Removal of Malathion from Various Waters by Advanced Oxidation Processes

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Summary: The degradation of malathion was investigated under various conditions, including ultrasound (US) irradiation, ultraviolet (UV) irradiation, and the combination of US/UV, UV/ZnO, UV/H_2O_2, and $US/UV/ZnO/H_2O_2$. In addition, the effect of the operational parameters, such as the initial concentration of the catalyst, the initial malathion concentration, the initial salt concentration ($NaHCO_3$ and Na_2SO_4), and pH, were studied. Analyses were performed by a gas chromatography-mass spectroscopy instrument. The k values were in the following order: $US/UV/H_2O_2/ZnO$ > US/UV > UV/ZnO > UV/H_2O_2 > UV > US. ZnO concentration of 100 mg/l, malathion initial concentration of 200 µg/l, H_2O_2 concentration of 30 mg/l, pH of 9, and irradiation time of 105 min were the optimum conditions for degrading malathion by the $US/UV/H_2O_2/ZnO$ system. Additionally, the optimized parameters were also tested for the treatment of an actual water sample containing the pesticide. As a result, the efficiency of the $US/UV/H_2O_2/ZnO$ system was higher in the distilled water sample than in the actual water sample.

Keywords: Malathion; Advanced oxidation processes; Water.

Introduction

Malathion, an organophosphorus pesticide for a large variety of pests, has been widely used in agriculture [1]. The metabolism and toxicology of malathion in mammals have been intensively studied and reviewed; this pesticide is a potent inhibitor of acethylcholinesterase (AChE) [2]. In the environment, the thiophosphoryl bonds(P=S) of malathion can be oxidized to their corresponding (P=O) oxon by different oxidizing agents such as ultraviolet irradiation, ultrasound irradiation, hydrogen peroxide, and zinc oxide [3]. There have been conducted extensive studies for the removal of malathion in the environment, such as ozonation [3], TiO_2 nanotube film ($Au-Pd-TiO_2$) [4], the heterogeneous reactions of nitrate (NO_3) radicals [5], dinitrogen tetraoxide and nitric acid [6], and using of photo-Fenton's process [7]. Advanced oxidation processes (AOP_s) have also been extensively investigated for treating water and aqueous solutions; these processes could be applied as the sole treatment or as the pretreatment for removing pesticides [8, 9]. Several reports have proven that AOP_s are promising and attractive alternatives for the treatment of organic pollutants that are either toxic or persistent to the biological treatments [10-12]. AOP_s mainly rely on the generation of highly oxidative free radicals; in most cases, the hydroxyl radical ºOH with an electropotential of 2.8 ev [13]. A variety of effective treatment methods, such as ultrasonic irradiation, direct photolysis, ultra-violet (UV) irradiation in the presence of TiO_2, ozone, and Fenton reagent, have been applied for degrading pesticides in contaminated waters [14, 15].

No studies have so far been reported on the nanosonophotocatalysis or the nanosonophoto-chemical process for removing malathion, and a detailed study of the nanosonophotocatalysis degradation process might provide useful information for optimizing the overall nanosonophotodegradation system. This investigation has the following objectives:

(i) to evaluate the effects of US in the UV/US system; (ii) to determine the effects of ZnO in the UV/ZnO system; (iii) to determine the effects of ZnO dosage in the UV/ZnO system; (iv) to determine the effects of H_2O_2 dosage in the UV/H_2O_2 system; (v) to measure the effects of adding radical scavengers (sulphate and bicarbonate) to the $US/UV/H_2O_2/ZnO$ system; (vi) to evaluate the impact of pH, initial malathion concentration, and time in the $US/UV/H_2O_2/ZnO$ system; and (vii) to determine the optimum conditions in the $US/UV/H_2O_2/ZnO$ system.

Experimental

Reagents

The ZnO catalyst was purchased from FLUKA. The diameter specific surface area and band gap energy of ZnO were 14 nm, 10 $m^2.g^{-1}$, and 2.92 ev respectively. The tested compounds in this study were malathion (from supellco), NaOH, and HNO3 (obtained from Merck co., Germany). The reaction solutions were sodium bicarbonate ($NaHCO_3$, Merck) and sodium sulphate (Na_2SO_4, Merck). The initial concentration of H_2O_2 was obtained by adding a pre–determined amount of the stock solution prepared

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from a 30% H_2O_2 solution (Merck). Hydrogen-peroxide-assisted degradation was conducted using 10 and 30 mgL^{-1} H_2O_2 from a 30% stock solution.

