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Role of aqueous electron and hydroxyl radical in the removal of endosulfan from aqueous solution using gamma irradiation

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HIGHLIGHTS

- Removal of endosulfan was assessed by gamma irradiation under different conditions.
- Removal of endosulfan by gamma irradiation was mainly due to reaction of aqueous electron.
- The radiation yield value decreased while dose constant increased with increasing gamma-ray dose-rate.
- Second-order rate constant of endosulfan with aqueous electron was determined by competition kinetic method.
- Degradation pathways were proposed from the nature of identified by-products.

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ABSTRACT

The removal of endosulfan, an emerging water pollutant, from water was investigated using gamma irradiation based advanced oxidation and reduction processes (AORPs). A significant removal, 97% of initially 1.0 μM endosulfan was achieved at an absorbed dose of 1020 Gy. The removal of endosulfan by gamma-rays irradiation was influenced by an absorbed dose and significantly increased in the presence of aqueous electron (e_{aq}^-). However, efficiency of the process was inhibited in the presence of e_{aq}^- scavengers, such as N_2O, NO_3^-, acid, and Fe^{3+}. The observed dose constant decreased while radiation yield (*G*-value) increased with increasing initial concentrations of the target contaminant and decreasing dose-rate. The removal efficiency of endosulfan II was lower than endosulfan I. The degradation mechanism of endosulfan by the AORPs was proposed showing that reductive pathways involving e_{aq}^- started at the chlorine attached to the ring while oxidative pathway was initiated due to attack of hydroxyl radical at the S=O bond. The mass balance showed 95% loss of chloride from endosulfan at an absorbed dose of 1020 Gy. The formation of chloride and acetate suggest that gamma irradiation based AORPs are potential methods for the removal of endosulfan and its by-products from contaminated water.

1. Introduction

Pesticides are chemical substances, either natural or synthetic, commonly used on crops that aim to increase the production of food with better quality and get ride from epidemic disease [1]. Thus the use of pesticides is highly vital in the struggle to improve human life. Among these pesticides, one important include endosulfan (ES), a chlorinated pesticide that is commonly found as a mixture of two stereoisomers, 64–70% endosulfan I and 29–32% endosulfan II [2]. Most common uses of endosulfan include as a wood preservative as well as an insecticide on various crops and vegetable etc. to control pests, mites and pests causing diseases [3–5]. Owing to beneficial aspects, endosulfan has been extensively used throughout the world. Besides, endosulfan has been reported to be highly toxic to aquatic life and is implicated in mammalian toxicity [6], genotoxicity [7] and neurotoxicity [8]. The US Environmental Protection Agency (US EPA) classified endosulfan as a category 1b (highly hazardous) pesticide as well as highly persistent with a long half life ranging from nine months to six years [9]. Due to greater persistency, residues of endosulfan have been detected in surface water, soil, and air samples in many areas of the world [10]. Water is an essential element of life and its pollution by endosulfan can lead to global environmental problems.

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Therefore, it is highly crucial to eradicate endosulfan from contaminated water.

Advanced oxidation (and reduction) processes (AOPs or AORPs) are introduced as the most adequate treatment technologies that carry dechlorination and mineralization of the target contaminant or in other way the target contaminant is converted into simple biodegradable and harmless products [11–14]. AORPs are chemical oxidation methods that rely on in situ generation of reactive radicals (i.e., hydroxyl radical, •OH) and refer to a set of different methods, such as Fenton and Fenton-like reactions (Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2), photo-Fenton and photo-Fenton-like reactions ($UV/H_2O_2/Fe^{2+}$, $UV/H_2O_2/Fe^{3+}$), UV/H_2O_2, UV/TiO_2 and ionizing radiation etc. [12–16]. Among the different AORPs, ionizing irradiation technique is quite efficient since oxidizing as well as reducing reactive species (i.e., •OH and e_{aq}^-, respectively) are produced simultaneously, it gives promising results and is also promoted by the international agencies, such as the IAEA, FAO, WHO to accomplish favorable goals in the removal of hazardous wastes [16–18]. Hydroxyl radical is a powerful oxidant with an oxidation potential of +2.72 V that reacts non-selectively with organic contaminant through three different ways, i.e., addition to unsaturated bond at near diffusion-controlled rates, abstraction of hydrogen from saturated C-H bond and electron transfer reactions [19,20]. On contrary, aqueous electron is a strong reducing agent with a reduction potential of −2.9 V that prefers to react through dissociative electron capture reactions with organic compounds containing electron withdrawing substituent, such a chlorine as shown by the following equation [21]:

$$R - X + e_{aq}^- \rightarrow {}^{\bullet}R + X^- \quad (1)$$

Therefore, e_{aq}^- could potentially dechlorinate endosulfan and related organochlorine compounds.

The main objective of the present study was removal of endosulfan by oxidative and reductive pathways involving •OH and e_{aq}^-, respectively. The removal of endosulfan by oxidative pathways involving hydroxyl radical (•OH) has been explained in previous studies. However, halogenated organic compounds including endosulfan showed greater reactivity towards e_{aq}^-, therefore, removal of endosulfan by gamma-rays irradiation involving both reductive and oxidative pathways was investigated for potential practical application. The effects of radical scavengers, inorganic ions and humic substances commonly found in water, different initial concentrations of endosulfan, and dose-rate were investigated. The main degradation pathways of the removal of endosulfan by both reductive and oxidative Schemes were examined.

