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SONODEGRADATION OF ORGANOPHOSPHORUS PESTICIDES IN WATER

Organophosphorus pesticides (OPP$_s$), such as diazinon and malathion, are widely found in water resources. When absorbed by human organisms, OPP$_s$ are very toxic mainly because they deactivate acetyl cholinesterase. In the present study, the degradation of diazinon and malathion was investigated. The experiments were conducted for diazinon concentrations of 100, 300, 500 µg/dm^3 and malathion concentrations of 200, 400, 600 µg/ dm^3. Sonochemical examination was done using an ultrasonic reactor at 130 kHz and 500 W for five times, and then the amount of the pesticide in a sample was measured by the gas chromatography with a flame ionization detector (GC-FID).The highest degradation of malathion and diazinon by the sonolysis process occurred at pH 9 and 3, respectively. The study demonstrates that malathion and diazinon could be effectively degraded by ultrasonic irradiation.

1. INTRODUCTION

Organophosphorus pesticides (OPP$_s$) are of great significance in pest control actions and have been increasingly used instead of organochlorine pesticides. Application of pesticides has recently become an essential part of the modern agriculture. Their fate in the environment is of great concern, since most of them as well as their degradation products have been found both in surface and ground waters [1, 2].

Diazinon and malathion are organophosphorus insecticides used to control pests in soil, on fruit, and on vegetable field crops. Diazinon (O, O-diethylo-[2-isopropyl -6-methylpyrimidin-4-yl] thiophosphate), and malathion [diethyl(dimethoxythio-phosphorylthio) succinate] are classified by the World Health Organization (WHO) as moderately hazardous (Class II) [1]. Toxic effects of diazinon and malathion are at-

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tributed to the inhibition of the acetylcholinesterase enzyme. Adverse effects have been reported regarding mortality and illness to fish and wild life [2].

Removal of pesticides from drinking, surface, and ground water is an extremely complex problem due to a wide range of pesticides with various chemical structures and properties. Several techniques have so far been used to eliminate pesticides [3–5], including adsorption by activated coke [6–8] and ultraviolet irradiation combined with hydrogen peroxide [8–14]. Recently, studies have been conducted on sonochemical treatment of water and wastewater [14–16]. Ultrasound has been used for many applications, including cell disruption, nanotechnology, water and wastewater treatment, chemical reactions, food preservation, and so forth. Ultrasound has been extensively used as an advanced oxidation process for water and wastewater treatment. This is owing to the production of hydroxyl radicals in aqueous solutions and subsequent oxidation of pollutants in the presence of ultrasound [16].
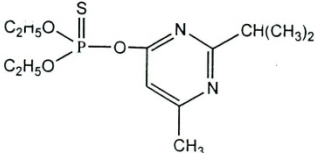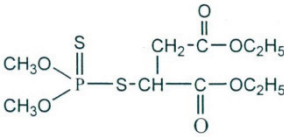
The present research deals with the sonodegradation of the selected pesticides, i.e. diazinon and malathion using a ultrasound reactor. The main objective was to determine the efficiency of a batch reactor for degradation of diazinon and malathion in various operational conditions, including sonication time, initial concentration, and pH.

2. EXPERIMENTAL

The tested samples in this study were diazinon and malathion purchased from the Supellco Company. The chemical structure and other characteristics are listed in Table 1. NaOH, HNO_3, and methanol were obtained from Merck CO., Germany.

Table 1

Physical and chemical properties of organo-phosphorus model substances used in this study [23]

Parameter	Diazinon	Malathion
Chemical formula	$C_{12}H_{21}N_2O_3PS$	$C_{10}H_{19}O_6PS_2$
Molecular weight(g/mol)	304.3	330.36
Density, g/cm^3 (at 20 °C)	1.117	1.23
Chemical structure		

The ultrasonic instrument used in this study (Fig. 1) was a T_1-H-5 model, Germany, with the following characteristics: the capacity of 3.7 cm^3, dimensions 30×25×32 cm high, a batch flow type; altered number 2, ultrasonic irradiation of 200 cm^3 of diazinon or malathion solution, operating at the frequency of 130 kHz with

500 W power, the operational temperature of 25±1 °C by circulating water in a double jacket cooling array. The sonication time was monitored with a stop watch. In the present study, we used synthetic samples of diazinon and malathion in deionized water. The concentrations of diazinon in the samples were 100, 300, and 500 µg/dm^3 and that of malathion were 200, 400, and 600 µg/dm^3. The samples were adjusted in the reactor in 5 time intervals (30, 45, 60, 90, and 105 min). pH of the samples was 3, 7, 9.