Procedures

The concentration of malathion in samples was 200, 400, and 600 µg.L^{-1}, which were prepared using a 30% insecticides. The samples were adjusted in the reactor in 5 detention times (60, 90, 120, 150, and 180 S). The pH of the sample solutions of malathion were 3, 7, and 9, and reaction temperature was kept at 25 ± 1°C. For all of the systems, study samples were synthesized from deionized water. For the photodegradation of malathion, a solution containing a known concentration of the pesticide and ZnO nanopowder was prepared and was allowed to equilibrate for 30 min in the darkness; then, 50 ml of the prepared suspension was transferred to a 800 ml Pyrex reactor. Irradiation was carried out with a 125 W medium pressure mercury lamp (Philips, Holland), which was placed above the batch photo reactor. The distance between the solution and the UV source was constantly kept at 3.75 cm for all experiments. In the surface of the solution, the light intensity was 80 Wm^{-2}, measured by a Hanger – Detector (EC1- UV-C, Swede). For the sonophotolysis of malathion, a solution containing pesticide and double distilled water was used. Then, 800 ml of the prepared suspension was transferred to a 800 ml Pyrex reactor. Irradiation was carried out with a 150 W medium pressure mercury lamp, which was placed above the batch photoreactor. After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by magnetic stirrer (IKA, werke , Germany) to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. Temperature was kept at 25± 1°C by circulating water in a double jacket cooling array. The ultrasonic instrument used in this study was model (T1-H-5, Germany): capacity 3.7 lit, dimensions L = 30 cm, W = 25 cm, H= 32 cm, flow type batch, altered number 2. The 800 ml malathion solution was irradiated using an ultrasound operating at 130 kHz working frequency and 500 W power at a temperature of 25 ± 1 ^{o}C kept constant by circulating water in a double jacket cooling array. The samples were adjusted in the reactor in 5 detention times (30, 45, 60, 90, 105 min). The sonication time was monitored with a stop watch. The pH of the reaction was adjusted using HNO3 or NaOH and then the pH values were measured with a pH meter (Sartorius, Germany). Dispersive liquid – liquid microextration (DLLME) techniques were used for the extraction of malathion [16].

5 ml of the sample (water + analyte) was mixed with 500 ml of the extraction solution (2 ml internal standard: chlorpyrifos 1000 mgL^{-1}, 10 ml chloroform with 100 ml acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper aqueous phase was collected by pipette, the droplets were sedimented at the bottom of the conical test tube, and 1 ml of it was injected into a GC/MS instrument. Analyses were performed by a gas chromatography-mass spectroscopy (GC-MS) instrument. For identification, 1 ml samples were injected into the GC-MS instrument (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was 270 ^{o}C, and the analysis was done using a capillary column (Varian DB-5 column; 30m 250µm I.D., film thickness 0.25 µm). The method was started at 150 ^{o}C , which was held for 2 min, then ramped to 120 ^{o}C at a rate of 25 ^{o}C/ min, followed by an increase to 270 ^{o}C (held for 2 min). The method used a split ratio of 1:10. Helium (99.999%) was used as the carrier gas at 1 ml/min. Data were analyzed using T – test and one-way ANOVA test.

