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Degradation of the Antibiotic Sulfamethoxazole in Aqueous Solutions by γ-Irradiation

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This study focused on the degradation of antibiotic sulfamethoxazole (SMX) in aqueous solutions by γ-irradiation. The influences of initial sulfamethoxazole concentration, solution pH, various additives (H_2O_2, CH_3OH, humic acid and thiourea) and absorbed dose on sulfamethoxazole degradation were investigated. At a sulfamethoxazole concentration of 26.4 mg L^{-1} and an absorbed dose of 1.1 kGy, the extent of sulfamethoxazole degradation was 99 %. The degradation reaction of sulfamethoxazole followed first-order like kinetics. Added humic acid or 0.3 % H_2O_2 enhanced the sulfamethoxazole degradation, while CH_3OH, 0.9 % H_2O_2 and thiourea additives significantly inhibited sulfamethoxazole degradation. The degradation efficiency was higher under acidic conditions than in neutral or alkaline media. The solution pH and total organic carbon became lower as the absorbed dose increased. The possible degradation pathway was proposed.

Key Words: Sulfamethoxazole, Degradation, γ-Irradiation.

INTRODUCTION

Recently, the pharmaceutical pollutants in the environment have received much attention due to their potential impact on the environment and their possible damage to plant kingdom[1]. These compounds and their metabolites can reach sewage systems, where they are not easily degraded under the typical biological treatments in the municipal wastewater treatment plants[2]. Antibiotics are an important group of pharmaceuticals in today's medicine. They are widely used to treat human infections disease and also used in veterinary medicine[3]. Of all emerging contaminants, antibiotics are probably the major problem because they may cause long-term and irreversible change to a microorganism's genome, making them resistant in their presence, even at low concentrations[4,5]. Now, the environmental risks of antibiotics have attracted special research attentions[6].

One of the antibiotics, sulfamethoxazole (SMX), one of the most widely synthesized sulfonamides[7], is currently prescribed to treat urinary infections and it is also being used in veterinary practice, aquaculture and livestock breeding both for treating diseases promoting growth. Now, some authors have found evidences of the presence of sulfonamides in wastewaters[8,9] and therefore it is necessary to develop a suitable method to remove these compounds from wastewater, in order to avoid an increase of antibiotic resistance in humans[10]. Now, a lot of enhanced technologies that can reduce SMX presence in the environment have been carried out, such as advanced oxidation processes[11,12], photodegradation and solar photodegradation methods[13,14], biological treatments[15], adsorption methods[16], electro-Fenton treatment[17].

γ-Irradiation is an advanced oxidation method, based on the production of the strongest oxidizing agent in the aqueous systems-the active $^{\bullet}OH$ radicals[18]. It has been employed for decomposition of various pollutants. Numerous publications were devoted to the degradation of organic compounds by gamma irradiation[19]. It is a promising treatment technology in the environmental remediation of drinking and wastewater.

In this work, the degradation of SMX by γ-irradiation was investigated. The primary aim of this research was to study the effect of operational parameters, such as solution pH and various additives (H_2O_2, CH_3OH, humic acid and thiourea) on SMX degradation in aqueous solutions by γ-irradiation. These researches will contribute to determine experimental conditions for γ-irradiated SMX in natural aquatic environments. The secondary aim of this research was to investigate the degradation kinetics of SMX. In addition, the possible degradation mechanism was proposed.

EXPERIMENTAL

Sulfamethoxazole, CH_3CN, CH_3COOH and CH_3OH were purchased from Sigma-Aldrich and HPLC grade. Humic acid was high purity product and also purchased from Sigma-Aldrich. H_2O_2, $(NH_2)_2CS$, HCl, NaOH were analytical-grade and obtained from Shanghai Chemicals Factory, China. The deionized water was obtained from milli-Q system (Elix5 + milliQ A10, USA).

Sample preparation: Following on the studies of Xekoukoulotakis *et al.*[13] a 26.4 mg L^{-1} SMX solution was used to test the effect of absorbed dose on degradation efficiency and to examine the changes of pH and total organic carbon (TOC) after γ-irradiation. Different additives (H_2O_2, CH_3OH, humic acid and thiourea) at various concentrations were added into the SMX aqueous solutions to examine their effects on SMX degradation. Dilute HCl and NaOH aqueous solutions were used to vary the pH of the SMX aqueous solutions and test the effect of pH value on degradation.

