



New insights into atrazine degradation by cobalt catalyzed peroxymonosulfate oxidation: Kinetics, reaction products and transformation mechanisms

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HIGHLIGHTS

- Cobalt catalyzed peroxymonosulfate oxidation of atrazine.
- Atrazine oxidation by Co(II)/PMS was more efficient than Fe(II)/PMS.
- Higher oxidation efficiency was achieved at neutral pH.
- Natural organic matter, chloride, and bicarbonate showed inhibitory effects.
- Pathways included dealkylation, chain oxidation, and dechlorination-hydroxylation.

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ABSTRACT

The widespread occurrence of atrazine in waters poses potential risk to ecosystem and human health. In this study, we investigated the underlying mechanisms and transformation pathways of atrazine degradation by cobalt catalyzed peroxymonosulfate (Co(II)/PMS). Co(II)/PMS was found to be more efficient for ATZ elimination in aqueous solution than Fe(II)/PMS process. ATZ oxidation by Co(II)/PMS followed pseudo-first-order kinetics, and the reaction rate constant (k_{obs}) increased appreciably with increasing Co(II) concentration. Increasing initial PMS concentration favored the decomposition of ATZ, however, no linear relationship between k_{obs} and PMS concentration was observed. Higher efficiency of ATZ oxidation was observed around neutral pH, implying the possibility of applying Co(II)/PMS process under environmental realistic conditions. Natural organic matter (NOM), chloride (Cl^-) and bicarbonate (HCO_3^-) showed detrimental effects on ATZ degradation, particularly at higher concentrations. Eleven products were identified by applying solid phase extraction-liquid chromatography-mass spectrometry (SPE-LC/MS) techniques. Major transformation pathways of ATZ included dealkylation, dechlorination-hydroxylation, and alkyl chain oxidation. Detailed mechanisms responsible for these transformation pathways were discussed. Our results reveal that Co(II)/PMS process might be an efficient technique for remediation of groundwater contaminated by ATZ and structurally related s-triazine herbicides.

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1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most widely used herbicides in agriculture due to its high effectiveness in inhibiting the growth of weeds and algae by interfering with the normal function of photosynthesis [1]. The

widespread and long-term use of ATZ resulted in high residue in soil, which further causes the surface and groundwater contamination via rain runoff and leakage [2,3]. Numerous studies have reported the occurrence of ATZ in groundwater because ATZ has the properties of high leaching potential, resistance to microbial degradation, slow hydrolysis, low vapor pressure, and moderate aqueous solubility [4–8]. ATZ is classified as a possible carcinogen and endocrine disrupting chemical by the U.S. EPA, thus water contamination by ATZ has raised growing concerns to the public and scientific agencies, especially when the water is used as drink-

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ing water source. Therefore, reliable and effective techniques for removing ATZ from groundwater are desirable.

In situ chemical oxidation (ISCO) is a potentially promising technology for groundwater remediation [9]. ISCO technology is based on the generation of highly reactive species arising from the oxidants with or without activation. Ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), and persulfate ($S_2O_8^{2-}$) are commonly used oxidants in ISCO. Of them, persulfate attracts particular attention due to its high redox potential ($E^0 = 2.01$ V) and chemical stability [9]. Persulfate has a relatively long lifetime in aquifers and can be easily delivered to target sites. Persulfate can be activated by heat, UV light, chelated or unchelated transition metals, H_2O_2 , and base to generate highly oxidative sulfate radical ($SO_4^{\bullet-}$, $E^0 = 2.5$ – 3.1 V). $SO_4^{\bullet-}$ is known to react with a variety of organic compounds with a second-order-rate constant ranging from 10^6 to 10^9 $M^{-1}s^{-1}$ [10]. $SO_4^{\bullet-}$ -mediated degradation of TCE, PAHs, PCBs, and PPCPs have been extensively documented [11–16]. Unlike the well-known HO^{\bullet} , $SO_4^{\bullet-}$ is believed to react with organic compounds mainly through electron transfer mechanism, which makes it more selective than HO^{\bullet} . As a result, $SO_4^{\bullet-}$ is less likely being scavenged by dissolved natural organic matter (NOM) ubiquitously present in waters [16]. Therefore, $SO_4^{\bullet-}$ -based oxidation processes appear advantageous in relative to conventional HO^{\bullet} -based AOPs in certain water treatment and remediation scenarios.

