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PHOTODEGRADATION OF 2, 4, 5, 6-TETRACHLOROISOPHTHALONITRILE (CHLOROTHALONIL) BY VISIBLE AND ULTRAVIOLET LIGHT IN THE PRESENCE OF ZnO AND TiO$_2$

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ABSTRACT:

photocatalytic degradation of fungicides (chlorothalonil) in suspension aqueous solution with semiconductors (TiO$_2$, ZnO) and without semiconductor has been investigated. the influence of different parameters such as light sources, the concentration of fungicides, type of semiconductors and temperature were studied by uv-visible spectrophotometer at 232 and 254 nm. the degradation reaction order spectra of chlorothalonil were determined which first order at 232 nm and second order at 254 nm. in addition, the rate constant, arrhenius factor and energy of activation can be estimated for both peaks. moreover, conductivity of chlorothalonil has been recorded during the photo-degradation and the rate of reaction also has been determined that dependent on product formation.

KEYWORDS: Chlorothalonil, Semiconductor, Rate constant, Photo-degradation, Activation energy.

1. INTRODUCTION

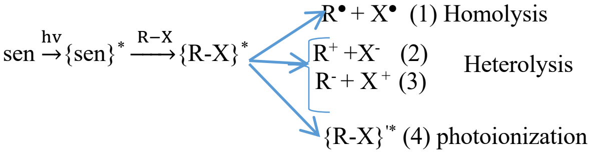
Pesticides are conceder natural and synthesized substances. They may be non-biodegradable and harmful to the environment. When pesticides are used in agriculture or any purpose it is converted to many chemical forms due to degradation by hydrolysis, oxidation, and photolysis by the environment (Ormad, Cortes, Puig, & Ovelleiro, 1997). The degradation of pesticides is due to microbial degradation, hydrolysis and photo degradation (Toshiyuki, 2004). To improve the agriculture sector there are many types of a chemical substance (pesticides) are produced which they are used in these sectors. Moreover, pesticides used to protect plants also humans from many diseases, in agriculture lands and in urban green areas (Polyxeni, Sotirios, Chrysanthi, Panagiotis, & Luc, 2016). Pesticides are diffusing in the environment by spray it in agriculture purposes. Moreover, the removal of such toxic compounds is essential to reduce the harm from it. It is removal by a process called degradation (Shinwar, Naman, & Anees, 2015). Degradation is the process by which a pesticide is transformed into a benign substance that is environmentally compatible with the site to which it was applied (Fenner, Canonica, Wackett, & Elsner, 2013). The degradation process is occurring by chemical, biological, thermal or photochemical processes (Sheren, Naman, & Lazgin, 2010). Moreover, the pesticide was removed by photo catalytic degradation by using semiconductor (TiO$_2$, ZnO) in the local water in Duhok (Fatma, Naman, & Lazgin, 2006). In addition, photo-degradation of chlorothalonil was also determined in various type of waters like (lake, river, and sea) in addition distilled water was used in this process in visible light or sun light. The effect of fulvic and humic substance is also determined on the rate of photo-degradation of chlorothalonil by sunlight (Sakkas, Lambropoulou, & Albanis, 2002).

1.1. Thermal degradation:

Thermal degradation is breaking down of pesticides molecule into other product which depending on the medium temperature (Girouda, Dorgea, & Trouvéa, 2007). Increasing the temperature by heating or light in the presence of Oxygen (oxidative condition) or without oxygen changes the rate of degradation (Osvaldo, Fabio, & Alfredo, 2007).

1.2. Photo degradation:

Degradation of pesticides are possible through photochemical processes including light sources, weather natural light from the sun or artificial sources of light like ultraviolet lamp high, medium or low pressure and visible light like home lamp 60 to 500 watt (Chiron, Fernandez-alba, Rodriguez, 2000). Ultraviolet lamp is used to remove pesticides from water (Shayeghi, Dehghani, Alimohammadi, & Goodini, 2007). Catalyst or semiconductor has been used to increase the degradation process of Pesticides, which we called sensitizers which absorb the light radiation and are excited to a higher energy state to transfer the excess energy to the target compound (laxma, & Ki-Hyun, 2015).



1.3. Semiconductor Based photo catalysis

The basis of the photo catalysis is the photo-excitation of a semiconductor due to the absorption of electromagnetic radiation in either ultraviolet or visible a range wavelength. Upon absorption of light, electrons in the valence band of a semiconductor are excited to the conduction band, leaving a positive hole in the valance band (Laxma, Ki-Hyun, & Hocheol, 2013).

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$$\text{Sc.} + h\nu \rightarrow e^-_{(CB)} + h^+_{(VB)} \tag{5}$$

$$\text{A (pest.)} + e^- \rightarrow A^-_{(CB)} \tag{6}$$

$$\text{B (pest.)} + h^+ \rightarrow B^+_{(VB)} \tag{7}$$

1.4. Kinetic and thermodynamic process:

The rate constant of pesticides degradation depends on the type of radiation, temperature, conductivity, pH. It is possible to calculate the activation energy of a reaction by using Arrhenius equation (Atkin's, & Julio, 2006).

2. EXPERIMENTAL PART

In general, the experiments have been carried out in different temperatures, in order to calculate the energy of activation. Moreover, the visible and ultraviolet light with and without semiconductor (ZnO, TiO_2) has been used in this work. The solvent was consisting of water fifty percent and fifty percent was acetonitrile. Acetonitrile is added in order to dissolve chlorothalonil completely. The optical density (absorbance) of chlorothalonil during Photo-degradation has been measured by spectrophotometer at 232 nm and 254 nm.

2.1. Chemical:

-The fungicide was supplied by Syngenta Company as a soluble liquid (SL) concentration, with active ingredients (% 72).
- Titanium dioxide supplied by Alpha chemika^{TM} Mumbai 200002, India.
- Zinc oxide supplied by BHD chemicals Ltd. Pool England.
- Acetonitrile supplied by Carl Roth GmbH + Co. KG with purity (99.95%).
- deionized water

2.2. Apparatus:

- Analytical balance type de ADAM pw 254 max 250g.
- Centrifuge type KUBOTA 2010.
- Thermo circulator type lab teach.
- Magnetic bar and magnetic stirrer type lab teach.
- UV.vis. Spectrophotometer type perkin-Elmer lambda 25
- Quartz UV. Cells
- Conductivity meter type Wagteach.
- GC/Mass type Perkin-Elmer (Gas chromatograph Clarus® 580) (Mass Spectrometer Clarus® SQ 8 S).

2.3 Construction of our Photocell:

The part of photolytic system is shown in the figure 1.

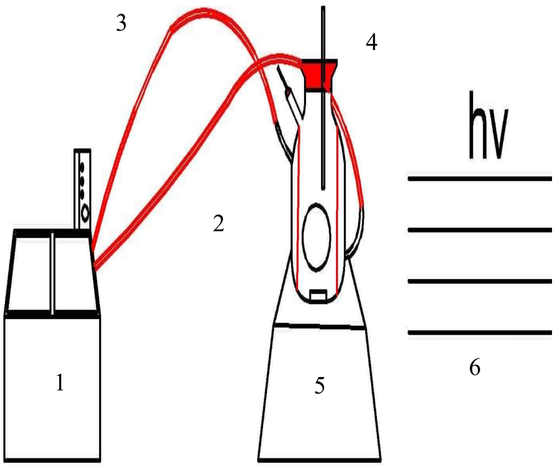


Figure 1. Schematic diagram of photo-degradation system. (1) Thermostat for controlling of temperature (2) Inlet water tube (3) outlet water tube (4) A photolytic cell made of Borosilicate, which is transparent for ultraviolet and visible light (5) Magnetic stirrer (6) Light source (visible or ultraviolet light).

