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Degradation of trimethoprim by gamma irradiation in the presence of persulfate

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HIGHLIGHTS

- Trimethoprim (TMP) degradation by gamma irradiation was investigated.
- Persulfate significantly enhanced TMP degradation.
- The effect of pH values (6.5, 7.5 and 8.5) on TMP degradation was determined.
- The possible degradation pathway of TMP was tentatively proposed.

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ABSTRACT

The degradation and mineralization of trimethoprim (TMP) by gamma irradiation was investigated in the presence of persulfate (PS). The TMP was degraded at initial concentration of 20 mg/L in aqueous solution with addition of 0, 0.5, 1, 1.5, 2 mM persulfate respectively. The effect of pH values (6.5, 7.5 and 8.5) on TMP degradation was also determined. The experimental results showed that the degradation and mineralization of TMP could be significantly enhanced by persulfate at acidic condition (pH=6.5). Several intermediate products generated during gamma irradiation process through hydroxylation, demethylation and cleavage were identified using liquid chromatography with tandem mass spectrometry (HPLC-MS). The degradation pathway of TMP was tentatively proposed based on the identification of intermediate products.

1. Introduction

Trimethoprim (TMP) is a dihydrofolate reductase inhibitor which is widely used as sulfonamide synergist in both veterinary and human medicine. It has been detected in the effluents of several wastewater treatment plants in Beijing, with concentration of 100–370 ng/L and removal efficiency of 1–35% (Sui et al., 2010; Sun et al., 2014; Qi et al., 2015). As the seasons change, trimethoprim is also detected in surface water of Beijing in concentrations varying from 35 ng/L to 120 ng/L (Heeb et al., 2012). Although its concentrations detected in waters are far below the levels which may cause acutely toxicity to aquatic organisms, trimethoprim is believed to have the potential for chronic environmental risk (Zhou et al., 2010) and can enhance the toxicity via association with other pharmaceuticals existing in municipal wastewaters (Brain et al., 2004; Göbel et al., 2005; Lindberg et al., 2005). It is necessary to develop cost-effective and environment-friendly treatment techniques to eliminate TMP and minimize the associated risks.

In the light of its low degradability (Junker et al., 2006) and toxicity (Batt et al., 2006), advanced oxidation processes (AOPs) is more suitable and efficient than biological methods (Wang and Xu, 2012). As one of the AOPs, gamma irradiation is an effective technology for removing persistent organic pollutants such as pharmaceuticals, endocrine disrupting chemicals (EDCs) from water and wastewater (Abe et al., 2003; Wojnarovits and Takacs, 2008; Xue and Wang, 2008; Kimura et al., 2012; Ahn et al., 2012; Wojnarovits and Takacs, 2013; He et al., 2014; Liu et al., 2014; Wang and Chu, 2016). During water radiolysis, large amounts of free radicals are generated. Except for hydroxyl radical ($HO\cdot$), several other reactive species were also produced in this process

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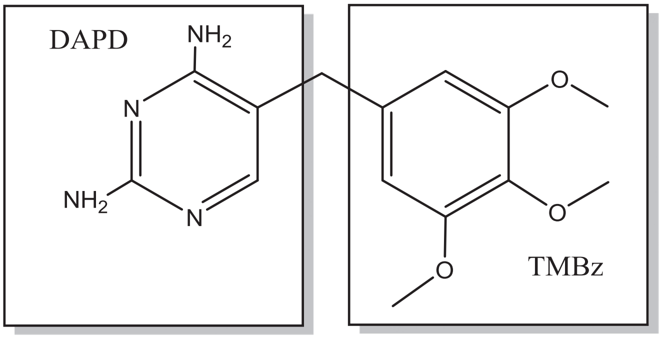

Fig. 1. Molecular structure of trimethoprim (TMP) and its substructural moieties, DAPD (2,4-diaminoprimidine) and TMBz (1,2,3-trimethoxybenzene).

as follows:

$$H_2O \rightarrow [2.8]HO\cdot + [2.7]e^-_{aq} + [0.6]H\cdot + [0.72]H_2O_2 + [2.7]H_3O^+ + [0.45]H_2 \quad (1)$$

In previous studies, HO· was considered to be the main radical that attribute to the degradation of toxic compounds, while e^-_{aq} and H· are generally neglected. In the presence of $S_2O_8{}^{2-}$, e^-_{aq} and H· could lead to the generation of sulfate radical ($SO_4{}^{\cdot -}$) (Roshani et al., 2011), which has a high standard redox potential (E^0=2.5–3.1 V, depending on pH), similar to HO· (E^0=1.9–2.7 V) (Guan et al., 2011; Ji et al., 2016). The difference between $SO_4{}^{\cdot -}$ and HO· is that $SO_4{}^{\cdot -}$ decomposes the organic compounds mainly through electron-transfer mechanism, which makes $SO_4{}^{\cdot -}$ more selective.

$$S_2O_8^{2-} + e^-_{aq} \rightarrow SO_4^{\cdot -} + SO_4^{2-}, \quad k = 1.1\times10^{10}\ M^{-1}S^{-1} \quad (2)$$

$$S_2O_8^{2-} + H\cdot \rightarrow SO_4^{\cdot -} + H^+ + SO_4^{2-}, \quad k = 2.5\times10^{7}\ M^{-1}S^{-1} \quad (3)$$

With addition of $S_2O_8{}^{2-}$ at alkaline pH, the formed $SO_4{}^{\cdot -}$ will react with OH^- to generate HO· (Kasiri et al., 2008; Chen et al., 2015), as shown in Eq. (4).

