Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.928795

55 (2015) 555–563
June

Taylor & Francis
Taylor & Francis Group

Photocatalytic degradation and mineralization of diazinon in aqueous solution using nano-TiO_2(Degussa, P25): kinetic and statistical analysis

Roshanak Rezaei Kalantary[a,b], Yousef Dadban Shahamat[a,c,*], Mahdi Farzadkia[a], Ali Esrafili[a], Hosseinali Asgharnia[a]

[a]*Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran, Tel. +9888 622721; Fax:+9821 88622707; email: roshanak_rezaeikalantary@yahoo.com (R.R. Kalantary), Tel. +9891 11789457; Fax: +9817 14436107; email: ydadban@yahoo.com (Y. Dadban Shahamat), Tel. +9888 622721; Fax:+9821 88622707; emails: mahdifarzadkia@gmail.com (M. Farzadkia), a_esrafili@tums.ac.ir (A. Esrafili), eha_ali1@yahoo.com (H. Asgharnia)*
[b]*Center for Water Quality Research (CWQR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran*
[c]*Environmental Health Research Center, Golestan University of Medical Sciences, Gorgan, Iran*

Received 19 October 2013; Accepted 20 April 2014

ABSTRACT

In this study, photocatalytic degradation of diazinon was investigated using nano-TiO_2, Degussa P25, as a photocatalyst and the effects of some operational parameters such as aeration, pH, photocatalyst concentration, and the irradiation time were also examined. Dispersive liquid-liquid microextraction technique was used to extract and pre-concentration of residual diazinon from the liquid samples and all experiments were carried out by gas chromatography. Amount of degradation and mineralization were determined by gas chromatograph with flame ionization detector (GC/FID) and COD measurements, respectively. The optimum condition for degradation of diazinon has been obtained in the pH 6, [nano-TiO_2] = 0.2 g/L, and [time] = 120 min. In the optimal condition the removal efficiency of diazinon and COD were 99.64 and 65%, respectively. The results have shown that the nano-TiO_2, aeration and time of reaction have a positive effect on photocatalytic degradation of diazinon and COD removal. Statistical analysis showed that the maximum removal of diazinon and COD were due to UV irradiation (71%, 41%), exposure time (16%, 39%), aeration (7%, 4%), and increased concentration of nano-TiO_2 (0.4%, 2%), respectively; and the kinetics of photodegradation were found to follow a first-order kinetic model and the constant rate, at optimal condition, was 0.038 (min^{-1}).

Keywords: Diazinon; Mineralization; Nano-TiO_2; Photocatalytic degradation

---

1. Introduction

Diazinon (*O*,*O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) is an organophosphorus (OP) pesticide used to control a variety of insects in agriculture and household environment [1,2] and classified by the World Health Organization (WHO) as "moderately hazardous" Class II.

It was associated with toxicity to aquatic organisms at a concentration of 350 ng/L [3,4]. Fetal human doses were found to be in the range from 90 to 444 mg/kg [3,5].

---

*Corresponding author.

They have replaced organochlorine pesticides because of the low persistence and accumulation of OPs in the environment situations. OP pesticides do not accumulate in organism bodies and they could be destructed easily in the environment [6].

Diazinon is relatively water soluble (40 mg/Lat 25℃), non-polar, moderately mobile, and persistent in soil, hence, it is of concern for groundwater and surface derived drinking water. Diazinon has a log K_{ow} of 3.3, vapor pressure of 1.4×10^{-4} mm Hg at 20℃, and Henry's law constant of 1.4×10^{-6} atmm^3/mol which indicate that it would not easily volatilize from soil or water [3,7].

Like other OPs, the main toxic effect of diazinon is the inhibition of acetyl cholinesterase activity (AChE, EC 3.1.1.7) by phosphorylation of the serine hydroxyl group in the substrate-binding domain of the enzyme which results in accumulation of acetylcholine and associated neurotoxicity [7–11]. In addition, researches have demonstrated that diazinon has an immunotoxic, cytotoxic, and genotoxic effects [12].