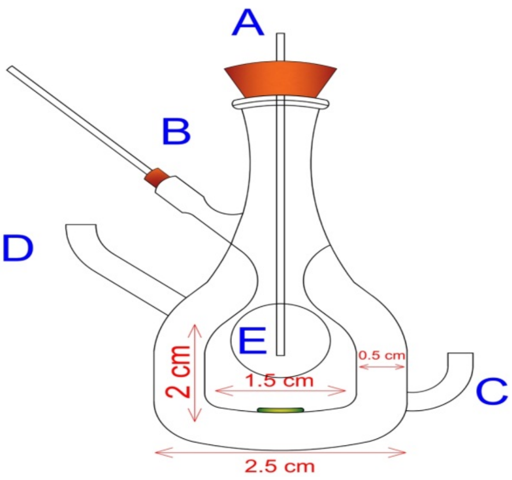


Figure 2. Scheme and dimension of the photolytic cell (A) sample inlet and outlet (B) opening for ventilation (C) water inlet (D) water outlet (E) quartz window.

2.4 Instrumentation:

Photo degradation of chlorothalonil has occurred in the thermostatic cell that illustrates in figure (1 and 2) and the changes in the absorbance were recorded with irradiation time by using UV-vis. Spectrophotometer type Perkin-Elmer lambda 25 as shown in the figure (3) with the time, the peaks at 232 nm is decreased faster than the peaks at 254 nm. In addition, figure (4) illustrates the photo-degradation of chlorathalonil of both spectra peaks 232 and 254 nm by ultraviolet light with time.

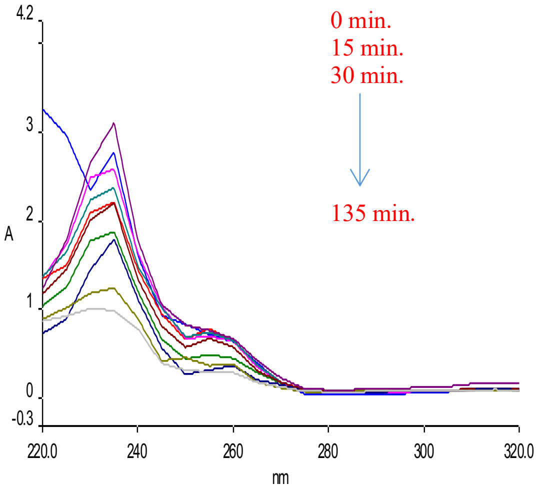


Figure 3. UV-Vis. Spectral change for the degradation of 15 ppm Chlorothalonil by visible light in different times.

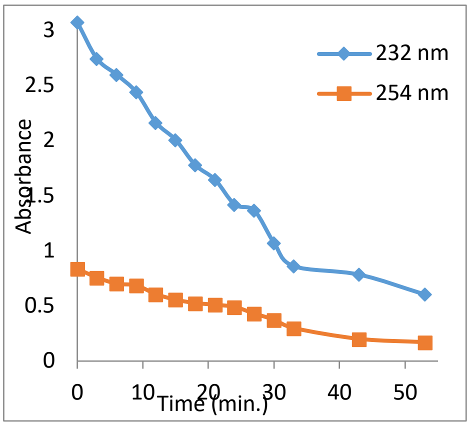


Figure 4. Degradation of 15ppm chlorothalonil by ultraviolet light as a function of irradiation time in a wavelength of 232 and 254 nm at 298 K.

2.5 Electrical conductivity measurement:

Measurements of electrical conductivity depend on the number of ions released during photo-degradation.

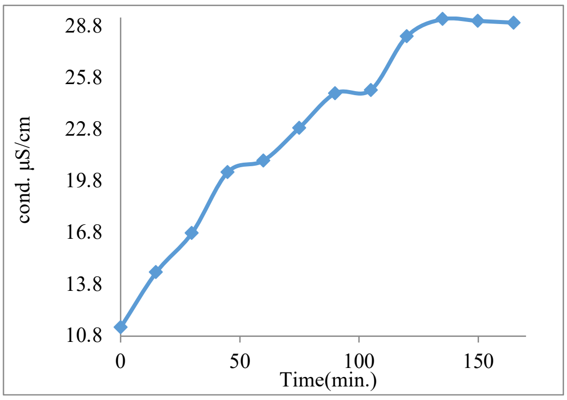


Figure 5. The conductivity of 15 ppm chlorothalonil by visible light as a function of irradiation time at 298 K.

It is shown from Figure (5) the reaction mixture it goes to equilibrium approximately in 150 minutes which depending on the type of the light sources (UV. or visible light).

3. RESULT AND DISCUSSION

A series of experiments have been done using two different light sources (visible and ultraviolet light). The rate of the optical density of peak 232 nm and 254 nm has been recorded with time as in figure (6 and 7) in a different medium as following:

3.1 Photolysis by visible light:

Photo-degradation of chlorothalonil has been done in % 50 water and % 50 acetonitrile using Tungsten-halogen lamp (500 W). The results are shown in figures (6 and 7) which is kinetic results.

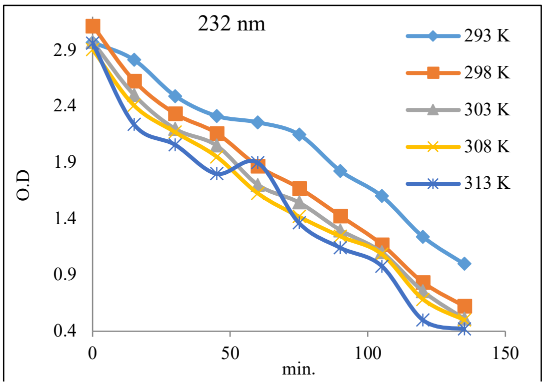


Figure 6. Degradation of 15 ppm of chlorothalonil by visible light as a function of irradiation time in different temperatures at 232 nm.

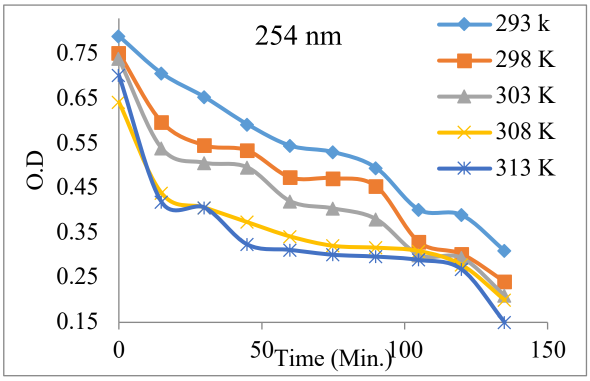


Figure 7. Degradation of 15 ppm of chlorothalonil by visible light as a function of irradiation time in different temperatures at 254 nm.

The results have shown that the degradation process increases with increasing temperature as illustrated in figures (6 and 7).

3.1.1 Product of chlorothalonil after photo-degradation: the product of chlorothalonil has been detected in figures (8 and 9) as it clears in GC/Mass which gives us the retention time of the product and mass number which may be chloro-1,3-dicyanobezene, dichloro-1,3-dicyanobezene, trichloro-1,3-dicyanobezene and 1,3-Benzene-dicarboxylic acid with the parent molecules. Major photoproducts illustrate in table (1).