Fig. 1. Laboratory ultrasonic reactor

Analyses were performed by the gas chromatography method with a flame ionization detector (GC-FID). A Varian CP-3800 (Australia) was used to determine the malathion and diazinon concentrations in the samples. The GC was fitted with a DB-5 capillary columns (30 m, 0.25 mm, I.d. 0.25 mm film thickness). The injector temperature was 250 °C, the initial oven temperature was 50 °C (held for 2 min) and increased to 100 °C at the rate of 25°C/min (held for 2 min as well). The inlet was operated in the splitless mode. Helium (99.999%) was used as the carrier gas at the flow rate of 1 cm^3/min. Dispersive liquid–liquid microextraction (DLLME) technique was used to extract diazinon and malathion. 5 cm^3 of the sample (water + analyte) was mixed with 500 cm^3 of the extraction solution (2 cm^3 internal standard: chlorpyrifos 1000 mg/dm^3, 10 cm^3 of chloroform, 100 cm^3 of acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the supernatant of the aqueous phase was collected with a pipette; the droplets deposited at the bottom of the conical test tube, and 1 µcm^3 of it was injected into GC. Acetone and chloroform were used as the disperser solvent and the extraction solvent, respectively. The results revealed a recovery rate in the range of 85–100% [17]. The definition of pesticide removal percentage (*RP*) was as follows:

$$RP = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 is the initial concentration of the pesticide (µg/dm^3), and C is the remaining concentration of the pesticide (µg/dm^3) after reaction for (*t*) time. Data were analyzed using T-test, one-way ANOVA, Post-Hoc test, Scheffe, Mann–Whitney, and Kruskal

–Wallis tests using SPSS software. The variables were pH, degradation time, and concentration, while the degradation percentage was the dependent variable.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF SONICATION TIME

The effect of time on the degradation of the pesticides is illustrated in Table 2, and Figs 2 and 3. As can be seen, the lowest degradation percentage was observed for the sonication time of 30 min (an average of 33.27±25.64%), while the highest degradation percentage occurred at the sonication time of 105 min (an average of 57.03±18.25%), suggesting that the degradation of the pesticides increased significantly over time ($P < 0.05$). Studies indicated that there is significant difference between sonication time and degradation percentage [18–19].

Table 2

Average removal percentage of pesticides at various sonication times

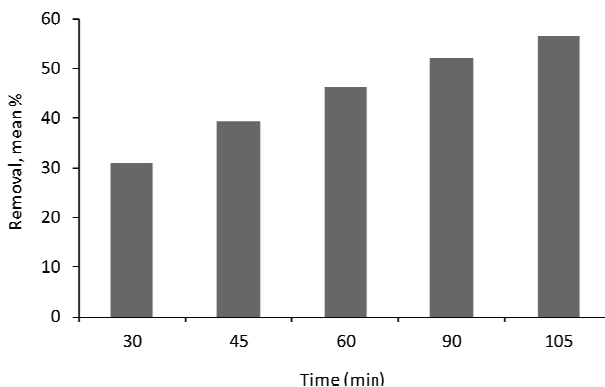| Time [min]	Average±SD [%]	95%confidence interval for the average value	
		Lower bound	Upper bound
30	33.27±25.64	20.51	46.02
45	39.12±24.22	27.08	51.17
60	44.51±23.72	32.72	56.31
90	52.83±19.39	43.19	62.48
105	57.03±18.23	47.96	66.1

P-value < 0.05.

Fig. 2. Dependence of the average removal percentage
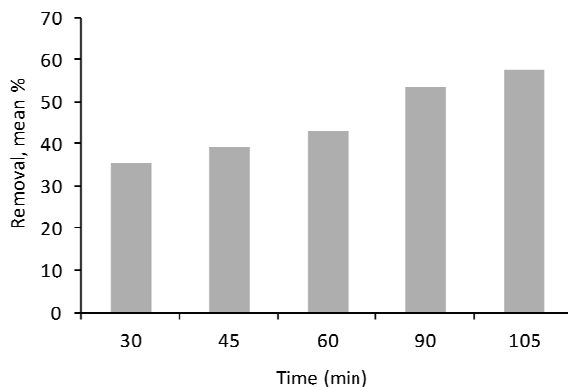of malathion on the irradiation time