More recent researches have focused on new methods such as ultrasonic technique [12], biodegradation [13], photodegradation [8], ozonation [10,14], radiolytic degradation [15], fenton treatment [16], UV/H_2O_2 treatment [3], and photocatalytic degradation [7,17,18].

When the nano-TiO_2 is irradiated with UV lamp, valence band holes (h_{vb}) and conduction band electrons (e_{cb}) are generated by Eq. (1). OH radicals, generated through water oxidation by photo-generated valence band holes following Eq. (2), are known to be the most oxidizing species [19,20].

$$TiO_2 + h \rightarrow h^+_{vb} + e^-_{cb} \tag{1}$$

$$h^+_{vb} + H_2O \rightarrow OH^{\cdot} + H^+ \tag{2}$$

OH radicals react with diazinon molecules leading to the generation of numerous oxidation byproducts. In the presence of air, other species, such as H_2O_2 or even superoxide radicals, might contribute to the oxidation of the diazinon molecules using Eqs. (3) and (4).

$$2H^+ + 2e^-_{cb} + O_2 \rightarrow H_2O_2 \tag{3}$$

$$e^-_{cb} + O_2 \rightarrow O_2^- \tag{4}$$

However, the dissipation of diazinon in aqueous solutions by nanophotocatalytic processes has rarely been studied which is an effective technique for the removal of recalcitrant contaminants. Therefore, in the present study, the photodegradation of diazinon, in aqueous solution, under UV irradiation and suspension of nano-TiO_2 was investigated. The effect of factors including initial concentration of nano-TiO_2, pH of solution, and initial concentration of pesticide, on the degradation of diazinon, was investigated in a bench-scale photoreactor.

2. Experimental

2.1. Materials

In this study, the nano-TiO_2 powder (P-25, mainly in anatase form) was purchased from Degussa Co. Table 1 shows specifications of nano-TiO_2 powder. High-purity diazinon (CAS number: 333-41-5) was purchased from Sigma–Aldrich and its chemical characteristics are listed in Table 2. In order to prepare the standard 16×10^{-2} M solution, 250 mg of pure diazinon was added to 5 mL of absolute methanol and 10 standard dilutions were then prepared by distilled and deionized water. Standard solutions were protected from light, and stored at 4℃. GC/FID was calibrated with more dilute extracted standards. Diazinon (21%) was purchased from Sudarshan of Pesticides Chemical Co. (India) and a volume of 2 L was used in each experiment. Analytical grade of Chlorobenzene (CAS number: 108-90-7), Sulfuric acid (CAS number: 7664-93-9), Sodium Hydroxide (CAS number: 1310-73-2), Potassium dichromate (CAS number: 7778-50-9), Silver sulfate (CAS number: 10294-26-5), Mercury(II) sulfate (CAS number: 7783-35-9) in and HPLC grade of methanol (CAS number: 67-56-1) and acetone (CAS number: 67-64-1) were obtained from Merck Co. (Germany).

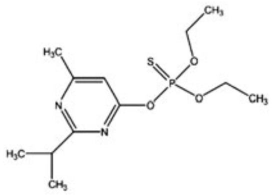
2.2. Photocatalytic treatment

Photocatalytic experiments were carried out in a 3 L cylindrical stainless steel reactor which improves

Table 1
Specifications of nano-TiO_2

Parameters	Decription
Chemical formula	TiO_2
Assay	99.5%
Behavior in water	Hydrophilic
Average particle size	15 nm
BET surface area	50 ± 15 m^2/g
Bulk density	130 g/L
pHpzc [21]	6.3
Crystalline phase	Anatase: 80% Rutile: 20%

Table 2
Chemical characteristics of diazinon

Parameters	Decription
Structure	
Molecular formula	$C_{12}H_{21}N_2O_3PS$
Mw (g/mol $^{-1}$)	304.3
Density (g/mL^{-1}) (20°C)	1.11
Solubility (mg/L^{-1}) (20°C)	40
WHO class	II
LD_{50} (Daphnia) (mg/kg^{-1})	1.4

the reflection and steady distribution of UV lamp in all parts of the reactor. In order to prevent the temperature increase of the solution (due to high electricity consumption of the UV source), the reactor was installed in a circulating water container. The UV exposure source (Fig. 1) was provided by OSRAM (125 W) high-pressure (HP) UV lamp (310–450 nm) with intensity of radiation of 35–50 W/m^2 installed inside the inner quartz tube in the reactor. Photocatalytic degradation studies of diazinon were performed in the batch reactor (Fig. 2).

