A novel advanced oxidation process using iron electrodes and ozone in atrazine degradation: Performance and mechanism

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HIGHLIGHTS

- A novel oxidation process using iron electrodes and ozone was proposed.
- In-situ formed Fe^{2+} was responsible for the generation of $OH^{\cdot}$ and ferryl ion.
- Individual contributions of the reactive species were predicted.

GRAPHICAL ABSTRACT
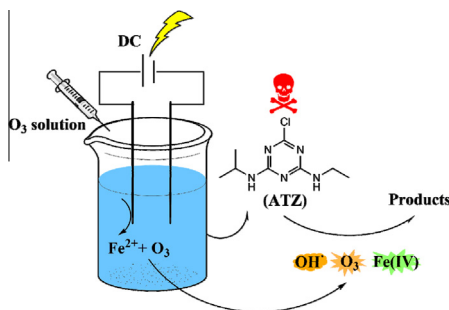
ABSTRACT

In this work, iron electrode was employed to enhance the reactivity of ozone (EC/O_3) in atrazine degradation. Compared to ozonation and Fe^{2+}-catalyzed ozonation, the elimination rate of atrazine by the EC/O_3 process increased significantly with increasing applied currents. The simultaneous formation of hydroxyl radical ($OH^{\cdot}$) and ferryl ion ($Fe(IV)$) from the reaction between ozone and in-situ formed Fe^{2+} was proposed and experimentally confirmed. The second order rate constant for atrazine reacting with $Fe(IV)$ was estimated to be 125 $M^{-1} s^{-1}$ using a relative rate method. The individual roles of the reactive species ($OH^{\cdot}$, $Fe(IV)$, and O_3) in atrazine degradation were modeled using a kinetic model and $OH^{\cdot}$ was the predominant reactive species in the EC/O_3 system. Furthermore, the effects of water quality parameters, such as initial pH and natural organic matters (NOM), on the performance of EC/O_3 process were also evaluated. The results demonstrated that higher initial pH is favorable for ozone consumption and atrazine degradation. The presence of NOM appreciably inhibited the degradation of atrazine, which may be attributed to the competition of NOM for $OH^{\cdot}$. This study provides a new approach to enhance ozonation, and broadens the knowledge of ozonation in removing organic contaminants from water.

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1. Introduction

Ozone (O_3) has been widely used in both drinking water plants and wastewater plants for disinfection or oxidation [1–3]. The latter application was employed for the control of cyanobacteria and its derivative products, elimination of emerging micropollutants, and decoloration [1]. Ozone is an electrophilic oxidant with high selectivity and involved in two-electron transfer reaction with organics, and predominantly reacts with organics containing double bonds, activated aromatic systems or non-protonated amines ($k > 10^5 M^{-1} s^{-1}$) [1], such as microcystin-LR [4], diclofenac [5] and sulfamethoxazole [6]. On the other hand, O_3 is inefficient for removing some other organics that consists of saturated ring systems or electron-withdrawing groups (e.g., geosmin [7], endrin

[8] and atrazine [9]). However, hydroxyl radical (OH·) generated from O_3 decomposition can react with various kinds of organics rapidly [10]. Therefore, ozone has to be transformed to OH· in the removal of ozone-resistant organics, but the normal rate of O_3 transforming to OH· is slow at acid and neutral conditions due to the lack of initiator (OH$^-$).

Catalytic ozonation (e.g., transition metals) has attracted extensive interests in last several decades due to the convenience and cheapness [11,12]. Ni et al. [13] reported that metallic ions including Pb$^+$, Cu^{2+}, Zn^{2+}, Fe^{2+}, Ti^{2+}, and Mn^{2+} are able to enhance ozonation, and Fe^{2+} is most widely used because it could be removed easily and cause low damages to water body.

However, unlike Fenton-like reaction in which fixed amounts of Fe^{2+} were directly added into solution, electrochemical oxidation at Fe anodes could continuously produce in-situ Fe^{2+} to catalyze ozonation [14]. Using Fe anode as a Fe^{2+} source could not only maintain the utilization of Fe^{2+}, but avoid the introduction of other anions (Cl$^-$ or SO$_4^{2-}$), which may affect the removal of contaminants [15]. In the last decade, the combination of electrochemistry and advanced oxidation processes (AOPs) has been frequently researched and Fe^{2+} generated from anode was used to activate hydrogen peroxide, persulfate, or peroxymonosulfate [16–18]. In this study, electrochemistry coupled with ozone (EC/O_3) was evaluated to remove organic micropollutants for the first time. And atrazine (ATZ, Table S1) was selected as a model contaminant since it is an ozone-resistant compound.

Furthermore, ferryl ion (known as FeO^{2+}) has been assigned to be an intermediate in the reaction of Fe^{2+} with O_3 [19,20], and yet OH· was still deemed as the major or only reactive species in some studies [21], and the contributions of Fe(IV) and O_3 itself are usually neglected or underestimated. To verify whether or not Fe(IV) existed in this study, nitrilotriacetic acid (NTA) was used to chelate Fe(IV) to improve its stability, but the individual contributions of reactive species were unclear. Fang et al. [22] chose a mathematical modeling approach to calculate the contributions of all reactive species for benzoic acid degradation in the UV/free chlorine system. Xie et al. [23] also built a kinetic model to distinguish the individual roles of OH· and sulfate radical in the UV/persulfate system. In this study, a simple modeling of ATZ degradation in the EC/O_3 system was established to investigate the individual contributions of three reactive species (OH·, Fe(IV), and O_3) in the EC/O_3 system.

