

Sonochemical kinetic model of diazinon and malathion pesticides degradation in aqueous solution

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Abstract

In this work, elimination two types of organophosphorus pesticides, diazinon and malathion spiked in aqueous solution by ultrasonic irradiation was investigated. Six different initial concentrations of diazinon and malathion (100, 300, 500, 200, 400, and 600 µg/L respectively) at different pH (3, 7, 9) and time (30, 45, 60, 90, 105 min) were investigated. Results showed that diazinon and malathion could be effectively and rapidly degraded by ultrasonic irradiation, and kinetics of both pesticides was strongly influenced by time, initial concentration and pH value. The results showed optimum condition degradation achieved at pH 3 and 9 for diazinon and malathion, respectively. Kinetic modeling applied for the obtained results showed that the degradation of diazinon and malathion by ultrasound followed first – order and second – order model.

Keywords: Ultrasonic, Pesticide, Diazinon, Malathion, Sonochemical kinetic, Aqueous solution

1. Introduction

Diazinon and malathion are high – effective pesticides those are extensively applied in agriculture (Liu et al., 2008). The summary of pesticides physicals is shown in Table 1 (Zang and Pagilla, 2010; Daneshvar et al., 2007). However, their residues have negative effects on the environment, even on the health of people because of its toxicity and stability (Zhang et al., 2007; Fadaei et al., 2012a). According to many researches, if the organophosphorous pesticide releases the suitable environmental conditions it is possible for them to persist in many environmental compartments for along period of time (Evgenidou et al., 2005).

These pollutants are usually poorly biodegradable or persistent to environmental conditions. Some techniques using for degradation of organophosphorus pesticide in aqueous solution were performed using nanofiltration (Zang and Pagilla, 2010), microwave (Zhang et al., 2007), ozonation (Ku et al., 1998), or chemical oxidation. Aqueous chlorine (Acero et al., 2008), and Fenton treatment (Wang and Lemley, 2008), ionizing radiation (Basfar et al., 2007) degradation were achieved through gamma – ray (Mohamed et al., 2009), X – ray (Trebse and Arcon, 2003), and ultraviolet ray (Okada et al., 2010; Dehghani et al., 2012). Some methods such as photocatalytic oxidation (Evgenidou et al., 2005; Dehghani and Fadaei, 2012), activated carbon (Foo, and Hameed, 2010) were performed. More recent studies have focused on some new methods such as biodegradation (Oller et al., 2010), and ultrasonic technique (Dehghani et al., 2008; Thangaradivel et al., 2009; Yao et al., 2010).

Ultrasonic irradiation is an attractive technique as the degradation of contaminants may occur under ultrasonic irradiation

without the addition of other chemicals. The most important mechanism responsible for the degradation of contaminants is acoustic cavitation (Schramm and Hua, 2001; Dehghani 2005; Dehghani et al., 2006; Dehghani et al., 2012; Shayeghi et al., 2012). The degradation of organic compound, (pesticides) mainly for either thermal decomposition or free radical reaction mechanism. Inside a cavitation bubble only thermal decomposition occurs in gas phase with the rupture of C – C, C = C, C – N, C – O bonds at a very high temperature (~ 5000 k). At the gas – liquid interface both thermal decomposition (~ 2000 k) and free radical (OH) reaction may occur side by side (Chowdhury and Viraraghavan, 2009; Shayeghi et al., 2011; Dehghani et al., 2012).

In this study, sonochemical degradation of diazinon and malathion are investigated. The objective of this study is to: 1. evaluate the effect of operation parameters (pH, time, initial concentration) on pesticides degradation. 2. Propose the degradation kinetics.

