

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 (SO₄-), 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 Rossmoore, 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 OH, e_{aq} , \cdot H) and molecular products (H₂, H₂O₂). 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 (.OH), hydrated electrons (e_{aq}) and hydrogen atoms (.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 .H scavenged by O₂ will be converted to O₂. and HO₂. (Eqs. (2) and (3)) (Getoff, 2002; Sampa et al., 2007). Therefore, in practice .OH is the major reactive species that will react with solutes, leading to their degradation.

$$e_{aa}^{-} + O_2 \rightarrow O_2^{-} \cdot k = 1.9 \times 10^{10} (mol/L)^{-1} / sec$$
 (2)

$$H \cdot +O_2 \rightarrow HO_2 \cdot k = 2.1 \times 10^{10} (mol/L)^{-1} / sec.$$
(3)

However, gamma irradiation is not a low cost method compared to other oxidation processes such as ozonation, ultraviolet (UV) irradiation and H₂O₂ 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 $(S_2O_8^{2-})$ in aqueous solution can be activated by ionizing radiation to form sulfate radicals (SO_4^{-}), which are more powerful oxidants ($E_0 = 2.6$ V) than persulfate anions. Therefore, addition of $S_2O_8^{2-}$ 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 $S_2O_8^{2-}$ solution is irradiated, the e_{aq}^- produced by water radiolysis can rapidly react with $S_2O_8^{2-}$ to form SO_4^{-} . (Eq. (4)). The rate constant of the reaction is comparable to that of the reaction between e_{aq}^{-} and oxygen (1.9 × 10¹⁰ (mol/L)⁻¹/sec). Persulfate can also react with the .H radical (Eq. (5)) or the ·OH radical (Eq. (6)), but the kinetics of these reactions are much slower.

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4 \cdot + SO_4^{2-} \ k = 1.1 \times 10^{10} (mol/L)^{-1} / sec$$
 (4)

$$S_2O_8^{2-} + H \rightarrow SO_4^{-} + H^+ + SO_4^{2-}$$
 $k = 2.5 \times 10^7 (mol/L)^{-1}/sec$ (5)

$$S_2O_8^{2-} + OH \rightarrow SO_4^{-} + HSO_4^{-} + 0.5O_2$$
 $k = 8 \times 10^4 (mol/L)^{-1}/sec$ (6)

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 $K_2S_2O_8$ 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 ⁶⁰Co 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 1.44×10^{15} 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:

Dose
$$(Gy) = Dose rate (Gy/min) \times Time (min)$$
 (7)

MBT-containing aqueous sample solutions were prepared in 30 mL glass tubes with an initial concentration of 20 mg/L. Extra $K_2S_2O_8$ 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 μ m membranes before analysis. The MBT removal was calculated as follows:

$$MBT Removal = (C_0 - C_i)/C_0$$
(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 × 4.6 mm, 5 μ m) (Shimadzu, Kyoto, Japan). HPLC separation was performed with an acetonitrile–water gradient. Distilled water, containing 4 mmol/L NaH₂PO₄ and adjusted to pH 4.5 with H₃PO₄, was employed as solvent A. Solvent B was acetonitrile:solvent A = 90:10, acidified to pH 4.5 with H₃PO₄. Elution started with 70% B and was linearly shifted to 80% B at 6 min. The column temperature was held at 40 °C and flow rate at 0.5 mL/min. 20 μ L aliquots were injected. UV detection was performed with time-programmed wavelength changes according to the absorption maxima of each compound: OBT was detected at 213 nm around 3.7 min, MBT at 325 nm between 4 min and 4.5 min, and BT at 250 after 4.7 min. This method was a modification of the previously reported analysis method by (Fiehn et al., 1994).

A UV-2450 spectrophotometer (Shimadzu, Kyoto, Japan) equipped with quartz cells (optical length = 1.0 cm) was used to detect the UV absorption of the samples. The scan range was 190–400 nm. The total organic carbon (TOC) was monitored by means of a TOC-V_{CPH} analyzer equipped with an OTC-18-port auto-sampler (both from Shimadzu, Kyoto, Japan). The amount of sulfate anion (SO₄^{2–}) was measured by an ICS-900 ion chromatograph with an IonPac AS 19 column (both from Dionex, Sunnyvale, USA). Conductivity detection was applied using the suppression technique. The eluent was a Na₂CO₃/NaHCO₃ solution at a flow rate of 1.0 mL/min.

