

# PHOTOLYSIS: Case Studies for Organophosphate Pesticides Treatment

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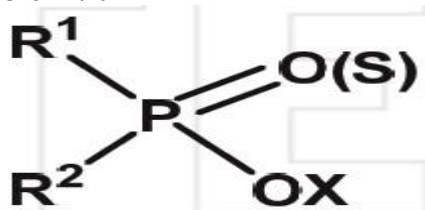
**Abstract** - Physical-chemical and biological methods are the main treatment processes with their own traits. Biological treatment is economical, but not so effective in refractory organic wastewater. The prolific dividends of photo-based methods in the treatment of pesticides are diverse enough to include low cost operations, easy handling, high efficiency, etc. When used to degrade pollutants rather than targeting microorganisms, photolytic treatment with UV is used as an advanced oxidation process (AOP) inducing photo degradation of organic and inorganic contaminants in water. The breakdown of pollutants into simpler compounds due to UV exposure is also called photolysis. UV treatment provides a number of benefits, including potentially complete oxidation of organics within a few hours. In general, UV has the potential for many compounds to provide more successful removal than other treatment procedures such as biodegradation, or activated carbon that involves a phase transfer of pollutants rather than their actual destruction. Low concentrations may also be treated, in the ppb range. Again, this varies by compound, but through the use of cost-effective catalysts that can be adapted to specific systems, photolysis can be optimized.

The pesticide and chemical industries are considered to generate wastewaters containing toxic and non-biodegradable compounds that remain in the environment even after their wastewaters have been subjected to conventional processing. It is very important to develop water and wastewater treatment technologies for the removal of toxic and refractory organic compounds from water and wastewater. Advanced oxidation processes are considered one of the most attractive methods for the treatment of water and wastewater containing toxic and non-biodegradable pollutants.

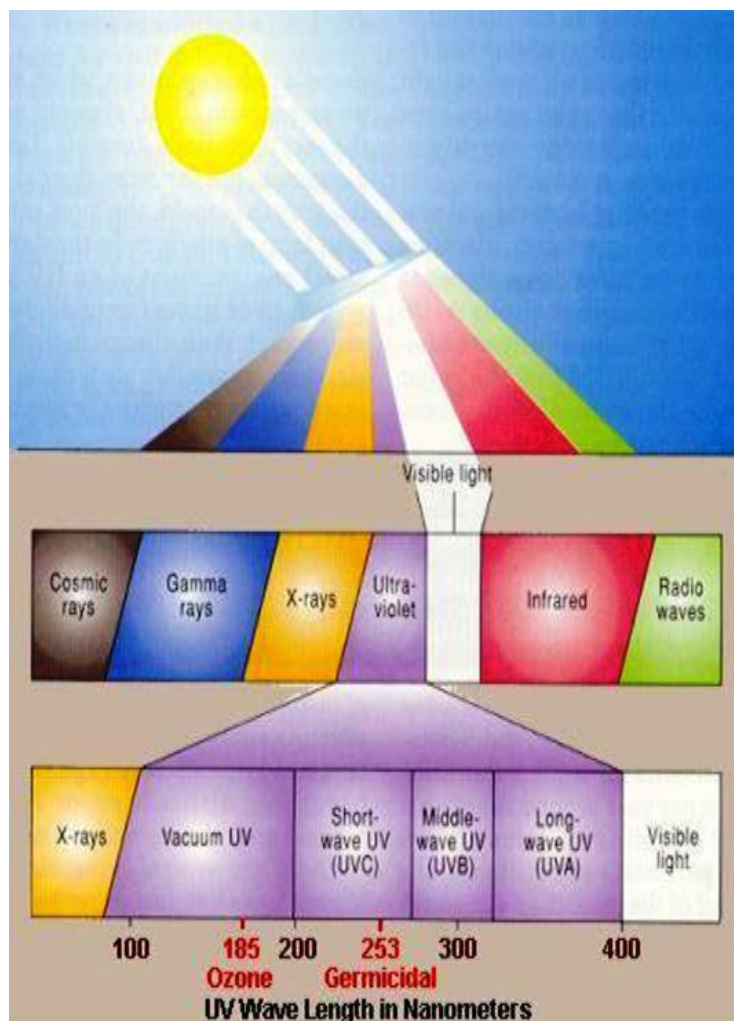
**Key Words:** Photolysis, UV treatment, Organophosphate Pesticides and Degradation