Table 1. Pesticides properties (Zang and Pagilla, 2010; Daneshvar et al., 2007)

pesticides	Molecular (g/mol)	Density at 20 °C (g/L)	Solubility at 20 °C (g/L)	Henry's law constant at 20 °C	melting point (atm.m ³ / mol)
Diazinon	304.3	1.11	0.04	10 ⁻⁶ × 1.4	No data
Malathion	330.36	1.23	0.13	10 ⁻⁹ × 4.89	2.9

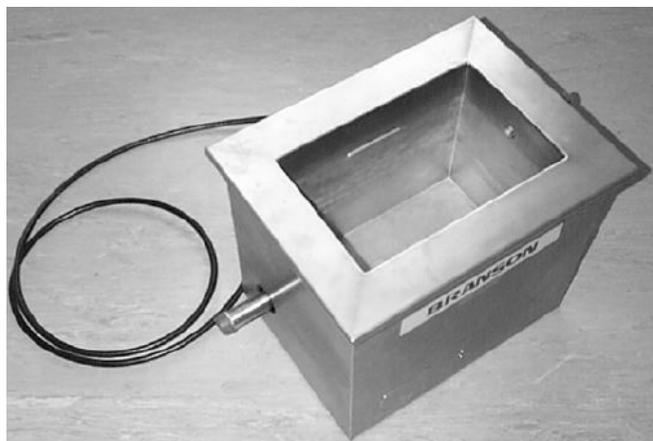
2. Materials and methods

All organophosphorus pesticide were gift from Merck Co. (Germany), and NaOH, HCl, chloroform, acetone and methanol were obtained Merck Co. (Germany). All solutions were prepared with deionized water.

Ultrasonic in this study was model ELMA, Germany) capacity 3.7 lit, dimensions: L = 30 cm, W = 25 cm, H = 32 cm, flow type batch (Fig 1). Samples of this study are synthetic from deionized water. The concentration of diazinon in samples was 100, 300, 500 µg/L.

The concentration of malathion in samples was 200, 400, 600 µg/L. The pH value of the original diazinon and malathion solution was adjusted to 3, 7, 9 (± 0.05) with 1 M NaOH and 1 M HCl and remained uncontrolled during the ultrasonic irradiation and reaction temperature in $25 \pm 1^\circ\text{C}$. Ultrasonic irradiation of 200 ml diazinon or malathion solution operating at 130 kHz frequency and 500 W power in 5 time of remaining 30, 45, 60, 90, 105 min, reaction temperature in $25 \pm 1^\circ\text{C}$. All the treated samples were stored at 4°C for a maximum of 24 for analysis. Each treatment was conducted in triplicate.

Fig.1. Ultrasonic reactor for degradation of pesticides



For the extraction of diazinon and malathion was used techniques (DLLME) dispersive liquid – liquid microextraction (Rezaee et al., 2010; Farajzadeh et al., 2009). A 5 ml of sample mixed with 500 ml extraction solution (2 ml internal standard: chlorpyrifos 1000 mg/l, 10 ml chloroform with 100 ml acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper of aqueous phase was collected by pipette; the droplets were sedimented at the bottom of the conical test tube and 1 ml injected in to GC.

Analyses were performed by gas chromatography with flame ionization detector (GC – FID) with CP – 3800 (Australia) was used to determine Varian malathion and diazinon concentration of samples. The GC was fitted with a DB – 5 capillary columns (30 m, 0.25 mm Id, 0.25 mm film thickness).

Injector temperature was 250°C , initial oven temperature was 50°C (held for 2 min) and increased to 100°C at a rate of $25^\circ\text{C}/\text{min}$,

held for 2 min. The inlet was operated in split less mode. Helium (99.999%) was used as carrier gas at 1 ml/min. sample solution (1 ml) was injected in split less mode.

Data were analyzed using the SPSS (11.5) software. The effects of ultrasonic on the reaction rate coefficient of malathion and diazinon in water were evaluated by Anova one way, Non-parametric test: Mann – Whitney, and Kruskal – Wallis test.

3. Results and discussion

The obtained data were fitted with different kinetics models first – order, second – order models.