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + HO\cdot, \quad k = 6.5\times10^{7}\ M^{-1}S^{-1} \quad (4)$$

Furthermore, under alkaline conditions, hydroxyl radicals exhibit a slightly higher redox potential than sulfate radicals (Deng et al., 2013). As a result, the generation of HO· in alkaline solution is expected to enhance the degradation of organic compounds.

The objective of this study was to investigate the degradation of trimethoprim by gamma irradiation with addition of $S_2O_8{}^{2-}$. The possible degradation pathway of TMP was tentatively proposed based on the identification of intermediate products.

2. Materials and methods

2.1. Chemicals

Trimethoprim was purchased from Aladdin with purity ≥99%, its chemical structure is presented in Fig. 1. Other chemicals used in the experiments, including $K_2S_2O_8$ (>99.5%); NaOH (>96%); H_2SO_4 (95–98%); ethanol (>99.9%); acetonitrile (>99.9%), were purchased from Beijing Chemical Plant Fine Chemicals Co., Ltd (Beijing, China), and they were used without further purification. All solutions used in the experiments were prepared with distilled water.

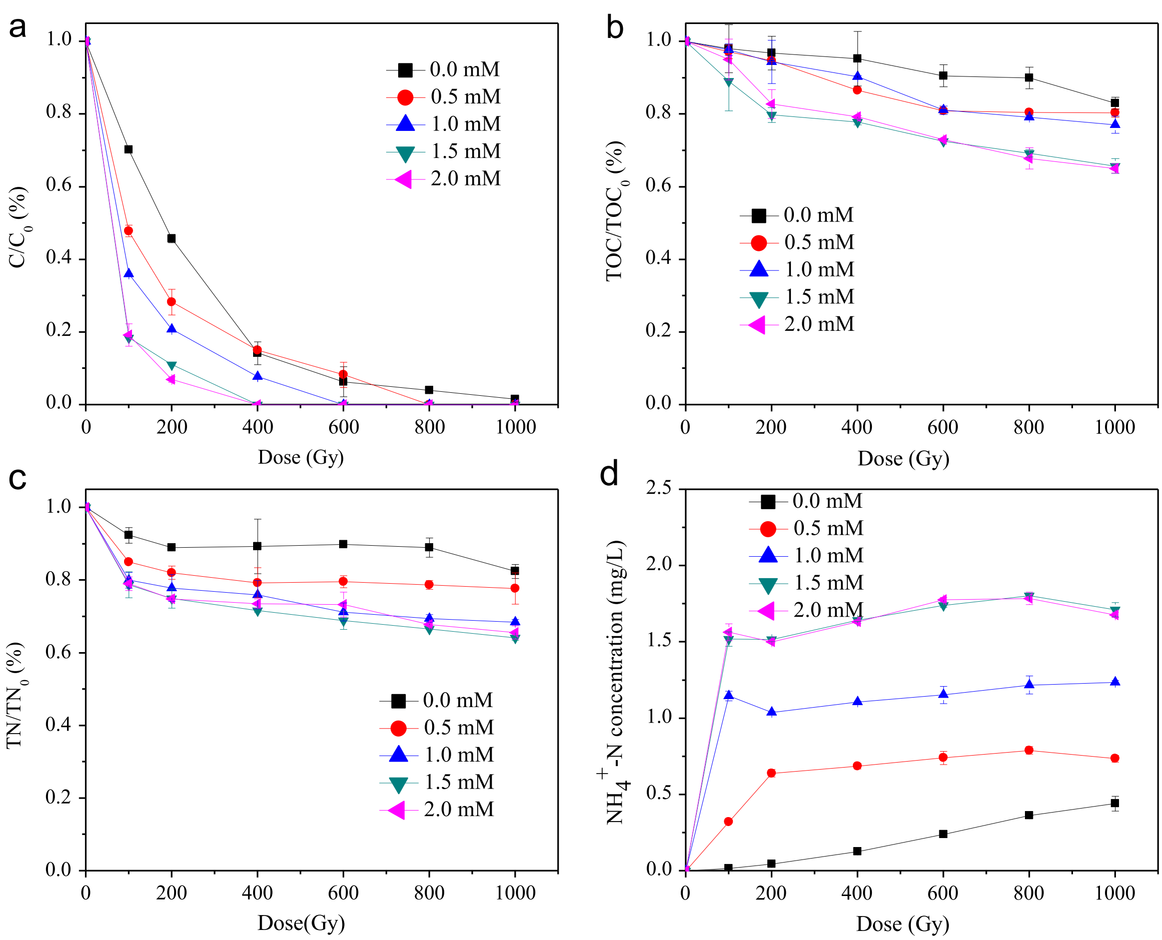

Fig. 2. Degradation of trimethoprim by gamma irradiation, TMP removal (a), TOC removal (b), TN removal (c) and $NH_4{}^+$–N generation (d) in the presence of PS.