



Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process



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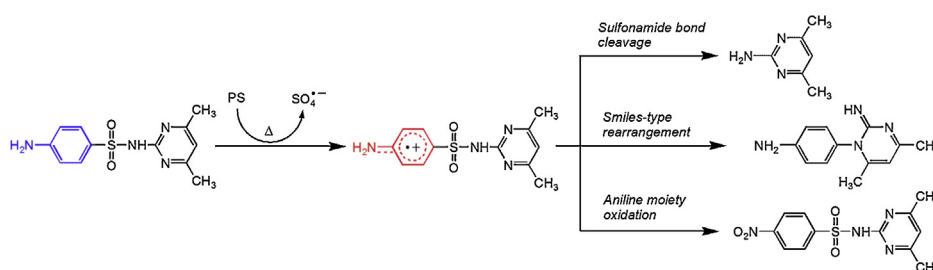
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HIGHLIGHTS

- Heat-activated persulfate induced sulfamethazine oxidation.
- Aniline moiety in sulfamethazine molecule was reactive site.
- Sulfate radical was identified as the predominant oxidizing species.
- Presence of bicarbonate and chloride enhanced SMZ degradation.
- Similes-type rearrangement followed SO_2 extrusion occurred during transformation.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfamethazine (SMZ) is widely used in livestock feeding and aquaculture as an antibiotic agent and growth promoter. Widespread occurrence of SMZ in surface water, groundwater, soil and sediment has been reported. In this study, degradation of SMZ by heat-activated persulfate (PS) oxidation was investigated in aqueous solution. Experimental results demonstrated that SMZ degradation followed pseudo-first-order reaction kinetics. The pseudo-first-order rate constant (k_{obs}) was increased markedly with increasing concentration of PS and temperature. Radical scavenging tests revealed that the predominant oxidizing species was $\text{SO}_4^{\bullet-}$ with HO^{\bullet} playing a less important role. Aniline moiety in SMZ molecule was confirmed to be the reactive site for $\text{SO}_4^{\bullet-}$ attack by comparison with substructural analogs. Non-target natural water constituents affected SMZ removal significantly, e.g., Cl^- and HCO_3^- improved the degradation while fulvic acid reduced it. Reaction products were enriched by solid phase extraction (SPE) and analyzed by liquid chromatography-electrospray ionization-triple quadrupole mass spectrometry (LC-ESI-MS/MS). 6 products derived from sulfonamide S–N bond cleavage, aniline moiety oxidation and Smiles-type rearrangement were identified, and transformation pathways of SMZ oxidation were proposed. Results reveal that heat-activated PS oxidation could be an efficient approach for remediation of water contaminated by SMZ and related sulfonamides.

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1. Introduction

Sulfamethazine (SMZ) is widely used in livestock and aquaculture as an antimicrobial agent and growth promoter [1]. Run-off from farms, leakage from septic tanks, and direct discharge from aquaculture are pathways responsible for the occurrence of SMZ in natural waters [2,3]. Environmental concentrations of SMZ generally range from nanogram per liter to microgram per liter.

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For example, SMZ concentration of 15–328 ng L⁻¹ was detected in tropical waters in Mekong Delta, Vietnam [4]. In China, comparable concentration of SMZ was observed in natural waters, e.g., 0.53–89.1 ng L⁻¹ in surface water of Yangtze estuary [5] and 2.05–623.27 ng L⁻¹ in Huangpu River, Shanghai [6]. Since SMZ is used primarily as veterinary medicine, the occurrence of SMZ in natural waters reflects the contamination derived from livestock wastes and aquaculture [4–6]. Natural attenuation processes, such as adsorption, photodegradation and microbial transformation are major pathways responsible for the fate of SMZ in environment [7,8]. For instance, photodegradation and adsorption to sediments were found to be the major pathways controlling SMZ's persistent in lakes [9]. Adsorption to minerals followed by oxidative transformation may be another important pathway for SMZ attenuation in environment [10]. However, owing to the lower attenuation rate and continuous releasing mode, SMZ and other antibiotics of concern show “pseudo-persistent” characteristics [2]. The widespread occurrence of these antibiotics may induce antibiotic-resistant genes, thus, have sublethal chronic and unpredictable effects on ecosystem and human health [3,11]. Therefore, developing cost-effective and environmental-friendly treatment techniques is required to removal SMZ and related antibiotics and associated risks.

Advanced oxidation processes (AOPs) are viable ways to remove sulfonamides like SMZ in water [12]. Traditional AOPs based on the generation of highly oxidative hydroxyl radical (HO•), such as Fenton (Fe²⁺/H₂O₂), electron-Fenton, UV/H₂O₂, O₃/H₂O₂ have been widely applied in wastewater treatment and pollution control [13,14]. More recently, sulfate radical (SO₄•⁻)-based AOPs gained growing attention. SO₄•⁻ can be produced via activation of persulfate (PS) and peroxymonosulfate (PMS) by ultraviolet light, transit metals, base and sonolysis [15]. SO₄•⁻ has a relatively high standard reduction potential of 2.6 V [15], which is comparable to that of HO• (E⁰ = 2.7 V) [16]. Second-order rate constants for reactions of SO₄•⁻ with organic compounds range from 10⁶ to 10⁹ M⁻¹ s⁻¹ [17]. SO₄•⁻ is thought to be a more selective radical than HO•. Reactions between SO₄•⁻ and organic compounds occurred mainly through electron transfer mechanism [17]. This characteristic renders SO₄•⁻ being less scavenged by nontarget water constituents (e.g., NOM), therefore increasing its steady-state concentration. SO₄•⁻-driven AOPs have become an emerging *in situ* chemical oxidation (ISCO) technique for remediation of contaminated groundwater and soil [15].