Irradiation process: γ-Irradiation was performed using high-level ^{60}Co source (1.85 Bq × 1016 Bq) at the Institute of Atomic Energy, Jiangsu Academy of Agriculture Sciences, P.R. China. Sulfamethoxazole solutions (25 mL each) were placed into 50 mL airtight glass vessels and all aqueous solutions were allowed to reach equilibrium with atmospheric pressure and room temperature (22 ± 2 ºC) before irradiation. Then they were placed in a radiation field with a specific distance from the source to achieve the desired series of absorbed dose. 0.3, 0.5, 0.7, 0.9 and 1.1 kGy were selected as the absorbed doses. The doses that samples absorbed were determined with silver dichromate dosimeter.

Detection method: The concentration of SMX was determined by using a HPLC system (Agilent, USA, 1200 series high-performance liquid chromatography) equipped with Hypersil ODS HPLC column (250 mm × 4.6 mm i.d., 5 µm, Agilent, USA), a multiple wavelength UV diode array detector and an auto sampler controlling under a chemstation data acquisition system. The mobile phase was 40:60 (v:v) of acetonitrile and deionized water with 0.1 % acetic acid and the flow rate was 1 mL min^{-1}. The determination wavelength was set at 270 nm and the column temperature was kept at 30 ºC.

The degradation efficiency of each sample was calculated from the following eqn. 1.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\ \% \tag{1}$$

where, η: degradation efficiency of SMX (%); C_t: residual concentration of SMX after γ-irradiation (mg L^{-1}). C_0: initial concentration of SMX (mg L^{-1}).

The identification of SMX and its degradation products resulted from the radiolytic degradation were performed by LC-MS (ThermoQuestLCQ Duo, USA) equipped with Beta Basic-C_{18} HPLC column (150 mm × 2.1 mm i.d., 5 µm, Finnigan, Thermo, USA). 20 µL SMX solutions after γ-irradiation were injected automatically into the LC-MS system. The eluent consisted of 65 % of 1.0 mM acetic acid in water and 35 % of acetonitrile. The flow rate was 0.2 mL min^{-1}. MS conditions were as follows: the electrospray ionization interface was selected. The capillary temperature was set to 275 ºC with a voltage of 19.00 V. The spray voltage was 5000 V and the sheath gas flow rate was 18 arb. The m/z range from 50-600.

Total organic carbon (TOC) was determined by TOC analyzer (Shimadzu, TOC-5000A). The pH value was measured by pH monitor (Shanghai Kangyi Instrument Co. Ltd. China, PHS-2C).

Sulfamethoxazole radiation chemical yield (G-value): Radiation chemical yield of SMX (defined by the number of molecules formed or destroyed in solutions absorbing 100 eV of radiation energy) can be calculated using eqn. 2[20].

$$G = \frac{(\Delta P)(N_A)}{(D)(6.24 \times 10^{16})} \tag{2}$$

ΔR: The amount of reduced SMX (mol L^{-1}); N_A: Avogadro constant, 6.023×10^{23} (molecules mol^{-1}); D: The absorbed dose (Gy); 6.24×10^{16}: Conversion constant from Gy to 100 eV L^{-1}.

RESULTS AND DISCUSSION

The energy of the ionizing radiation can be absorbed by water, resulting in the formation of several primary reactive species, such as hydrogen atoms ($H^\bullet$), hydrated electrons (e^-_{aq}), hydroxyl radicals ($^\bullet OH$) and less reactive species (H_3O^+)[20]. The effects of ionization radiation in water are described in eqn. 3. Under certain conditions, the reactions between these radicals occur in aqueous solutions during γ-irradiation. As follows: (i) In the presence of dissolved oxygen, the radicals $H^\bullet$ and e^-_{aq} are converted into $HO_2^\bullet$ and $O_2^{\bullet -}$, as in eqns. 4 and 5; (ii) At higher absorbed dose, the reaction between the $^\bullet OH$ and the e^-_{aq} can be represented by eqn. 6; (iii) under acidic conditions, the H^+ readily reacts with e^-_{aq} to generate $H^\bullet$, as in eqn. 7; (iv) $HO^\bullet_2$ and its conjugate base $O_2^{\bullet -}$ exist in a pH-dependent equilibrium, as in eqn. 8; (v) Any other reactions could occur during γ-irradiation, as in eqns. 9-11[21].

