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Removal of sulfonamide antibiotics from wastewater by gamma irradiation in presence of iron ions

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Abstract The presence of sulfonamide antibiotics in aquatic environments has received increasing attention in recent years. Sulfadiazine (SD), a widely used heterocyclic sulfonamide pharmaceutical, has entered into the receiving water body. In this paper, gamma rays are used to irradiate samples of sulfadiazine antibiotics-containing wastewater. The results demonstrate that SD can be effectively degraded by irradiation, but the mineralization degree of SD (in terms of TOC) is not as efficient as the SD degradation. The addition of Fe^{2+} can significantly enhance the SD degradation and mineralization through the generation of hydroxyl radical by catalytic decomposition of H_2O_2 from water radiolysis. Ion chromatography analysis indicates that sulfate ions (SO_4^{2-}) and formate ($HCOO^-$) are the main intermediate products. Gamma irradiation is a promising technology for removing low-concentration antibiotics from water and wastewater.

Keywords Sulfadiazine (SD) · Gamma radiation · Advanced oxidation process (AOP) · Wastewater treatment · Antibiotics

1 Introduction

As an important kind of emerging pollutants, pharmaceutically active compounds (PhACs) are of major concern for water quality and aquatic organisms. Sulfonamides (SAs) antibiotics are widely used for veterinary and human medicine [1, 2]. In recent years, antibiotics have been released increasingly into the environment. As a big environmental problem, SAs antibiotics become ubiquitous pollutants in different environmental media, causing hazardous effects on ecological systems. Also, it can cause the antibiotic resistance. The conventional wastewater treatment processes for sewage industrial wastewater are not effective for removing antibiotic contaminants [3, 4]. Physical methods, such as adsorption or membrane separation, can only transport the pollutants from one media to another, or concentrate the pollutants, rather than degrading or destroying the pollutants. Biological methods degrade biodegradable organic contaminants, but they are not effective for the degradation of antibiotics because of the toxicity and bacterial resistance.

Advanced oxidation processes (AOPs) are efficient for degrading toxic organic contaminants due to the generation of strong reactive oxidizing agents, such as hydroxyl radical. As a powerful and unique AOP, radiation technology has received more and more attention in recent years [5, 6]. The degradation of toxic organic pollutants in aqueous solution by irradiation has been extensively investigated, including chlorinated phenols [7–16], nitrophenols [17], sulfamethazine [18–21], diclofenac [22], oxytetracycline [23], cyclohexanebutyric acid [24], landfill leachate [25], dichloroacetic acid [26], imidacloprid [27], acephate [28], Ochratoxin A [29], carbamazepine [30], bromide [31], cyanide [32], 4-tert-octylphenol [33] and dimethyl phthalate [34].

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The Fenton reaction is an advanced oxidation process, in which the hydroxyl radicals are generated through the oxidation reaction between Fe^{2+} and H_2O_2, as shown in Eqs. (1–3), where RH represents the organic pollutants:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH, \tag{1}$$

$$RH + \cdot OH \rightarrow R \cdot + H_2O, \tag{2}$$

$$R \cdot + Fe^{3+} \rightarrow R^+ + Fe^{2+}, \tag{3}$$

Under irradiation, hydrogen peroxide (H_2O_2) is further decomposed to form hydroxyl radicals through the Fenton reaction [35]. In this way, more reactive hydroxyl radicals are converted and the oxidation process can be improved. As a result, the degradation reaction of the pollutants can be enhanced by adding Fe^{2+} in irradiation process.

The effects of gamma irradiation on degradation of sulfafurazole, sulfamethoxazole and sulfacetamide sodium were studied by several groups [36–38]. In this paper, we use ^{60}Co γ-rays to irradiate sulfadiazine (SD) solution samples added with Fe^{2+}, which can catalytically decompose H_2O_2 formed during the irradiation process to produce hydroxyl radical, so as to degrade and mineralize the SD effectively. Some inorganic ions and small-molecular organic acids produced during the degradation process are identified, and a possible pathway of sulfadiazine degradation is proposed.

2 Materials and methods

2.1 Chemicals

Sulfadiazine (SD) was obtained from Alfa Aesar Company. Its chemical structure is depicted in Fig. 1. $FeSO_4$ was AR grade (>99 %) and methanol was chromatography grade. All chemical solutions were prepared with deionized water.

