

Degradation of endosulfan and lindane using Fenton's reagent

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Abstract Advanced oxidation of endosulfan and lindane was investigated using Fenton's reagent ($\text{FeSO}_4/\text{H}_2\text{O}_2$) in aqueous phase. A pH of 3 was chosen as optimum with the degradation efficiency of 83 % for endosulfan and 92 % for lindane. FeSO_4 dose of 50 and 20 mg ml^{-1} was found to be optimum for endosulfan and lindane, respectively, with the degradation efficiency of ~ 83 % at pH 3. Further addition of FeSO_4 remained unutilized and contributed to the dissolved solid content. $\text{FeSO}_4:\text{H}_2\text{O}_2$ (w/w) ratio of 1:4.7 and 1:7 was optimized for endosulfan and lindane, respectively. First-order reaction kinetics (5, 7.5 and 10 ppm) were observed for both endosulfan and lindane degradations. Calculated rate constant values (k_{obs}) for initial endosulfan concentration of 5, 7.5 and 10 ppm were 0.021, 0.133, 0.046 min^{-1} , respectively. While rate constant values (k_{obs}) of 0.057, 0.035 and 0.034 min^{-1} were observed for kinetics performed with 5, 7.5 and 10 ppm initial lindane concentrations, respectively. GC–MS analysis revealed that degradation process for endosulfan was sequential with the formation of methyl cyclohexane followed by 1-hexene. While lindane degradation process was spontaneous with the formation of 1-hexene formed by benzene ring fission.

Keywords Dechlorination · Endosulfan · Lindane · Fenton's reaction

Introduction

Endosulfan and Lindane have been used as insecticides on a wide variety of crops (cotton, cereals, fruit trees and plantation crops such as tea and coffee), in public health programs to control vector-borne diseases, and as wood preservatives (Weber et al. 2009). These compounds have been chemicals of choice as a result of their low cost, easy availability and applicability (Andreozzi et al. 1999; Gogate and Pandit 2004). On the other hand, these pollutants are characterized by their high chemical stability, lipophilic nature, hydrophobicity, carcinogenicity, presence of chlorine atoms, and longer half-lives. Their toxic nature makes them recalcitrant and difficult to be completely mineralized by conventional biological treatment (Andreozzi et al. 1999).

Endosulfan acts as a neurotoxin and is considered to be an endocrine disruptor, a xenoestrogen (Edwards et al. 1984). Lindane has been reported to cause disturbances in the rat estrus cycle, lengthened gestation period, decreased fecundity, and increased fetal mortality (Colborn et al. 1993; Sharara et al. 1998). Thus, both endosulfan and lindane have been classified as highly toxic pesticides in EPA toxicity class I and class II, respectively, and are considered as chloroorganic contaminants in the European Union's black list of chemicals (Jaradat 2009; Rodriguez 2003). Due to their toxicity and high persistence in various environmental compartments (soil, water and living organisms), it becomes imperative to develop indigenous technologies for the

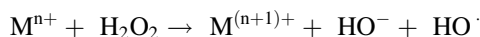
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remediation of these chlorinated pesticides (endosulfan and lindane) in contaminated sites. Recent advancement in the field of science and technology has suggested that these potentially harmful chemicals could be removed by Advanced Oxidation Processes (AOPs) (Zhou and Smith 2002; Titus et al. 2004; Chiro et al. 1999).

AOPs are defined as processes based on generation of highly reactive intermediates that initiate a sequence of reactions resulting in destruction and removal of organic pollutants at ambient temperatures (Chiro et al. 1999; Catalkaya and Kargi 2007). All AOPs are based mainly on hydroxyl radical (OH) chemistry. The hydroxyl radical species with a redox potential of 2.8 V react strongly with most organic substances by hydrogen abstraction or electrophilic addition to double bonds. Free radicals further react with molecular oxygen to give a peroxy radical, initiating a sequence of oxidative degradation reactions which may lead to complete mineralization of the contaminant (Chiro et al. 1999; Catalkaya and Kargi 2007). Among the well-known AOPs, Fenton's reagent is the most widely used and studied catalytic process based on the electron transfer between hydrogen peroxide (H_2O_2) and a metal acting as a homogeneous catalyst for the treatment of both organic and inorganic substances (Chiro et al. 1999). H_2O_2 is a strong oxidant and its combination with transition metal salt (iron salt) is used in Fenton's reagent for the treatment of refractory pollutants (Neyens and Baeyens 2003). The mechanism of Fenton's reagent is as follows:



where, M is a transition metal (Fe or Cu).

