

## The role of reactive oxygen species in sulfamethazine degradation using UV-based technologies and products identification



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### ABSTRACT

Sulfamethazine (SMT) is an emerging pollutant continuously delivered into water bodies that has attracted growing attention due to its recalcitrant behavior in the environment. Although UV-based technologies have been investigated for the treatment of both water and wastewater containing SMT, photosensitization of the target compound is not usually examined during photo-induced oxidation processes. It is not our intention to propose processes for water treatment, only to understand the phenomena induced by the interactions between UV radiation and pollutant molecule. In this way, the photo-initiated and photo-induced oxidation processes are compared in terms of changes in SMT degradation rates and photoproducts formed. A tubular photochemical reactor with a concentric low pressure mercury vapor lamp emitting at 254 nm was used and SMT concentrations were determined by ultra-fast liquid chromatography analysis. Hydrogen peroxide consumption was monitored spectrophotometrically and the photoproducts were analyzed by LCMS-IT-TOF. To characterize samples we used three spectroscopic methods based on: (1) UV-Vis absorption; (2) excitation-emission matrix (EEM) fluorescence; and (3) phosphorescence. Our results suggest that photolysis and photosensitization played an important role in sulfamethazine degradation during irradiation at 254 nm. The reaction with singlet oxygen and radical species promotes sulfamethazine degradation during a photosensitized process occurring simultaneously with direct photolysis. The photo-initiated oxidation process was advantageous over the photo-induced oxidation in terms of SMT degradation rates, achieving concentration below the detection limit after 47 min of irradiation. Compounds originated from the cleavage of the C–S and N–S bonds of the SMT molecule were detected as common transformation products during photo-initiated and photo-induced oxidation processes, whereas a degradation product resulting from the electrophilic addition of hydroxyl radicals to the aromatic ring was detected for the H<sub>2</sub>O<sub>2</sub>/UV system. The high efficiency of the photo-initiated oxidation process on the photodegradation of the recalcitrant sulfamethazine was verified, suggesting the formation of acidic subproducts probably from the oxidative cleavage of hydroxylated aromatic rings.

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### 1. Introduction

Human and livestock excretion is an important route for the disposal of antibiotics and their metabolites into the environment [1]. Special attention is given to the treatment of waters contaminated with sulfonamides, which are not efficiently degraded in sewage treatment plants and are therefore transferred into water bodies [2–4]. Sulfonamides are bacteriostatic antibiotics which may contribute to the development of pathogenic organisms more resistant to antibacterial action [5,6]. Among sulfonamides, sulfamethazine

(SMT) is commonly used for treating livestock diseases and is mentioned as the predominant sulfonamide found in livestock animal wastewater [7]. For example, SMT has been detected in wastewaters from swine farming at concentrations of  $600 \pm 30 \text{ ng L}^{-1}$  [8].

In view of the continuous input of sulfamethazine residues into water bodies, the development of more effective water and wastewater treatment technologies is of major concern. Non-destructive physicochemical technologies are often limited for the complete degradation of sulfamethazine [9], which is then often detected in effluents from wastewater treatment plants [2]. Because of its recalcitrant behavior, SMT was selected for the present study. As an attractive alternative to conventional treatment processes, UV-based technologies are considered efficient for wastewater treatment purposes [10]. Some examples are the

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degradation and detoxification of phenol derivatives in water [11], pesticides degradation [12], pre-treatment of hospital wastewater [13] and others.

In photo-excitation, photon absorption promotes electrons from their initial ground state to a higher energy excited state. An electron from a bonding  $\pi$  orbital can get excited to an antibonding  $\pi^*$  orbital, according to a  $\pi \rightarrow \pi^*$  transition, whereas a non-bonding electron can undergo transition to an antibonding  $\pi^*$  orbital ( $n \rightarrow \pi^*$  transition). Based on these events, UV-driven technologies include photo-induced oxidation and photo-initiated oxidation processes. The former rely on the absorption of electromagnetic radiation by organic pollutants to produce electronically excited species in the singlet state, which can undergo relaxation processes. This includes the decomposition of electronically excited species to photoproducts (photolysis processes) or the re-emission of radiation by fluorescence or phosphorescence. The existence of pollutant molecules in the triplet excited state is an important phenomenon for the photosensitized processes during the photo-induced oxidation reactions and is related to the formation of reactive oxygen species (ROS) [14]. The motivation for the present study is the hypothesis that reactive oxygen species could be formed during SMT photodegradation by using concentrations of the target compound higher than that found in the environment. Photons emitted from a low-pressure mercury lamp can be effective to degrade sulfonamides during photo-induced oxidation processes due to the presence of aromatic rings and double bonds in their chemical structure. The other UV-based technology involves photo-initiated oxidation in which pollutant degradation depends on the reactions initiated during the absorption of photon by a given auxiliary oxidant. The cleavage of chemical bonds of an auxiliary oxidant such as hydrogen peroxide, for example, leads to the formation of ROS [10,13,15], such as hydroxyl radicals ( $\text{HO}\cdot$ ).

In this study, the photodegradation of the antibiotic sulfamethazine (SMT) using UV radiation at 254 nm is evaluated by employing two UV-based technologies. The importance of photosensitization is investigated in the photo-induced oxidation of SMT in an attempt to understand the interaction between UV radiation and sulfonamide molecules. The contribution of molecular oxygen as electron/energy acceptor in photosensitization processes is studied using scavengers in aqueous solutions. Kinetic studies of SMT photodegradation is performed in terms of changes in the pollutant degradation rates. Furthermore, the concern with the elucidation of photochemical transformation products of SMT is taken into account. The degradation pathway is proposed based on the structural elucidation of the pseudo molecular ions of the photoproducts.