2.2 Irradiation procedures

The irradiation was performed in a ^{60}Co γ-rays source of 1.33×10^{15} Bq at the Institute of Nuclear and New Energy Technology, Tsinghua University [16]. Before irradiation, $FeSO_4$ concentration of 0.4 mM was added to the SD solution, being purged with argon gas to drive out of air (O_2, especially). The samples were irradiated to 0, 200, 400, 600, 800 and 1000 Gy. The irradiated samples were taken at a certain interval and filtered with 0.22-µm filters for analysis. All experiments were performed at room temperatures (22–25 °C), with duplicate samples to take the average.

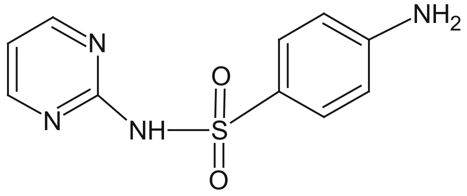

Fig. 1 SD molecular structure

2.3 Analyses

The SD concentration was determined using HPLC. Sulfate and formic acid were analyzed by IC. The TOC concentration was determined by TOC analyzer [14].

3 Results and discussion

3.1 Effect of dose on SD degradation

Figure 2 shows the effect of absorbed dose on SD removal, which increases with the dose. Without Fe^{2+}, over 80 % SD was removed at 1000 Gy, which is consistent with the results by Guo et al. [7], while in the presence of 0.4 mM Fe^{2+}, the SD removal efficiency increased to 90 % at 1000 Gy, and the required absorbed dose to reach 80 % removal efficiency is 600 Gy, indicating that addition of Fe^{2+} can significantly increase SD removal from wastewater.

The following reaction kinetic model can be used to simulate the data in Fig. 2.

$$C = C_0 e^{-dD} \quad \text{or} \quad -\ln(C/C_0) = dD, \tag{4}$$

where C_0 and C are SD concentration before and after irradiation, respectively, d is dose constant and D is absorbed dose. Figure 2 also shows (in the inset) the

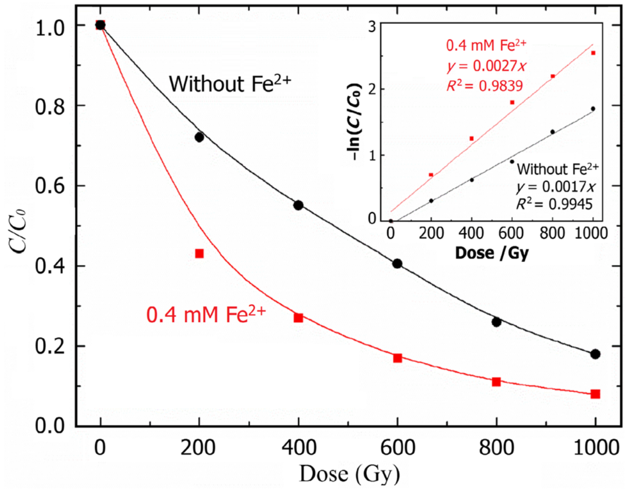

Fig. 2 SD concentration as function of the dose

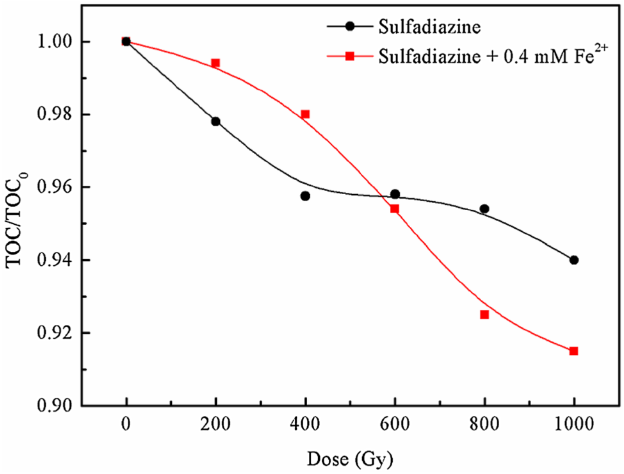

Fig. 3 Variation of TOC in the SD degradation

kinetics data of SD degradation with and without Fe^{2+}. In the presence of Fe^{2+}, the dose constant is 0.0027, while it is 0.0017 without Fe^{2+}.

As usual, in the irradiation process, the effect of H_2O_2 on SD degradation can be ignored due to its low *G* value. By adding Fe^{2+} ions, H_2O_2 is converted to hydroxyl radical, which is a stronger oxidizing agent with higher *G* value to break the C=C, C=N, C–N and C–C bonds of SD molecule, cleaving it to form intermediates and final products.

