

## Original Article

# Using Ultraviolet Irradiation for Removal of Malathion Pesticide in Water

M Shayeghi<sup>1</sup>, \*MH Dehghani<sup>2</sup>, M Alimohammadi<sup>2</sup>, K Goodini<sup>3</sup>

<sup>1</sup>Department of Medical Entomology and Vector Control, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

<sup>2</sup>Department of Environmental Health Engineering, School of Public Health, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran

<sup>3</sup>Department of Environmental Health, Ilam University of Medical Sciences, Ilam, Iran

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## Abstract

**Background:** Organophosphorus pesticides are one of the most consumable poisons. Such poisons can enter water sources by different routes. Since consuming some drinking water containing an amount of poison higher than the standard level, causes undesirable effects on human health. This research aimed to study the effectiveness of eliminating malathion from water by ultraviolet irradiation (UV) mercury lamp with a medium pressure.

**Methods:** In this experimental- applied study, variants of initial pHs and initial concentrations and exposure times were investigated. Initial concentrations of malathion were 0.5, 1 and 2 mg/l. The samples were then exposed to UV irradiation interruptedly the time periods of 10, 20, 30, 40, 50 and 60 minutes. The UV lamp used in the reactor was medium pressure (irradiation intensity= 200 W/m<sup>2</sup>). The amounts of malathion were determined before and after the irradiation by HPLC instrument. Moreover, the results obtained from the study were analyzed using SPSS software and ANOVA and *t*-test statistical trials.

**Results:** The minimum reduction occurs at 10 min (46%) and the maximum reduction in 60 min (87.25%) ( $P < 0.05$ ). In addition, the effectiveness of irradiation process decreases with increasing the poison concentration ( $P < 0.001$ ). However, the efficiency of the process increases with pH increase.

**Conclusion:** The results show the most effectiveness were achieved at 60 min and 0.5 mg/l and pH= 9. Therefore, the application of UV reactors could be considered as an appropriate method.

**Keywords:** Pesticide, Malathion, Water, Ultraviolet Irradiation

## Introduction

Organophosphate compositions are the largest and various groups of available pesticides and form about 40% of recorded pesticides in the world. The used pest down poisons enter to water sources by direct washing and irrigation from used places. In addition, rain fall on sprayed poison areas before break down these materials cause to enter them to sources of surface water (Agarawal 1991, Borner 1994). Furthermore pesticides can find a way to ground water table by way of soil layers and during water infiltration. Some pesticides can enter to air and conse-

quently enter to sources of surface water and soil while rain fall. Entrance these pollutants materials in sources of supply drinking water can have adverse effects on human health and environment (Videria et al. 2001, Safi 2002). In addition to remains of these poisons are dangerous for health people, also can have effect on economic of region people that subsist by aquatics selling. Malathion acts as one clean hereditary inhibitor operator in human that cause to find complications and problems in nervous system and create conditions like dizziness, nausea and

attention disorder (Videria et al. 2001, Fireston et al. 2005). This poison has very destructive effects on children nervous system especially in first years. So we must use sure and congruous ways for prevention of entrance these poisons to sources of water and air and soil (Alavanja et al. 2004, Rauh et al. 2006).

Recently, some investigations are done concerning being and remain of these poisons in environment in Iran. These studies shows that after usage of poison in short times, their amount have been more than allowable extent (Shayeghi et al. 2001, 2004, 2007, 2010, Tarahi 2002, Honarpajoh et al. 2003, Hejazinejad et al. 2004, Khodadadi 2008, Shayeghi and Dehghani 2011). For example investigations performed by Shayeghi et al. (2007) about malathion remains in drinking water showed that remains of these poisons exist for some months in environment. Shayeghi et al. (2004) appraised remains of malathion organophosphate poisons in rivers water like Shahpoormand and Dalkie in Booshehr, and concluded that amount of this poison has been more than allowable extent in each three rivers in Booshehr, Iran. In addition Shayeghi et al. (2001) investigated remains of these pesticides in Mazandaran River.