Various studies have shown the applicability of Fenton's reagent to treat a variety of industrial wastes containing a range of organic compounds like phenols, formaldehyde, pesticides, wood preservatives, plastic additives, and rubber chemicals. The process may also be applied to wastewaters, sludge, and contaminated soils to reduce the toxicity (Zhou and Smith 2002; Titus et al. 2004; Chiro et al. 1999).

Based on the above-discussed potential of Fenton's reaction, attempts were made to degrade two of the endocrine disrupting chemicals namely endosulfan and lindane in the present study. No such studies were found in the literature so far.

Materials and methods

Source of chemicals

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide), and Lindane (1*r*,2*R*,3*S*,4*r*,5*R*,6*S*)-1,2,3,4,5,6-hexachlorocyclohexane) were procured from Sigma-Aldrich Chemical

Company (USA) and were >98 % pure. All other chemicals were purchased from Fisher Scientific Ltd. (India) or from Merck Ltd. (India). All chemicals were of analytical grade.

Degradation reaction protocol

Separate batch experiments for the degradation of endosulfan and lindane were conducted in aqueous phase. 7.5 ppm initial concentration of endosulfan or lindane was achieved into reaction tubes by adding appropriate volume of 1,000 ppm stock solution of each pesticide prepared separately in acetone. Preliminary experiments conducted suggested that with naturally occurring aqueous concentrations of endosulfan and lindane, the rate of reaction was extremely fast and the authors were unable to study the degradation mechanisms. Hence, to carry out the reactions with higher concentrations of the pesticides, stock solutions were prepared in acetone to enhance the solubility of the two pesticides. Initial pH of the reaction mixture was maintained at two in case of endosulfan. In case of lindane, reaction was conducted at two variations of initial pH values, i.e., 2 and 3. pH was not maintained throughout the experiment. Various doses of FeSO_4 (20–50 mg ml^{-1} for endosulfan and 20–40 mg ml^{-1} for lindane degradation experiments) were added to the reaction mixture. The reaction was initiated by the addition of H_2O_2 (59–236 mg ml^{-1} for endosulfan and 59–118 mg ml^{-1} for lindane degradation). Table 1 depicts the contents of reaction mixtures for endosulfan and lindane. All reactions were conducted in quadruplicate under atmospheric pressure with continuous shaking in a water bath maintained at 130 rpm at 30 °C. No precautions were taken to alter redox potential of the reaction phase. Entire reaction mixtures were sacrificed after 1 h of reaction time, extracted twice using cyclohexane (2×4 ml; total 8 ml) and 0.2 μl of the pooled hexane extracts was injected for GC–ECD analyses. Control experiments were also conducted in exactly the similar way as the test experiment except that no FeSO_4 or H_2O_2 was added into the control reaction mixtures. All other processes (reaction conditions and time) were similar to the test experiments.

pH optimization for the degradation of endosulfan and lindane

Influence of pH on the degradation of endosulfan or lindane was studied in batch mode experiments with 7.5 ppm initial concentration of either endosulfan or lindane. The volume of the reaction mixture was 4 ml. The initial pH of the reaction mixtures was varied from 2 to 6 for both endosulfan and lindane. In case of endosulfan, reaction was conducted with 50 mg ml^{-1} of FeSO_4 and 236 mg ml^{-1} of

Table 1 Endosulfan and lindane disappearance by varying FeSO₄/H₂O₂ concentrations

S. no.	FeSO ₄ dose (mg ml ⁻¹)	H ₂ O ₂ dose (mg ml ⁻¹)	pH	Degradation of compound (%)
Endosulfan				
1	20	59	2	26
2	20	118	2	42
3	20	147.5	2	66
4	25	177	2	60
5	50	177	2	58
6	50	236	2	80
Lindane				
1	20	59	2	36
2	20	59	3	38
3	40	118	2	83
4	40	118	3	97
pH optimization				
Endosulfan				
1	50	236	3	83
2	50	236	4	76
3	50	236	5	66
4	50	236	6	61
Lindane				
1	40	118	4	71
2	40	118	5	62
3	40	118	6	39
FeSO₄ optimization				
Endosulfan				
1	30	236	3	39
2	37.5	236	3	57
3	45	236	3	64
4	50	236	3	83
Lindane				
1	10	118	3	45
2	20	118	3	84
3	30	118	3	83
H₂O₂ optimization				
Endosulfan				
1	50	59	3	61
2	50	118	3	68
3	50	177	3	69
Lindane				
1	20	47	3	73
2	20	71	3	74
3	20	94	3	80
4	20	142	3	94

Reaction conditions: initial concentration of endosulfan or lindane: 7.5 ppm, pH: 2, total volume of reaction solution: 4 ml, reaction time: 1 h, temperature: 25 °C (±1), shaking speed: 130 rpm (±2)

H₂O₂ while in case of lindane, 40 mg ml⁻¹ of FeSO₄ and 118 mg ml⁻¹ of H₂O₂ were chosen to carry out the degradation experiments. Reactions were conducted for 1 h at the ambient conditions as discussed in previous section.

