

Advanced Oxidation Processes for the Degradation of Organochlorine Pesticides

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Abstract

Advanced Oxidation Processes (AOPs) are a group of treatment technologies, which aim at efficient decomposition of pollutants. The AOPs are based on oxidation of pollutants using various single or combinational techniques generating free radicals, thereby leading to oxidative degradation and complete mineralization of pollutants. Conventional AOPs based on ultraviolet (UV) irradiation are commonly used for destruction of microorganisms in the household filters. These techniques have also been used to remediate conventional and upcoming pollutants like pesticides, Pharmaceuticals etc., which are normally persistent in nature. The various combinations used for generating reactive radicals in AOPs are fenton, photofenton, ozone, UV radiations, sonolysis etc.

In the present study, degradation using various AOPs and different pesticides was performed for the organochlorine group of pesticides. It was found to be effective for degradation of the targeted pesticides which are otherwise, persistent in nature. The response of the studied pesticides was different for all the AOPs used, which include, UV photolysis, H₂O₂ degradation, UV-H₂O₂, fenton's etc. Studies have been performed in the aqueous matrix and degradation rates are determined for the different reactions. The rate of degradation was found to be significantly enhanced in presence of H₂O₂ and fenton's reagent with UV irradiation rather than UV alone.

Keywords: Advanced Oxidation Processes, Organochlorines, Pesticides, UV, Fenton's reagent

Introduction

Pesticides and fertilizers play a substantial role in enhancing the crop productivity. However, the use of pesticides goes parallel with its residues in water and soil due to its indiscriminate use. The pesticides after being used in the fields, enter the environment through surface run-offs, aerial sprays etc. and some of persistent pesticides may bind with the soils and also get deposited in the sediments.

Humans may be exposed to pesticides by direct and indirect routes of exposure like dermal contact, inhalation etc. The exposure to these compounds may lead to acute and chronic health issues.

The pesticides can be classified into various classes depending upon their chemical composition, applications, origin etc. Under chemical classification, pesticides are categorized according to the chemical nature of the active ingredients. The various categories include Organochlorines (OCPs) Synthetic Pyrethroids (SPs) Organophosphate (OPPs) etc.

Of these, the OCPs is the most persistent of the group. They are synthetic organic compounds with five or more chlorine atoms. They have been used significantly in agriculture and mosquito control in the past. Some important representative compounds of this group are dichlorodiphenyl-trichloroethane (DDT), Hexachlorocyclohexane (HCHs), aldrin, dieldrin, chlordane, endosulphan etc.^{1,2}

OCPs have a high bioaccumulation potential, toxicity, and persistence in the environment³.

A good number of pesticides, particularly organochlorines, can also be seen among the Persistent Organic Pollutant list of Stockholm convention⁴. A share of about 40% of all the pesticides used belonged to organochlorines in the past⁵.

The various studies carried out on pesticide concentrations in the environment, indicate their presence not only in environmental matrices but also at various food chain levels.

During 2005-2007, 16 bird species in more than 100 samples were collected from Ahmedabad after being killed with kite flying threads. All carcasses were detected with pesticide contamination during the study, which makes the situation more alarming⁶. The blood plasma samples of Vultures collected from Ahmedabad indicated the presence of organochlorine pesticides (OCPs) and polychlorinated biphenyls⁷.

Some studies have also been carried out in the Cauvery river⁸ in the water, sediment, shrimps and fish samples indicate the presence of OCPs in these samples.

Another review⁹ reported OCPs in the Cauvery river which include compounds like hexachlorocyclohexane (HCH), dichloro-diphenyltrichloroethane (DDT), endosulfan, aldrin, dieldrin, heptachlor epoxide etc. The concentrations of HCHs, DDTs and endosulfan residues in water were observed up to 2.3microg/L, 3.6 microg/L and 15.4 microg/L, respectively.

Fate of pesticides

The fate of pesticide in environment depends on the chemical and physical properties of the pesticides, its environmental interactions and abiotic and biotic characteristics of the receiving matrix. Pesticides are degraded or immobilized through processes like, hydrolysis, photolysis, soil adsorption, degradation through microorganisms and plant uptake.

