Radiation Physics and Chemistry 103 (2014) 198–202

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Degradation of 2-mercaptobenzothiazole in aqueous solution by gamma irradiation

Qiburi Bao [a], Lujun Chen [a,b,*], Jinping Tian [a], Jianlong Wang [c]

[a] School of Environment, Tsinghua University, Beijing 100084, PR China
[b] Zhejiang Provincial Key Laboratory of Water Science and Technology, Jiaxing, Zhejiang, 314050, PR China
[c] Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- Radiation is an effective method to remove MBT from water.
- G-value and dose constant of MBT degradation under different conditions were discussed.
- Desulfuration of MBT molecule was observed during irradiation.
- γ-Irradiation can improve the biodegradability of MBT containing water.

ARTICLE INFO

Article history:
Received 20 March 2014
Accepted 1 June 2014
Available online 9 June 2014

Keywords:
Ionizing radiation
2-mercaptobenzothiazole
Degradation
Desulfuration
Biodegradability

ABSTRACT

Industrial wastewaters containing 2-mercaptobenzothiazole (MBT), a widely used chemical additive, usually cannot be treated properly by conventional biological methods, thus cause an environmental risk. Ionizing radiation was proposed as a method for abatement of several refractory pollutants from water. The paper investigated MBT degradation using irradiation technology. The decomposition kinetics was described, and the transformation and the change of biodegradability were discussed. The results of gamma radiation experiments on MBT-containing aqueous solutions indicated that reactive radicals resulting from water radiolysis effectively degrade MBT and improve the biodegradability of the solutions. At a 20 mg/L MBT concentration, the removal of 82% was achieved at the absorbed dose of 1.2 kGy. The results of specific oxygen uptake rate (SOUR) test showed that MBT was decomposed into biodegradable products, after irradiation at 20 kGy. Radicals attacked the sulfur atoms of the studied molecule leading to the release of sulfate ions, but the mineralization of organic carbons was rather weak. Initial concentration significantly affected the degradation efficacy of MBT by gamma radiation.

1. Introduction

As an important chemical additive, 2-mercaptobenzothiazole (MBT) is widely used in synthesis of antibiotics, pesticides, rubber, leather, etc. According to EPA Toxic Release Inventory in 2010, total on-site and off-site disposals of MBT in USA was 190575.42 lb, of which chemical industry released 6071 lb and plastic/rubber industry released 60749.6 lb.

MBT is a condensed heterocyclic compound with a molecular weight of 167 amu (Fig. 1; Table 1). Because of its antimicrobial effect, wastewater containing MBT is usually resistant to conventional biological treatment.

For example, in the activated sludge system, MBT was found to be resistant and toxic towards activated sludges (Chudoba et al., 1977; Devos et al., 1993). Moreover, MBT even inhibited the degradation of the other heterocycles in the degradation test of heterocycle mixtures. It was reported that microorganisms composing the activated sludge from municipal wastewater treatment plant could be killed after exposure to MBT solutions for 2–3 days (Repkina et al., 1983). Dewever et al. (1994) found that 100 mg/L of MBT was enough to completely inhibit bacterial growth. In addition to the conventional activated sludge process, two-stage anaerobic and aerobic process (Reemtsma et al., 1995), the Bayer tower system (DeWever and Verachtert, 1997), etc. have also been studied. However, microbial tolerance to MBT is limited, therefore a large scale of dilution and pH adaptation were always required in order to achieve satisfactory treatment efficiency.

Recently developed advanced oxidation processes (AOPs) have been considered as an alternative for MBT removal from wastewater.

* Corresponding author at: School of Environment, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 62776686; fax: +86 10 62797581.
E-mail address: chenlj@tsinghua.edu.cn (L. Chen).

http://dx.doi.org/10.1016/j.radphyschem.2014.06.001
0969-806X/

Ozonation could remove MBT and its derivatives from wastewater and reduce the COD, but showed little effect on mineralization (Puig et al., 1996). Fiehn et al. (1998) found that ozonation of MBT was nearly independent of pH-values and proposed that the oxidation product was an organic sulfite. There have been several investigations on direct photolysis (Malouki et al., 2004) and TiO_2-based photocatalysis of MBT. Habibi et al. (2001) found that MBT could be degraded by photocatalytic oxidation, and alkaline medium was favorable. Under optimized condition, 98% removal could be achieved with 8 h reaction time. To enhance the photocatalytic activity for MBT degradation, Li et al. (2005) improved the catalyst performance by doping TiO_2 with Ce^{3+}. In addition, peroxidase-catalyzed oxidation of MBT was recently reported (Al-Ansari et al., 2010).