Degradation of ATZ by reaction with $SO_4^{\bullet-}$ has been examined in previous studies. Ali Khan et al. carried out a comparative study on oxidative degradation of ATZ in aqueous solution by UV/ H_2O_2 / Fe^{2+} , UV/ $S_2O_8^{2-}$ / Fe^{2+} , and UV/ HSO_5^- / Fe^{2+} [17]. ATZ oxidation by homogenous cobalt-mediated activation of peroxy-monosulfate (PMS) and heterogeneous cobalt oxide photocatalysis was investigated by Chan and Chu [18]. Guan et al. recently explored the ATZ degradation by $CuFe_2O_4$ catalyzed PMS oxidation [19]. All studies showed efficient degradation of ATZ in $SO_4^{\bullet-}$ -based oxidation processes. However, comparing with the well established mechanisms of ATZ degradation in HO^{\bullet} -based oxidation [20], little is currently known about the underlying mechanisms in $SO_4^{\bullet-}$ -based processes. Although Chan and Chu identified 2-chloro-4-ethylamino-6-amino-s-triazine as an intermediate of ATZ [18], this finding does not support to construct a detailed map of degradation pathways. Recently, Ali Khan and co-workers investigated the mechanisms of photochemical degradation of atrazine with activated H_2O_2 , $S_2O_8^{2-}$, and HSO_5^- [21], and Yola et al. studied the photocatalytic degradation of atrazine by a novel efficient photocatalyst [22]. However, the mechanisms of atrazine reaction with $SO_4^{\bullet-}$ generated by Co(II) activated PMS remain unclear.

In the present study, we attempted to elucidate the underlying mechanisms and transformation pathways of the reactions between ATZ and $SO_4^{\bullet-}$. $SO_4^{\bullet-}$ was generated by Co(II) catalyzed PMS because Co(II) was found to be the most efficient transition metal for the activation of PMS, and freely diffusible sulfate radicals were the primary oxidative species in this system [23,24]. Solid phase extraction-liquid chromatography-mass spectrometry (SPE-LC/MS) as a powerful tool allowed us to identify a series of ATZ transformation intermediates and products, based on which the reaction mechanisms and detailed transformation pathways were proposed. Kinetics studies were also conducted for better understanding the influence of factors including pH and natural water constituents. Our study provides useful information about using sulfate radical-based technologies for remediation of the groundwater contaminated by atrazine and structurally related s-triazine herbicides.

2. Materials and methods

2.1. Chemicals

Atrazine (ATZ, $C_8H_{14}N_5Cl$, 99%), cobalt(II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), potassium monopersulfate triple salt (OXONE, $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, $\geq 47\%$ $KHSO_5$ basis), and humic acid (used as NOM, $\geq 90\%$) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, $\geq 99.0\%$) was obtained from Sigma-Aldrich (St. Louis, MO). HPLC grade acetonitrile (ACN), methanol (MeOH), and formic acid were purchased from Tedia (Fairfield, OH). Other reagents were at least of analytical grade and used as received. All the stock solutions were prepared by dissolving the reagents in Milli-Q water (>18 $M\Omega$ cm) prepared from a Millipore Milli-Q system and used within 1 week.

2.2. Kinetic experiments

Batch kinetic experiments were conducted in 65 mL cylindrical glass reactors at room temperature (20 ± 2 °C). Appropriate volume of Co(II) stock solution was spiked into the reactor containing ATZ, PMS, and constituents of interest to achieve a total 50 mL solution with predetermined molar ratios of ATZ, Co(II), and PMS. Control experiments with ATZ only, ATZ + Co(II), and ATZ + PMS were run concurrently under identical conditions. No removal of ATZ was found in the controls, indicating Co(II) or PMS alone could not cause ATZ degradation. ATZ oxidation by Fe(II)/PMS was also carried out for comparison with Co(II)/PMS system. The initial pH of the solution was adjusted by 0.01 M H_2SO_4 or NaOH to 7.0 unless specially mentioned. No buffer was used to rule out any complexities related to potential reactions between radicals and buffer species. Aliquots (0.5 mL) were then periodically collected and quenched immediately with equivalent volume of 10 mM $Na_2S_2O_3$ before quickly analyzed by HPLC. Note that, $Na_2S_2O_3$ has previously been examined as an effective $SO_4^{\bullet-}$ scavenger in Co(II)/PMS process [23]. Meanwhile, the quenching agent $Na_2S_2O_3$ was demonstrated to have little interference with the analysis of ATZ. 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 ($5 \mu m$, 4.6 mm I.D. \times 125 mm). An L-2300 column oven was used to maintain the column temperature as 30 °C. The isocratic elution consisted of 70% MeOH and 30% H_2O with a flow rate of 1.0 $mL \cdot min^{-1}$. The injection volume was 10 μL 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 using solid phase extraction (SPE) technique. A reaction solution (50 mL) containing 50 μM ATZ, 1 mM PMS, and 5 μM Co(II) was initially quenched by 50 mL 100 mM $Na_2S_2O_3$ after reaction of 60 min. The mixture was then concentrated by SPE workstation using HLB cartridge (WAT106202, Waters Oasis). Prior to extraction, the cartridge was activated by 5 mL MeOH followed by 5 mL Milli-Q H_2O . The quenched reaction solution was passed through the cartridge

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