperature, inorganic anions, and NOM in  $O_3$ /nZnO process.

### 2.2.1. nZnO dosage

The catalyst dosage is always a crucial factor in heterogeneous catalytic reactions. In order to make effective use of the catalyst in practical application, it is necessary to explore the impact of catalyst dosage on the degradation efficiency and determine the optimum dosage. The effects of nZnO dosage on the degradation of ATZ were investigated and the results are represented in Fig. 3. It can be observed from Fig. 3 that the removal efficiency of ATZ was enhanced from 62.7% to 97.2% and  $k$  was increased from  $0.6206$  to  $1.5534$  min $^{-1}$  as the dosage of nZnO was raised from 50 to 1000 mg/L. Based on the good linear relationship between the rate constants and the nZnO dosage (see inset in Fig. 3), we can speculate that nZnO could

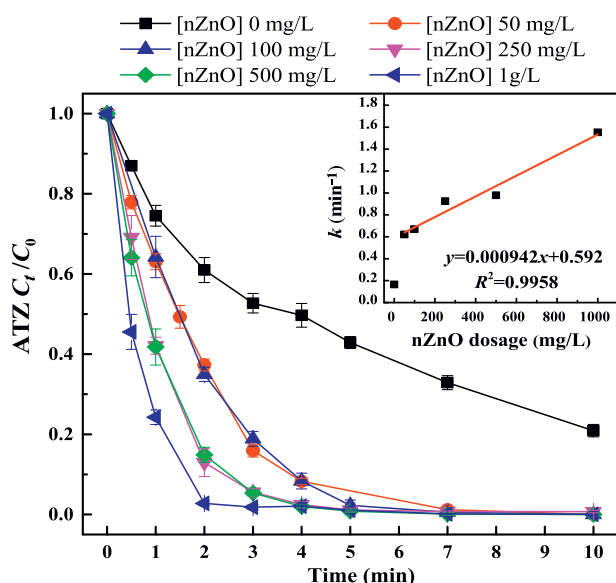


Fig. 3 – Effect of nZnO dosage on ATZ degradation in the  $O_3$ /nZnO process. Experimental conditions:  $[ATZ]_0 = 2$  mg/L,  $[O_3] = 10$  mg/L,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ C$ . Inset displays relationship between the pseudo-first-order constant ( $k$ ) and nZnO dosage.

enhance the transformation of  $O_3$  into  $\cdot OH$  and that its transformation efficiency was proportional to the concentration of nZnO, finally resulting in the observed enhancement of ATZ degradation. Zhai et al. (2010) also revealed that ZnO has the ability to enhance the decomposition of ozone and leads to the formation of highly oxidizing intermediates ( $\cdot OH$ ). It is well known that nano-materials including metal oxides tend to form aggregates when they are suspended in water, and that the self-aggregation rate depends on the particle dosage and the pH (Huang et al., 2005). Hence, 250 mg/L of nZnO catalyst, as a moderate dosage, was used in all other experiments.

### 2.2.2. Initial ATZ concentration

The concentration of pollutants, as an important parameter in wastewater treatment, has great influence on the required  $O_3$  quantity and the treatment time. Therefore, it is very important from a practical point of view to study how the initial ATZ concentration affects the removal of pollutants in the nZnO-catalytic ozonation process. The ATZ degradation under different initial concentrations varied from 0.5 to 5 mg/L, as displayed in Fig. 4. It was observed that the removal efficiency and rate constant decreased gradually as the initial ATZ concentration increased. The degradation efficiency at initial ATZ concentration of 0.5, 1, 2, 3 and 5 mg/L was 100%, 99.5%, 94.5%, 92%, and 90.2% after 3 min reaction, respectively (Fig. 4). On the contrary, a higher amount of ATZ was degraded as the initial ATZ concentration increased, which is attributed to the increase in the probability of collision between pollutants and oxidants. In addition, the quantity of induced active oxidants was constant in the  $O_3$ /nZnO process. With the increase of initial ATZ concentration, more intermediates will be generated that would compete for the available oxidants against ATZ, resulting in a lower ATZ degradation efficiency. An initial ATZ concentration of 2 mg/L was selected in order to simulate the

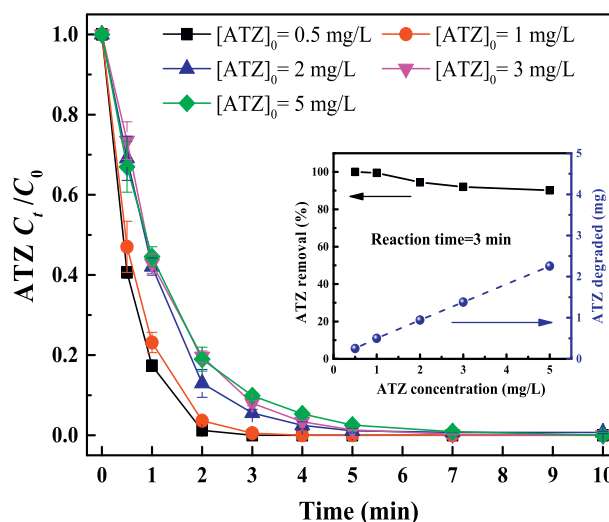


Fig. 4 – Effect of initial ATZ concentration on its degradation efficiency in the  $O_3$ /nZnO process. Experimental conditions:  $[nZnO] = 250$  mg/L,  $[O_3] = 10$  mg/L,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ C$ . Inset shows the removal rate and degraded amount of ATZ versus the initial ATZ concentration.



trace levels present in real conditions and to ensure a sufficient amount of ATZ degradation.

