



Using Sonophotodegradation Technology for Removal of Organophosphorus Pesticides in Aqueous Solution

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Advanced oxidation processes (AOPs) such as sonolysis and sonophotolysis (sonophotodegradation) may be used to remove organic pollutants from an aqueous solution. Malathion and diazinon are both of highly effective organophosphorus pesticides that are used extensively in agriculture. The objective of this study was to investigate degradation of these pesticides (diazinon and malathion) using sonophotodegradation technology. The operational parameters used in the study to evaluate the processes were irradiation time, pH and initial concentrations of pesticide and the synergistic effect was also documented. Gas chromatography mass spectroscopy (GC-MS) was used to analyze the pesticides. Results showed that sonophotolysis was more effective than individual sonolysis and that degradation of both pesticides increased with a decrease in the initial concentration. The sonophotodegradation rate of the malathion pesticide was more than that of diazinon but the sonolysis rate of both pesticides was about equal, hence photolysis was used effectively to remove the pesticides from water.

Key Words: Pesticides, Advanced oxidation processes, Organophosphorus, Sonophotodegradation, Water.

INTRODUCTION

Organophosphorus pesticides are widely found in water resources, they are released in to the environment from industrial wastewater, as agricultural runoff and from agricultural waste¹. The maximum upper limit for a permissible level has been proposed by the European Union for organopesticide in drinking water. The EU has proposed 0.1 and 0.5 mg/L for individual and total levels of organopesticides in drinking water, respectively². Measurement of organophosphorus pesticides in water is usually carried out by methods involving GC, GC-MS and HPLC³.

The organophosphorus pesticides used in this study were diazinon and malathion. Diazinon is an organophosphorus insecticide classified by the World Health Organization (WHO) as "moderately hazardous" class II. It is associated with toxicity to aquatic organisms at a concentration of 350 ng/L⁴, with an LC₅₀ level that kills fish (48 h) of 4.4 mg/L⁵. Fatal human doses were found to range from 90-444 mg/Kg⁴. Diazinon is relatively water soluble (40 mg/L at 25 °C)⁶. Diazinon undergoes fast hydrolysis at acidic and basic conditions⁵.

When diazinon was irradiated at $\lambda < 290$ nm in a water/soil suspension it was isomerized to a product containing a

S-(P=O)-group than O-(P=O)- group other products were diazoxon and hydroxyl diazinon⁶. Malathion is an organophosphorus insecticide in use from as early as 1950. Malathion has a vapour pressure 3.38×10^{-6} mm Hg at 30 °C, water solubility 130 mg L⁻¹ Henry's law constant of 4.89×10^{-9} atm/m³. mol⁷. Lethal Dose for mammat was 390 mg/Kg⁸.

The half-life range of malathion is 0.2 weeks at pH 8 compared to 21 weeks at pH 6⁷. The metabolites resulting from hydrolysis are as follows; malaaxon, malathion α - and β -monoacid, diethyl fumarate, diethyl thiomalate, O,O-dimethyl phosphorodithioic acid, diethylthiomalate and O,O-dimethyl phosphorothionic acid⁷. The toxic effects of diazinon and malathion are caused by an ability to inhibit activity of the enzyme acetylcholinesterase^{9,10}.

In recent years, advanced oxidation processes (AOPs) have attracted attention for an ability to directly convert pollutants in water and wastewater into harmless substances¹¹. AOPs are those processes that are based on the production and utilization of hydroxyl radicals¹¹.

There have been many studies related to the degradation of selected pesticides (atrazine, diuron, isoproturon, alachlor, pentachlorophenol and chlorfenvinphos) by UV photolysis and AOPs (such as UV/H₂O₂, UV, ZnO/UV and UV/TiO₂)¹²⁻¹⁴. The

