Experimental and Theoretical Study for The Photo
degradation of Chlorpyrifos and Cypermethrin Insecticides on
γ-Alumina Surface

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ABSTRACT

In this research, experimental and theoretical study of the adsorption
and photodegradation of two insecticides (chlorpyrifos and cypermethrin)
using the (UV) light and (gamma-alumina) as sensitizer. The photolysis of
insecticides by using water and hexane as solvents at (pH=7-7.5) and (0.1g)
of sensitizer were found increase the rate of decomposition of both
insecticides. The reactions of photodegradation of insecticides followed the
first order reactions. It was observed that the increasing in reaction
temperature led to increase the rate constant of the reaction (0.8×10^{-2}
1.4×10^{-2})min^{-1} for chlorpyrifos and(1×10^{-2}-1.6×10^{-2})min^{-1} for cypermethrin.
Activation energy of degradation were calculated and found (22.971KJ.
mol^{-1}) for chlorpyrifos and (13.127 KJ. mol^{-1}) which was relatively low, it
explain the rapid reactions of insecticides. The values of heats of formation
were calculated for both insecticides experimentally and theoretically using
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the hyper chem.8.0/semi-empirical(PM₃) and the values were as follows (20.452 KJ. mol⁻¹, (21.56)ₚ KJ. mol⁻¹) for chlorpyrifos and (10.608KJ.mol⁻¹, (17.348)ₚ KJ. mol⁻¹) for cypermethrin, they showed a positive values which means that the decomposition processes of insecticides is an endothermic process. The electronic and vibrational spectra of both insecticides were identified experimentally and theoretically and found obvious changes.

INTRODUCTION

Chlorpyrifos and cypermethrin are two of the most important insecticides, which are widespread use. Chlorpyrifos as organophosphorus insecticides is a crystalline solid dissolves in water in addition to the solubility in acetone and ethylacetate and have a short half-life, the chemical name is (O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl)phosphorothioate(1). Cypermethrin is pyrethroid insecticide, low solubility in water but it soluble in organic solvents such as hexane, cyclohexane and chloroform(2).

Heterogeneous photocatalytic study were carried out for both insecticides experimentally by using UV light as a source and gamma-alumina as a catalyst(3), its formula is (γ-alumina) and molecular weight (101.96), insoluble in water and organic solvents. The reason for use of alumina is the presence within the contents of the soil well proportioned. The figure (1) show the crystal structure of γ-alumina(4):

These two insecticides were studied theoretically using the program(hyper chem..8.0/semi-empirical (PM₃)), this method is the most computational
speed and accuracy, applied to large molecules and are useful in the study of reactions of organic compounds(5).

Experimental

Chemical Materials

<table>
<thead>
<tr>
<th>Common name</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Purity</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>C₉H₁₁Cl₃NO₃PS</td>
<td>350.5</td>
<td>98%</td>
<td>IPROCHEM(China)</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>C₂₂H₁₉Cl₂NO₃</td>
<td>416.3</td>
<td>93.5%</td>
<td>BILAG(Gordan)</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₆</td>
<td>78</td>
<td>99.8</td>
<td>GCC</td>
</tr>
<tr>
<td>γ- alumina</td>
<td>γ-Al₂O₃</td>
<td>101.69</td>
<td>99%</td>
<td>BDH</td>
</tr>
</tbody>
</table>

Instruments
1- UV-Visible spectra measurements by CARY 100 from VARIAN Co.
2- Infrared spectra measurements by SHIMADZU
3- pH meter (HANA)
4- Gas-Chromatography by Buck Model 910
5- Electronic balance AE220 Model by METLER

Preparation of Standard Solutions
1- Preparation of Standard Solution for Active Ingredient of Chlorpyrifos

The standard solution of chlorpyrifos was prepared by dissolving (0.3505g, 1mmol) of chlorpyrifos in 100ml of distilled water to get a concentration of (1×10⁻²M), which represents (Stock Sol.) of the active ingredient of chlorpyrifos and using the law of mitigation to prepare concentrations used in the process of Irradiation (2×10⁻³…………9×10⁻³)M.