The chemical oxygen demand (COD) was photometrically determined after dichromate oxidation with a DRB200 digital reactor and a DR890 colorimeter (Hach, Colorado, USA). The biochemical oxygen demand (BOD₅) was manometrically determined with a BODTrak[™] II apparatus (Hach, Colorado, USA). Lake water was used as inoculum.

2. Results and discussion

2.1. Decomposition of MBT by gamma irradiation in the presence of $S_2 O_8^{2^-}$

2.1.1. Influence of persulfate $(S_2 O_8^{2-})$ addition on radiolytic degradation of MBT

In order to study the influence of added $S_2O_8^{2-}$ on MBT decomposition efficiency, irradiation experiments were performed for the dose range of 100-2000 Gy with or without $S_2O_8^{2-}$. Results obtained are shown in Fig. 1. Gamma irradiation decay curves of MBT in aqueous solution were plotted (Fig. 1a). The MBT concentration was progressively reduced with increasing absorbed dose. The addition of persulfate induced a significant improvement in MBT degradation in the early stage. In the absence of persulfate, 20% of MBT was degraded for a dose of 200 Gy, while an abatement of 61% was obtained for the same dose in the presence of 200 μ mol/L $S_2O_8^{2-}$. After this point, the decay curves began to flatten with increasing dose, and the difference between them became smaller. The removals for a dose of 1200 Gy with and without $S_2O_8^{2-}$ were 93% and 89%, respectively. This indicates that the radiolytic degradation of MBT followed a trend towards a balanced state.

The changes in the UV spectra of MBT after irradiation with or without persulfate were examined in the range of wavelengths of 190–350 nm (Fig. 1b). The unsaturated bonds (double bonds and aromatic rings) in the organic compound generate a



Fig. 1 – Influence of persulfate addition on the degradation of 2-mercaptobenzothiazole (MBT) in aqueous solution by gamma irradiation. (a) residual ratio of MBT, (b) ultraviolet (UV) absorption spectra, (c) TOC, (d) release of sulfate ion. MBT = 20 mg/L; $S_2O_8^{2-}$ = 200 μ mol/L.

characteristic UV spectrum (Qiburi et al., 2014b). After absorbing the energy of γ -rays, the reactive radicals formed attack the bonds in the molecule and destroy the chromophore. A major difference was observed between non-irradiated MBT and irradiated MBT. In the presence of $S_2O_8^{2-}$, the difference became greater. MBT had a strong absorption at 230 nm and 306 nm wavelengths. After irradiation, the absorption intensity of both peaks decreased, while additional absorption peaks were found around 260 nm and 190–220 nm, indicating the degradation of the original compound and formation of by-products.

Usually, it takes several steps to mineralize a heterocyclic compound: oxidation of rings, ring opening and transformation to carboxylic acids, and finally transformation to inorganic molecules, which is reflected in the reduction of TOC. As a sulfur compound, MBT degradation involves the breakage of C-S bonds, namely the transformation of sulfur from carbon-bound atoms to free ions. In previous studies Habibi et al. (2001) and Qiburi et al. (2014b) reported the release of sulfate (SO_4^{2-}) from MBT decomposition by AOPs, therefore in this work the sulfate concentration was detected during the gamma irradiation experiment. The mineralization and desulfuration of MBT during gamma radiation with or without persulfate are shown in Fig. 1c and d. The TOC content of MBT aqueous solution without S₂O₈²⁻ was not significantly reduced by gamma irradiation within the applied dose range, while in the presence of $S_2O_8^{2-}$, the removal of TOC increased to a certain extent (18% at 1800 Gy). This indicates that most radiolytic products exist in organic forms and the mineralization of these products is difficult.

As for sulfur transformation, it can be seen that $SO_4^{2^-}$ was generated from gamma-induced decomposition of MBT (Fig. 1d). The formation of sulfate gradually increased with the cumulative absorbed dose. For the dose of 1500 Gy, without additional $S_2O_8^{2^-}$, 3.8 mg/L sulfate was detected in the sample solution, accounting for around 17% of the calculated final sulfate concentration (23 mg/L) assuming total oxidation of all sulfur atoms in the MBT molecule. In the presence of persulfate, the formation of sulfate was dramatically promoted. At 1500 Gy, the final $SO_4^{2^-}$ concentration reached 25.6 mg/L with 200 μ mol/L $S_2O_8^{2^-}$. That is because the irradiation of persulfate solutions with ionizing radiation produces a large amount of sulfate ions (Eq. (4)). In these cases, both MBT and persulfate provide a source of sulfate ions.

