



Kinetic and mechanism investigation on the gamma irradiation induced degradation of endosulfan sulfate



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H I G H L I G H T S

- Removal of endosulfan sulfate was assessed by gamma-rays under different conditions.
- Removal of endosulfan sulfate by gamma-rays was mainly due to aqueous electron.
- Removal of endosulfan sulfate was significantly affected by pH of aqueous solution.
- Second-order rate constants of endosulfan sulfate with hydroxyl radical and aqueous electron were determined.
- Degradation pathways of endosulfan sulfate were proposed from the nature of by-products evolved.

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The gamma irradiation was investigated for potential removal of endosulfan sulfate, an emerging water pollutant and central nervous system disruptor. A removal efficiency of 99.5% of initially 1.30 μM endosulfan sulfate was observed at an absorbed dose of 1020 Gy. Aqueous electron (e_{aq}^-) was found to play primary role in the removal of endosulfan sulfate which was possibly due to greater reactivity of e_{aq}^- with endosulfan sulfate, considering the second-order rate constant of 8.1×10^9 and $3.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for hydroxyl radical ($\cdot\text{OH}$) and e_{aq}^- , respectively, with endosulfan sulfate. The removal efficiency of endosulfan sulfate was affected by the pH of aqueous solution, with observed removal efficiency of 99.5%, 98.3% and 31.3% at pH 6.2, pH 10.0, and pH 2.6, respectively. The efficiency was also influenced by inorganic anions and humic acid in the order of nitrate > nitrite > bicarbonate > carbonate \approx humic acid. The initial degradation rate increased while degradation constant decreased with increasing initial concentrations of endosulfan sulfate. The degradation pathways showed that oxidative pathway was initiated at the SO_2 bond while reductive pathways at the chlorine attached to the ring of endosulfan sulfate. The mass balance showed removal of 98% chloride and 72% sulfate ions from endosulfan sulfate at an absorbed dose of 1020 Gy. The removal of endosulfan sulfate followed by subsequent loss of by-products under extended treatment showed that gamma irradiation is potential technique for the remediation of organic pollutants from a water environment.

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1. Introduction

Pesticides are chemical substances, either natural or synthetic, widely used in different forms on crops and vegetables etc. so as to increase the agricultural yield (Liu et al., 2009). The extensive use of pesticides led to contamination of various environmental matrices, such as water and thus has become a worldwide concern (Lu et al., 1999). One important among these pesticides include

endosulfan, a chlorinated cyclodiene insecticide that is commonly found as a mixture of two stereoisomers, 64–70% endosulfan I and 29–32% endosulfan II (Rice et al., 1997). It has been reported that in soil and water endosulfan readily undergo microbiological oxidation at the sulfite functional group and transform into endosulfan sulfate (Burns et al., 2008). Endosulfan sulfate is the most common and stable transformation product that together with endosulfan is the most frequent form of water contamination. Endosulfan sulfate has been found to be highly toxic and even more than endosulfan in some cases, it causes acute toxicity (Lemke, 1980; Sunderam et al., 1994), affects embryo development and estrogenic activity in human estrogen-sensitive cells (Soto et al., 1995). Moreover it

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is reported to be highly persistent with long half life ranging from two to six years depending on the environmental conditions (Herrmann, 2003). Therefore, residues of endosulfan sulfate have been detected in environmental matrices, such as water, soil and air in different countries of the world (Shivaramaiah et al., 2005). These factors make endosulfan sulfate of greater concern than the parent compound to be investigated in the present study.

Conventional treatment processes, e.g., coagulation, adsorption, hydrolysis, flocculation and filtration have been reported to be inefficient and may not effectively remove endosulfan sulfate from water (He et al., 2014). Advanced oxidation and/or reduction processes (AOPs or AORPs) are introduced alternatively as the most efficient and promising techniques for water remediation (Lu et al., 1999; He et al., 2014).

AORPs are chemical oxidation methods that involve in situ generation of a power oxidant, hydroxyl radical that can degrade a wide range of contaminants in water, wastewater, air and soil (He et al., 2014). AORPs are class of different methods with most common involving ionizing radiation treatment that generate oxidizing as well as reducing reactive species (i.e., $\cdot\text{OH}$ and e_{aq}^-) simultaneously (Guo et al., 2012; Ismail et al., 2013). The gamma irradiation gives promising results and is also promoted by the international agencies, such as the IAEA, FAO and WHO to accomplish favorable goals in the removal of hazardous wastes (FAO/WHO, 1984; Guo et al., 2012).

In this study Co-60 source was used for generation of gamma radiation to degrade endosulfan sulfate. The removal efficiency as well as degradation pathways of endosulfan sulfate by gamma irradiation under both oxidative and reductive systems were investigated. The removal of organic pollutants by oxidative systems has been widely investigated, however, halogenated organic compounds, such as endosulfan sulfate show high reactivity toward reducing reactive species, e.g., e_{aq}^- . The effects of inorganic anions, humic acid (HA), initial concentration of endosulfan sulfate and pH were investigated on the removal efficiency of endosulfan sulfate. The effects of pH of solution, HA and some of the inorganic anions have been investigated in previous studies, such as by Basfar et al. (2009), Zheng et al. (2011) and Zheng et al. (2012). These studies investigated the effects of only few of these factors, besides their study was mainly concerned to hydroxyl radical based AOPs. The main aim of the present study was the removal of endosulfan sulfate from water containing inorganic anions and humic acid commonly found in natural water and under different pH conditions and to suggest guideline for the removal of persistent halogenated organic contaminant from natural water by both hydroxyl radical and aqueous electron based advanced oxidation and reduction processes (AORPs) for practical applications. The removal of halogenated organic contaminant has been only limited studied using gamma irradiation base AORPs. Further the technique was investigated for the removal of common by-products and dechlorination of endosulfan sulfate and to study change in toxicity of aqueous solution.