2- Preparation of Standard Solution for Active Ingredient of Cypermethrin

The standard solution of cypermethrin was prepared by dissolving (0.416g 1mmol,) of cypermethrin in (100ml) of hexane to get a concentration of (1×10⁻²M), which represents (Stock Sol.) of the active ingredient of cypermethrin and using the law of mitigation to prepare concentrations used in the process of irradiation (4×10⁻⁵…………8×10⁻⁵)M

Procedure
Placed 100ml of a solution of the active ingredient for chlorpyrifos or cypermethrin using the concentrations founding in (1,2) and (0.1g) of catalyst (gamma–aluminia) was added. The mixture was placed in irradiation cell and connecting plastic pipes to the thermostat to regulate temperature, the samples using a UV-Visible light source (125 W), medium mercury pressure lamp. The pyrex cell has a quartz window, which was 15cm a put from the light source with a magnetic stirrer.
RESULTS AND DISCUSSION

Catalyst Effect

The effect of the presence of a catalyst (γ - alumina) on the rate of photolysis of the active ingredients of chlorpyrifos and cypermethrin through a comparison between the presence of the catalyst and its absence. This process has been carried on by irradiation of chlorpyrifos at concentration \((8 \times 10^{-3} \text{mol/L})\) and cypermethrin at concentration \((8 \times 10^{-5} \text{mol/L})\) at a temperature of \((303^\circ \text{K})\) and in the presence \((0.1 \text{g})\) of a catalyst (γ-alumina). The change in the concentration of the active ingredients through the process of irradiation were followed in different times. Figures (3) and (4) showing the effect of the catalyst on the degradation rate of the active ingredients for chlorpyrifos in water and cypermethrin in hexane at temperature \((303^\circ \text{K})\) using \((\text{UV})\) light.

![Figure 3: the effect of catalyst on degradation of chlorpyrifos](image3)

![Figure 4: The effect of catalyst on degradation of cypermethrin](image4)

The results have shown that the degradation of the active ingredients of chlorpyrifos and cypermethrin using light through providing the
compounds with energy that needed and decomposition for excitation (6) as it has proved that the presence of the catalyst (gamma - alumina) increases the rate of reaction due to increase the absorption of a photon by the catalyst, leading to different mechanical degradation of the materials and this has proven by other researchers (7), where they have observed increasing the real concentration for the active ingredients with the addition of the catalyst and before irradiation process (t = 0) and the reason is due to adsorption of the active substances on the surface of alumina and the occurrence of reaction between them.

**Effect of initial concentration change**

The study of initial concentration change of chlorpyrifos and cypermethrin on the reaction rate using UV light and gamma-alumina of weight (0.1g) in different times at constant temperature:

**Kinetic studies**

The UV-Visible spectroscopy is a good technology for follow-up the change in the concentration of chlorpyrifos in water at (pH=7.5) and cypermethrin in hexane at (pH=7) in different times with constant temperature (303 K) at wavelengths of (λ_{max}= 318nm) for chlorpyrifos and (λ_{max}=278nm) for cypermethrin at a range between (200-500)nm during the irradiation of (105min) for chlorpyrifos and (75min) for cypermethrin. Figures (7) and (8) show the absorption spectra in the ultraviolet region for the active ingredients of chlorpyrifos in water and cypermethrin in hexane before and after irradiation process.
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Figure 7: UV-Vis. absorption spectra for chlorpyrifos in water after and before irradiation process

Figure 8: UV-Vis. Absorption spectra for cypermethrin in hexane after and before irradiation process

The decline in absorbance during the irradiation process every (15min) led to a decline in concentration of compounds, which was also accompanied by changing the pH from basic to the acidic medium and this is evidence for the degradation of both compounds (8).

Theoretically by using the hyper chem. 8.0/semi-empirical(PM$_3$), table (1) show the comparison between the spectrum of electronic for active ingredients of chlorpyrifos and cypermethrin experimentally and theoretically.