2. Materials and methods

2.1. Materials

All the chemicals used in the present study were of high purity and used as received. Solid endosulfan, endosulfan I, endosulfan II, endosulfan ether, endosulfan lactone, and chlorendic acid with a purity of 99.6% were obtained from Supelco (PA, USA). Other chemicals, such as tertiary butyl alcohol (*t*-BuOH) and isopropyl alcohol (*i*-PrOH), perchloric acid ($HClO_4$) sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$), potassium chloride (KCl), sodium bicarbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), ferric chloride ($FeCl_3{\cdot}6H_2O$), sodium acetate (CH_3CO_2Na), phenol (C_6H_5OH) and humic acid (HA) were also of high purity and obtained from Scharlau. Nitrogen (N_2) and nitrous oxide (N_2O) gases with a purity of 99.5% were used for sparging an aqueous solution of endosulfan. Ultra pure water with a resistivity of 18.2 MΩ cm from Milli-Q® system (Millipore) were used for preparation of different solutions used in the present study.

2.2. Analysis

An Agilent 6890 series gas chromatography (GC) equipped with Ni^{65} electron capture detector (ECD) and an HP-5 (5% phenyl methylsiloxane) capillary column (30 m, i.d. 0.25 μm) was used for the analysis of endosulfan as well as some of its by-products. The temperature of the injector, inlet, and detector were set at 250 °C, 220 °C, and 320 °C, respectively. The temperature of the oven was started from 80 °C (hold time 2 min), increased to 150 °C (hold time 0 min) by 20 °C/min rate and finally increased to 220 °C (hold time 10 min) at a rate of 10 °C/min. N_2 gas was used as a carrier gas at a flow rate of 1.0 mL/min. Solid phase microextration (SPME) with the fiber (made up of polydimethsiloxane (PDMS) and purchased from Supelco, USA) was used for the extraction of endosulfan and its by-products from water. The SPME was fitted with CTC autosampler (CombiPAL, Switzerland) for directly injecting the extracted sample into the injector of the GC.

Ion chromatography (IC, Metrohm) with electrical conductivity detector was used for the analysis of chloride (Cl^-) and acetate (CH_3COO^-) ions in irradiated aqueous endosulfan solution. This was done by the method for anion determination using Assup-5 column (250/4.0 mm), with 3.2 mM Na_2CO_3/1 mM $NaHCO_3$ as an eluent at a flow rate of 0.75 mL/min.

The by-products were identified by comparison of retention time with that of authentic standard compounds under the same conditions [22].

2.3. Gamma irradiation source and procedure

The gamma irradiation treatment of aqueous endosulfan solution was conducted using a cobalt-60 gamma ray source (model Issledovadel, origion USSR) available at the Nuclear Institute for Food and Agriculture (NIFA), Tarnab, Peshawar. The source was calibrated using ferrous sulphate solution (Fricke dosimetery) [23] and typical dose-rate was found to be 296 Gy/h. Air tight 17 mL Pyrex glass test tubes were used for sample irradiation. Typical irradiation was done using 15 mL of solution in the test tube, sparging with N_2 or N_2O gases for 25 min and then putting the stoppered tubes in the gamma-ray source for irradiation treatment for predetermined period of time. The effect of dose-rate was investigated using brass and iron/brass containers. All the irradiation treatments were done at room temperature.

3. Results and discussion

3.1. Gamma-rays irradiation of endosulfan

Aqueous solution of endosulfan was irradiated with gamma-rays for different absorbed doses from 150 to 1020 Gy at a constant dose-rate of 296 Gy/h. Upon irradiation, dilute aqueous solution of endosulfan undergoes radiolysis of water, yielding reactive species as shown by the following equation [16]:

$$H_2O \text{ --^-^-- } > {}^{\bullet}OH(0.29), {}^{\bullet}H(0.06), e_{aq}^-(0.28), H_2(0.047), H_2O_2(0.07), H_3O^+(0.27) \quad (2)$$

The bracketed values in Eq. (2) represent *G*-values (μmol/J) of the primary reactive species in air free medium and pH range from 3–11 [24,25]. Among the species in Eq. (2), hydroxyl radicals (•OH), hydrogen atom (•H) and aqueous electron (e_{aq}^-) are the most reactive and readily attack the target contaminant [16,24].

In aerated aqueous endosulfan solution, e_{aq}^- and •H react with oxygen which led to scavenging of these radicals as shown by Eqs. (3) and (4) [26]. The reaction of oxygen with e_{aq}^- and •H produces superoxide ($O_2^{\bullet-}$) and hydroperoxy ($HO_2^{\bullet}$) radicals, respectively,

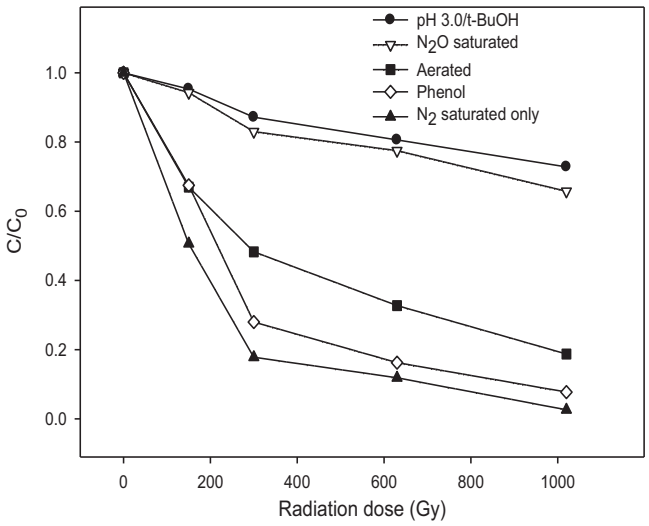


Fig. 1. Removal of endosulfan under different conditions: N_2 and N_2O gases only, aerated only, and in the presence of phenol and acid (pH 3.0)/*t*-BuOH with N_2 gas. Experimental conditions: $[endosulfan]_0 = 1.0\ \mu M$, $[t\text{-BuOH}]_0 = 60$ mM, $[phenol]_0 = 1$ mM, [perchloric acid] = 0.05 mM.

that together with some of the species in Eq. (2), e.g., •OH react with the target contaminant [24,26,27].