Oxygen was introduced to the reactor from an air pump at a regulated flow rate of 3.5 L/min. Solutions with the desired diazinon concentration and nano-TiO_2 loading were fed into the reactor and the initial pH was adjusted by addition of either NaOH or HCl solutions (1 M).

The suspension was circulated for 10 min and then the lamp was switched on to start the photocatalytic reaction. Samples were filtered and then appropriate amounts were extracted and prepared for GC/FID injection at regular time intervals. The extent of degradation of the organic matter was also followed by COD analysis by digestion of diazinon solution with KCr_2O_7 solution [22].

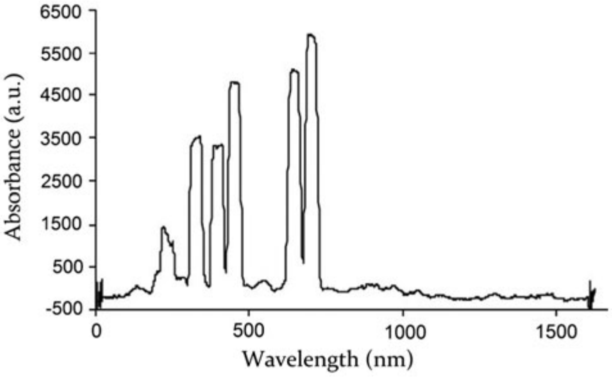


Fig. 1. Spectrum distribution of the UV irradiation source provided by OSRAM (125 W) lamp.

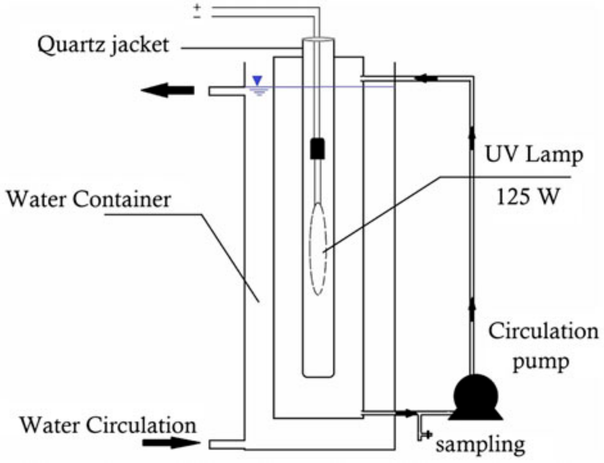


Fig. 2. Scheme of cylindrical photocatalytic reactor.

The concentration of diazinon and COD in each degraded sample was determined by using calibration curve (Fig. 3). The degradation of pesticide has been investigated under variable conditions: pH, diazinon dosage, nano-TiO_2 dosage, time, presence or absence of UV, and aeration.

2.3. Extraction and measurement analysis

Sampling was carried out from 0 to 120 min, in time intervals of 20 min. To eliminate the nano-TiO_2 particles, samples (ca. 12 mL) were filtered by 0.22-μm pore polytetrafluoroethylene syringe filters and centrifuged in 5,000 rpm for 10 min.

A new microextraction technique known as dispersive liquid–liquid microextraction, was applied to extract diazinon from aqueous phase to solvent phase, is a very simple and rapid method for extraction and pre-concentration of organic pesticides from water samples [23,24]. In this method, the mixture of extraction solvent (100.0 μL chlorobenzene) and disperser solvent (2.0 mL acetone) containing 50 mg/L phenanteren as an internal standard were injected into the aqueous sample (10.0 mL) by syringe, rapidly. After 3 min of shaking and centrifugation (5,000 rpm, 4 min, 25°C), the fine particles of extraction solvent were deposited in the bottom of the conical glass tubes with extraction recovery and enrichment factor of 89 ± 6% and 500 ± 10, respectively.

