# The radiolytic mineralization of 2-mercaptobenzothiazole, an emerging contaminant in aqueous solution

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**Abstract:**The ability of high-energy ionizing radiation has been demonstrated for environmental remediation processing. γ-rayswere applied to treat a solution of 2-mercaptobenzothiazole (2-MBT). 2-MBT (125 µM) was decomposed and mineralized by the γ-radiation. The absorbed doses for 50 and 90% 2-MBT degradation were 0.170 and 0.650 kGy, respectively. Organic by-products were almost fully mineralized when high-absorbed doses in the range of 5-60 kGy were applied. Sulfate radicals ($SO_4^{\bullet-}$) produced through the rapid reaction of persulfate ions ($S_2O_8^{2-}$) with hydrated electrons($e_{aq}^-$; $k_{e_{aq}^-/S_2O_8^{2-}} = 1.1 \times 10^{10}$ $M^{-1}.s^{-1}$) had a significant effect on the 2-MBT mineralization yield. Because of 2-MBT decomposition,sulfate ions ($SO_4^{2-}$) were formed, and thepH and dissolved oxygen concentration were decreased. The degradation efficiency decreased when $HCO_3^-$was added to the 2-MBT solution. No significant effects of $NO_3^-$ and $Cl^-$ ions on 2-MBT radiolytic eliminationwere observed.
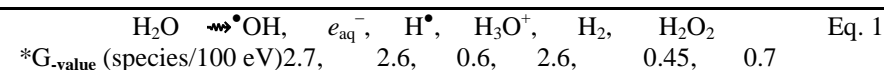
**Keywords:** 2-Mercaptobenzothiazole; Mineralization; Ionizing radiation;Persulfate ions.

**Highlights**

●Hydroxyl radicals issuing from high-energy irradiation are good species for environmental remediation.

● γ-Irradiation effectively mineralizes the 2-MBT heterocyclic compound in aqueous solution.

●Acidification, desulfurization and dissolved oxygen consumption are observed and discussed.

●$SO_4^{\bullet-}$ radicalshave a high impact on the elimination of organic carbon.

## I.      Introduction

Since the 1970s, high-energy ionizing radiation has been demonstrated to possess high efficiency and reliability for water remediation [1]. A large and growing body of literature has focused on high-energy ionizing radiation as one of the most effective advanced oxidation processes (AOPs) that can effectively be applied for water remediation, because of the predominant simultaneous formation of roughly equivalent amounts of two active oxidizing and reducing species, hydroxyl radical ($^\bullet OH$; $E^\circ = 1.9$ V; [2]) and hydrated electrons ($e_{aq}^-$; $E^\circ = -2.9$ V), respectively, by the phenomenon of water radiolysis, as shown in Eq. 1 [3, 4].

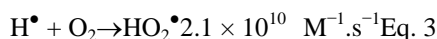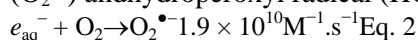| $H_2O$ | $\rightsquigarrow ^\bullet OH$, | $e_{aq}^-$, | $H^\bullet$, | $H_3O^+$, | $H_2$, | $H_2O_2$ | Eq. 1 |
|---|---|---|---|---|---|---|---|
| *G-**value** (species/100 eV)2.7, | | 2.6, | 0.6, | 2.6, | 0.45, | 0.7 | |

*The yield in µmol/J of those species per unit of radiation at neural pH.

Additionally, this technology can be used at room temperature and often requires no additional hazardous chemicals to enhance its efficiency. Several studies (at both laboratory and industrial scale) have demonstrated the potential of this promising technology and its suitability for environmental remediation aspects, especially in the field of water treatment. For example, it has been tested for municipal wastewater plant and sludge [5,6,7], effluents from the dye industry [8], industrial wastewater [9,10] and gas treatment [11]. In addition, there are many studies on the elimination of organic contaminants in aqueous solution by ionizing radiation at the laboratory or semi-industrial scale,e.g., pharmaceutical compounds and endocrine disruptors [12-15], persistent

contaminants [16,17], sulfonated aromatic compounds [18], dyes [19,20], pesticides [21,22], carboxylic acids [23,24],and phenols [25,26].