use of high UV fluencies (1000-2000 mJ/cm^2) can promote the degradation of photolabile organic compounds by direct photolysis due to their potentials to absorb light^{15,16}. Most advanced oxidation processes utilize UV irradiation to catalyze catalysts that involve the generation of an extremely powerful and non-selective oxidizing agent, such as the hydroxyl radical, to destroy pollutants. However, the utilization efficiency of UV is low because some catalysts can screen out UV waves. This limitation can be overcome by utilizing ultrasound (US) irradiation. Ultrasonic irradiation causes acoustic cavitation and consequent bubble collapse causes intense local heating, high pressures and very short lifetimes of bubbles; these transient, localized hot spots drive high energy chemical reactions. The enhanced mass transfer and phase transfer properties of solid surfaces caused by US irradiation can accelerate oxidation^{17,18}. There has been much research related to the degradation of organic pollutants by a combination of UV with US¹⁷⁻²⁰. The mechanism employed for the degradation of pesticides can be by means of reactions; either to produce free radicals by cavitation or by pyrolysis with a collapsing bubble or by means of a combination of both of these processes²¹. Therefore, the AOPs in this work can be divided into three categories:

Photolysis: The use UV irradiation without the presence of any catalyst, to irradiate polluted water. Photolysis does not totally dissociate the organic pollutant but replaces it with the generation of intermediate products from the pollutant, which could be more hazardous than the primary pollutant.

Sonolysis: The use of ultrasonic technology, without the presence of any catalyst, to generate hydroxyl radicals in solution. Sonolysis suffers the same problems as photolysis.

Sonophotolysis: The use of ultrasonic and ultraviolet irradiation contemporaneously without the presence of any type of catalyst^{22,23}.

The purpose of this study was to determine the effects of US direct sonolysis and AOPs (using US and UV) on degradation of the selected pesticides diazinon and malathion. These effects were determined using a polychromatic UV source (medium pressure Hg vapour UV lamp) at pH values 3, 7 and 9, as well as with an ultrasonic source (130 kHz, 500 W) at 30, 45, 60, 90, 105 the influence of various parameters on sonolysis and sonophotolysis to remove diazinon and malathion from water. There was no background study on this procedure available from publications.

EXPERIMENTAL

The tested compounds in this study diazinon and malathion (from supelco), NaOH and HNO_3 were obtained from Merck co. (Germany).

Concentrations of malathion in the samples were 200, 400, 600 $\mu\text{g}/\text{L}$. Concentrations of diazinon in the samples were 100, 300, 500 $\mu\text{g}/\text{L}$ and used the 30 % insecticides. The samples were adjusted in a reactor at setting 5 and for the following times; 30, 45, 60, 90, 105 min. The pH of the solutions of the malathion and diazinon samples was 3, 7, 9 and reaction temperature in 25 ± 1 °C. The samples used in this study were synthetic, from deionized water.

Diazinon and malathion, were in solutions containing pesticide and double distilled water for the sonophotolysis

procedure. Then 850 mL of each prepared suspension was transferred to a 1000 mL Pyrex reactor. Irradiation was carried out with a 150 w medium pressure mercury lamp (Philips, Holland), which was above the batch photo reactor. The distance between the solution and the UV source remained constant at 3.75 cm in all experiments. In the surface of the solution the light intensity was $80 \text{ w}/\text{m}^2$ and was measured with a Hagner-Detector (EC1-UV-C, Swede), the pH of the reaction of HNO_3 or NaOH and then the pH values were measured with a pH meter (Sartorius, Germany). After that the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained with a magnetic stirrer (IKA, Werke, Germany) to keep the suspensions homogeneous and the suspension samples were tested after the appropriate illumination time. Ultrasonic irradiation of 850 mL diazinon or malathion solution operating at 130 kHz working frequency and 500 w power. Temperature 25 ± 1 °C by circulating water in a double jacket cooling array. Ultrasonic application in this study used the model (T1-H-5, Germany). The ultrasound application time was monitored with a stopwatch.

Analyses were performed by gas chromatography mass spectroscopy (GC-MS). For identification, 1 mL samples were injected into the GC-MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). The injector temperature was 270 °C and analysis was done using a capillary column (varian DB-5 column; 30 m 250 μm I.D., film thickness 0.25 μm). The method started at 150 °C, which was held for 2 min, then raised to 120 °C at a rate of 25 °C/min, followed by an increase to 270 °C (held for 2 min) the method used a split, split ratio 1:10 helium (99.999 %) as a carrier gas at 1 mL/min. Data were analyzed using *t*-test, ANOVA one-way test using SPSS software.