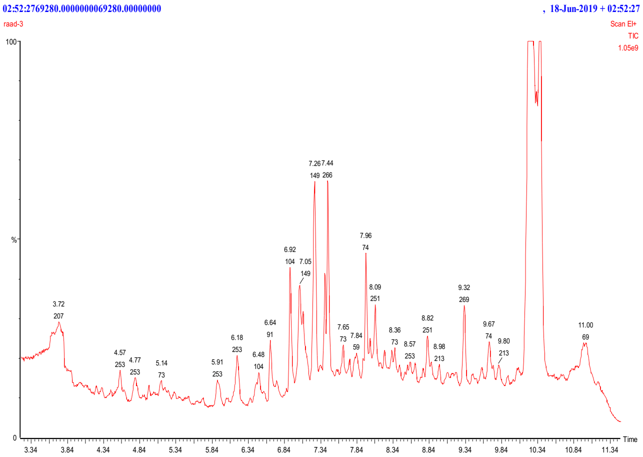


Figure 8. GC/Mass of 15 ppm of chlorothalonil in (99.9% acetonitrile) after 30 minutes by visible light. The upper number of each peak is retention time and the below one is the mass number.

Table 1. GC/MS retention times (Rt) and spectral characteristics of chlorothalonil major photoproducts.

No.	Compound	R_t (min)	molecular ions (*m/z*)	Fragments (*m/z*)
1	1,3-Benzene-dicarboxylic acid	7.05, 7.26		149
2	Chloro-1,3-dicyanobenzene	7.65, 7.96		104
3	Trichloro-1,3-dicyanobenzene	7.65, 7.96		74, 73
4	Dichloro-1,3-dicyanobenzene	7.65, 7.96		74, 73
5	Unidentified	6.64, 3.72 8.91, 6.18	91, 207, 251, 253	
6	Chlorothalonil	7.44, 9.32	266, 269	

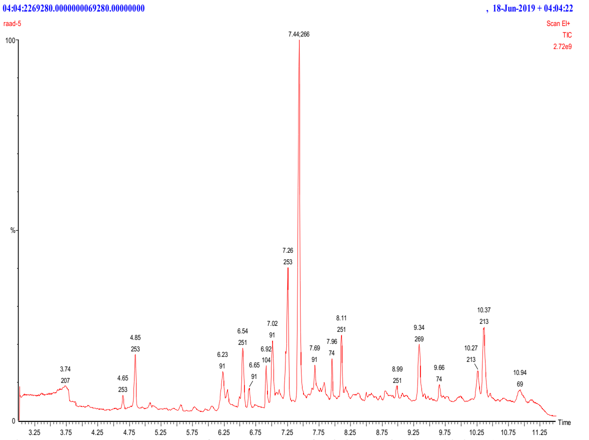
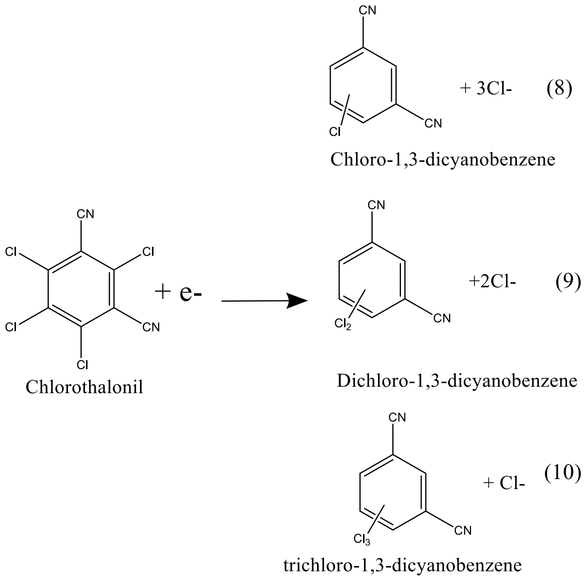


Figure 9. GC/Mass of 15 ppm of chlorothalonil in (99.9% acetonitrile) after 5 hours by visible light. The upper number of

each peak is retention time and the below one is the mass number.

de chlorination products from equation (8, 9, 10) are formed by the interaction of the trapped electron on the semiconductor surface with chlorothalonil which releasing chloride ion and give us the peaks of the derivatives of chlorothalonil, also the increasing of conductivity indicates that the Cl^- ions, and CN^- ions formed in the solution during photo-degradation.



The Proposed mechanism for chlorothalonil photoproduct at 254 nm is illustrated in figure (10).

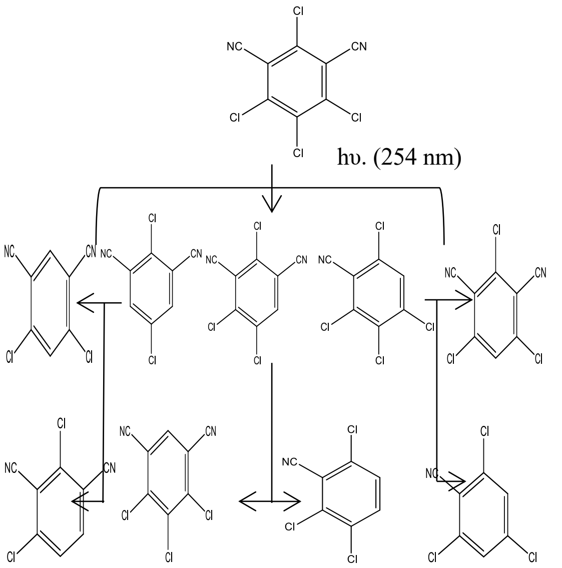


Figure 10. Proposed photo-degradation of chlorothalonil photoproduct (Cooke, Oviedo, Pelaez, & Argüello, 2017).

3.2 Photolysis by visible light with TiO2:
Photo-degradation of chlorothalonil has been done by visible light with semiconductor (TiO_2) 0.3 g/dm^3. Moreover, the solvent used in this work consisting of water fifty percent and fifty percent was acetonitrile. The optical density (absorbance) of chlorothalonil during Photo-degradation has been measured by spectrophotometer at 232 and 254 nm.

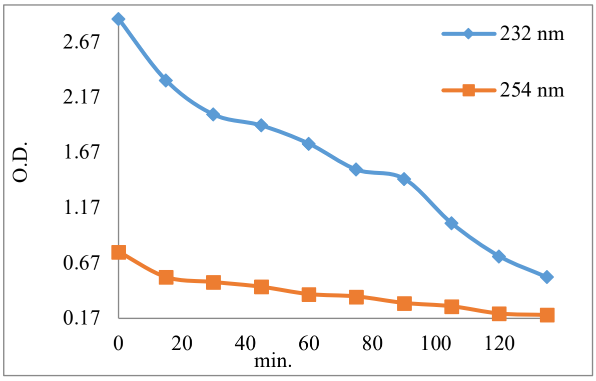


Figure 11. Degradation of 15 ppm of chlorothalonil by visible light with TiO_2 as a function of irradiation time at a Wavelength of 232 and 254 nm at 298 K.

3.3 Photolysis by visible light with ZnO:
Photo-degradation of chlorothalonil has been done in the presence of suspension ZnO 0.3 g/dm^3. The results are shown in the following figure.