The objectives of this study were as follows: (1) to comparatively investigate the degradation efficiency of ATZ by the EC/O_3, Fe^{2+}/O_3 and ozonation processes, and confirm the reactive species responsible for ATZ degradation in the EC/O_3 system; (2) to improve the understanding of all the reactive species responsible for organics degradation in the EC/O_3 system using a kinetic modeling; (3) to evaluate the effects of water quality parameters on the performance of the EC/O_3 system.

2. Materials and methods

2.1. Materials

All chemicals were commercially available and used as received without further purification. Atrazine was supplied by Aladdin Industrial Co. (China). Methanol (MeOH, HPLC grade, ≥99.9%), phosphoric acid (H$_3$PO$_4$, ≥99.9%), and potassium indigotrisulfonate was purchased from Sigma-Aldrich Chemical Co. Ltd. (USA). Benzoic acid (BA, ≥99.0%), ferrous sulfate (FeSO$_4$·7H$_2$O, ≥99.0%), sodium thiosulfate (Na$_2$S$_2$O$_3$·5H$_2$O, ≥99.0%), sodium sulfate (Na$_2$SO$_4$, ≥99.0%), sodium ethylene diamine tetracetate (EDTA, ≥99.0%), sodium pyrophosphate (PP, ≥99.0%) and NTA (≥98.0%) were obtained from Sinopharm Chemical Reagent Co.

(China). Suwannee River natural organic matter (SRNOM) was purchased from the International Humic Substances Society (USA). Glass microfiber filters (GF/F) were purchased from Whatman (UK). Ozone was produced by an ozone generator (Qingdao Guolin, China) using high purity-oxygen as gas source (≥99.999%) and the ozone stock solutions were prepared by dissolving a high concentration of gaseous ozone into deionized water at 4 °C. All solutions were prepared with ultrapure water, unless otherwise specified.

2.2. Experiment procedures

Batch experiments were conducted in an open electrolytic cell containing 500 mL ATZ solution of 5 μM at a certain pH (5.6). The electrodes with dimensions of 5 cm × 2 cm were set in parallel at a distance of 2 cm. A direct current (DC) source was used to supply the power of the system. 3.0 mM Na$_2$SO$_4$ were added to raise the conductivity of the solution.

Ozonation reactions were performed by adding an aliquot of ozone stock solution to achieve the desired concentration (0.1 M). The applied current was fixed at 10 mA except for the investigation of the effect of current, which ranged from 5 mA to 20 mA. NaOH and H$_2$SO$_4$ (0.1 M) were used to adjust the solution pH when the effect of initial pH on the performance of EC/O_3 system was evaluated. Besides, 1~3 mg-C/L NOM were added into the reaction solution to simulate the ATZ removal in actual waters. To determine the consumption of O_3 and the generation of Fe^{2+} with time, we performed experiments at different applied currents, and the concentrations of O_3 and Fe^{2+} were measured. To identify the primary reactive species in the EC/O_3 system, quenching experiments were conducted with the addition of excess MeOH. To calculate the second rate constant of ATZ and Fe(IV), benzoic acid was used as model compound. In parallel experiments, Fe^{2+}-catalyzed ozonation (Fe^{2+}/O_3) process without EC were also performed to offer reference, where the Fe^{2+} dosage was calculated according to Faraday law (Eq. (1)) with a reaction time of 10 min.

$$C = \frac{I \times t}{F \times Z \times V} \tag{1}$$

where, C is the generated molecular concentration of Fe^{2+} (mol/L), Z is the number of electrons (2 equivalents/mol), F is Faraday's constant (96485.3 Coulombs/mol), I is the given current (A), t is the reaction time (s), and V is the volume of electrolyte (L).

At each designated time intervals, samples were collected and mixed immediately with appropriate amounts of Na$_2$S$_2$O$_3$ solution (0.5 M) to quench the residual oxidants. Then the samples were filtered with 0.70 μm pore size filter membranes to filter the particulates of Fe(OH)$_3$ before analysis. All the experiments were duplicated at room temperature (25 °C). The relative standard deviations (RSD) for different batches were normally less than 10%.

2.3. Analytical methods

ATZ and BA was measured by a high performance liquid chromatography (HPLC) (Agilent 1260, USA) equipped with a Symmetry C18 column (150 mm × 4.6 mm × 5 μm, Agilent, USA) and a variable wavelength detector (Agilent, USA). The concentrations of ATZ were measured at λ = 221 nm, and a mixture of ultrapure water and methanol (v:v = 30:70) was used at a flow rate of 1.0 mL/min and the injection volume was 10 μL. The concentrations of BA were determined at λ = 227 nm, and a mixture of ultrapure water (1‰ phosphoric acid) and methanol (v:v = 50:50) was used at a flow rate of 1.0 mL/min and the injection volume was 30 μL. The residual concentration of ozone was determined by the indigo method using an UV–vis spectrophotometer (Hitachi, U-3900, Japan) according to the method of Bader and Hoigné [24]. The concentrations of Fe^{2+} without ozone were determined