Ferrous sulfate (FeSO₄) dose optimization for endosulfan and lindane degradation

Reactions for FeSO₄ dose optimization were conducted in 4 ml aqueous phase containing 7.5 ppm of either endosulfan or lindane. Initial pH of 3 was chosen to carry out the experiments in case of both endosulfan and lindane. The doses of FeSO₄ were varied from 30 to 50 mg ml⁻¹ at fixed H₂O₂ dose (236 mg ml⁻¹) in case of endosulfan. In case of lindane, FeSO₄ doses were varied from 10 to 40 mg ml⁻¹ with fixed H₂O₂ dose (118 mg ml⁻¹). Reaction time of 1 h was chosen to study the extent of disappearance of each pesticide.

Hydrogen peroxide (H₂O₂) dose optimization for endosulfan and lindane degradation

Based on the FeSO₄ dose optimization experiments, FeSO₄ dose of 50 and 20 mg ml⁻¹ was chosen to optimize H₂O₂ doses for endosulfan and lindane degradation, respectively. In case of endosulfan, H₂O₂ dose was varied from 59 to 236 mg ml⁻¹ while in case of lindane, H₂O₂ dose was varied from 47 to 142 mg ml⁻¹. For both endosulfan and lindane, the reaction was conducted in aqueous phase with the 7.5 ppm initial concentration of endosulfan or lindane at initial pH 3.

Kinetic study of endosulfan and lindane degradation using Fenton's reagent

In case of endosulfan, kinetic studies were conducted in 4 ml aqueous phase to determine the rate and extent of dechlorination of 5, 7.5 and 10 ppm initial concentrations of endosulfan using 50 and 236 mg ml⁻¹ dose of FeSO₄ and H₂O₂, respectively. In case of lindane, FeSO₄ dose of 20 mg ml⁻¹ and H₂O₂ dose of 142 mg ml⁻¹ were selected to study the degradation kinetics of 5, 7.5 and 10 ppm initial concentration of lindane. For both endosulfan and lindane, initial pH of the reaction mixtures was maintained at 3. The corresponding control experiments were also conducted to determine the extent of degradation of endosulfan and lindane under same conditions as for the test samples. All reactions were conducted under similar conditions as described above in the degradation reaction protocol.

Gas chromatography–electron capture detection (GC–ECD) analyses

Extracted samples were analyzed using a gas chromatograph equipped (Agilent, model no. 6890 N) with Ni⁶³ electron capture detector (ECD). The column used was HP-5 capillary column of 0.32 mm ID, 0.25 μm film thickness and 30 m length. Injections were made in splitless mode using nitrogen as the carrier gas. The following temperature programming was used: initial oven temperature of 150 °C with hold time for 2 min, then ramped to 200 °C at 6 °C min⁻¹ with hold time of 2 min, again ramped to 250 °C at 10 °C min⁻¹ with a hold time of 2 min. Injector and detector temperatures were set at 200 and 290 °C, respectively. The residual concentrations of endosulfan, lindane, partially chlorinated intermediates and the end products were quantified from peak areas obtained through automated integration and also by comparison with known concentrations of the pure standard compounds.

Gas chromatography–mass spectroscopy (GC–MS) analyses

GC–MS analyses were carried out using TRACE GC ULTRA (Thermo make) equipped with MS (model DSQII). The column used for GC–MS analysis was TR-5 column of 0.25 mm I.D., 0.25 μm film thickness and 30 m length. 1 μl volume of samples was injected for analyses. Helium (He) was used as carrier gas. The temperature programming used was: initial oven temperature of 40 °C with the hold time of 1 min, ramped to 53 °C at 1 °C min⁻¹ with hold time of 1 min, again ramped 53–60 °C at 10 °C min⁻¹ with hold time of 1 min and finally ramped from 60 to 250 °C with hold time of 1 min. Injector and detector temperatures were set at 200 and 300 °C, respectively. The mass spectral data coupled with the systematic reduction in the retention times of the dechlorinated products (due to loss of chlorine atoms) allowed identification of the intermediates and end products with reasonable certainty. Wiley Registry (8e Mass Spectral Library) was used to identify the intermediate and end products.