Results and Discussion

Removal in the US/UV system

Effect of pH

The changes of removal percentage of malathion with pH are shown in Fig. 1 and Table-1 It was observed that the pesticide removal was significantly influenced with increasing pH, and the highest removal efficiency was achieved at pH 9. The results indicated that the degree of sonophotolysis increased with increasing pH. The reason for this phenomenon was that $\overline{OH}$ ions with an elevated concentration would increasingly scavenge ultrasonic-generated holes that concurrently yielded highly oxidative ^{o}OH species [17].
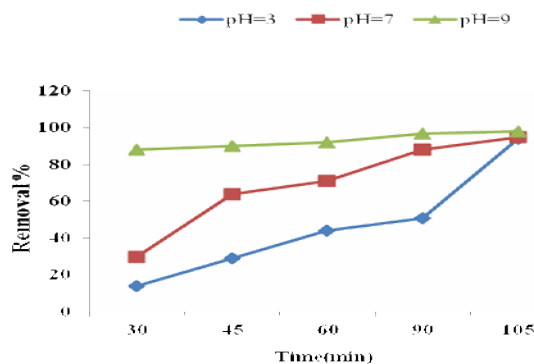

Fig. 1: Comparison of removal percentage for US/UV process at different pH of malathion, [malathion]0=600 µgL-1

Table-1: Reaction rate constants and correlation coefficients of various system [malathion]0=200 µgL-1, H2O2=30 mgL-1 and ZnO= 100mgL-1.

Systems	K(min-1)	r2
US(pH3)	0.0001	0.9913
US(pH7)	0.0075	0.9312
US(pH9)	0.0088	0.9610
UV(pH3)	0.0131	0.9551
UV(pH7)	0.0151	0.9810
UV(pH9)	0.0171	0.9900
US/UV(pH3)	0.0271	0.8782
US/UV(pH7)	0.0197	0.9345
US/UV(pH9)	0.0341	0.9781
UV/ZnO(pH3)	0.0182	0.9441
UV/ZnO(pH7)	0.0195	0.9910
UV/ZnO(pH9)	0.0311	0.9924
UV/H2O2(pH3)	0.0161	0.9510
UV/ H2O2 (pH7)	0.0181	0.9869
UV/ H2O2 (pH9)	0.0197	0.9855

Effect of initial Malathion Concentration

The effect of the initial pesticide concentration on the sonophotolysis is presented in Table-2. The degree of sonophotolysis decreased with increased initial pesticide concentration. In general, the decomposition percentage decreased as the initial concentration of contaminant increased under ultrasonic treatment [18].

Assuming that the production of hydroxyl radical concentration is constant, radical recombination reactions would dominate at low concentrations of the pesticide, which increase the degradation. Similar results have also been reported by previous studies [19-21].

Effect of synergetic US/UV

The effect of the synergy on the sonophotolysis was studied and the obtained results are illustrated in Fig. 2 and 3. The degree of decomposition by sonophotolysis was more than that by sonolysis. The reason for the observed enhancement in the rate may be due to increased generation of highly reactive free radicals such as hydroxyl (^{o}OH), hydrogen (H^{o}), and hydroperoxy (HO_2^{o}). These reactive radicals are the main species that degrade pesticide [12]. Various researches reported that sonophotolysis was more effective than the individual sonolysis for the removal of organic pollutants from aqueous solutions. For example, the decolorization efficiency of US/UV was higher than that of US [22]. In addition, the degradation of dimethoate by synergetic sonophotolysis [23].
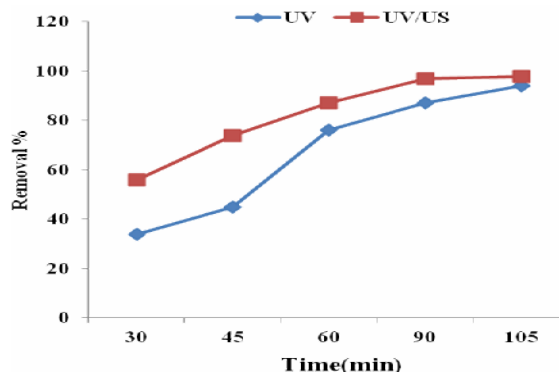

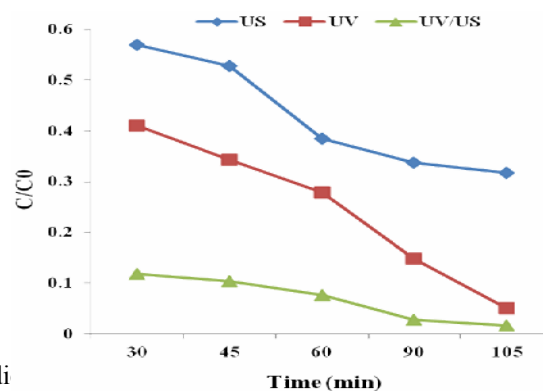Fig. 2: Effect of UV and US on sonophotodegradation of malathion. [malathion] 0=400µgL-1; pH neutral

Fig. 3: Comparison of removal percentage for different processes of malathion [malathion] 0=600 µgL-1,pH=9.