### 2.2.3. Initial pH

$O_3$  may attack organic compounds through either direct oxidation with molecular  $O_3$  or indirect oxidation with highly reactive  $\cdot OH$ , which is highly pH-dependent. The initial pH is an important operational parameter because it influences the  $\cdot OH$  generation rate, the utilization efficiency of ozone, the surface properties of catalysts and the charge of ionic or ionizable organic molecules (Kasprzyk-Hordern et al., 2003; Zhao et al., 2008). As illustrated in Fig. 5, the effects of initial pH on ATZ degradation in the  $O_3/nZnO$  process were studied from 3.0 to 9.0.

It was observed that little ATZ was removed (less than 3%) by catalyst adsorption under all the tested pH conditions. The hydrophobicity of ATZ could be an important factor hindering its adsorption on the nZnO surface in aqueous solution. In addition, the weak ATZ adsorption on nZnO revealed that the oxidation reactions may occur in the bulk solution rather than on the catalyst surface. It can be seen from Fig. 5 that the presence of nZnO promoted the ozonation greatly at each pH value, and therefore over 84% of ATZ was degraded over a wide pH range of 3.0–9.0 after 5 min reaction. It can be clearly seen that the degradation efficiency of ATZ in the  $O_3/nZnO$  process is slightly affected by the solution pH, whereas ozonation without catalyst addition is much more sensitive to pH change (Elovitz et al., 2000; Sotelo et al., 1987). Moreover, the removal efficiency of ATZ in the  $O_3/nZnO$  process increased 22.2%–42% compared to  $O_3$  alone in the pH range of 3.0–8.0. At pH 9.0, due to the increased decomposition rate of molecular  $O_3$  by  $OH^-$ , the catalysts were less effective compared to other pH values or  $O_3$  alone (Roshani et al., 2014).

The overall result was that the variation of initial pH did not notably affect the removal of ATZ in the  $O_3/nZnO$  process.

The results also indicated that a heterogeneous catalytic reaction mechanism occurs in the  $O_3/nZnO$  process, and except for  $OH^-$ , nZnO was assumed to be responsible for initiating the decomposition of  $O_3$ . The pH value of nZnO at the point of zero charge was 9.3, which was determined by the titration method (not shown here). In the pH range of 3.0–9.0 in bulk solution, the nZnO surface was negatively charged and  $O_3$  would be strongly attracted towards the nZnO surface due to its electrophilic characteristics (Jung and Choi, 2006; Kasprzyk-Hordern et al., 2003; von Gunten, 2003).

### 2.2.4. Temperature

The effect of temperature on ATZ degradation in the  $O_3/nZnO$  process is shown in Fig. 6. It is noted that ATZ degradation efficiency increased as the temperature rose from 10 to 40°C. The rate constants  $k$  of ATZ degradation were  $0.3048 \text{ min}^{-1}$  ( $R^2 = 0.9759$ ) at 10°C,  $0.9255 \text{ min}^{-1}$  ( $R^2 = 0.9728$ ) at 20°C,  $1.1664 \text{ min}^{-1}$  ( $R^2 = 0.9965$ ) at 30°C, and  $1.4139 \text{ min}^{-1}$  ( $R^2 = 0.9658$ ) at 40°C, respectively (Fig. 6). It is known that a relatively high temperature should reduce the reaction activation energy and then increase the reaction rate. However, the increase of the temperature does not benefit the solubility and stability of ozone in solution (Elovitz et al., 2000), affecting the interaction between  $O_3$  and nZnO in the liquid phase, and further forming radicals (such as  $\cdot OH$ ) that react with organics. Therefore, the following ozonation experiments were performed at 20°C in this study.