2.1.2. Synergetic effect of persulfate and radiation

The additional persulfate effectively enhanced the degradation of MBT by gamma radiation according to the above results. However, we note that persulfate has the nature of a strong oxidant ($E_0 = 2.01$ V), and tends to cause the oxidation of MBT without irradiation. Therefore, a pertinent question is whether the benefit from persulfate addition was merely due to its chemical oxidation or due to some synergetic action of the oxidant with gamma rays. In order to evaluate the synergetic effect of persulfate addition, a comparison was made between the combination of γ -S₂O₈²⁻, and the simple summation of the effects of S₂O₈²⁻ oxidation and γ radiation applied separately.

The comparison between the combination and summation of effects is shown in Fig. 2. After radiation at 100, 200 and 400 Gy, the solution containing 100 μ mol/L persulfate showed



Fig. 2 – Comparison of combined γ -S₂O₈² treatment with single S₂O₈²⁻ oxidation and single γ radiation. S₂O₈²⁻=100 μ mol/L, MBT = 20 mg/L.

MBT removal of 34%, 44% and 62%, respectively. By comparison, the sums of the removals by 100 µmol/L persulfate oxidation and γ radiation applied separately at the three doses were only 18%, 31% and 57%, respectively. The results indicated that removal of MBT in combined γ -S₂O₈²⁻ treatments was greater than that obtained from a simple summation of $S_2O_8^{2-}$ removal and radiation removal for the applied dose range. The formation of reactive SO₄⁻ radicals from the reaction of persulfate with hydrated electrons (Eq. (4)) was assumed to explain the synergetic effect of the combined γ -S₂O₈²⁻ system. However, we note that the longer the gamma exposure time, the more similar the effect of combination and summation. In other words, with the accumulation of radiation dose, the synergetic effect of combined γ -S₂O₈²⁻ treatment gradually decreased, and finally disappeared at 600 Gy. That trend can be explained by the competitive reactions for e_{aq}^{-} between MBT molecules and SO_4^- radicals. At lower doses, persulfate anions can be transformed by radiation into sulfate radicals, which have a more powerful oxidation effect than $S_2O_8^{2-}$ oxidation on MBT; at higher doses, the increasing amount of radical species leads to a greater probability of the side reaction between SO₄- radicals and e_{aq}^{-} radicals, transforming reactive SO_{4}^{-} into inert SO_{4}^{2-} ions (Eq. (9)) (Boukari et al., 2011; Criquet and Karpel Vel Leitner, 2012).

$$SO_4 \cdot - + e_{ag} \to SO_4^{2-}$$
 $k < 1 \times 10^6 (mol/L)^{-1} / sec$ (9)

2.2. Transformation of MBT during gamma-induced degradation

The release of sulfate ions during irradiation indicates the oxidation of sulfur atoms in the MBT molecule. However, in principle, there are two sites in MBT that may react with radicals, the thiol group and the benzothiazole skeleton. In order to determine the exact site of radical attack, the breakdown products of MBT in the radiation process were investigated.

2.2.1. Identification of breakdown products

In this study, all samples were analyzed by HPLC. The parent compound and products were identified using a UV detector. HPLC chromatograms of samples are shown in Fig. 3. With increasing absorbed dose, the MBT peaks declined and two emerging major peaks appeared successively, for which the retention times were about 4.7 and 3.7 min, respectively. The two peaks were identified as BT (C_7H_5NS 135 g/mol) and OBT (C_7H_5NS 151 g/mol) by comparing samples with the corresponding standards *via* HPLC analysis.

The sequence of occurrence of the transformation products and their concentrations during the radiation process are shown in Fig. 4. With the accumulation of absorbed dose, the BT concentration first increased and then decreased. The maximum content of BT (36.1 μ mol/L) was observed after 500 Gy radiation. In contrast, the concentration of OBT increased much more slowly and reached 17.1 μ mol/L after 1200 Gy radiation. It seems that greater doses are needed to achieve the degradation of OBT. In AOPs, a higher oxygen to carbon ratio in a molecular structure means lower reactivity with radicals. That is why OBT was more difficult to degrade than BT. As OBT showed a slower reaction than that observed in the destruction of BT, the former might be a transformation product of the latter.

