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Gamma irradiation of 2-mercaptobenzothiazole aqueous solution in the presence of persulfate

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ABSTRACT

Recently, water treatment by ionizing radiation has gained increasing attention as a powerful technology for the destruction of refractory pollutants. 2-Mercaptobenzothiazole (MBT) is known as a widespread, toxic and poorly biodegradable pollutant. This paper studied the gamma irradiation of aqueous solutions of MBT. Moreover, the effect of the addition of persulfate ($S_2O_8^{2-}$) on the radiolytic destruction of MBT was investigated. The main transformation products of the studied compound were detected and the sequence of occurrence of the products was described. The change of biodegradability of MBT solution was also observed. The main results obtained in this study indicated that gamma radiation was effective for removing MBT in aqueous solution. Persulfate addition, which induced the formation of reactive sulfate radicals ($SO_4\cdot^-$), greatly enhanced the degradation of MBT. Benzothiazole was identified as the first radiation product, followed by 2-hydroxybenzothiazole. Decomposition of MBT started with the oxidation of $-SH$ groups to sulfate ions. Possible pathways for MBT decomposition by gamma irradiation were proposed. The BOD/COD ratios of MBT samples were increased after radiation, indicating the improvement of biodegradability and reduction of toxicity.

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Introduction

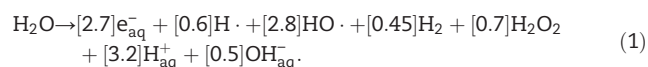
2-Mercaptobenzothiazole ($C_7H_5NS_2$) is used widely in various industries, for example synthesis of antibiotics, pesticides, rubber and leather (Azam and Suresh, 2012; Rodriguez et al., 2004). 2-Mercaptobenzothiazole (MBT) exists in numerous industrial effluents, resulting in a large amount of release into the environment every year. With a heterocyclic ring structure and molecular weight of 167 amu, this compound is characterized by water insolubility, a high octanol–water distribution coefficient ($K_d > 90$) and weak acidity ($pK_a = 6.94$). These properties lead to the antimicrobial activity of MBT. Some researchers (De Wever et al., 1994) suggested that

MBT might distribute in hydrophobic cell membranes and interact with the respiratory chain. Several studies discovered that MBT was likely to attack enzymes in bacteria and thus inhibit their growth (Czechowski and Rossmore, 1981; Shuto et al., 1989). The toxicity of MBT towards microorganisms makes it difficult to degrade in biological treatment systems (De Wever et al., 2001; Gaja and Knapp, 1998; Reemtsma et al., 2002). Therefore, new technologies are being investigated for the purpose of effectively removing MBT from waters.

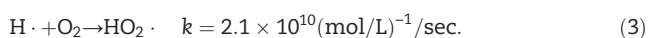
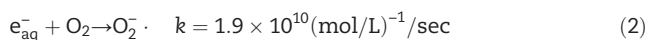
In recent years, advanced oxidation processes (AOPs) have been considered as alternative methods for elimination of many organics in wastewaters and effluents. Regarding treatment of MBT, there have been reports on ozonation

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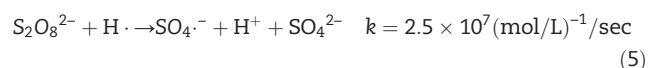
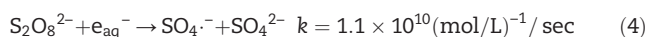
(Fiehn et al., 1998; Puig et al., 1996), direct photolysis (Malouki et al., 2004), photocatalytic oxidation (Habibi et al., 2001; Li et al., 2005) and hydrogen peroxide oxidation (Al-Ansari et al., 2010). Among AOPs, ionizing radiation (gamma irradiation or electron beam irradiation) has demonstrated potential as an efficient method for degradation of recalcitrant water pollutants (Kim et al., 2009; Sun et al., 2013a, 2013b; Vahdat et al., 2010). After absorbing energy from ionizing radiation, water molecules are electronically excited and ionized into many kinds of reactive primary species ($\cdot\text{OH}$, e_{aq}^- , $\cdot\text{H}$) and molecular products (H_2 , H_2O_2). The overall reaction taking place and the yields (number of molecules formed per 100 eV absorbed dose) of primary products in aqueous solutions at pH 7 are as follows (Chmielewski, 2005; Wojnarovits and Takacs, 2008):



Hydroxyl radicals ($\cdot\text{OH}$), hydrated electrons (e_{aq}^-) and hydrogen atoms ($\cdot\text{H}$) are much more reactive with organic compounds than the other species produced. Due to the presence of dissolved oxygen in the water, the reductive species e_{aq}^- and $\cdot\text{H}$ scavenged by O_2 will be converted to O_2^- and $\text{HO}_2\cdot$ (Eqs. (2) and (3)) (Getoff, 2002; Sampa et al., 2007). Therefore, in practice $\cdot\text{OH}$ is the major reactive species that will react with solutes, leading to their degradation.



