



## Synergistic enhancement of oxidative degradation of atrazine using combined electrolysis and ozonation

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### ABSTRACT

In the current study concurrent electrolysis and ozonation was compared with the processes applied separately to degrade the herbicide atrazine in aqueous solution at pH 2, 7, and 12. Ozone containing gas was injected at a rate of 0.3 L/min into an electrolysis reactor with a boron-doped diamond anode and stainless steel cathode operating with an anodic current density of 10 mA/cm<sup>2</sup>. When electrolysis and ozonation were applied together, the rate constant of atrazine degradation could not be explained simply from considering the processes when applied separately. In particular, at pH 7, the measured first-order rate constant was 0.3441 min<sup>-1</sup>, a rate 4.78 times as large as the estimated additive rate (0.072 min<sup>-1</sup>) from electrolysis and ozonation separately in the same conditions. Across the pH range, the rate constant increased from 0.0516 min<sup>-1</sup> at pH 2 to 0.3441 min<sup>-1</sup> at pH 7 and 0.3065 min<sup>-1</sup> at pH 12. Use of *tert*-butanol as a radical scavenger elucidated that HO· contributed to a majority of the reaction at pH 7 and 12. The increasing impact of HO· was due to ozone decomposition into HO· through reaction with hydroxide (OH<sup>-</sup>) in both the bulk solution and at the cathode. Through LC-QTOF-MS analysis, acetamide and imine transformation of atrazine's alkyl groups were observed at pH 7 and initial dechlorination by HO· to form hydroxyatrazine was observed at pH 12.

### 1. Introduction

One of several pesticides of environmental concern, atrazine (ATZ) is still applied heavily across the world. It is one of the two most widely applied pesticides in the United States, with the United States Environmental Protection Agency (USEPA) estimating annual domestic application at 76.5 million pounds [1]. Atrazine has been the subject of controversy, and has been heavily studied and reviewed for its impacts as an endocrine disrupting compound [2,3], possible carcinogen [4,5], and environmentally persistent contaminant [6]. The United States Geological Survey (USGS) Watershed Regression for Pesticides (WARP) tool predicts that for the most recent year in which data are available, 2012, that substantial surface water in the US is in danger of exceeding the maximum contaminant level (MCL) for ATZ [7]. In addition to the specific health risks of atrazine contamination, ATZ shares a similar triazine structure with an entire class of pesticides, making it a good candidate for study as a surrogate for related triazine pesticides. Chemical information for ATZ and major degradation products as well as a depiction of the general triazine structure can be found in Table 1 below.

Removal of ATZ from water has been studied extensively due to the

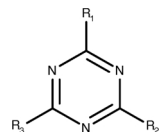
regulation of ATZ concentration in drinking water by the EPA with an MCL of 3 µg/L (ppb). Commonly studied methods for ATZ treatment include adsorption [12,13], ozonation [14], electrolysis [15,16], and several advanced oxidation processes (AOPs): Fenton's reagent [17–19], electrolysis using radical-generating electrode materials such as boron-doped diamond (BDD) [20], catalysis by dissolved manganese [21], and peroxide/ozone [9]. Boron-doped diamond is a popular anode material due to its large working potential window, high resistance to fouling, and in-situ hydroxyl radical (HO·) generation [22–24]. The AOP based processes are centered around the generation of HO·, a highly reactive and indiscriminate reactant able to effectively degrade organic compounds. Despite the desirability of HO· as an oxidizing agent, many processes require the addition of chemicals (Fenton's reagent, peroxide-ozone) or the use of expensive equipment and large amounts of energy (electrolysis, BDD, ozone). Despite these drawbacks, researchers continue to develop new processes and enhance the performance of current technology. This paper discusses a new and promising AOP that combines electrolysis with the addition of aqueous ozone to catalyze the generation of HO·.

Kishimoto et al. [25,26] first reported in 2005 that the combination of electrolysis with ozonation (E + O) produced a synergistic effect on

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**Table 1**  
Chemical information on ATZ and major degradation products.



Name	Abbreviation	R1	R2	R3	Reference
atrazine	ATZ (CIET)	Cl	NHCH <sub>2</sub> CH <sub>3</sub>	NHCH(CH <sub>3</sub> ) <sub>2</sub>	[8]
desethyl-atrazine	ADE (CIAT)	Cl	NH <sub>2</sub>	NHCH(CH <sub>3</sub> ) <sub>2</sub>	[8]
desisopropyl-atrazine	ADI (CEAT)	Cl	NHCH <sub>2</sub> CH <sub>3</sub>	NH <sub>2</sub>	[8,9]
desethyl-desisopropyl-atrazine	ADEDI (CAAT)	Cl	NH <sub>2</sub>	NH <sub>2</sub>	[8]
cyanuric acid	CYN (OOOT)	OH	OH	OH	[10]
2-chloro-4-ethylimino-6-isopropylamino-s-triazine	ATZ-imine	Cl	N=CHCH <sub>3</sub>	NHCH(CH <sub>3</sub> ) <sub>2</sub>	[8]
6-amino-2-chloro-4-ethylimino-s-triazine	ADI-imine	Cl	N=CHCH <sub>3</sub>	NH <sub>2</sub>	[8]
4-acetamido-6-amino-2-chloro-s-triazine	CDAT	Cl	NHC=OCH <sub>3</sub>	NH <sub>2</sub>	[9]
2-chloro-4,6-diacetamido-s-triazine	CDDT	Cl	NHC=OCH <sub>3</sub>	NHC=OCH <sub>3</sub>	[9]
4-acetamido-2-chloro-6-ethylamino-s-triazine	CDET	Cl	NHC=OCH <sub>3</sub>	NHCH <sub>2</sub> CH <sub>3</sub>	[8]
4-acetamido-2-chloro-6-isopropylamino-s-triazine	CDIT	Cl	NHC=OCH <sub>3</sub>	NHCH(CH <sub>3</sub> ) <sub>2</sub>	[8]
ammeline	OAAT	OH	NH <sub>2</sub>	NH <sub>2</sub>	[9,11]
2-amino-4-ethylamino-6-hydroxy-s-triazine	OAET	OH	NH <sub>2</sub>	NHCH <sub>2</sub> CH <sub>3</sub>	[10]
2-amino-4-hydroxy-6-isopropylamino-s-triazine	OAIT	OH	NHCH(CH <sub>3</sub> ) <sub>2</sub>	NH <sub>2</sub>	[10]
atrazine-2-hydroxy	OIET	OH	NHCH <sub>2</sub> CH <sub>3</sub>	NHCH(CH <sub>3</sub> ) <sub>2</sub>	[10]