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \quad k = 1.9 \times 10^{10}\,(M\,s)^{-1} \tag{3}$$

$$^{\bullet}H + O_2 \rightarrow HO_2^{\bullet} \quad k = 2.1 \times 10^{10}\,(M\,s)^{-1} \tag{4}$$

$$HO_2^{\bullet} \rightleftarrows H^+ + O_2^{\bullet -} \quad (pKa = 4.8) \quad k = 8.0 \times 10^5\,(M\,s)^{-1} \tag{5}$$

Fig. 1 shows that 78% removal of endosulfan was observed in an aerated solution at an absorbed dose of 1020 Gy. The radiolytic degradation of endosulfan was studied in the absence of dissolved oxygen as well by sparging an aqueous solution with N_2 gas, as a result the reactions (3) and (4) are avoided. Therefore, the reactive radicals (i.e., •OH, •H and e_{aq}^-) are all available for reaction with endosulfan. Fig. 1 shows that at an absorbed dose of 1020 Gy, 97% removal of endosulfan was achieved in the presence of N_2 gas. The comparatively lower removal of endosulfan in aerated solution suggested significant importance of reactive radicals in gamma irradiation treatment.

The study of common radicals scavengers, such as N_2O, phenol and perchloric acid/*t*-BuOH were carried out to investigate the involvement of •OH, e_{aq}^- and •H in the removal of endosulfan by gamma-rays irradiation.

N_2O gas reacts efficiently with e_{aq}^- as shown by Eqs. (6), therefore, N_2O was used as a scavenger of e_{aq}^- in the present study [26].

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^{\bullet}OH + N_2 + OH^- \quad k = 9.1 \times 10^9\,(M\,s)^{-1} \tag{6}$$

The scavenging of e_{aq}^- by N_2O yield •OH and as result increase the concentration of •OH as shown by Eq. (7) which led to primary role of •OH in the removal of endosulfan by gamma-rays irradiation in the presence of N_2O.

$$G\text{-value}(^{\bullet}OH) = G\text{-value}(^{\bullet}OH) + G\text{-value}(e_{aq}^-) = 0.29 + 0.28 = 0.57\,\mu mol/J \tag{7}$$

Phenol reacts fast with •OH due to its high bimolecular rate constant as shown by Eq. (8) and thus can scavenge •OH greatly, leaving e_{aq}^- free for reaction with endosulfan [26].

$$^{\bullet}OH + C_6H_5OH \rightarrow \text{Dihydroxycyclohexadienyl} \quad k = 1.8 \times 10^{10}\,(M\,s)^{-1} \tag{8}$$

The involvement of hydrogen atom (•H) in the removal of endosulfan was assessed by spiking perchloric acid (for study at pH 3.0) and *t*-BuOH in an aqueous solution followed by sparging with N_2 gas. The presence of acid (i.e., H^+) and *t*-BuOH efficiently scavenges e_{aq}^- and •OH due to their fast reaction as show by Eqs. (9) and (10), respectively [26].

$$e_{aq}^- + H^+ \rightarrow {}^{\bullet}H \quad k = 2.3 \times 10^{10}\,(M\,s)^{-1} \tag{9}$$

$$^{\bullet}OH + t\text{-BuOH} \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2O \quad k = 6.0 \times 10^8\,(M\,s)^{-1} \tag{10}$$

The scavenging of e_{aq}^- by H^+ yield •H which led to increase concentration of •H.

Fig. 1 depicts that at an absorbed dose of 1020 Gy, radiolytic degradation of endosulfan was 34%, 92% and 27% in the presence of N_2O, phenol and acid/*t*-BuOH, respectively, as compared to 97% in the absence of either scavenger. The lower removal of endosulfan in the presence of N_2O and acid/*t*-BuOH could be due to their scavenging of e_{aq}^-. The removal efficiency (%) was less inhibited in the presence of air despite its fast reaction with e_{aq}^- as shown by Eq. (3) that could be due to involvement of $O_2^{\bullet -}$ and $HO_2^{\bullet}$ along with •OH in the removal of endosulfan [27]. The study of radical scavengers as well as N_2 and air revealed the contribution of e_{aq}^-, •OH, •H as well $O_2^{\bullet -}$ and $HO_2^{\bullet}$ in the radiolytic degradation of endosulfan with primary involvement of e_{aq}^-. The removal of endosulfan was found to increase with an increase in absorbed dose under all the studied conditions.