There are the various technologies for removal of organophosphate pesticides. Recently the modern ways have been used for removal or decrease of pesticides poisons like using of ultrasonic waves ultraviolet radiation and advanced oxidation technology (Samanidou and Fytianos 1988, Huston and Pignatello 1999, Hequet et al. 2001, Burrows et al. 2002, Walid et al. 2002, Badawy et al. 2006, Maldonado et al. 2006, BavconKralj et al. 2007, Li-An et al. 2011, Shayeghi and Dehghani 2011). But ultraviolet radiation is one of the functional and safe technologies that can be profitable in treatment of surface and ground water sources polluted by pesticides with its resultant advantages. Certainly one of protection reasons and welcome this

technology is necessity that has existed for purpose of compulsion in laws observance and new rules of water treatment. The advantages of this system as compared with other ways of water treatment are as follows (Samanidou and Fytianos 1988, Hequet et al. 2001, Burrows et al. 2002, BavconKralj et al. 2007, Vaezi and Bazrafshan 2008):

1. It does not need to add chemical materials,
2. It does not need to absorbent media,
3. The reactor profits by good pliable,
4. The property of produced sewage is limpid and odorless and ideal,
5. The most of pesticides are degraded in the reactor considerably,
6. The less connection with pH changes and water temperature in compared with other chemical materials,
7. To have safety and acceptability from the viewpoint of refineries workers and the general public and be propounded as a green technology.

A variety of researches have been done on removal of pesticides by ultraviolet radiation, like Hequet et al. (2001) on effect of medium pressure lamp on atrazine. The results were indicative of perfect influence this way in atrazine pesticide degradation. Bavconkralj et al. (2007) got products of gotten mineral perfectly by photo-oxidation process by ultraviolet irradiation and visible light. Samanidou and Fytianos (1988) did research for assessments of photo-oxidation process effect on the carbamate. This research performed by medium pressure mercurial lamp. The results were indicative of perfect influence ultraviolet irradiation in degradation of this material. Huston et al. (1999) used process of ultraviolet radiation and photo-Fenton for degradation of some commercial pesticides in natural waters.

The aims of this study were survey on effectiveness of ultraviolet irradiation for degradation of malathion pesticide from water and the effect of irradiation time, initial concentration and pH changes influence on potential of ultraviolet radiation effectiveness in degradation of malathion in water.

## Materials and Methods

This research is the experimental-applicable study that performed in chemical laboratories of environment health engineering and Entomology of the Tehran University Medical Sciences in 2009–2010. Malathion poison was prepared in the different concentrations and analyzed. In this study, malathion poison has prepared and analyzed.

The confrontation times to ultraviolet wave were selected on the basis of done pre examinations in lab and also the discussed concentrations in this research considering to done studies about the existing remains of malathion poison in country surface water (Shayeghi et al. 2001, 2004, 2007, 2010, 2011, Tarahi 2002, Honarpajoh et al. 2003, Hejazinejad et al. 2004, Khodadadi 2008).

### The method of samples preparation

The extraction stages and samples preparation done for analyzing were:

First, 500 ml of noted water sample was added to separator funnel that has 1 L size. In some cases, the sample was passed from the Atman filter (0.45  $\mu$  m) because it had turbidity of suspended particles; Then, 30 ml dichloromethane was added to noted sample. For better separating two phases 15–20 gr NaCl was added to contents of separator funnel; next, funnel contents intensively was mixed and leaved its valve in continual times for decreasing of the funnel inside pressure. In order to separating organic phase from watery phase while passing from column that consist the sodium sulphate for deletion of water molecule from organic phase.

In this stage, 30 ml dichloromethane was again added to that and mixed to separate organic phase from watery phase. In order to evaporation of extracted liquid by the Rotary set, the evaporation of under vacuum, thus the bulk of extracted liquid is reduced 2–3 ml. At the end of the processes 1 ml organic solvent chloroform was used for extracting.

### The concentration reading

Considering to the suggested way of Standard Method Book for measuring of malathion poison because the considering to the conditions of HPLC set following stages was done:

-The standard solution was prepared from noted poison by HPLC grade material and with high pureness percent in the different concentrations and then it was injected to HPLC set.

2.1  $\mu$  L was extracted and injected to HPLC set. The thermal program of this set was as follows:

- First temperature equal 110°C for 1 min.
- To reach to temperature of 188°C with additive velocity 25°C/min for 4 min.
- To reach to temperature of 190°C with additive velocity 20°C/min for 1 min.
- To reach to temperature of 244°C with additive velocity 25°C/min for 6.21 min.
- Keeping noted temperature for samples concentration reading.
- Using of helium gas with > 99% pureness percent and velocity of flowing 0.7 cm/s.

