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Kinetics and degradation pathway of sulfamethazine chlorination in pilot-scale water distribution systems

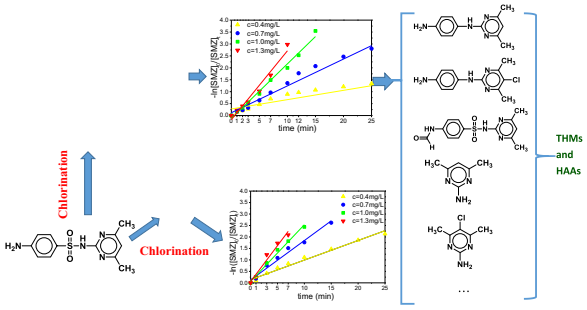
Feilong Dong, Cong Li *, Guilin He, Xinbo Chen, Xinwei Mao

College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310027, China

HIGHLIGHTS

- Degradation of BPA differed in pilot-scale water distribution systems and beaker test.
- Degradation of SMZ by chlorine decreased with an increase in temperature, and is optimal at neutral pH.
- Degradation of SMZ by chlorine varies with pipe material in water distribution systems.
- Nine identified byproducts of SMZ including and HAAs describe the reaction pathways.
- The inhibition halo of the SMZ solutions increases during SMZ chlorination in water distribution systems.

GRAPHICAL ABSTRACT



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ABSTRACT

As a new type of environmental micro-organic pollutant, sulfonamides (SAs) have been shown to damage organisms if they are exposed to them over the long term. Moreover, an increasing number of SAs has been detected in natural water and urban water supply systems in recent years because they cannot be completely removed through conventional water treatment processes. Therefore, sulfamethazine (SMZ) in urban water systems was selected as a target to be investigated. The reaction kinetics of sulfamethazine chlorination were studied in a pilot-scale water distribution system (WDS) under the influence of different factors, including pH, temperature, flow rate and pipe materials, to determine the optimal factors for removing SMZ and to provide a reference for water quality in urban drinking water systems.

According to the experimental results, the kinetics models of SMZ chlorination fitted a second-order reaction in pure water. The degradation of SMZ was not only affected by the water quality conditions but also the operating temperatures, flow rates and pipe materials. The rate constants of SMZ chlorination under different temperatures were related to the Arrhenius equation. Different flow rates had little effect on SMZ degradation. In different pipes, the degradation rates of SMZ followed the order stainless-steel pipe > polyethylene pipe (PE) > ductile iron pipe. Moreover, eight reaction intermediates during SMZ degradation were observed and identified, and a degradation pathway was proposed. The concentrations of trihalomethanes (THMs) and haloacetic acids (HAAs) during the degradation of SMZ in WDS were also determined.

* Corresponding author.
E-mail address: congil@zju.edu.cn (C. Li).

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1. Introduction

Sulfonamides (SAs) are the first antibacterial agents successfully applied in human infectious diseases [1] and are important synthetic antimicrobial agents that are still widely used in human and veterinary medicine [2,3]. SAs are used to prevent infection in humans and livestock. However, SAs are not fully metabolized in human or livestock bodies and are excreted in urine or feces. Therefore, the ubiquitous occurrence of SAs in the environment has received widespread attention from the worldwide scientific community, and the biological effects of these antibiotics have been increasingly studied in recent decades [4–6]. They enter into the environment in different ways, including mainly through human and animal excretion, medical waste, and wastewater discharges. SAs have frequently been detected in surface water and drinking water worldwide [7–9]. Although the concentrations of SAs are quite low (μg/L) in natural water or soil, ecotoxicity at μg/L levels has been reported [10]. Their presence in soil and water promote the growth of antibiotic-resistant bacteria and reduce the numbers of soil bacteria, destroying the natural ecosystem structure [11]. In addition, excessive use of SAs will impair the human immune system and inhibit the germination of plants [12].

A variety of technologies have been investigated for removing sulfamethazine (SMZ), such as physical, biological and chemical methods [13]. As a traditional method, chlorine oxidation has exhibited high efficiency in oxidizing a great variety of organic compounds [14]. So far, this method is most widely used for the disinfection of drinking water. However, investigations on the SAs of chlorinated reactions have been conducted in a purified water matrix. Dodd and Huang [15] studied the oxidation of sulfamethoxazole with chlorine and estimated rate constants. In addition, these researchers also proposed oxidation byproducts and a degradation pathway with chlorine [16,17], though SMZ chlorination in water distribution systems (WDS) has not been the subject of intensive research.