Fig. 3. Dependence of the average removal percentage
of diazinon on the irradiation time

3.2. EFFECT OF pH

For diazinon, the highest degradation efficiency was observed at pH 3 (an average of 79.52±5.5%), while the highest degradation efficiency occurred at pH 7 (an average of 25.71±12.51%), and the difference was statistically significant ($p < 0.001$). For malathion, however, the highest degradation efficiency was observed at pH 9 (an average of 66.51±9.98%), while the highest degradation efficiency occurred at pH 7 (an average of 35.42±15.33%); this difference was also statistically significant ($p < 0.001$) (Table 3 and Fig. 4).

T a b l e 3

Average removal percentage of pesticides at various pH

Pesticide	pH	Average±SD%	95% confidence interval for the average value	
			Lower bound	Upper bound
Malathion	3	35.42±15.33	26.93	43.31
	7	33.06±12.97	25.88	40.24
	9	66.51±9.98	60.98	72.04
Diazinon	3	79.52±5.5	76.47	82.56
	7	25.71±12.51	18.78	32.64
	9	31.9±15.68	23.22	40.59

P-value < 0.05.

Statistical analysis showed that both pesticides were significantly influenced by the pH of the solution, and the highest degradation efficiency was achieved at pH 9 for malathion and at pH 3 for diazinon. In acidic solutions, the protonated form of diazinon dominates ($pk_a = 2.4$), while its deprotonated form dominates in neutral and alka-

line solutions. Self decomposition and sonolysis into hydroxyl radicals at pH 9 might explain the observed inhibition in the degradation of diazinon at the alkaline solution, as compared to pH 3. This is mainly the reason why the degradation percentage of diazinon increases with decreasing pH [20]. On the contrary, the highest degradation efficiency of both pesticides was achieved at pH 7 under the ultrasonic irradiation [21].
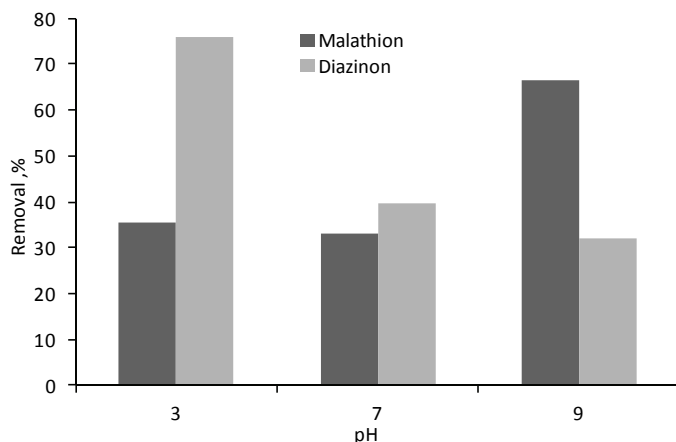

Fig. 4. Average removal percentage of pesticides at various pH

Under these conditions, the influence of pH of the solution on the degradation of both pesticides was not consistent with their basic characteristics. This has probably resulted from the occurrence of complex degradation pathway under the ultrasonic irradiation. The presumed reason is generation of hydroxyl radicals in the solution. Similar results have also been observed in the sonochemical degradation of methyl parathion, indicating that the degradation rates increased significantly upon increasing initial pH [18, 22].

3.3. EFFECT OF INITIAL CONCENTRATION

For diazinon, the highest removal percentage was observed at the concentration of 100 μg/dm^3 (an average of 48.61±26.04%), while the lowest removal percentage occurred at the concentration of 500 μg/dm^3 (an average of 38.11±21.39%), suggesting a decrease in the removal percentage with an increase in the initial diazinon concentration; however, this difference was not significant ($P > 0.05$). For malathion, the highest removal percentage was observed at a concentration of 200 μg/dm^3 (an average of 53.33±19.29%), while the lowest removal percentage occurred at the concentration of 600 μg/dm^3 (an average of 38.41±15.97%), suggesting a decrease in the removal percentage with an increase in the initial malathion concentration; however, this difference was not significant ($P > 0.05$) either (Table 4 and Figs. 5 and 6).