### The specifications of HPLC

High Performance Liquid Chromatography device (HPLC), equipped with visible-ultraviolet disclosure and auto sampler. The used column for separating of these compounds is C<sub>18</sub> made in Water Company in USA, with 25 mm length and 4.6 mm diameter in 30°C temperatures. The moving phase flowing velocity and the used moving phase were considered in order 1 mL/min and methanol, acetonitrilic and water with ratio (15:45:40). The used wave length was ascertained 140 nm for disclosure of these compounds. The used separating column of HPLC set was capillary column DB5.6.25 kind. By the performance of correct thermal program and the set preparing was observed the pertaining vertex to malathion in 10.23 minutes. The used set exactness in research was estimated as nearly 1  $\mu$ g/L.

### The specifications of ultraviolet reactor

The used reactor in this study contains one closed bottom cylinder with 3 liters size and kind of the rustproof steel made in Tehran Steel of Iran Company. In this cylinder one magnetic mixer has been used in order to complete mixing of the sample for radiation in the reactor. In this pilot, on account of too much heat making that is the result of lamp radiation was used the chiller for temperature reducing. For this purpose, one bocal of 4 L was used that cylinder fits its inside. The empty space of cylinder and bocal was filled by ice for temperature reducing.

All the analyses were performed according to the procedures outlined in standard methods (APHA 2005).

### Calculation of degradation percentage

The definition of malathion degradation percentage (DP) was as follows:

$$DP = (C_1 - C_2) / C_1 \times 100$$

Where DP (%) is the degradation percentage of the ultraviolet reactor,

$C_1$  is the initial concentration of malathion (mg/l).

$C_2$  is the concentration of malathion (mg/l) after reaction for (t) time.

### Statistical method

The results were analyzed by SPSS software, 11.5 version and 2003 excel. The data were analyzed using ANOVA and *t*-test. The variables were irradiation time, initial concentration and pH degradation was variable depended.

### Results

The malathion poison was affected by ultraviolet mercurial lamp with medium pres

sure in 0.5, 1, 2 mg/L and 10, 20, 30, 40, 50, 60 min and pH= 6, 7, 9.

### Effect of pH value

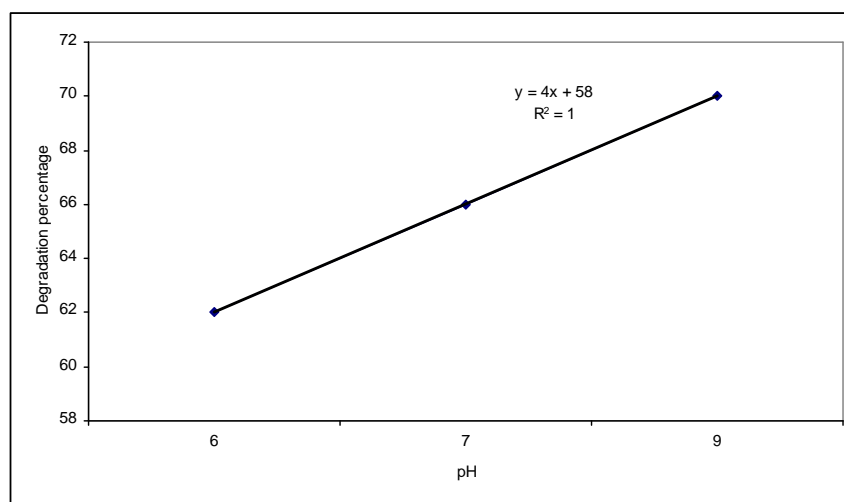
The investigation results of pH changes on the utility of malathion concentration shows that the utility of concentration increases by pH augmentation, so that malathion in 0.5, 1, 2 concentrations and pH= 6 have the concentration utility 62%, 57%, 54.5 % but the measure of utility reaches to 70%, 65%, 63.5 % in pH = 9 (Fig. 1, 2 and 3). The analysis test of ANOVA showed in this case is the meaningful statistical difference too.