The distribution of pesticides in the environmental matrices is dependent on physico-chemical characteristics of pesticide like solubility, partition coefficient, half-life and photolysis, etc.¹⁰. The immobilized pesticides can remain in the soil/sediment till they are degraded by the soil microbes or other reactions. Mostly, the more hydrophobic pesticides tend to get locked in soil/sediment.

Due to potential water contamination by these pesticides there is a need to develop techniques for destruction of these compounds in water. Advanced Oxidation Processes (AOPs) have been recently studied as a promising techniques for many applications¹¹.

AOPs are relatively cleaner in context of environmental applications. They use various combinations of oxidants, UV irradiation and some catalysts for hydroxyl radical (OH[•]) generation in solutions. This radical is non-selective and strong chemical oxidant that can react rapidly with most organic compounds. AOPs have also been successfully used to remove, upcoming pollutants like pharmaceuticals and other endocrine disrupting chemicals¹².

The organic pollutants are oxidized by free radicals and can be ultimately mineralized to water, carbon dioxide and mineral salts. Ozonation alone or oxidation of organic compounds through H₂O₂ may or may not completely oxidize organics to CO₂ and H₂O in many cases. Supplementing the reaction with UV radiation would aid in the reaction completion¹¹.

Process efficacy is dependent on the rate of hydroxyl radical generation and their contact with the contaminant molecules. Earlier studies have been performed on the removal of Lindane

from soil and water using certain AOPs¹³⁻¹⁶. Lindane is reported to be difficult to degrade by ozonation and requires addition of oxidant like H₂O₂ for efficient degradation¹⁶.

A few studies have reported photolytic degradation of endosulphan using UV irradiation¹⁷ and biodegradation of endosulphan¹⁸⁻¹⁹.

A study¹¹ on comparative operating costs of some of the AOPs reported a high oxidant cost in the ozonation/UV and ozonation /H₂O₂ process. In the present study we have not used ozonation but attempted to degrade the studied pesticides using UV irradiation, H₂O₂, fenton's reagent and a combination of both, that is, UV/H₂O₂ and UV/Fenton. These five AOPs are optimized to achieve maximum degradation of lindane and endosulphan isomers.

Lindane and Endosulphan are persistent pesticides and are listed amongst POPs (Persistent Organic Pollutant) in Annexure A under the Stockholm Convention⁴. Lindane (1,2,3,4,5,6-hexachlorocyclohexane) is an organochlorine pesticide with a broad-spectrum of activities and was commonly used for a wide range of soil-dwelling and plant-eating insects. It was previously used on numerous crops, as a seed treatment. Another common use of Lindane is treatment of scabies and lice in humans⁴. Throughout the world, it had been used for agricultural applications as a mixture of technical grade HCH or in pure form, since 1940s. The effective component of technical grade HCH is lindane²⁰.

Lindane has the potential for long-range environmental transport, tendency of bioaccumulation and carcinogenic characteristics⁴. Hydrolysis of lindane happens in alkaline pH and it reduces to its half concentration in nearly 50 hours at pH 9, it is reported to be completely stable at pH 5²¹. Due to widespread use during earlier times and resistance to degradation, lindane and other HCH isomers occurred frequently in soils and groundwater all over the world causing environmental issues²². Due to its toxicity and non-biodegradability in the environment, most of the countries have restricted its use²⁰.

Endosulphan is chlorinated- cyclodiene insecticide with broad spectrum activities. Technical grade Endosulphan consists of two stereoisomers, α and β endosulphan in an approximate ratio of 7:3¹⁸. In the environment, it hydrolyzes to a less toxic species, endosulphan diol, due to O-S double-bond breakage. It can also be oxidized to a more persistent compound that is endosulphan sulphate which requires degradation; Photolysis produces endosulphan diol¹⁷. Endosulphan is toxic to aquatic organisms²³⁻²⁴. The lethal concentration 50 of endosulphan is relatively higher than DDT²⁵.

Due to the persistence of these two organochlorines and their extensive use in the previous times, they were selected as model compounds for studying the degradation of pesticides through AOPs.

Materials and Methods

Chemicals

All the solvents (Merck) used for standard preparation and sample extractions were of HPLC grade. FeSO_4 (Loba) was used as received. Neat Standards of Lindane, Alpha and Beta Endosulphan were procured from Sigma Aldrich. A working solution of 5 ppm was prepared from the stock. The stock and working solutions were prepared in n-hexane.

