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Degradation of sulfamethoxazole by ionizing radiation: Identification and characterization of radiolytic products

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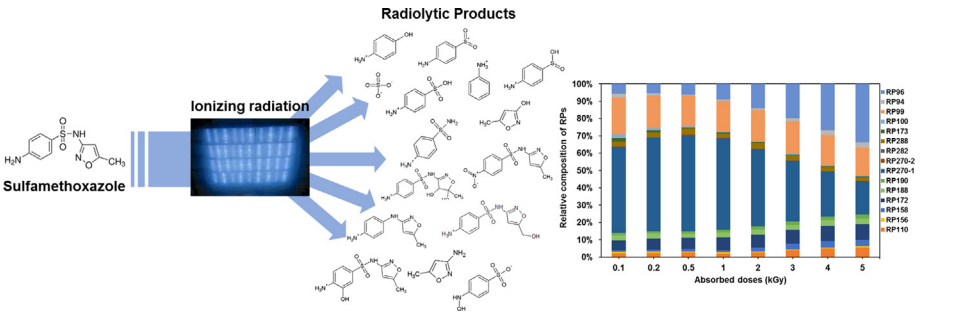
HIGHLIGHTS

- The radiolytic products (RPs) of antimicrobial sulfamethoxazole were identified.
- The relative abundances of fifteen RPs were compared with increasing irradiation doses.
- RP270-1, RP99, RP172, and RP96 were predominant, accounting for 86.9% at 1 kGy.
- The main degradation mechanisms and the proposed pathways for RPs were suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfamethoxazole (SMX) is a widely prescribed pharmaceutical compound to treat bacterial infections in both human and animals. As an alternative treatment process for non-degradable pharmaceuticals by conventional water treatment processes, radiolysis using gamma radiation has been applied as one of the radical-based advanced oxidative processes. However, further information was limited with regard to the production mechanism and fate of radiolytic products after treatment. Therefore, the degradation characteristics of SMX using ionizing radiation were investigated in this study. In addition, some radiolytic products of SMX were identified, and a degradation pathway as a result of the radiolysis of SMX was proposed. The radiolytic products were analyzed using liquid chromatography quadrupole time-of-flight mass spectrometry, liquid chromatography tandem mass spectrometry, and ion chromatography. Molecular structures of the radiolytic products were elucidated by the interpretation of MS^2 fragmentation patterns of each product. In total, fifteen products were elucidated as a result of ionizing radiation treatment of aqueous SMX in the range 0.1–5.0 kGy. Hydroxylation, bond-cleavage, and the combined mechanism of cleavage and transformation were proposed as the predominant mechanisms, inducing the various radiolytic products. In particular, based on the comparison of the relative intensity and the quantified concentration using authentic standards, RP270-1 (hydroxylated SMX) and RP172 (sulfanilic acid), RP99 (3-amino-5-methylisoxazole), and RP96 (sulfate) were the most abundant products. Chromatographic profiles of radiolytic products also revealed the change of major products with increasing absorbed doses, from compounds that have high molecular weight (MW), to relatively lower MW. The results of this study lead to an understanding of the role of ionizing radiation on the fate of the parent compound and its degradation products when applied to pharmaceutical pollutants.

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1. Introduction

The environmental impact of pharmaceuticals as emerging contaminants has generated severe concerns. Sulfonamide antibiotics (SAs), including sulfamethoxazole (SMX), are widely prescribed pharmaceutical compounds that are used to treat bacterial infections in both veterinary and human medicines. SMX is included as a high priority pharmaceutical compound, when considering the high frequency of environmental detection, persistence, bioaccumulation, and its toxicity [1]. Once absorbed into the body, pharmaceuticals undergo biotransformation reactions, including phase I and II, and are metabolized to more polar compounds [2]. However, pharmaceuticals are not completely metabolized, and parent compounds are excreted into the water body [3]. Improperly discarded drugs via household waste are also one of the major sources of pharmaceuticals entering the environment [4].

Recently, efforts have been made to study the degradation efficiency of various pharmaceuticals. In the case of antibiotics, low and inconsistent degradation efficiency have been reported when treated in conventional wastewater treatment plants (WWTPs), and the compounds were still detected in effluent [5–9]. In detail, Göbel et al. obtained no significant elimination in primary treatment processes, including screen, aerated grit removal, and primary clarifier. The elimination rates in secondary treatment that consists of activated sludge and membrane bioreactor ranged between 60 and −138% [10]. In our previous study, the compound-dependent manner of the degradation rates of antibiotics when treated with UV and activated sludge were also observed [11]. The persistence of antibiotics in treatment processes resulted in their frequent detection in effluent and surface water in the range of ng L^{-1} to μg L^{-1} [12–15].

