

# Gamma radiolytic decomposition of endosulfan in aerated solution: the role of carbonate radical

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**Abstract** The present study elaborates the removal of endosulfan, an emerging water pollutant and potential carcinogenic, in aerated solution. The influence of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_3^{2-}$ , and humic acid was assessed on the radiolytic degradation of endosulfan. A strong inhibition on the radiolytic degradation of endosulfan was observed in the presence of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_3^{2-}$ . Instead, a slight increase in the removal efficiency of endosulfan was observed at high concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . The formation of  $\text{CO}_3^{\bullet-}$  in radiolytic degradation of endosulfan in the presence of

$\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  was demonstrated by adding  $\text{SO}_3^{2-}$  that rapidly react with  $\text{CO}_3^{\bullet-}$ . The results indicate that  $\text{CO}_3^{\bullet-}$  formed from the reactions of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  and commonly found in natural water can play an important role in the degradation of endosulfan and other sulfur containing electron-rich compounds. The study showed faster degradation of endosulfan at lower concentration compared to high concentration and removal was found to follow *pseudo-first-order* kinetic. Endosulfan ether was found as the main degradation product and degradation pathway was found to be initiated at the S=O bond of endosulfan. The efficiency of gamma irradiation in the removal of endosulfan was examined in terms of formation of short chain organic acids and chloride ion accumulation.

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**Highlights** • Removal of endosulfan was assessed by gamma irradiation in aerated solution.

- Superoxide and carbonate radical played significant role in endosulfan degradation.
- Removal efficiency and dose constant decreased with increasing endosulfan concentration.
- By-products and short chain organic acids were evaluated.
- Gamma radiation proved to be effective in toxicity reduction of chlorinated compounds.

**Keywords** AOPs · Carbonate radical · Endosulfan · Gamma irradiation · Water treatment

## Introduction

Organochlorine pesticides (OCP) are a large group of pesticides that have been extensively used throughout the world for control of pests and pests causing diseases in agriculture as well as in household (Jiang et al. 2009). Most classes of OCP have been banned due to their high toxicity and persistent nature; however, some are reported to be still synthesized and used on a large scale in different countries of the world (Wandiga 2001). Endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1-heptene-2,3-bis-hydroxymethane-5,6-sulfite) is one of the important class of OCPs that is still synthesized on a large scale and used in many, mostly developing, countries of the world. The extensive applications had led to the presence of endosulfan (ES) in many environmental matrices, such as water (Shah et al. 2014). The US Environmental Protection

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Agency (US EPA) classified endosulfan to be highly hazardous pesticide (category Ib) as well as highly persistent in water with half life ranging from several months to several years depending upon the conditions under study (US EPA 2002). Endosulfan is reported to be highly toxic and is concerned in mammalian toxicity (Verma et al. 2011), genotoxicity (Lu et al. 2000), neurotoxicity (Paul and Balasubramaniam 1997), as well as affect soil fertility, crop productivity, and ecological balance (Shah et al. 2015a). Therefore, increased contamination of water resources with endosulfan has become an important issue of worldwide concern. Thus, cost-effective, efficient, and environmentally friendly technologies for removal of endosulfan from contaminated water are necessary to be hypothesized.

Advanced oxidation processes that rely on the in situ generation of reactive radicals have proved to be effective in the treatment of a wide class of emerging water pollutants (Pera-Titus et al. 2004; Pozo et al. 2006; Khan et al. 2013, 2014a, 2015a; Shah et al. 2015a). Advanced oxidation processes (AOPs) are innovative treatment technologies for conversion of organic pollutant into simple biodegradable and harmless products and even mineralization to carbon dioxide, water, and other inorganics (Cavalcante et al. 2013; Pera-Titus et al. 2004; Pozo et al. 2006; Khan et al. 2014b, 2015b; Shah et al. 2015b). Among different AOPs, ionizing radiation has been proven to be the most significant, efficient, environmentally friendly, and can yield both reducing and oxidizing reactive species (Shah et al. 2014).

A few studies account on the removal of endosulfan and related organochlorine pesticides from water by AOPs used hydroxyl and sulfate radicals, and aqueous electron (Shah et al. 2013; Shah et al. 2014). Recently, carbonate radical ( $\text{CO}_3^{\cdot-}$ ) formed through the reaction of reactive radical with carbonate and/or bicarbonate ion has been gaining researchers' attention because of its high reactivity and redox potential ( $E_0 = 1.78 \text{ V}$ ) (Wu and Linden 2010). The  $\text{CO}_3^{\cdot-}$  exists in natural water in the concentration range from  $10^{-13}$  to  $10^{-15} \text{ M}$  and is highly selective in reaction with the target contaminant and react primarily through electron transfer reaction (Wu and Linden 2010).

The previous study on the removal of endosulfan by reactive radicals from gamma irradiation was concerned to deaerated (oxygen-free) solutions (Shah et al. 2014). There is, however, very limited study for removal of endosulfan and related compounds in aerated (oxygenated) solutions. Natural water contains high concentrations of oxygen; removal of endosulfan from aerated aqueous solution is highly vital for literature information and potential practical applications.

The present study investigated the removal of endosulfan by gamma irradiation in aerated aqueous solution. The effects of carbonate and superoxide radicals on the removal of endosulfan was assessed. The effects of initial concentrations and radical scavengers were also studied for potential practical

applications on a large-scale treatment of endosulfan by gamma irradiation. Toxicity evaluation and main degradation products of endosulfan in aerated solution were also suggested.

## Materials and methods

### Materials

The chemicals used were solid endosulfan and endosulfan ether with a purity of 99.6 %, purchased from Supelco (PA, USA). Other chemicals, e.g., sodium nitrite ( $\text{NaNO}_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), potassium chloride (KCl), sodium bicarbonate ( $\text{NaHCO}_3$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), sodium acetate ( $\text{CH}_3\text{CO}_2\text{Na}$ ), and sodium formate ( $\text{HCO}_2\text{Na}$ ) were also of high purity and purchased from Scharlau. Ultra pure water (resistivity,  $18.2 \text{ M}\Omega \text{ cm}$ ) obtained from Milli-Q® system (Millipore) was used as a solvent for preparation of all solutions.