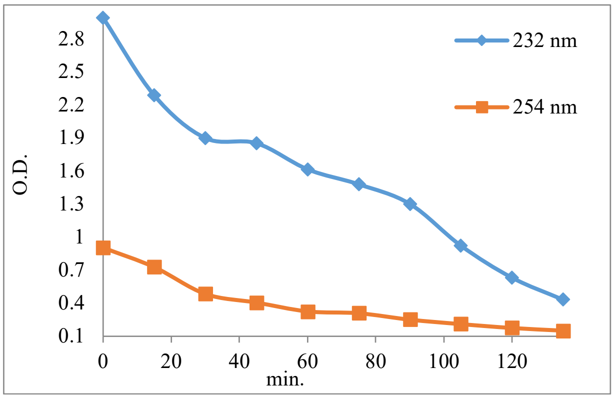


Figure 12. Degradation of 15 ppm of chlorothalonil by visible light with ZnO as a function of irradiation time at a Wavelength of 232 and 254 nm at 298 K.

The results have shown that the degradation process increase by adding semiconductor particularly in case of zinc oxide which is more active than the titanium dioxide and without catalyst.

3.4 Determination of order of chlorothalonil degradation by visible light with and without catalyst:
3.4.1 Determination order by using the integral equation: The order of chlorothalonil also determined by integral rate laws. The most fitted linear curve by measuring the correlation coefficient determines. Equation (11) illustrates the first order equation (Atkin's, & Julio, 2006):

$rate = k[A]$ (11)

Equation (12) illustrates the second order equation (Atkin's, & Julio, 2006):

$rate = k[A]^2$ (12)

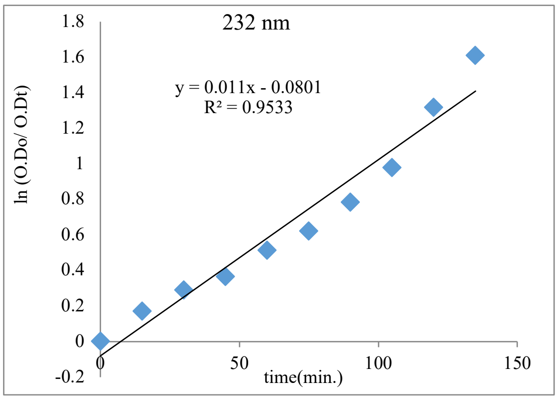


Figure 13. First order plot at 232 nm for degradation of 15 ppm of chlorothalonil by visible light 298 K.

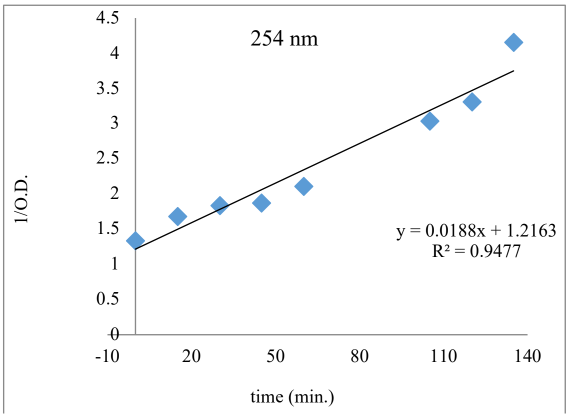


Figure 14. Second order plot at 254 nm for degradation of 15 ppm of chlorothalonil by visible light 298 K**.**

First order plot and second order plot is not good straight line from that reason we did the theoretical order (differential equation) to determine the order of reaction as mention in section (3.4.2).

3.4.2 Determination of order of chlorthalonil degradation by using differential equation: The rate of chlorothalonil degradation has been done by examining of each peak 232 and 254 nm. It appears that the degradation of peak 232 nm is the first order and 254 nm is the second order through plotting log-log graphical method as in figure (15).

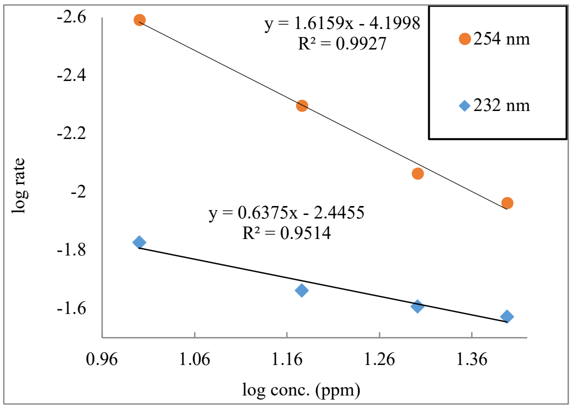


Figure 15. Log rate with log (conc.) graphical plot for 15 ppm of chlorothalonil degradation (232 and 254 nm) by visible light at 298 K.

Table 2. Order of chlorothaolnil degradation at 232 nm and 254 nm peaks by differential equation by visible light with and without catalyst.

Light source	Order at peak	
	232 nm	254 nm
Visible only	0.6	1.6
Visible + TiO_2	1.08	1.6
Visible + ZnO	0.9	2.1

3.5 Photolysis by Ultraviolet light:

Another series of experiments have been done by ultraviolet light. Photo degradation of chlorothalonil has been done in % 50 water and % 50 acetonitrile using Ultraviolet (UV) water sterilization lamp (8 W). Optical density (absorbance) of chlorothalonil during Photo degradation has been measured by spectrophotometer at 232 nm and 254 nm.

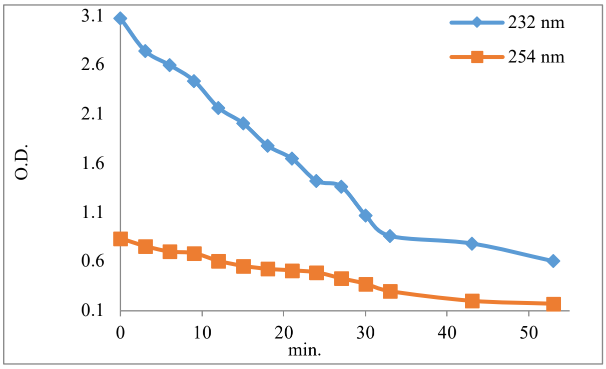


Figure 16. Degradation of 15 ppm of chlorothalonil by Ultraviolet light as a function of irradiation time at a wave length of 232 and 254 nm at 298 K.

As shown in figure (16) the photo-degradation of chlorothalonil in ultraviolet light is faster than the visible light.

3.5.1 Product of chlorothalonil after photo degradation: The product of chlorothalonil was analyzed by GC/Mass as illustrated in figures (17 and 18).

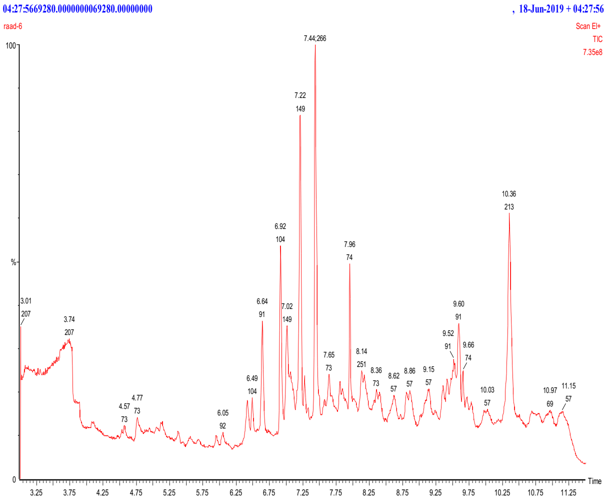


Figure 17. GC/Mass of 15 ppm of chlorothalonil in (99.9% acetonitrile) after 30 minutes by ultraviolet light. The upper number of each peak is retention time and the below one is the mass number.