3.1 First – order kinetics model

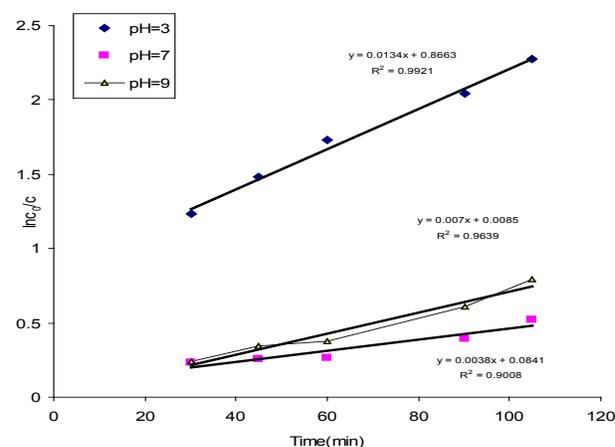
In this model the experimental data were fitted according to simple first – order rate: $C = C_0e^{-kt}$ to obtain a liner fitting Eq. (1), rearranged to: $\text{Ln}C_0/C = kt$.

Where: -k is the first – order rate constant and it is estimated from the slope by plotting $\text{Ln} C_0/C$ versus time t, as shown in Fig. 2.

C_0 is the initial diazinon concentration and R^2 is the correlation factor.

All the correlation factors (R^2) were larger than 0.9, indicating that the degradation of diazinon obey first – order kinetics model. This was in accordance with the description in degradation kinetics of dichlorous by ultrasonic treatment in aqueous solution (Zhang et al, 2010). The results are illustrated in Fig. 2. The kinetics constants are 0.0134 min^{-1} , 0.0038 min^{-1} , 0.007 min^{-1} .

Fig.2. The first-order model at 100 ppb initial concentration for diazinon



3.2 Second – order kinetics model

The proposal of having a second – order kinetic model is examined here. The change in the degradation concentration can be fitted by using the second – order kinetic equation model described by Eq. (2): $\frac{dc}{dt} = -kc^2$ for liner fitting the equation can be

$$\text{rearranged as: } \frac{1}{c} - \frac{1}{c_0} = kt$$

Where:

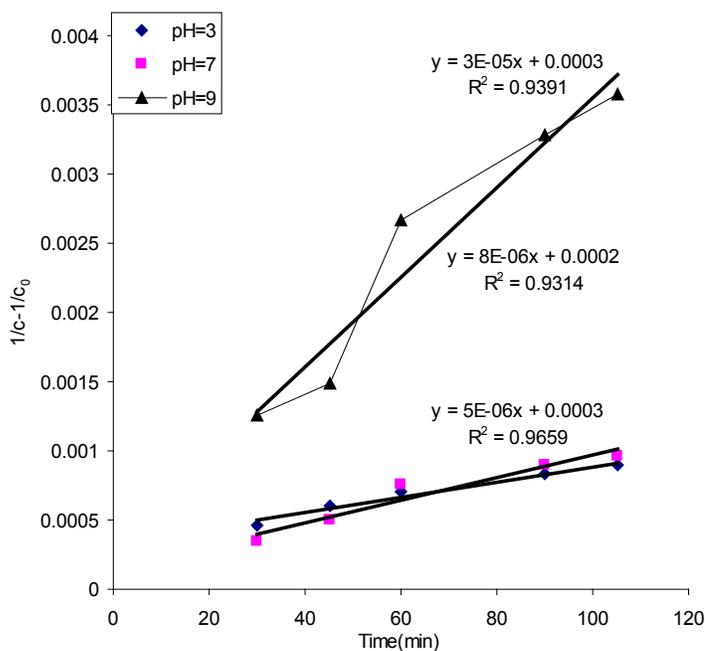
k is the second – order degradation rate constant and it can be estimated from the slope after plotting $\frac{1}{c} - \frac{1}{c_0}$ versus t, as shown in Fig. 3.

C_0 is the initial malathion concentration

In analyzing the experimental results, decomposition of malathion and diazinon appeared t, follow first – order and second – order kinetics, but first – order model is shown to be much more correct than second – order model.