Moreover, interestingly, high-energy ionizing radiation has been successfully and commercially used for food preservation [27-29], materials improvement [30,31] and medical device sterilization [32,33]. In addition, there have been several recent studies on the progress of irradiation methods for petroleum processing and curing [34,35].

When the samples to be irradiated are air saturated (7-8 mg $O_2$/L), reducing species ($e_{aq}^-$ and atomic hydrogen; ${}^\bullet$H) are scavenged by the dissolved oxygen to convert it to superoxide radical anion ($O_2^{\bullet-}$) andhydroperoxyl radical ($HO_2^\bullet$), respectively, (Eqs. 2 and 3) [3,4].

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-} \quad 1.9 \times 10^{10} M^{-1}.s^{-1} \quad Eq.\ 2$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \quad 2.1 \times 10^{10} \ M^{-1}.s^{-1} \quad Eq.\ 3$$

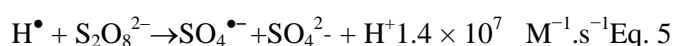$$HO_2^\bullet H^+ \leftrightarrow O_2^{\bullet-} \quad pk = 4.8$$

Benzothiazole compounds are among the most widely used heterocyclic compounds in industry. They are used in the rubber industries, fungicide manufacture, photography photosensitizers, paper production, and wood preservation. Because of their wide application, benzothiazolesare considered to be environmental contaminants for aquatic systems [36,37].

2-MBT is thebenzothiazolemost frequently represented in the literature. This xenobiotic compound is considered resistant to conventional biological treatment. It is toxic and can inhibit bacterial growth [37-39]. 2-MBT and its derivatives have been detected in aquatic environments in the 0.04 ng/L to 20 mg/L range [40,41], includingin rivers [42-44], lakes [45], wastewater plants [40,46,47], ground water [48], surface water [49,50], tannery wastewater [51,52], marine water [53] and drinking water [54]. In addition, it has been found in street runoff [55], street dust [56], and atmospheric aerosol [57] and in some biota samples [58].

Various AOP treatmentsto degrade 2-MBT and its derivatives in aqueous solutions have been tested including:ozonation [40, 59], resultsobtained by Fiehn et al. [59] showed that 2-MBT (600 μM, $pH_i$ 7) had been eliminated in pure water and in industrial effluents at short time of ozonation, an oxidation pathway had also been suggested.Puig et al. [40] found that after ozone decontamination, the acute toxicity measured as $EC_{50}$ was three time less; photolysis [60-62], $H_2O_2$/UV and Fe (II)-photoassisted Fenton system were investigated on the removing of the 2-MBT and its deriviatives;photodegradation [63,64], the effect of ion oxide and oxalate on the photdegradation of 2-MBT was investigated by Liu et al. [64];photocatalysis [65-67], Li et al., [66], found that 2-MBT (0.278 mM) was fully eliminated using the photo-Fenton reaction,also,according to Habibi and co-workers [67], 2-MBT and its derivatives were almost completely mineralized by photo-catalytic process; Manganese oxides [68]; andby ionizing radiation (γ-irradiation) [16, 38, 69].Bao et al. [38] applied 1.2 kGyto remove 82% of 2-MBT (20 mg/L, 120 μM, $pH_i$ 9). Additionally, they reported that the absorbed doses needed for 2-MBT radiolytic elimination were not proportional to the initial concentration of 2-MBT. Bao et al. [16] found that the addition of 0.2 mM $S_2O_8^{2-}$ for the radiolytic elimination of 2-MBT (120 μM; $pH_i$ = 9) only enhanced the early stage of its degradation. Their results showed that at an absorbed dose of 1.2 kGy, the removals with and without $S_2O_8^{2-}$ were 93% and 89%, respectively. High-energy γ-irradiation technology has been used as a pretreatment for 2-MBT-containing wastewater. However, the TOC and BOD values remained unchanged [69]. Generally, in these studies, 2-MBT and its derivatives were found to be degraded. Nevertheless, mineralization could not be achieved completely.