The composition of Fenton's reagent used was 1mM FeSO_4 + 10mM H_2O_2 for most of the experiments unless otherwise mentioned.

Photochemical Experiments

The laboratory scale photodegradation experiments were performed in an immersion well quartz reactor of 650 mL capacity. The photochemical reactor was cylindrical in shape with a water recirculation arrangement to maintain the temperature close to 25°C. It was irradiated using a 400 W medium pressure mercury lamp (SAIC, India), which emits radiation at various wavelengths ranging from 200nm-400 nm.

Batch experiments were performed using individual pesticide solutions (lindane and endosulphan isomers) of 5 ppm (200 mL) prepared in ultrapure water (Millipore). The reaction solution was continuously stirred with a magnetic bar during reaction.

For light reactions, the time of turning on UV lamp was turned time zero for light experiments and addition of hydrogen peroxide was the beginning time for dark.

Analytical Method

After completion of irradiation time, the sample was removed from the photoreactor and methanol was immediately added to it to stop further reaction¹⁶. The sample was extracted thrice using dichloromethane (10 ml each) by vigorous manual shaking for 5 min and then removing the organic layer after separation. The collected organic phase was combined and dried with a small amount of anhydrous Na_2SO_4 . The extract was concentrated before injecting into the gas chromatograph. Final sample concentrate was made up in n-hexane.

Concentration was quantified using gas chromatograph with ^{63}Ni electron capture detector (Perkin Elmer, Clarus 500). Fused-silica capillary DB-5 column (30m x 0.25mm x 0.25 μm film thickness) was used for analysis. Nitrogen was used as a carrier gas.

The recovery of γ -HCH was 81-95%, α and β -Endosulphan was 80-85% obtained in the working range for three replicates. The detection limits for these compounds were 0.1 ± 0.02 $\mu\text{g/l}$.

Results and Discussion

The purpose of this study was to obtain maximum degradation of critical POP lindane and other persistent pollutants, α and β Endosulphan. The degradation rates of three pesticides were different for all the studied AOPs.

Lindane showed a slower degradation under UV irradiation as compared to endosulphan isomers. The degradation rate of lindane was enhanced in presence of H_2O_2 . Lindane also gave faster degradation using fenton's and fenton's /UV process. However, fenton's reagent did not play a significant role in the degradation of α and β Endosulphan. Also, in presence of H_2O_2 , α and β Endosulphan did not show a significant degradation as compared to lindane. The individual degradation processes are detailed in the following sub-sections.

Degradation using UV Irradiation

A number of organic contaminants absorb UV radiation in the range of 200–300 nm and get decomposed either due to direct photolysis or indirectly through radical generation. On irradiation of solutions containing lindane and endosulphan isomers, photolytic degradation of both the compounds occurred.

Fig. 1 shows the trends of photolytic degradation of lindane and endosulphan isomers. It can be observed that the degradation of lindane in presence of UV alone was slow as compared to endosulphan. Complete degradation was observed in 300 min of irradiation with an observed rate constant of $2.2 \times 10^{-4} \text{ s}^{-1}$ ($r^2 = 0.83$) as shown in Table 1. The initial degradation rate of lindane was slow upto 90 minutes and then the reaction proceeded at a faster rate, indicating that isomerization of lindane occurred in 90 minutes and finally a complete degradation of breakdown products occurred in 300 minutes of irradiation. No significant peak was observed in the chromatogram by the end of reaction.

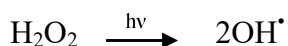
Alpha endosulphan degraded faster than beta isomer. In 240 min, 96% of α and 89% of β Endosulphan was degraded. A photolysis study²⁶ of α -endosulphan and β -endosulphan was