RESULTS AND DISCUSSION

Effect of irradiation time: The effect of time is an important parameter that determines degradation of sonolysis and sonophotolysis processes. In order to study the effect of time on the degradation of malathion and diazinon degradation, experiments were carried out at the various times of 30, 45, 60, 90, 105 min. A significant enhancement to the rate of degradation was observed when the time was increased (Table-1) (Figs. 1 and 2). For example when the UV/US time was 30 min, the percentage of malathion removed from the solution amounted to 53.17 ± 22.77 , whereas at 105 min, the mean percentage of removal was about 94.98 ± 3.66 . When the contact time was increased, the percentage removal of the pesticides increased. The reason for the observed enhancement in the rate at longer times may be due to an increased number of cavitation bubbles and hence the generation of more hydroxyl radicals and hydrogen peroxide^{24,25}.

Effect of pH values: The pH value influenced the processes of sonolysis and sonophotolysis on the pesticides. The sonophotolysis and sonolysis of malathion and diazinon were studied at three pH values. Results demonstrate the changes to percentage of removal of malathion and diazinon associated with various pH values are shown in Table-2 and Fig. 3. From Table-2 and Fig. 3, it can be seen in the UV/US process, the removal mean followed the order of pH: alkaline

TABLE-1
COMPARISON OF DECOMPOSITION MEAN PERCENTAGE PESTICIDES WITH US AND UV/US PROCESS AT DIFFERENT TIME

Time (min)	Malathion		Diazinon	
	US	UV/US	US	UV/US
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
30	31.01±22.69	53.17±22.72	35.52±29.52	32.54±17.81
45	39.12±19.14	68.49±20.12	39.12±22.67	57.19±13.83
60	46.15±17.14	77.70±16.77	42.87±29.94	70.29±10
90	51.09±16.44	86.07±15.04	53.57±21.19	80.75±7.21
105	56.6 ± 16.03	94.98 ± 3.66	57.96±21.99	86.21±5.41

p value < 0.001.

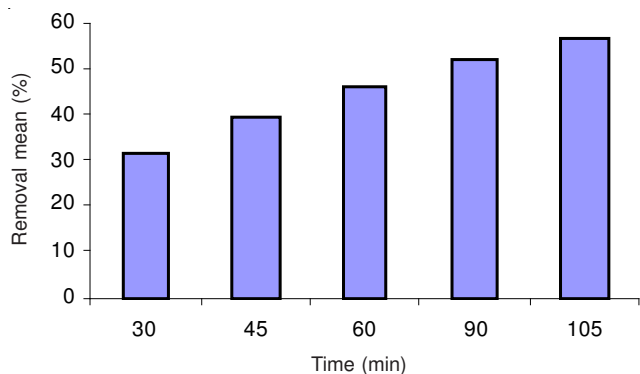


Fig. 1. Comparison of removal percentage for sonolysis of malathion at different time

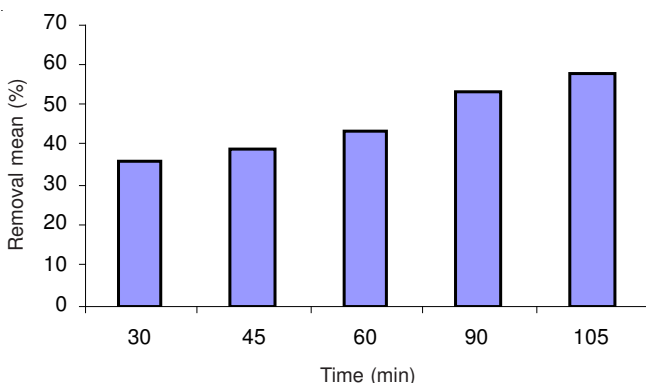


Fig. 2. Comparison of removal percentage for sonolysis of diazinon at different time

TABLE-2
COMPARISON OF DECOMPOSITION MEAN PERCENTAGE PESTICIDES WITH US AND UV/US PROCESS AT VARIOUS pH

Time (min)	Malathion		Diazinon	
	US	UV/US	US	UV/US
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
3	35.42±15.33	68.2±27.34	79.52±5.50	72.22±23.69
7	33.06±12.97	73.12±19.87	25.71±12.51	59.91±21.22
9	66.51±9.98	86.95±12.27	31.90±15.68	64.03±22.04

p < 0.001 = 0.047 < 0.001 = 0.317

p-Value < 0.001.