### Effect of irradiation time

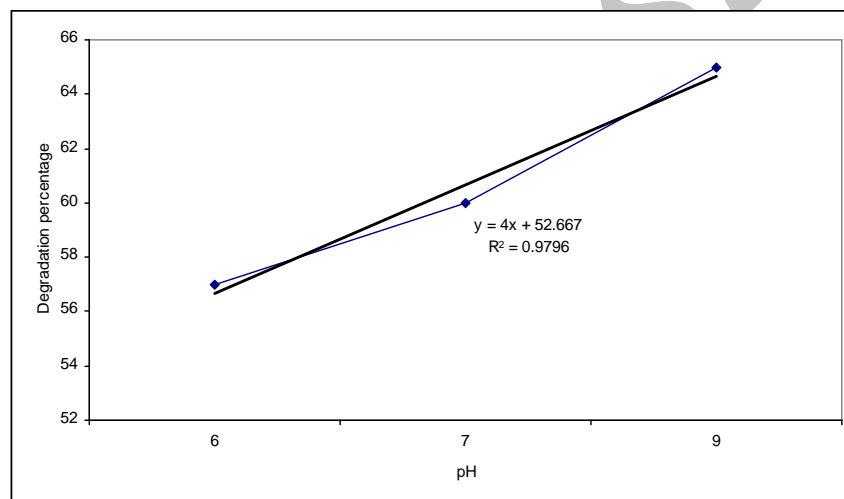
The results showed that measure of malathion poison reduction augmentation by increasing of irradiation time. The regression statistical test shows that the concentration of extant poison decreases in pilot by increasing time. The analysis test of ANOVA showed the significant differences among times.

### Effect of initial concentration

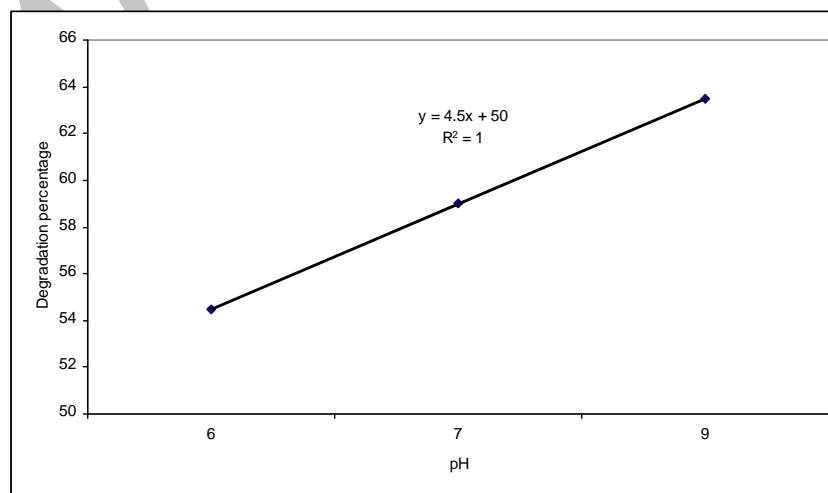
The concentration changes are influential on the utility of ultraviolet. The measure of malathion degradation has the most utility in 0.5 mg/L in 60 min period and the alkali pH among the other concentrations. In other words, by increasing of poison concentration drops the degradation. The figures 4, 5 and 6 show the degradation percentage vs. time period for different concentrations of malathion. According to ANOVA test, the effect of concentration changes on efficiency is significance.



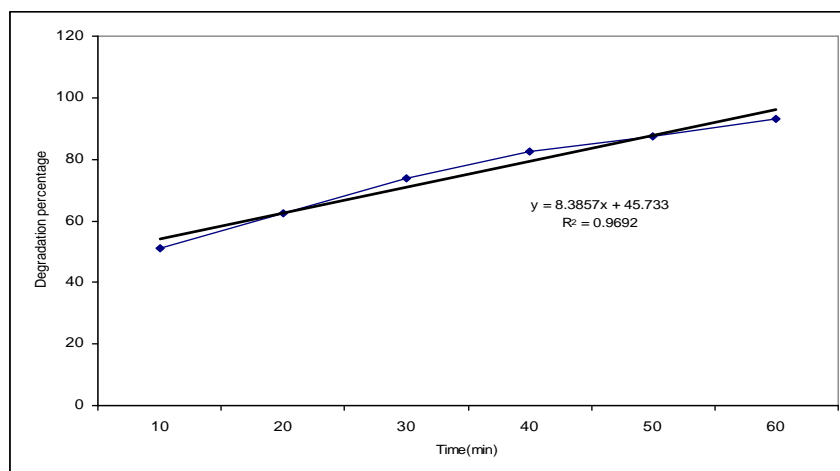
**Fig. 1.** Degradation percentage vs. pH for 0.5 mg/l