Therefore, various advanced oxidation processes (AOPs), including ozonation, UV, Fenton oxidation, heterogenous photocatalytic treatments, ultrasound irradiation, and wet air oxidation, have been currently applied to treat non-degradable pharmaceuticals by conventional water treatment processes. [16–18]. Among the various AOP technologies, pharmaceuticals have been most studied by ozone and heterogenous photocatalysis [17]. Radiolysis is a new treatment technology in the field of radiation-induced degradation for environmental pollutants. The ionizing radiation process is an alternative method to eliminate a variety of non-degradable compounds, and shows higher removal efficiency and non-specific degradative action [11,19–21]. Radiolysis has advantages in minimizing the required energy cost for treatment, and is a fast and clean process, without chemical addition for oxidation. In our previous study, a lower energy requirement of radiolysis was obtained when compared with ozone and UV [22]. It is known that the radiolytic decomposition of aqueous pollutants is dominated by reactive species produced by water radiolysis, such as hydroxyl radical (·OH), and hydrated electron (e^-_{aq}) [19]. These reactive radicals are known to be predominantly responsible for the degradation of organic pollutants in aqueous phase AOPs [23].

However, some environmental pollutants were not completely mineralized by powerful AOPs, but yield a number of intermediates or products, which can be more stable than the parent compound when released into environment. Studies considering pharmaceuticals and personal care products (PPCPs) degradation by various AOPs revealed that each technique exhibited unique mechanism to remove pollutants, resulted in the different degradation products. Although studies considering the degradation of recalcitrant compounds with ionizing radiation have increased [20,21,24–28], kinetic studies alone were not enough to understand the radiolysis process, and there has been insufficient information of intermediates and byproducts produced by this treatment. In case of sulfonamide antibiotics (SAs), some studies have conducted degradation of SAs using gamma radiation treatment. The influence of solution pH, additives, and radical scavengers on the degradation of sulfadiazine [29] and sulfamethoxazole [30] were broadly investigated. Recently, Sági et al., also conducted pulse radiolysis of SAs and observed gradual oxidation of target compounds with various intermediates, especially including the hydroxylated and inorganic ion products [31]. However, the fate of SAs and their degradation intermediates treated by ionizing radiation with high selectivity and accurate structural information is not sufficient. Therefore, the aims of the present study were to systematically identify the radiolytic degradation products of antibiotic SMX, and to evaluate the radiolysis kinetics of products as well as the parent compound. The radiolytic products during the irradiation process were identified using LC-QTOF-MS, and some of them were confirmed by MS/MS data matching with authentic standards. A tentative radiolytic degradation pathway of SMX was also proposed, according to the structural characterization and kinetics of the products with increased radiation energy. Product analysis coupled with total organic carbon (TOC) and inorganic ions was complementally conducted to understand the overall radiolysis efficiency and their degradation mechanisms.

2. Material and methods

2.1. Chemicals and reagent

The target sulfonamide class of antibiotic compound was sulfamethoxazole (SMX, CAS No. 723-46-6). Other chemicals including aniline (AN), sulfanilic acid (SAA), sulfanilamide (SA), 3-hydroxy-5-methylizoxazole (HMI), and 3-amino-5-methylisoxazole (AMI) for the radiolytic products confirmation were all purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade solvents for the mobile phase, including water (Fisher scientific, NJ, USA), acetonitrile (J.T. Baker, PA, USA), methanol (J.T. Baker, PA, USA), and formic acid (Sigma-Aldrich, St. Louis, MO, USA) were also obtained from various chemical suppliers.

2.2. Radiolysis experiments

The aqueous SMX were prepared for all radiolysis experiments. The test solution containing 394.82 μM of target compound (SMX) was treated using ionizing radiation, with the range of absorbed doses from 0.1 to 5 kGy (1 kGy = 1 kJ kg^{-1}, dose rate 1 kGy h^{-1}). Ionizing irradiation was achieved using a high-level ^{60}Co source (Nordion Inc., Canada) at the Korea Atomic Energy Research Institute (KAERI, Republic of Korea). The dose rates of the source ranged from 6.3 to 14.3 kGy h^{-1}, which rates were dependent on the distance of the sample from the source. The initial radioactivity was about 1.47×10^{17} Bq (=397,949 Ci). The absorbed dose was measured using the alanine-EPR dosimetry system (IOS/ASTM 51607:2003). Before ionizing radiation was applied, 1 L glass bottles containing the SMX solution were allowed to reach equilibrium at room temperature (22 ± 1 °C). After irradiation, the samples were stored at 4 °C until further analysis. Oxygen or air was not supplied for the irradiation treatment.

2.3. Analytical methods

2.3.1. Product identification and qualitative/quantitative analysis

Agilent 6520 quadrupole time-of-flight liquid chromatography mass spectrometer (LC-QTOF-MS, Agilent Technologies, Santa Clara, USA) was used for the qualification analysis of radiolytic products (RPs) irradiated at 1 kGy of absorbed dose. Ten micro-

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