> neutral > acidic and acidic > alkaline > neutral for malathion and diazinon, respectively.

It was observed that both pesticides were significantly influenced by the pH value of the solution and that the highest removal efficiency was achieved at pH 9 for malathion and pH 3 for diazinon. The results indicated that the degree of

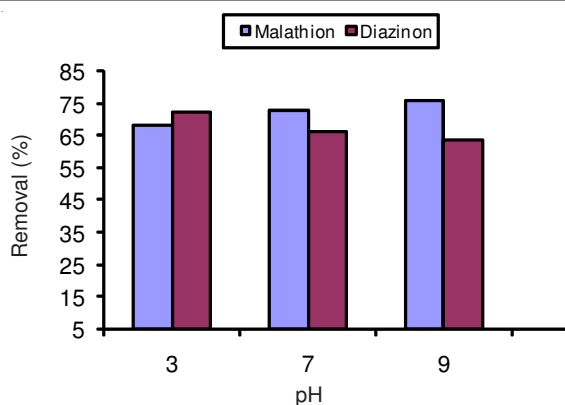


Fig. 3. Comparison of removal percentage for sonophotolysis of pesticides at different pH

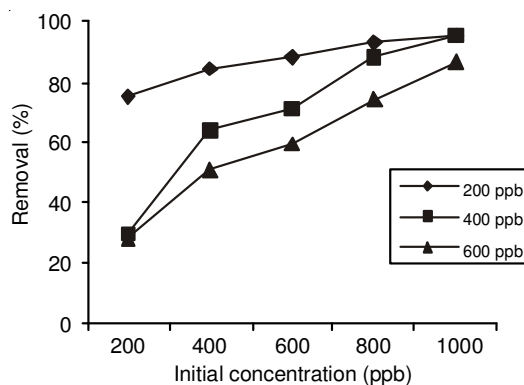


Fig. 4. Comparison of degradation rate for sonophotolysis of malathion at different concentration (pH = 7)

effectiveness of the sonolysis and sonophotolysis procedures increased with increasing pH for malathion but for diazinon the effect of increasing the pH level decreased the effectiveness of the sonolysis and sonophotolysis procedures. The reason for the first phenomenon was that OH⁻ ions with an elevated concentration would increasingly scavenge ultrasonic generated holes that concurrently yielded highly oxidative •OH species²⁶.

The reason for the second phenomena was that the breakdown rate of diazinon in acidic water is quicker than in other solutions²⁷, also fraction in the molecular state of diazinon was larger when the pH was smaller. The diazinon ions cannot vapourize in to cavitation bubbles, they can react only outside the bubble film with •OH radicals cleaved from the solution. However, in the molecular state diazinon vapourize into cavitation bubbles and react both inside by thermal cleavage and outside with OH radicals as an oxidation reaction. Hence the smaller pH (pH < pK_a) was effective for degradation²⁸.

Effect of initial concentration and pesticide type: The effect of the initial pesticide concentration on the processes of sonolysis and sonophotolysis are presented in Tables 3-4 and Figs. 5-6. The sonophotodegradation efficiency of malathion decreases from 85.93 to 69.6 % when the initial concentration increases from 200 to 600 µg/L and for diazinon decreases from 59.55 to 72.6 % when the initial concentration increases from 100 to 500 µg/L. In general, the percentage decomposition decreased as the initial concentration of contaminant increased under ultrasonic treatment²⁹. Assuming that the production of hydroxyl radical concentration is constant,