They have reported the rates of degradation of pesticides in a number of sonodegradation reactors. Matouq et al. (2008) have reported the kinetics model of sonodegradation obey first – order, second – order and pseudo first – order model. Farooq et al. (2008) have reported the kinetics model of sonochemical degradation follow first – order model. Wang et al. (2006) have reported the kinetics model of sonochemical degradation follow first – order model. Wang et al. (2006) have reported the kinetics model of sonochemical degradation obey first – order model. Yuo et al. (2010) have reported the kinetics model of sonodegradation obey pseudo first – order model. Finally, most investigators have observed the kinetics of sonodegradation of pollutants to be either first – order or zero order (Adewayi, 2001).

Fig.3. The second order model at 600 ppb initial concentration for malathion



3.3 The effect of pH

The effect of pH on the degradation of malathion and diazinon was investigated and the results are shown in Table 2. The results showed that the highest mean rank = 5.33 at pH 3, and 7 at pH 9 for diazinon and malathion, on the other hand the highest degradation in sonolysis process for malathion at pH 9 and

diazinon at pH 3. Diazinon degraded rapidly at 3 but very slow at pH 7 and 9. The presumed reason for diazinon is that the fraction in the molecular state of diazinon was larger when the pH

Table 2. Comparison of the mean rank rate constant at different pH

Pesticide	pH	Mean rank (k/1000)	Parameters
Diazinon	3	5.33	$\chi^2 = 0.089$ d.f = 2 P = 0.95
	7	5	
	9	4.67	
Malathion	3	4.67	$\chi^2 = 2.75$ d.f = 2 P = 0.25
	7	3.33	
	9	7	

χ^2 = Chi-Square, d.f = degree of freedom, ρ = p-value, Z = z-value

was smaller and the smaller pH (especially less than the pK_a) was effective for decomposition similar results was also observed in the sonochemical degradation of methidathion and the reason for malathion is that the generation of $^{\circ}OH$ radicals on the solution (Farooq et al., 2008).

As show in Table 2, 3, there is no significant effect of initial pH on malathion and diazinon of degradation rate constant other researchers have also reported that initial concentration and pH has no significant effect on the degradation of organic compound due to sonication (Bhatnagar and Cheung, 1994). An increase in pH stimulated the degradation rate of most of the pesticides, with exception of diazinon and permethrin (Zhang et al., 2010; Shayeghi et al., 2011). Under the ultrasonic irradiation, the influence of pH range of solution on the degradation of the both pesticides was not consistent with their basic characteristic. This probably resulted from the occurrence of complex degradation pathway under the ultrasonic irradiation.

Table 3. Comparison of the mean rank rate constant of pesticides (malathion and diazinon) at different pH

pH	Mean rank (k/1000)	Parameters
3	9.67	$\chi^2 = 1.067$ d.f = 2 P = 0.58
7	7.83	
9	11	

3.4 The effect of initial concentration

The effect of initial concentration on the degradation rate constant of malathion and diazinon are shown in Table 4. It can be seen that as the increase of initial concentration pesticides, the degradation rate constant declined at high concentration bulk solution; at low concentration levels an additional removal mechanism may be proposed and free radical reactions in the bubble-

liquid interfacial region are likely to be important (Drijvers et al., 1996; Shayeghi et al., 2010; Fadaei et al., 2012b). The initial concentrations have significant effect on the degradation of diazinon ($p < 0.05$). The reason is that the role of hydroxyl radical induced by ultrasound (Tauber et al., 2000) and in general, the decomposition rate decreased as the initial concentration of compound increased due to ultrasonic irradiation (Singla et al., 2009).

