



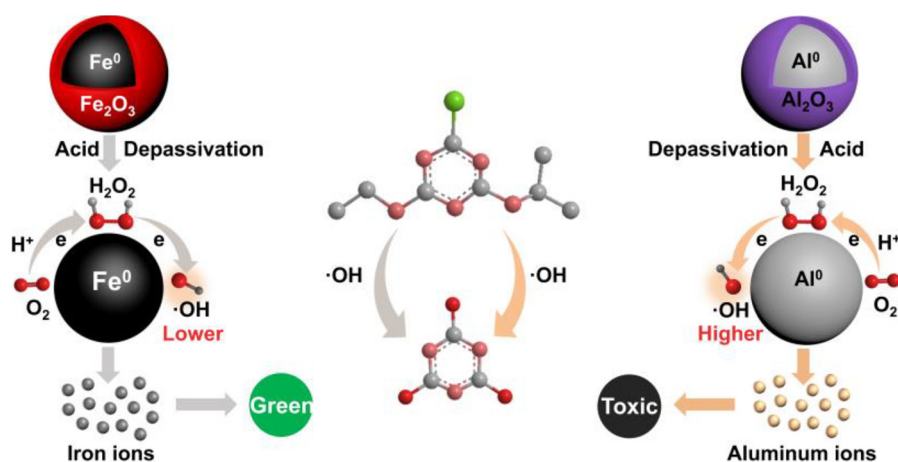
## Comparison of aerobic atrazine degradation with zero valent aluminum and zero valent iron

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### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Zero-valent aluminum  
Zero-valent iron  
Molecular oxygen activation  
Atrazine  
Reactive oxygen species

### ABSTRACT

This study systematically compared the degradation of atrazine (ATR) with aerobic zero-valent aluminum (ZVAL/Air) and zero-valent iron (ZVI/Air) systems. By comparing the ATR degradation curves and rate in the ZVAL/Air and the ZVI/Air systems, a significant induction period was observed in the ZVAL/Air system, and the pseudo-first-order rate constant of ATR degradation in the second stage by ZVAL was 6.4 times faster than that by ZVI. The differences in ATR degradation patterns of the two systems stemmed from the different redox nature and electrical conductivity of aluminum (oxide) and iron (oxide). Reactive oxygen species measurement and electron spin spectra analysis indicated that more hydroxyl radical was generated through molecular oxygen activation in the ZVAL/Air system, leading to enhanced ATR degradation in the ZVAL/Air process. By analyzing the intermediates of atrazine degradation, we found that ATR underwent an oxidative dealkylation and hydroxyl-dechlorination degradation pathway, and the low toxicity cyanuric acid was the final product in both systems. However, aluminum ions released in the ZVAL/Air system exceeded the regulated standard value, which might cause environmental pollution. Finally, the pros and cons of potential environmental remediation of the ZVAL/Air and ZVI/Air processes were evaluated.

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<https://doi.org/10.1016/j.jhazmat.2018.06.029>

Received 25 December 2017; Received in revised form 1 June 2018; Accepted 11 June 2018

Available online 15 June 2018

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## 1. Introduction

Molecular oxygen ( $O_2$ ) is a kind of clean and abundant oxidant in chemosphere. Due to the spin forbidden nature of  $O_2$  molecule, it hardly reacts with organic pollutants directly under mild circumstance [1]. Stable oxygen molecules could be activated under certain conditions to generate reactive oxygen species (ROS), like  $\cdot O_2^-$ ,  $H_2O_2$ , and  $\cdot OH$ , which could degrade organic pollutants efficiently. Therefore, tremendous efforts have been devoted to the development of molecular oxygen activation strategies for environment pollutants remediation [2–4]. Among the various strategies, molecular oxygen activated by zero-valent iron (ZVI) was considered as an friendly way to aerobically degrade organic pollutants (ZVI/Air) [5–9]. But the aerobic ZVI/Air process in the absence of ligand still suffered from its low efficiency, for instance, the yield of methanol/ethanol oxidation was only 6% in the aerobic ZVI/Air system due to the poor iron cycling [6,10].

Compared with the common used ZVI ( $E^\circ(Fe^{2+}/Fe) = -0.44 V$ ), the zero-valent aluminum (ZVAL) possesses a more negative redox potential ( $E^\circ(Al^{3+}/Al) = -1.67 V$ ), which could result in faster electron transfer rate and higher  $O_2$  activation efficiency (ZVAL/Air) (Eqs. (1) and (2) [[11]]. It has been reported that ZVAL was of reduction and adsorption properties. For example, the scrap zero-valent aluminum exhibited superior reducing capacity for Cr(VI) and imidacloprid reduction [12,13]. The released aluminum ions by ZVAL could adsorb 90–95% of perchlorate within 24 h at acid pH ( $4.5 \pm 0.2$ ) [14]. Meanwhile, the oxidation ability of the aerobic ZVAL/Air system was utilized to degrade phenol, methyl tert-butyl ether nitrobenzene, bisphenol A, acid orange 7, acetaminophen, and arsenate [9,15–19]. However, the performance and pros/cons of the aerobic ZVI/Air and ZVAL/Air processes for aqueous pollutants remediation have never been well discussed.