Table 1: Comparison between the electronic spectrum of active ingredients for chlorpyrifos and cypermethrin

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Band (I)</th>
<th>Band (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda$(nm)</td>
<td>$\lambda$(nm)</td>
</tr>
<tr>
<td>1</td>
<td>C$<em>9$H$</em>{11}$Cl$_3$NOPS</td>
<td>318 (322)$_p$</td>
<td>237 (250)$_p$</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>{22}$H$</em>{19}$Cl$_2$NO$_3$</td>
<td>278 (273)$_p$</td>
<td>218 (228)$_p$</td>
</tr>
</tbody>
</table>

P: semi-empirical(PM$_3$)

Figures (9) and (10) show the theoretical UV spectra for chlorpyrifos and cypermethrin theoretically:
The reaction order was determined by the following equation:
\[ \ln \text{Rate} = \ln k + n \ln [\text{Conc.}] \]  
\[ \ldots (1-3) \]

\( k \): rate constant  
\( n \): reaction order

A straight line was given by draw \( \ln \text{Rate} \) versus \( \ln [\text{Conc.}] \). The slope of the straight line represent the reaction order. Figures (11) and (12) represent the relationship between \( \ln[\text{conc.}] \) and \( \ln \text{Rate} \) of chlorpyrifos and cypermethrin:

The catalytic photodegradation reaction for both insecticides showed first order reaction and therefore these reactions are simple reactions (one step). The reaction rate constant is calculated by drawing the relationship between \( \ln [\text{conc.}] \) versus irradiation time for insecticides. Figures (13) and (14) demonstrated the relationship between \( \ln [\text{conc.}] \) versus time of irradiation for chlorpyrifos and cypermethrin at a temperature of (303\(^{\circ}\)K).
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Figure 13: The relationship between ln[chlor.] versus irradiation time

The relationship was obtained the rate constants. The half-life time of the reactions as a first order were obtained through the following relationship:

\[ t_{1/2} = \frac{0.693}{K} \]  

…..(2-3)

Table (2) shows the values of rate constant (K) and half-life time (t_{1/2}) of chlorpyrifos and cypermethrin:

**Table 2: The values of K and t_{1/2} for chlorpyrifos and cypermethrin**

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>K×10^{-2} (min^{-1})</th>
<th>t_{1/2} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_5H_{11}Cl_3NOPS</td>
<td>0.8</td>
<td>86.62</td>
</tr>
<tr>
<td>2</td>
<td>C_{22}H_{19}Cl_2NO_3</td>
<td>1</td>
<td>69.3</td>
</tr>
</tbody>
</table>

**Effect of Temperature Change**

The effect of temperature change on rate constant of photolysis reaction were studied for the active ingredients of chlorpyrifos and cypermethrin in the solvents water and hexane using (UV) light and the presence of (0.1g) catalyst (gamma–alumina). The irradiation process carried out under different thermal conditions \((303^0, 313^0, 323^0, 333^0)K\). Where the following equation was applied to find the rate constant:

\[ \ln [C_t] = \ln [C_0] - k_{obs} \cdot t \]  

…..(3-3)

Table (3) represent the values of rate constant in different temperatures for both insecticides:
Table 3: The values of rate constant in different temperatures for chlorpyrifos and cypermethrin

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>303°</th>
<th>313°</th>
<th>323°</th>
<th>333°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K \times 10^{-2} \text{(min}^{-1}) ) for chlorpyrifos</td>
<td>0.8</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>( K \times 10^{-2} \text{(min}^{-1}) ) for cypermethrin</td>
<td>1</td>
<td>1.2</td>
<td>1.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

It was observed that increasing temperature led to increase the rate constant of decomposition.

The activation energy which show the type of the reactions were calculated, it was showed whether the reaction rapid or slow from arrhenius equation

\[
k = A \cdot e^{-\frac{E_a}{RT}} \quad \text{.....(4-3)}
\]

By taking the logarithm of the parties….

\[
\ln k = \ln A - \frac{E_a}{RT} \quad \text{.............(5-3)}
\]

Plotting the relationship between \(1/T\) versus \(\ln K\) as in figures (15) and (16). the slope gave activation energy.