## 1. Introduction

Organophosphorous pesticides contain a phosphate group as their basic structural framework as defined by Schrader's formula:



Where, R1 and R2 are usually methyl or ethyl groups, the O in the OX group can be replaced with S in some compounds, whereas the X group can take a wide diversity of forms. Organophosphorous pesticides are generally more toxic to vertebrates and invertebrates as cholinesterase inhibitors leading to a permanent overlay of acetylcholine neurotransmitter across a synapse. As a result, nervous impulses fail to move across the synapse causing a rapid twitching of voluntary muscles and hence paralysis and death.



The electromagnetic spectrum (Cane 2013)

## 2. Photolysis

It is the chemical decomposition of compounds when a photon of light is absorbed. This however, does not fully degrade them. This is often a successfully destructive pathway for pesticides in surface water or on plant or soil surfaces that are therefore contacted by sunlight. The absorption of a photon induces molecular excitation and elevation from a ground state to an elevated state. This excited molecule may then undergo a degradation reaction through "direct" photolysis, or contact a ground state molecule which will then undergo the reaction through "indirect" photolysis. Many photoreactions then involve bond cleavage. Typical photoreactions involve isomerization, dealkylation, carbon oxidation, dehalogenation, ester cleavage, cyclization, or sulfur oxidation. Oxidation involves the transfer of electrons when two compounds are combined. In the case of UV degradation, UV creates active bonding radicals that oxidize carbon (gain electrons from the carbon) and other organic and inorganic components of pesticides. Oxygen replaces hydrogen or other bonded molecules and, if complete oxidation is achieved, oxygen replaces all potential bonding sites provided by carbon's valence electrons. Hydroxyl radicals are often the oxidizing species. If the pesticide is completely mineralized, the final products are carbon dioxide as well as other fully oxidized compounds containing any other inorganic elements in the base compound. If incomplete degradation occurs, any number of byproducts may be formed and will vary in composition based on the parent compound and water quality overall.

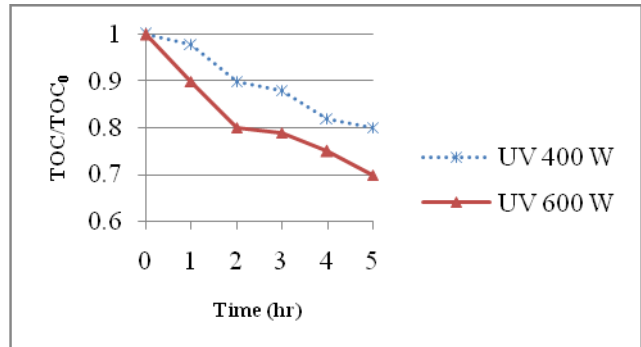
## 3. Case Studies

**3.1.** Treatment of wastewater streams containing three pesticides, i) acephate, ii) glyphosate and iii) malathion. The degradation of acephate increased and malathion decreased at their higher initial concentrations whereas no significant effect related to concentration was observed for glyphosate. Results show that the degradation followed a first order kinetics and the degradation rates were: malathion > acephate > glyphosate. (Nik Raihan et.al)