the degradation of aqueous 4-chlorobenzoic acid through cathodic reduction of aqueous ozone. Cathodic reduction of oxygen gas to form hydrogen peroxide has also been proposed as an important mechanism creating the observed synergism [27,28]. Zhou et al. [29] and Zhang et al. [30] built on the combined process by adding iron electrodes to release Fe<sup>2+</sup> and catalyze radical generation with the dissolved ozone.

The overall oxidative degradation of ATZ in the context of electrolysis (E), ozonation (O), and (E + O) systems can be simplified to five main pathways based on previously published studies: (I) direct reaction with molecular ozone [8], (II) reaction with HO· formed through the decomposition or reduction of ozone [8,25,31], (III) direct oxidation at the surface of the anode [20], (IV) reaction with HO· generated at the anode [20], and (V) reaction with HO· formed from the reaction of H<sub>2</sub>O<sub>2</sub> with O<sub>3</sub> [27,32,33]. Pathway (II) is the focus of this manuscript. It describes the pathway that is responsible for the formation of hydroxyl radical species through several different mechanisms, creating the potential for synergism. Pathway (V), the unique feature of a process referred to as electro-peroxone, also produces an enhancement in radical production, but requires carbon-based cathodes that are suited to H<sub>2</sub>O<sub>2</sub> generation. Metal cathodes, in contrast to carbon, do not favor H<sub>2</sub>O<sub>2</sub> production [34]. In Pathway (II) decomposition of ozone is initiated by reaction with hydroxide ion (OH<sup>-</sup>) generated at the cathode. The decomposition of ozone and the start of a radical chain reaction leading to generation of HO· have been studied extensively with one of the first studies dating back to 1935 [35]. Two major pathways have been studied previously: direct decomposition of ozone in water to form HO· directly (Eq. (1)) and reaction between ozone and OH<sup>-</sup> to initiate several propagation reactions leading to HO· formation (Eq. (2)) [14,35–37]. Ozone stability in water strongly relates to pH as a result of the reaction between ozone and OH<sup>-</sup> described in Eq. (2) [38]. Specifics on the propagation steps and formation of transient species can be found in previously published research [14,37].



Electrolysis combined with ozonation has been shown to enhance the degradation of organics through the generation of radical oxidants; however, the process needs further investigation, especially relative to other AOPs and traditional treatment methods such as adsorption. For this process to gain traction as a viable method for removal of organic contaminants, continued study is required to elucidate and confirm the reaction mechanisms reported in previously published work and determine the impact of reactor operating conditions to optimize

efficiency and synergism. This paper discusses the impact of combining BDD electrolysis with ozonation at various pH conditions on the rate constant, reaction mechanisms and pathways of ATZ degradation in aqueous solution.

## 2. Material and methods

### 2.1. Material

All pesticides used in the study, ATZ, ADE, ADI, ADEDI and CYN, were analytical standard grade purchased from Sigma Aldrich (USA) and all other compounds, including buffers and solvents, were ACS grade and were purchased from Thermo Fisher Scientific (USA). All water used in the study was deionized and distilled using a Corning Mega-Pure<sup>®</sup> water purification still. Boron-doped diamond (monopolar/mono-Si) electrodes were obtained from Adamant (Switzerland), and stainless steel (SS) electrodes were manufactured in-house using 316 grade stainless steel. All electrodes were rectangular plate electrodes with dimensions 25 × 50 × 2 millimeters (mm) for BDD and 25 × 50 × 1.2 mm for SS. The reference electrode used was the RE-5 B Ag/AgCl reference electrode from BASi (USA).

### 2.2. Reactor system

The reactor system used in the current study consists of an acrylic cylinder with a total volume of 600 mL (mL) and working volume of 470 mL. A diagram of the reactor is presented in Fig. 1. The reactor was stirred magnetically, with a porous polytetrafluoroethylene (PTFE) tube with 3 μm pores used to diffuse ozone gas into the system. Electrodes were mounted to the lid of the reactor and suspended partially into the solution to achieve a solution contact area of 23.7 cm<sup>2</sup>. The electrodes and ozone gas diffuser were present in the system during all experiments regardless of operating mode.

Ozone gas was produced using the Ozonia LAB2B Ozone Generator fed with 99.6% pure extra-dry oxygen from a compressed gas cylinder at a rate of 2 L/min, the minimum recommended by the manufacturer. Once the ozone gas left the ozone generator the flow was split, with 1.7 L/min flowing to waste bypass (via a potassium iodide trap) and 0.3 L/min flowing into the reactor. A Princeton Applied Research Model 362 Scanning Potentiostat was used in galvanostatic mode to apply 237 mA of current to the reactor, resulting in an applied anodic current density of 10 mA/cm<sup>2</sup>. Current density was held constant to allow for investigation of pH as the main factor in this set of experiments.

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