



## Iodine-enhanced ultrasound degradation of sulfamethazine in water

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### ABSTRACT

This study investigated sulfamethazine (SMT) ultrasound degradation, enhanced by iodine radicals, generated by potassium iodide (KI) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) *in situ*. The results showed that the ultrasound/H<sub>2</sub>O<sub>2</sub>/KI (US/H<sub>2</sub>O<sub>2</sub>/KI) combination treatment achieved an 85.10 ± 0.45% SMT removal (%) in 60 min under the following conditions: pH = 3.2, ultrasound power of 195 W, initial SMT concentration of 0.04 mmol·L<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> concentration of 120 mmol·L<sup>-1</sup>, and KI concentration of 2.4 mmol·L<sup>-1</sup>. UV-Vis spectrophotometric monitoring of molecular iodine (I<sub>2</sub>) and triiodide (I<sub>3</sub><sup>-</sup>) revealed a correlation between the SMT degradation and the iodine change in the solution. Quenching experiments using methanol, *t*-butanol and thiamazole as radical scavengers indicated that iodine radicals, such as I· and I<sub>2</sub><sup>-·</sup>, were more important than hydroxyl radicals (HO·) for SMT degradation. SMT degradation under the US/H<sub>2</sub>O<sub>2</sub>/KI treatment followed pseudo-first order reaction kinetics. The activation energy (*E*<sub>a</sub>) of SMT degradation was 7.75 ± 0.61 kJ·mol<sup>-1</sup>, which suggested the reaction was controlled by the diffusion step. Moreover, TOC removal was monitored, and the obtained results revealed that it was not as effective as SMT degradation under the US/H<sub>2</sub>O<sub>2</sub>/KI system.

### 1. Introduction

Sulfonamides (SAs), such as sulfamethazine (SMT), are an important group of broad-spectrum antibiotics, which are particularly effective in the inhibition of most gram-positive bacteria. They have been extensively applied in humans and livestock [1–3]. However, SAs can enter the environment via faecal excretion, wastewater discharge, or leachate from solid waste landfill [4]. Therefore, they are frequently detected in various aquatic environments [5]. Recent studies have reported the potential toxicity and development of antibiotic resistance arising from residual SAs [1–3,5,6]. Consequently, public health concerns pertaining to the presence of SAs in the environment demand the development of effective treatments for their removal [7].

Efficient removal of organic contaminants in water was achieved by advanced oxidation processes (AOPs), such as photolysis [5,8,9], gamma irradiation [2,10], Fenton-based reactions [11], ozonation [4], ultrasound irradiation [12], and their combinations [13]. Among various AOPs, ultrasound irradiation has drawn increased attention due to its simple operation and convenient control. Two mechanisms are involved in the removal of organic compounds by ultrasound irradiation: 1) direct thermal decomposition in cavitation bubbles and 2) oxidation by hydroxyl radicals (HO·) generated from cavitation bubbles [12,14].

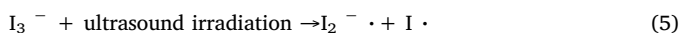
The first one is assumed to be the major removal mechanism for hydrophobic and volatile compounds, and the second one is considered to be more relevant to hydrophilic and less/non-volatile compounds [14]. Nevertheless, the degradation involving HO· radical oxidation tends to be limited by the trace amount of HO· radicals in aqueous solutions [15–17]. Thus, considerable efforts have been made to enhance the production of reactive species with additional catalysts or chemicals. Accordingly, ultrasound degradation of a textile dye, Reactive Blue 19, enhanced by the Fenton process, was reported [16]. Ultrasound combined with ozone showed the effective degradation of sulfamethoxazole (SMX), a SA antibiotic [17]. Sono-degradation of levofloxacin was also shown to be increased by carbon tetrachloride [18,19]. Furthermore, oxidative decomposition using sulfate radicals (SO<sub>4</sub><sup>-·</sup>) promoted the ultrasound degradation of the antibiotic, amoxicillin, with oxone (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) [20]. A similar result was also observed in degrading norfloxacin with peroxydisulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) [21]. In addition, sono-degradation enhancement using carbonate radicals (HCO<sub>3</sub><sup>-·</sup> and CO<sub>3</sub><sup>-·</sup>), generated from bicarbonate or carbonate ions, was reported [22]. Markedly, the generation of highly reactive radicals is a proven mechanism to enhance ultrasound degradation.

Recently, iodine radicals, i.e., I· (*E*<sup>0</sup>(I·/I<sup>-</sup>) = +1.33 V) and I<sub>2</sub><sup>-·</sup> (*E*<sup>0</sup>(I<sub>2</sub><sup>-·</sup>/I<sup>-</sup>) = +1.03 V), were found to be very efficient in the

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photochemical degradation of several environmental pollutants, such as arsenite (As(III)) [23], chromium (Cr(VI)) [24] and 2,4,6-trichlorophenol [8], where iodine radicals were generated from the transformation of the iodide ion or molecular  $I_2$  under light irradiation. Molecular  $I_2$  ( $E^0(I_2/I^-) = +0.54$  V) has received considerable attention as an inexpensive, non-toxic, readily available catalyst in organic synthesis, such as for esterification and transesterification, allylation of aldehydes, cycloaddition, etc. [25,26]. Moreover, the covalent I–I bond of molecular  $I_2$  can be broken under light irradiation ( $\lambda \geq 450$  nm), subsequently generating iodine radicals [8]. Light and ultrasound irradiation can contribute to the generation of active free radicals [27] and considering the safer and easier operation of ultrasound irradiation treatment, iodine radicals produced from the decomposition of molecular iodine under ultrasound irradiation, for the first time, was investigated. Moreover, the effect of the catalytic degradation of aqueous SMT was studied. In this treatment, molecular  $I_2$  was generated by  $H_2O_2$  oxidation of  $I^-$ , which was added to the solution as KI (Eqs. (1) and (2)) [28–30]. Molecular  $I_2$  further reacts with existing  $I^-$  to produce  $I_3^-$  (Eq. (3)), in which  $I_3^-$  may enhance the solubility of  $I_2$  in solution [8,24,30,31]. Subsequently, the covalent I–I bond in  $I_2$  and  $I_3^-$  was broken by ultrasound irradiation and iodine radicals, such as  $I\cdot$  and  $I_2^{\cdot-}$ , were formed (Eqs. (4) and (5)), which would facilitate SMT degradation. In addition, chain termination reactions (Eqs. (6) and (7)) would enhance the regeneration of iodine in the proposed system.