$$H_2O \rightarrow e_{aq}^- \ (2.6) + H\cdot \ (0.55) + \cdot OH \ (2.7) + H_2 \ (0.45) + H_2O_2 \ (0.71) + H_3O^+ \tag{3}$$

(2.6) (the values in brackets are the radiation chemical yields of these species (G values) per 100 eV of absorbed energy)

$$H^\bullet + O_2 = HO_2^\bullet \qquad k = 2.1 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \tag{4}$$

$$e^-_{aq} + O_2 = O_2^{\bullet -} \qquad k = 1.9 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \tag{5}$$

$$e^-_{aq} + {}^\bullet OH = OH^- \qquad k = 3.0 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \tag{6}$$

$$e^-_{aq} + H^+ = H^\bullet \qquad k = 2.3 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \tag{7}$$

$$HO^\bullet_2 = O_2 + H^+ \qquad k = 8 \times 10^5\ S^{-1} \tag{8}$$

$$HO^\bullet_2 + O_2^{\bullet -} = H_2O_2 + O_2\ (pH < 7) \qquad k = 9.7 \times 10^7\ L\ mol^{-1}\ S^{-1} \tag{9}$$

$$HO^\bullet_2 + HO^\bullet_2 = H_2O_2 + O_2 \quad k = 8.3 \times 10^5\ L\ mol^{-1}\ S^{-1} \tag{10}$$

$$H^\bullet + OH^- = e^-_{aq} + H_2O \quad k = 2.2 \times 10^7\ L\ mol^{-1}\ S^{-1} \tag{11}$$

γ-Irradiation of SMX in aqueous solutions was conducted at absorbed doses of 0.3, 0.5, 0.7, 0.9 and 1.1 kGy. The concentration variations of SMX with absorbed doses are compared in Fig. 1. It could be observed that the concentration of SMX decreased with the increasing of absorbed does. When 1.1 kGy was selected as the absorbed dose, SMX degradation efficiency was 99 %. γ-Irradiation is an effective method to remove SMX in aqueous solutions.

According to eqn. 2, the SMX radiation chemical yield (G value) at different absorbed dose is shown in Table-1. It showed that the SMX radiation chemical yield was decreased with the increasing of absorbed dose. The reason is that the radical species increase at higher absorbed dose, the absolute rates for radical-radical recombination reactions (eqns. 12-15)

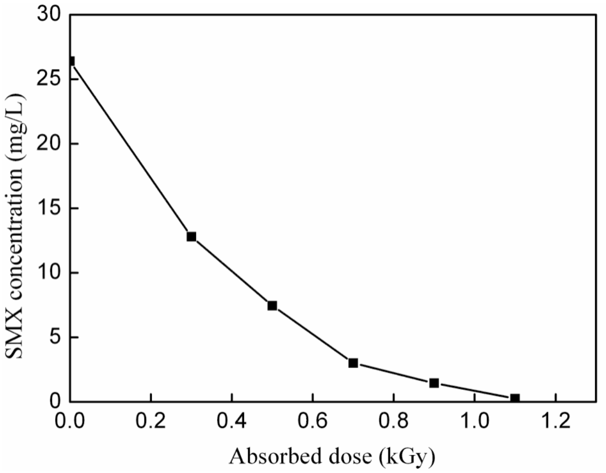

Fig. 1. Degradation of SMX under different absorbed dose

TABLE-1
G VALUE OF SMX REMOVALS UNDER DIFFERENT ABSORBED DOSE (× 10^{-5} MOLECULES/(100 eV))

Absorbed dose (kGy)	G (molecules/(100 eV))
0.3	1.73
0.5	1.45
0.7	1.27
0.9	1.05
1.1	0.91

also increase, reducing the effective ${}^{\bullet}OH$ radical concentrations for reaction with sulfamethoxazole, so the sulfamethoxazole G value is decreased[21].