### Analysis

The analysis of endosulfan and endosulfan ether was carried out using an Agilent 6890 series gas chromatography (GC) equipped with  $\text{Ni}^{63}$  electron capture detector (ECD) and an HP-5 (5 % phenyl methylsiloxane) capillary column ( $30 \text{ m} \times 0.25 \text{ mm I.D.}$  and  $0.25\text{-}\mu\text{m}$  thickness). The detail operational conditions were explained in our previous publication (Shah et al. 2014). Solid phase microextraction (SPME) with the polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber purchased from Supelco (USA) and fitted with CTC autosampler (CombiPAL, Switzerland) was used for extraction of endosulfan and endosulfan ether as well as directly injecting into the injector of the GC.

The analysis of chloride, acetate, and formate ions formed from the radiolytic degradation of endosulfan in aerated aqueous solution was carried out using ion chromatography (IC, Metrohm) with electrical conductivity detector. This was done following the method for anion determination on IC using Assup-5 column ( $250/4.0 \text{ mm}$ ), with  $3.2 \text{ mM Na}_2\text{CO}_3/1 \text{ mM NaHCO}_3$  as an eluent at a flow rate of  $0.75 \text{ mL min}^{-1}$ .

The by-products, both organic and inorganic, were identified by comparison of retention time with that of authentic standard compounds under the similar experimental conditions (Choi et al. 2010; Shah et al. 2014).

### Gamma irradiation source and procedure

Cobalt-60 gamma-ray source (model Issledovadel, origion USSR) installed at the Nuclear Institute for Food and Agriculture (NIFA), Tarnab, Peshawar, was used for gamma radiation treatment of aqueous endosulfan solution. The

calibration of radiation source for dose rate determination and treatment of endosulfan in the radiation chamber are explained in our previous study with a typical dose rate reported to be 296 Gy h<sup>-1</sup> (Shah et al. 2015b).

An aqueous solution of endosulfan was sparged with oxygen gas for 25 min. The sparging of aqueous solution of the target contaminant with O<sub>2</sub> has been reported to contain 1.4 × 10<sup>-3</sup> M of dissolved oxygen (Földváry and Wojnárovits 2009). The pH of all irradiated solutions was 6.5, except in the case of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> where pH 10.5 and 7.4, respectively, were used.

## Results and discussion

Gamma radiations are highly energetic electromagnetic radiations with an energy level that ranges from around 10 keV to several hundred kiloelectron volts and thus have high penetrating power. When treated with gamma irradiation, dilute aqueous solution of endosulfan undergoes radiolysis of water and as a result, reactive radicals and molecular products are formed as shown by Eq. (1) (Khan et al. 2015b; Shah et al. 2014). The values in small bracket with reactive radicals and molecular products in Eq. (1) show radical and molecular products yields (μmol J<sup>-1</sup>) of the primary radiolytic products of water radiolysis (Shah et al. 2014). Among the primary radiolysis products, e<sub>aq</sub><sup>-</sup> and <sup>•</sup>OH have been reported to be highly reactive due to their high redox potential (Shah et al. 2013, 2014). Both e<sub>aq</sub><sup>-</sup> and <sup>•</sup>OH react fast with endosulfan due to their high second-order rate constant values, i.e., 5.9 × 10<sup>9</sup> and 1.83 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively (Shah et al. 2014). Under certain conditions, however, the reactive radicals undergo competitive reactions and thus affect their reactivity with the target contaminant: (1 = in the presence of dissolve oxygen (aerated solution), e<sub>aq</sub><sup>-</sup> and <sup>•</sup>H are converted into superoxide radical (O<sub>2</sub><sup>•-</sup>) and hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>) as shown by Eqs. (2) and (3), respectively (Buxton et al. 1988; Shah et al. 2014); (2 = in aerated solution and in the presence of chloride ion, the <sup>•</sup>OH is scavenged yielding ClOH<sup>•-</sup> (Eq. (4)) that further reacts and yield reactive chlorine radical (Cl<sup>•</sup>/Cl<sub>2</sub><sup>•-</sup>) (Buxton et al. 1988; Shah et al. 2013); (3 = in aerated solution and in the presence of carbonate and bicarbonate ions, the <sup>•</sup>OH is scavenged yielding carbonate radical (CO<sub>3</sub><sup>•-</sup>) as shown by Eqs. (5) and (6) (Buxton et al. 1988).

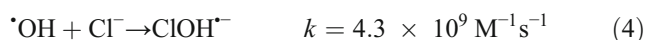
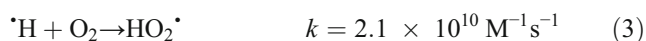
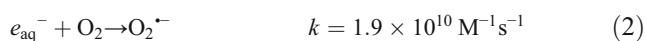
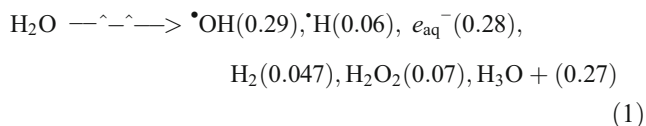
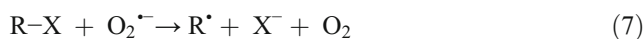