### 2.2.5. Inorganic anions

There is a wide variety of inorganic anions such as chloride ion ( $Cl^-$ ), nitrate ion ( $NO_3^-$ ), sulfate ion ( $SO_4^{2-}$ ), bicarbonate ion ( $HCO_3^-$ ) and phosphate ion ( $PO_4^{3-}$ ) ubiquitously existing in wastewater and surface water, which could have significant impacts on the degradation of organic compounds during catalytic ozonation. Some studies have shown that most of

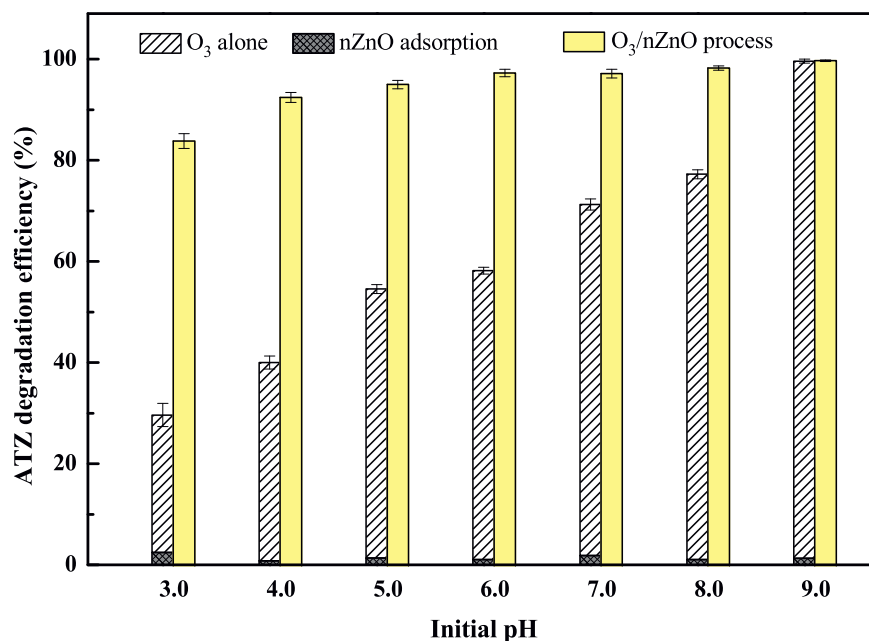
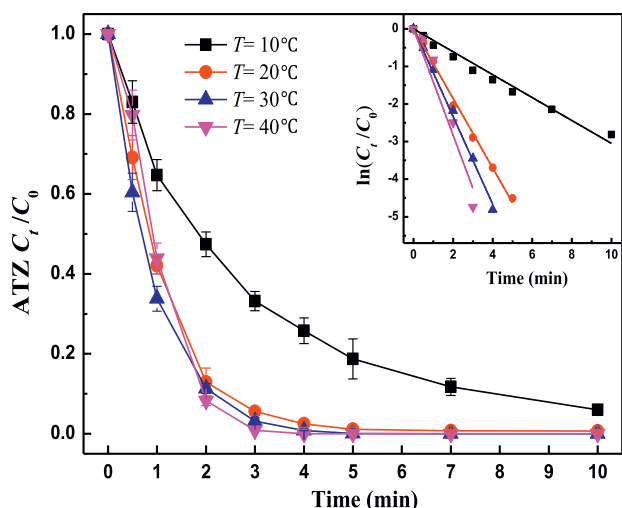


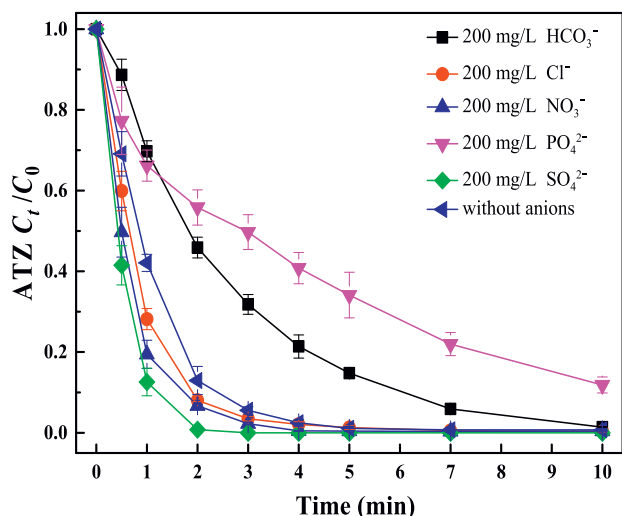
Fig. 5 – Effect of initial pH on ATZ degradation in the  $O_3/nZnO$  process. Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $T = 20^\circ\text{C}$ , reaction time = 5 min.



**Fig. 6 – Effect of reaction temperature on ATZ degradation in the  $O_3/nZnO$  process. Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ .**

these inorganic anions exhibit an inhibitory effect on the degradation of organic compounds (Parfitt and Russell, 1977; Yuan et al., 2013). In this study, known concentrations of these inorganic anions were added separately to the  $O_3/nZnO$  process, so as to investigate the influence of various inorganic anions on ATZ degradation. As illustrated in Fig. 7, the effects of  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$  and  $PO_4^{3-}$  were different.

$PO_4^{3-}$ , a common ligand, has a relatively strong affinity for transition metal ions. In the presence of  $PO_4^{3-}$ , a significant inhibitory effect on ATZ degradation was observed, leading to a 33% decrease in ATZ removal at 5 min.  $PO_4^{3-}$ , as a stronger Lewis base than water, can lead to maximum substitution of surface OH groups, which could negatively affect the catalytic reaction (Afzal et al., 2016; Li et al., 2012). The aforementioned



**Fig. 7 – Effect of inorganic anions on ATZ degradation in the  $O_3/nZnO$  process. Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ .**

results provided evidence that the catalytic activity was due to the bonding of  $O_3$  with the Lewis acid sites of  $nZnO$ .