Second-order rate constant of endosulfan (ES) with e_{aq}^-, i.e., $k_{e_{eq}^-/ES}$ was determined by competition kinetic method as shown in Eq. (11) [28] using 2-chlorophenol (2-CP) as the competitor for e_{aq}^- ($k_{e_{eq}^-/2\text{-CP}} = 1.3 \times 10^9\,(M\,s)^{-1}$) [26] and isopropanol (*i*-PrOH) as the scavenger for •OH and •H (due to their high bimolecular rate constant as shown by Eqs. (12) and (13)) [26].

$$\ln\left[\frac{ES_D}{ES_0}\right] = \frac{k_{e_{eq}^-/ES}}{k_{e_{eq}^-/2-CP}} \ln\left[\frac{2\text{-}CP_D}{2\text{-}CP_0}\right] \tag{11}$$

$$^{\bullet}OH + i\text{-PrOH} \rightarrow (CH3)_2{}^{\bullet}COH + H_2O \quad k = 1.9 \times 10^9\,(M\,s)^{-1} \tag{12}$$

$$^{\bullet}H + i\text{-PrOH} \rightarrow (CH3)_2{}^{\bullet}COH + H_2 \quad k = 7.4 \times 10^7\,(M\,s)^{-1} \tag{13}$$

A plot of $\ln\left[ES_D/ES_0\right]$ vs $\ln\left[2\text{-}CP_D/2\text{-}CP_0\right]$ gave straight line with slope equal to $k_{e_{eq}^-/ES}/k_{e_{eq}^-/2\text{-CP}}$. Consequently, second-order rate constant of endosulfan with e_{aq}^- was determined and found to be $5.9 \times 10^9\,(M\,s)^{-1}$, much higher than the second-order rate constant of hydroxyl radical with endosulfan, i.e., $k_{\bullet OH/ES} = 1.83 \times 10^9\,(M\,s)^{-1}$ [29].

The primary role of aqueous electron in the removal of endosulfan was consistent with previous studies involving removal of halogenated compounds, such as dichlorobiphenyls and halomethanes by gamma-rays irradiation [21,30].

Radiation yield or *G*-value, defined as "the concentration of species (i.e., molecules, radicals or ions) produced or consumed by absorption of one joule of radiation energy" was determined for the radiation-induced degradation of endosulfan using the following equation [31]:

$$G\text{-value} = \frac{[R]}{D} \times 1.0 \times 10^6\ \mu mol/J \tag{14}$$

In Eq. (14), [*R*] refers to a change in concentration of the target compound in moles per liter (mol/L) at a respective absorbed dose and D is the absorbed dose in Gy. Table 1 shows that *G*-values of endosulfan decreased with an increase in absorbed gamma-ray dose, possibly due to increase in the concentration of by-products

Table 1
G-values (μmol/J) for the degradation of endosulfan under different conditions: N_2 and N_2O gases saturated only, aerated only, and in the presence of phenol and acid (pH 3.0)/*t*-BuOH with N_2 gas. Experimental conditions: $[endosulfan]_0 = 1.0\ \mu M$, $[t\text{-BuOH}]_0 = 60$ mM, $[phenol]_0 = 1$ mM, [perchloric acid] = 0.05 mM.

Absorbed dose (Gy)	*G*-value (μmol/J)				
	N_2 saturated only	Phenol	Aerated	N_2O saturated only	pH 3.0/*t*-BuOH
150	2.9×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	3.8×10^{-4}	3.0×10^{-4}
300	2.7×10^{-3}	2.4×10^{-3}	1.7×10^{-3}	5.7×10^{-4}	4.2×10^{-4}
630	1.4×10^{-3}	1.3×10^{-3}	1.0×10^{-3}	3.6×10^{-4}	3.0×10^{-4}
1020	9.3×10^{-4}	9.0×10^{-4}	7.9×10^{-4}	3.4×10^{-4}	2.7×10^{-4}

with increasing absorbed dose which led to significant competition with the target contaminant for reactive radicals [31–34].

The radiolytic degradation of endosulfan was the highest in N_2 saturated solution and was further studied to investigate the effects of common inorganic ions and humic acid, initial concentration of endosulfan, gamma-ray dose-rate and degradation comparison of endosulfan I and endosulfan II.

3.2. Effects of inorganic ionic species and humic acid

Inorganic ions, e.g., nitrite (NO_2^-), nitrate (NO_3^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and ferric (Fe^{3+}) and humic acid are common constituents of natural water, distributed with varying concentrations depending on geographical locations and anthropogenic activities [29,35,36]. The inorganic ions exhibit high bimolecular rate constants with •OH, •H and e_{aq}^- as shown by Eqs. (15)–(21) and possibly scavenge these radicals to greater extent, however, HA has been reported to efficiently scavenge •OH only [26,37].

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} \quad k = 1.0 \times 10^{10}\,(M\,s)^{-1} \tag{15}$$

$$^\bullet H + NO_3^- \rightarrow HNO_3^- \quad k = 1.0 \times 10^{7}\,(M\,s)^{-1} \tag{16}$$

$$^\bullet OH + NO_2^- \rightarrow NO_2^\bullet + OH^- \quad k = 8.0 \times 10^{9}\,(M\,s)^{-1} \tag{17}$$

$$e_{aq}^- + Fe^{3+} \rightarrow Fe^{2+} \quad k = 6.0 \times 10^{10}\,(M\,s)^{-1} \tag{18}$$

$$^\bullet OH + CO_3^{2-} \rightarrow CO_3^{\bullet-} + OH^- \quad k = 4.0 \times 10^{8}\,(M\,s)^{-1} \tag{19}$$

$$e_{aq}^- + HCO_3^- \rightarrow \text{Product} \quad k = 1.0 \times 10^{6}\,(M\,s)^{-1} \tag{20}$$

$$^\bullet OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O \quad k = 1.0 \times 10^{7}\,(M\,s)^{-1} \tag{21}$$