2.2.2. Pathway of MBT degradation by gamma radiation

The stability of the condensed heterocyclic structure of benzothiazole explains the lack of identified organic ringcleavage products. Therefore, the oxidation of the substituent group (–SH) was hypothesized to be the main pathway for MBT degradation. As mentioned above, like many other advanced oxidation processes, the degradation of MBT during gamma irradiation was mainly due to oxidation by .OH radical produced in water radiolysis. .OH attack caused thiol cleavage from the MBT molecule to yield BT in the beginning of the radiation process. SO_4^{2-} ion was generated at the same time. Then BT was further oxidized to OBT. Derived from the combined data of HPLC and ion chromatography analyses, a degradation pathway for MBT in pure water is suggested (Fig. 5).



Fig. 3 – High Performance Liquid Chromatograph (HPLC) chromatogram of the radiation products of MBT at different absorbed doses. MBT = 20 mg/L.



Fig. 4 - Concentrations of the radiation products of MBT.

2.3. Biodegradability assessment

The effectiveness of a treatment process is not only determined by its power to degrade contaminants but also by its capacity to generate benign degradation products that are less toxic than the parent compound (Drzewicz et al., 2004; Rizzo, 2011; Sánchez-Polo et al., 2009). Many reports have stated that



CO₂, H₂O and other small molecules

Fig. 5 – Proposed pathways for MBT degradation by gamma irradiation in aqueous solution.



Fig. 6 – Biodegradability of MBT solution during gamma irradiation. MBT = 200 mg/L. B/C: biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio.

ionizing radiation could effectively destroy the stable structure of some recalcitrant pollutants, making them more easily degraded biologically (Bao et al., 2009; Chmielewski, 2011; Sun et al., 2012). Hence, we focus on the change of the biodegradability of MBT samples during gamma irradiation.

The biodegradability of MBT samples was assessed by the biochemical oxygen demand (BOD₅) to chemical oxygen demand (COD) ratio (B/C). BOD₅ and COD were measured for the aqueous solutions of MBT irradiated at different absorbed doses (0-20 kGy). The initial concentration of MBT was set to 200 mg/L, which was the threshold value of complete inhibition of Escherichia coli growth (De Wever et al., 1994, 2001; De Wever and Verachtert, 1997). There were no additional carbon sources or nutrients in the solution, hence MBT served as the only substrate. The result is shown in Fig. 6. Within the range of applied doses, no significant removal of COD was observed. After irradiation at 20 kGy, the COD of the sample only declined by 13%; while the BOD of the sample rose significantly with the increase of absorbed dose. Therefore, the B/C value of irradiated samples was increased, indicating the improvement of biodegradability. After irradiation by 5, 10, 15 and 20 kGy, the B/C values of 200 mg/L MBT solutions were 134%, 151%, 167% and 162% the unirradiated B/C values. The values of COD, BOD₅ and B/C tested in the study were consistent with a published report (Tolgyessy et al., 1986). The above results confirmed that the transformation products are more readily degraded biologically than MBT. Therefore, toxicity reduction of MBT-containing wastewater should easily be achieved by gamma irradiation.

3. Conclusions

Gamma irradiation is an effective way to eliminate refractory pollutants from water. In this study, the benefit of persulfate addition was demonstrated for the degradation of a heterocyclic compound. The degradation of MBT was substantially promoted by adding persulfate to the aqueous solution. Moreover, the mineralization was enhanced to a certain extent. The synergetic effect of persulfate and radiation is due to the action of reactive SO_4^- radicals formed in the reaction of persulfate with hydrated electrons.

Breakdown products in the radiation process were identified and quantified for the elucidation of the degradation pathway of MBT. Radical attack was directed towards the –SH group, leading to the cleavage of the C–S bond. In this way, MBT was transformed into BT, releasing SO_4^2 ions at the same time. OBT was identified as an oxidation product of BT. The biodegradability experiment showed that radiation products were easier for microorganisms to degrade than the parent compound. Thus, the toxicity of MBT-containing wastewater should be reduced remarkably through radiation treatment.

Further work will focus on the application of ionizing radiation as pretreatment in a biological treatment system of MBT-containing wastewater.