$${}^{\bullet}OH + {}^{\bullet}OH = H_2O_2 \qquad k = 5.5 \times 10^{9}\ L\ mol^{-1}\ S^{-1} \quad (12)$$

$${}^{\bullet}OH + H^{\bullet} = H_2O \qquad k = 7.0 \times 10^{9}\ L\ mol^{-1}\ S^{-1} \quad (13)$$

$${}^{\bullet}OH + e^{-}_{aq} = OH^{-} \qquad k = 3.0 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \quad (14)$$

$$H_2O + H^{\bullet} + e^{-}_{aq} = H_2 + OH^{-} \quad k = 2.5 \times 10^{10}\ L\ mol^{-1}\ S^{-1} \quad (15)$$

The changes in ln (C_0/C_t) as the absorbed dose are described in Fig. 2. It shows a trend and the slope of this plot yielded the first order dose constant. When the initial concentration of sulfamethoxazole was 26.4 mg L^{-1}, the dose constant was 3.54 kGy^{-1}. However, when the initial concentrations were 37.8, 49.6 and 59.8 mg L^{-1}, the dose constants were 2.16, 1.59 and 1.32 kGy^{-1}. The dose constant increased with lower initial sulfamethoxazole concentrations.

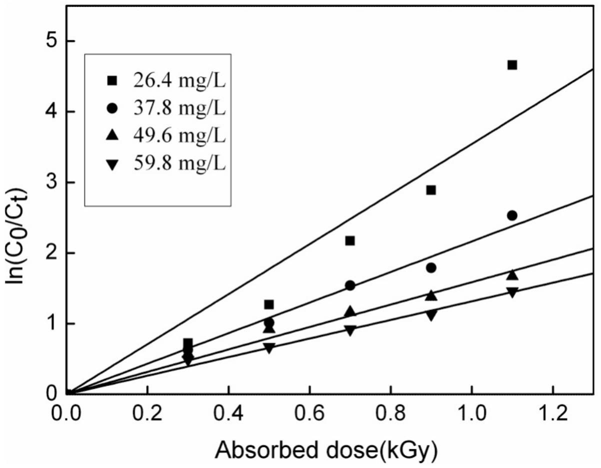

Fig. 2. Effects of sulfamethoxazole concentrations on its degradation kinetics

Influence of operational parameters on the sulfamethoxazole degradation

Effect of solution pH: Fig. 3 shows the significant effect of solution pH on SMX degradation. With an absorbed dose of 0.7 kGy, SMX degradation efficiency was 89.2 % at pH 3.13, whereas the degradation efficiency was only 81.3 % at pH 10.21 with the same absorbed dose. Acidic conditions enhanced the SMX degradation, because of the higher relative concentration of $H^{\bullet}$ present eqn. 7. However, in alkaline solutions, OH^{-} readily reacts with the $H^{\bullet}$ to generate e^{-}_{aq} eqn. 11, thereby increasing the concentration of e^{-}_{aq}, enhancing the probability of recombination between ${}^{\bullet}OH$ and e^{-}_{aq} eqn. 14 and reducing the effective ${}^{\bullet}OH$ concentration, leading to a decrease in the degradation efficiency of SMX[19].

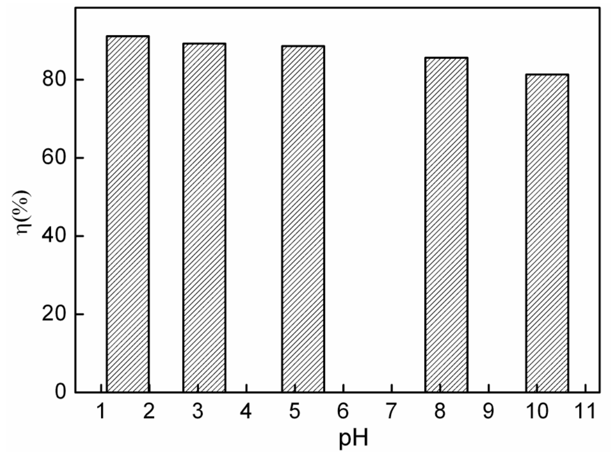

Fig. 3. Effect of pH on sulfamethoxazole degradation by γ-irradiation

Effects of H_2O_2 and humic acid on SMX degradation: It is well known that H_2O_2 is an ${}^{\bullet}OH$ promoter, which can accelerate the degradation of pollutants in aqueous solutions[21]. Fig. 4 shows the effect of H_2O_2 on SMX degradation. 0.3 % H_2O_2 accelerated the SMX degradation as a result of increased ${}^{\bullet}OH$ in the medium. However, 0.9 % H_2O_2 inhibited SMX degradation, indicating that a massive dosage of H_2O_2 not lead to more available ${}^{\bullet}OH$ in the aqueous solutions. Instead, it may compete with SMX for ${}^{\bullet}OH$ and thus reduce the SMX degradation efficiency.