Average removal percentage of pesticides at various initial concentrations

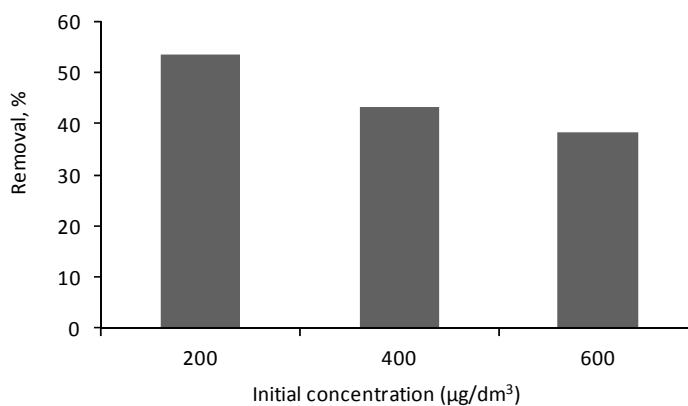| Pesticide	Initial concentration [μg/dcm^3]	Average±SD%	95% confidence interval for the average value	
			Lower bound	Upper bound
Malathion	200	53.33±19.29	42.65	64.02
	400	40.25±22.31	30.89	55.81
	600	38.41±15.97	29.01	50.99
Diazinon	100	48.61±26.04	34.18	63.03
	300	40.42±33.9	28.98	58.86
	500	38.11±21.39	32.26	59.96

$P < 0.05$.

Fig. 5. Effect of initial concentration of malathion
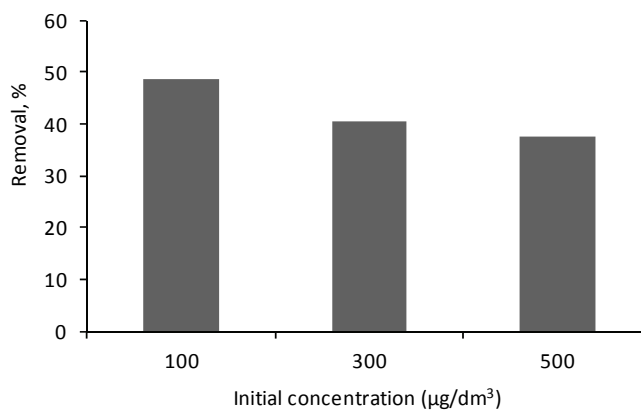on the average removal percentage

Fig. 6. Effect of initial concentration of diazinon
on the average removal percentage

The study showed that there was no significant relationship between initial pesticides concentrations and their degradation percentages. Similar result have also been observed in the sonochemical degradation of diazinon [23]. Experiments indicated that the degradation percentage of pesticides varies according to the initial concentration after being exposed to irradiation, which is basically the steady state phase [19, 21, 22]. A number of studies reported that the initial pesticide concentration decreases with sonication time up to a certain point, when the steady state phase is achieved [23]. In general, the degradation percentage decreases as the initial concentration of the contaminant increases under ultrasonic treatment [24]. This could be attributed to the role of hydroxyl radicals induced by ultrasound, implying that hydroxyl radicals could take part in the degradation of contaminants, although a considerable part of these hydroxyl radicals would recombine to yield H_2O_2 [25]. Assuming that the production rate of hydroxyl radicals is constant, radical recombination reactions would dominate at low diazinon concentrations. Upon increasing concentrations of diazinon and malathion, an increasing proportion of hydroxyl radicals attack the pesticide molecules, thus leading to an increase in the degradation. Finally, sonodegradation of pesticides was successfully achieved at various concentrations, sonication times, and pH. It has been shown that ultrasonic reactor can be used to reduce the pesticides concentrations at 130 kHz and 500 W.

The decomposition process of malathion and diazinon can be described using the effectiveness of ultrasonic irradiation by the formation of hydroxyl radicals. Hydroxyl radicals, which are produced in the hot vapour phase, may either react there or diffuse into and react within the surrounding liquid phase. The hydroxyl radicals react with malathion and diazinon by addition of hydrogen abstraction to double bonds.

4. CONCLUSIONS

In conclusion, the ultrasound technique was successfully used to degrade two organophosphorus pesticides, i.e. diazinon and malathion, from aqueous solutions. It should be kept in mind that complete mineralization by ultrasonic irradiation was a slow process and the complete degradation may require combination with other advanced oxidation processes (AOP$_s$) to thoroughly dissipate the pesticides. Further studies are needed to investigate the effect of ultrasonic treatment on the quality of pesticides, in order to provide the complete information for the application of ultrasonic technique.

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