Therefore, the effects of these species on the removal of endosulfan by gamma irradiation were considered highly important in our study for potential practical applications. An aqueous solution of endosulfan spiked with each of these specie and sparged with N_2 gas was irradiated with gamma-rays. Table 2 shows that at an absorbed dose of 630 Gy, radiolytic degradation of endosulfan was 15%, 24%, 84%, 85%, 75% and 82%, in the presence of NO_3^-, Fe^{3+}, HCO_3^-, CO_3^{2-}, NO_2^- and HA, respectively, as compared to 92% in the absence of either specie. The lower removal efficiency of endosulfan in the presence of NO_3^- and Fe^{3+} could be due to their faster reaction with e_{aq}^- as shown by Eqs. (15) and (18), suggesting their significant competing effect with endosulfan for e_{aq}^-. The relatively higher removal of endosulfan in the presence of HCO_3^- and CO_3^{2-} could be either due to their slower reaction with e_{aq}^- or involvement of $CO_3^{\bullet-}$ (formed from the reaction of HCO_3^- and CO_3^{2-} with •OH as shown by Eqs. (19) and (21)) in the removal of endosulfan [38]. The $CO_3^{\bullet-}$ react fast with sulfur containing electron rich compounds and might have played role in the removal of endosulfan in the present study [38]. Besides, removal efficiency of endosulfan was inhibited in the presence of NO_2^- that scavenges e_{aq}^- up to certain extent in addition to •OH [26]. The lower inhibition of removal efficiency of endosulfan in the presence of HA could be either due their scavenging of •OH only or involvement of radiolytic products of HA in the removal of endosulfan [37]. The effect of inorganic ions and HA also revealed the primary role of e_{aq}^- in the radiolytic degradation of endosulfan.

3.3. Effect of initial concentration of endosulfan

This study is useful to assess the impact of contaminant load on the removal of the target contaminant by gamma-ray irradiation. When the initial concentration of endosulfan was increased, the removal efficiency (%) of endosulfan decreased correspondingly [36]. The removal of endosulfan followed *pseudo-first-order* kinetics at different initial concentration and observed dose constants (k_{obs}, Gy^{-1}) were determined using integrated *pseudo-first-order* rate equation as shown in the following equation [39]:

$$-\ln\left(\frac{C}{C_0}\right) = k_{obs}D \tag{22}$$

Table 3 shows that k_{obs} decreased with increasing initial concentrations of endosulfan which can be attributed to the general trend of predominant chemical reactions in steady-state radiolysis of aqueous solution of the target contaminant as shown by the following equations (23–25):

$$\text{Reactive species} + \text{ES} \rightarrow \text{degradation intermediates} \tag{23}$$

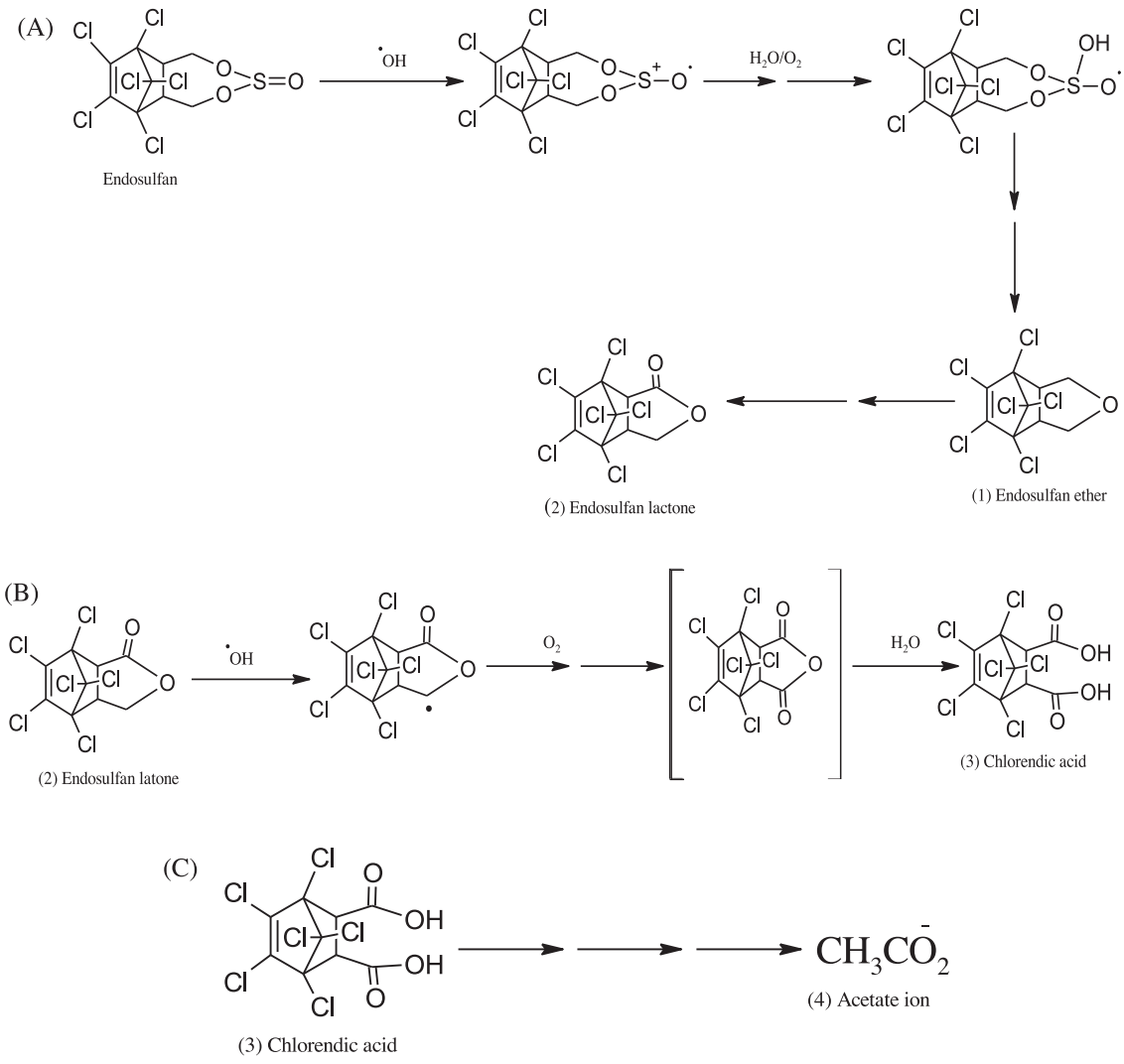
$$\text{Reactive species} + \text{degradation intermediates} \rightarrow \text{degradation products} \tag{24}$$

$$\text{Reactive species} + \text{reactive species} \rightarrow \text{steady molecule} \tag{25}$$