Table 1 shows the radiolytic degradation of endosulfan in aerated solution in the absence and presence of 1 mM of each chloride, carbonate, and bicarbonate ions for a radiation dose of 0–1020 Gy. At an absorbed dose of 1020 Gy, radiolytic degradation of endosulfan was 80 % in aerated solution as compared to 76, 78, and 77 % in the presence of Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>, respectively. In aerated solution as already said somewhere in the present study, e<sub>aq</sub><sup>-</sup> and <sup>•</sup>H are converted into superoxide radical (O<sub>2</sub><sup>•-</sup>) and hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>) thus leaving O<sub>2</sub><sup>•-</sup>, HO<sub>2</sub><sup>•</sup>, and <sup>•</sup>OH for reaction with endosulfan (Al-Sheikhly et al. 1997). The high second-order rate constant of <sup>•</sup>OH with endosulfan (ES) (k<sub>OH/ES</sub> = 1.83 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) (Shah et al. 2013) might be one of the possible reason for high degradation of endosulfan in aerated solution in the present study. Besides, O<sub>2</sub><sup>•-</sup> has been reported to induce reductive dechlorination of halogenated compounds (R–X), such as endosulfan and yield carbon-centered radical as shown by Eq. (7) (Sampa et al. 2007). The carbon-centered radical further react with air and converted into peroxy radicals (Eq. 8) that after several complicated unimolecular and bimolecular stepwise reactions converted into final products (Eq. 9) (Sampa et al. 2007).



The high second-order rate constant of <sup>•</sup>OH with endosulfan and the faster reductive dechlorination reaction by O<sub>2</sub><sup>•-</sup> suggest involvement of <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> in the radiolytic degradation of endosulfan in aerated solution. Based on the reported second-order rate constant of e<sub>aq</sub><sup>-</sup> with endosulfan (ES, k<sub>ES/e<sub>aq</sub><sup>-</sup></sub> = 5.1 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) (Shah et al. 2014) and with O<sub>2</sub> (k<sub>O<sub>2</sub>/e<sub>aq</sub><sup>-</sup></sub> = 1.9 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>) (Buxton et al. 1988) and concentration of dissolved oxygen in aerated solution (i.e., [O<sub>2</sub>] = 1.4 × 10<sup>-3</sup> M) (Földváry and Wojnárovits 2009) and

**Table 1** Removal efficiency (%) of endosulfan in aerated solution by gamma irradiation in the presence of carbonate, bicarbonate, and chloride ions. Experimental conditions: [endosulfan]<sub>0</sub> = 0.83 μM, [CO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = [Cl<sup>-</sup>]<sub>0</sub> = 1.0 mM, gamma-ray dose rate = 296 Gy/h

Absorbed dose (Gy)	Percent degradation (%) = $\frac{(C_0 - C)}{C_0} \times 100$			
	Aerated only	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
0	0.00	0.00	0.00	0.00
150	20.0	19.1	18.5	12.7
300	34.5	33.1	32.2	27.0
630	57.1	55.7	53.4	49.5
1020	80.0	78.2	77.1	76.0

that of endosulfan used in the present study (i.e., [ES] = 0.83 × 10<sup>-6</sup> M), the reactivity (*r*) of hydrated electron with ES ( $r(\text{ES}/e_{\text{aq}}^-)$ ) and with O<sub>2</sub> ( $r(\text{O}_2/e_{\text{aq}}^-)$ ) was calculated using Eqs. (10 and 11).

$$r(e_{\text{aq}}^-/\text{ES}) = k_{e_{\text{aq}}^-/\text{ES}} [\text{ES}] \tag{10}$$

$$r(e_{\text{aq}}^-/\text{O}_2) = k_{e_{\text{aq}}^-/\text{O}_2} [\text{O}_2] \tag{11}$$

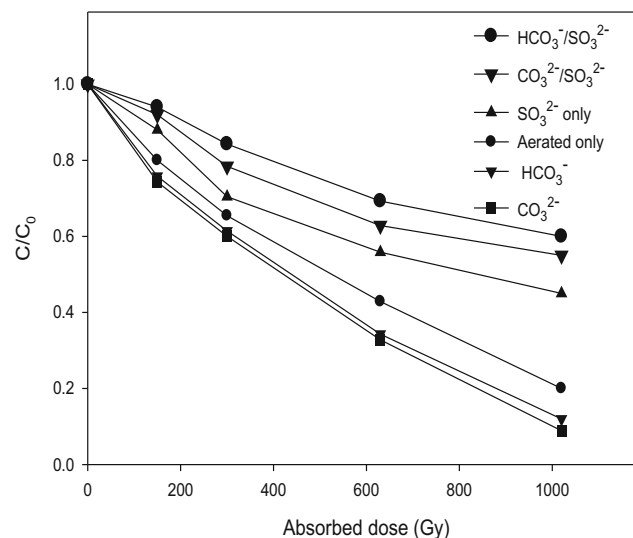
Putting the values of  $k_{\text{ES}/e_{\text{aq}}^-}$ , [ES],  $k_{\text{ES}/\text{O}_2}$ , and [O<sub>2</sub>] in Eqs. (10) and (11), the reactivity of  $e_{\text{aq}}^-$  with ES and with O<sub>2</sub> was found to be 4233 and 2,660,000 s<sup>-1</sup>, respectively, showing the faster kinetic of  $e_{\text{aq}}^-$  with O<sub>2</sub> than with ES at the mentioned concentrations of O<sub>2</sub> and ES.