$HCO_3^-$  is well known as a  $\cdot OH$  scavenger, which could react with  $\cdot OH$  to produce carbonate radical ions ( $k = 8.5 \times 10^6 \text{ mol/(L}\cdot\text{sec)}$ ) (Faria et al., 2009). When  $HCO_3^-$  was introduced into the reaction system, the results indicated that  $HCO_3^-$  significantly inhibited ATZ degradation, with a 13% decrease in ATZ removal at 5 min. Nevertheless, the presence of  $SO_4^{2-}$  and  $NO_3^-$  significantly improved the degradation of ATZ and the introduction of  $Cl^-$  showed a slight enhancement compared to control. Zhang et al. (2015a) also found that the introduction of  $Cl^-$  and  $SO_4^{2-}$  promoted p-chloronitrobenzene degradation in the  $O_3/Zn(0)$  process, which was attributed to complex formation between the ligands  $Cl^-$  or  $SO_4^{2-}$  and  $Zn(II)$  and the presence of a different dominant oxidation radical ( $O_2^{\cdot -}$ , not  $\cdot OH$ ).

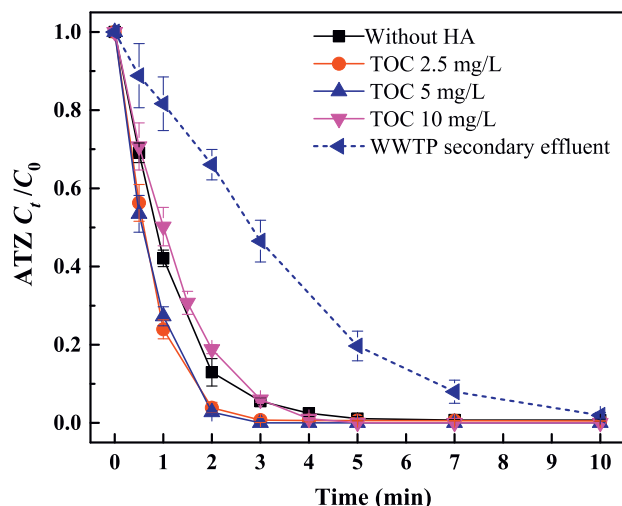
#### 2.2.6. The presence of NOM

NOM is ubiquitous in surface and ground waters, and as an important component of NOM, HA can directly or indirectly react with  $O_3$  (von Gunten, 2003). It is important to understand the role of HA in the mechanism of  $nZnO$ -catalytic ozonation, since in other studies it has been shown that HA can act as a radical initiator, promoter and scavenger (Staehelin and Hoigne, 1985; Xiong and Graham, 1992). The influence of HA and municipal secondary effluent on ATZ degradation in  $O_3/nZnO$  process was investigated and the results are shown in Fig. 8.

As illustrated in Fig. 8, with the increase in concentration of HA from 2.5 to 10 mg/L, the  $k$  of ATZ declined from 1.6754 to  $1.0024 \text{ min}^{-1}$ . It is noted here that HA has a substantial influence on ATZ degradation in the  $O_3/nZnO$  process. In the presence of a low HA concentration (e.g.,  $\leq 5 \text{ mg/L}$  as TOC), the  $nZnO$ -catalyzed ozonation is clearly enhanced. However, with the further increase of HA concentration (TOC 10 mg/L), a slight inhibitory effect by HA on ATZ degradation is observed. Our previous study (Yuan et al., 2015) also revealed that the presence of HA (TOC 4.7 mg/L) significantly enhanced the degradation of four reactive organophosphate esters in  $O_3$  treatment. Ma and Graham (1999) reported a measurable enhancement of ATZ degradation in the presence of a small amount of HA (dissolved organic carbon 1 mg/L) in Mn-catalyzed ozonation.

HA ozonation could inherently lead to considerable  $\cdot OH$  production as a result of the reactions between  $O_3$  and the electron-rich moieties of HA (von Gunten, 2003). It has also been reported (Jung and Choi, 2006) that  $O_3$  decomposition in the presence of ZnO leads to generation of  $\cdot OH$ . Therefore, at low concentrations of HA, both  $nZnO$  and HA may initiate and promote the formation of  $\cdot OH$  during ozonation, which enhances the degradation of ATZ. At higher concentrations, HA may compete with ATZ for both  $O_3$  and the highly reactive  $\cdot OH$  (Xiong and Graham, 1992; Yuan et al., 2013), thus decreasing the ATZ oxidation efficiency (Fig. 8).