Among various activation methods, heat activation is of particular interest. In heat activation, PS is usually utilized as a precursor of SO₄•⁻, and symmetrical cleavage of the peroxide bond results in the formation of SO₄•⁻, which further oxidizes the pollutants [15]. Several recent studies documented the effectiveness of heat-activated PS oxidation of herbicides [18,19], industrial chemicals [20,21], and pharmaceuticals [22,23]. Heat-activation possesses several advantages compared with other activation approaches. For instance, heat activation requires no additional chemicals, which minimizes the consumption of PS during its pre-mixing with activators [15]. Owing to its high chemical stability, PS can be delivered through a long distance to contaminant zone in aquifers prior to activation [24]. Heat-activation was also frequently employed to explore the reaction mechanisms between SO₄•⁻ and various contaminants due to its simplicity and higher efficiency [25]. In field application, heat activation was commonly combined with *in situ* thermal remediation (ISTR) [15]. However, identifying the optimal operational parameters is crucial for successful application of heat-activated PS oxidation process. For example, increasing temperature facilitates PS decomposition and contaminants oxidation, therefore, shortening the remediation time [15]. However, higher temperature increases the operational cost and may also favor radical-to-radical

reactions instead of radical-to-contaminant reactions, thus, lowering the treatment efficiency [15]. In addition, the effects of various natural water constituents which are expectedly to be encountered in treatment are not well-documented and warrant further study in heat-activated PS oxidation.

In this work, we attempted to assess the feasibility of employing heat-activated PS to degrade SMZ in aqueous solution. The motivation of this study is to explore a viable method to eliminate SMZ and related sulfonamide antibiotics in waters. Kinetic studies were performed to gain insights into the influence factors including temperature, PS dosage, pH, dissolved natural organic matter (NOM), chloride, and bicarbonate. Solid phase extraction followed by liquid chromatography–tandem mass spectrometry (SPE-LC–MS/MS) was used to identify reaction intermediates and products. Based on the structural elucidation of the intermediates/products, detail mechanisms and transformation pathways for SMZ oxidation by heat-activated PS were proposed.

2. Materials and methods

2.1. Reagents and materials

Chemicals, suppliers, and purities are listed in the Supplementary data, Text S1.

2.2. Experimental setup

Batch kinetic studies were conducted in 33 mL screw-cap cylindrical glass vials with Teflon septa at predetermined temperature (i.e., 40–60 °C) controlled by a thermostated water bath (Xianou Instrument Manufacture Co., Ltd., Nanjing). The temperature range adopted herein was consistent with previous reports [18–20]. Prior to heat activation, appropriate volume of SMZ stock solution (150 μM) and PS stock solution (100 mM) were transferred into the vials to achieve a total 20 mL solution with predetermined molar ratio of SMZ and PS. Control experiments without PS were carried out under identical conditions and showed no loss of target compounds, indicating SMZ and substructural analogs are hydrolysis-resistant and thermally stable. The reactions for aniline (AN), sulfanilic acid (SAA), and 2-amino-4,6-dimethylpyrimidine (ADPD) were performed under identical conditions. Initial pH was adjusted by 0.01 M H₂SO₄ or NaOH to desired value. No buffer was used in the present study to avoid potential reactions between these additives and SO₄•⁻. The effects of HCO₃⁻, Cl⁻ and SRFA were studied to evaluate the effects of typical natural water constituents on heat-activated PS oxidation of SMZ. Aliquots (0.5 mL) were withdrawn at predetermined time intervals and chilled in an ice bath for 10 min to stop the reaction and kept in a 4 °C refrigerator thereafter until further treatment and analysis. All the experiments were carried out in duplicates, and the data were averaged. The standard deviations were usually within 5–10% unless otherwise stated.

2.3. Analytical methods

SMZ was analyzed by a Hitachi L-2000 high performance liquid chromatography (Hitachi, Japan) equipped with an L-2455 diode array detector. Detailed HPLC setup can be found in Table S1, Supplementary data. Quantification of analytes was based on multipoint standard calibration. Degradation products were concentrated by solid phase extraction (SPE) using Waters Oasis hydrophilic–lipophilic balance (HLB) cartridges. Detailed experimental procedures are given in Text S2, Supplementary data. Reaction products were identified using HPLC with tandem mass spectrometry (HPLC–MS/MS), consisting of an Agilent 1200 series HPLC coupled to a G6410B triple quadrupole mass spectrometer (Agilent Technologies, USA). Separation was accomplished using a

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