In the presence of chloride ion in aerated solution, besides scavenging of  $e_{\text{aq}}^-$  and <sup>•</sup>H by air, the <sup>•</sup>OH is effectively scavenged by Cl<sup>-</sup> and yield highly reactive Cl<sup>•</sup>/Cl<sub>2</sub><sup>•-</sup> thus under this condition the species for reaction with endosulfan come out to be Cl<sup>•</sup>/Cl<sub>2</sub><sup>•-</sup> in addition to O<sub>2</sub><sup>•-</sup> and HO<sub>2</sub><sup>•</sup> (Buxton et al. 1988). Besides greater scavenging of <sup>•</sup>OH by Cl<sup>-</sup>, the high removal efficiency of endosulfan, i.e., 76 % (Table 1) in aerated solution in the presence of chloride ion suggest contribution of Cl<sup>•</sup>/Cl<sub>2</sub><sup>•-</sup> in the removal of endosulfan in addition to O<sub>2</sub><sup>•-</sup>. The removal of endosulfan was investigated in aerated solution in the presence of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> as well, with 78 and 77 % removal of endosulfan, respectively, achieved (Table 1). As mentioned earlier in the present study, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> scavenges <sup>•</sup>OH and yield CO<sub>3</sub><sup>•-</sup>, the CO<sub>3</sub><sup>•-</sup> in return has been reported to be highly reactive towards sulfur containing electron-rich organic compounds, such as endosulfan (Wu and Linden 2010). The performance of CO<sub>3</sub><sup>•-</sup> as well as the effect of other operational parameters on the radiolytic degradation of endosulfan in aerated solution was further explained in detail in the following sections.

### Role of carbonate radical on the removal of endosulfan

Carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) anions are common constituents of natural water distributed with varying concentrations. Various studies elaborate the inhibition effects of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> on the removal of emerging water pollutants by <sup>•</sup>OH due to their high second-order rate constants (Eqs. (5) and (6)) (Guo et al. 2015; Liu et al. 2015). The removal of endosulfan by gamma irradiation in aerated solution in the presence of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> with <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> as the primary reactive species was however, not influenced in the present study as discussed earlier. The reaction of <sup>•</sup>OH with both CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> yield CO<sub>3</sub><sup>•-</sup> that has been reported to be highly reactive towards sulfur containing electron-rich compounds, such as endosulfan (Wu and Linden 2010). According to Wu and Linden (2010), CO<sub>3</sub><sup>•-</sup> react rapidly with

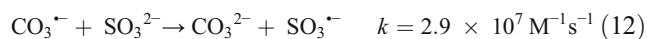
sulfur containing compounds with a second-order rate constants of 10<sup>6</sup>–10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>. The role of carbonate radical in the removal of endosulfan in the present study was investigated using high concentration, i.e., 5 mM of each of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> and using sulfite anion (SO<sub>3</sub><sup>2-</sup>) as a scavenger for CO<sub>3</sub><sup>•-</sup>. At an absorbed dose of 1020 Gy, the presence of 5 mM CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> resulted in 91 and 88 % removal of endosulfan (Fig. 1) contrary to 78 and 77 % in the presence of 1 mM of each of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> (Table 1), respectively. This slight increase in the removal efficiency of endosulfan with increasing initial concentrations of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> suggest increase in the rate of formation of CO<sub>3</sub><sup>•-</sup> and its contribution in the removal of endosulfan. The role of CO<sub>3</sub><sup>•-</sup> in the removal of endosulfan was further assessed by using SO<sub>3</sub><sup>2-</sup> as a scavenger of CO<sub>3</sub><sup>•-</sup> due to their high second-order rate constant value as shown in Eq. (12) (Buxton et al. 1988). The removal efficiency of endosulfan was found to be 45 and 40 % at 1020 Gy in aerated solution in the presence of SO<sub>3</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, respectively (Fig. 1). This high inhibition of removal efficiency of endosulfan in the presence of SO<sub>3</sub><sup>2-</sup> with both CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> reveals the possible role of CO<sub>3</sub><sup>•-</sup> in the removal of endosulfan. The SO<sub>3</sub><sup>2-</sup> has been reported to react faster with <sup>•</sup>OH as well due to their high second-order constant value as shown in Eq. (13) and might compete strongly with endosulfan for <sup>•</sup>OH and consequently, removal of endosulfan might be influenced (Buxton et al. 1988). Thus, the presence of SO<sub>3</sub><sup>2-</sup> with CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> scavenges <sup>•</sup>OH in addition to CO<sub>3</sub><sup>•-</sup>. Besides, the faster reaction of <sup>•</sup>OH with SO<sub>3</sub><sup>2-</sup> (Eq. (13)) than with CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, as shown in Eqs. (5) and (6), might retard the formation of CO<sub>3</sub><sup>•-</sup>. The removal of endosulfan in aerated solution in the presence of SO<sub>3</sub><sup>2-</sup> only was also investigated



**Fig. 1** Removal of endosulfan in aerated solution by gamma irradiation in the presence of carbonate, bicarbonate, and sulfite ions. Experimental conditions: [endosulfan]<sub>0</sub> = 0.83 μM, [CO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = [SO<sub>3</sub><sup>2-</sup>]<sub>0</sub> = 5.0 mM, gamma-ray dose rate = 296 Gy/h



and was found to be only 55 % at 1020 Gy (Fig. 1). This lower removal efficiency of endosulfan in the presence of  $\text{SO}_3^{2-}$  only revealed scavenging of  $\cdot\text{OH}$ , which, in return, could influence the formation of  $\text{CO}_3^{\cdot-}$ . However, removal efficiency of endosulfan in the presence of  $\text{SO}_3^{2-}$  only was inhibited to slightly lesser extent than in the presence of either  $\text{SO}_3^{2-}$  and  $\text{CO}_3^{2-}$  or  $\text{SO}_3^{2-}$  and  $\text{HCO}_3^-$  suggesting the formation of  $\text{CO}_3^{\cdot-}$  by reaction of carbonate and/or bicarbonate with  $\cdot\text{OH}$  as well as the involvement of  $\text{CO}_3^{\cdot-}$  in the removal of endosulfan in aerated solution. However, further study is needed to elaborate in detail the contribution of  $\text{CO}_3^{\cdot-}$  in the removal of endosulfan and related sulfur containing compounds.



