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Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms

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ABSTRACT

Gamma irradiation-induced removal of sulfadiazine (SD) under different conditions was investigated. The results show that SD can be effectively degraded using gamma irradiation. The removal efficiencies of low-concentration SD can be remarkably improved in an acid solution, and SD degradation was in accordant with the pseudo-first-order kinetic model. The additives, such as H_2O_2 and Fenton reagent, were favorable for removing SD during gamma irradiation. However, SD removal was restrained with the addition of Na_2CO_3. Adding CH_3OH in solution, we found that SD removal was restrained at low-irradiation dose while markedly promoted at high-irradiation dose. Based on the results of quantum chemical calculations and LC–MS analysis, SD degradation using gamma irradiation in aqueous solution is mainly ascribed to •OH oxidation and the direct decomposition of SD molecules.

1. Introduction

Pharmaceutical antibiotics have been widely used as veterinary drugs in recent decades and become the subject of growing attention [1–3]. The discharged antibiotics can enter the aqueous environment from soil and sediments by surface runoff, leaching and desorption [4], and eventually flow into drinking water for their high stability towards conventional biodegradation [5]. Sulfonamides antibiotics are synthetic antimicrobials derived from sulfanilic acid. Sarmah et al. [6] have reported that sulfonamides represent from 2% (USA) to 22% (UK, Kenya) of used veterinary antibiotics. Sulfadiazine (SD) belonging to sulfonamide class of antibiotics is commonly used as veterinary medicine. From applied sulfadiazine to animals, about 50% are excreted as parent compound and about 30% as acetyl conjugate [7]. Once sulfadiazine with its metabolites present in manure is released to land, it may interact with different soil components and may be washed off into surface water or leached to ground water. Thus, it may enter the food chain and have an impact on environment and human health [8].

Under these circumstances, various technologies to remove SD have been developed. Turkdogan and Yetilmezsoy [9] found that the removal efficiency of antibacterial drugs from biosphere using biological treatment was frequently low. However, many researches have showed that technologies based on advanced oxidation processes have highly effective in degrading of pharmaceutical compounds in aqueous solution. Justyna et al. [10] found that the highest efficiency of sulfonamides degradation was achieved in the presence of TiO_2-P25/$FeCl_3$ mixture and UV irradiation. Garoma [11] observed that SD from aqueous solution could be completely removed by ozonation. Besides, SD can be effectively degraded and mineralized with α-MnO_2 [12].

Gamma irradiation, as an advanced oxidation process, has been widely used in many countries for the degradation of stable organic pollutants. Ocampo-Perez [13] studied the degradation of antineoplastic cytarabine in aqueous solution by gamma irradiation. The results demonstrated that cytarabine degradation was achieved via oxidative pathway. Abdoua [14] systemically studied the removal efficiencies of dye solutions during gamma irradiation. It is noteworthy that the azo dyes were more easily decolored by gamma irradiation than the anthraquinone dyes. Meanwhile, it is observed that the removal efficiency of dye solution with electron beam treatment was higher compared to that with gamma irradiation, which is mainly ascribed to the rapid and high intensity of energy during electron beam irradiation. In addition, Kim [15] concluded that gamma irradiation was useful for the solubilization of waste sewage sludge. Zheng [16] found that gamma irradiation could

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effectively degrade ibuprofen in aqueous solution using gamma irradiation. At the absorbed dose of 1.1 kGy, ibuprofen degradation efficiency was 100%. Melo [17] also highlighted the potential of gamma irradiation for wastewater treatment.

To our knowledge, the radiolytic decomposition of SD in aqueous solution was seldom investigated. Although we have studied gamma radiation-induced bisphenol A removal from the aqueous solution [18], the structure of SD is more complex than BPA molecule for SD molecule contains both oxidative groups (—SO_2) and reductive groups (—NH_2, —NH—), which inevitably results in the uncertainties on SD removal efficiency and degradation mechanism during gamma irradiation. Consequently, the purposes of this study are to investigate the effects of irradiation dose, initial concentration and pH value on SD removal using gamma irradiation; to examine the effects of different additives, such as H_2O_2, Fenton, Na_2CO_3 and CH_3OH. Gaussian 03 software was used to optimize geometry structure of SD at Density functional theory (DFT) in the level of B3LYP/6-31G(d) [19], which aims to predict SD degradation mechanism based on the charge distribution of SD by Gaussian calculation. LC–MS analysis was simultaneously conducted for determining SD degradation intermediates to confirm the degradation process during gamma irradiation.

2. Materials and methods

2.1. Materials

SD (>99%) was purchased from Sigma–Aldrich. HPLC-grade acetonitrile and methanol, A.R.-grade hydrogen peroxide (H_2O_2, 30%), ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and sodium acetate (CH_3COONa) are from Shanghai chemical factory. Solution pH was adjusted using H_2SO_4 (0.05 mol/L) or NaOH (0.1 mol/L) solution. All solutions were prepared with twice-distilled water.