However, gamma irradiation is not a low cost method compared to other oxidation processes such as ozonation, ultraviolet (UV) irradiation and H_2O_2 oxidation. With the goal of improving efficiency and reducing cost, recent researchers have tentatively combined ionizing radiation with oxidants or catalysts. Liu and Wang (2013) suggested that the addition of H_2O_2 could promote the removal of sulfamethazine during gamma irradiation because activated hydrogen peroxide molecules generated extra hydroxyl radicals. A similar result was obtained in the radiation process of polyvinyl alcohol with the addition of O_3 gas (Sun et al., 2015). Some other studies indicated that persulfate anions ($\text{S}_2\text{O}_8^{2-}$) in aqueous solution can be activated by ionizing radiation to form sulfate radicals ($\text{SO}_4^{\cdot-}$), which are more powerful oxidants ($E_0 = 2.6 \text{ V}$) than persulfate anions. Therefore, addition of $\text{S}_2\text{O}_8^{2-}$ can affect the radiation-induced degradation of target pollutants (Criquet and Karpel Vel Leitner, 2012; Criquet and Leitner, 2011; Roshani and Karpel Vel Leitner, 2011a, 2011b). When $\text{S}_2\text{O}_8^{2-}$ solution is irradiated, the e_{aq}^- produced by water radiolysis can rapidly react with $\text{S}_2\text{O}_8^{2-}$ to form $\text{SO}_4^{\cdot-}$ (Eq. (4)). The rate constant of the reaction is comparable to that of the reaction between e_{aq}^- and oxygen ($1.9 \times 10^{10} (\text{mol/L})^{-1}/\text{sec}$). Persulfate can also react with the $\cdot\text{H}$ radical (Eq. (5)) or the $\cdot\text{OH}$ radical (Eq. (6)), but the kinetics of these reactions are much slower.



However, very little information is available in the open literature on the radiation-induced degradation of MBT or the impact of additional oxidants on its radiolytic behavior. In the present research, we report for the first time the radiolytic degradation of MBT in aqueous solution in the presence of persulfate. This work examined the decomposition efficiency, the radiolytic products and the transformation pathway. Particular attention was paid to the change of biodegradability.

1. Materials and methods

1.1. Solution and chemicals

Because of the very low solubility of MBT in neutral distilled water, a stock solution of MBT was prepared by dissolving the solid in 5 mol/L NaOH aqueous solution. Then the solution pH was adjusted to 7 using HCl. MBT solution used in this study was diluted from the stock solution.

MBT and benzothiazole (BT) were obtained from the Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. 2-Hydroxybenzothiazole (OBT) was obtained from Sigma-Aldrich (Shanghai, China). MBT, BT, OBT and $\text{K}_2\text{S}_2\text{O}_8$ used were of analytical grade. Methanol was of chromatographic purity. All chemicals were used as received without further purification.

1.2. Irradiation experiments

The irradiation experiments were carried out using γ -rays from a ^{60}Co irradiation source located at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University (Qiburi et al., 2014a). The initial activity of the source was about $1.44 \times 10^{15} \text{ Bq}$, with dose rate of 274 Gy/min at the core channel. The absorbed dose (in gray, 1 Gy = 1 J/kg) is determined from the relation:

$$\text{Dose (Gy)} = \text{Dose rate (Gy/min)} \times \text{Time (min)} \quad (7)$$

MBT-containing aqueous sample solutions were prepared in 30 mL glass tubes with an initial concentration of 20 mg/L. Extra $\text{K}_2\text{S}_2\text{O}_8$ was added into the solutions just before exposure to γ -rays. Samples were irradiated at different absorbed doses ranging from 100 to 2000 Gy. All the experiments were performed at ambient temperature. All samples were filtered with 0.22 μm membranes before analysis. The MBT removal was calculated as follows:

$$\text{MBT Removal} = (C_0 - C_i)/C_0 \quad (8)$$

where C_0 (mg/L) and C_i (mg/L) are the MBT concentrations before and after irradiation.

1.3. Analytical methods

MBT and organic breakdown products were quantified by an LC-20AT High Performance Liquid Chromatograph (HPLC) with SPD-20A UV detection and a C_{18} reverse-phase column (150 mm \times 4.6 mm, 5 μm) (Shimadzu, Kyoto, Japan). HPLC separation was performed with an acetonitrile–water gradient.

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