## 2. Experimental

### 2.1. Chemicals

All the solutions were prepared using ultrapure water (Millipore Milli-Q®). A 30% (w/w)  $\text{H}_2\text{O}_2$  solution (Merck) was used. Sulfamethazine (SMT,  $\text{MM} = 278 \text{ g mol}^{-1}$ , Sigma–Aldrich > 99%) was used as a standard in ultra-fast liquid chromatography (UFLC) analysis and in photochemical experiments. The molecular structure of SMT is

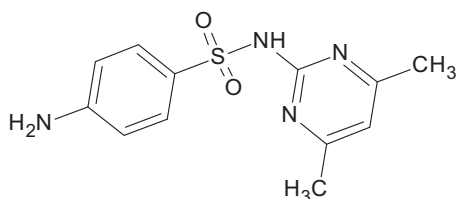


Fig. 1. Molecular structure of sulfamethazine (SMT).

shown in Fig. 1. The sulfamethazine standard solution was prepared in methanol and after was diluted up to a maximum of 0.1% methanol in ultrapure water to avoid hydroxyl radicals scavenging. High-purity nitrogen was purchased from Air Products (99.99%). Acetonitrile and methanol (HPLC grade) were purchased from Sigma–Aldrich.

### 2.2. Equipment and procedures

Photochemical degradation experiments were performed in batch in a tubular photochemical reactor, which consists of a borosilicate glass tube with a concentric low-pressure (LP) mercury vapor lamp (TUV Philips 36W), emitting short-wave UV radiation with a peak at 253.7 nm. It is important to mention that the glass of this lamp filters out the 185 nm ozone-forming line.

The reactor is connected to a circulation tank, from which samples were withdrawn using an automatic pipette. The initial concentration of the antibiotic was  $0.100 \text{ mmol L}^{-1}$  ( $27.8 \text{ mg L}^{-1}$ ). The initial pH of the solutions was adjusted using both  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ ; in this investigation, all the experiments were carried out at pH 6, which was adjusted in the beginning but not corrected over time. The experiments were carried out at room temperature. The solution was recirculated at a flow rate of  $80.0 \text{ mL min}^{-1}$  through the reactor and the tank by means of a centrifugal pump, which enabled the continuous oxygenation of the reaction medium. The flow rate was adjusted using a needle valve and read with a rotameter.

The irradiation time ( $t_{\text{irrad}}$ ) was calculated according to  $t_{\text{irrad}} = (t_{\text{total}} \times V_{\text{reactor}}) / V_{\text{total}}$ , where  $t_{\text{total}}$  represents total time,  $V_{\text{reactor}}$  is the reactor volume and  $V_{\text{total}}$  is the total volume of the SMT solution. The total and irradiated volumes of SMT solutions were 5.00 L and 3.93 L, respectively. The monitoring time ( $t_{\text{total}}$ ) started when the reaction vessel was completely filled and the lamp was switched on. In this study, standard deviations were calculated from three replicates of the experiments carried out at each experimental condition. To evaluate the photo-induced oxidation of SMT in the absence of dissolved oxygen, the solution was deoxygenated by bubbling pure nitrogen for 60 min before and during irradiation.

### 2.3. Chemical analysis

Sulfamethazine (SMT) concentration was determined by Ultra-Fast Liquid Chromatography analysis using a Shimadzu equipment (LC 20AD), equipped with a UV–visible detector (SPD 20A) and a  $\text{C}_{18}$  column (Phenomenex Synergi Fusion-RP,  $250 \text{ mm} \times 4.60 \text{ mm}$ ,  $4 \mu\text{m}$ ); the detection wavelength of SMT was 268 nm. The oven temperature and sample injection volume were  $40^\circ\text{C}$  and  $50.0 \mu\text{L}$ , respectively. The eluents were (A)  $\text{H}_2\text{O} + 0.2\%$  acetic acid and (B) acetonitrile at 80:20 ratio and  $1.00 \text{ mL min}^{-1}$  flow rate. Under these conditions, the detection and quantification limits were  $0.611 \mu\text{mol L}^{-1}$  ( $0.170 \text{ mg L}^{-1}$ ) and  $1.80 \mu\text{mol L}^{-1}$  ( $0.500 \text{ mg L}^{-1}$ ), respectively.

Hydrogen peroxide concentration was determined spectrophotometrically by measuring the sample absorption at 450 nm after reaction with ammonium metavanadate [16]. The photoproducts in samples were analyzed with a Shimadzu LCMS-IT-TOF High Speed Liquid Chromatography–Mass Spectrometer (LC-20AD with an electrospray ionization source), employing a  $\text{C}_{18}$  column (Shimadzu,  $50 \text{ mm} \times 2.1 \text{ mm}$ ,  $5 \mu\text{m}$ ). The injection volume was  $50.0 \mu\text{L}$ . The eluents were (A)  $\text{H}_2\text{O} + 0.2\%$  acetic acid and (B) acetonitrile at 80:20 ratio and  $0.200 \text{ mL min}^{-1}$  flow rate. The mass-spectral data were obtained in positive mode between  $m/z$  50 and 500 and the operating conditions were as follows: desolvating gas flow,  $1.50 \text{ L h}^{-1}$ ; source and desolvation temperatures,  $250^\circ\text{C}$  both; capillary voltage, 4.50 kV. The collision energy (CE) was held at 50% for MS analysis; the collision gas applied was argon.

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