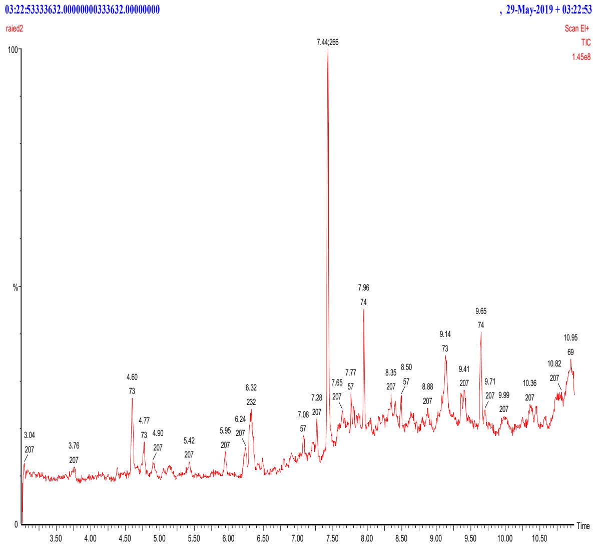


Figure 18. GC/Mass of 15 ppm of chlorothalonil in (99.9% acetonitrile) after 5 hours by ultraviolet light. The upper number of each peak is retention time and the below one is the mass number.

The results have shown that the product of the reaction in ultraviolet light is faster and smaller peaks at five hours, it may be going to mineralization as in figure (18). In addition, Ultraviolet light which is more stronger than the visible light the pesticide reached equilibrium in fifty minutes, The results show that in thirty minutes the product it may be chloro-1,3-dicyanobezene, dichloro-1,3-dicyanobezene, trichloro-1,3-dicyanobezene and with the parent molecules.

3.6 Photolysis by ultraviolet light with TiO2:

Photo degradation of chlorothalonil has been done in the presence of suspension TiO_2 0.3 g/dm^3. The results are shown in Figure (19).

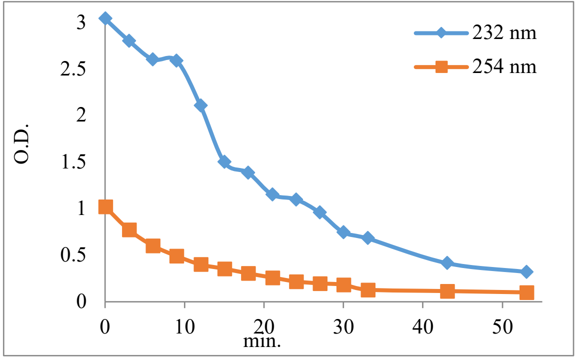


Figure 19. Degradation of 15 ppm of chlorothalonil by Ultraviolet light with TiO_2 as a function of irradiation time at a Wavelength of 232 and 254 nm at 298 K.

3.7 Photolysis by Ultraviolet light with ZnO:

Photodegradation of chlorothalonil has been done by ultraviolet light with semiconductor (ZnO) 0.3 g/dm^3. Moreover, the solvent used in this work consisting of water fifty percent and fifty percent was acetonitrile. Optical density (absorbance) of chlorothalonil during photodegradation has been measured by spectrophotometer at 232 and, 254 nm.

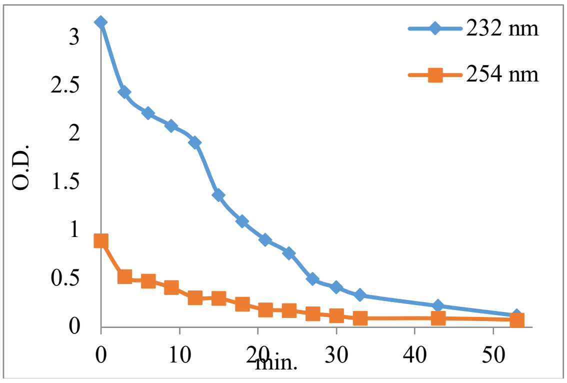


Figure 20. Degradation of 15 PPM of chlorothalonil by Ultraviolet light with ZnO as a function of irradiation time at a Wavelength of 232 and 254 nm at 298 K.

The results show that the degradation process increase by adding semiconductor particularly in case of zinc oxide which is more active than titanium dioxide and without catalyst

3.8 Determination of order of chlorothalonil degradation by Ultraviolet light with and without catalyst:

3.8.1 Determination of order of chlorothalonil degradation by using the integral equation: The order of chlorothalonil also determined by integral rate laws. The most fitted linear curve by measuring correlation coefficient determines.

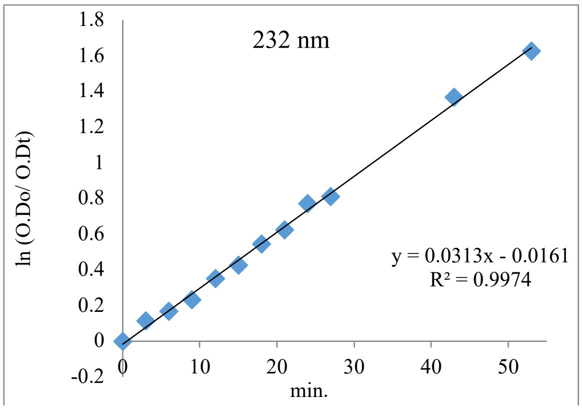


Figure 21. First order plot at 232 nm for degradation of 15 ppm of chlorothalonil by Ultraviolet light 298 K.

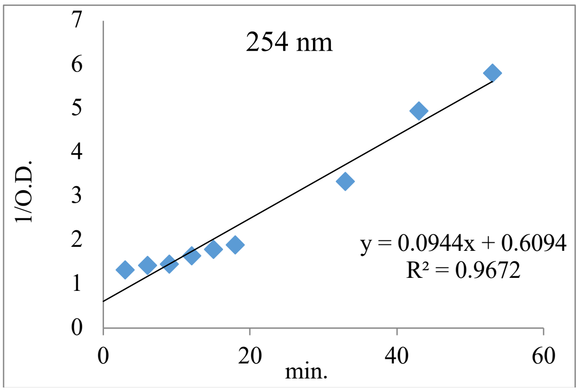


Figure 22. Second order plot at 254 nm for degradation of 15 ppm of chlorothalonil by Ultraviolet light 298 K.

First order plot and second order plot is not good straight line from that reason we did the theoretical order (differential equation) to determine the order of reaction as mention in section (3.8.2).

3.8.2 Determination of order of chlorothalonil degradation by using differential equation: The rate of chlorothalonil degradation has been done by examining of each peak of (232 nm, 254 nm). It appears that degradation of the peak 232nm first order and 254 nm is second order through plotting log-log graphical method. The table (3) illustrates the results of log-log graphical method.

Table 3. Order of chlorothaolnil degradation at 232 nm and 254 nm peak by differential equation by ultraviolet light with and without catalyst.

Light source	Order at peak	
	232 nm	254 nm
UV. only	0.63	1.6
UV. + TiO_2	0.62	1.52
UV. + ZnO	0.62	1.6

3.9 Determination of activation energy:

The activation energy for the degradation of chlorothalonil (15 ppm) by visible and ultraviolet light without and with the catalyst was calculated for temperature range (288 to 313 K).

