Oxidation of lindane in contaminated water under solar irradiation in the presence of photocatalyst and oxidizing agents

G. Krishnamurthy[1,*], M. Sona Bai[2]

[1] *Department of Chemistry, Bangalore University, Central College Campus, Bangalore-560 001, India,*
[2] *Department of Chemistry, Goutham College, Bangalore, India*

The oxidation of lindane is investigated by photooxidation and photocatalytic procedures using solar light irradiation. The photocatalyst used in photocatalysis is Degussa P25 TiO_2. The degree of oxidation is followed by chemical oxygen demand (COD) measurements. The oxidation process is carried out at different initial concentrations of lindane varying from 0.05×10^{-2} M to 1.0×10^{-2} M. The photooxidation and photocatalytic oxidation are studied in the presence of $H_2O_2/K_2Cr_2O_7$ to check the effect of oxidizing agents on the rate of oxidation. The higher rate of oxidation is observed in the presence of H_2O_2 when compared to $K_2Cr_2O_7$ in photocatalysis. The decrease in the concentration of lindane during oxidation is also followed by UV-visible absorption studies. The oxidation of lindane follows the first order kinetics and the value of the rate constant k, as calculated, is 0.43×10^{-4} s^{-1}.

Key words: photooxidation, solar irradiation, photocatalyst, COD measurement, lindane.

INTRODUCTION

Wastewater treatment is one of the challenging areas of the environmental pollution control as our hydrosphere is getting contaminated with significantly high concentrations of various chemicals. These chemicals include the pesticides used mainly in agriculture; dyes used in the textiles, laboratory reagents, *etc*. Pesticides constitute one of the major classes among pollutants. In recent years pesticide compounds (insecticides, herbicides, fungicides, nematodes, rodenticides, *etc*.) are being increasingly used in the control of pests. Many of these chemicals persist for long periods causing contamination of water, soil and air environment. Many of these pesticides and organochlorine compounds are toxic, carcinogenic and mutagenic. The contamination of water by these chemicals has become a major and serious problem globally and removal of these contaminants has become very challenging.

There are several techniques of removal of contaminants from the water [1–4] and some of them are found to be inefficient procedures. Biological oxygen demand (BOD) and the chemical oxygen demand (COD) [5–7] are among the waste water quality indicators, which are essentially laboratory tests to determine the pollutant content. Any oxidizable material present in a natural waterway or in an industrial or wastewater will be oxidized both by biochemical (bacterial) or chemical processes. Recent developments in the domain of chemical water treatment have led to improved oxidative degradation procedures, which are generally referred to as advanced oxidation processes (AOP). Among AOP the photooxidation has attracted much attention for the degradation of pesticides and organic pollutants in contaminated water [8–11]. Photooxidation uses the energy in light to destroy environmental contaminants, applicable both as a waste clean-up and a pollution control technique.

In photocatalysis TiO_2 is a widely used photocatalyst [8–11]. A wide range of photonic efficiencies are observed among various TiO_2 phases and formulations. Studies have shown that mixtures of anatase and rutile TiO_2 perform better than either individual rutile or anatase phases of TiO_2 [12] and the high photocatalytic activity is reported in some mixed-phase TiO_2 preparations such as Degussa P25. The commercial Degussa P25 TiO_2 contains 80 to 90% of anatase and 10 to 20% of rutile [12]. The inactivity of pure-phase rutile is due in part to rapid rates of recombination. In mixed-phase TiO_2, charges produced on rutile by visible light are stabilized through electron transfer to lower energy anatase lattice trapping sites. These results suggest that within mixed-phase titania (P25) there is morphology of nanoclusters containing typically small rutile crystallites interwoven with anatase crystallites. The transition points between these two phases allow for rapid electron transfer from rutile to anatase. Thus, rutile acts as an antenna to extend the photoactivity into visible wavelengths [13] and the structural

* To whom all correspondence should be sent:
E-mail: gkmurthy_2005@yahoo.com

arrangement of the similarly sized TiO_2 crystallites creates catalytic "hot spots" at the rutile-anatase interface. Hence, the commercial Degussa P25 TiO_2 photocatalyst has been chosen for the photocatalytic oxidation study in order to compare with direct photooxidation and chemical oxidation.