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REFERENCES

- Al-Ansari, M.M., Steevensz, A., Taylor, K.E., Bewtra, J.K., Biswas, N., 2010. Soybean peroxidase-catalyzed removal of an aromatic thiol, 2-mercaptobenzothiazole, from water. Water Environ. Res. 82 (11), 2285–2289.
- Azam, M.A., Suresh, B., 2012. Biological activities of 2mercaptobenzothiazole derivatives: a review. Sci. Pharm. 80 (4), 789–823.
- Bao, H., Gao, J., Liu, Y., Su, Y., 2009. A study of biodegradation/ γ -irradiation on the degradation of *p*-chloronitrobenzene. Radiat. Phys. Chem. 78 (12), 1137–1139.
- Boukari, S.O.B., Pellizzari, F., Leitner, N.K.V., 2011. Influence of persulfate ions on the removal of phenol in aqueous solution using electron beam irradiation. J. Hazard. Mater. 185 (2–3), 844–851.
- Chmielewski, A.G., 2005. Application of ionizing radiation to environment protection. Nukleonika 50, S17–S24.
- Chmielewski, A.G., 2011. Electron accelerators for environmental protection. Rev. Accel. Sci. Technol. 4, 147–159.
- Criquet, J., Karpel Vel Leitner, N., 2012. Electron beam irradiation of citric acid aqueous solutions containing persulfate. Sep. Purif. Technol. 88 (0), 168–173.
- Criquet, J., Leitner, N.K.V., 2011. Electron beam irradiation of aqueous solution of persulfate ions. Chem. Eng. J. 169 (1–3), 258–262.
- Czechowski, M., Rossmoore, H.W., 1981. The effect of selected industrial biocides on lactate metabolism in *Desulfovibrio desulfuricans*. Dev. Ind. Microbiol. 22, 797–804.
- Drzewicz, P., Nałęcz-Jawecki, G., Gryz, M., Sawicki, J., Bojanowska-Czajka, A., Głłuszewski, W., Kulisa, K., Wolłkowicz, S., Trojanowicz, M., 2004. Monitoring of toxicity during degradation of selected pesticides using ionizing radiation. Chemosphere 57 (2), 135–145.
- De Wever, H., Demoor, K., Verachtert, H., 1994. Toxicity of 2-mercaptobenzothiazole towards bacterial growth and respiration. Appl. Microbiol. Biotechnol. 42 (4), 631–635.
- Fiehn, O., Reemtsma, T., Jekel, M., 1994. Extraction and analysis of various benzothiazoles from industrial wastewater. Anal. Chim. Acta 295 (3), 297–305.

- Fiehn, O., Wegener, G., Jochimsen, J., Jekel, M., 1998. Analysis of the ozonation of 2-mercaptobenzothiazole in water and tannery wastewater using sum parameters, liquid- and gas chromatography and capillary electrophoresis. Water Res. 32 (4), 1075–1084.
- Gaja, M.A., Knapp, J.S., 1998. Removal of 2-mercaptobenzothiazole by activated sludge: a cautionary note. Water Res. 32 (12), 3786–3789.
- Getoff, N., 2002. Factors influencing the efficiency of radiation-induced degradation of water pollutants. Radiat. Phys. Chem. 65 (4–5), 437–446.
- Habibi, M.H., Tangestaninejad, S., Yadollahi, B., 2001.
 Photocatalytic mineralisation of mercaptans as environmental pollutants in aquatic system using TiO₂ suspension. Appl. Catal. B Environ. 33 (1), 57–63.
- Kim, H.Y., Yu, S.H., Lee, M.J., Kim, T.H., Kim, S.D., 2009. Radiolysis of selected antibiotics and their toxic effects on various aquatic organisms. Radiat. Phys. Chem. 78 (4), 267–272.
- Li, F.B., Li, X.Z., Hou, M.F., Cheah, K.W., Choy, W.C.H., 2005.
 Enhanced photocatalytic activity of Ce³⁺-TiO₂ for
 2-mercaptobenzothiazole degradation in aqueous suspension for odour control. Appl. Catal. A Gen. 285 (1–2), 181–189.
- Liu, Y., Wang, J., 2013. Degradation of sulfamethazine by gamma irradiation in the presence of hydrogen peroxide. J. Hazard. Mater. 250, 99–105.
- Malouki, M.A., Richard, C., Zertal, A., 2004. Photolysis of 2-mercaptobenzothiazole in aqueous medium: laboratory and field experiments. J. Photochem. Photobiol. A Chem. 167 (2–3), 121–126.
- Puig, A., Ormad, P., Roche, P., Sarasa, J., Gimeno, E., Ovelleiro, J.L., 1996. Wastewater from the manufacture of rubber vulcanization accelerators: characterization, downstream monitoring and chemical treatment. J. Chromatogr. A 733 (1–2), 511–522.
- Qiburi, B., Chen, L., Wang, J., 2014a. Radiation induced decomposition of a refractory cefathiamidine intermediate. J. Environ. Sci. (China) 26 (12), 2406–2411.
- Qiburi, B., Lujun, C., Jinping, T., Jianlong, W., 2014b. Degradation of 2-mercaptobenzothiazole in aqueous solution by gamma irradiation. Radiat. Phys. Chem. 103, 198–202.
- Reemtsma, T., Zywicki, B., Stueber, M., Kloepfer, A., Jekel, M., 2002. Removal of sulfur-organic polar micropollutants in a membrane bioreactor treating industrial wastewater. Environ. Sci. Technol. 36 (5), 1102–1106.
- Rizzo, L., 2011. Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. Water Res. 45 (15), 4311–4340.
- Rodriguez, D.M., Wrobel, K., Jimenez, M.G.G., 2004. Determination of 2-mercaptobenzothiazole (MBT) in tannery wastewater by high performance liquid chromatography with amperometric detection. Bull. Environ. Contam. Toxicol. 73 (5), 818–824.