As shown in Fig. 8, ATZ degradation was strongly inhibited in the municipal secondary effluent (TOC 10.75 mg/L, pH 7.82, COD 36.92 mg/L) and the ATZ degradation rate constant was only  $0.331 \text{ min}^{-1}$ . The effluent organic matter (EfOM) could react with both  $O_3$  and  $\cdot OH$ , thus considerably impacting the degradation of ATZ. EfOM was reported to be the main  $\cdot OH$  scavenger in municipal secondary effluents, due to its moderate reactivity towards  $\cdot OH$  and its relatively high



**Fig. 8** – Effect of HA on ATZ degradation in the  $O_3/nZnO$  process. Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ . TOC: total organic carbon; WWTP: wastewater treatment plant; HA: humic acid.

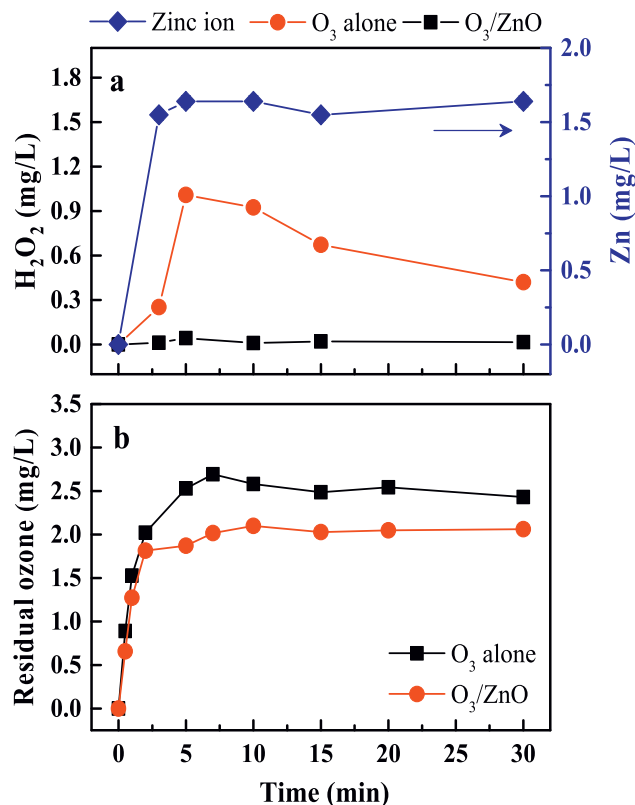
concentration (Keen et al., 2014; Rosario-Ortiz et al., 2008). Note that there were various ions (e.g.,  $HCO_3^-$ ,  $CO_3^{2-}$ ) present in the municipal secondary effluent, which also could act as radical scavengers.

### 2.3. Exploration of $nZnO$ -catalytic ozonation mechanisms

#### 2.3.1. Stability of $nZnO$ and residual $O_3$ concentration in aqueous solution

To further explore the stability of  $nZnO$  for practical application, the leaching of zinc ion into solution and  $nZnO$  recycling experiments was investigated. As shown in Fig. 9a, there was weak leaching of zinc ion, and the maximum concentration was below  $2 \text{ mg/L}$  with the prolonging of reaction time. The released zinc ion in the solution showed no effects on ozonation. The corrosive dissolution of  $nZnO$  could be the reason for zinc ion release, and further research on the reduction of zinc release and improvement of catalyst stability should be carried out, such as by reducing the  $nZnO$  dosage or loading  $nZnO$  onto a support. For the recycling experiment, the recovered  $nZnO$  was centrifuged, dried at  $60^\circ\text{C}$  for 24 hr, and then reused for a subsequent run. As illustrated in Fig. 10, there was no obvious loss of catalytic properties after the 6th run, and  $nZnO$  exhibited good stability in the catalytic ozonation process.

The residual  $O_3$  concentration was monitored in  $O_3$  alone and  $O_3/nZnO$  processes over a reaction time of 30 min (Fig. 9b). The residual  $O_3$  increased gradually as a function of reaction time and reached maximum values of 2.69 and  $1.90 \text{ mg/L}$  in  $O_3$  alone and  $O_3/nZnO$  processes. The results showed that  $nZnO$  decreased the residual  $O_3$  concentration, which might help to initiate the production of oxidative intermediate species derived from  $O_3$  decomposition.



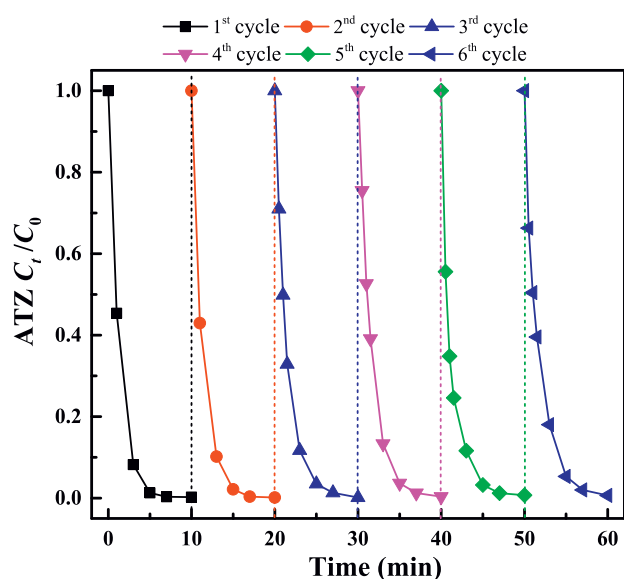
**Fig. 9** – Concentration of  $H_2O_2$ , released zinc ion and residual ozone as a function of time in the experimental processes. Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ .

