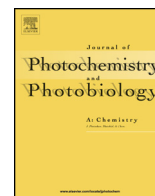




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Comparative studies of various iron-mediated oxidative systems for the photochemical degradation of endosulfan in aqueous solution



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ABSTRACT

This study investigated iron-mediated oxidative processes for the photochemical degradation of endosulfan, a chlorinated insecticide and central nervous system disruptor. At UV fluence of 360 mJ/cm², 52.4% and 32.0% removal of 2.45 μM initial endosulfan was observed by UV/Fe³⁺ and UV/Fe²⁺ processes, respectively, at an initial concentration of 17.8 μM iron. The degradation of endosulfan by UV/Fe³⁺ or UV/Fe²⁺ was dramatically enhanced by adding peroxide (i.e., H₂O₂, S₂O₈²⁻ or HSO₅⁻). Among the UV/peroxide/Fe processes, the highest degradation efficiency of 99.0% at UV fluence of 360 mJ/cm² was observed by UV/HSO₅⁻/Fe²⁺ with 2.45 μM [endosulfan]₀, 17.8 μM [Fe²⁺]₀, and 49.0 μM [HSO₅⁻]₀. The observed degradation rate constant of endosulfan was promoted either by increasing [Fe²⁺]₀ and/or [peroxide]₀ or by decreasing [endosulfan]₀, while the initial degradation rate of endosulfan increased with increasing [Fe²⁺]₀, [peroxide]₀, or [endosulfan]₀. At UV fluence of 6000 mJ/cm², 45.0% mineralization as represented by the decrease in total organic carbon content was observed by UV/HSO₅⁻/Fe²⁺ at 9.80 μM [endosulfan]₀, 980 μM [HSO₅⁻]₀, and 17.8 μM [Fe²⁺]₀. The major by-product of endosulfan was observed in all cases to be endosulfan ether which was further degraded with an extended reaction time. The results suggest that iron-mediated advanced oxidation processes (AOPs) have a high potential for the removal of endosulfan and its by-product from contaminated water.

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1. Introduction

Organochlorine insecticides are an important class of pesticides, commonly used on wood, crops and vegetables for the control of mites, pests, and pest causing diseases [1]. However, many of them have been reported to be highly toxic and can affect the crop productivity [2], soil fertility [3], ecological balance [4], and human health [5]. One of the most known organochlorine insecticides is endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1-heptene-2,3-bis(hydroxymethyl)-5,6-sulfite). It is commonly used on fruits, cotton, vegetables, tobacco, sugarcane, and tea for the control of tsetse fly, mites, home garden pests, Colorado potato beetles, and cabbage worms; it can also be used as a wood

preservative [6,7]. The acute and chronic toxicity of endosulfan is widely recognized in a number of mammals including humans [8]. Moreover, endosulfan is non-volatile and is highly persistent in the environment, with a long half-life ranging from several months to several years [9,10]. Residues of endosulfan have therefore been detected in various environmental matrices such as water [11]. Considering its health risk, the US Environmental Protection Agency has classified endosulfan as a “priority pollutant (category Ib)” [12]. However, no control guidelines have been proposed for this emerging organic pollutant [13]. It is thus highly important to develop effective technologies for the detoxification of water contaminated with endosulfan.

Advanced oxidation processes (AOPs) are innovative treatment technologies that rely on in situ generation of reactive hydroxyl radical ([•]OH) [14]. Various AOPs have been developed and studied including Fenton (Fe²⁺/H₂O₂) and Fenton-like (e.g., Fe³⁺/H₂O₂) reactions, photo-Fenton (UV/H₂O₂/Fe²⁺) and photo-Fenton-like (e.g., UV/H₂O₂/Fe³⁺) reactions, UV/H₂O₂, UV/TiO₂, microwave decomposition and ionizing radiation treatment [15–18]. More

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recently, sulfate radical ($\text{SO}_4^{\bullet-}$) based AOPs have also been gaining researchers' attention in degrading organic contaminants [19]. Both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ have high redox potentials of 2.72 V [20] and 2.5–3.1 V [21], respectively, depending on the measurement conditions, and therefore, readily attack organic contaminants including endosulfan having a comparable reported second-order rate constant of $1.83 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with $\bullet\text{OH}$ and $1.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with $\text{SO}_4^{\bullet-}$ [22]. Hydrogen peroxide (H_2O_2), peroxymonosulfate (PMS, HSO_5^-), and persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) are capable of generating $\bullet\text{OH}$ and/or $\text{SO}_4^{\bullet-}$ after activation, such as by UV irradiation and transition metals [19,23–25]. Iron (Fe), on the other hand, is naturally abundant, cheap and non-toxic, and consequently has been widely investigated for the catalytic decomposition of peroxides and subsequently the enhancement in the degradation of organic pollutants in water [25–27].

In this study, Fe^{3+} or Fe^{2+} was combined with germicidal UV-254 nm and the dual activation of peroxide by iron and UV was further investigated for the degradation of endosulfan. To minimize the reagent cost while establishing environmentally friendly and economical treatment methods, low concentrations of iron and peroxide were used. A kinetic study on the degradation of endosulfan was assessed by varying initial concentrations of the oxidant, iron, or the target contaminant. Mineralization of endosulfan was elucidated by the UV/peroxide/ Fe^{2+} process. Major transformation by-products were also investigated.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals used in the present study were of high purity and used as received. Standard endosulfan ($\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3\text{S}$, 406.9 g/mole, 99.5%) and endosulfan ether ($\text{C}_9\text{H}_6\text{Cl}_6\text{O}$, 342.86 g/mole, 99.5%) were obtained from Supelco (Bellefonte, PA, USA). Sodium persulfate and potassium peroxymonosulfate (active component of a potassium triple salt, commonly known as Oxone[®], $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Hydrogen peroxide (50%, v/v), ferrous sulfate, ferric chloride, methanol, and hydrochloric acid (37.5%, w/w) were purchased from Fischer Scientific (Pittsburgh, PA, USA).