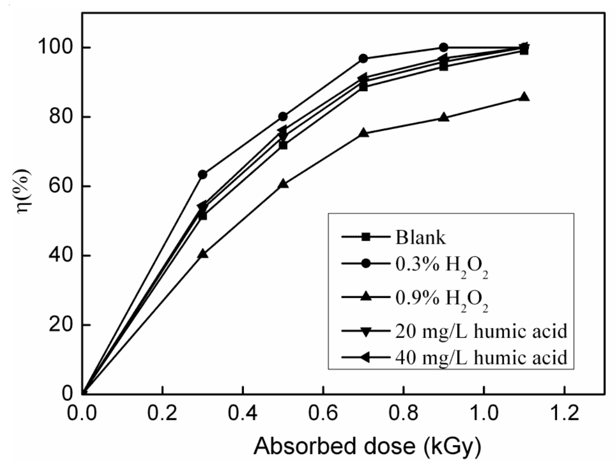

Fig. 4. Effect of H_2O_2 and humic acid on sulfamethoxazole degradation by γ-irradiation

When humic acid was added to aqueous solutions, SMX degradation efficiency was enhanced. The results are similar with the previously reported result[22]. The reason is that humic acid could absorb irradiation and generate excited triplet states ($^3HA^*$) and various reactive oxygen species, including hydroxyl radicals ($^{\bullet}OH$), singlet oxygen ($^1O_2$) and hydrogen peroxide (H_2O_2)[23], thus increasing the concentrations of radicals for reaction with SMX was increased.

Effects of CH_3OH and thiourea on SMX degradation: Fig. 5 shows the effects of CH_3OH and thiourea on SMX degradation by γ-irradiation. In the presence or absence of these additives, SMX degradation efficiency increased with increasing absorbed dose. When CH_3OH was added, the SMX degradation efficiency was much lower than in the absence of CH_3OH with the same absorbed dose. The reason was CH_3OH reacted more rapidly than SMX with $^{\bullet}OH$ and in aqueous solutions (eqns. 16 and 17)[22]. The results also showed that $^{\bullet}OH$ radicals play an important role in SMX degradation by gamma irradiation, it was closely associated with the radiolytic degradation of SMX, since an increase in CH_3OH concentration produced a remarkable decrease in degradation efficiency.

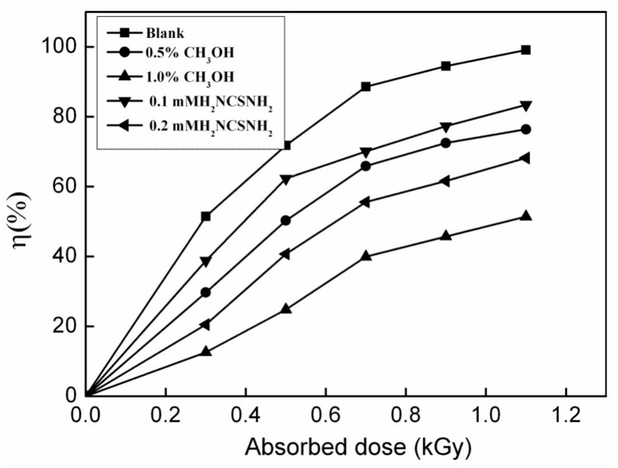

Fig. 5. Effect of CH_3OH and thiourea on sulfamethoxazole degradation by γ-irradiation

$$^{\bullet}OH + CH_3OH \rightarrow H_2O + {}^{\bullet}CH_2OH + CH_3O^{\bullet} \quad k = 4.7 \times 10^8\ L\ mol^{-1}\ s^{-1} \tag{16}$$

$$e^-_{aq} + CH_3OH \rightarrow H^{\bullet} + CH_3O^- \quad k = 1.0 \times 10^4\ L\ mol^{-1}\ s^{-1} \tag{17}$$