Results and discussion

Table 1 depicts the extent of endosulfan and lindane degradation using various doses of FeSO₄ and H₂O₂. It is clear from the table that about 80 % of 7.5 ppm initial concentration of endosulfan disappeared within 1 h of the reaction time at FeSO₄ dose of 50 mg ml⁻¹ and H₂O₂ dose of 236 mg ml⁻¹ at initial pH 2. When H₂O₂ dose was reduced to 177 mg ml⁻¹, endosulfan degradation decreased to

about 58 %. On further reducing the dose of FeSO₄ and H₂O₂ (20 and 59 mg ml⁻¹, respectively), minimum endosulfan degradation (26 %) was observed at initial pH 2. Based on the results provided in Table 1, FeSO₄ dose of 50 mg ml⁻¹ and H₂O₂ dose of 236 mg ml⁻¹ were selected to carry out further degradation studies on endosulfan degradation. The increase in pH at the end of the reaction was observed in all experimental set-ups with pH reaching to neutral/alkaline levels. No degradation or disappearance of pesticides was observed in any of the control experiment.

Table 1 also reveals that about 97 % degradation of lindane (initial concentration 7.5 ppm) was achieved at FeSO₄ dose of 40 mg ml⁻¹ and H₂O₂ dose of 118 mg ml⁻¹ at a pH of 3. Further, when pH of the reaction mixture was reduced to two at same doses of FeSO₄ and H₂O₂, 83 % degradation of lindane was observed after 1 h of the reaction time. On decreasing FeSO₄ and H₂O₂ further (20 and 59 mg ml⁻¹, respectively); significant reduction in disappearance of lindane was witnessed (36 and 38 % at pH 2 and 3, respectively). Thus, a FeSO₄ dose of 40 mg ml⁻¹ and H₂O₂ dose of 118 μl ml⁻¹ were selected to conduct further experiment on lindane degradation.

pH optimization for dechlorination of endosulfan and lindane

pH of the reaction mixture plays an important role in the degradation of endosulfan and lindane. The maximum degradation of both pesticides was observed at a pH value of 3 (83 and 97 %, respectively, for endosulfan and lindane) followed by pH 2 (80 and 83 %, respectively). Above pH 4, the degradation efficiency of Fenton's reagent begins to drop and this may be due to the decrease in the dissolved fraction of iron species by the formation of complexes which inhibits the formation of free radicals. This further hinders the regeneration of ferrous ions with the increase in pH.

Our results are in agreement with the results reported by Kwon et al. (1999) for the decomposition of *p*-chlorophenol by Fenton oxidation. It was observed that decomposition progressed at higher rates at pH 2–4. Above pH 4, decomposition rates were significantly decreased. However, in another study conducted by Li et al. (2009) for the removal of triazophos with Fenton reagent, it was observed that synthesized waste water containing triazophos had efficient chemical oxidation demand (COD) removal at a pH value of 4. It was also observed that at pH values lower than 4, the reaction rate of Fe³⁺–Fe²⁺ decreased and at pH above 4, H₂O₂ decomposed very slowly and fewer hydroxyl radicals were produced.

Thus, a pH of 3 was chosen as optimum to carry out further degradation studies of both endosulfan and lindane.

Ferrous sulfate dose optimization for the dechlorination of endosulfan and lindane

Ferrous sulfate dose optimization for the degradation of endosulfan and lindane was done by varying FeSO_4 dose at fixed H_2O_2 dose (236 and 118 mg ml^{-1} for endosulfan and lindane, respectively). In case of endosulfan, varying FeSO_4 dose has a profound influence on the extent of degradation. On FeSO_4 dose of 30 mg ml^{-1} , only 39 % degradation of endosulfan was observed. When FeSO_4 dose was gradually increased to 37.5 and 45 mg ml^{-1} , about 57 and 64 % removal of endosulfan was achieved, respectively. Further, the maximum degradation of endosulfan (83 % removal) was witnessed at a FeSO_4 dose of 50 mg ml^{-1} . Based on these results, FeSO_4 dose of 50 mg ml^{-1} was selected to conduct further endosulfan degradation study.

In case of lindane, about twofold increase (45–84 %) in the degradation was observed when FeSO_4 dose was increased from 10 to 20 mg ml^{-1} . However, further increase in FeSO_4 dose (to 30 mg ml^{-1}) did not influence lindane degradation (83 % degradation). The maximum lindane degradation (97 %) was observed at FeSO_4 dose of 40 mg ml^{-1} . Based on this observation, 20 mg ml^{-1} dose of FeSO_4 was chosen as optimum for further degradation studies of lindane despite of having the maximum degradation of lindane at 40 mg ml^{-1} dose of FeSO_4 . The authors would like to point out that the optimum degradation, here stands for the satisfactory range of degradation achieved by economically favorable concentrations of reactants (Hydrogen peroxide and Iron). As in this case, only a difference of 13 % degradation was achieved by doubling the concentration of FeSO_4 which does not seem to be an economical choice.

