



Oxidation of sulfonamide antibiotics by chlorine dioxide in water: Kinetics and reaction pathways



Weiwei Ben^a, Yanwei Shi^{b,c}, Weiwei Li^d, Yu Zhang^a, Zhimin Qiang^{a,*}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 18 Shuang-qing Road, Beijing 100085, China

^b Beijing Enterprises Water Group of China Co., Ltd., 101 Baiziwan, Beijing 100124, China

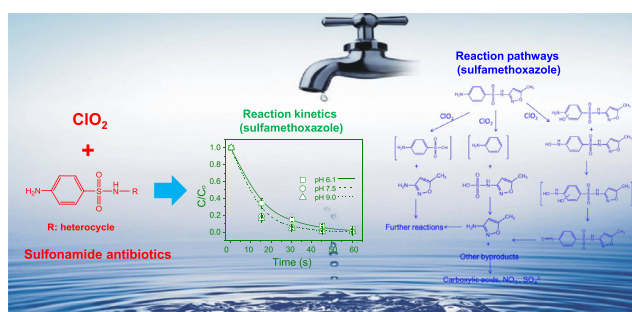
^c Beijing Engineering Research Center of Reclaimed Water Quality Security Guarantee, 101 Baiziwan, Beijing 100124, China

^d PKU UES-Techand Ecology Joint Research and Development Center, 5 Yiheyuan Road, Beijing 100871, China

HIGHLIGHTS

- Sulfonamides (SAs) were effectively oxidized by ClO₂ following second-order kinetics.
- The reactivity of SAs with ClO₂ showed a strong dependence on pH and temperature.
- Breakage of S–N and C–S bonds and hydroxylation of aniline group induced SAs removal.
- Antibacterial functional moieties of SAs were disrupted by ClO₂.
- Effective removal of SAs can be expected under practical water treatment conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfonamides (SAs), commonly used as human and veterinary antibiotics, are of great concerns because of their frequent detections in aquatic environment. This study investigated the oxidation of six SAs (i.e., sulfamethoxazole (SMX), sulfamethizole, sulfamethazine, sulfadimethoxine, sulfamerazine, and sulfathiazole) by chlorine dioxide (ClO₂). The results indicate that the reactions followed the second-order kinetic model, with rate constants ranging from 3.85×10^3 to $2.59 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.0 and 20 °C. For each SA, the rate constant increased by 1.6–2.2 orders of magnitude as the solution pH increased from 4.0 to 9.5. The activation energies of the selected SAs ranged from 31.6 to 39.8 kJ mol⁻¹. In addition, SMX was selected as a model compound to explore the degradation pathways during ClO₂ oxidation. The reactivity of SMX toward ClO₂ was strongly related to the ionization equilibrium of the amido-nitrogen in SMX molecule. The cleavage of S–N and C–S bonds and the hydroxylation of aniline moiety in the SMX molecule constituted the major degradation pathways. ClO₂ oxidation was likely to decrease the antibacterial activity of SMX solution because of the destruction of *p*-aminobenzenesulfonamide moiety. The obtained rate constants could well predict the fate of SAs during ClO₂ oxidation in a surface water, where an effective removal of SAs by ClO₂ can be expected under practical water treatment conditions.

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1. Introduction

Antibiotics in the environment have attracted intensive concerns due to the possibility of inducing the proliferation of resistant bacterial strains. Moreover, antibiotics may also pose other

* Corresponding author.

E-mail address: qiangz@cees.ac.cn (Z. Qiang).

risks to ecosystems, such as causing toxic effects on aquatic species and affecting plant growth [1]. As an important antibiotic class, sulfonamides (SAs) are extensively used in human and animal medical practices. Because of their stable chemical property and high environmental mobility [2,3], SAs have been frequently detected in a variety of aqueous media, such as effluents of wastewater treatment plants, surface water and even drinking water [4–6].

In previous studies, various chemical and photo-catalytic oxidation processes have been applied to oxidize SAs in water, such as free chlorine, ozone, ferrate (Fe(VI)) and TiO₂ photocatalytic treatments [7–12], and fast reactions were generally observed. However, SAs can only be partly removed in practical ozonation and free chlorine disinfection units [6,13], while ferrate and photocatalytic oxidations have not been practically applied in water treatment plants. Hence, further studies on SAs removal by other water oxidants/disinfectants are still necessary.

Chlorine dioxide (ClO₂), a commonly-applied water disinfectant, shows a higher disinfection efficiency, less pH dependence, and less formation of disinfection byproducts than free chlorine. Many studies have been conducted on the reactions between ClO₂ and micro-pollutants in water, such as methiocarb [14], phenylurea herbicides [15], β -lactams [16], fluoroquinolones [17] and tetracyclines [18]. With regard to SAs, an appreciable reactivity of ClO₂ with sulfamethoxazole (SMX) has been reported in water treatment [19]. However, the reaction kinetics and degradation pathways of other SAs during ClO₂ oxidation still remain unclear.

Hence, in this study, the reaction kinetics of six SAs (i.e., SMX, sulfamethizole (SML), sulfamethazine (SMN), sulfadimethoxine (SDM), sulfamerazine (SMR), and sulfathiazole (STZ)) with ClO₂ were individually determined at different pHs and temperatures. Thereafter, SMX was selected as a model compound to clarify the degradation pathways. The reaction kinetics of two substructural compounds of SMX, namely, 3-amino-5-methylisoxazole (AMI) and 4-aminophenyl methyl sulfone (APMS), with ClO₂ were determined and the oxidation byproducts of SMX were identified. Finally, the applicability of obtained rate constants to surface water was assessed.

