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Degradation of sulfamethazine in sewage sludge mixture by gamma irradiation

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HIGHLIGHTS

- Gamma irradiation was effective in removing SMT from sludge mixture.
- SMT removal efficiency from sludge mixture reached 98% at a dose of 2.5 kGy.
- 93–97% of SMT was observed in the supernatant.
- Sludge activity decreased by 85–98% with increasing dose from 1.0 to 5.0 kGy.
- Addition H_2O_2 exhibited synergetic effect on SMT degradation by gamma irradiation.

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ABSTRACT

The gamma-irradiation-induced degradation of antibiotics sulfamethazine (SMT) in sludge mixture was investigated. The results showed that gamma irradiation was effective in removing SMT from contaminated sludge mixture. With an initial SMT concentration of 10 mg/L, the SMT removal efficiency reached 65% at 1.0 kGy and increased to 98% at 2.5 kGy. The SMT degradation rate was lower in the sludge mixture than that in pure water. The pseudo first-order kinetic constant of SMT degradation in pure water was 2.3 times higher than that in the sludge mixture. Analysis of the SMT concentrations in the supernatant and sludge residue revealed that 93–97% of SMT was observed in the supernatant and the detected SMT in the sludge residue was 168 ± 29, 147 ± 4, and 87 ± 9 μg/g dry weight following irradiation at doses of 0, 1.0 and 2.5 kGy, respectively. The sludge solubilization slowly increased from 1.5% to 3.5% with increasing dose from 1.0 to 5.0 kGy, while the sludge activity decreased by 85–98%. Addition of H_2O_2 exhibited a synergetic effect on the degradation of SMT, with the pseudo first-order kinetic constant k increasing by around 25%.

1. Introduction

Recently, environmental research study has been considerably focused on the pharmaceutical compounds, namely antibiotics, which were more frequently detected in aqueous solution, soil and sediments (Homem and Santos, 2011). A major concern regarding the occurrence of antibiotics in the environment is their potential role in the development of resistant bacterial strains, thus making them ineffective in disease treatment (Lai and Hou, 2008).

It has been reported that the standard biological treatment processes commonly used for water treatment are not successful in degrading antibiotics (Homem and Santos, 2011; Le-Minh et al., 2010). Chemical oxidation processes, involving ozonation, Fenton and Fenton-like oxidation, and semiconductor catalysis, are considered highly effective in removal of antibiotics from aqueous matrices (Xekoukoulotakis et al., 2011; Zhou et al., 2013). In addition, some combined methods such as ozonation with hydrogen peroxide, UV irradiation, or catalyst and photo-Fenton have been developed to improve the oxidation efficiency. Uslu and Balcioglu (2009) studied the degradation of sulfamethazine (SMT) and oxytetracycline (OTC) from manure slurry by ozonation, Fenton and persulfate oxidation. Approximately 98% of SMT and OTC were removed by increasing the oxidant doses.

Gamma radiation is a promising and powerful alternative to degrade antibiotics (Sanchez-Polo et al., 2009). The reactive primary species produced during gamma irradiation of aqueous solution are hydroxyl radicals, hydrated electrons, and hydrogen atoms, which play an important role in the decomposition of refractory organic compounds (Spinks and Woods, 1990). Liu and

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Wang (2013) showed that gamma irradiation at a dose of 1.0 kGy removed more than 90% of SMT from distilled water, while Guo et al. (2012) observed that 95% of sulfadiazine in water solution (initial concentration of 10 mg/L) was removed at an absorbed dose of 1.1 kGy. Furthermore, Kimura et al. (2012) investigated the gamma-irradiation-induced decomposition of five kinds of pharmaceuticals in real wastewater containing 50 mg total organic carbon (TOC)/L. They found that carbamazepine, clofibric acid, and diclofenac degraded faster with their concentrations decreasing from 5.0 to less than 0.05 μmol/L at an absorbed dose of 1.0 kGy, while mefenamic acid and ketoprofen were eliminated at 2.0 kGy. Studies by Takacs's group at the Institute of Isotopes, Hungarian Academy of Sciences, Hungary, showed that gamma irradiation was successful in removing chloramphenicol (Csay et al., 2012), 2,6-dichloroaniline (Homlok et al., 2012), and paracetamol (Szabo et al., 2012) from pure water. Moreover, an improvement of gamma-irradiation-induced degradation was achieved with addition of H_2O_2 and Fe^{2+} (Guo et al., 2012; Liu et al., 2014).