performed in aqueous solution and in hexane reported that α -endosulphan and β -endosulphan were more stable under UV light in aqueous solution than in hexane. Also, the degradations of both the isomers in both matrices were of first-order kinetics. The observed rate constant in the present study was $2.3 \times 10^{-4} \text{ s}^{-1}$ for α and $1.5 \times 10^{-4} \text{ s}^{-1}$ for β endosulphan ($r^2 = 0.99$). An earlier study¹⁹ reported that 38% of alpha and 25% of beta degraded by UV irradiation in 30 min. Similar values were obtained in this study for the two pesticides in 30 minutes irradiation. It is also reported¹⁷ that the major product of UV irradiation of endosulphan is endosulphan diol which is a less toxic species. Also, endosulfan is fairly resistant to phototransformation particularly in air but its degradation products endosulfan sulfate and endosulfan-diol are susceptible to photolysis²⁷. This will lead to a complete degradation of the endosulphan molecule with a possible pathway of formation of endosulphan sulphate or endosulphan diol and then complete dissociation of these breakdown products. These trends were also confirmed by the chromatograms obtained in the study, which showed no significant peak of endosulphan sulphate, by the end of reaction.

Degradation using UV/H₂O₂

To improve the reaction rate, H₂O₂ was added as an oxidizing agent to the aqueous solution of lindane. Initially, dark experiments (without UV irradiation) were performed in presence of H₂O₂.

The direct photolysis of hydrogen peroxide leads to the formation of 2 OH[•] radicals²⁸:



In the absence of UV irradiation, 36.7% degradation of lindane was observed in 30 min for a 2mM of H₂O₂ concentration. On increasing the concentration of H₂O₂ to 10mM, a three-fold increase (90%) was observed in same time period indicating an increase in the number of hydroxyl radicals generated.

On irradiating the solution of 5 ppm of lindane with 2mM of H₂O₂, the reaction became even faster. Rate constant of $5.3 \times 10^{-4} \text{ s}^{-1}$ was observed with 97% degradation in 90 min (Fig. 2). The suggested mechanism for photolysis in presence of H₂O₂ follows breakdown pathway of the molecule with two OH[•] radicals generated with each quantum of radiation absorbed²⁹.

On addition of H₂O₂, no significant dark degradation was observed for endosulphan isomers. Fig.2 shows the degradation trends for UV-H₂O₂ (2mM) reactions. 49.2% of alpha and 46% of beta endosulphan was degraded in 90 min of UV irradiation in presence of H₂O₂ with a

rate constant of $1.1 \times 10^{-4} \text{ s}^{-1}$ and $0.97 \times 10^{-4} \text{ s}^{-1}$ respectively. It has been reported ³⁰ that endosulphan isomers and endosulphan sulphate show no appreciable reaction with $\text{OH}^\bullet$ radicals produced by H_2O_2 photolysis in air matrix. The endosulphan degradation seems to be proceeding more through direct photolysis rather than being mediated by hydroxyl radicals. It is also reported that UV based photolysis and hydrogen peroxide synergistic reaction will be useful only for the contaminants, which need comparatively higher oxidation conditions due to higher activation energies ³¹. Endosulphan isomers are reported to have low activation energies. (Around 44 to 59 KJ/mol) ²⁵.

Reverse is observed for lindane. Presence of H_2O_2 drastically improved degradation of lindane. During UV/ H_2O_2 treatment, during which $\text{OH}^\bullet$ radical is generated rapidly, the $\text{OH}^\bullet$ radical attack of lindane is majorly observed than direct photolysis or reaction with H_2O_2 as the initial reaction step.

Degradation in Fenton's and Photo-fenton's process

To improve the process further, fenton's oxidation using a mixture of ferrous ion and H_2O_2 was used. Free radicals could be generated from a catalytic reaction of Fe salt with H_2O_2 either in absence or presence of UV light. The use of Fe(II)/ H_2O_2 as an oxidizing agent for water treatment is useful due to abundance and non-toxicity of iron and easy handling of environmentally benign hydrogen peroxide ¹¹.

Degradation of lindane using fenton's reagent (1mM FeSO_4 + 10mM H_2O_2) is given in Fig. 3. Complete degradation of lindane was obtained in 120 min in dark. The basic reaction for the fenton's process can be described as follows ³²:

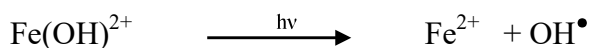


In the photofenton process greater numbers of hydroxyl radicals are generated in comparison to the conventional Fenton method or photolysis, thus promoting faster rates of degradation of organic pollutants.