2. Materials and methods

2.1. Chemicals

The chemical structures of SAs, AMI and APMS are shown in Fig. S1, and their corresponding standards were purchased from Sigma-Aldrich (St. Louis, USA) with purities of >98%. Methanol, acetonitrile and formic acid of high performance liquid chromatography grade were obtained from Fisher Scientific (Pittsburgh, USA). The stock solutions of SAs, AMI and APMS were prepared individually in methanol at a concentration of 100 mg L⁻¹. To identify the oxidation byproducts of SMX, a stock solution of about 1000 mg L⁻¹ was purposely prepared in water by adding HCl. ClO₂ stock solution (350 mg L⁻¹) was prepared according to our previous work [14] and stored in brown bottles at 4 °C. All other reagents used (e.g., buffers, reductant sulfite, carboxylic acids, sulfate, nitrate) were of at least analytical grade quality. High purity Milli-Q water (resistivity of >18 M Ω ·cm) was used to prepare the aqueous solutions.

2.2. Experimental procedures

The reaction kinetics of SAs, AMI and APMS with ClO₂ were individually examined with at least 10-fold excess of ClO₂ (5–12.5 μ M), where the ClO₂ concentration could be considered as constant over the reaction course and the pseudo-first-order rate

constant of a target compound could be determined experimentally. The effect of pH on SAs degradation was investigated in a pH range of 4.0–9.5 with 10 mM acetate (pH 4.0–5.0), phosphate (pH 6.0–8.0) and borate buffer (pH > 8.0). The effect of temperature was tested from 5 to 34 °C. The reaction was initiated by adding a desired amount of ClO₂ stock solution into 20 mL of a buffered solution containing a target compound (0.5 μ M) under magnetic stirring. Water samples (1 mL each) were withdrawn at pre-selected time intervals and the residual oxidant was quenched immediately with excess sodium thiosulfate.

To identify the oxidation byproducts of SMX reacting with ClO₂, the initial molar ratios ([ClO₂]₀/[SMX]₀) of 1:1 and 4:1 were used and the SMX solution was prepared with an initial concentration of 40 μ M (i.e., about 1000 mg L⁻¹) at pH 7.5. After reaction for 1 h, water samples were taken for byproduct identification.

Degradation experiments of all selected SAs by ClO₂ were also carried out in a filtered surface water collected from Jingmi Trench in Beijing. The main characteristics of the filtered surface water were as follows: pH 7.8, dissolved organic carbon 4.8 mg L⁻¹, UV₂₅₄ 0.031 cm⁻¹, and alkalinity 1.8 mM. The filtered water was buffered with 5 mM phosphate and then spiked with each selected SA individually. The prepared reaction solutions were subject to ClO₂ oxidation with an initial dosage of 1.0 mg L⁻¹, which is typically applied for water disinfection. All kinetic experiments were conducted in triplicate.

2.3. Analytical methods

ClO₂ concentration was measured with Hach method 10126 at 530 nm on a DR 5000 UV-Vis spectrophotometer (Hach, Loveland, USA). The concentrations of SAs, AMI and APMS were analyzed by an ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS, Agilent 6240, USA) equipped with an Agilent SB-C18 column (2.1 \times 150 mm, 1.8 μ m). The mobile phases consisted of an aqueous solution of formic acid (0.2%, v/v) and acetonitrile with a total flow rate of 0.3 mL min⁻¹, whose gradient ratio varied from 65:35 to 80:20 depending on different target compounds. The MS parameters were set as follows: capillary 4000 V, nebulizer 35 psi, drying gas 10 L min⁻¹, gas temperature 350 °C, and fragmentor 90–115 V. The limits of quantification for SMX, SML, SDM, SMN, SMR and STZ were determined to be 0.8, 1.7, 1.1, 1.0, 1.1 and 0.5 μ g L⁻¹, respectively.

Oxidation byproducts of SMX were identified by an ultra-performance liquid chromatography/hybrid quadrupole time-of-flight mass spectrometry (UPLC-Q/ToF-MS, AcQuity UPLC/Xevo G2 Q-ToF, Waters, USA) with an Eclipse plus C-18 column (2.1 \times 150 mm, 3.5 μ m). Mobile phases A and B were formic acid aqueous solution (0.2%, v/v) and acetonitrile, respectively. The gradient program with a total flow rate of 0.3 mL min⁻¹ was set as follows (t (min), A (%)): (0–4, 5), (4–10, 75), and (10–14, 5). The MS parameters were as follows: capillary 3000 V, source temperature 100 °C, desolvation temperature 250 °C, cone gas 50 L h⁻¹, desolvation gas 600 L h⁻¹, cone voltage 40 V, and collision energy 6 V. The MS spectra were acquired over an *m/z* range of 50–400. Carboxylic acids, sulfate and nitrate were analyzed with an ion chromatograph (IC, ICS-2000, Dionex, USA) equipped with an IonPac AS19 column (4 \times 250 mm).

3. Results and discussion

3.1. Determination of reaction order

For the reaction of ClO₂ with an organic pollutant, first-order kinetics was generally observed with respect to each reactant [14,20]. Fig. 1a shows a logarithmic representation of the kinetic

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