- Roshani, B., Karpel Vel Leitner, N., 2011a. Effect of persulfate on the oxidation of benzotriazole and humic acid by e-beam irradiation. J. Hazard. Mater. 190 (1–3), 403–408.
- Roshani, B., Karpel vel Leitner, N., 2011b. The influence of persulfate addition for the degradation of micropollutants by ionizing radiation. Chem. Eng. J. 168 (2), 784–789.
- Sampa, M.H.O., Takacs, E., Gehringer, P., Rela, P.R., Ramirez, T., Amro, H., Trojanowicz, M., Botelho, M.L., Han, B., Solpan, D., Cooper, W.J., Emmi, S.S., Wojnarovits, L., 2007. Remediation of polluted waters and wastewater by radiation processing. Nukleonika 52 (4), 137–144.
- Sánchez-Polo, M., López-Peñalver, J., Prados-Joya, G., Ferro-García, M.A., Rivera-Utrilla, J., 2009. Gamma irradiation of pharmaceutical compounds, nitroimidazoles, as a new alternative for water treatment. Water Res. 43 (16), 4028–4036.
- Shuto, A., Ohgai, M., Eto, M., 1989. Screening of tryptophan synthase inhibitors as leads of herbicide candidates. J. Pestic. Sci. 14 (1), 69–74.
- Sun, W., Chen, L., Tian, J., Wang, J., He, S., 2013a. Degradation of a monoazo dye Alizarin Yellow GG in aqueous solutions by gamma irradiation: decolorization and biodegradability enhancement. Radiat. Phys. Chem. 83, 86–89.
- Sun, W., Chen, L., Tian, J., Wang, J., He, S., 2013b. Radiation-induced decomposition and polymerization of polyvinyl alcohol in aqueous solutions. Environ. Eng. Manag. J. 12 (7), 1323–1328.
- Sun, W., Chen, L., Zhang, Y., Wang, J., 2015. Synergistic effect of ozonation and ionizing radiation for PVA decomposition. J. Environ. Sci. (China) 34, 63–67.
- Sun, W., Tian, J., Chen, L., He, S., Wang, J., 2012. Improvement of biodegradability of PVA-containing wastewater by ionizing radiation pretreatment. Environ. Sci. Pollut. Res. 19 (8), 3178–3184.
- Tolgyessy, P., Kollar, M., Vanco, D., Piatrik, M., 1986. The radiation treatment of waste water solutions containing 2-mercaptobenzothiazole and N-oxydiethylene-2benzothiazolesulfenamide. J. Radioanal. Nucl. Chem. Lett. 107 (5), 315–320.
- Vahdat, A., Bahrami, S.H., Arami, M., Motahari, A., 2010. Decomposition and decoloration of a direct dye by electron beam radiation. Radiat. Phys. Chem. 79 (1), 33–35.
- Wojnarovits, L., Takacs, E., 2008. Irradiation treatment of azo dye containing wastewater: an overview. Radiat. Phys. Chem. 77 (3), 225–244.
- De Wever, H., Besse, P., Verachtert, H., 2001. Microbial transformations of 2-substituted benzothiazoles. Appl. Microbiol. Biotechnol. 57 (5–6), 620–625.
- De Wever, H., Verachtert, H., 1997. Biodegradation and toxicity of benzothiazoles. Water Res. 31 (11), 2673–2684.