To enhance the process efficiencyof eliminating organic contaminants by ionizing radiation, there has been increasinginterest in coupling persulfate ions ($S_2O_8^{2-}$) dissolved in aqueous solution with high-energy radiation, which induces the formation of sulfate radical ($SO_4^{\bullet-}$, $E^\circ$ = 2.43 V; [2]) by the reaction majority between $S_2O_8^{2-}$ and the reducing species ($e_{aq}^-$; $H^\bullet$, Eqs. 4; 5 [3]).

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad 1.1 \times 10^{10} M^{-1}.s^{-1} \quad Eq.\ 4$$

$$H^\bullet + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \quad 1.4 \times 10^7 \ M^{-1}.s^{-1} \quad Eq.\ 5$$

The effectiveness of $SO_4^{\bullet-}$ radical was evaluated based on the removal and mineralization of organic pollutants in aqueous solutions i.e. phenol [70], endocrine disruptors and pharmaceutical compounds [12-14], pesticide and refractory pollutants [16,71].

## II. Experimental

### II.I.      Reagents and chemicals

All chemical reagents used in this study were of high-purity analytical grade and were used without any further purification. Methanol (HPLC plus-gradient grade) was purchased from AppliChem Panreac (Germany).Sodium persulfate ($S_2O_8^{2-}$, 98%) was purchased from Acros Organics (USA),while sodium chloride (NaCl),sodium bicarbonate ($NaHCO_3$), sodium nitrate ($NaNO_3$) and orthophosphoric acid (85%) were purchased from Sigma-Aldrich (USA).

As stated previously, 2-mercaptobenzothiazole (2-MBT) ($C_7H_5NS_2$; CAS number 149-30-4; pKa = 6.95;water solubility =0.12 g/L at 25 °C; log $K_{ow}$=2.4) was selected as the model industrial heterocycliccontaminant; thiswas also supplied by Sigma-Aldrich (USA) (97%). Its chemical structure is presented in Fig. 1.
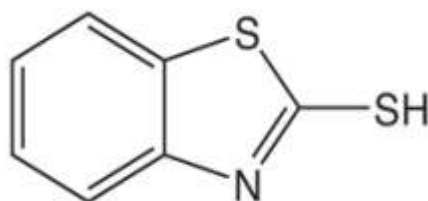


**Figure 1**Chemical structure of heterocyclic 2-MBT

### II.II.      Solution preparation and experimental setup

Aqueous solutions of 2-MBTwith an initial concentration of126± 2μM were prepared in deionized water (Milli-Q device,Elix Technology inside Integral 5 Millipore) and placed in 40 mL or 2 mL vials using airtight caps with Teflon-based silicone septa. These solutions were irradiated. The initial solution concentration of dissolved oxygen was 7.5± 0.6 mg/L, and the initial pH was 6.8. The sample irradiation was conducted using Co-60 Gamma Cell 220 from MDS-Nordion, Canada. The source was calibrated using aqueous ferrous sulfate (Fricke solution; [72]). The dose rate for all experiments was 4.1 kGy/h, and the transit dose was estimated to be 7 Gy. Aqueous solutions were irradiated over the range 0.1−60 kGy. To verify the stability of 2-MBTwith the $S_2O_8^{2-}$, theconcentrations of 2-MBT were determined at the beginning and end of each experiment. Significant changes were observed in2-MBTconcentration (without irradiation).However, the major advantage of combined γ-ray/$S_2O_8^{2-}$was observed on removal of organic by-products.

### II.III.      Analytical methods

The initial and residual concentrations of 2-MBT were determined by ultra-performance liquid chromatography (UPLC-Nexera X2, SHIMADZU). UV detection was performedat322 nm. The column was a Raptor™ ARC−18 (5 μm,150×4.6 mm; Restek), the flow rate was 0.7 mL/min, the injection volume was 20 μL, and the mobile phase contained 50% methanol and 50% ultra-pure water acidified with 0.1% orthophosphoric acid (pH = 2.2). A good peak shape of 2-MBT solution was obtained. The expected ions that could be formed (nitrate,$NO_3^{2-}$; sulfate,$SO_4^{2-}$) were analyzed using an ion chromatograph (HIC-20A SUPER, SHIMADZU).The TOC content was determined using a Shimadzu TOC analyzer (TOC-L) connected to an ASI-L auto-sampler system. pH and dissolved oxygen were measured before and after irradiation of the solutions using a Cello 325 oxygen probe (WTW model 740) and a Sentix 81 pH electrode, respectively; calibration of the pH and oxygen meters was performed in prior experiments. The 2-MBT degradation yield was calculated from the relation:

$$\text{2-MBT degradation yield, \%}=([\text{2-MBT}]_0-[\text{2-MBT}]_i)/[\text{2-MBT}]_0\text{x}100$$

Where [2-MBT]$_0$and [2-MBT]$_i$are the concentration before and after irradiation respectively.

# III. Results and discussion

## III.I. 2-MBT degradation

The elimination of 2-MBT (126 µM) by γ-radiation is shown in Fig. 2. The residual concentration of 2-MBT dramatically decreased with increasing absorbed dose, which can be effectively attributed to the formation of $^\bullet$OH radical from the radiolysis of the 2-MBT aqueous solution (Eq. 6) [60]. The elimination efficiency could reach almost 100% at an absorbed dose of 2.5 kGy. For absorbed doses of 0.17 and 0.4 kGy, the concentration of 2-MBT decreased by 50% and 80%, respectively. As shown in the inset of Fig. 2, the relationship between the absorbed dose and $-\ln(C/C_\bullet)$ was found to be linear, thus suggesting that the elimination of 2-MBT followed pseudo-first-order kinetics.
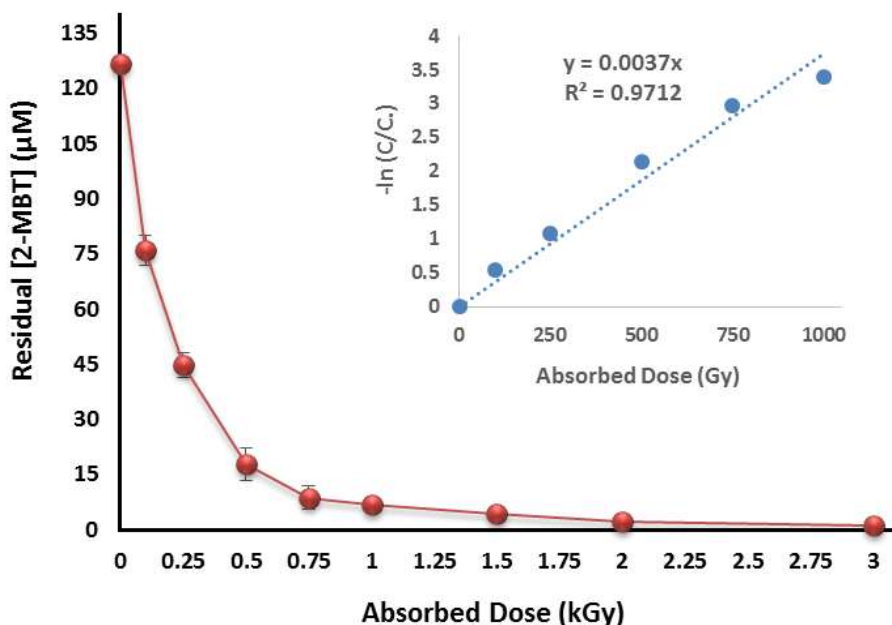
$$HO^\bullet + \text{2-MBT} \rightarrow \text{by-products} \qquad 4.3 \times 10^9 \ M^{-1}.s^{-1} \qquad \text{Eq. 6; [60]}$$



**Figure 2** 2-MBT degradation by γ-irradiation ($pH_i$=6.7±0.15; $[O_2]_i$=7.5±0.65 mg/L)

The $G_{value}$ at an absorbed dose of 0.5 kGy was calculated to be 0.22 µmol/J; at this value, the elimination yield was 86%. The study conducted by Bao et al. [38] cited 1.75 µmol/J for 60% elimination of 2-MBT at an absorbed dose of 0.5 kGy. They also observed that the $G_{value}$ increased and that the dose constant decreased as the initial concentration of 2-MBT increased. Table 1 shows the removal efficiency of 2-MBT by γ-irradiation.