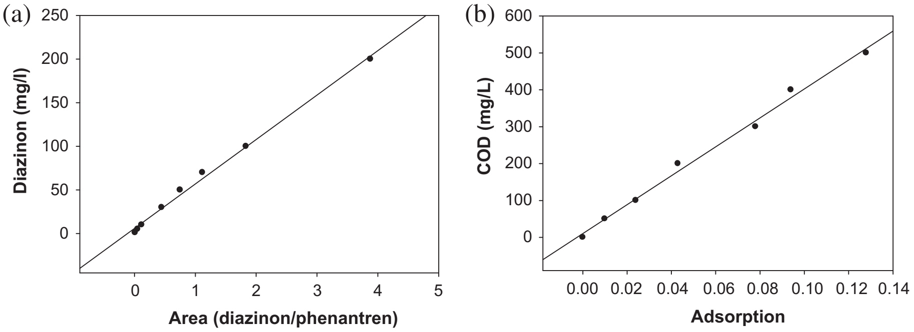


Fig. 3. Calibration curve for the determination of diazinon concentration in aqueous solution (a). Calibration curve for the determination of COD concentration at wavelength 600 nm (b).

Diazinon was analyzed using a CP 9001 Chrompack GC/FID equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 µm film thickness). The operating conditions were as follows: the temperature of the column was initially set at 70˚C for 2 min, then increased by 18˚C per min to 280˚C and maintained at this isothermal temperature for the final 1 min. Injector and detector temperatures were set at 250 and 270˚C, respectively. Nitrogen was used as a carrier gas at a flow rate of 4.0 mL/min and the injections were made in the split mode with a split ratio of 1:5.

2.4. Kinetic and statistical studies

The kinetic study using nano-TiO_2 (0.2 g/L) was carried out with seven different concentrations (12.0, 16.5, 22.5, 38.0, 65.0, 192.0, and 450.0 mg/L) of diazinon and at optimum pH.

Pseudo-first-order model expression was used to calculate the photocatalytic degradation rate using the kinetic study data. The kinetic expression is given by Eq. (5):

$$-\ln\frac{C}{C_0} = kt \qquad (5)$$

where k is the pseudo-first-order rate constant, C and C_0 are the concentrations of diazinon at time t, and $t = 0$, respectively.

Results analyses were accomplished by applying analysis of variance (ANOVA) test to statistically compare the diazinon photodegradation efficiency in different variable parameters.

In order to evaluate the effect of conditions of time reaction, nano-TiO_2 concentration with presence or absence of UV light and aeration during the degradation of diazinon and COD, a four-level factorial design (4^2) was performed.

3. Results and discussion

3.1. Effect of initial pH

In order to investigate the degradation behavior of diazinon, at pH values ranging from 4 to 10, the suspension was prepared by mixing 40 mg/L of diazinon solutions for reaction times of 30 and 60 min with a fixed nano-TiO_2 dose (0.4 g/L) and UV light.

The suspension was kept for given times at exposure of the UV lamp under the conditions of circulation, and then filtered after being centrifuged. The effect of pH (initially at 4, 6, 7, 8, and 10) on degradation of diazinon is shown in Fig. 4. The maximum degradation of diazinon was achieved at pH 6.

$$\mathrm{Ti^{IV}-OH + H^+ \rightarrow Ti^{IV}-OH_2{}^+} \quad K_{a1} \qquad (6)$$

$$\mathrm{Ti^{IV}-OH + H^- \rightarrow Ti^{IV}-O^- + H_2O} \quad K_{a2} \qquad (7)$$

pH_{pzc} of TiO_2 by using Eqs. (6) and (7) can be calculated as $pH_{pzc} = (pK_{a1} + pK_{a2})/2$. The pH_{pzc} of TiO_2 Degussa P-25 was 6.5 as it is reported in the range of 6.3–6.9 by various researchers [21,25].

The nano-TiO_2 catalyst surface will be charged negatively when pH > pzc, positively when pH < pzc, and neutrally when pH ≈ pzc. Also, the structural properties of the pollutant will change with pH. The effect of pH on the photocatalytic degradation can be explained as electrostatic interaction between the catalyst surface and the target material.