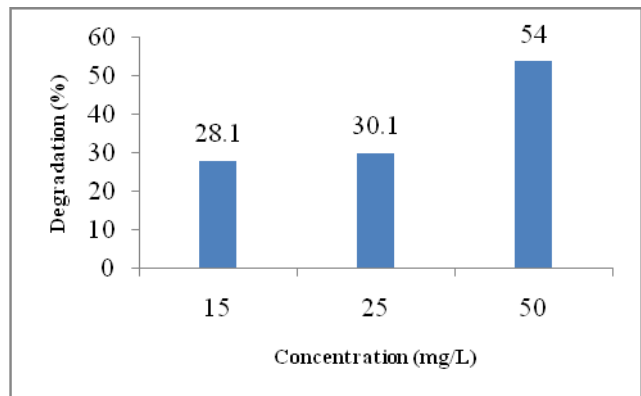
### Photo degradation of Acephate

#### Effect of UV source

The effect of the UV source on the photo degradation of acephate is studied.



**Fig 1: Effect of the UV source on the photo degradation of acephate**



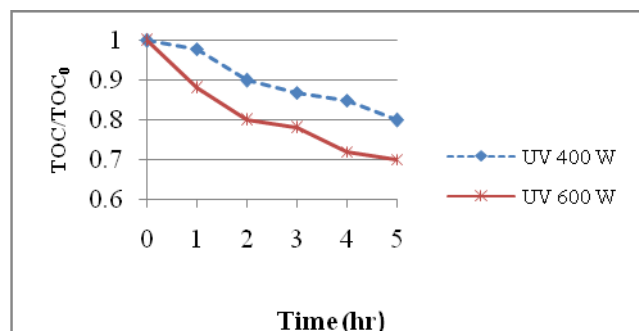
**Fig 2: Effect of Initial concentration of Acephate**

Percentage degradation increased from 28.1% to 54.0% when the initial concentration was increased from 15 mg/L to 50 mg/L after 5 h UV irradiation.

### Photo degradation of Glyphosate

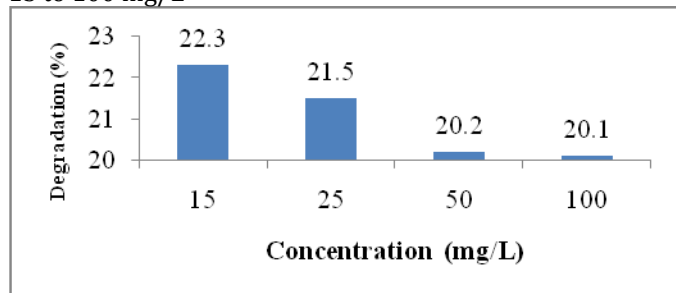
#### Effect of UV source

The effect of UV light is studied for the photo degradation of glyphosate and the results are as below.



**Fig 3: Effect of UV irradiation source on photodegradation of glyphosate.**

The percentage degradation of glyphosate using a 400 W UV source was 22.3% and this value slightly increased to 30.5% when the UV source was changed from 400 W to 600 W. The effect of initial concentration on photodegradation of commercial glyphosate is investigated over the range from 15 to 100 mg/L



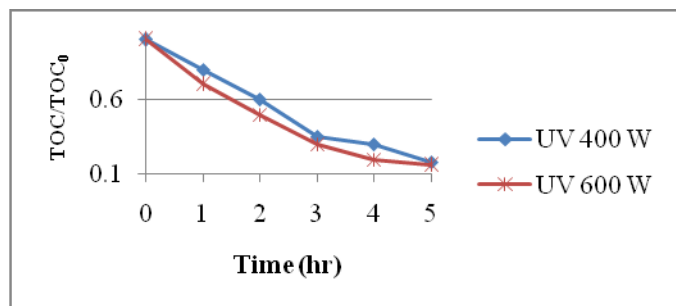
**Fig 4: Effect of initial concentration of glyphosate**

The results show a slight drop in the degradation of glyphosate when the concentration was increased from 15 to 100 mg/L.