The basic reactions for the Photofenton process at pH 3 lead to the formation of $\text{Fe}(\text{OH})^{2+}$ complex because of the acidic environment ¹¹:



Further UV exposure leads to the complex being decomposed as follows:



On UV irradiation in presence of Fenton's reagent, 92% degradation was obtained in 60 min of irradiation with an observed rate constant of $6.3 \times 10^{-4} \text{ s}^{-1}$. pH of reaction is an important factor affecting photo-Fenton degradation. Oxidation is much favorable at strongly acidic pH. The effect of like Bicarbonate and carbonate ions have a negligible activity as radical scavengers under the acidic conditions³¹, in the present study the operating pH was 2.5 for fenton's reactions.

On changing the concentration of FeSO_4 in fenton's reagent, no noticeable change was observed in the degradation rate. However, on changing the concentration of H_2O_2 , faster degradation rates were achieved as depicted in Fig.4. Ninety-six percent degradation was observed in 30 min of time in double and triple H_2O_2 concentration in fenton's reagent. The first order rate constant was increased to $7.8 \times 10^{-4} \text{ s}^{-1}$ for 20 mM of H_2O_2 . For 30mM of H_2O_2 , similar rate constant value was observed indicating saturation.

The effect of iron content in the fenton's reagent did not play a major role, indicating that the used millimolar concentration of iron was sufficient for catalyzing the reaction.

Alpha and beta endosulphan did not show significant degradation in presence of fenton's reagent.

Conclusions

The major conclusions from the above study are:

More than 95% of Degradation of lindane was observed for all the AOPs used (UV, H_2O_2 , UV/ H_2O_2 , fenton's reaction, UV/fenton). The degradation rate was significantly enhanced in presence of H_2O_2 . The photo- fenton's process produced the highest reaction rate $6.3 \times 10^{-4} \text{ s}^{-1}$ of all the five AOPs studied.

Significant degradation of α and β -endosulphan (96% and 89% respectively) was observed on UV irradiation in absence of any additive. No significant dark degradation was observed for endosulphan isomers on addition of H_2O_2 , which increased to 49.2% of alpha and 46% on UV irradiation. No significant degradation was observed in presence of fenton's reagent.

Of all the AOPs studied, UV/ H_2O_2 can be suggested as an efficient technique for degradation of lindane as it does not generate any byproduct (viz. iron sludge in fenton's reactions) and the cost of oxidant (H_2O_2) is also low. For endosulphan isomers UV irradiation is the suggested as an efficient AOP.

Acknowledgement

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Figures:

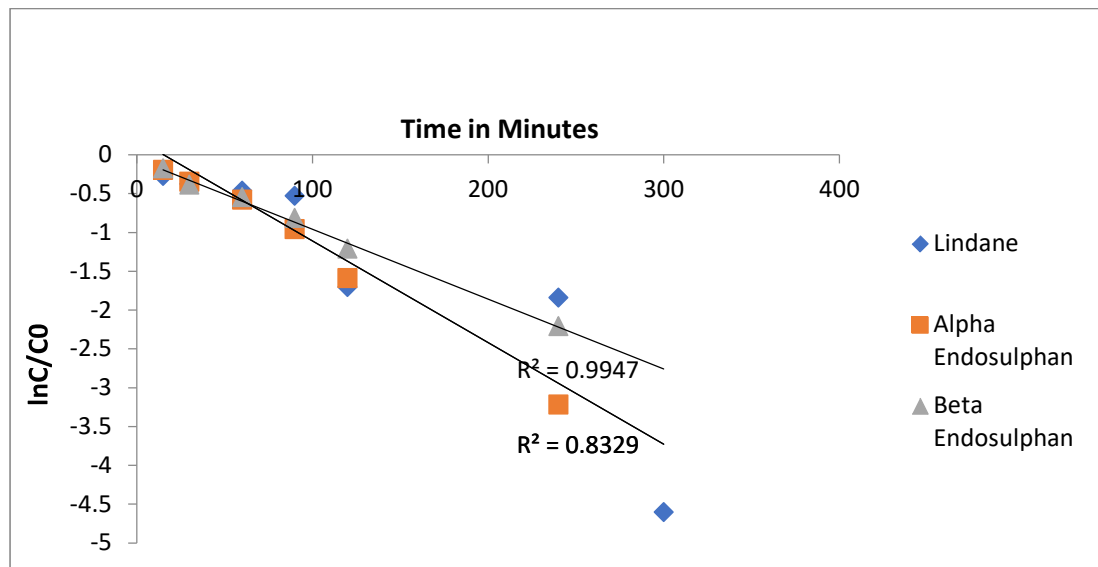


Fig. 1: First Order Kinetics for Pesticide Photodegradation with UV

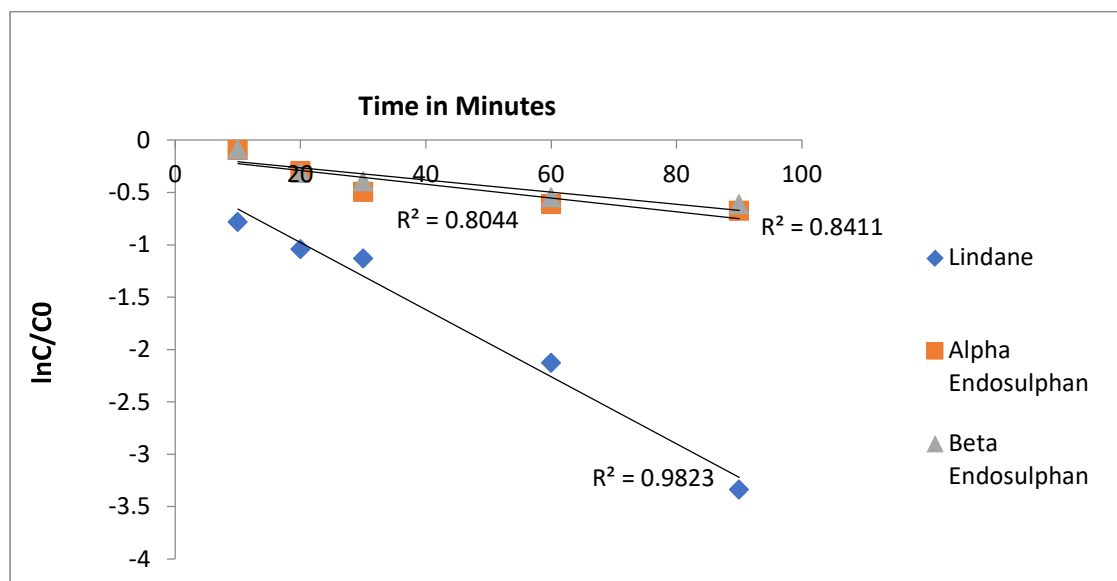


Fig. 2: First Order Kinetics for Pesticide Photodegradation with UV-H₂O₂

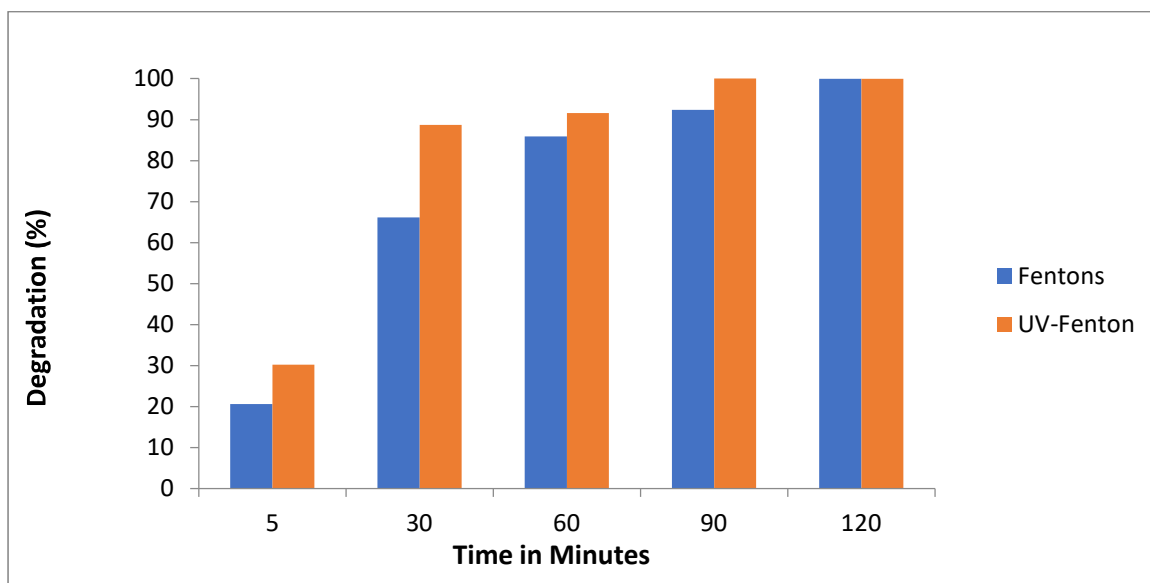


Fig. 3: Degradation of Lindane using Fentons and UV-Fentons Process

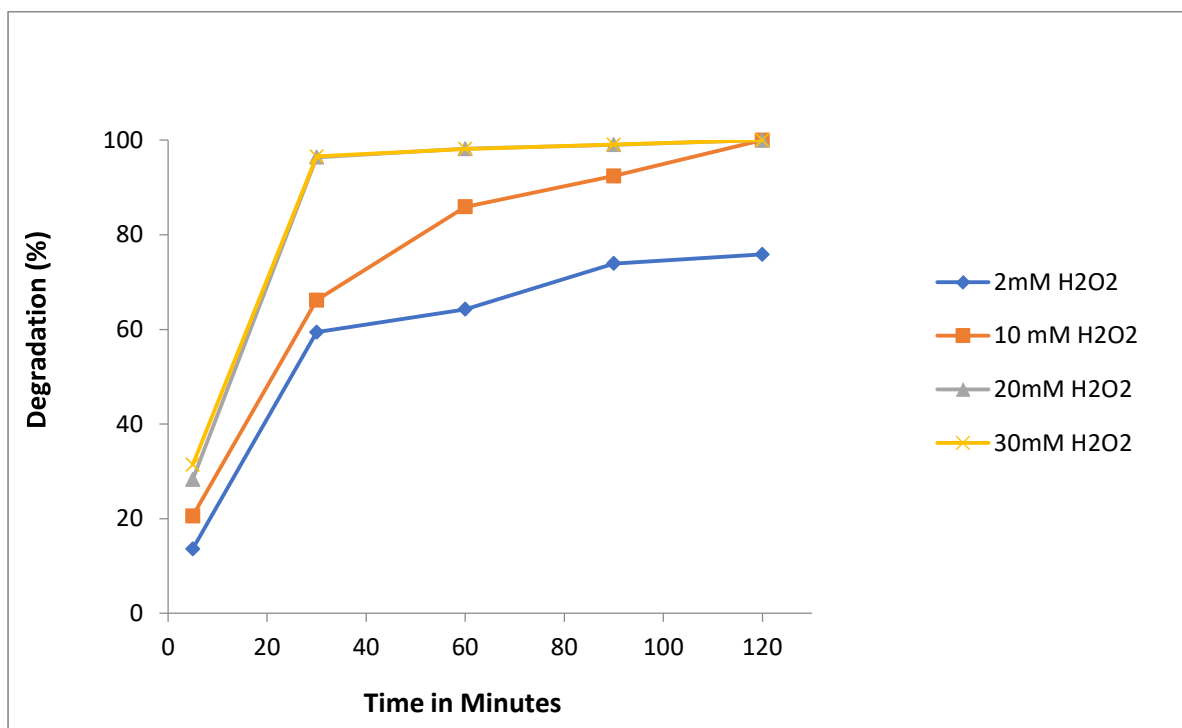


Fig. 4: Effect of H₂O₂ concentration on photodegradation of Lindane

Table:**Table 1:** First order rate constants (s^{-1}) for pesticide degradation using various Advanced Oxidation Processes

Pesticide	UV	UV/H ₂ O ₂	Fenton's	UV/Fenton
Lindane	2.2×10^{-4}	5.3×10^{-4}	4.6×10^{-4}	6.3×10^{-4}
α -endosulphan	2.3×10^{-4}	1.1×10^{-4}	-	-
β -endosulphan	1.5×10^{-4}	0.97×10^{-4}	-	-

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