2.2. Analytical methods

An Agilent 7890 gas chromatography (GC) equipped with an Agilent 5975 mass spectrometric detector (MS) and an HP-5MS (5% phenyl methylsiloxane) capillary column (30 m, i.d., 0.25 μm) was used for the detection of endosulfan and its by-products. Solid phase microextraction (SPME) technique with the fiber made of polydimethylsiloxane (PDMS) and fitted with a manual holder (Supelco) was used for a direct injection of samples into the GC. Spectral measurement of the samples was done using an ion trap

operated at 70 eV with a scan mode ranging from m/z 50 to 450. Other instrumentation conditions of the GC–MS method are reported in our previous study [22]. The concentration of endosulfan in the present study was the sum of endosulfan stereoisomers, endosulfan I and endosulfan II. The determination of by-products was performed based on comparison of the spectra of the by-products with those of the standards in the NIST library (USA) installed in the GC–MS [22].

A colorimetric method by UV–vis Spectrophotometer (Hewlett Packard, 8452) was used for the quantification of PMS [28]. A Shimadzu VCSH-ASI TOC analyzer was used for monitoring the total organic carbon (TOC).

2.3. Experimental procedure

The photo-assisted experiment was conducted using a UV photochemical apparatus housing two 15 W low-pressure Hg UV lamps (Cole-Parmer) emitting light primarily at $\lambda_{\text{max}} = 254 \text{ nm}$, with an average UV fluence rate of 0.1 mW/cm^2 in the reaction solution [22,29]. This study was conducted at pH 3.0 if not stated otherwise and the pH was adjusted using 0.1 N HCl. Samples were quenched with methanol prior to analysis by GC–MS. Due to the limit of instrumental analysis, a higher initial concentration of 2.45 μM endosulfan was generally used. Other detailed experimental parameters are shown in the figures and tables shown below. For monitoring the TOC removal, an immediate analysis after each treatment was performed without adding any quenching agent. All the experiments were carried out in triplicate with error bars representing the standard error of the mean.

3. Results and discussion

3.1. Performance of UV/Fe and UV/peroxide/Fe

The degradation of endosulfan was evaluated by three different sets of processes, namely, UV only, UV/Fe (i.e., UV/ Fe^{3+} and UV/ Fe^{2+}), and UV/peroxide/Fe (i.e., UV/peroxide/ Fe^{3+} and UV/peroxide/ Fe^{2+}), with the peroxide evaluated to be H_2O_2 , PS, or PMS). The UV fluence based pseudo *first-order* rate constant for each reaction condition was determined and is shown in Table 1. The presence of Fe and UV improved the degradation of endosulfan compared to direct UV photolysis, with the degradation under UV/ Fe^{3+} being much faster than UV/ Fe^{2+} .

After the excitation of organic molecule by light, both the collision between the excited organic molecule and Fe^{3+} [30] and the transfer of an electron from organic molecule to the center of Fe^{3+} in its complex [31] were reported to be responsible for the destruction of organic compounds. A different mechanism was proposed by De Laat et al. [27] who observed that $\text{Fe}(\text{OH})^{2+}$ in acidic aqueous solution of Fe^{3+} is highly photosensitive with a molar extinction coefficient at 254 nm of $1500\text{--}3500 \text{ M}^{-1} \text{ cm}^{-1}$.

Table 1

Comparison of different processes in the removal of endosulfan in terms of degradation efficiency (%) (calculated at UV fluence of 360 mJ/cm^2), UV fluence based pseudo *first-order* degradation rate constant (k_{obs}), and EE/O value. Experimental conditions: $[\text{endosulfan}]_0 = 2.45 \text{ }\mu\text{M}$, $[\text{peroxide}]_0 = 49.0 \text{ }\mu\text{M}$, $[\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 17.8 \text{ }\mu\text{M}$, pH 3.0.

	Percent degradation (%)	k_{obs} (cm^2/mJ)	UV fluence for one-order removal of endosulfan (mJ/cm^2)	EE/O value ($\text{kWh m}^{-3}/\text{order}$)
UV only	19.8	6.18×10^{-4}	3.72×10^3	20.2×10^{-1}
UV/ Fe^{2+}	32.0	1.11×10^{-3}	2.07×10^3	11.5×10^{-1}
UV/ Fe^{3+}	52.4	2.09×10^{-3}	1.10×10^3	6.24×10^{-1}
UV/ $\text{H}_2\text{O}_2/\text{Fe}^{3+}$	69.4	3.45×10^{-3}	6.67×10^2	3.62×10^{-1}
UV/PS/ Fe^{3+}	76.8	4.19×10^{-3}	5.50×10^2	3.01×10^{-1}
UV/PMS/ Fe^{3+}	86.0	5.83×10^{-3}	3.95×10^2	2.11×10^{-1}
UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$	91.3	6.82×10^{-3}	3.38×10^2	1.82×10^{-1}
UV/PS/ Fe^{2+}	93.1	7.62×10^{-3}	3.02×10^2	1.64×10^{-1}
UV/PMS/ Fe^{2+}	99.0	12.1×10^{-3}	1.90×10^2	1.03×10^{-1}

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