The pKa for diazinon is 2.6 [26]. It is negatively charged above pH 2.6, whereas catalysts are positively charged below pH 6.5. As expected, optimal conditions were found at $pK_a^{diazinon} < pH < pH_{ZPC}^{TiO_2}$ at which the positively charged nano-TiO_2 and negatively charged diazinon molecules should readily attract each other. In this situation both of them combine by

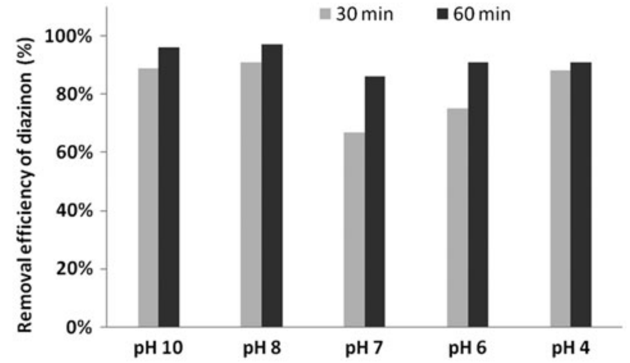


Fig. 4. Effect of initial pH on photocatalytic degradation of diazinon at irradiation times of 30 and 60 min.

hydrogen bonding easily and thus elevates the amount of adsorption and enhances the decomposition rate.

Hasnat et al. reported similar findings during comparative photocatalytic studies of decolorization of an anionic and a cationic dye [27].

3.2. Effect of irradiation time

Irradiation time plays an important role in photocatalytic decomposition of pollutant. Generally, the efficiency of photocatalytic processes may improve by increasing the irradiation time. In this study, different irradiation times of 0–120 min (20, 60, 90 and 120 min) were considered. As shown in Figs. 5 and 6, the photodegradation of diazinon and COD are increased in longer radiation times. However, the rate of degradation of pesticide during the first 20 min of UV irradiation was fast and then it leveled off at further times. Statistical test (ANOVA) also confirmed that degradation efficiency of diazinon and COD were significantly increased in longer irradiation times (p value < 0.05). As shown in Fig. 6, the removal of COD derived from diazinon content effluents is lesser than the degradation trend of diazinon pollutant which may be due to the formation of smaller intermediates [20]. Applying nano-TiO_2 (0.2 g/L) can increase the efficiency of pesticide removal significantly (13%) compared with the case of no application of nano-particles during 90 min process; while this increase for the case of COD removal efficiency (28%) was more than pesticide removal. This shows that complete mineralization can due to presence of nano-TiO_2 and generation of hydroxyl radicals, Although UV irradiation can effectively remove diazinon [3,28].

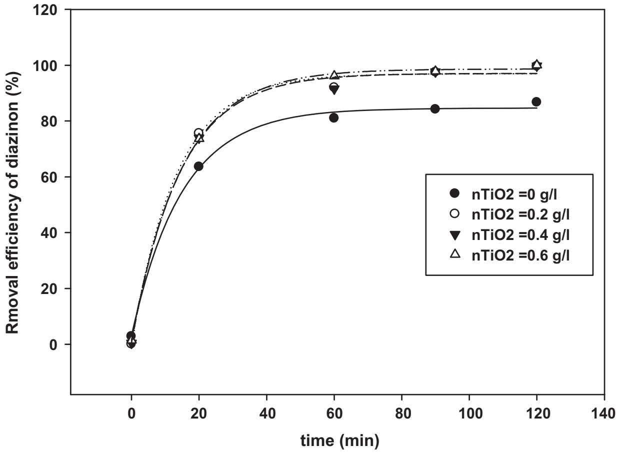


Fig. 5. Effect of nano-TiO_2 dosages on photocatalytic degradation of diazinon ($C_0 = 40$ mg/L) in presence of UV lamp (125 W) and aeration (3.5 L/min) and pH 6.