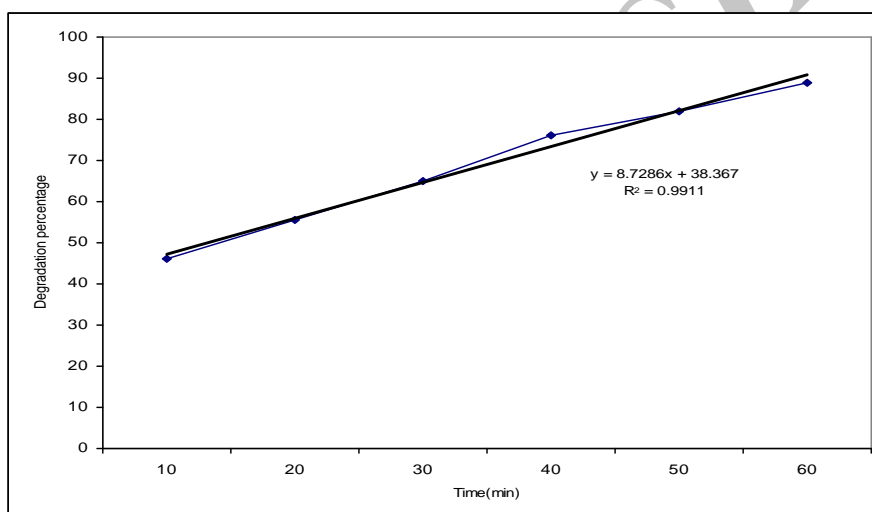
**Fig. 2.** Degradation percentage vs. pH for 1 mg/l



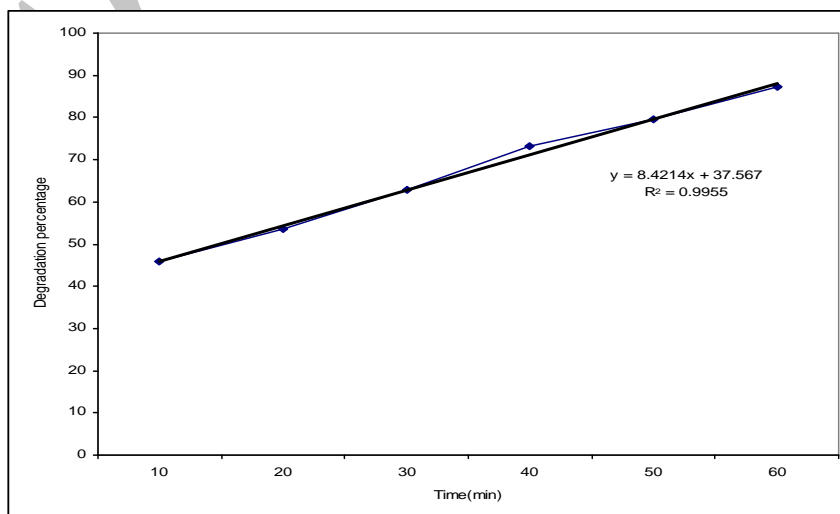
**Fig. 3.** Degradation percentage vs. pH for 2 mg/l



**Fig. 4.** Degradation percentage vs. time period for 0.5 mg/l



**Fig. 5.** Degradation percentage vs. time period for 1 mg/l



**Fig. 6.** Degradation percentage vs. time period for 2 mg/l

## Discussion

This study showed that the effectiveness of malathion degradation from water by ultraviolet irradiation depends on three parameters; the initial concentration, the irradiation time and the pH. This study showed that initial concentration decreases with irradiation time. These researches results conform to Khodadadi (2008), Walid et al. (2006) and Maladonado et al. (2006) too. In other words, when the irradiation time increases, lots of free radicals has formed in the liquid and this event cause to the much decomposition of malathion poison.

Khodadadi (2008) investigated pH changes in 6, 7, 9 limits on the concentration in time period of 1 hour and founded that the concentration increased by pH augmentation. The founded results of Walid's studies (2006) and also Freed et al. (1979) confirm to the results of this research. Besides the studies of Burrows (2002) and Badawy et al. (2006) showed that the velocity of poison decomposition increased by pH augmentation. His research results conform to this study. According to these researches, the principal reason of this event is the augmentation of  $\text{OH}^-$  ions producing and the hydroxyl free radicals in the alkali environment.

Finally, using chemical oxidation ways are not too much safe because they can impose too much energy and costs in the process of water treatment. Because of this, is given preference that will use the integrative ways of water refining for reducing of costs and using energy in order to will founded the ideal reduction efficiency in the short time and by using low energy.

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27-02-90. The authors declare that there is no conflict of interests.

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