In the present work the oxidation of lindane by direct photolysis and photocatalytic oxidation by chemical oxygen demand (COD) measurement method is discussed. Lindane is an organochlorine insecticide. Consumption or acute exposure to lindane can cause health hazards in humans, aquatic animals and birds [14]. Hence, the suitable procedure for the decontamination of lindane from the aquatic environment is needed. In this regard, in the present study the oxidation of lindane by solar light irradiation and by an oxidizing agent in the presence/absence of catalyst has been explored. The analyses are made by oxygen demand measurements (COD tests) and also by UV-visible absorption studies.

EXPERIMENTAL

Materials

Lindane is obtained from Rallis India Ltd., an Agrochemical Research Station, Bangalore, India. The purity of the compound was about 98.5% and it was used as obtained from the industry without further purification. Benzene hexachloride (BHC) is the 100% pure form of the product while lindane is slightly less pure (> 99% pure). There are eight separate three dimensional forms (isomers) of BHC; the gamma configuration being one of those forms. Lindane refers only to the γ-isomer of BHC [14].

The other materials such as potassium dichromate, ferrous ammonium sulphate (FAS), silver sulphate, mercuric sulphate, hydrogen peroxide, H_2SO_4 and Ferroin indicator of Merck chemicals are used for the study. Degussa P25 TiO_2 as supplied by the company has surface area of about 50 m^2/g and anatase and rutile ratio is 4:1 (80%:20%).

Analytical Methods

Photooxidation and photocatalytic oxidation procedures are employed to study the oxidation of lindane in which COD measurement and absorption studies are used as analytical methods to follow the degradation of lindane. The value of COD indicates the concentration of the lindane in the solution. The COD values give the extent of degradation of lindane under solar illumination.

The UV-visible spectra of the samples were obtained using Shimadzu UV-VIS-160 model instrument. The decrease in the absorption intensity of the bands corresponds to the wavelengths, 198 nm and 190 nm indicating the degradation of lindane.

Reactors

Photoreactor. The photoreactor unit consists of the optical convergence lens of circumference of 39 cm which was fixed at the appropriate height in such a way that the entire area of the reaction vessel would focused by the sun light and it was maintained carefully throughout the experiment. It consists of a glass reaction vessel of circumference 34 cm, 1 litre capacity, which was mounted on a magnetic stirrer. The entire set up is encased in a cabinet.

COD (chemical oxidation) reactor. The experimental setup used for COD test is a round bottom flask fitted with reflux condenser (water cooled). The heating was done using heating mantle.

Experimental procedure

Photooxidation of lindane at 0.1×10^{-2} M concentration has been studied under solar light irradiation. The solution of about 500 ml was kept under constant stirring during irradiation. The solar irradiation was performed between 11 a.m. to 2 p.m. during June and September months in 2008. The experimental setup was made on the roof of the research laboratory in Bangalore, India. The latitude and longitude are 12.58 N and 77.38 E, respectively. The average intensity of sunlight was around 1.16×10^3 $W \cdot cm^{-2}$. The solar light was concentrated by using convex lens and the reaction mixture was exposed to this concentrated solar light. The samples were withdrawn before the start of irradiation and at 30, 60, 90 and 120 min during irradiation in about 30 ml quantities each time. The similar procedure was involved in photocatalysis, but in the presence of Degussa P25 TiO_2 photocatalyst. The samples from the photocatalysis were centrifuged to remove suspended photocatalyst. Then COD measurements were made for these samples using strong oxidizing agent potassium dichromate. The process is largely followed by measuring chemical oxygen demand (COD) of the solution and also studied by UV-visible absorption measurements. The COD determination involves the use of oxidizing agent, such as potassium dichromate, to oxidize the chemical in acidic aqueous medium. The other reagents such as silver sulfate were added as catalyst and mercury sulfate in order to avoid the formation of silver halide [5–7, 15, 16].

RESULTS AND DISCUSSION

Chemical Oxygen Demand (COD) measurement

The degree of oxidation is followed by chemical oxygen demand (COD) measurements. The samples of photooxidation and photocatalytic oxidation experiments are used for COD measurements. In general the COD value indicates the extent of contamination of water by the pollutants. In this study, it also implies the concentration (amount) of lindane oxidized. The general reaction of potassium dichromate with lindane is given by the equation:

$$C_6H_6Cl_6 + 2Cr_2O_7^{2-} + 2H_2SO_4 \rightarrow$$
$$\rightarrow 6CO_2 + 2H_2O + 6HCl + 2Cr_2SO_4 \qquad (1)$$
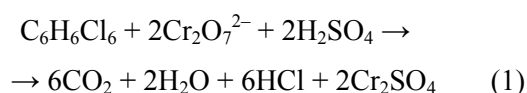
The COD calculations are made using the following relationship:

$$COD = 8000\,(V_2 - V_1)N/V \qquad (2)$$

Where V_2 is the volume of FAS used in the blank sample, V_1 is the volume of FAS in the original sample, and N is the normality of FAS. If millilitres are used consistently for volume measurements, the result of the COD calculation is given in mg/L.