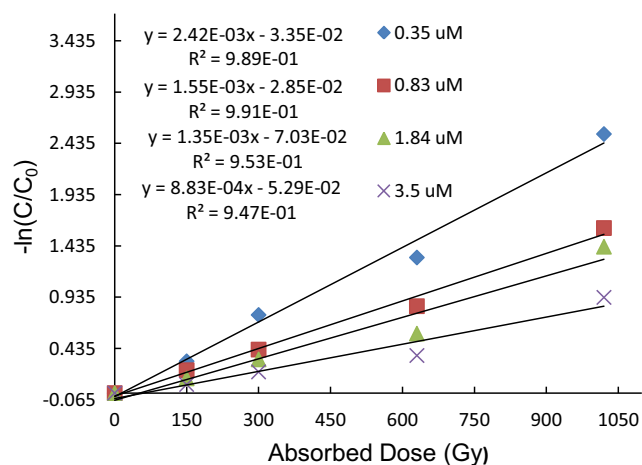
Influence of operational parameters on the radiolytic degradation of endosulfan in aerated solution are discussed in the following sections.

### Effects of initial endosulfan concentration

Table 2 shows the radiolytic degradation efficiency (%) at an absorbed dose of 1020 Gy for different initial concentrations of endosulfan, 0.35–3.5  $\mu\text{M}$ . The radiation dose needed for decomposition of endosulfan was not proportional with initial concentration, and at an absorbed dose of 1020 Gy, removal efficiency of endosulfan was 60 and 92 % for an initial endosulfan concentration of 3.5 and 0.35  $\mu\text{M}$ , respectively, and this result was similar to the findings in previous studies (Ocampo-Pérez et al. 2011; Sánchez-Polo et al. 2009). The removal of endosulfan followed *pseudo-first-order* kinetics at different initial concentrations of endosulfan and observed dose constants ( $k_{\text{obs}}$ ,  $\text{Gy}^{-1}$ ) were determined using integrated pseudo-first-order rate equation (Eq. 14) (Fig. 2) (Shah et al. 2014).

$$-\ln\left(\frac{C}{C_0}\right) = k_{\text{obs}}D \quad (14)$$

Table 2 shows that  $k_{\text{obs}}$  decreased with increasing initial concentrations of endosulfan. The decrease in removal efficiency (%) and  $k_{\text{obs}}$  of endosulfan with increasing initial concentration is attributed to the competition between endosulfan and its by-products for reactive radicals. The increased initial



**Fig. 2** Pseudo-first-order degradation kinetics of endosulfan at different initial concentrations:  $[\text{endosulfan}]_0 = 0.35, 0.83, 1.84, \text{ and } 3.5 \mu\text{M}$ , gamma-ray dose rate = 296 Gy/h

concentration of endosulfan is expected to increase the concentration of by-products and subsequently led to higher competition for reactive radicals with the target contaminant (Shah et al. 2014; Khan et al. 2015b).

The relationship between  $k_{\text{obs}}$  and initial concentration of endosulfan can be expressed as a power function as shown by Eq. (15).

$$k_{\text{obs}} = 0.0015C_0^{-0.403} \quad R^2 = 0.971 \quad (15)$$

The  $k_{\text{obs}}$  obtained was used to calculate the dose required for 50 and 90 % removal of endosulfan, i.e.,  $D_{0.50}$  and  $D_{0.90}$  (Gy) for the studied initial concentrations using Eqs. (16) and (17), respectively (Table 2).

$$D_{0.50} = \frac{\ln 2}{k_{\text{obs}}} \quad (16)$$

$$D_{0.90} = \frac{\ln 10}{k_{\text{obs}}} \quad (17)$$

Radiation chemical yield, defined as the number of species (i.e., atoms, ions, and molecules) in micromole ( $\mu\text{mol}$ ) formed or consumed by absorption of 1 J of radiation energy, were calculated for different initial concentrations of endosulfan using Eq. (18).

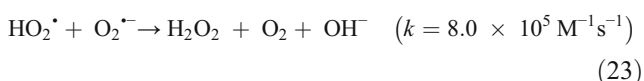
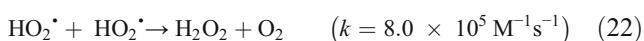
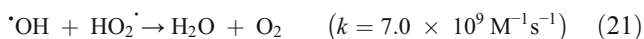
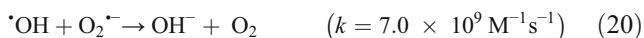
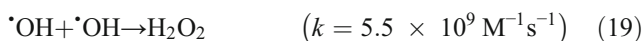
$$\text{Radiation chemical yield} = \frac{[R]}{D} \times 1.0 \times 10^6 \mu\text{mol J}^{-1} \quad (18)$$

**Table 2** Variation of removal efficiency (%),  $k_{\text{obs}}$  ( $\text{Gy}^{-1}$ ), radiation chemical yield ( $\mu\text{mol J}^{-1}$ ) and dose required for 50 and 90 %, i.e.,  $D_{0.50}$  and  $D_{0.90}$  (Gy), respectively, as a function of different initial concentrations of endosulfan. Experimental condition: gamma-ray dose rate = 296 Gy/h

Concentration ( $\mu\text{M}$ )	% degradation	$k_{\text{obs}}$ ( $\text{Gy}^{-1}$ )	Radiation chemical yield ( $\mu\text{mol J}^{-1}$ )	$D_{0.50}$ (Gy)	$D_{0.90}$ (Gy)
0.35	92.01	$2.42 \times 10^{-3}$	0.0008	289	959
0.83	80.00	$1.55 \times 10^{-3}$	0.0012	462	1540
1.84	76.31	$1.35 \times 10^{-3}$	0.0022	533	1770
3.5	60.40	$8.83 \times 10^{-4}$	0.0031	770	2560

Table 2 shows that radiation chemical yield increased from 0.0008 to 0.0031  $\mu\text{mol J}^{-1}$  with increasing initial concentrations of endosulfan from 0.35 to 3.5  $\mu\text{mol L}^{-1}$  (Lee and Lee 2005; Shah et al. 2014). The increase in radiation chemical yield of endosulfan with increasing initial concentrations could possibly be due to the increased number of molecules of the target contaminant exposed to reactive radicals at higher initial concentrations than that at lower initial concentration and was consistent to the findings in previous studies [Sánchez-Polo et al. 2009; Shah et al. 2014, 2015b; Khan et al. 2015a]. However, radiation chemical yield decreased with increase in absorbed dose for all the studied initial concentrations with possible reason explained in our previous study (Shah et al. 2014).