When thiourea was added, the SMX degradation efficiency was lower than that in the absence of additive with the same absorbed dose. Thiourea inhibited the degradation process. These results indicated that primary active species, such as e^-_{aq} and $H^{\bullet}$, also participate in the degradation reaction of SMX, since thiourea was a very strong scavenger of all three radicals ($^{\bullet}OH$, e^-_{aq} , $H^{\bullet}$)[22], the reaction patterns are shown by eqns. 18-20[21].

$$^{\bullet}OH + H_2NCSNH_2 \rightarrow \text{Unknown products} \quad k = 3.9 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{18}$$

$$H^{\bullet} + H_2NCSNH_2 \rightarrow \text{Unknown products} \quad k = 6 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{19}$$

$$e^-_{aq} + H_2NCSNH_2 \rightarrow \text{Unknown products} \quad k = 2.9 \times 10^9\ L\ mol^{-1}\ s^{-1} \tag{20}$$

Variation of solution pH: The effect of γ-irradiation on solution pH value is shown in Fig. 6. The pH value decreased with increasing absorbed dose, going from a value of 5.17 without irradiation to 5.07, 4.73, 4.68, 4.34 and 4.29, at absorbed doses of 0.3, 0.5, 0.7, 0.9 and 1.1 kGy, respectively. This decrease in pH is possibly due to the production of a large amount of H_3O^+ during the irradiation process eqn. 3.

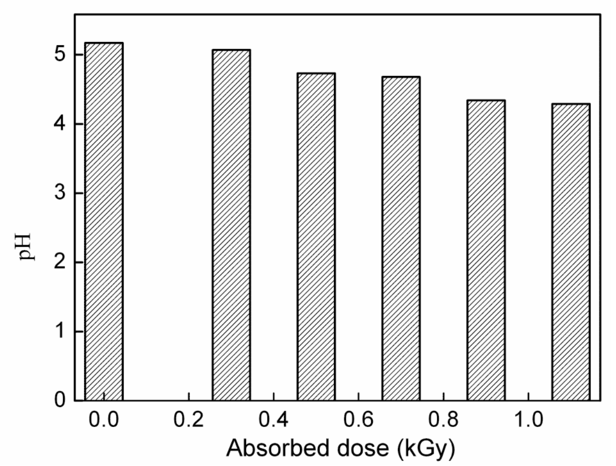

Fig. 6. Variation of solution pH

Variation total organic carbon during the radiation: Fig. 7 describes the total organic carbon change of sulfamethoxazole aqueous solutions (26.4 mg L^{-1}) after irradiation. The solution total organic carbon value decreased with increasing absorbed dose, which indicated that γ-irradiation could lead to both degradation and partial mineralization of sulfamethoxazole in aqueous solutions.

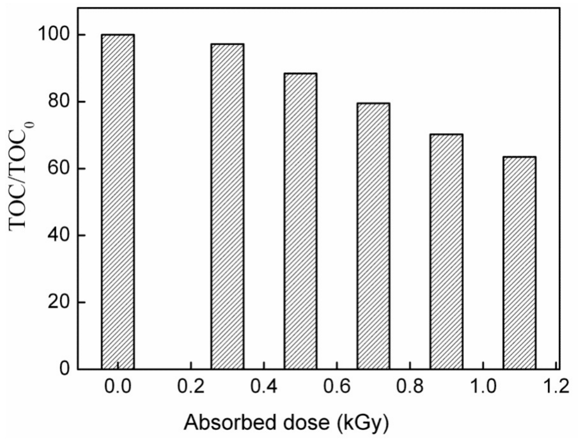

Fig. 7. Variation of solution total organic carbon

Identification of degradation products: In order to identify the SMX derivatives, sample collected at the absorbed dose of 0.9 kGy was analyzed by means of LC-MS. Six intermediates during SMX degradation by γ-irradiation was identified, as it is observed in the mass spectrum. Table-2 shows the information obtained from the accurate mass spectra of the detected compounds, that is, measured ions mass, the empirical formula proposed in each case.