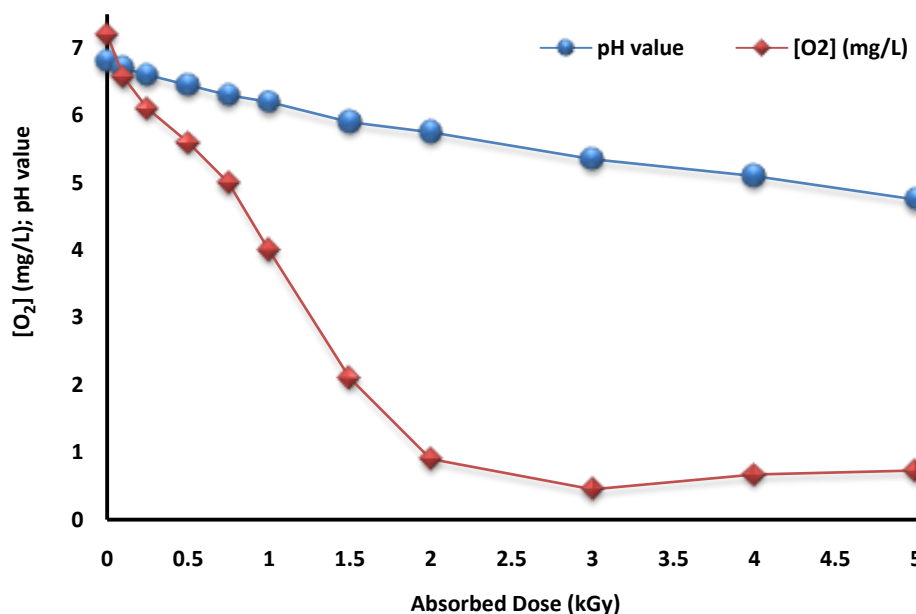**Table 1** Removal efficiency of 2-MBT by γ-radiation.

| [2-MBT]$_i$=125 µM; pH$_i$=6.8 | $D_{50; 90\%}$ (kGy) | k (Gy$^{-1}$) | $G_{value}$ 0.5kGy (µmol J$^{-1}$) | R$^2$ |
|---|---|---|---|---|
| | 0.170; 0.650 | 0.0037 | 0.221 | 0.97 |

Additionally, the results reveal that 2-MBT was not stable in the presence of two initial concentrations of $S_2O_8^{2-}$ (0.5 and 1 mM), and no peaks of 2-MBT were detected by UPLC with either concentration. This indicates that the 2-MBT was oxidized without irradiation by $S_2O_8^{2-}$ ($E^\circ = 2$ V; [73]). Nevertheless, results obtained by Bao et al. [16] show that the addition of $S_2O_8^{2-}$ induced a significant enhancement for 2-MBT elimination in the early stage of its elimination. For an absorbed dose of 0.5 kGy, 28% and 48% of 2-MBT was degraded without and with $S_2O_8^{2-}$ (0.2 mM) respectively. However, its addition to the 2-MBT aqueous solution clearly enhanced the TOC radiolytic elimination.

*III.II. Evolution of dissolved oxygen, pH and $SO_4^{2-}$ ions*

As illustrated in Fig. 3, the radiolytic elimination of 2-MBT induced a noticeable decrease in pH with an increase in the absorbed doses. The pH values were 6.6 and 4.75 at absorbed doses at 0.25 and 5 kGy.