The observed radiation chemical yield values were very small for all the studied concentrations. The possible reason that concentrations of reactive radicals, i.e., 0.094, 0.189, 0.397, and 0.643 mM at the studied absorbed doses of 150, 300, 630, and 1020 Gy, respectively, is much greater than the initial concentrations of endosulfan studied, e.g., 0.35, 0.83, 1.84, and 3.5  $\mu\text{M}$ . The high concentrations possibly increased the probability of recombination reactions of reactive radicals with each other due to their high second-order rate constants as shown in Eqs. (19)–(23) and consequently decreased the probability of their reaction with the target contaminant, i.e., endosulfan (Khan et al. 2015a). As a result, less number of molecules of endosulfan are decomposed by reactive radicals and consequently yielded lower radiation chemical yield.

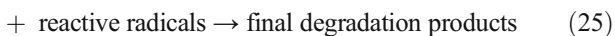


In addition, the decomposition of endosulfan by reactive radicals yielded intermediate by-products that also start reacting with reactive radicals as shown by Eqs. (24) and (25).

Endosulfan



Intermediate by-products

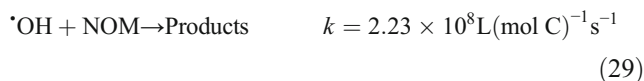
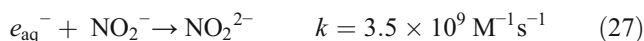
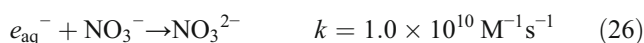


The competition between endosulfan and intermediate by-products for reactive radicals might also lead to decomposition of low number of molecules of endosulfan because some of the reactive radicals will be consumed by intermediate by-

products (Khan et al. 2015a). The lower radiation chemical yield values obtained in the present study was similar to the findings in our previous study that each of the reactive radical produced from water radiolysis cannot decompose target contaminant molecule (Khan et al. 2015a).

### Effect of inorganic anions and natural organic matter

Besides the target contaminant, natural water contains several other entities with most common including inorganic anions and natural organic matter (NOM), i.e., humic acid (HA). The inorganic anions and HA have been reported to react faster with  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  due their high second-order rate constant value as shown in Eqs. (26)–(29) and might compete with the target contaminant for reactive radicals, therefore, removal of the target contaminant could be influenced (Buxton et al. 1988).



The effects of these anions on the removal of endosulfan in deaerated solution has been investigated in our previous study (Shah et al. 2014). However, for treatment of the target contaminant in natural water containing high concentration of oxygen (aerated solution), effect of inorganic anions, and HA is also very crucial. At an absorbed dose of 1020 Gy, radiolytic degradation of endosulfan was 28, 45, and 76 %, in aerated solution in the presence of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and HA, respectively, as compared to 80 % in aerated solution in the absence of either additive (Table 3). The lower removal efficiency of endosulfan in the presence of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  could be from the faster kinetic of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  with  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  (Eqs. (26) - (28)) leading to greater competition with the target contaminant for reactive radicals (Buxton et al. 1988). Based on the initial concentrations of 1 mM for each of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  and 0.83  $\mu\text{M}$  for endosulfan used in the present study and the second-order rate constant values of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  with  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$ , which is in the order of  $10^9$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (as shown in Eqs. (26) – (28)) and that of endosulfan with  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$ , the reactivity of  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  with  $\text{NO}_3^-$  and  $\text{NO}_2^-$  comes out to be more than 1000 times faster than with endosulfan. The faster kinetic of these inorganic anions with  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  effectively scavenge  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  and might influence the rate of formation of secondary reactive species, such as superoxide radical, that along with hydroxyl radical, has been suggested to play a role in the degradation of endosulfan in aerated solution.

**Table 3** Removal efficiency (%) of endosulfan by gamma irradiation in the presence of inorganic ions (i.e.,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) and HA. Experimental condition:  $[\text{endosulfan}]_0 = 0.83 \mu\text{M}$ ,  $[\text{HA}]_0 = 35 \text{ mg/L}$ ,  $[\text{inorganic anions}]_0 = 1.0 \text{ mM}$

Absorbed dose (Gy)	Percent degradation (%) = $\frac{(C_0 - C)}{C_0} \times 100$			
	Aerated only	$\text{NO}_3^-$	$\text{NO}_2^-$	HA
0	0.00	0.00	0.00	0.00
150	20.0	6.0	11.1	16.0
300	34.5	12.5	20.0	30.0
630	57.1	21.0	35.2	52.5
1020	80.0	28.5	45.1	76.0