Removal in the UV/ZnO system

Effects of ZnO level

Comparisons of removal percentage in UV/ZnO system of malathion at different catalyst dose in Fig.4. As the concentration of ZnO increased, the removed percentage increased. The highest removal percentage was observed when 100 mgL^{-1} of ZnO was used. The results indicated that the degree of photodegradation increases with catalyst loading and then decreases at higher values, mainly because of high scattering and screening effects. The tendency towards agglomeration (particle – particle interaction) also increases at high solids concentrations, which results in a reduction in the catalyst surface area available for light absorption and, hence, a drop in the photocatalytic degradation rate. Although the number of active sites in the solution will increase with catalyst loading, a point appears to be reached where light penetration is

compromised because of excessive particle concentration. A further increase in the catalyst loading beyond the optimum will result in a non-uniform light intensity distribution, so that the reaction rate would indeed be lower with increased catalyst dosage. Generally, the amount of photocatalyst to be used should maintain a balance between these two opposing effects in order to ensure efficient absorption of photons and to avoid excess catalyst, so the photocatalytic reactor should be operated at optimum catalyst loading. Consistently similar results have been reported for degradation of metamitron [24], terepthalic acid [25], and 2-4-dinitrophenol [26] .

Effect of pH

The K values of UV/ZnO system was determined at pH 3, 7, and 9 (Table-1). The K values for the UV/ZnO system increased with pH (Table-1).

The results indicated that the degree of photodegradation increased with increasing pH. Generally, the characteristics of the organic pollutants in the aqueous solution differ greatly is several parameters, particularly in their speciation behavior, solubility in water, and hydrophobicity. This variation can also significantly influence their photocatalytic degradation behavior [27]. The pH at which the surface of an oxide is uncharged is defined as the zero point charge (pHzpc). The surface of the catalyst is positive below pH 9.0 [28]. Optimal conditions were found at which the positively charged ZnO and negatively charged insecticide molecules should readily attract each other. Therefore, the pH of the solution can play a vital role in the adsorption and photocatalytic oxidation of pollutants. Similar observation have also been reported for the degradation of methamidophos [29], carbofuran [30], and thiram [31].

Effect of initial Malathion concentration

The influence of initial Malathion concentration the photocatalytic degradation is an important aspect of study. The results are given in Table-2. The degree photodegradation decreased with increasing of init concentration of pesticide [27, 32, 33]. An increase in substrate concentration can lead to the generation of intermediates, which may be adsorbed on the surface of the catalyst. Slow diffusion of the generated intermediates from the catalyst surface can result in the deactivation of active sites on the photocatalyst and result in a reduction in the degradation rate.

Table-2: Comparsion of removal percentage of Malathion at different process

Systems	Initial concentration (μgL-1)	Mean±SD
US	200	53.33±19.29
	400	43.25±22.31
	600	38.41±15.97
UV	200	75.93±12.15
	400	72.64±18.61
	600	69.69±29
UV/US	200	80.21±17.73
	400	80.02±26.87
	600	74.35±23.55
UV/ZnO	200	78.31±15.89
	400	77. 14±17.91
	600	75.20±18.10
UZ/H2O2	200	81.54±15.70
	400	71.54±22.10
	600	69.47±24.06

Removal in the UV/H$_2$O$_2$ system

Effects of pH

The highest removal efficiency was achieved at pH 9, as shown in Table-1. The reason for this phenomenon was that $O\overline{H}$ ions with elevated concentrations would increasingly scavenge yielded highly oxidative ºOH species [34].