Higher COD value indicates higher concentration of contaminants in the water. On treating any particular waste water (of particular concentration) the COD should decrease. Here, COD test itself is considered as the chemical oxidation. However, this method itself introduces lots of toxicants such as chromium ions, acid, *etc*., along with the degradation of lindane. Hence, a suitable environmental friendly method is essential for removal of water contaminants. In this regard, photooxidation by natural or artificial light irradiation is prominent.

Optimal concentration of lindane

The optimal concentration of lindane was determined by conducting COD experiments at various concentrations such as 0.05×10^{-2} M, 0.1×10^{-2} M, 0.5×10^{-2} M and 1.0×10^{-2} M in the presence of fixed amount of oxidizing agent and catalyst. The COD value is doubled for 0.1×10^{-2} M concentration of lindane and further there is a slight decrease in the proportional COD values. This may be due to decrease in the catalytic activity of the silver ions and competitive reactions with the degradation metabolites. Therefore, 0.1×10^{-2} M solution of lindane is used as optimum concentration for this study. The corresponding COD values are given in Table 1. Similarly, optimal refluxing time was determined and it was found to be 1.5 h for the above optimal concentration.

Table 1. The COD (chemical oxidation) values corresponding to various concentrations of lindane.

Concentration, $\times 10^{-2}$ M	COD value, $\times 10$ mg/L
0.05	15.34
0.1	33.21
0.5	131.30
1.0	228.57

Photooxidation and photocatalytic oxidation

The photooxidation is carried out under solar light at various concentrations of lindane as mentioned above. The COD values of the samples are determined in these experiments after 120 minutes of irradiation. The decrease in the COD values implies the increase in the oxidation of lindane. The COD values at the various initial concentrations of lindane used in the photooxidation experiments are plotted as shown in Fig. 1. The higher COD values in chemical oxidation indicate the greater amount of oxygen required for the oxidation of lindane. The lower COD values in the photooxidation and photocatalytic oxidation imply the oxidation of lindane by these processes as shown in Fig. 1. The COD values in photocatalytic oxidation are significantly less than 50% (curve a) of that of photooxidation (curve b) as depicted in the figure. This implies the effect of catalyst on the oxidation of lindane. The concentration of lindane has become zero after 90 min. of solar irradiation. It can also be seen from the figure that the maximum in oxidation has occurred for 0.1×10^{-2} M lindane, which is the optimal concentration. The COD values for the photooxidation and photocatalytic oxidation of lindane for 0.1×10^{-2} M concentration, at different time intervals are given in Table 2. The decrease in COD values with increase in solar irradiation time implies an increase in the oxidation of lindane.
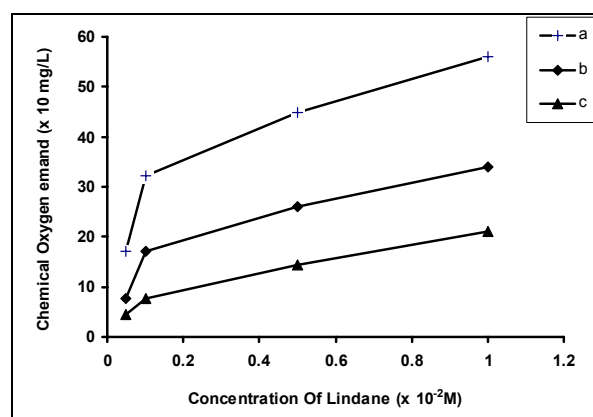

Fig. 1. Plots of COD values as a function of concentration of lindane in which the curves, a, b and c correspond to chemical oxidation, photooxidation and photocatalytic oxidation, respectively.

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Table 2. COD values for the photooxidation and photocatalytic oxidation of lindane $(0.1 \times 10^{-2}$ M$)$ at different time intervals.