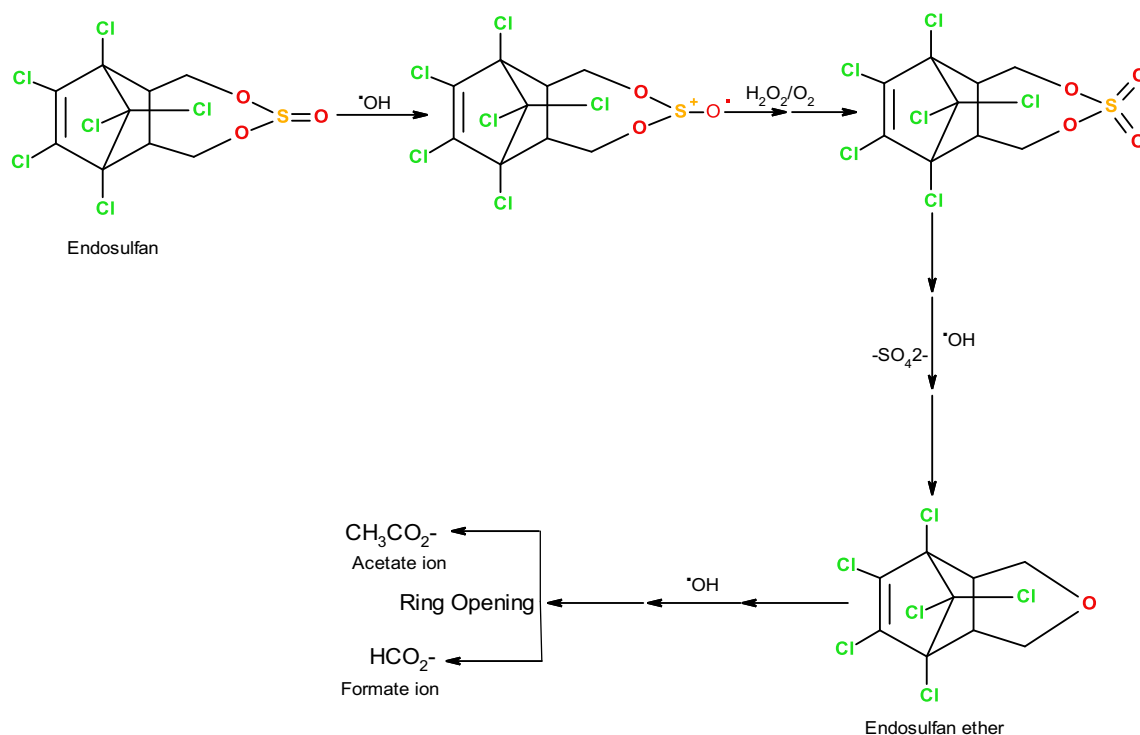
The influence of HA, acting as a major scavenger of hydroxyl radical (Eq. (29)); however, did not influence the removal efficiency of endosulfan in aerated solution. The possible reason for this could be the formation of small degradation products from the radiolytic degradation of HA and their role in the removal of target contaminant as explained in our previous study (Shah et al. 2014).

### Formation of organic by-products and small chain organic acids

The decomposition of endosulfan in aerated solution is expected to result in several organic by-products including larger molecules and short chain organic acids (possibly formed before

mineralization of the target organic contaminants). The radiolytic degradation of endosulfan in aerated solution was found to result in the formation of endosulfan ether, reported to be formed as the main degradation product of endosulfan in our previous studies as well (Shah et al. 2013, 2014) and short chain organic acids, i.e., formate and acetate ions. The proposed pathway for the formation of endosulfan ether involve electron abstraction of  $\cdot\text{OH}$  from the S=O bond of endosulfan, yielding first radical-cation intermediate which after a series of reactions is transformed to endosulfan sulfate having two S=O bonds (product not identified in the present study) through oxidation followed by hydrolysis as shown in Scheme 1 (Shah et al. 2013). The endosulfan sulfate is then converted into endosulfan ether through a series of reactions by  $\cdot\text{OH}$  yielding possibly the first oxygen-centered radical, which through a route of elimination reactions (with the loss of sulfate ion) is transformed to endosulfan ether as shown in Scheme 1 (Shah et al. 2013). The formation of short chain organic acids from endosulfan ether involve ring opening by  $\cdot\text{OH}$  after several intermediate steps as shown in Scheme 1 (Shah et al. 2014; Khan et al. 2015b).

The formation of short chain organic acids reveal potential decrease in mass concentration of the target contaminants. The three organic by-products were identified but not quantified successfully at the studied concentrations of endosulfan (i.e.,  $0.83 \mu\text{M}$ ). However, when the initial concentration of endosulfan was increased to  $3.5 \mu\text{M}$ , the three by-products were quantified successfully. The rapid increase in the concentrations of endosulfan ether, formate, and acetate ions was reported initially with decomposition of the target contaminant

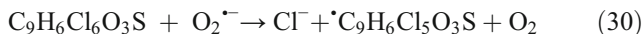


**Scheme 1** Proposed degradation pathways of endosulfan in an aerated solution

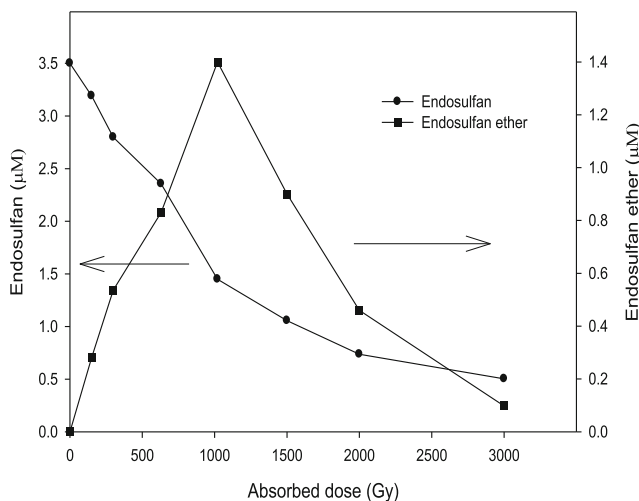
(Figs. 3 and 4). However, after extended treatment by gamma irradiation (i.e., up to 3000 Gy), concentration of endosulfan ether, formate, and acetate ions as well, decreased potentially with the decrease in concentration of the target contaminant (Figs. 3 and 4). The decrease in concentration of endosulfan ether, formate, and acetate ions after extended treatment suggest contribution of reactive radicals in the removal of by-products as well. Besides, this study verifies competition between the target contaminant and by-products for reactive radicals.