**Figure**3 Changes of dissolved oxygen concentration and pH

This decrease of pH could be attributed to the release of $SO_4^{2-}$ ions by the decomposition of 2-MBT and the formation of carboxylic acid (carboxyl group) from the degradation of 2-MBT. Hence, water radiolysis leads to a decrease in pH (Eq. 1). These results are consistent with those obtained by Alkhuraiji and Leitner [18] and Boukari et al. [25]. As withpH, the dissolved oxygen concentration decreases with increases in the absorbed dose. The reduction of dissolved oxygen during the radiolytic elimination of 2-MBT indicates that the mechanism of 2-MBT oxidation involves dissolved oxygen, from the reaction of organic radical ($^•$R) with dissolved oxygen [4]. A second cause could be related to the consumption of dissolved oxygen by hydrated electron (Eqs. 2-3). These observations also agree with those obtained by Alkhuraiji and Leitner [18] and Criquet and Leitner [23]. Almost 94% of the initial concentration of dissolved oxygen was consumed at an absorbed dose of 3 kGy. Then, a tendency toward less consumption was observed. This result could be attributed to the fully oxygenated organic compounds formed and to the full destruction of the aromatic ring.
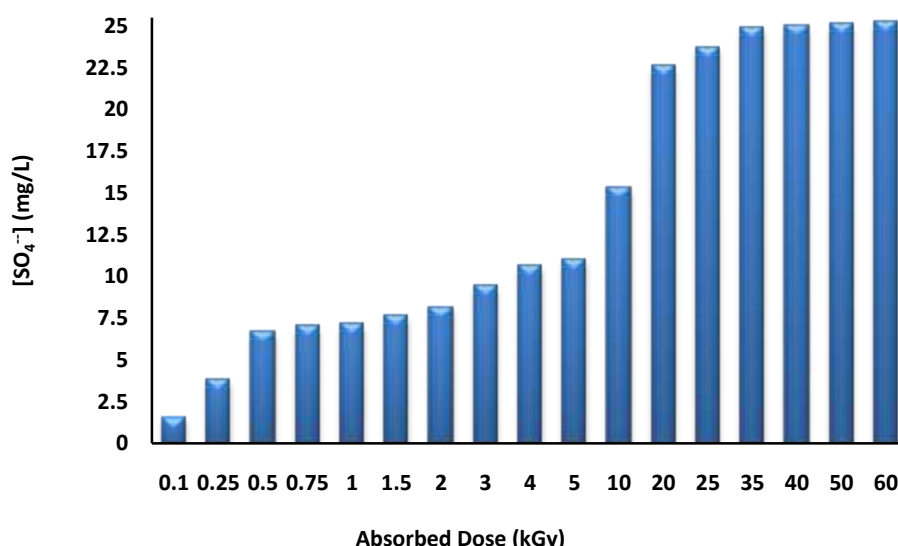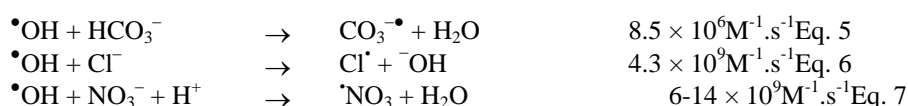
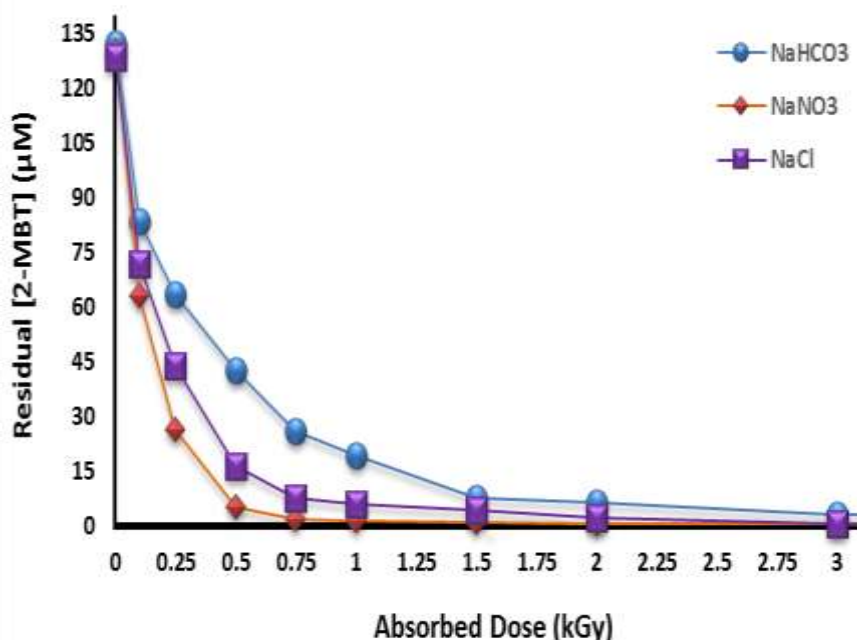**Figure**4$SO_4^{2-}$ formation from 2-MBT as a function of absorbed dose.