#### 2.3.2. Influence of the addition of radical scavengers

To further clarify the degradation mechanisms of ATZ in the  $O_3/nZnO$  process, experiments were performed to investigate ATZ degradation by addition of radical scavengers. TBA is a typical  $\cdot OH$  scavenger, which can react with  $\cdot OH$  ( $k_{\cdot OH} = 5 \times 10^8 \text{ mol/(L}\cdot\text{sec)}$ ) and generates inert intermediates, leading to the termination of the radical chain reactions (Ma and Graham, 2000). The experimental results are shown in Fig. 11.

As the concentration of TBA increased, the degradation efficiency of ATZ decreased gradually. For example, with a reaction time of 3 min, the ATZ degradation efficiency in the  $O_3/nZnO$  process was 94.5%, 56.0%, 52.9% and 43.6% with addition of TBA at 0, 5, 10 and 25  $\text{mg/L}$ , respectively (Fig. 11a). Therefore, the presence of TBA clearly exhibited a negative effect on ATZ degradation, which indicated that the degradation followed the  $\cdot OH$  mechanism. However, there was still a ATZ degradation efficiency of 86.4% at TBA concentrations up to 25  $\text{mg/L}$  after 10 min reaction, which probably was due to direct oxidation via molecular  $O_3$  and the existence of some active intermediate oxidants other than  $\cdot OH$  in the  $O_3/nZnO$  process.

It was hypothesized that another highly active species, superoxide radical ( $O_2^{\cdot -}$ ) might have participated in the reaction and accounted for part of the degradation of ATZ. In order to further confirm whether  $O_2^{\cdot -}$  participated in ATZ degradation, BQ, as an effective scavenger of  $O_2^{\cdot -}$ , was added



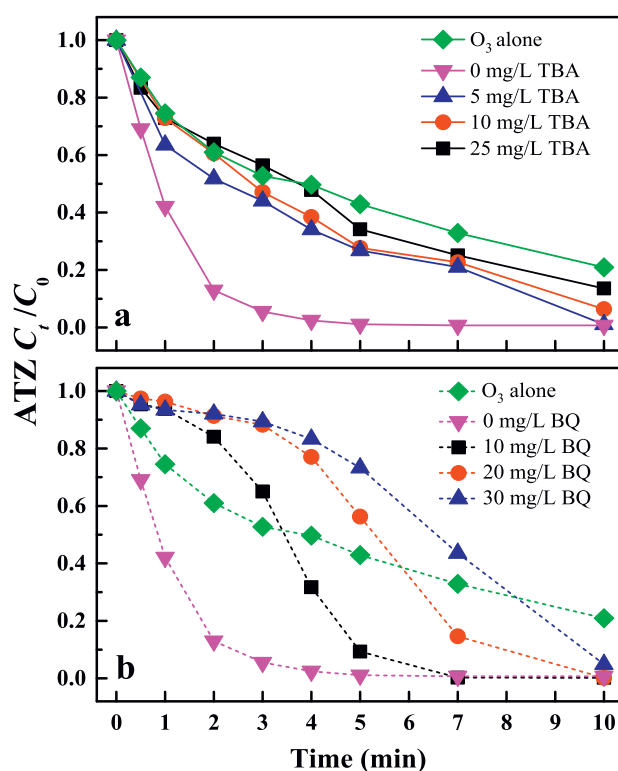
**Fig. 10 – Stability of nZnO in catalytic ozonation over six cycles.** Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ .

to the  $O_3/nZnO$  system (Umare et al., 2013). It can be observed from Fig. 11b that the degradation of ATZ was significantly suppressed with introduction of BQ, especially in the first few minutes of the reaction. The inhibiting effects on ATZ degradation became more distinct as the concentration of BQ increased, and the ATZ removal was 94.5%, 35.0%, 11.8% and 10.7% with BQ addition of 0, 10, 20 and 30 mg/L, respectively (Fig. 11b). For ATZ and BQ, the reaction rates with  $\cdot OH$  are  $3.0 \times 10^9$  and  $1.2 \times 10^9 \text{ mol/(L}\cdot\text{sec)}$  (Buxton et al., 1988). The suppression of ATZ degradation in the first few minutes of the reaction was probably due to the rapid reaction between BQ and  $\cdot OH/O_2^{\cdot-}$ . The results revealed that  $O_2^{\cdot-}$  could be an essential oxidative intermediate species participating in the  $O_3/nZnO$  process.