TABLE-3
COMPARISON OF DECOMPOSITION MEAN
PERCENTAGE MALATHION WITH US AND UV/US
PROCESS AT DIFFERENT CONCENTRATION

Concentration (ppb)	US	UV/US
	Mean \pm SD	Mean \pm SD
200	53.33 \pm 19.29	85.93 \pm 12.15
400	43.25 \pm 22.31	72.64 \pm 18.61
600	38.41 \pm 15.97	69.60 \pm 29
<i>p</i> -Value	0.111	0.093

TABLE-4
COMPARISON OF DECOMPOSITION MEAN
PERCENTAGE DIAZINON WITH US AND UV/US
PROCESS AT DIFFERENT CONCENTRATION

Concentration (ppb)	US	UV/US
	Mean \pm SD	Mean \pm SD
100	48.61 \pm 26.04	72.6 \pm 21.73
300	45.11 \pm 21.39	64.07 \pm 19.98
500	40.42 \pm 33.9	59.55 \pm 22.73
<i>p</i> -Value	0.65	0.274

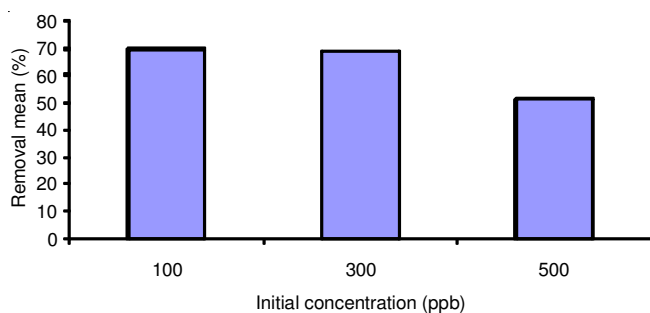


Fig. 5. Comparison of removal percentage for sonophotolysis of diazinon at different concentration

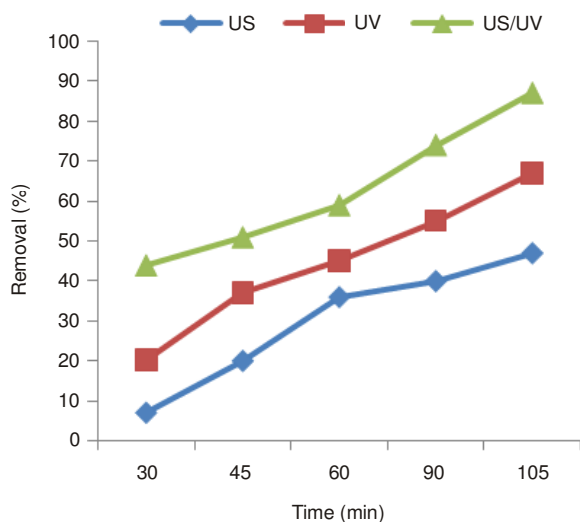


Fig. 6. Comparison of removal percentage for different processes of malathion (400 μ g/L, pH = 7)

radical recombination reactions would dominate at low concentrations of pesticide to increase degradation, similar results have been reported in other research.³⁰⁻³². Both of the pesticides were about equal, hence, photolysis was effective for the removal of pesticides from water. Results for the effect of type of pesticide in the processes of sonolysis and sonophotolysis are illustrated in Table-5. The mean rank of k

for the US/UV system was higher than US system. The sonophotodegradation rate of malathion was more than that of diazinon.

TABLE-5
COMPARISON OF DECOMPOSITION MEAN PERCENTAGE
AND MEAN RANK (k) PESTICIDES WITH US AND UV/US
PROCESS AT VARIOUS PESTICIDE

Pesticide	US	UV/US	US	UV/US
	Mean \pm SD	Mean \pm SD	Mean rank (k/1000)	Mean rank (k)
Malathion	45 \pm 19.94	76.09 \pm 21.81	11.67	12
Diazinon	45.71 \pm 26.99	65.38 \pm 22.4	7.33	7
<i>p</i> value	0.88	0.024	0.09	0.047

Effect of synergetic: The synergetic effect on the process of sonophotolysis was studied and the results are presented in Figs. 6-8. From Figs. 6-8 it can be seen the removal mean of processes US, UV and UV/US were 45, 67.8, 76.09, 45.71, 58.8 and 65.38 % for malathion and diazinon, respectively.