2.2. Irradiation treatment

Gamma irradiation was carried out in a ^{60}Co source (1.85×10^{16} Bq), located at the Institute of Application of Atomic Energy in Agriculture, Jiangsu Academy of Agricultural Sciences. Samples (100 mL each) were preserved in 125 mL airtight glass vessels, which were placed in the irradiation field to a specific distance from the source to achieve the desired series of absorbed doses. The absorbed doses were determined by a silver dichromate dosimeter.

2.3. Radiation process

100 mL (2–50 mg/L) SD solution was preserved in 125 mL airtight glass vessels for treatment using gamma irradiation. H_2SO_4 or NaOH was used to adjust solution pH at 3–11. According to experiment design, we added different additives to the solution, such as H_2O_2 (0–20 mg/L), Fenton (H_2O_2 10 mg/L, Fe^{2+} (0.5–2 mg/L), Na_2CO_3 (0–20 mg/L) and CH_3OH (0–5%). All experiments were made parallel experiments to examine its stability.

2.4. High-performance liquid chromatography (HPLC) analysis

SD concentration was measured by HPLC (Agilent 1100) coupled with a C_{18} reversed phase column (150 mm × 4.5 mm, 5 μm, Agilent, USA) at 30 °C. Detection was performed with an ultraviolet (UV) detector at the wavelength of 275 nm. The mobile phase is a mixture of acetonitrile and sodium acetate solution (0.02 mol/L, pH 4.75) with a ratio of 25:75(v/v) and a flow rate of 0.8 mL/min. The sample loop volume is 20 μL. The detection limit for the experiment method is 20 μg/L.

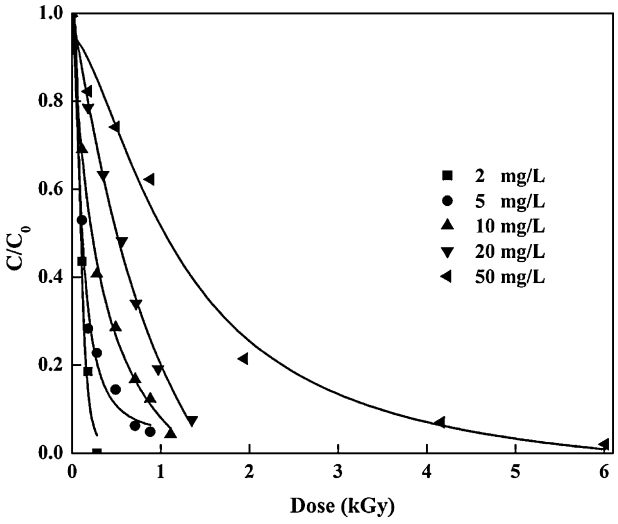

Fig. 1. Effect of the initial concentrations on gamma irradiation-induced SD degradation.

2.5. Liquid chromatography and mass spectrometer (LC/MS) analysis

SD degradation products were analyzed by LC–MS (Finnigan LCQ Advantage MAX) with a 10 μL solution injected to column. Mobile phase is a mixture of 50% acetonitrile and 50% water with a flow rate of 0.2 mL/min. The ESI–MS analysis was performed in the negative mode, with a spray voltage of 45 kV and an ion-transfer capillary temperature of 300 °C. Nitrogen was used as sheath gas at a flow rate of 35 arb units.

3. Results and discussions

3.1. Gamma irradiation-induced degradation of SD

SD removals at different initial concentration by gamma irradiation are shown in Fig. 1. It can be observed that the removal percentages of SD increased with the increasing absorbed doses, but decreased with an increase in SD initial concentrations at a given dose. When the initial concentrations of SD were 2, 5, 10, 20 and 50 mg/L, the required irradiation doses to 95% removal of SD were approximately 0.28, 0.88, 1.11, 1.35 and 6.01 kGy, respectively. This indicates that gamma irradiation is an effective method in removing SD from aqueous solution.

In diluted solution, gamma irradiation of water produces some active species, such as solvated electrons e^-_{aq}, hydrogen atoms H• and hydroxyl radicals •OH, which can be described in formula (1) (numbers in the brackets present the amount of produced radicals/100 eV energy) [20]. We note that SD molecule is not only presence of oxidative radicals (—SO_2—), but also reductive radicals (—NH_2, —NH—), therefore, SD may be deoxidized by e^-_{aq} and H•, or oxidized by •OH radicals.

$$H_2O \rightarrow e^-_{aq}(2.6) + H^{\bullet}(0.55) + {}^{\bullet}OH(2.7) + H_2(0.45) + H_2O_2(0.71) + H_3O^+(2.6) \quad (1)$$

We note that SD molecule is not only presence of oxidative radicals (—SO_2—), but also reductive radicals (—NH_2, —NH—), therefore, SD may be deoxidized by e^-_{aq} and H·, or oxidized by •OH radicals, which results in SD removal from the solution. By combining the appropriately selected experimental conditions, it is possible to decrease or increase the concentrations of some reactive radicals, and consequently to obtain useful information about the possible mechanism of the undergoing reaction.