Furthermore, the formation of  $\cdot OH$  was measured by EPR, and the intensity of DMPO and  $\cdot OH$  (DMPO- $\cdot OH$ ) adduct signals was compared in  $O_3$  alone and  $O_3/nZnO$  processes. As illustrated in Fig. 12, a typical four-line EPR spectrum of the DMPO- $\cdot OH$  adduct with a peak intensity ratio of 1:2:2:1 was observed in ozonation without catalyst addition. With the addition of nZnO, there was a marked increase in the signal intensity of the DMPO- $\cdot OH$  adduct, representing more  $\cdot OH$  radicals being formed (Fig. 12). The spin-adduct of DMPO and  $O_2^{\cdot-}$  (DMPO- $O_2^{\cdot-}$ ) was not detected in the aqueous system. This is probably because the facile disproportionation reaction of superoxide in water precludes the slow reactions between  $O_2^{\cdot-}$  and DMPO ( $k = 10 \times 10^3 \text{ mol/(L}\cdot\text{sec)}$ ) (Chen et al., 2002). Besides, the DMPO- $O_2^{\cdot-}$  adduct is unstable in aqueous solution and tends to convert into DMPO- $\cdot OH$  by combination with  $H^+$  (Sanders et al., 1994), which could enhance the DMPO- $\cdot OH$  adduct signal.

### 2.3.3. Possible reaction mechanisms

If  $O_2^{\cdot-}$  plays an important role in the oxidation of ATZ in the  $O_3/nZnO$  process, it is expected that  $H_2O_2$  could be detected. As shown in Fig. 9a, the concentration of  $H_2O_2$  rose rapidly in



**Fig. 11 – Effect of (a) tert-butyl-alcohol (TBA) and (b) benzoquinone (BQ) on ATZ degradation in the  $O_3/nZnO$  process.** Experimental conditions:  $[ATZ]_0 = 2 \text{ mg/L}$ ,  $[nZnO] = 250 \text{ mg/L}$ ,  $[O_3] = 10 \text{ mg/L}$ ,  $pH_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ .

the first few minutes, up to maximum values of 0.04 and 1.0 mg/L in  $O_3$  alone and  $O_3/nZnO$  processes. After that, the concentration of  $H_2O_2$  decreased with reaction time, indicating that  $H_2O_2$  took part in the process of ATZ degradation. The reactions can be expressed as follows:



Fig. 9a also reveals that nZnO had a positive effect on the formation of  $H_2O_2$ . The enhanced generation of  $H_2O_2$  in the catalytic ozonation process provides evidence for the presence of  $O_2^{\cdot-}$  and the improvement of ATZ degradation. Qi et al. (2015) also identified the generation of  $H_2O_2$  and observed the same variation pattern of  $H_2O_2$  concentration during the degradation of phenacetin in catalytic ozonation by the



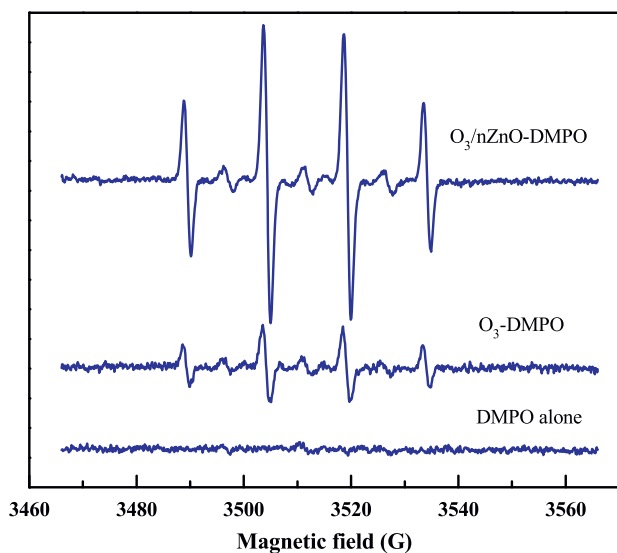
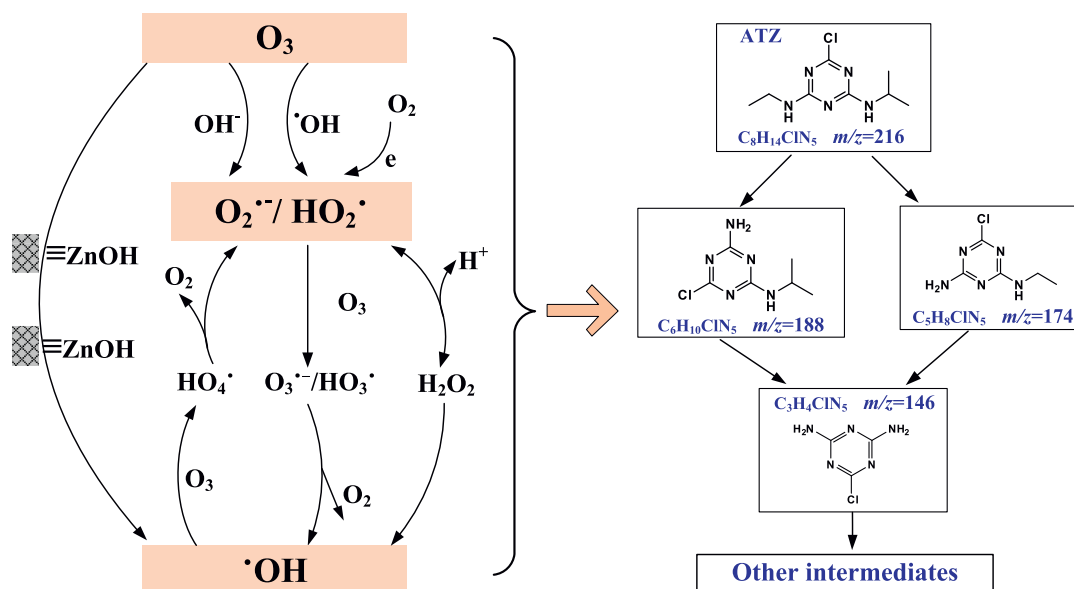