**Time-course of chloride ion accumulation and toxicity evaluation**

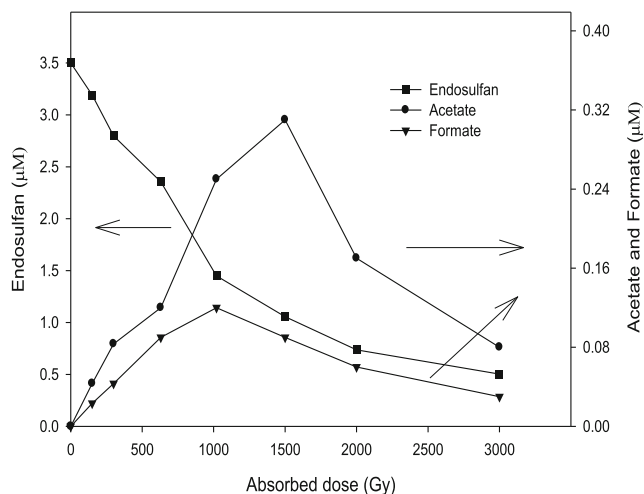
The reductive dechlorination of endosulfan (C<sub>9</sub>H<sub>6</sub>Cl<sub>6</sub>O<sub>3</sub>S), a hexachlorinated insecticide, is expected to result in the formation of chloride ion by reaction with reactive radicals, i.e., O<sub>2</sub><sup>•-</sup> as shown in Eq. (30).



The analysis of irradiated aqueous endosulfan solution (i.e., 3.5 μM) is expected to yield 21 μM; however, 17 μM of chloride ion was formed at an absorbed dose of 3000 Gy in the present study, showing a mass balance of 80 % loss of chloride ion (Fig. 5). The reductive dechlorination of endosulfan in aerated solution was rapid initially for the first few hours with the formation of 13.2 μM at an absorbed dose of 1020 Gy. However, the rate of loss of chloride ion was leveled off at a much slower rate afterward, and finally reached 17 μM at an absorbed dose of 3000 Gy. The fast accumulation of chloride ion initially for few hours and leveling off afterward suggest the persistence of some aliphatic compounds containing chlorine towards further mineralization. The mass balance of the loss of chloride ion was 95 % in deaerated solution (Shah et al. 2014) as compared to 63 % in aerated solution



**Fig. 3** Changes in concentration of endosulfan and endosulfan ether with absorbed dose in aerated solution only. Experimental conditions: [endosulfan]<sub>0</sub> = 3.5 μM, gamma-ray dose rate = 296 Gy/h



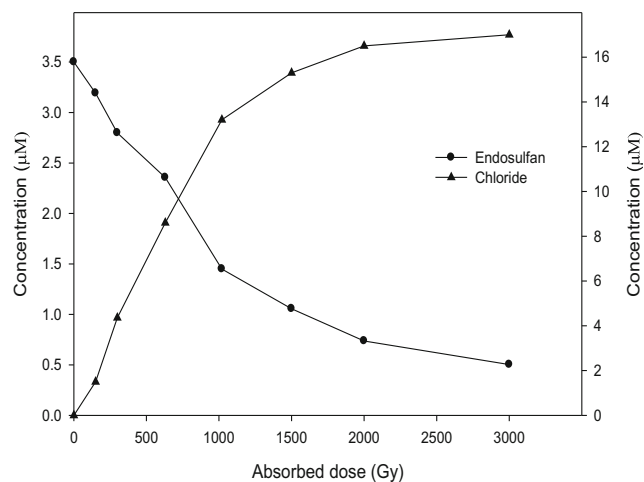
**Fig. 4** Changes in the concentration of endosulfan, acetate, and formate ions with absorbed dose in aerated solution only. Experimental conditions: [endosulfan]<sub>0</sub> = 3.5 μM, gamma-ray dose rate = 296 Gy/h

at an absorbed dose of 1020 Gy, suggesting slower rate of dechlorination of endosulfan in aerated solution.

The chlorine group has been reported to be responsible for toxicity of chlorinated organic compounds and their by-products; therefore, dechlorination achieved in water treatment reveals significant decrease in toxicity of the water contaminated with chlorinated organic compounds (Shah et al. 2014, Khan et al. 2015b). The mass balance showing 80 % loss of chloride ion in aerated solution at an absorbed dose of 3000 Gy implicates significant decrease in toxicity of endosulfan.

**Conclusions**

Endosulfan was significantly removed by gamma irradiation in aerated solution. The removal efficiency of endosulfan was



**Fig. 5** Changes in the concentration of endosulfan and chloride ion with absorbed dose in aerated solution only. Experimental conditions: [endosulfan]<sub>0</sub> = 3.5 μM, gamma-ray dose rate = 296 Gy/h



primarily due to hydroxyl and superoxide radical in aerated solution. The carbonate radical was found to contribute significantly to the removal of endosulfan. The removal of endosulfan was inhibited in the presence of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_3^{2-}$ . The removal efficiency and  $k_{\text{obs}}$  decreased while radiation chemical yield increased with increasing initial concentrations of endosulfan. The contribution of  $\text{O}_2^{\cdot-}$  and  $\text{CO}_3^{\cdot-}$  in removal of endosulfan implicates significant role of these radicals in treatment of water contaminated with chlorinated and sulfur containing organic compounds. The formation of endosulfan ether reveals that oxidation of endosulfan occurs at the S=O bond through electron transfer reaction by  $\cdot\text{OH}$  while the loss of chloride ion occur through reductive dechlorination by  $\text{O}_2^{\cdot-}$ . A decrease in mass concentration of some of the by-products after extended treatment reveals significant competition between parent compound and by-products for reactive radicals. The formation of small chain organic acids and chloride ion implicate potential decrease in mass concentration of the target contaminant and detoxification of an aqueous solution. The efficient removal of endosulfan in aerated solution suggests potential applications of gamma irradiation for treatment of contaminant in natural water.

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