At a fixed initial concentration of pesticides and H_2O_2 , continuous increase in FeSO_4 dose enhances the degradation of pesticides. This is mainly due to the presence of sufficient concentration of catalytic ferrous ions in the reaction system. However, after a certain saturation point, any further increase in FeSO_4 dose does not influence the degradation reaction. This is also supported by other studies conducted to degrade alkylbenzene sulfonate and landfill leachate (Lin et al. 1999; Kang and Hwang 2000). For the removal of non-biodegradable landfill leachate (evaluated as COD), it was observed that COD removal efficiency increased with an increase in FeSO_4 dose till a concentration of 500 mg l^{-1} , beyond which the removal efficiency remained unchanged.

Hydrogen peroxide dose optimization for degradation of endosulfan and lindane

H_2O_2 plays a crucial role in the overall efficacy of the degradation process. In case of endosulfan (7.5 ppm initial concentration), 61 % removal was noticed at 59 mg ml^{-1} dose of H_2O_2 (1:1.2 w/w FeSO_4 : H_2O_2 ratio). Whereas the continual increase of H_2O_2 dose to 118 and 177 mg ml^{-1} (1:2.4 and 1:3.5 w/w FeSO_4 : H_2O_2 ratio, respectively) showed 68 and 69 % disappearance of endosulfan. Further increase in H_2O_2 dose to 236 mg ml^{-1} (1:4.7 w/w FeSO_4 : H_2O_2 ratio) resulted in 83 % removal of the endosulfan.

In case of lindane (7.5 ppm initial concentration), it was observed that increase in H_2O_2 dose from 47 to 71 mg ml^{-1} (1:2.4 and 1:3.5 w/w FeSO_4 : H_2O_2 ratio) did not significantly increase degradation of lindane (73 and 74 %, respectively). However, at a H_2O_2 dose of 118 mg ml^{-1} (1:5.9 w/w FeSO_4 : H_2O_2 ratio), about 84 % of lindane was degraded. Further, 94 % removal of lindane was observed when H_2O_2 dose was increased to 142 mg ml^{-1} (1:7 w/w FeSO_4 : H_2O_2 ratio).

The feature of the optimal dose of H_2O_2 is characteristic of Fenton's reagent. The typical ranges of FeSO_4 and H_2O_2 as suggested by Titus et al. (2004) and Gogate and Pandit (2004) are 1 part iron per 5–25 parts of H_2O_2 similar to our results obtained for FeSO_4 dose optimization. Further, it was observed that as the concentration of H_2O_2 increases, the degradation efficiencies of both the pesticides tend to increase probably because of the increase in the amount of oxidant present in the reaction system for the same initial concentration of pesticides and catalytic ferrous ions. Results by other researcher groups have also shown similar results while removing COD (Idil 2007) and chlorophenols (Barbeni et al. 1987). Any further addition of H_2O_2 dose after a certain saturation point has no major influence on degradation as the residual H_2O_2 would contribute to COD and hence excess amount is not recommended (Lin and Lo 1997).

Kinetic study for the dechlorination of endosulfan and lindane by Fenton's reagent

Figure 1 depicts the kinetic profile of endosulfan degradation (5, 7.5 and 10 ppm initial concentrations) as a function of time for endosulfan removal by FeSO_4 dose of 50 mg ml^{-1} and H_2O_2 dose of 236 mg ml^{-1} at initial pH 3. At initial endosulfan concentrations of 5, 7.5 and 10 ppm, ~3, 60 and 50 % disappearance, respectively, was witnessed within 2 min of the reaction time. As the reaction proceeded, gradual increase in endosulfan degradation was noticed and about 67, 94 and 81 % of 5, 7.5,

Fig. 1 Kinetics of the degradation of endosulfan by Fenton's reagent [reaction conditions: initial endosulfan concentration: 5, 7.5 and 10 ppm, pH: 3, reaction volume: 4 ml, reaction time: 1 h, temperature: 25 °C (± 1), shaking speed: 130 rpm (± 2), FeSO₄: 50 mg ml⁻¹, and H₂O₂: 236 mg ml⁻¹]