Irradiation time, min	COD value, $\times 10$ mg/L	
	Photooxidation	Photocatalytic oxidation
0	33.44	33.21
30	25.24	10.56
60	21.80	7.88
90	18.16	0.0
120	17.68	0.0

The UV-visible spectral studies have also been employed. The spectra for the initial sample (before irradiation) and for the samples after 30, 60, 90 and 120 minutes of solar irradiation are shown in Fig. 2. The λ_{max} for lindane is found to be at 198 nm. The intensity of absorption decreases with increase in irradiation. The absorption intensity is decreased considerably after 120 min. of irradiation. This indicates nearly 70% oxidation of lindane, whereas in photocatalysis in the presence of Degussa P25 TiO_2, the complete oxidation of lindane takes 0 min. of irradiation. The bands at 198 nm and at 190 nm are characteristic of aromatic $\pi \rightarrow \pi^*$ transition. The decrease in intensity of absorption bands shows the degree of oxidation of the compound in other words the degradation of lindane.
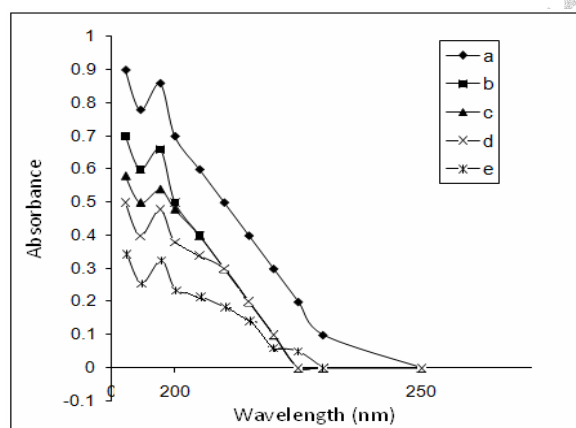

Fig. 2. Superimposed UV-visible absorption spectra: a. sample before solar irradiation; b. sample after 30 min. of irradiation; c. sample after 60 min; d. sample after 90 min.; e. after 120 min..

However, in photo/photocatalytic oxidation experiments for efficient oxidation, the intensity of the solar light focused on to the reaction solution is very important. The amount of radiation intercepted by a planetary body varies inversely proportional to the square of the distance between the star and the planet. The Earth's orbit and obliquity change with time (over thousands of years), sometimes forming a nearly perfect circle, and at other times stretching out to an orbital eccentricity of 5% (currently 1.67%).

The total solar illumination remains almost constant but the seasonal and latitudinal distribution and intensity of solar radiation received on the Earth's surface also varies [17]. Fig. 3 is the solar spectrum, which shows the absorption of sun light at different wavelength regions. However in the present research work photo/photocatalytic oxidation using solar light was performed as described previously.
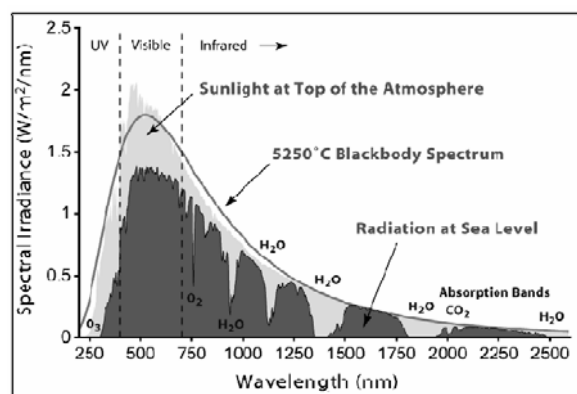

Fig. 3. Solar radiation spectrum which shows the radiation of sunlight at the top of the atmosphere, at sea level and black body radiation.