Scheme 1(A–C) depicts that large number of by-products are formed from the radiation-induced degradation of endosulfan

Table 2
Removal efficiency (%) of endosulfan by gamma-rays irradiation in the presence of inorganic ions (i.e., NO_2^-, CO_3^{2-}, HCO_3^-, NO_3^-, and Fe^{3+}) and HA. Experimental condition: $[endosulfan]_0 = 1.0\ \mu M$, $[HA]_0 = 35$ mg/L, $[inorganic\ ions]_0 = 1$ mM.

Absorbed dose (Gy)	Percent degradation (%) $= \frac{(C_0-C)\times 100}{C_0}$						
	N_2 saturated only	CO_3^{2-}	HCO_3^-	NO_3^-	NO_2^-	Fe^{3+}	HA
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
150	49.0	49.1	44.0	10.0	11.1	16.0	33.0
300	60.1	59.2	49.0	12.0	42.0	20.5	70.0
630	92.3	85.0	84.2	15.2	75.2	24.0	82.5
1020	97.0	92.4	91.3	39.0	90.1	26.5	89.0



Scheme 1. Degradation mechanism of endosulfan by hydroxyl radical based AORPs.

whose concentration is expected to increase with increasing initial concentration and consequently led to greater competition for reactive radicals with the target contaminant. This led to increased probability of reaction (24) than reaction (23) and resulted in lowering of k_{obs} [29,40,41].

The relationship between k_{obs} and initial concentration of endosulfan can be expressed as a power function as shown in the following equation:

$$k_{obs} = 0.003\, C_0^{-0.114} \quad R^2 = 0.9943 \tag{26}$$

The values of k_{obs} was used to calculate the dose required for 50% and 90% removal of endosulfan, i.e., $D_{0.50}$ and $D_{0.90}$ (Gy), respectively, as a function of different initial concentrations using the following equations (27) and (28):

$$D_{0.50} = \frac{\ln 2}{k_{obs}} \tag{27}$$

$$D_{0.90} = \frac{\ln 10}{k_{obs}} \tag{28}$$

Table 3 shows that initial degradation rate (calculated by the change in concentration with time at an initial reaction time of 60 min) and *G*-value increased with increasing initial concentrations of endosulfan [29,42,43]. When initial concentration of endosulfan was increased, the number of molecules exposed to reactive species increased correspondingly which led to increased probability of reaction between reactive radicals and molecules of endosulfan. As a result, *G*-value and degradation rate increased, suggested by linear increase in *G*-value from 0.0036 to 0.0144 μmol/J (R^2 = 0.999) and degradation rate from 0.0065 to 0.024 μM/min (R^2 = 0.998) when initial concentration of endosulfan was increased from 0.5 to 2.0 μM [29,42,44].

Table 3
Variation of k_{obs} (Gy^{-1}), degradation rate (μM/min), *G*-value (μmol/J) and dose required for 50% and 90% removal of endosulfan i.e., $D_{0.50}$ and $D_{0.90}$ (Gy), respectively, as a function of different initial concentration. Experimental condition: $[endosulfan]_0$ = 0.5, 1.0 and 2.0 μM.

Concentration (μM)	k_{obs} (Gy^{-1})	Degradation rate (μM/min)	*G*-value (μmol/J)	$D_{0.50}$ (Gy)	$D_{0.90}$ (Gy)
0.5	3.3×10^{-3}	0.0065	0.0036	212	704
1.0	3.0×10^{-3}	0.013	0.0072	231	767
2.0	2.8×10^{-3}	0.024	0.0144	248	822

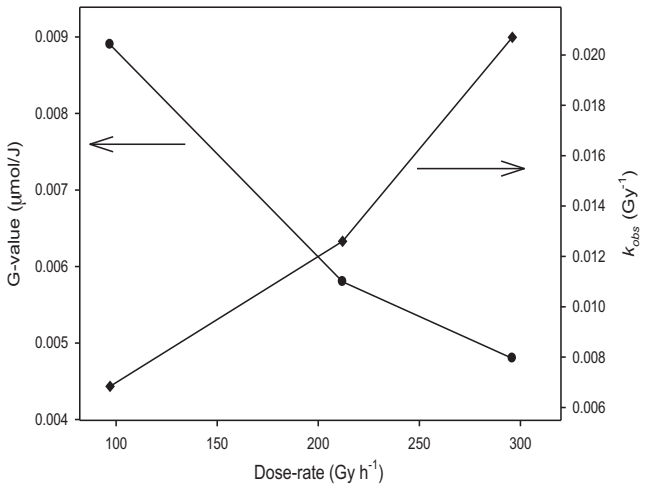


Fig. 2. Effect of dose-rate on the k_{obs} (Gy^{-1}) and *G*-value (μmol/J) of endosulfan. Experimental conditions: [endosulfan]$_0$ = 1.0 μM, dose-rates = 296, 212 and 97 Gy/h.