Table 4. Comparison of the mean rank rate constant at various initial concentrations

Pesticides	Initial concentration	Mean rank (k/1000)	Parameters
Diazinon	200	6.33	$\chi^2 = 1.15$ d.f = 2 P = 0.56
	400	4.67	
	600	4	
Malathion	100	7.67	$\chi^2 = 6.48$ d.f = 2 P = 0.039
	300	5.53	
	500	2	

The comparisons of both pesticides are shown in Table 5. The k values of malathion were 1.6 times higher those of diazinon, indicating that malathion is much more labile to ultrasonic treatment than diazinon also, this indicated that diazinon was more resistant to ultrasonic treatment than malathion, but there was no significant difference between pesticide type and degradation rate constant.

Table 5. Comparison of the mean rank rate constant of pesticides (all of concentrations)

Pesticides	Mean rank (k/1000)	Parameters
Malathion	11.67	Z = -1.7
Diazinon	7.33	P = 0.09

3.5 The effect of ultrasonic irradiation time

The effect of the ultrasonic irradiation time on the degradation of malathion and diazinon were also considered in the range from 30 to 105 min. As shown in Fig 4, 5 the decreasing in concentration profiles with the increasing of irradiation exposing time the two pesticides. It is clear that the concentration decreases with time which means that the rate of degradation is proportional to the time of exposing to ultrasound (Matouq, et al., 2008; Wang et al., 2006).

4. Conclusions

This work demonstrated that malathion and diazinon could be effectively degraded by ultrasonic irradiation under various experimental conditions such as pH, irradiation time and initial concentration. The rate constant for both pesticide was affected by pH, irradiation time and initial concentration. Degradation rate constant increased with the decrease of initial concentration

pesticide. The degradation kinetics of both pesticides could be described by the first – order and second – order kinetics model, but malathion is shown to be much more labile to ultrasonic irradiation than diazinon.

Fig.4. Comparison of initial concentration on sonolytic degradation of diazinon at different time (pH=7)

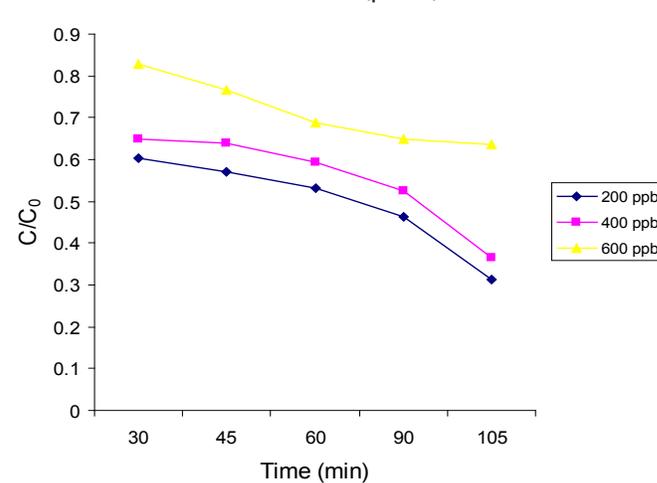
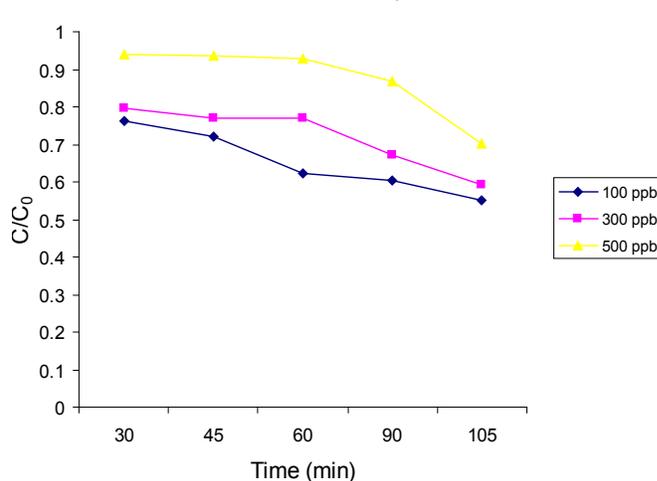


Fig.5. Comparison of initial concentration on sonolytic degradation of malathion at different time (pH=7)



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