Effect of oxidizing agent on the rate of photo/photocatalytic oxidation

The degree of conversion is depending on several factors and one of them is the formation of photo-generated reactive radical species. Therefore, the photo/photocatalytic oxidation experiments were conducted in the presence of oxidizing agents such as H_2O_2 and $K_2Cr_2O_7$. The presence of oxidizing agents causes the formation of OH radicals under light illumination more efficiently in the presence of photocatalysts. The OH radicals are highly potent oxidants, which enhance the rate of oxidation. The oxidation of lindane in these processes is analyzed by COD determination at different time intervals during illumination. The COD values from the photo-oxidation and photocatalytic oxidation experiments in the presence of $H_2O_2/K_2Cr_2O_7$ are plotted against the illumination time as shown in Fig. 4. The curves a, b and c correspond to photooxidation of lindane carried out in the absence of oxidizing agent, in the presence of H_2O_2 (5 ml of 0.01 M) and in the presence of $K_2Cr_2O_7$ (5 ml of 0.01 M), respectively. The higher rate of oxidation is observed in the presence of H_2O_2 than that in the presence of $K_2Cr_2O_7$ (Table 3). The reason may be the ease of formation of greater number of OH radicals in the presence of H_2O_2 when compared to $K_2Cr_2O_7$. The dichromate may directly oxidize lindane to some extent since it is a strong oxidant provided the media is acidic, but the formation of the essential

OH radicals is considerably less. Hence, the higher rate can be expected in the presence of H_2O_2. However, the rate of oxidation of lindane is much higher in the presence of both catalyst and oxidizing agents, i.e. in the photocatalysis. There is a rapid decrease in the COD values in these experiments (curves d, e and f). The curves d, e and f correspond to photocatalytic oxidation of lindane carried out in the absence of oxidizing agent, in the presence of H_2O_2, and in the presence of $K_2Cr_2O_7$ at 5 ml of 0.01 M concentration, respectively. The highest rate of oxidation is observed with H_2O_2, when compared to dichromate.
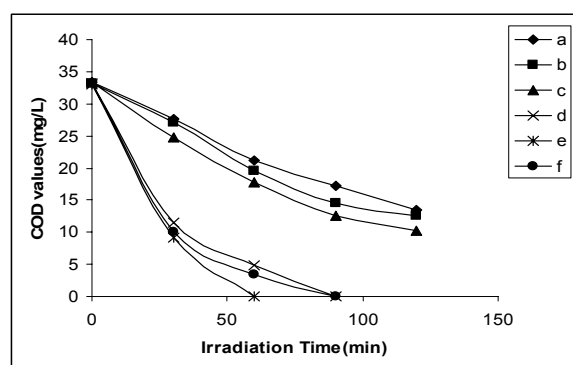

Fig. 4. Plot of COD values as a function of solar irradiation time for the oxidation of lindane in which the curves a, b and c correspond to the photooxidation experiments and the curves d, e and f correspond to photocatalytic oxidation experiments. The curves a and d, b and e, and c and f correspond to the experiments carried out in the absence of oxidizing agent, in the presence of H_2O_2 and in the presence of $K_2Cr_2O_7$, respectively.

Table 3. COD values for the photooxidation and photocatalytic oxidation of lindane (0.1×10^{-2} M) in the presence of H_2O_2 and $K_2Cr_2O_7$ as additional oxidizing agents.

Irradiation time, min	COD values in photooxidation experiments			COD values in photocatalytic oxidation experiments		
	Without Oxidant	With H_2O_2	With $K_2Cr_2O_7$	Without Oxidant	With H_2O_2	With $K_2Cr_2O_7$
0	33.34	33.25	33.3	33.22	33.0	33.12
30	27.6	27.0	24.8	10.56	8.72	9.12
60	21.2	19.5	17.8	7.88	0.0	1.35
90	17.3	14.6	12.5	0.0	0.0	0.0
120	13.5	12.5	10.2	-	-	-

Efficiency and kinetics of photooxidation and photocatalytic oxidation

The efficiency 'η' of photo/photocatalytic oxidation is defined by conversion degree as follows:

$$\eta = [(COD_0 - COD)/COD_0] \times 100 \quad (\%) \quad (3)$$

Where, COD_0 and COD denote the concentrations at the initial moment and given time t, res-

pectively. Fig. 5 is a plot of $\eta(\%)$ *versus* irradiation time, which implies the percentage of conversion of lindane to product to be high at the beginning and later it became almost constant. About 70% efficiency of total oxidation is achieved within 90 min of irradiation in photooxidation. However, 100% efficiency is achieved in photocatalysis in 90 min of irradiation.
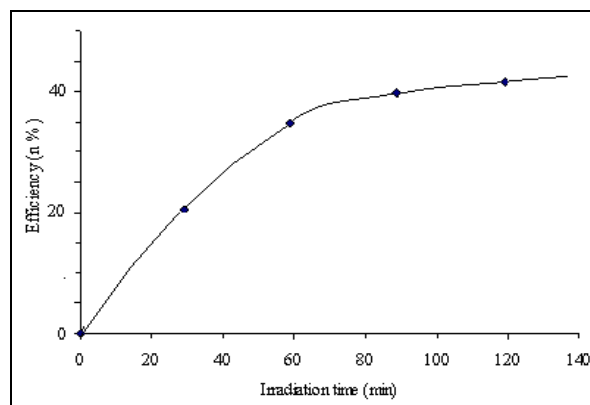

Fig. 5. Plot of oxidation efficiency '$\eta(\%)$' *versus* irradiation time.