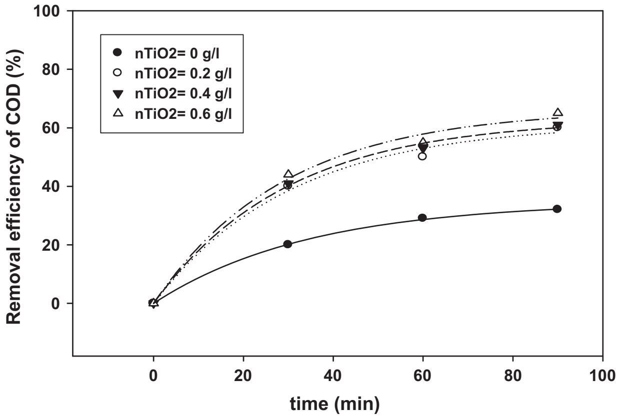


Fig. 6. Effect of nano-TiO_2 dosages on COD degradation of diazinon ($C_0 = 40$ mg/L) in the presence of UV lamp (125 W) and aeration (3.5 L/min) and pH 6.

3.3. Effect of photocatalyst concentration

After optimizing the pH conditions (pH 6), the photocatalytic degradation of diazinon was carried out by varying concentration of the nano-TiO_2 from 0.2 to 0.6 g/L in order to investigate the appropriate amount of catalyst concentration. Fig. 5 shows the effect of catalyst loading on the degradation of diazinon at optimum pH.

It can be seen that the rate of photodegradation increases with increase in the catalyst loading up to 0.6 g/L. Increase in the catalyst dosage increases the total active surface area, hence the availability of more active sites on the catalyst surface for adsorption and reaction. The removal efficiency of pesticide by photocatalyst loading from 0.2 to 0.6 g/L for reaction time of 120 min was 99.64 and 99.98% respectively. When the nano-TiO_2 concentration was very high, turbidity impedes further penetration of UV light in the reactor. It has been observed that above a certain concentration, the reaction rate levels off and becomes independent of the catalyst concentration [20,29,30]. Thus, optimum catalyst concentration has been found, 0.2 g/L, in order to avoid the excess of catalyst that ensure absorption of efficient photons brought about as a result of excess photocatalyst particles [17].

3.4. Effect of initial concentration of diazinon

Photocatalytic degradation of diazinon, after optimizing the pH conditions and catalyst concentration (pH 6 and catalyst dose 0.2 g/L), was carried out by varying the initial concentration of the diazinon from 12 to 450 mg/L.

As the concentration of diazinon was increased, the percentage of photodegradation decreased (Fig. 7).

In case of diazinon solutions of 12 and 16.5 mg/L, 100% degradation occurred within 90 min, and in cases of 22.5 and 38 mg/L, they took almost 120 min for the complete degradation and the percentage degradation further decreased on increasing the concentration of pesticide.

The possible explanation for this behavior is that increase in the initial concentration of diazinon can lead to the generation of high concentration of intermediates, which may adsorb on the surface of the catalyst that deactivate or block the catalytic sites of nano-TiO_2 and consequently, a reduction in the rate of degradation was observed. The other reason is at higher substrate concentration, the increased amount of reactant molecules may also occupy and/or block all the active catalytic sites present on the surface of the nano-TiO_2 and lead to decrease in degradation rate. Many researchers have reported similar results earlier [19,29].

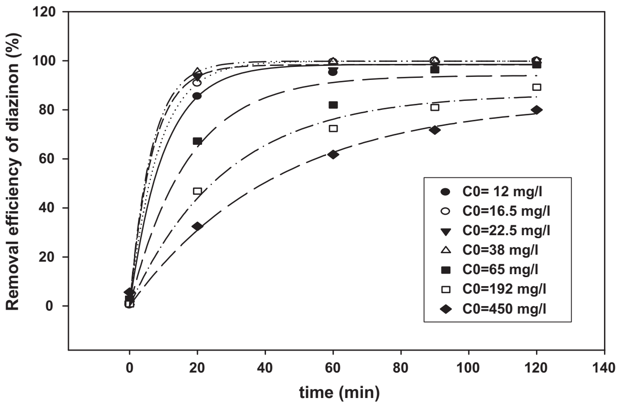


Fig. 7. Effect of initial concentration of diazinon on photocatalytic degradation in the presence of UV lamp (125 W) and aeration (3.5 L/min) and pH 6.