While most of the studies on antibiotics degradation by gamma irradiation had been focused on antibiotic-contaminated aqueous solution, limited information is available about antibiotics degradation in sewage sludge mixture. Antibiotics can potentially enter activated sludge by sorption during the sewage treatment processes and subsequently get released into the environment through biosolids application to agricultural land or landfill (Le-Minh et al., 2010; Musson and Townsend, 2009). Gobel et al. (2005b) reported that some antibiotics such as sulfapyridine, sulfamethoxazole, and trimethoprim were detected in activated sludge in the range of 28–68 μg/kg of dry weight. Thus, the objective of the present study was to investigate the degradation of antibiotics in sludge mixture following gamma irradiation. The enhancement of gamma-irradiation-induced degradation with H_2O_2 addition and the changes in the physicochemical characteristics of sewage sludge during irradiation were evaluated. SMT, which belongs to the group of sulfonamide antibiotics and is widely used in both human and veterinary medicine (Zhou et al., 2013), was chosen as the target antibiotic. This will provide useful information regarding the treatment of antibiotics-contaminated sludge.

2. Materials and methods

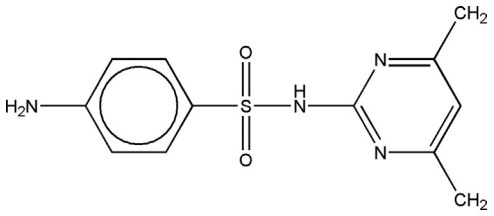
2.1. Sludge source and chemicals

The sludge used in the present study was collected from an aerobic tank of a Municipal Wastewater Treatment Plant in Beijing, China. The sludge was settled before use and the applied initial total suspended solid (TSS) concentration was around 9000 mg/L. The ratio of volatile suspended solid (VSS) to TSS was 65%.

SMT ($C_{12}H_{14}N_4O_2S$, molecular weight of 278.36 g/mol) was purchased from Alfa Aesar (China) Chemical Company with purity > 99% and used as received. It must be noted that SMT is characterized by a common sulfanilamide group and a distinct six-member heterocyclic ring with two nitrogen atoms and two methyl groups (Scheme 1).

2.2. Experimental procedures

The SMT stock solution was prepared by dissolving SMT in pure water at a concentration of 200 mg/L and stored in a refrigerator. The SMT-contaminated sludge mixture was prepared by adding SMT stock solution into the sludge mixture and mixing adequately, and subsequently was subjected to 0–5 kGy irradiation. To examine the enhancement of gamma-irradiation-induced degradation with H_2O_2 addition, H_2O_2 at an initial concentration of 10 mg/L was added to the SMT-contaminated sludge mixture before irradiation. An aqueous solution containing the same concentration of SMT was operated in parallel for comparison. After irradiation the sludge mixture was centrifuged at 10,000 rpm for 10 min. The SMT concentration in the supernatant and sludge residue was separately determined, and the physicochemical characteristics of sewage sludge, involving sludge solubilizaton and activity after exposure to gamma irradiation, were evaluated.



Scheme 1. The chemical structure of SMT. .

The gamma irradiation experiments were carried out using a gamma irradiator developed at the Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China. The activity of the ^{60}Co source was 3.6×10^{14} Bq. The sludge samples were irradiated in glass tubes with a working volume of 40 mL at ambient temperature. The dose rate was 184–201 Gy/min.

2.3. Analytical methods

The SMT concentration was measured with a high-performance liquid chromatography (HPLC) (Agilent 1200 Series, Agilent, USA) using a diode array detector DAD with an XDB-C18 analytical HPLC 5-μm reversed-phase column. The mobile phase consisted of distilled water and ethanol with a ratio of 55:45 flowing at 1.0 mL/min. The detection wavelength was 255 nm and the temperature of the column was kept at 30 °C.

The SMT in the sludge residue was extracted using ultrasonic solvent extraction as described by Gobel et al. (2005a) and Loffler and Ternes (2003). Briefly, the sludge samples were first freeze-dried in a vacuum freeze dryer (LGJ-18, Huaxing Technology Development Company, Beijing). Then, the freeze-dried sludge was successively dissolved in methanol and acetone and ultrasonicated for 5–10 min in each extraction step. The supernatant was combined, filtered using 0.45-μm filters, evaporated, and then analyzed by HPLC.

Sludge solubilization, which was used to evaluate sludge decomposition, was determined as follows (Eq. (1)):

$$\text{Sludge solubilization}\,(\%) = \frac{\text{SCOD} - \text{SCOD}_0}{\text{TCOD}_0} \quad (1)$$

where $SCOD_0$ and $TCOD_0$ represent the initial soluble chemical oxygen demand (COD) and initial total COD, respectively.

The colony forming units (CFU) were enumerated using a beef peptone agar plate incubated at 30 °C for 48 h to represent the sludge activity. The TOC and total nitrogen (TN) were determined using a TOC analyzer (multi N/C 2100, Analytik Jena, Germany). COD was evaluated according to the Chinese SEPA Standard Methods (SEPA, 2002).

3. Results and discussion

3.1. Effect of gamma irradiation on the degradation of SMT in the sludge mixture

Analysis of the SMT concentrations in the supernatant and sludge residue revealed that 93–97% of SMT existed in the