2-MBT contains two sulfur atoms (-SH group and thiazole cycle) and one nitrogen atom (thiazole group) in its heterocyclic structure (Fig. 1). The degradation of 2-MBT by γ-radiation was followed by the release of $SO_4^{2-}$, whereas no formation of nitrite ($NO_2^-$) or nitrate ($NO_3^-$) ions was observed. The concentration of $SO_4^{2-}$ formed increased notablywith increasing absorbed dose (Fig. 4). However, the dose applied (2.5 kGy) for the total elimination of 2-MBT yielded 30% desulfuration, with 7.6 mg/L of $SO_4^{2-}$formed, thus demonstrating the presence of organic by-products with sulfur in their chemical structure. It has been reported that $HO^\bullet$ radical will preferentially attack the −SH group [16]. For absorbed doses of 1, 5 and 20 kGy, 7.1, 11 and 22.5 mg/L $SO_4^{2-}$were formed, respectively. For an absorbed dose of 20 kGy, 94% of sulfur atoms were oxidized to $SO_4^{2-}$ ions, while at the same absorbed dose, Bao et al. [16] obtained 26% desulfuration.In addition to $SO_4^{2-}$ formation, ammonium ($NH_4^+$) and nitrate have been reported to be formed during 2-MBT photodegradation (F. Li et al.[66]).

*III.III.    Effect of inorganic salts on 2-MBT degradation*

Three sets of experiments were conducted to evaluate how the radiolytic degradation of 2-MBT by γ-radiation was affected by the addition of $NaHCO_3$ (300 mg/L; $pH_i$=8.7), $NaNO_3$ (520 mg/L; $pH_i$=6) or NaCl (480 mg/L; $pH_i$=5.8). The experimental results (Fig. 5) showed that 2-MBT degradation was affected by the presence of $NaHCO_3$ (Eq. 5) whereas the presence of $NaNO_3$ and NaCl had no significant effect on the radiolytic elimination of 2-MBT (Eqs. 6, 7 [3]).

$$^\bullet OH + HCO_3^- \quad \rightarrow \quad CO_3^{-\bullet} + H_2O \qquad 8.5 \times 10^6 M^{-1}.s^{-1} \text{Eq. 5}$$
$$^\bullet OH + Cl^- \quad \rightarrow \quad Cl^\bullet + {}^- OH \qquad 4.3 \times 10^9 M^{-1}.s^{-1} \text{Eq. 6}$$
$$^\bullet OH + NO_3^- + H^+ \quad \rightarrow \quad {}^\bullet NO_3 + H_2O \qquad 6\text{-}14 \times 10^9 M^{-1}.s^{-1} \text{Eq. 7}$$
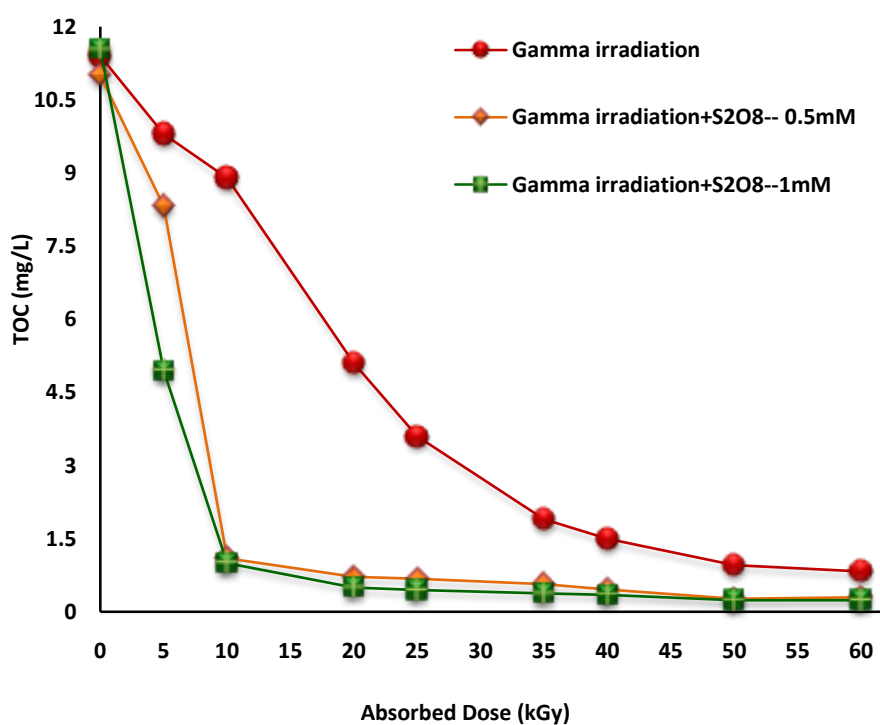
**Figure**5Removal of 2-MBT in aqueous solutions by γ-rayinthe presence of NaHCO$_3$, NaNO$_3$ and NaCl