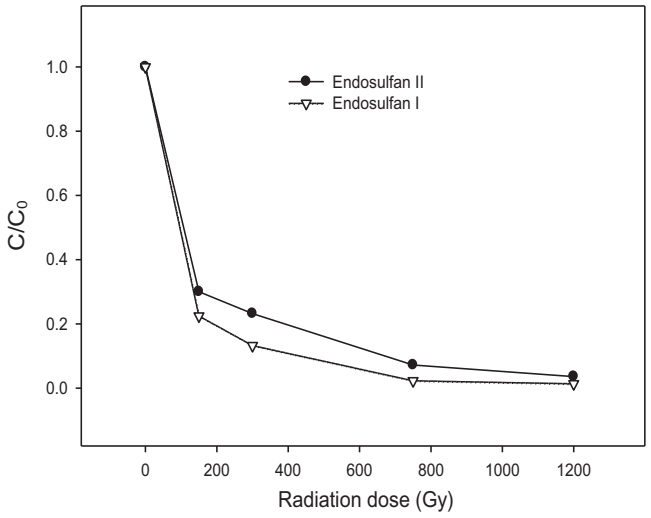


Fig. 3. Degradation comparison of endosulfan I and endosulfan II. Experimental conditions: [endosulfan I]$_0$ = [endosulfan II]$_0$ = 0.61 μM.

3.4. Effect of gamma ray dose-rate

Fig. 2 illustrates *G*-value and k_{obs} for the radiolytic degradation of endosulfan as a function of different gamma-ray dose-rate (D_r). When the dose-rate was increased from 97 to 296 Gy/h, the k_{obs} increased from 0.00684 to 0.0207 Gy^{-1} while *G*-value decreased from 0.00890 to 0.00480 μmol/J correspondingly [41]. At a fix concentration of the target contaminant, an increase in D_r correspondingly increased the steady-state concentration of reactive radicals which led to higher k_{obs} (equal to the product of steady-state radical concentration and second-order rate constants of reaction between reactive radicals and the target contaminant) [41]. However, an increase in steady-state concentration of reactive radicals with increasing dose-rate could increase the probability of radicals recombination reaction as shown by Eq. (25) that significantly compete with the reaction between reactive radicals and the target contaminant (Eq. (23)) and thus led to lowering of *G*-value [41].

3.5. Comparative degradation of endosulfan I and endosulfan II

Table 4 shows that endosulfan in the present study was a stereoisomer of endosulfan I and endosulfan II. The two isomers might show different radiolytic degradation due to difference in their structure, therefore, radiolytic degradation of the two isomers was compared under similar conditions. The study is beneficial to investigate kinetic study of the removal of endosulfan by the AORPs. Fig. 3 shows that at the same absorbed dose, radiolytic degradation of endosulfan I was comparatively more than endosulfan II. The possible reasons for the observed trend look to be the greater persistency of endosulfan II than endosulfan I or involvement of more intermediate steps in the removal of endosulfan II than endosulfan I [45,46]. The difference in degradation of endosulfan I and endosulfan II suggest the influence of structure on the radiolytic degradation of the target contaminant.

3.6. Reaction by-products of endosulfan

The degradation of endosulfan by gamma-rays irradiation resulted in several by-products. The by-products identified were endosulfan ether, endosulfan lactone, chlorendic acid, chloride and acetate ions as shown in Table 4 with their respective molecular structure, molecular weight (MW), and retention time (RT) along with analytical techniques for their determination. All the by-products, except **3** identified as chlorendic acid, were assessed quantitatively. Based on the identified by-products, degradation pathways for endosulfan were proposed and are shown in Scheme 1(A–C) and Eq. (29). The by-products endosulfan ether, endosulfan lactone, chlorendic acid, and acetate ions were found to be resulted from oxidation pathways, however, chloride ion was formed as a result of reduction pathways.

In oxidation pathways, endosulfan is attacked by •OH at the S=O bond through electron transfer mechanism and resulted in radical cation intermediate that quickly hydrolyzed in the presence of oxygen to oxygen-centered radical intermediate (Scheme 1(A)) [29]. The oxygen-centered radical intermediate through a rout of beta-elimination yielded endosulfan ether (product **1**, Scheme 1(A), Figs. 4 and 5) [29,47].

The conversion of ether by-product into endosulfan lactone (product **2**) is explained somewhere else [29].

The lactone by-product is attacked by •OH through hydrogen abstraction reaction yielding carbon-centered radical [21]. The carbon-centered radical react with dissolved oxygen in an aqueous solution that underwent through several intermediate reactions, possibly yielding first chlorendic anhydride (product not identified

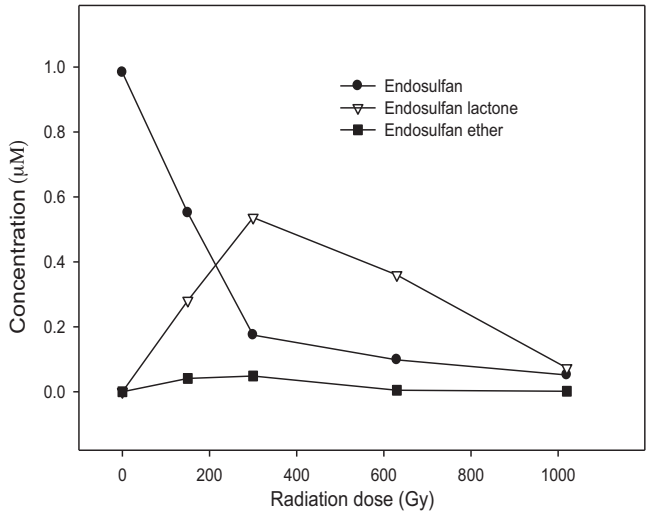
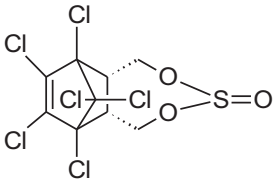
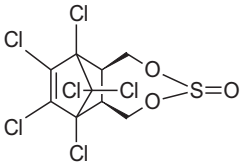
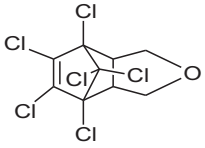
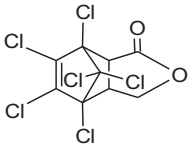
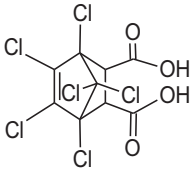