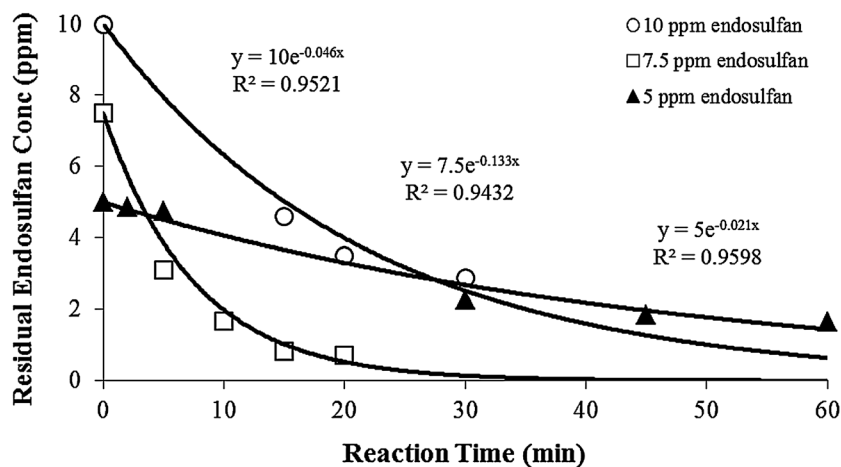
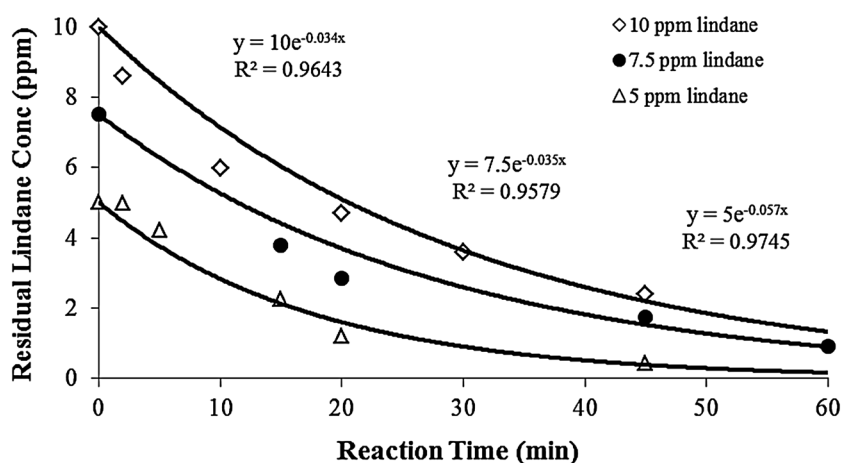


Fig. 2 Kinetics of the degradation of lindane by Fenton's reagent [reaction conditions: initial lindane concentration: 5, 7.5, and 10 ppm, pH: 3, reaction volume: 4 ml, reaction time: 1 h, temperature: 25 °C (± 1), shaking speed: 130 rpm (± 2), FeSO₄: 20 mg ml⁻¹, and H₂O₂: 142 mg ml⁻¹]



and 10 ppm initial concentrations, respectively, of endosulfan were degraded within 1 h of reaction. The set of data in Fig. 1 could be fitted into exponential curves thereby suggesting first-order kinetics of the reaction. The rate constant (k_{obs}) values for the set of kinetics performed were 0.021, 0.133, 0.046 min⁻¹, respectively, for 5, 7.5 and 10 ppm initial concentration of endosulfan.

Figure 2 shows the degradation kinetic profile of 5, 7.5 and 10 ppm initial concentrations of lindane as a function of time and time course profile for lindane removal by FeSO₄ dose of 20 mg ml⁻¹ and H₂O₂ dose of 142 mg ml⁻¹ at a pH value of 3. At initial lindane concentrations of 5, 7.5 and 10 ppm, ~5, 27 and 14 % degradation was observed within 2-min reaction time. However, after 1 h of reaction, about 93, 88 and 81 % of lindane degradation was observed for 5, 7.5 and 10 ppm initial concentrations of lindane, respectively. The set of data in Fig. 2 was well fitted into exponential curves thereby suggesting first-order kinetics of the reaction. The rate constant values (k_{obs}) for the set of kinetics performed for lindane (5, 7.5 and 10 ppm initial concentrations) degradation were calculated to be 0.057, 0.035 and 0.034 min⁻¹, respectively.

It can be noticed from Figs. 1 and 2 that optimum degradation and rate constant values were achieved at 10 ppm initial endosulfan concentration and at 5 ppm initial lindane concentration, respectively. Our results for lindane degradation are in agreement with work carried out by Kwon et al. (1999) and Benitez et al. (2001) for the decomposition of *p*-chlorophenol and *p*-hydroxyl phenyl-acetic acid, respectively, wherein the percentage degradation of pollutant decreased with the increase in the initial concentration of pollutant and that efficient removal of the pollutant is favored usually at lower initial concentrations of the pollutants.