2. Experimental

2.1. Materials

Endosulfan sulfate, endosulfan ether and endosulfan lactone with a purity of 99.6% were purchased from Supelco (PA, USA). Sodium nitrate (NaNO_3), sodium nitrite (NaNO_2), potassium carbonate (K_2CO_3), potassium bicarbonate (KHCO_3), ferrous sulfate (FeSO_4), humic acid (HA), sodium hydroxide (NaOH), perchloric acid (HClO_4), sodium sulfate (Na_2SO_4), potassium chloride (KCl), sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$) and isopropyl alcohol were also of high purity and obtained from Scharlau. Ultra pure water with a resistivity of 18.2 M Ω cm was used for preparation of all solutions.

Nitrogen (N_2) and nitrous oxide (N_2O) gases with purity of 99.5% were used for sparging of aqueous endosulfan sulfate solutions.

2.2. Apparatus

The analysis of endosulfan sulfate and some of its by-products were carried out with an Agilent 6890 series gas chromatography (GC) using Ni^{65} electron capture detector (ECD) and an HP-5 (5% phenyl methylsiloxane) capillary column (30 m, i.d. 0.25 μm). Solid phase microextraction technique (SPME) with the fiber made up of polydimethylsiloxane/divinylbenzene (PDMS/DVB) and purchased from Supelco (PA, USA) was used for extraction of samples and directly injecting into the injector of the GC. Analysis was performed under the instrumental conditions using temperature of the injector, inlet and detector at 250 $^\circ\text{C}$, 220 $^\circ\text{C}$ and 350 $^\circ\text{C}$, respectively. The temperature of the oven was programmed from initially 80 $^\circ\text{C}$ (hold for 2 min) followed by increase to 150 $^\circ\text{C}$ (hold time 2 min) at a rate of 20 $^\circ\text{C min}^{-1}$ and finally moved to 220 $^\circ\text{C}$ (hold time 10 min) at 10 $^\circ\text{C min}^{-1}$ rate. Nitrogen gas with a purity of 99.99% was used as a carrier gas at a flow rate of 1.0 mL min^{-1} .

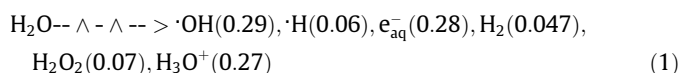
The analysis of anionic by-products, e.g., sulfate ion (SO_4^{2-}), chloride ion (Cl^-) and acetate ion (CH_3COO^-) in irradiated endosulfan sulfate solutions was carried out with ion chromatography (IC, Metrohm, Switzerland). The IC was equipped with an electrical conductivity detector and Assup-5 column (250/4.0 mm). The analysis was carried out by the method for anions determination using 3.2 mM Na_2CO_3 /1 mM NaHCO_3 as an eluent at a flow rate of 0.75 mL min^{-1} .

The identification of by-products was carried out by comparing the retention time of the by-products formed with that of authentic standard compounds under similar experimental conditions (Guivarch et al., 2003).

2.3. Gamma irradiation treatment procedure

Cobalt-60 source (model Issledovadel, origin: USSR), installed at the Nuclear Institute for Food and Agriculture (NIFA), Tarnab, Peshawar and used for research purposes, was used for gamma irradiation treatment of aqueous endosulfan sulfate solution. The source was calibrated using Fricke dosimetry (ferrous sulfate solution) and typical dose-rate was found to be 296 Gy h^{-1} (Ismail et al., 2013).

When irradiated with gamma-ray, dilute aqueous solution of endosulfan sulfate undergo radiolysis of water and reactive species as shown in Eq. (1) are produced (Spinks and Woods, 1990). The numbers in small bracket show G-values (the number of species (molecules, atoms or ions) produced or consumed by absorption of 1 J of radiation energy) of reactive species in $\mu\text{mol J}^{-1}$ in air free medium (Getoff, 1996; Ismail et al., 2013).



Among the species in Eq. (1), the $\cdot\text{H}$, e_{aq}^- and $\cdot\text{OH}$ are highly reactive while the other can be neglected due to their less reactivity and lower concentration formed (Getoff, 1996; Ismail et al., 2013). These radicals attack endosulfan sulfate and caused their degradation through a chain of reactions. The radical scavengers, such as N_2O gas, isopropyl alcohol and inorganic anions were used to investigate the contribution of $\cdot\text{H}$, e_{aq}^- and $\cdot\text{OH}$ in the radiolytic degradation of endosulfan sulfate.

The radiation treatment of aqueous endosulfan sulfate solutions was performed in a 17 mL air tight Pyrex glass tube at a normal pH (pH 6.2) of ultra pure water. The radiolytic degradation of endosulfan sulfate was carried out at other pH, such as pH 10.0 and pH 2.6 as well for studying the effect of pH using NaOH and HClO_4 for pH

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