The HCO$_3^-$ ions were scavenged by $^•$OH radicals (Eq. 5). However, the elimination of 2-MBT in the presence of NaCl and NaNO$_3$was still significant, and no difference in its elimination with or without the presence of NaCl and NaNO$_3$ was observed. At an absorbed dose of 0.75 kGy, the removals achieved were approximately 80% (NaHCO$_3$), 98.5% (NaNO$_3$) and 94% (NaCl).

*III.IV. Mineralization of 2-MBT and the effect of $S_2O_8^{2-}$*

The elimination of organic carbon of 2-MBT (11.05±0.35 mg C/L) was conducted at several high-absorbed doses, and the effects of two concentrations of $S_2O_8^{2-}$ (0.5 and 1 mM) were examined. The results presented in Fig. 6 show that the elimination of TOC without $S_2O_8^{2-}$ addition required a high-absorbed dose. However, a very notable improvement of TOC elimination was obtained by adding the two concentrations of $S_2O_8^{2-}$ ions. The removal of TOC for both concentrations of persulfate ions was similar.

**Figure** 6 TOC concentration (mg C/L) for 2-MBT as a function of the absorbed dose in the presence of $S_2O_8^{2-}$ ion

For absorbed doses of 5, 10 and 25 kGy, the reductions in TOC removal were 14, 22 and 68%. However, at an absorbed dose of 35 kGy, where the desulfuration was total, the mineralization yield was approximately 83%. This result indicates that the organic by-products remaining in the system contained no sulfur in their chemical structures. The combined system of $\gamma$-rays/$S_2O_8^{2-}$ led to a dramatic decrease in the energy needed to eliminate the organic carbon. Almost full mineralization was observed at an absorbed dose of 25 kGy. The improvement of the mineralization efficiency with the $\gamma$-ray/$S_2O_8^{2-}$ systemwas clearlyattributable to the generation of $SO_4^{\bullet-}$radical, whichis considered to be more selective than $HO^{\bullet}$ radical (Eq.4).

## V. Conclusion

The application of high-energy radiation from Co-60 has been demonstrated to degrade theheterocyclic 2-MBT compound and its by-products with high efficiency. The efficiency of the 2-MBT degradation increased by increasing the absorbed dose. For an initial 2-MBT concentration of 126 µM, the doses necessary to eliminate 50 and 90% of 2-MBT were 0.170 and 0.650 kGy. The 2-MBT degradation process followed first-order kinetics. The dose constant for 2-MBT elimination was determined to be 0.0037 $Gy^{-1}$. The $G_{value}$ at an absorbed dose of 0.5 kGy was calculated to be 0.22 µmol/J, where the degradation yield was 86%. The degradation efficiency of 2-MBT was affected when $HCO_3^-$ion was added to the solution. The combination of $\gamma$-rays/$S_2O_8^{2-}$ was very favorable towards organic carbon elimination.

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