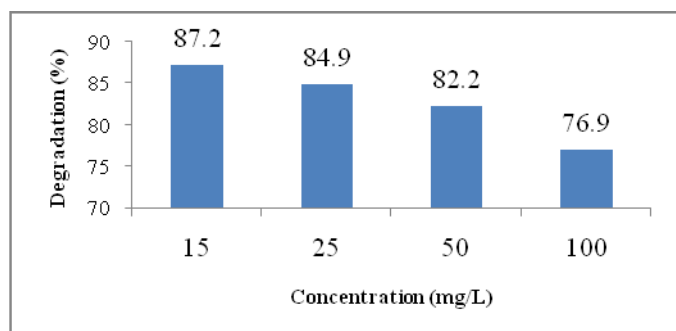
### Photodegradation of Malathion

#### Effect of UV source

The results show that the degradation of malathion was slightly higher when a 600 W UV source was used to irradiate the aqueous solution containing 15 mg/L malathion



**Fig 5: Effect of different watt of UV light irradiation on photodegradation of malathion**



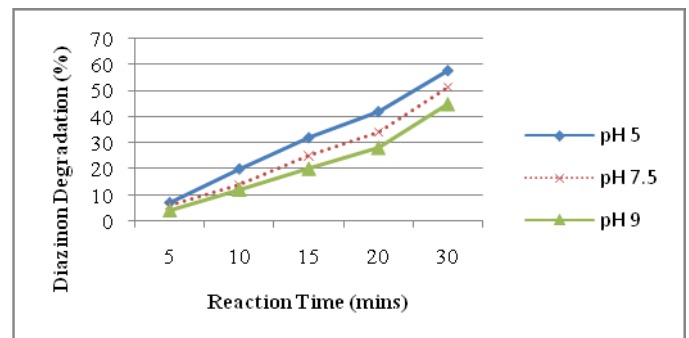
**Fig 6: Effect of initial concentration of malathion**

The results show that the higher the initial commercial malathion concentration (100 mg/L), the lower the

percentage degradation (76.9%). When the concentration of malathion reduced to 15 mg/L, the percentage degradation (87.2%) occurred.

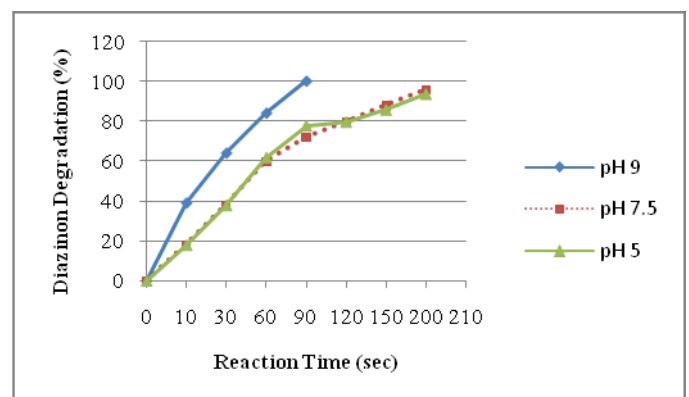
**4.2 Performance of UVC and vacuum UV (VUV) processes for the degradation of diazinon is divided into two phases.** In the first phase, the photo-reactor operated in batch mode and the influence of pH, diazinon concentration and reaction time on diazinon degradation in the VUV and UVC processes using contaminated distilled water was recorded. In the second phase, the most efficient process for degradation and mineralization of diazinon (VUV) is further examined in continuous mode and the influence of hydraulic retention time (HRT = volume/flow) is tested for degradation of diazinon in contaminated tap water.

The performance of the UVC process for degradation of diazinon (10 mg/L) in distilled water is investigated in acidic (pH 5), neutral (pH 7.5), and alkaline (pH 9) solutions as a function of reaction time