Compounds **C1** yielded an m/z ratio of 268.1, which the best fit formula was $C_{10}H_{11}N_3O_4S$. This formula was consistent

TABLE-2
ACCURATE MASS MEASUREMENTS FOUND BY LC-MS SPECTRA OF SMX DEGRADATION PRODUCTS IDENTIFIED IN AQUEOUS SOLUTIONS

Compound	Retention (min	Formula	Mass (m/z)
C1	1.772	$C_{10}H_{11}N_3O_4S$	268.1
C2	2.502	$C_6H_8N_2O_2S$	171.1
C3	2.732	$C_7H_9N_3O_3S$	214.0
C4	3.248	$C_4H_6N_2O$	97.1
C5	7.347	$C_{10}H_{13}N_3O_5S$	286.1
C6	14.977	$C_{10}H_{10}N_2O_5S$	269.1
SMX	20.026	$C_{10}H_{11}N_3O_3S$	252.1

with the addition of a hydroxyl radical to the SMX structure, to yield monohydroxylated derivatives. Compounds **C1** is subsequently oxidized to the dihydroxylated compound **C6** (m/z 269.1; $C_{10}H_{10}N_2O_5S$), as a results of the substitution of the amino group by the hydroxyl group in the benzene aromatic ring. Dihydroxylated compound **C5** was identified at m/z 286.1, as a result of the attack of ·OH radicals to the double bond on the isoxazole ring. These results are consistent with published findings for the solar photo-Fenton degradation of SMX[24]. The opening of the isoxazole ring and the loss of one carbonyl group in compound **C5** was assessed by identifying compound **C3** at m/z 214.0, which fits the formula $C_7H_9N_3O_3S$. Compounds **C2** and **C4** were also identified at m/z 171.1 and 98.1 in 0.9 kGy irradiated SMX aqueous solutions, both compounds had been reported as SMX derivatives by TiO_2 photocatalysis and photo-Fenton treatment[24,25]. The transformation pathways, which involve hydroxyl radical attack either on the benzenic or isoxazole aromatic rings (Fig. 8).

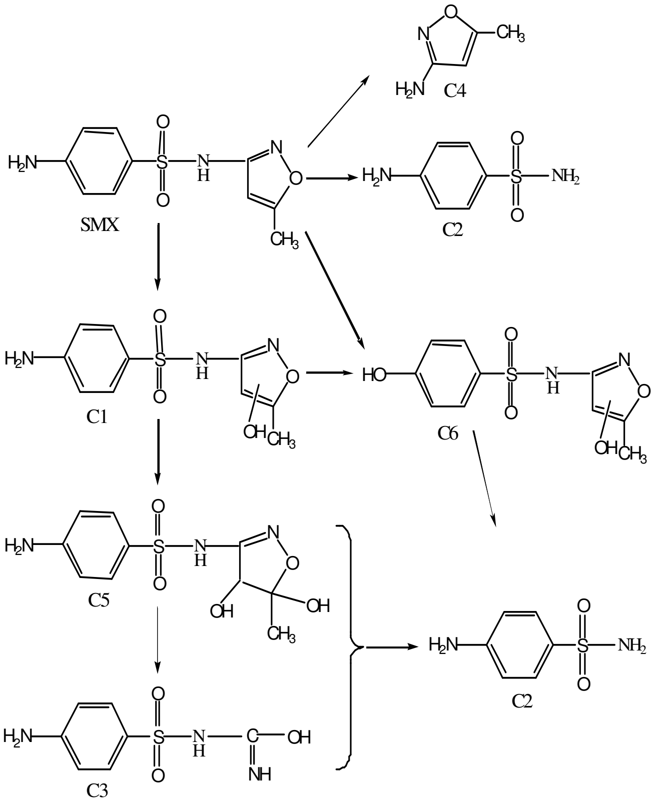

Fig. 8. Possible degradation pathway of sulfamethoxazole by γ-irradiation in aqueous solutions

Conclusion

γ-Irradiation effectively degraded SMX in aqueous solutions. At an absorbed dose of 1.1 kGy, SMX degradation efficiency was 99 %. The SMX degradation process followed first-order like kinetics. The degradation yield was higher under acidic conditions than in neutral or alkaline media. Addition of humic acid or 0.3 % H_2O_2 enhanced the SMX degradation. But SMX degradation was inhibited by addition of 0.9 % H_2O_2, CH_3OH or thiourea. The solution pH and TOC decreased after γ-irradiation. The possible degradation pathway of SMX was proposed.

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