Like other types of SAs, SMZ is an important member of the synthetic SAs and is generally used on a larger scale than other antibiotics; however, the effects of treatments commonly used in the laboratory were not well understood in WDS. Therefore, SMZ was selected as the target in WDS experiments. SMZ compounds contain two moieties connected to both sides of the characteristic sulfonamide linkage (see Supplementary Information Fig. S1). The aniline moiety is in para-connection to the sulfonyl S, which is present in all SAs, and the other moiety connected to the sulfonamide N is unique [18]. Compared with the beaker experiment, halogenation of SMZ in an actual WDS is affected by more factors, including drinking water disinfectants, pipe scales and pipe materials, than in laboratory tests. A pilot-scale WDS in Zhejiang University was chosen as a platform to explore the impact of factors by controlling variables. In addition, GC/MS and HPLC were utilized in conjunction with supplementary analytical techniques to identify intermediate products, and all of the results were combined to deduce the reaction mechanisms and pathways related to the degradation of SMZ by chlorine in WDS.

It is evidently more important to consider the degradation products of many drugs when studying their presence in the environment [1]. Therefore, this study focused on the effects of chlorination for the halogenations and degradation of SMZ in a pilot-scale WDS. The main objectives were: (1) to investigate the degradation of SMZ in a WDS as a function of the concentrations of free chlorines (FC), flow rates and types of WDS pipe materials, which were simultaneously compared with the degradation of SMZ in a beaker; (2) to identify the principle intermediates produced during the reaction process and to propose the degradation pathway of SMZ in WDS; and (3) to evaluate the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) during the degradation of SMZ in WDS.

2. Materials and methods

2.1. Chemicals

Sulfamethazine (SMZ) was obtained from Aladdin (Shanghai, China) (purity > 98%), which was used without further purification. Free chlorine stock solutions were prepared by dilution from a purchased 5% sodium hypochlorite solution (Aladdin) (Shanghai, China). Methanol, acetonitrile and methyl *tert*-butyl ether (MTBE) used in the HPLC and GC-MS measurements were of chromatography grade and supplied by Sigma-Aldrich (Shanghai, China). A mixture of four trihalomethanes (THMs, gas chromatographic grade) and a mixture of eight haloacetic acids (HAAs, gas chromatographic grade) were obtained from Supelco (Supelco Park, PA, USA). Other reagents, including sodium hydroxide (NaOH, analytical grade), sulfuric acid (H_2SO_4, analytical grade) and bicarbonate ($NaHCO_3$, analytical grade) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All solutions were prepared with ultra-pure water (Heal Force ultra-pure system) obtained from a Milli-Q system with resistivity >18 MΩ cm.

2.2. Analytical procedures

The concentrations of sulfamethazine in each sample were monitored by HPLC (Agilent 1200 Series, Agilent, Santa Clara, CA, U.S.) according to the method of R. Fernandez-Torres et al. [19], which used a XDB-C18 with a particle size of 5 μm (4.6 mm × 150 mm) and a diode array detector (DAD, G1314B, Agilent Technologies, Santa Clara, CA, U.S.) set at 270 nm. The column temperature was 30 °C, and the injection volume was 20 μm. The mobile phase was a mixture of methanol and distilled water at a ratio of 35:65 (v/v). The flow rate was 1.0 mL min^{-1}. The retention time of SMZ was 2.031 min.

A solid-phase extraction was used to analyze the degradation byproducts. Analytes were extracted using solid phase extraction (SPE) cartridges (CNWBOND HC-18 SPE cartridges; CNW Technologies GmbH, Düsseldorf, Germany). Cartridges were preconditioned with 3 mL of methanol, then 3 mL of 0.1 mol/L HCl, followed by 5 mL of distilled water [20]. Water samples were then passed through the cartridges at 5 mL min^{-1}. After isolation, cartridges were rinsed with 3 mL of distilled water to remove excess impurities. Then, the analytes were eluted using 5 mL of MTBE into a test tube. Finally, the extracts were concentrated to a final volume of 0.2 mL under a flow of nitrogen. Then, 0.8 mL of mobile phase MTBE was added.

Most intermediate products of the SMZ halogenation were analyzed by gas chromatography–mass spectrometry (SHIMADZU, GCMS-QP2010 SE, Kyoto, Japan) equipped with a HP-5 MS capillary column (30 m × 0.25 mm × 0.25 lm, Agilent, Santa Clara, CA, U.S.) in a GC oven [13]. Conditions: injector temperature 260 °C, the initial temperature was 40 °C (held for 3.5 min), increased at a rate of 6.0 °C min^{-1} to 280 °C (held for 2.0 min), and finally to 300 °C (held for 3.0 min); the injected volume was 1.0 μL in splitless mode, and the carrier gas was high purity (99.99%) helium with a flow rate of 1.0 mL min^{-1}. The injector and detector temperatures were 250 °C and 280 °C, respectively. The analysis was performed in the selected ion monitoring mode with mass-to-charge ratios ranging from m/z 20 to 450.

Separation and identification of THMs and HAAs were detected by a gas chromatograph (Varian, GC-450, Palo Alto, CA, U.S.) according to the method of Li and colleagues [21] using a splitless injector and a SP-Sil 8 CB capillary column