Fig. 4. Changes in the concentration of endosulfan, endosulfan ether and endosulfan lactone with absorbed dose in N_2 saturated solution only. Experimental conditions: [endosulfan]$_0$ = 1.0 μM.

Table 4
List of by-products formed from the radiolytic degradation of endosulfan under different conditions (conditions for analysis by GC-ECD and IC are given in the text). Experimental condition: $[endosulfan]_0$ = 1.0 μM.

Compound	Structural formula	MW	RT (min)	Analytical techniques applied
Endosulfan I		406.9	17.1	GC-ECD
Endosulfan II		406.9	19.7	GC-ECD
(1) Endosulfan ether		342.0	13.2	GC-ECD
(2) Endosulfan lactone		356.0	16.0	GC-ECD
(3) Chlorendic acid		388.8	14.7	GC-ECD
(4) Acetate ion	CH_3COO^-	59.0	7.6	IC
(5) Chloride ion	Cl^-	35.5	10.5	IC

here) that quickly hydrolyzed into chlorendic acid (product **3**) as shown by Scheme 1(B) [21].

The formation of acetate ion (product **4**) concluded that product **3** undergo further oxidative cleavages involving various intermediate pathways as shown in Scheme 1(C), however, further study is needed to explain the pathway.

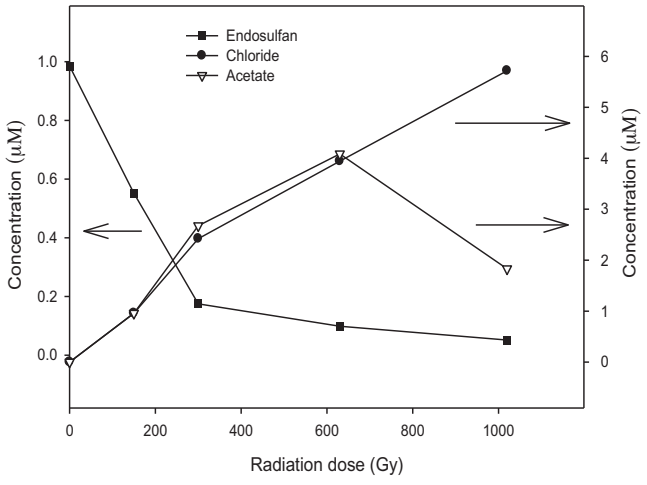


Fig. 5. Changes in the concentration of endosulfan, chloride and acetate ions with absorbed dose in N_2 saturated solution only. Experimental conditions: $[endosulfan]_0$ = 1.0 μM.

In reductive pathways, e_{aq}^- attack endosulfan at the position of chlorine attached to the ring, resulting in the loss of chloride (product **5**) and generation of carbon-centered radical as shown in the following equation [21,48]:

$$e_{aq}^- + C_9H_6Cl_6O_3S \rightarrow Cl^- + {}^{\bullet}C_9H_6Cl_5O_3S \quad (29)$$

This is followed by step wise loss of chloride and formation of intermediate by-product.

The removal of endosulfan followed by significant formation of endosulfan ether, endosulfan lactone, acetate and chloride by the AORPs implicates important role of radical species (Figs. 4 and 5). Under extended treatment by the AORPs, the by-products endosulfan ether, endosulfan lactone and acetate were eliminated, however, formation of chloride steadily increased.

The study is useful to provide literature database on the removal of endosulfan and the further toxicity evaluation on the destruction of this compound. The chlorine group is considered to be essential for the toxicity of organochlorine compounds as well as their by-products, the overall toxicity of these compounds has been reported to be closely related to the extent of de-chlorination achieved in water treatment [12,49]. The mass balance showed that 95% of chloride was removed from endosulfan under reductive pathways at an absorbed dose of 1020 Gy, suggesting a significant decrease in

the toxicity of the target contaminant. Besides, formation of ether and lactone by-products from the degradation of endosulfan under oxidative pathways in our study have been reported to be non-toxic and formation of these by-products suggest detoxification of endosulfan [50]. Nevertheless, more study is needed for the evaluation of the toxicity of the degradation by-products of endosulfan.

4. Conclusions

This study showed that removal of endosulfan by gamma-rays was influenced by an absorbed dose and significantly increased under conditions where e_{aq}^- was the primary reacting specie. The removal of endosulfan was inhibited in the presence of e_{aq}^- scavengers, e.g., acid, N_2O, NO_3^-, and Fe^{3+}. The k_{obs} increased while *G*-value decreased with decreasing initial concentration of endosulfan and increasing gamma-ray dose-rate. The endosulfan II was found to be more persistent than endosulfan I to gamma irradiation treatment. The degradation pathways of endosulfan were suggested from the degradation of endosulfan and by-products evolution, suggesting the attack of •OH at the S=O bond while e_{aq}^- attacked at the chlorine attached to the ring. Results of the study suggest that gamma irradiation based AORPs are promising treatment techniques for the removal of pesticides, such as endosulfan and its products, from a water environment.

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