3.9.1 Determination of activation energy by visible light with and without catalyst: The activation energy for the degradation of chlorothalonil (15 ppm) by visible light without and with catalyst was calculated for temperature range (293 to 313 K).

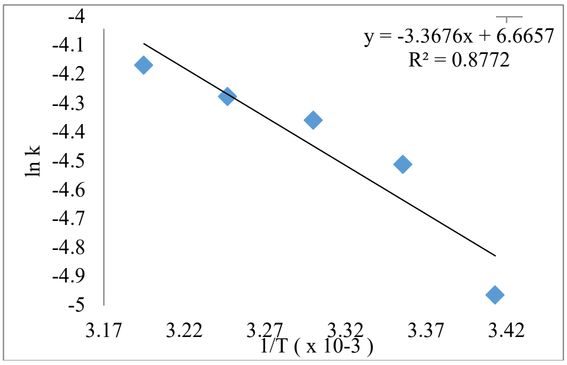


Figure 23. Arrhenius activation energy plot at 232 nm for chlorothalonil degradation by visible light for 15 ppm.

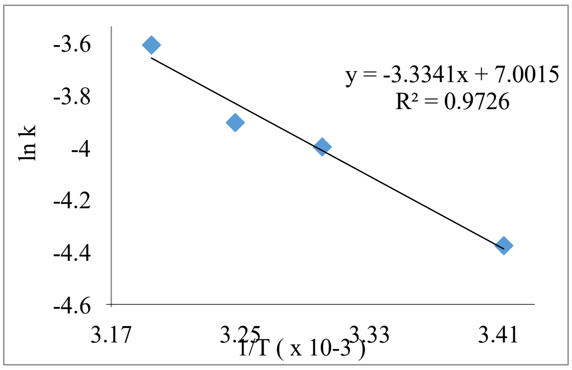


Figure 24. Arrhenius activation energy plot at 254 nm for chlorothalonil degradation by visible light for 15 ppm.

The Arrhenius plot is not good straight line that was due to the fact the degradation is not pure first and second order reaction and we used these plots to calculate the activation energies.

Table 4. Arrhenius activation energy for the degradation of chlorothalonil by visible light with and without catalyst at 232 nm and 254 nm.

peaks	Activation energy (kJ.mol^{-1})		
	Visible only	Visible + TiO_2	Visible + ZnO
232 nm	27.998	25.302	22.806
254 nm	27.719	24.725	23.197

As shown in Table (4) the activation energy decreases when we added the catalyst partially in case ZnO that is more active and has the lowest activation energy.

3.9.2 Determination of activation energy by ultraviolet light with and without catalyst: The activation energy for the degradation of chlorothalonil (15 ppm) by ultraviolet light without and with catalyst was calculated for temperature range (288 to 313 K).

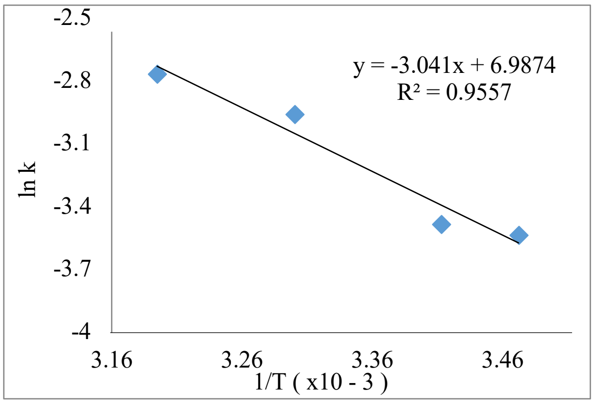


Figure 25. Arrhenius activation energy plot at 232 nm for chlorothalonil degradation by UV light for 15 ppm.

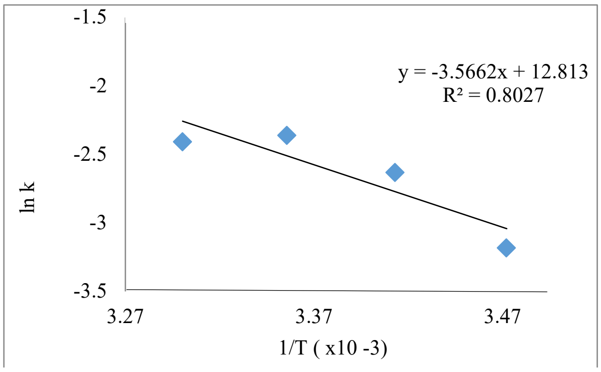


Figure 26. Arrhenius activation energy plot at 254 nm for chlorothalonil degradation by UV light for 15 ppm.

The Arrhenius plot is not good straight line that was due to the fact the degradation is not pure first and second order reaction and we used these plots to calculate the activation energies.

Table 5. Arrhenius activation energy for the degradation of chlorothalonil by Ultraviolet light with and without catalyst at 232, and 254 nm.

peaks	Activation energy (kJ . mol^{-1})		
	UV only	UV + TiO_2	UV + ZnO
232 nm	25.282	22.746	20.422
254 nm	29.647	22.225	17.567

As shown in Table (5) the activation energy decreases when we added the catalyst partially in case ZnO which is more active and has the lowest activation energy.

Table 6. Comparison between rates constant

Light source	Rate constant	
	232 nm k1(min.$^{-1}$)	254 nm k2(L.mol^{-1}. min^{-1})
Visible only	0.0110	0.0177
Visible +TiO_2	0.0111	0.0259
Visible +ZnO	0.0126	0.0397
UV only	0.0313	0.0856
UV + TiO_2	0.0463	0.1815
UV + ZnO	0.0644	0.2404

The rate constant increase with the increase of temperatures, also when we added catalyst the rate constant increase as shown in Table (6).

Table 7. Comparison between activation energy

Light source	Activation energy	
	232 nm (kJ/mol)	254 nm (kJ/mol)
Visible only	27.998	27.719
Visible +TiO_2	25.302	24.725
Visible +ZnO	22.806	23.197
UV only	25.282	29.647
UV + TiO_2	22.746	22.225
UV + ZnO	20.422	17.567

However, as shown in table (7) the activation energy is decreased when adding the catalysts for both peaks and its low value in ultraviolet with ZnO when compare with another value.

3.10 Measurement of Conductivity

Another series of experiments have been done for product by measuring conductivity. Conductivity is measure of ions when produced in photolytic solution. In this work, the conductivity was also monitored during photo degradation of chlorothalonil before and after photolysis of pesticides. The results of conductivity study show that the first part of plot conductivity versus time is kinetic part and the final part after 140 minutes in visible light and 50 minutes in ultraviolet light is equilibrium part as in figure (27 and 28).

3.10.1 Conductivity by visible light: The conductivity is also measured in different temperatures as it is shown in figure (27).

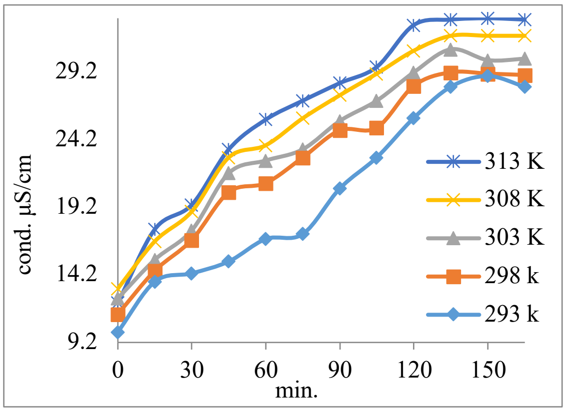


Figure 27. The conductivity of 15 ppm of chlorothalonil by visible light as a function of irradiation time in different temperatures.

