



# Heat-activated persulfate oxidation of atrazine: Implications for remediation of groundwater contaminated by herbicides

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## HIGHLIGHTS

- Heat-activated persulfate induced atrazine oxidation.
- Oxidation efficiency was highly temperature-dependent.
- Sulfate and hydroxyl radical were involved in oxidation process.
- Chloride and bicarbonate exhibited inhibitory effect at higher concentration.
- Pathways included dealkylation, chain oxidation, and dechlorination–hydroxylation.

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## ABSTRACT

Contamination of herbicides such as atrazine (ATZ) poses a significant threat to human health and aquatic ecosystem. In this study, we demonstrated that heat-activated persulfate could effectively degrade ATZ in water. Complete disappearance of 50  $\mu\text{M}$  ATZ could be obtained after 2 h reaction in the presence of 1 mM persulfate under 60  $^{\circ}\text{C}$ . Increasing the initial persulfate concentration or temperature significantly enhanced the degradation efficiency. Natural organic matter (NOM) decreased the degradation rate, but complete removal of ATZ could still be obtained. The presence of chloride ( $\text{Cl}^-$ ) and bicarbonate ( $\text{HCO}_3^-$ ) had little effects on ATZ degradation at lower concentration (e.g., 5 mM). However, inhibitory effects were observed when concentrations of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  increased (e.g., 100 mM). Radical scavenging test revealed that sulfate radical ( $\text{SO}_4^{\cdot-}$ ) was the predominant radical species at acidic to neutral pH, while hydroxyl radical ( $\text{HO}^{\cdot}$ ) was predominant at basic pH. Eight intermediates and products were identified by applying solid phase extraction and liquid chromatography–tandem mass spectrometry (SPE–LC–MS/MS) techniques. Transformation pathways including dealkylation, alkyl chain oxidation, and dechlorination–hydroxylation were proposed, and the underlying mechanisms for each pathway were systematically analyzed.

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## 1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine, ATZ) is one of the most heavily used herbicides in agriculture to control broadleaf and grassy weeds in corn and other croplands [1]. ATZ has a high potential to contaminate natural waters due to its persistence, widespread, and long-term use [2,3]. Waters contamination by ATZ and structurally related s-triazine herbicides has been reported globally [4,5]. The U.S. EPA classified ATZ as a possible carcinogenic and endocrine disrupting chemical [6].

Consumption of contaminated water causes the potential risks for human exposure to ATZ. Technologies that can effectively remove or destroy ATZ in water are desirable to minimize such risks.

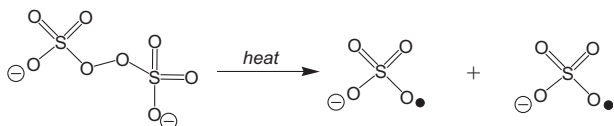
*In situ* chemical oxidation (ISCO) technology using persulfate as oxidant for remediation of groundwater and soil attracts a growing attention in recent years [7]. Persulfate has a relatively higher redox potential ( $E^0 = 2.01 \text{ V}$ ) and greater oxidant persistence compared to conventional oxidants used in ISCO such as ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and permanganate ( $\text{MnO}_4^-$ ), therefore can be delivered long-distance in the subsurface to reach the contaminated zone [8,9]. Persulfate can be activated by heat, transit metal, UV light, and base to generate highly oxidative sulfate

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radical ( $\text{SO}_4^{\cdot-}$ ,  $E^0 = 2.5\text{--}3.1\text{ V}$ ), which is known to react with a variety of organic compounds with a second-order-rate constant ranging from  $10^6$  to  $10^9\text{ M}^{-1}\text{ s}^{-1}$  [10]. Compared with  $\text{HO}^{\cdot}$ ,  $\text{SO}_4^{\cdot-}$  is less likely to be scavenged by nontarget water constituents because  $\text{SO}_4^{\cdot-}$  reacts with organic compounds predominantly through electron transfer mechanism [11]. Thus, chemical oxidant demands can be comparatively lower using activated persulfate for environmental remediation. In addition, persulfate, and its final product sulfate, have little impact upon native soil microorganisms [12]. These characteristics make persulfate-based ISCO a promising technology for remediation of contaminated groundwater and soil.

Among various activation methods, heat activation is particularly attractive, especially when this technology is combined with *in situ* thermal remediation (ISTR) [7]. Homolysis of the peroxide bond occurs in persulfate molecule during heat activation, leading to the formation of  $\text{SO}_4^{\cdot-}$ , which further oxidizes the pollutants.



Previous studies have documented the effective oxidation of chlorinated ethenes [13,14], bisphenol A [15], perfluorocarboxylic acids [16], herbicides [17,18], and pharmaceuticals [19–21] by heat-activated persulfate. Compared with other activation technologies, heat activation offers some advantages. For example, because no additional chemicals are required, it can minimize the consumption of persulfate caused by pre-mixture of the persulfate and the activator before injection. Increasing the activation temperature can locally increase the site temperature and thus raise the reaction rates to shorten the remediation time. In addition, heat-activated persulfate is usually employed to study the reaction mechanism between contaminants and  $\text{SO}_4^{\cdot-}$  due to the simplicity of the system [22].