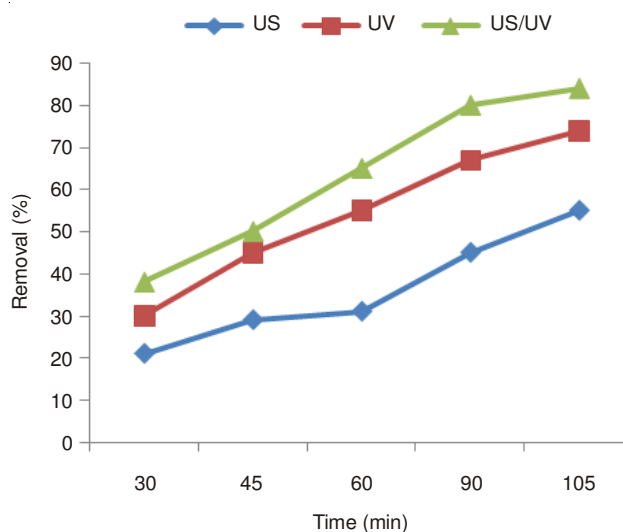


Fig. 7. Comparison of removal percentage for different processes of diazinon (100 μ g/L, pH = 9)

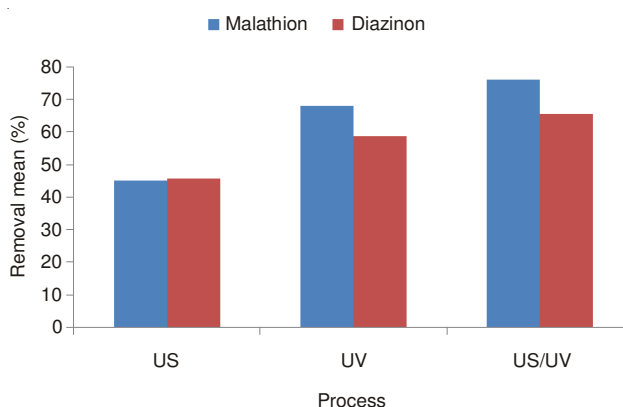


Fig. 8. Comparison of removal mean of pesticides at different processes

The malathion broke down at a faster rate with increases of pH, temperature and light irradiation³³. The rate of photodegradation of malathion was higher than that of diazinon³⁴. The degree of decomposition from the process of sonophotolysis

was more than that of sonolysis. The reason for the observed enhancement in the rate may be due to increased generation of highly reactive free radicals such hydroxyl ($\cdot\text{OH}$), hydrogen (H^\bullet) and hydroperoxy (HO_2^\bullet). These reactive radicals are the main species that degrade pesticides²². Various researches reported that the process of sonophotolysis was more effective than that of sonolysis for the removal of organic pollutants from aqueous solutions for example: the decolorization efficiency of US/UV was higher than US¹⁸ or the degradation of dimethoate by the synergetic process of sonophotolysis³⁵. Thus it is evident that the degradation of pesticides under (UV/US) irradiation is more than the sum of degradation under individual UV and US irradiation, thereby showing a synergistic effect.

Conclusion

Finally the use of sonolysis and sonophotolysis techniques for the degradation of the pesticides malathion and diazinon. The role of various operating parameters on the sonophotodegradation of various pesticides such as initial concentration, initial pH, time, pesticide types and effect of synergetic can significantly influence the sonophotodegradation rate of pesticides. The obtained results indicate that the degradation effect from sonophotolysis was higher than that of the individual process of sonolysis. The sonophotodegradation efficiency decreased with an increase in the initial concentration of pesticides. The process of sonolysis combined with other techniques can be used as a way to improve the degradation of organic pollutants (pesticides) or their intermediates. The sonophotodegradation rate of the malathion pesticide was more than that of diazinon, but the rate of sonolysis on both pesticides was about equal, hence photolysis was effective for the removal pesticides from water. The highest removal efficiency was achieved at alkaline for malathion and acidic for diazinon.

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