Ionizing radiation, as a special kind of AOPs technology has demonstrated potential as a powerful method for degradation of recalcitrant pollutants (Kim et al., 2009; Sampa et al., 2007; Sun et al., 2013b; Vahdat et al., 2010) like halogenated organic compounds, pesticides, antibiotics, sulfonated aromatic compounds and azo dyes. This technology is also used for incomplete decomposition of the target pollutants into less toxic by-products in order to improve their biodegradability (Chmielewski, 2011; Sun et al., 2012, 2013a). The chemistry behind this technology is under extensive investigation (Al-Sheikhly et al., 2006; Homlok et al., 2011; Zacheis et al., 2000). But there is only one brief piece of report available regarding the ionizing radiation of MBT. Tolgyessy et al. (1986) carried out γ irradiation on 115 mg/L MBT solutions and found no significant change in COD, TOC or BOD_5 within the absorbed dose range of 0–16 kGy. However, neither MBT removal efficacy nor the influence of operational parameters was mentioned.

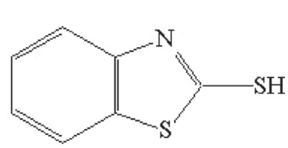
To our knowledge, this is the first study giving an insight into the radiolytic behavior of MBT in aqueous solution. The objectives of the present work were (1) to study the radiation-induced decomposition and transformation of MBT, and the change of its biodegradability; (2) to investigate the decomposition kinetics of this compound.

2. Materials and methods

2.1. Chemicals

MBT (2-mercaptobenzothiazole) was obtained from the SCR Corporation. The chemical structure and characteristics are displayed in Fig. 1 and Table 1. MBT and NaOH were of analytical grade. Methanol was of chromatographic purity. All chemicals were used as received without further purification.

MBT solution used in this study was diluted from the stock solution. Because of the very low solubility of MBT in neutral distilled water, stock solution was prepared from MBT solid dissolved in 5 mol/L NaOH aqueous solution. Solution pH was adjusted using NaOH or HCl.



pKa = 6.94; [MBT] → [MBT$^-$] + [H$^+$]

Fig. 1. Chemical structure and acidity constants of MBT.

2.2. Irradiation experiments

MBT-containing aqueous sample solutions were placed into 30 mL glass tubes and irradiated with a ^{60}Co irradiation source (Institute of Nuclear and New Energy Technology, Tsinghua University). The initial activity of the source was about 1.44×10^{15} Bq, with dose rate of 274 Gy/min at the core channel.

2.3. Specific oxygen uptake rate test

Biodegradability of samples was investigated through the specific oxygen uptake rate test by a Warburg respirometer (SKW-3, Shanghai University). The activated sludge was obtained from the aeration tank of the Reclaimed Water Station I, Tsinghua University. The sludge was aerated for 24 h in advance to reach the endogenous respiration (ER) state. The mixed liquor volatile suspended solids (MLVSS) in the reaction vials was controlled at about 5 g/L. The reaction temperature was fixed at 35 °C.

2.4. Analytical methods

A method for the detection and quantification of MBT was developed in our laboratory by a Shimadzu series LC-20AT HPLC with SPD-20A UV detection and a C_{18} reverse-phase column (150 mm × 4.6 mm, 5 μm) using a methanol:water = 65:35 as mobile phase flowing at 1.0 mL/min, $\lambda = 329$ nm.

A Shimadzu series UV-2450 spectrophotometer equipped with quartz cells (optical length = 1.0 cm) was used to detect the UV absorption of each samples. The scan range was 190–600 nm.

The total organic carbon (TOC) was monitored by means of a Shimadzu series TOC–V_{CPH} analyzer.

The amount of SO_4^{2-} in solutions was measured by a Dionex series ICS-900 ion chromatograph.

2.5. Calculation of dose constant

The removal of compounds by gamma irradiation can usually be expressed by Eq. (1) (Criquet and Karpel Vel Leitner, 2012; Sánchez-Polo et al., 2009). The dose constant, k, is the slope of natural logarithm (ln) of the compound concentration versus dose.

$$\ln(C/C_0) = -kD \quad (1)$$

where C is the concentration after irradiation (mg/L), C_0 the initial concentration, k the dose constant (kGy^{-1}) and D the absorbed dose (kGy).

Dose constants were used to calculate the doses required for 50% and 90% MBT degradation ($D_{0.5}$ and $D_{0.9}$ values) by using

$$D_{0.5} = (\ln 2)/k \quad (2)$$

$$D_{0.9} = (\ln 10)/k \quad (3)$$

Table 1
Characteristics of MBT.

Molecular formula	Molecular weight (g/mol)	Melting point (°C)	LD_{50} (mg/kg)	Solubility	log (oil/water)	pK_a
$C_7H_5NS_2$	167.24	179	100	Insoluble in water. Soluble in alkaline solution and ethanol.	2.4	6.94