In the present study, we attempted to evaluate the feasibility to employ heat-activated persulfate to degrade ATZ. The motivation of this study is to explore a viable method to destroy or eliminate ATZ and related *s*-triazine herbicides in contaminated groundwater. Detailed kinetics studies were performed for better understanding the influence of factors including the pH, dissolved natural organic matter (NOM), chlorine, and bicarbonate. Solid phase extraction followed by liquid chromatography–tandem mass spectrometry (SPE–LC–MS/MS) as a powerful tool allowed to identify a series of intermediates and products. Based on the structural elucidation of the products, detail mechanisms and transformation pathways for ATZ oxidation by heat-activated persulfate were proposed. To the best of our knowledge, this is the first study on heat-activated persulfate oxidation to destruct ATZ in aqueous solution.

## 2. Materials and methods

### 2.1. Chemicals

Atrazine (ATZ,  $\text{C}_8\text{H}_{14}\text{N}_5\text{Cl}$ , 99.0%), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , 99.5%) and humic acid (used as a representative of NOM,  $\geq 90\%$ ) were purchased from Aladdin Chemistry Co. Ltd. Sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) was obtained from Sigma–Aldrich. HPLC grade acetonitrile (ACN), methanol (MeOH), and formic acid were purchased from Fisher Chemical. Other reagents were at least of analytical grade and used as received without further purification. All the stock solutions were prepared by dissolving the chemical agents into Milli-Q water (18 M $\Omega$  cm) prepared from a Millipore Milli-Q system and used within 1 week.

### 2.2. Kinetic experiments

Heat-activated persulfate oxidation of ATZ was performed on batch reaction for 120 min. Appropriate volume of ATZ stock solution was transferred into a series of cylindrical glass vials and specific aliquots of persulfate stock solution were added to achieve a total 50 mL reaction solution with predetermined molar ratios of ATZ and persulfate, e.g., 50  $\mu\text{M}$  ATZ and 1 mM persulfate. Thereafter, vials were immersed in a thermostated water bath (Xianou Instrument Manufacture Co., Ltd., Nanjing) at desired temperature (20–60  $^{\circ}\text{C}$ ). Control experiments with ATZ only were run concurrently under identical conditions. No degradation of ATZ was found in the control experiments, indicating ATZ was hydrolysis-resistant and thermally stable. The initial pH of the reaction solution was adjusted by 0.01 M  $\text{H}_2\text{SO}_4$  or NaOH to desired value. Solution pH decreased to approximately 3.75 after 120 min reaction. No buffer solution was used in the present study to avoid potential complexity due to reaction between these additives and  $\text{SO}_4^{\cdot-}$  [14]. Reaction aliquots (0.5 mL) were periodically withdrawn and quenched immediately with equivalent volume of 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$ . Note that,  $\text{Na}_2\text{S}_2\text{O}_3$  has previously been examined as an effective  $\text{SO}_4^{\cdot-}$  scavenger in Co(II)/PMS oxidation process [23]. All the experiments were carried out in duplicates or triplicates, and the data were averaged. The standard deviations were usually within 5–10% unless otherwise stated.

### 2.3. Analytical methods

ATZ concentration was analyzed by a Hitachi L-2000 high performance liquid chromatography system (Hitachi, Japan) equipped with an L-2200 autosampler, L-2130 binary pump, and an L-2455 diode array detector. Analytical separation was performed by a Hitachi La Chrom C18 column (5  $\mu\text{m}$ , 125  $\times$  4.6 mm). An L-2300 column oven was used to maintain the column temperature as 30  $^{\circ}\text{C}$ . The isocratic elution consisted of 70% methanol and 30% water with a flow rate of 1.0 mL  $\text{min}^{-1}$ . The injection volume was 10  $\mu\text{L}$  and the detection wavelength was 222 nm. Quantification of ATZ was determined by using multipoint standard calibration curves.

ATZ degradation products were separated and concentrated by using solid phase extraction (SPE) technique. An aqueous solution (50 mL) contained 50  $\mu\text{M}$  ATZ and 1 mM persulfate was allowed to react for 60 min at 60  $^{\circ}\text{C}$  and then quenched by 50 mL 100 mM  $\text{Na}_2\text{S}_2\text{O}_3$ . The mixture was concentrated by SPE workstation using HLB cartridge (WAT106202, Waters Oasis). Prior to extraction, the cartridge was activated by 5 mL methanol followed by 5 mL Milli-Q water. The quenched reaction solution was percolated through the cartridge at a flow rate of 5 mL  $\text{min}^{-1}$ . The extracts were eluted with 2 mL methanol twice. The eluents were combined and purged gently with highly purified  $\text{N}_2$  to approximately 1 mL.

Reaction products were identified using liquid chromatography with tandem mass spectrometry (HPLC–MS/MS), consisting of an Agilent 1200 series HPLC coupled to a 6410 triple quadrupole mass spectrometer (Agilent Technologies, USA). Separation was accomplished using a Waters Symmetry C18 column (3.5  $\mu\text{m}$ , 2.1  $\times$  150 mm). Elution was performed at a flow rate of 0.25 mL  $\text{min}^{-1}$  with  $\text{H}_2\text{O}$  containing 0.1% (v/v) formic acid as eluent A and ACN containing 0.1% (v/v) formic acid as eluent B, employing a linear gradient from 10% B to 60% B in 0–10 min, 60% B to 100% B in the next 2 min. Mass spectral analysis was conducted in positive mode using an electrospray ionization (ESI) source. Instrument parameters were as follows: capillary voltage 3.8 kV, fragmentor 125 V, desolvation gas (nitrogen,  $\geq 99.995\%$ ) flow 10 L  $\text{min}^{-1}$ , temperature 350  $^{\circ}\text{C}$ , nebulizer pressure 940 psi, and nitrogen ( $\geq 99.999\%$ ) was used as collision gas. Mass analyzer was operated in full scan mode ( $m/z$  range 50–500) in order to identify the

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