3.2 Effect of dose on sulfadiazine mineralization

The concentration of total organic carbon was determined, which can be used to evaluate the degree of SD mineralization (Fig. 3). TOC removal was low at low doses, being ∼6 % and 9 % at 1000 Gy without and with 0.4 mM Fe^{2+}, respectively, indicating that hydroxyl radicals preferred to react with SD molecules rather than the formed intermediate products at low doses. Although the addition of Fe^{2+} can significantly increase the SD degradation, the removal of TOC increased slightly, suggesting that mineralization of SD is not as easy as its degradation.

3.3 Intermediate products and degradation pathway

The formation of sulfate (SO_4^{2-}) and formic acid (HCOOH) in SD degradation was detected as shown in Fig. 4. Figure 4a shows the formed SO_4^{2-} concentration in the irradiation process, that is to say, the SO_4^{2-} concentration from 0.4 mM $FeSO_4$ is subtracted from the total SO_4^{2-} concentration. The sulfate formation, and the formation of formic acid, increased with the dose. Adding Fe^{2+} ions enhanced the sulfate and formate formation because of increased generation of hydroxyl radicals. Acetate was not formed in the SD degradation or its concentration was below the detection limit, so it can be ignored.

At 1000 Gy, the final concentration of SO_4^{2-} was 0.032 and 0.079 mmol/L for the samples with and without 0.4 mM Fe^{2+}, respectively; its concentration increased from 0.027 to 0.030 mmol/L. These show that adding Fe^{2+} ions enhances the SD degradation efficiently.

Based on the intermediate products detected, and according to studies, the possible degradation pathway can be proposed as follows: Hydroxyl radical attacks the pyrimidine ring, sulfonamide bond and aromatic ring of SD molecule, e.g., breaking the C–N bond in SD molecule to form intermediate products, which are further degraded to generate phenolic compounds, such as 4-aminophenol and 4-nitrophenol; sulfur containing in SD molecule was

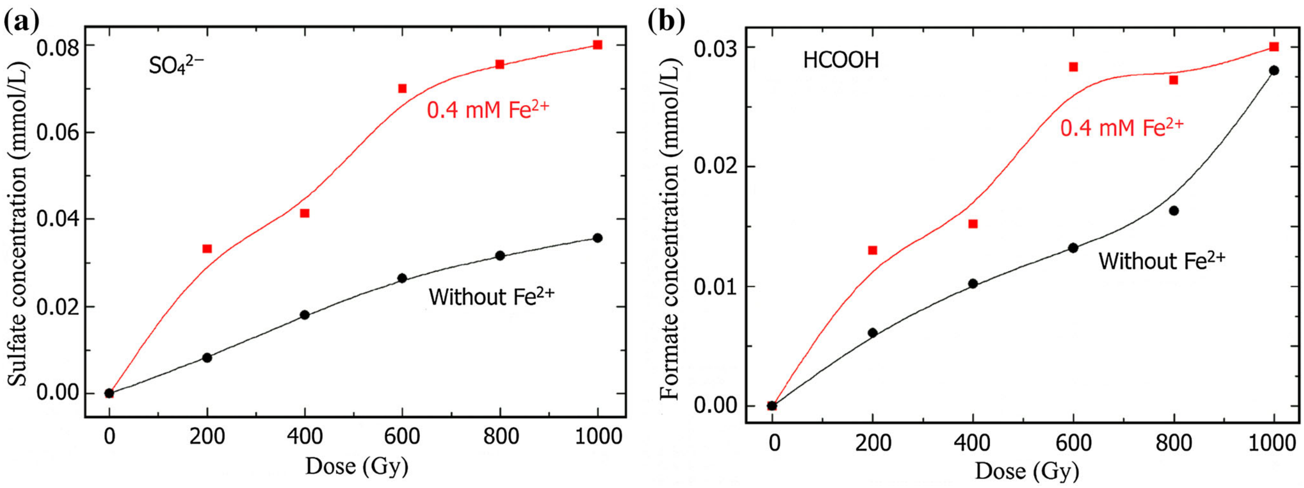

Fig. 4 Concentration variations of SO_4^{2-} (**a**) and HCOOH (**b**) in radiation degradation of sulfadiazine

oxidized to SO_4^{2-} and released into the solution. Further studies are needed for exact reaction pathway of radiation-induced degradation of sulfadiazine.

4 Conclusions

The results indicate that SD can be effectively degraded, but SD mineralization is not effective. The presence of Fe^{2+} can obviously improve the degradation and mineralization of SD. The formation of SO_4^{2-} and HCOOH is identified and quantified. The addition of Fe^{2+} decreases the dose required for SD degradation and mineralization. By adding Fe^{2+} ions into the water, gamma irradiation can remove low-concentration antibiotics from wastewater.

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