Hence, this study focuses on (1) evaluating the effectiveness of the  $US/H_2O_2/KI$  combination treatment on SMT degradation, (2) validating the reactivity of iodine radicals on SMT degradation, (3) assessing the process parameter effects on SMT removal (%), (4) determining the activation energy ( $E_a$ ) of SMT degradation, and (5) investigating the mineralization of SMT during its degradation under the  $US/H_2O_2/KI$  treatment system.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals were used as received without further purification.  $H_2O_2$  (30 wt%), was purchased from Sinopharm Chemical Reagent Co. Ltd, China. KI (analytical grade) was obtained from Tianjin Fu Chen Chemical Reagents Factory, China. SMT, ( $\geq 99\%$  purity) was supplied by J&K Chemical Technology, China, with the structure and relevant

data of SMT shown in Table 1. Thiamazole ( $\geq 98\%$  purity) was purchased from Shanghai Yanchen Co. Ltd., China. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (analytical grade, Tianjin Ao-ran Fine Chemical Industry Research Institute, China) were used to adjust the initial pH value of SMT solutions. All solutions were prepared with ultra-pure grade water throughout the study.

### 2.2. Ultrasound irradiation experiments for SMT degradation

SMT ultrasound irradiation experiments were carried out in glass beakers (250 mL) using a JY92-II ultrasonic cell crusher (Ningbo Xinzhi Instruments Co. Ltd, China), which was equipped with a titanium probe (8 mm diameter). The tip of the probe was placed 10 mm below the surface of the reaction solution, and the sonication was set in a pulse mode of 1.0 s on and 1.0 s off. A thermostat bath (DC-1006, Ningbo Xinzhi Instruments Co. Ltd, China) was used to keep the reaction temperature constant by cycling the cooling water. Unless stated otherwise, all degrading reactions were conducted in the open atmosphere, the ultrasound power was set at 195 W, and the initial concentration of SMT,  $H_2O_2$ , and KI was 0.04, 120.0 and  $2.4 \text{ mmol}\cdot\text{L}^{-1}$ , respectively. The initial pH value of reaction solution was adjusted to 3.2 using  $0.5 \text{ mol}\cdot\text{L}^{-1}$  HCl or NaOH. At given irradiation time intervals, samples (1.5 mL) were withdrawn and filtered using a  $0.22 \mu\text{m}$  micro-filtration membrane before the HPLC analysis. The percent loss of SMT in solution for each treatment is shown in Eq. (8),

$$\text{Removal}(\%) = \frac{[SMT]_0 - [SMT]_t}{[SMT]_0} \times 100\% \quad (8)$$

where  $[SMT]_0$  and  $[SMT]_t$  are the SMT concentration at the initial and time  $t$  (min), respectively.

### 2.3. Analytical methods

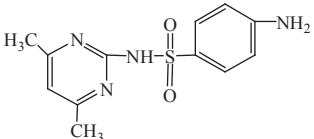
SMT concentration was quantified by HPLC (high-performance liquid chromatography) analysis (Agilent 1200 Series, Agilent, USA) equipped with a  $C_{18}$  reverse phase column ( $4.6 \times 150 \text{ mm}$ ,  $5 \mu\text{m}$ ) and UV detector. The column temperature was  $30^\circ\text{C}$ , with an injection volume of  $10.0 \mu\text{L}$ . The mobile phase was a mixture of 50% (v/v) methanol and 50% (v/v) water with a flow rate of  $0.50 \text{ mL}\cdot\text{min}^{-1}$ ; the UV detection wavelength was 275 nm.

UV-Vis spectrophotometry was used to quantify  $I_2$  and  $I_3^-$  in the reaction solution. The molar absorption coefficients of  $I_2$  at 350 and 460 nm are 30 and  $730 \text{ M}^{-1}\cdot\text{cm}^{-1}$ , while those of  $I_3^-$  at 350 and 460 nm are 25,800 and  $980 \text{ M}^{-1}\cdot\text{cm}^{-1}$ , respectively. Thus,  $I_2$  and  $I_3^-$  have maximum absorption at 460 nm and 350 nm, respectively, for quantification [8]. UV-Vis spectrophotometry was conducted with a UV-Vis spectrophotometer (DR 5000, Hach, USA). Total organic carbon (TOC) was measured using a vario TOC cube (Elementar, Germany).

### 2.4. Statistical analysis

All experiments were conducted in triplicate, and the average of three replicates for each experiment was calculated. SMT degradation

**Table 1**  
Physiochemical characteristics of sulfamethazine.

Name	Chemical structure	Molecular formula	$m_w^*$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$\lambda_{\text{max}}^*$ (nm)
Sulfamethazine		$C_{12}H_{14}N_4O_2S$	278	276

\*  $m_w$  represents molar mass of sulfamethazine;  $\lambda_{\text{max}}$  represents the maximum absorption wavelength of sulfamethazine.

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