



## Study on enhanced degradation of atrazine by ozonation in the presence of hydroxylamine



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### HIGHLIGHTS

- The presence of hydroxylamine (HA) enhanced the atrazine degradation by ozonation.
- •OH was produced from the reaction of ozone with HA with a yield of 25.8%.
- •OH primarily contributed to the enhanced degradation of atrazine (ATZ).
- HA still enhanced the atrazine degradation in the real water, especially at acidic pHs.
- Based on the identified products, the ATZ degradation pathway was proposed.

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### ABSTRACT

Degradation of atrazine (ATZ) by ozonation in the presence of hydroxylamine (HA) was experimentally investigated in this study. The results showed approximately 80% of ATZ was degraded by ozonation in the presence of HA, while only 20% was degraded by ozonation alone. The obvious inhibition of the ATZ degradation by *tert*-butanol suggested the enhanced ATZ degradation by ozone/HA was primarily attributed to •OH. The •OH yield was determined to be 25.8%. Additionally, the optimum HA dosage for the ATZ degradation was 4 μM, when the ozone dosage was 20 μM. The effects of pH, bicarbonate and temperature on ATZ degradation by ozone/HA were investigated in details. Most importantly, the enhanced ATZ degradation by ozonation in the presence of HA was still observed in real water especially at acidic pHs. Furthermore, the potential mechanism of •OH formation during the reaction of ozone with HA was proposed herein. Nine products were identified by UPLC/Q-TOF-MS system. The ATZ degradation involved dealkylation, dechlorination-hydroxylation and olefination. The evolutions of the concentrations of three available transformation products including deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine in ozone/HA were evaluated and compared with that in ozonation alone.

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## 1. Introduction

Atrazine (ATZ) is one of the most widely applied herbicides in agriculture, which has been detected in many surface and ground water [1–3]. Various advanced oxidation processes for the production of •OH or SO<sub>4</sub><sup>•-</sup> were applied to remove ATZ in aqueous solutions, such as the peroxone [4,5], catalytic ozonation [6], Fen-

ton or Fenton-like processes [7], and the activation of persulfate or permonosulfate by UV [8,9], transition metal [10], or heat [11].

Atrazine (ATZ) is resistant to the degradation by ozone due to its low reactivity towards ozone ( $k_{(\text{ozone,ATZ})} = 6 \text{ M}^{-1} \text{ s}^{-1}$ ) [5]. However, ATZ and other ozone refractory compounds were eliminated to a certain extent during ozonation alone in the real water as reported in many previous literatures. The authors ascribed this phenomenon to the production of •OH during ozonation in the real water. And many researchers constantly focused on the role of the dissolved organic matter on the •OH formation during ozonation of the real waters as reported in previous literature. For example, research on •OH production during the reaction of ozone

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with phenol was carried out by Mvula and C. von Sonntag. They proposed that an electron transfer reaction would occur during ozonation of phenol, which produced  $\bullet\text{OH}$  with a yield of 22% [12]. In addition, many nitrogen-containing organic compounds, such as aliphatic amines, have been found to activate ozone to produce  $\bullet\text{OH}$  and subsequently enhance the degradation of some recalcitrant compounds [13]. In the case of the reaction of ozone with tertiary amines,  $\text{O}_3^{\bullet-}$  is generated, which then decomposes into  $\bullet\text{OH}$  [14–17]. However, few inorganic reducing compounds have been reported to enhance the  $\bullet\text{OH}$  formation during ozonation as well as the degradation of the refractory contaminants.

Hydroxylamine (HA) is widely used throughout industry as a typical inorganic reducing agent. Moreover, it is commonly produced as an intermediate from the nitrification and reduction of some nitrogen-containing compound and detected in natural waters [18–20]. HA was found to activate some oxidants, thereby producing radicals in a  $\text{Fe}^{2+}$ -facilitated manner in recent studies. Chen and coworkers proposed that HA significantly enhances the production of  $\bullet\text{OH}$  in Fenton process via accelerating  $\text{Fe(II)/Fe(III)}$  redox cycles [21]. A similar mechanism was applied by Zou et al. to the ferrous iron/peroxymonosulfate oxidation system, in which HA promotes the formation of  $\text{SO}_4^{\bullet-}$  [22]. Recently, it is reported that  $\bullet\text{OH}$  formation was found via activating  $\text{H}_2\text{O}_2$  by HA directly with quite a low reaction rate, even if without employing  $\text{Fe}^{2+}$  as an electron shuttle [23]. All the mentioned above suggest that HA is likely to serve as an activator for  $\bullet\text{OH}$  production based on its reaction with ozone as well. However, the  $\bullet\text{OH}$  formation from the reaction of ozone with HA has not been experimentally investigated so far. The influence of the presence of HA on the degradation of the ozone refractory contaminants during ozonation still remains unknown.

The objectives of this study were (1) to examine the effect of the presence of HA on the degradation of ATZ during ozonation; (2) to investigate the influence of HA concentration, pH, temperature and alkalinity on the degradation of ATZ in the ozone/HA reaction; and (3) to propose a possible mechanism for the degradation of ATZ in the ozone/HA process.