**Fig 7: Effect of solution pH on diazinon degradation in UVC process**

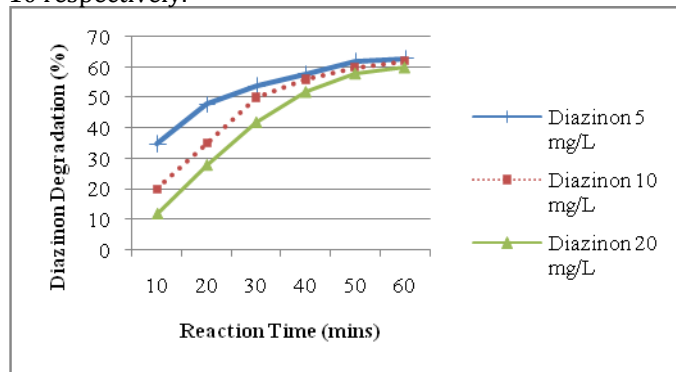
The efficiency of UVC process in diazinon degradation at solution pHs of 5, 7.5 and 9 was 57.8%, 51.4% and 44.8%, respectively, at a reaction time of 30 min.



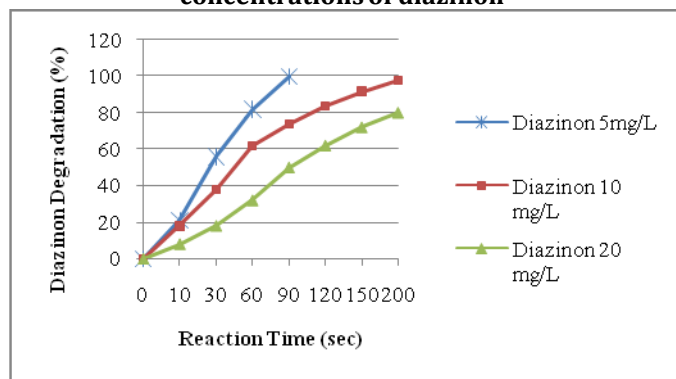
**Fig 8: Effect of solution pH on diazinon degradation in VUV process**

The performance of UVC and VUV processes for the degradation of diazinon is compared at different diazinon concentrations. The percentage of degradation for different

concentrations of diazinon as a function of reaction time for the UVC and VUV processes are shown in Figure 9 and Figure 10 respectively.

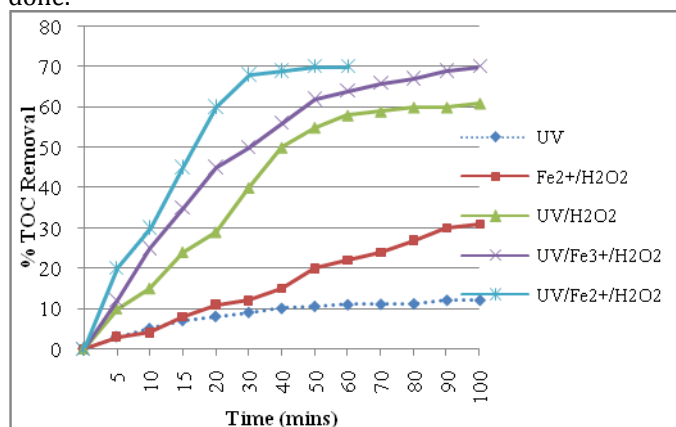


**Fig 9: Performance of UVC process for different concentrations of diazinon**



**Fig 10: Performance of VUV process for different concentrations of diazinon**

**4.3 Degradation of organophosphorus containing substrates such as fenitrothion, diazinon and profenofos with UV is done.**



**Fig 11: Degradation of Mixtures of Profenofos, Diazinon and Fenitrothion by Different AOPs.**

#### 4. CONCLUSIONS

From above studies it is concluded that photolysis can be effectively used to degrade organophosphate pesticides in wastewater as pre treatment method.

Efficiency of photolytic treatment is around 60% for nearly all organophosphate compounds.

Degradation efficiency depends on chemical content of respective compounds and not much on UV source.

Different compounds in same Organophosphate Group of Pesticides have been found to have different degradation efficiencies for same UV source and initial Concentrations. Thus, all compounds in Organophosphate group cannot be summarized/clubbed together for degradation efficiency, concentration, UV source, etc.

Photolysis if assisted with other means showed good degradation efficiencies than just only photolysis for mixture of Different organophosphate compounds.

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