In this study, we comparatively investigated the aerobic ZVAL/Air and ZVI/Air system by using atrazine (ATR, 2-chloro-4-(ethylamino)-6-isopropylamino-s-triazine) as a model containminant. ATR is a typical endocrine disruptive hercide and was abundantly used around the world decades ago [20–22]. As the ATR degradation products were widely identified, it is feasible to clarify the mechanism by monitoring the degradation pathway of ATR in the ZVAL/Air and the ZVI/Air systems [23]. Aluminum was a toxic agent in neurological disorders and a kind of potential risk factors for Alzheimer's disease, while iron was environmental friendly. In order to evaluate the possible application of ZVAL/Air [24], we monitored the dissolution of aluminum ions and discussed their environmental risk. We aimed to clarify the ATR degradation mechanisms in the ZVAL/Air and ZVI/Air systems, as well to reveal the pros and cons of the ZVAL/Air and ZVI/Air processed for their potential environmental remediation.

## 2. Experimental section

### 2.1. Chemical and materials

Zero-valent aluminum and zero-valent iron were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Atrazine of guaranteed reagent was obtained from Sigma-Aldrich Reagent Co., Ltd. Catalase (CAT) and superoxide dismutase (SOD) were bought from Shanghai Kayon Biological Technology Co., Ltd.  $CH_2Cl_2$ ,  $CH_3CN$ , and  $CH_3OH$  were guaranteed reagent and brought from Shanghai Aladdin Reagent Co. Ltd. All reagents were used without further purification.

### 2.2. Aerobic degradation of atrazine

Aerobic atrazine degradation was conducted in a 50 mL erlenmeyer

flask at room temperature ( $25 \pm 1^\circ C$ ). In a typical process, 0.6 g ZVAL or ZVI was added into 20 mL stock solution containing of 20 ppm atrazine under air or argon bubbling ( $1.5 L min^{-1}$ ) to initiate the reaction. The initial pH was adjusted to acid or alkaline condition by 1 M  $H_2SO_4$  or 2 M NaOH respectively. Samples were collected at regular intervals with 1 mL syringe and filtered immediately through 0.22  $\mu m$  nylon filter for next analysis. All the degradation experiments were replicated three times.

### 2.3. Analytical methods

The concentration of atrazine was analyzed by high performance liquid chromatograph (HPLC, Ultimate 3000, Thermo) equipped with an Acclaim 120 column ( $250 mm \times 4.6 mm$ ,  $5 \mu m$ , Dionex) at 220 nm by a UV-vis detector. The mobile phase was a mixture of acetonitrile and water (v/v 1:1) with a flow rate of  $1.0 mL min^{-1}$ . Anions generated in ATR degradation process were determined by ion chromatography (ICS-900, Thermo) equipped with AS23 analytical column. A mixture of sodium carbonate ( $Na_2CO_3$ ,  $4.5 \times 10^{-3} mol L^{-1}$ ) and sodium bicarbonate ( $NaHCO_3$ ,  $8.0 \times 10^{-4} mol L^{-1}$ ) were used as the mobile phase at a flow rate of  $1.0 mL min^{-1}$ . The intermediates of atrazine were detected by high performance liquid chromatography coupled with tandem mass spectrometric (HPLC-MS/MS) (TSQ Quantum Access MAX, Thermo) equipped with Hypersil GOLD-C18 column ( $150 mm \times 2.1 mm$ ,  $5 \mu m$ ). The pretreatment of samples was reported in our previous study [8]. The HPLC-MS/MS was operated in the positive electrospray mode (ESI+) with gradient elution of water and acetonitrile at a flow rate of  $0.5 mL min^{-1}$  (Table 1). Electrospray source settings (with nitrogen) were as follows: capillary voltage, 3200 V; tube lens voltage, 89 V; vaporizer temperature,  $550^\circ C$ ; sheath gas pressure,  $50 L h^{-1}$ ; ion sweep gas pressure,  $20 L h^{-1}$ ; auxiliary gas pressure,  $20 L h^{-1}$ ; capillary temperature,  $320^\circ C$ . Concentrations of metal ions in aqueous solution were determined with an atomic adsorption spectrometer (AAS, Hitachi 180-70). Total organic carbon (TOC) was measured on a total organic carbon analyzer (TOC-VCPH, Shimadzu). Electron spin resonance (ESR) spectra were collected with a Bruker A300 in a mixture of 25 mM DMPO and 5 mg ZVAL (or ZVI) powder.

### 2.4. Characterizations

X-ray diffraction (XRD) patterns of ZVAL and ZVI before and after the aerobic reaction were carried out by a Bruker D8 Advance X-ray diffractometer collecting at 40 kV and 40 mA with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Scanning electron microscopy (SEM) analysis was performed on a LEO 1450 VP scanning electron microscope. Free corrosion potential measurement was performed in a conventional three-electrode cell with a platinum plate ( $1 \times 1 cm^2$ ) as the auxiliary electrode and a saturated calomel electrode as the reference electrode on CHI 660C workstation (Shanghai, China). The work electrode was prepared by pressing 8 mg ZVAL or ZVI powder into the electrode cavity. The electrolyte was 50 mL of  $NaSO_4$  (50 mM) solution.

**Table 1**  
HPLC-MS/MS parameters for analysis of ATR and its intermediates.

Time (min)	Formic acid (0.1%)	Acetonitrile
0	95	5
2	95	5
35.5	10	90
40	10	90
40.5	95	5
45	95	5

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