In experiments carried out by Kwon et al. (1999), Benitez et al. (2001), and Zhou and Lei (2006) for the decomposition of wastewater containing alkylbenzene sulfonate, *p*-chlorophenol, 4-chlorophenol and *p*-nitrophenol, respectively, using Fenton's reagent highlighted that degradation reaction follows first order of reaction. However, pseudo-first-order reaction kinetics was observed by Arslan and Balcioglu (2001) for the degradation of Remazol black B dye and its simulated dyebath wastewater. Balci et al. (2009) also reported that the degradation of

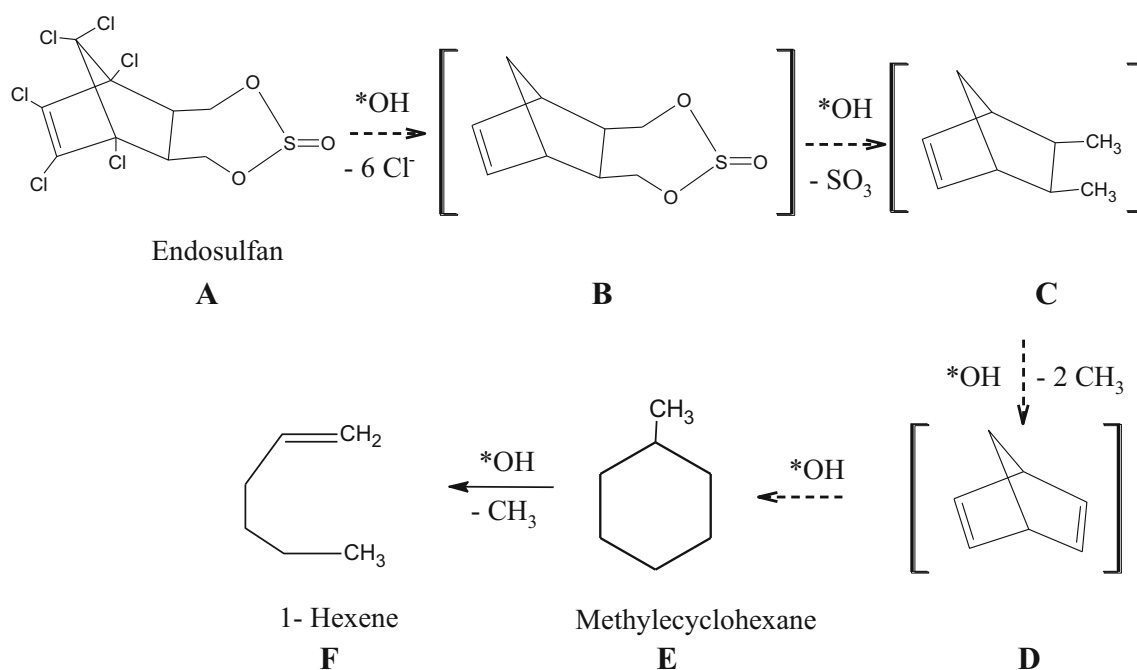


Fig. 3 Proposed endosulfan degradation pathway by Fenton's reagent

atrazine in aqueous medium using Fenton's reagent follows pseudo-first order.

GC–MS analysis of degradation products formed from Endosulfan and Lindane following reaction with Fenton's reagent

No partially dechlorinated intermediate of endosulfan and lindane degradation using Fenton's reagent could be detected using GC–ECD. Thus, GC–MS analyses were carried out to detect and identify the intermediates formed, if any along with the end products of degradation.

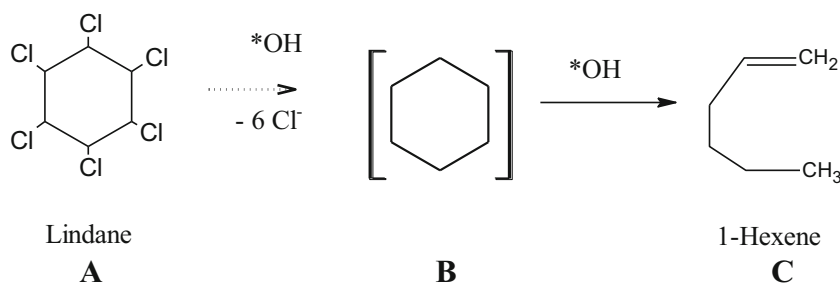
GC–MS analysis for endosulfan degradation was carried out with initial endosulfan concentration of 10 ppm in 4 ml aqueous phase with FeSO_4 dose of 50 mg ml^{-1} and H_2O_2 of 236 mg ml^{-1} at pH 3 and the entire reaction mixtures were sacrificed after 10 and 30 min of reaction time, extracted using dichloromethane and analyzed. MS elution profile after 10 min reaction time showed an abundant peak at 4.25 min. Based on the molecular ion fragmentation pattern of this peak (characterized m/e of 98), it was identified as methyl cyclohexane using Wiley library (8e Mass Spectral Library). However, the MS elution profile after 30-min reaction time did not show any peak at 4.25 min indicating its total disappearance and a new peak at 3.01 min appeared. This peak eluting at 3.01 min was identified as 1-hexene based on its molecular ion fragmentation pattern characterized by m/e of 84. 1-hexene might have formed by the fission of methyl cyclohexane molecule. Based on the above, endosulfan degradation