The results have shown that the conductivity increases as temperature increases due to more degradation occurs when the temperature increases and more ions produce so the conductivity increases.

3.10.2 Conductivity by Ultraviolet light: The conductivity is also measured in different temperatures as it is shown in figure (28).

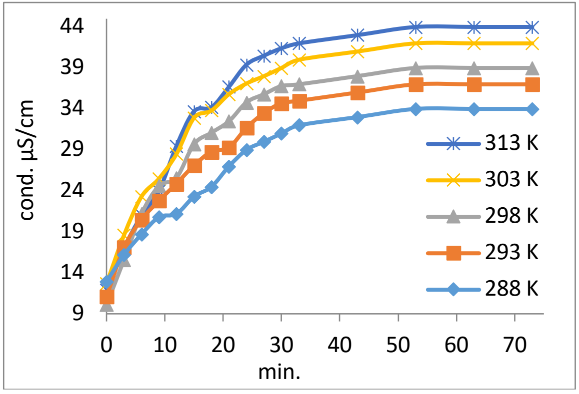


Figure 28. Conductivity of 15 ppm of chlorothalonil by UV light as a function of irradiation time in different temperatures.

The results have shown that the conductivity increases as temperature increases due to more degradation occurs when temperature increases and more ions produce and the conductivity increases and after 50 minutes, it goes to equilibrium.

3.10.3 Conductivity by the visible light with TiO_2: The conductivity is also measured in different temperatures as it is shown in figure (29).

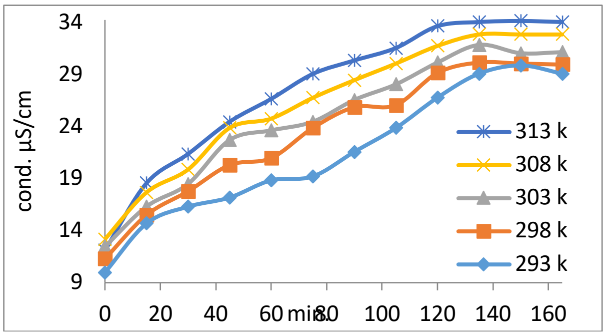


Figure 29. Conductivity of 15 ppm of chlorothalonil by visible light with TiO_2 as a function of irradiation time in different temperatures.

The results have shown that conductivity increases as temperature increases due to more degradation occurs when temperature increase and more ions produce so the conductivity increases with reach approximately to 34 (µS/cm) but in visible light without catalyst is reach to (30 µS/cm)

3.10.4 Conductivity by Ultraviolet light with TiO_2: The conductivity is also measured in different temperatures as it is shown in figure (30).

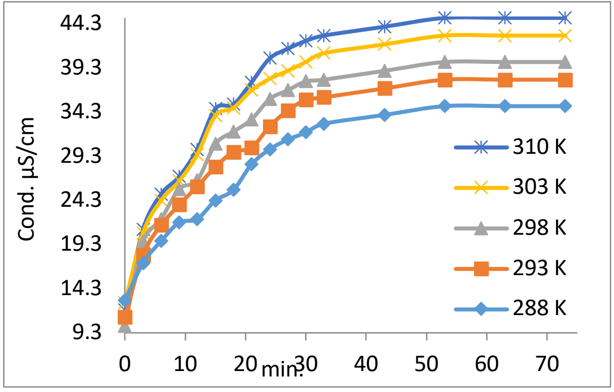


Figure 30. Conductivity of 15 ppm of chlorothalonil by UV. light with TiO_2 as a function of irradiation time in different temperatures.

The results have shown that the conductivity increases as temperature increases due to more degradation occurs when the temperature increases and more ions produce and the conductivity increases and after 40 minutes, it goes to equilibrium.

3.10.5 Conductivity by visible light with ZnO: The conductivity is also measured in different temperatures as it is shown in figure (31).

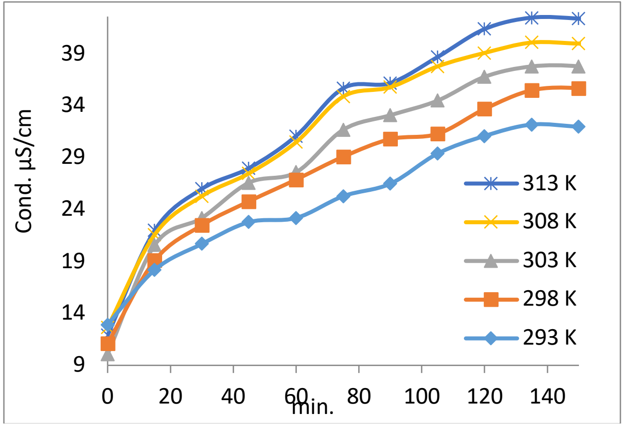


Figure 31. Conductivity of 15 ppm of chlorothalonil by visible light with ZnO as a function of irradiation time in different temperatures.

The results have shown that the conductivity increases as temperature increases due to more degradation occurs when temperature increases and more ions produce so the conductivity increases and after 130 minutes it goes to equilibrium.

3.10.6 Conductivity by Ultraviolet light with ZnO: The conductivity is also measured in different temperatures as it is shown in figure (32).

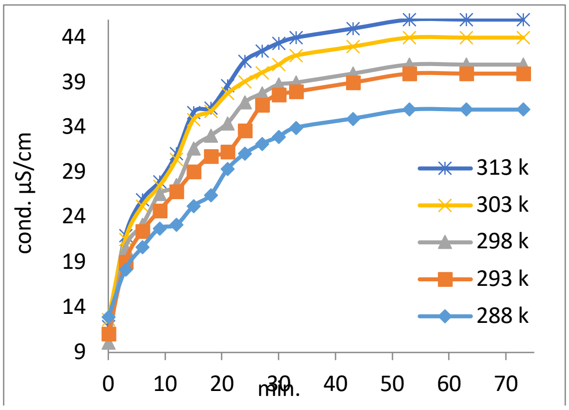


Figure 32. Conductivity of 15 ppm of chlorothalonil by UV light with ZnO as a function of irradiation time in different temperatures.

The results have shown that the conductivity increases as temperature increases due to more degradation occurs when temperature increases and more ions produce and the conductivity increases and after 30 minutes, it goes to equilibrium.

Table 8. Comparison between conductivity when reach equilibrium.

Light source	minute
Visible only	150
UV only	50
Visible +TiO_2	140
UV + TiO_2	40
Visible +ZnO	130
UV + ZnO	30

3.11 Determination of order by Conductivity

The order of reaction in this time is determined by measurement of ions in reaction products which will be different from there rate order in a spectroscopic measurement which is reactant dependence. The cell constant was measured by moving electrodes up-down to fix approximately cell constant =L/A.

We determine the order by plotting log conductivity with time and 1/conductivity with time.

3.11.1 Determination of order by visible and ultraviolet light: log conductivity with time and 1/conductivity as a function of time was done as shown in figure (33 and 34) respectively.