Fig. 12 – Electron paramagnetic resonance spectra of the adduct of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and  $\cdot\text{OH}$  formed in the selected systems. Experimental conditions:  $[\text{nZnO}] = 250 \text{ mg/L}$ ,  $[\text{O}_3] = 10 \text{ mg/L}$ , DMPO concentration  $50 \text{ mmol/L}$ ,  $\text{pH}_0 = 6.0 \pm 0.1$ ,  $T = 20^\circ\text{C}$ , reaction time = 10 min.

magnetic spinel ferrite. It has been previously reported by Zhang et al. (2015a, 2015b) that  $\text{O}_2^{\cdot-}$  rather than  $\cdot\text{OH}$  is the dominant active species responsible for the degradation of aniline and *p*-chloronitrobenzene in the  $\text{O}_3/\text{ZnO}$  process.

Meanwhile,  $\text{O}_2^{\cdot-}$  could react with  $\text{O}_3$  to produce  $\text{O}_3^{\cdot-}$ , and the protonation of  $\text{O}_3^{\cdot-}$  forms  $\text{HO}_3^{\cdot-}$ , which would further decompose into  $\cdot\text{OH}$ . The reactions are presented as follows (Wen et al., 2014):



Scheme 1 – The possible mechanism and pathways of atrazine (ATZ) degradation in the  $\text{O}_3/\text{nZnO}$  process. nZnO: nano-ZnO;  $m/z$ : mass to charge ratio of the detected ions.



Hence, it can be concluded that both  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  are reactive oxygen species and participate in ATZ ozonation enhanced by nZnO. Moreover, Fig. 9a demonstrates that the ATZ degradation efficiency at the catalyst–solution interface was higher than that on the catalyst surface. The surface OH groups generated by the lattice oxygen in aqueous solution and Lewis acid sites of nZnO were the active reaction sites.  $\text{O}_3$  was adsorbed on the catalyst surface, and subsequently formed active oxygen species ( $\cdot\text{O}$ ,  $\cdot\text{OH}$ , or  $\text{O}_2^{\cdot-}$ ) at the interface, which further resulted in the rapid oxidation of ATZ. Elevated concentrations of  $\cdot\text{OH}/\text{O}_2^{\cdot-}$  produced by the reaction of  $\text{O}_3$  with nZnO at the solid–liquid interface were the main factor responsible for the enhanced ozonation.

Finally, in order to elaborate the ATZ degradation in the  $\text{O}_3/\text{nZnO}$  process, the intermediates were further analyzed by UPLC–MS/MS. Several main intermediates were detected and based on the MS spectra, possible pathways of ATZ degradation were described as shown below (Scheme 1).

### 3. Conclusions

The combination of  $\text{O}_3$  with nZnO exhibited an obvious synergetic effect in ATZ degradation. The degradation efficiency of ATZ markedly increased with an increase of nZnO dosage. The process was pH-dependent, and the maximum enhanced degradation efficiency occurred at solution pH 3.0 in the  $\text{O}_3/\text{nZnO}$  process. HA could enhance the catalytic ozonation activity at low concentration due to HA acting principally as an initiator and promoter of ozone decomposition, thereby enhancing the ATZ degradation. Chloride ion, sulfate ion and nitrate ion improved the degradation of ATZ,

while bicarbonate ion and phosphate ion significantly inhibited ATZ degradation. Based on the inhibiting effects of TBA and BQ, the production of  $\text{H}_2\text{O}_2$ , and residual ozone concentration, it is proposed that nZnO enhanced ozone decomposition in bulk solution, and the effective degradation of ATZ in the  $\text{O}_3/\text{nZnO}$  process is primarily attributed to  $\cdot\text{OH}$ . It is concluded that ozone combined with nZnO is a very effective and promising approach for degrading organic pollutants, which could also be combined with UV/Vis to further degrade refractory pollutants. However, there is a slight zinc ion release, and future research could consider to loading nZnO onto a support to improve the stability of the catalyst.

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