mechanism is proposed in Fig. 3. However, the compounds shown in brackets (b–d) were not identified and detected, but based on the identified end products; the authors propose that reaction would proceed in depicted fashion. Appearance of no partially chlorinated intermediate suggests that either the removal of chloride atoms is simultaneous or too fast to be captured.

In case of lindane, GC–MS analysis was carried out with initial lindane concentration of 10 ppm with FeSO_4 dose of 20 mg ml^{-1} and H_2O_2 dose of 142 mg ml^{-1} at pH 3. Reaction mixtures were sacrificed at 10- and 30-min reaction time, extracted using dichloromethane and analyzed. MS elution profile after 10-min reaction time showed a major peak at 2.99 min, which was identified as 1-hexene based on the molecular ion fragmentation pattern characterized by m/e of 84. The absence of any other partially chlorinated intermediate suggests that removal of chlorine atoms occurs simultaneously or in a very fast manner. The proposed mechanism of lindane degradation using Fenton's reagent is shown in Fig. 4. However, the compound shown in brackets (cyclohexane, b) was not identified and detected, but based on the identified end products, the authors propose that reaction may proceed in the depicted fashion.

However, earlier reports have suggested that the reaction proceeds in sequential way. Catalkaya and Kargi (2007) reported that the degradation of diuron using Fenton reagent proceeds in a sequential way with the formation of aniline and 3,4-dichloroaniline as major intermediates. In another study conducted by Masomboon et al. (2010), the

Fig. 4 Proposed lindane degradation pathway by Fenton's reagent



degradation of 2,6-dimethylaniline by Fenton's reagent resulted in formation of several stable intermediates, viz, 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid. Zhou and Lei (2006) while studying the degradation of *p*-nitrophenol observed that degradation process was sequential with the formation of hydroquinone, *p*-nitrocatechol, benzoquinone and carboxylic acids such as fumaric acid and oxalic acid as intermediates.

Conclusion

The following salient points have emerged from the present study:

1. Fenton's reagent is an efficient system to dechlorinate endosulfan and lindane completely.
2. GC–MS analyses reveal that Fenton's system is capable of complete dechlorination of the endosulfan with 1-hexene as an end product.
3. The dechlorination reaction proceeds at ambient temperature and pressure. No precaution is required to exclude oxygen or reduce redox potential of the reaction.

As the presented experiments were conducted under controlled conditions at a laboratory scale set-up, the cost of pure analytical grade chemicals (endosulfan, lindane, H_2O_2 , iron) contributes significantly to the cost of the treatment. However, when the technology would be taken to the field scale, a reduction in the cost is expected, mainly due to (a) the naturally occurring concentrations of the endosulfan and lindane in the environment and (b) reduced cost of bulk quantities of Hydrogen peroxide and iron. Further, as the contaminated sites are located in the western coast of India which is naturally abundant in laterite soils; the iron present in these soils may be a source of iron leading to the further reduced cost of the treatment. The authors plan to upscale the technology in two phases; (a) pilot scale experiment with real water contaminated

with the pesticides in large volume reactors and (b) field level demonstration of the technology. The former phase would enable the authors to study the synergistic or antagonistic impacts of other co-existing components in the natural water systems. This would lead to the correction and revised optimization of the reaction parameters. This can be followed by the field scale treatment.

Overall, Fenton's reagent is a promising technology for in situ chemical oxidation of chlorinated pesticides for soil and ground water remediation as an alternative to the conventional treatment methods. Fenton's reaction could provide fast and efficient treatment of contaminant sites and thus lowering the treatment cost. Also Fenton's reagent has an advantage of using hydrogen peroxide, which is safe, easy to use and a cheaper oxidant than other chemical oxidants. Use of iron as a catalyst has an added advantage as it is the second most abundant metal and the fourth most abundant element on earth. Further, it would be worthwhile to evaluate the degradation efficiency of Fenton's reagent in combination with ozonation or photocatalysis to achieve immediate mineralization of organics.

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