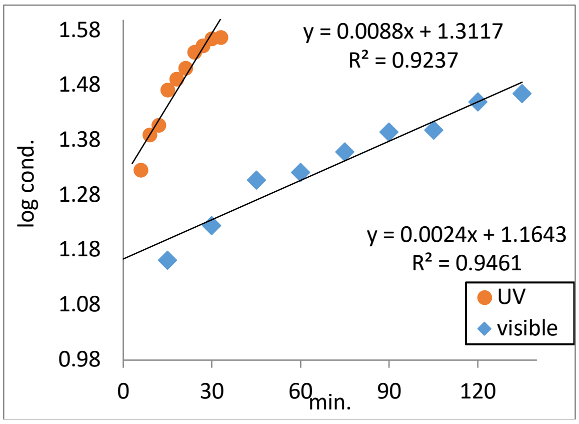


Figure 33. Log conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet Light based on conductivity at 298 K.

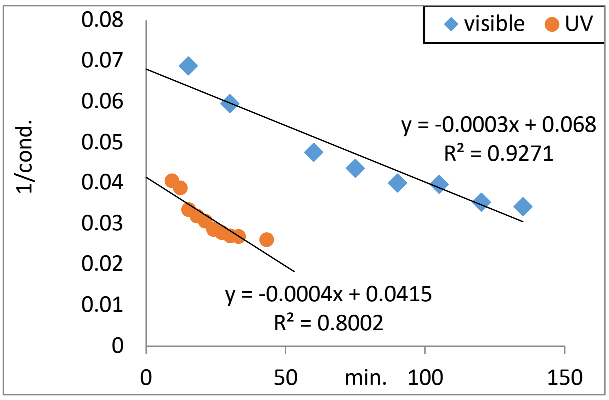


Figure 34. 1/conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet Light based on conductivity at 298 K.

The results in figure 33 show that the order of chlorothalonil is first order with both light sources ultraviolet and visible light. Will the shapes of curve in Figure 34 shows it is not second order. Putting into our account it is the product that deals with ions.

3.11.2 Determination of order by visible and ultraviolet light with TiO_2: log conductivity with time and 1/conductivity as function of time was done as shown in Figure (35 and 36) respectively.

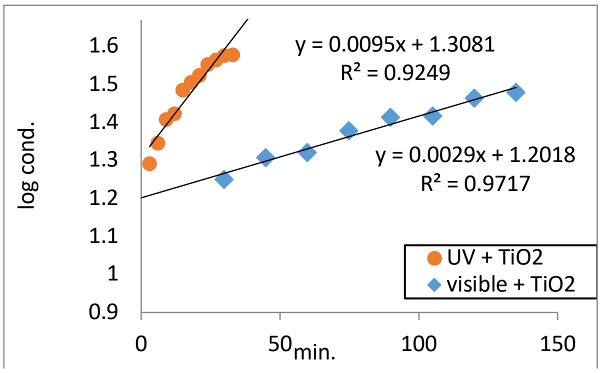


Figure 35. Log conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet light with TiO_2 based on conductivity at 298 K.

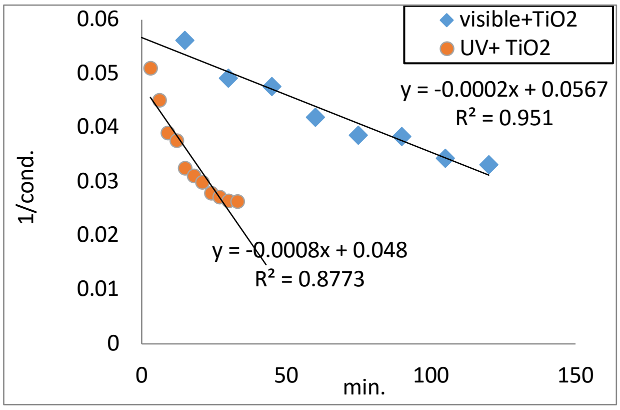


Figure 36. 1/conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet light with TiO_2 based on conductivity at 298 K.

3.11.3 Determination of order by visible and Ultraviolet light with ZnO: log conductivity with time and 1/conductivity as function of time was done as shown in figure (37 and 38) respectively.

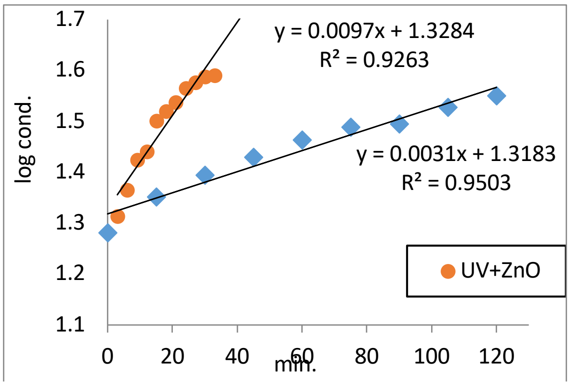


Figure 37. Log conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet light with ZnO based on conductivity at 298 K.

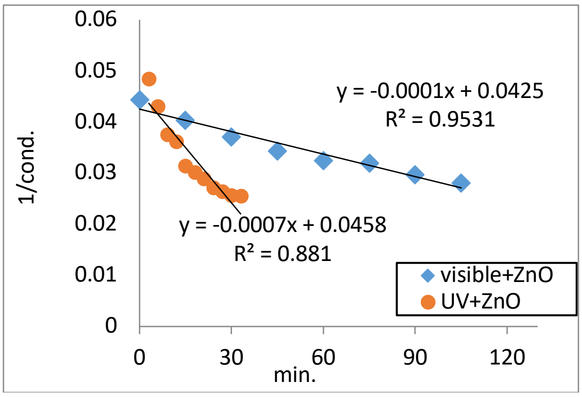


Figure 38. 1/conductivity as a function of time for the photo degradation of chlorothalonil 15 ppm by visible and ultraviolet Light with ZnO based on conductivity at 298 K.

Table 9. Comparison between conductivity rates constant

Light source	Rate constant	
	k1	k2
Visible only	0.0024	-0.0003
UV only	0.0088	-0.0004
Visible +TiO_2	0.0029	-0.0002
UV + TiO_2	0.0095	-0.00088
Visible +ZnO	0.0031	-0.0001
UV + ZnO	0.0097	-0.0007

As illustrated in Table 9 the value of k1 is increasing by adding a semiconductor or when changing the visible light to ultraviolet light. But the value of k2 is make sane because putting into our account it is the product which deals with ions.

4. CONCLUSION

This study gives us the fact the rate constant of chlorothalonil may proceed faster for ultraviolet radiation than visible light as in table (6) which indicates that the Photo-degradation of chlorothalonil is possible by visible or ultraviolet light but ultraviolet light is more efficient. In addition, this rate constant will increase when we added semiconductor like (TiO_2 and ZnO) as in table (6). Moreover, Arrhenius energy shows that the degradation by ultraviolet light is more sensitive to temperature than in case of visible light and activation energy decreases when we add catalyst especially with ZnO as illustrated in the table (7). The reaction rate constant depending on 232 nm is faster than 254 nm this may be due to fragmentation of this molecule during photolysis. The order of reaction has been measured by spectra and conductivity. However, in spectra we got two orders of reaction of chlorothalonil 232 nm which is first order, and 254 nm is second order and 232 nm, is faster than 254 nm. The order of reaction by conductivity is first order in both ultraviolet and visible light. However, the conductivity of chlorothalonil during Photo-degradation also increases with increasing temperature and it is more in case of ultraviolet with ZnO. In addition, GC/Mass gives us an indication that the product may be chloro-1,3-dicyanobezene, dichloro-1,3-dicyanobezene, trichloro-1,3-dicyanobezene and 1,3-Benzene-dicarboxylic acid and it goes to mineralization after five hours.

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