Effect of H$_2$O$_2$ concentration

The results in Fig. 5 show that the mean removal percentage of pesticide is higher at 30 mgL^{-1} H$_2$O$_2$ concentration than at 10 mgL^{-1}. Addition of hydrogen peroxide increased the UV degradation rates of malathion, mainly due to the formation of hydroxyl radicals through the photolysis of H$_2$O$_2$ [22].
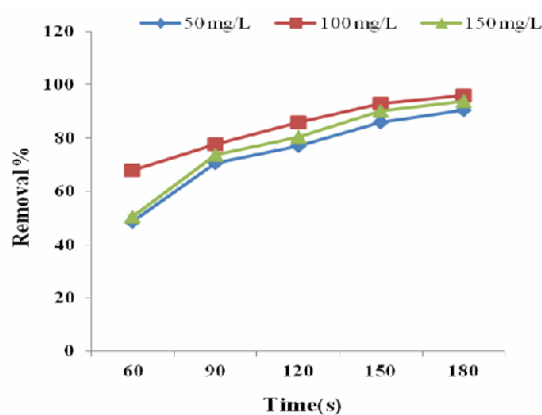
Removal in the US/ UV/H$_2$O$_2$/ZnO system

Fig. 4: Comparisons of removal percentage in UV/ZnO system of Malathion at different catalyst dose. [malathion]0=200 μgL-1, pH=7.
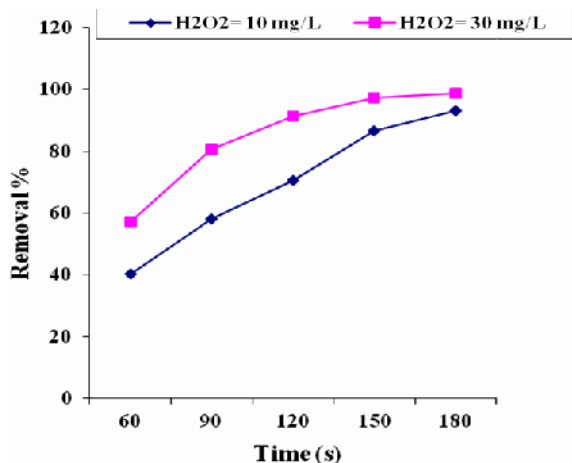
Fig. 5: Comparison of decomposition mean percentage pesticides with UV/ H2O2 process at different hydrogen peroxide concentration. [diazinon]0=600 µgL-1,pH=9

The results in Fig. 6 show that the mean removal percentage of pesticide is higher in the UV/ US system than in other systems. Moreover, in all systems, the degradation rate was higher at pH 9 than at pH 3 or 7. In addition, in all systems, the degradation rate decreased with increasing of initial concentration of pesticide (Table-2).
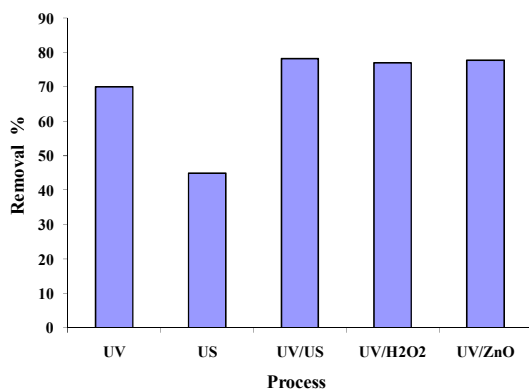

Fig. 6: Comparison of removal percentage malathion at different processes.

Salt Effect

The effect of salt on the nanosonophotodegradation of malathion was studied using sodium bicarbonate and sodium sulfate. The influence of different concentrations of the salts (50 – 400 mgL^{-1}) on the nanosonophotodegradation of malathion is presented in Figs. 7 and 8. Nano sonophotodegradation in the presence of sodium bicarbonate and sodium sulfate was slower in

comparison to the reactions without salts. The decrease in the reaction rate in the presence of salts is due to the hydroxyl scavenger property of sulfate and bicarbonate ions.
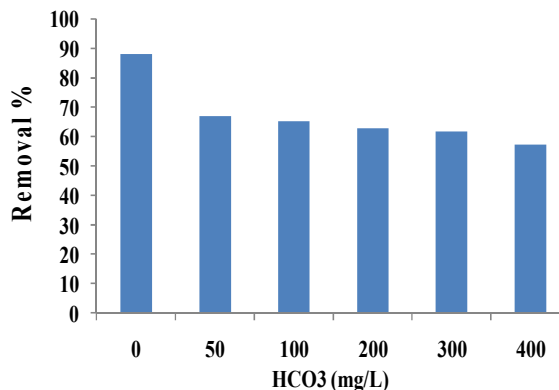

Fig. 7: Comparison of removal percentage for degradation of malathion in the presence of bicarbonate.[H2O2]=30 mgL-1,[ZnO] =100 mgL-1, pH=9, irradiation time =105 min.