We note that the value of activation energy \((E_a=22.971\text{KJ.mol}^{-1})\) for chlorpyrifos and \((E_a=13.127\text{KJ.mol}^{-1})\) for cypermethrin, these values are low that means the reactions were fast and the reason is the surface of alumina contributes to reduce the activation energy by adsorbing the insectices molecules on the surface and makes it easier to decompose\(^{(9)}\).

The heats of formation values for the two insecticides are calculated experimentally by using the equation(10):

\[
E_a = \Delta H + RT \quad \text{...........(6-3)}
\]

Theoretically by using hyper chem.8.0/semit-empirical(PM3), table (4) show the values of heats of formation for chlorpyrifos and cypermethrin experimentally and theoretically.
Table 4: The values of $\Delta H_f$ for chlorpyrifos and cypermethrin experimentally and theoretically

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>$\Delta H_f$ (KJ. mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$<em>9$H$</em>{11}$Cl$_3$NOPS</td>
<td>20.452 (21.56)$_p$</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>{22}$H$</em>{19}$Cl$_2$NO$_3$</td>
<td>10.608 (17.348)$_p$</td>
</tr>
</tbody>
</table>

P: semi-empirical (PM$_3$)

I.R. Spectroscopy

Active ingredients for chlorpyrifos and cypermethrin possess many of the bands belonging to the groups consisting in molecules (chlorpyrifos and cypermethrin). Figures (17), (18), (19) and (20) show the IR spectra for chlorpyrifos and cypermethrin before and after the photolysis process:
Theoretically by using hyper chem.8.0/semi-empirical(PM$_3$), tables(5) and (6) show the comparison between the spectrum of IR for chlorpyrifos and cypermethrin experimentally and theoretically.

**Table 5: The comparison between the vibrational spectra of chlorpyrifos experimentally and theoretically**

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>$V_{\text{P=S}}$</th>
<th>$V_{\text{C=N}}$</th>
<th>$V_{\text{C=C}}$</th>
<th>$V_{\text{C-H}}$</th>
<th>$V_{\text{C-H}}$</th>
<th>$V_{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C$<em>9$H$</em>{11}$Cl$_3$NOPS</td>
<td>850.2 (837.67)$_p$</td>
<td>1550.8 (1555.28)$_p$</td>
<td>1647.26 (1667.9)$_p$</td>
<td>1411.9 (1411)$_p$</td>
<td>3053.4 (3004)$_p$</td>
<td>1274.9 (1277)$_p$</td>
</tr>
</tbody>
</table>

P: semi-empirical(PM$_3$)

**Table 6: The comparison between the vibrational spectra of cypermethrin experimentally and theoretically**

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>$V_{\text{C-Cl}}$</th>
<th>$V_{\text{C=N}}$</th>
<th>$V_{\text{C=O}}$</th>
<th>$V_{\text{C=C}}$</th>
<th>$V_{\text{C=C}}$</th>
<th>$V_{\text{Aryl-O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C$<em>{22}$H$</em>{19}$Cl$_2$NO$_3$</td>
<td>694.4 (686.2)$_p$</td>
<td>2100 (2019)$_p$</td>
<td>1741.78 (1752.8)$_p$</td>
<td>1410.01 (1403.8)$_p$</td>
<td>1487.47 (1511)$_p$</td>
<td>1247 (1253.4)$_p$</td>
</tr>
</tbody>
</table>

P: semi-empirical(PM$_3$)

Figures (21) and (22) show the vibrational spectra for chlorpyrifos and cypermethrin theoretically by using hyper chem.8.0/semi-empirical(PM$_3$)
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**Figure 21:** The vibrational spectra of chlorpyrifos theoretically

**Figure 22:** The vibrational spectra of cypermethrin theoretically

- **The photolysis mechanism for chlorpyrifos and cypermethrin**
  A mechanism for degradation of chlorpyrifos and cypermethrin were suggested depending on the results of the UV-Vis., I.R. technique and determination of Cl. Figs. Figures (23) and (24) show the mechanism for the both compounds:

![Mechanism of Photolysis of Chlorpyrifos and Cypermethrin](image)

**Figure 23:** The photolysis mechanism for chlorpyrifos
Figure 24: The photolysis mechanism for cypermethrin

REFERENCES


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