COD concentration can be fitted well by the following apparent first-order kinetics:

$$\ln(COD_0/COD) = kt \quad (4)$$

Where, k is the apparent first-order reaction rate constant, which is found to be 0.43×10^{-4} s^{-1} for the oxidation of lindane. Fig. 6 represents the plot of $\log(COD_0/COD)$ *versus* irradiation time, in which the initial rate of oxidation is high. About 70% of degradation (of total oxidation) has taken place in the course of 1.5 h of irradiation, whereas the rate constant for photocatalytic oxidation is 1.27×10^{-4} s^{-1}, in which 100% oxidation has taken place.
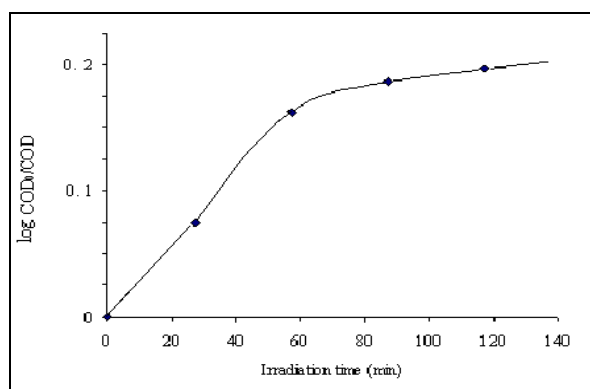

Fig. 6. Plot of $\log(COD_0/COD)$ *versus* irradiation time.

CONCLUSION

In this research work a comparative study of photooxidation and photocatalytic oxidation of lindane has been explored by using oxygen demand

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measurement procedure. The photocatalytic oxidation is found to be doubly efficient than direct photooxidation at 0.1×10^{-2} M concentration of lindane in the presence of commercially available Degussa P25 TiO_2. The method is more simple and cost effective as it uses the more abundant solar light for the oxidation of lindane. This procedure can be extended to study the detoxification of other water contaminants. The efficiency of the solar photo/photocatalytic oxidation is enhanced considerably in the presence of oxidizing agents. Decrease in the COD values in the presence of oxidizing agents implies an increase in the oxidation of lindane. Comparatively higher rate of degradation is observed with H_2O_2 than that with potassium dichromate.

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ОКИСЛЕНИЕ НА ЛИНДАН В ЗАМЪРСЕНИ ВОДИ ПОД ДЕЙСТВИЕ НА СЛЪНЧЕВА СВЕТЛИНА В ПРИСЪСТВИЕ НА ФОТОКАТАЛИЗАТОР И ОКИСЛИТЕЛЕН АГЕНТ

Г. Кришнамурти[1,]*, М. Сона Бай[2]

[1] *Департамент по химия, Университет на Бангалор, Бангалор 560001, Индия*
[2] *Департамент по химия, Колеж Гутам, Бангалор, Индия*

(Резюме)

Изследвано е окислението на линдан чрез фотоокисление и във фотокаталитични процеси с използване на слънчева светлина. Използван е фотокатализатор TiO_2 Degussa P25. Степента на окисление е определена чрез измерване на химически потребния кислород (ХПК). Окислителният процес е провеждан при различни начални концентрации на линдан - от 0.05×10^{-2} М до 1.0×10^{-2} М. Фотоокислението и фотокаталитичното окисление са изследвани в присъствие на H_2O_2 и $K_2Cr_2O_7$ за да се проследи ефекта на окислителни агенти върху скоростта на окисление. При фотокатализа по-висока скорост на окисление е наблюдавана в присъствие на H_2O_2 в сравнение с $K_2Cr_2O_7$. Намалението на концентрацията на линдан по време на окислението е следено чрез абсорбцията в УВ-видима област. Окислението на линдан следва кинетиката на реакция от първи порядък и изчислената стойност на скоростната константа k е 0.43×10^{-4} s^{-1}.