## 2. Methods and materials

### 2.1. Materials

The chemicals used in this study were the following: nitrobenzene ( $\geq 99.0\%$ ), and potassium indigotrisulfonate, all from Sigma-Aldrich; hydroxylamine hydrochloride (HA,  $\geq 99.0\%$ ), *tert*-butyl alcohol (*t*-BuOH,  $\geq 99.8\%$ ), atrazine (ATZ), deethylatrazine (DEA), deisopropylatrazine (DIA), deethyldeisopropylatrazine (DEIA) and sodium sulfite (98.0%) from Aladdin Industrial Corporation; and sulfuric acid, sodium hydroxide, phosphoric acid, sodium phosphate dibasic, sodium dihydrogen phosphate, sodium nitrite and sodium nitrate from Sinopharm Chemical Reagent Co., Ltd. Ozone stock solution was prepared by passing an oxygen/ozone mixture gas into ultrapure water by means of an ice-cooling system to maintain the solution at  $4^\circ\text{C}$ . The surface water used in this study was characterized as following: pH 7.7, DOC = 2.67 mg/L, alkalinity = 0.18 mM.

### 2.2. Ozonation procedure

Experiments were conducted using Milli-Q-filtered water that was pre-ozonated to prevent the potential influence of any ozone-consuming impurities. All experiments were performed in a 150 mL screw-top bottle with a bottle-top dispenser (Brand) for sampling. ATZ with the desired concentrations was spiked to the solution and adjusted to the predetermined pH with  $\text{H}_2\text{SO}_4$  (0.1 M) and NaOH (0.1 M). The desired concentration of the ozone dose to the solution

was then achieved by injecting a certain volume of ozone stock solution with a syringe. Samples were withdrawn at predetermined time intervals by operating the dispenser and then were quenched with excess sodium sulfite solutions.

### 2.3. Quantification of the hydroxyl radical yield

The hydroxyl radical yield in the ozonation process can be evaluated by the *t*-BuOH method [24]. In this method, *t*-BuOH in a large excess is spiked to solutions to scavenge the hydroxyl radical formed in the reaction. And the primary end product of the scavenging reaction, formaldehyde, can be quantified as its 2,4-dinitrophenylhydrazones by high performance liquid chromatography (HPLC). 0.2 mL of 2,4-dinitrophenylhydrazine solution (9 mM in acetonitrile) and 0.1 mL of perchloric acid (1 M in acetonitrile) were spiked into 1.7 mL sample and mixed well. The mixed solution was kept in the dark for 45 min, and then was analyzed by HPLC at a wavelength of 350 nm. The  $\bullet\text{OH}$  yield in the ozone/HA reaction was taken twice as the measured formaldehyde yield [24].

### 2.4. Analytical methods

The dissolved ozone concentrations were determined by the indigo method [25]. ATZ and its degradation products were measured with an eluent containing 0.1% acetic acid and acetonitrile (20:80, v/v%) at  $\lambda = 221$  nm. The amount of hydroxylamine was determined by measuring the acetoxime, which is the derivative of the hydroxylamine reaction with acetone. The amount of acetoxime was determined by a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID) as described in [22]. The nitrate and nitrite fractions were quantified using ion chromatography (Dionex ICS-3000) with an eluent containing 30 mM KOH.

The ATZ degradation products were identified by a UPLC/Q-TOF-MS system, consisting of an Eksperit ultraLC110HPLC coupled with an AB Sciex 5600 Triple quadrupole time-of-flight mass spectrometer (Q-ToF-MS). The sample was injected with an eluent of ammonia acetate/acetonitrile at a flow rate of 0.2 mL/min. An Agilent reversed phase C18 column (3.0 mm  $\times$  50 mm, 2.7  $\mu\text{m}$ ) was used for separation.

## 3. Results and discussion

### 3.1. Degradation of ATZ in the different processes

The degradation efficiency of ATZ was evaluated and compared in different processes including HA alone, ozonation alone, ozone/ $\text{Cl}^-$ , ozone/HA and ozone/HA/ $\text{Cl}^-$  at the ozone dosage of 1 mg/L and pH 7 in Fig. 1. ATZ was eliminated by approximately 80% in the process of ozone/HA within 8 min, while only about 20% of initial concentration of ATZ was destructed by ozonation alone. No degradation of ATZ was observed for HA alone. The effect of chloride ion on the degradation of ATZ was investigated, since HA was introduced into the experimental solutions in the form of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . The experiments were carried out under the same conditions as applied in the ozonation alone and ozone/HA processes but with the addition of 10  $\mu\text{M}$  chloride ion. No change was observed in the degradation of ATZ with or without spiking the chloride ion, which excluded the effect of chloride ion on the enhanced degradation of ATZ in the process of ozone/HA. One can thus infer that the enhanced degradation of ATZ in the process of ozone/HA is attributed to the synergistic effect of ozone and HA.

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