The effects of salts are compared in Figs 7 and 8. It can be seen that sodium bicarbonate was the most powerful inhibitor studied, while sodium sulfate was the weakest one.
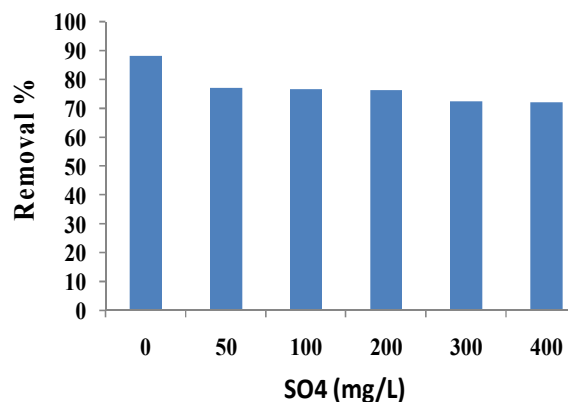

Fig. 8: Comparison of removal percentage for degradation of malathion in the presence of sulfate.[H2O2]=3 mgL-1,[ZnO] =100 mgL-1, pH=9, irradiation time =105 min.

Degradation of malathion in an actual water sample

The actual water samples were obtained from the drinking water of Tehran and Babolrood river in Mazandaran , Iran. The results are shown in Fig. 3, which illustrate that the

nanosonophotodegradation rate was higher in the distilled water than in the natural water (tap and river waters). Nanosonophotodegradation rate followed the following order: distilled water> tap water> river water. This inhibition is undoubtedly due to their ability to act as hydroxyl radicals scavengers by the following reaction: [24, 35].

$$SO_4^{2-} + °OH \rightarrow SO_4^{o-} + OH^- \qquad (1)$$

$$HCO3^- + °OH \rightarrow CO3^{o-} + H_2O \qquad (2)$$
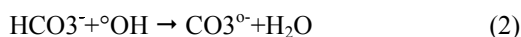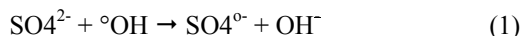
This may be due to the presence of organic carbon in natural water, which inhibits the degradation rate of the pesticide. These organic matters absorb most of the photons emitted there by slowing down the degradation reaction of pesticides [36]. Finally, under the studied conditions, the optimum conditions for the degradation of malathion by US/UV/H_2O_2/ZnO system were: a ZnO concentration of 100 mgL^{-1} , a malathion initial concentration 200 μgL^{-1}, a H_2O_2 concentration 30 mgL^{-1}, pH=9, and an irradiation time 105 min.

Conclusion

The present study investigated the nanosonophotodegradation of malathion and evaluated the removal efficiency of US, UV, **US**/UV, UV/ZnO, UV/H_2O_2, and US/UV/H_2O_2/ZnO systems for its removal.

The k values of US, UV, US/UV, UV/H_2O_2, and US/UV/H_2O_2/ZnO systems all increased with increasing of pH. The k values followed the order: US/UV/H_2O_2/ZnO > US/UV > UV/ZnO > UV/H_2O_2 > UV > US. There was a decrease in the removal efficiency of malathion in all processes with increasing initial malathion concentration. We also observed that the optimal amount of the catalyst was 100 mgL^{-1}. Adding sodium bicarbonate and sodium sulfate decreased the removal efficiency of the US/UV/H_2O_2/ZnO system. It was found that sodium bicarbonate was the most powerful inhibitor. Finally, the rate of nanosonophotodegradation was higher in the distilled water than in the natural water.

Acknowledgments

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