3.5. The study of kinetics and statistical calculations

Degradation rate constants (k, min^{-1}) of diazinon for the various conditions are shown in Table 3.

The maximum degradation rate was in UV/aeration/nano-TiO_2 condition (0.038/min). Kaur and Sud reported this rate for quinalphos (other organophosphate pesticide) equal to 0.00567/min [31].

Four independent variables varied at different levels were irradiation time (A), aeration (B), UV light (C), and $nTiO_2$ (*C*) concentrations and response functions are percent diazinon (Y_1) and COD (Y_2) removals.

p-values less than 0.05 indicate the model terms are significant. Based on the models and the related constraint conditions, numerical optimization was carried out with the help of Design Expert software version 7.0.0.1 considering each value of response. As shown in Table 4, it is clearly observed that variables (irradiation time, aeration and UV light) had significant effect on diazinon degradation [32]. However, based on *F* value, presence of UV light was the most strong factor that could affect the removal efficiency of diazinon (*F*-percent = 71%). The variations of nano-TiO_2 concentration had no significant effect on diazinon photodegradation that it can be due to the limitation of penetration of UV light in the reactor by enhancement of nano-TiO_2 concentration. The best condition for diazinon photodegradation (100%), in neutral pH and nano-TiO_2 concentration (0.55 g/L) with irradiation time of 95 min under UV irradiation and aeration, was determined through the experimen-

Table 3
Parameters (k and R^2) for pollutant degradation at various conditions. Nano-TiO_2 = 0.2 g/L; $(\text{diazinon})_0$ = 40 mg/L; pH 6

Conditions	Rate constant (min^{-1})	R^2
Adsorption only	0.001	0.97
Aeration only	0.005	0.98
UV/aeration	0.025	0.91
UV/aeration/*n*-TiO_2	0.038	0.97

Table 4
Results of ANOVA test of various variables for diazinon removal (Y_1). pH 6

Source	Sum of squares	df	Mean square	*F*-value	*p*-value
Model	100,569	36	2,793.6	48.6	< 0.0001
A- irradiation time (min)	39,481	4	9,870.2	171.7	< 0.0001
B-aeration (+/−)	3,951	1	3,950.7	68.7	< 0.0001
C-UV (+/−)	42,704	1	4,2704.0	743.0	< 0.0001
D-nTiO_2 (g/L)	742	3	247.2	4.3	0.9482
AB	1,273	4	318.3	5.5	< 0.0001
AC	11,291	4	2822.8	49.1	0.0097
AD	288	12	24.0	0.4	0.3090
BC	446	1	445.5	7.8	0.0011
BD	182	3	60.5	1.1	0.3789
CD	213	3	70.9	1.2	0.0079
Residual	2,471	43	57.5		
Cor total	103,041	79		1052.8	

Table 5
Results of ANOVA test of various variables for COD removal (Y_2). pH 6

Source	Sum of squares	df	Mean square	*F*-value	*p*-value
Model	19,048	24	794	108	<0.0001
A-irradiation time (min)	9,433	2	4,716	641	<0.0001
B-aeration (+/−)	438	1	438	60	<0.0001
C-UV (+/−)	4,941	1	4,941	672	<0.0001
D-nTiO_2 (g/L)	844	3	281	38	<0.0001
AB	223	2	111	15	<0.0001
AC	2,534	2	1,267	172	<0.0001
AD	431	6	72	10	<0.0001
BC	63	1	63	9	0.0076
BD	9	3	3	0	0.7573
CD	133	3	44	6	0.0035
Residual	169	23	7		
Cor total	19,217	47		1,623	

tal design used to model the behavior of the diazinon removal.

As shown in Table 5, statistical test confirmed that degradation efficiency of COD removal were significantly affected by the time of reaction, concentration of nano-TiO_2, presence of UV light, and aeration (p value < 0.05), however, based on F value, presence of UV light was the most strong factor that could affect the COD removal efficiency (F-ratio = 672/1,623). The results showed that presence of UV light can break the structure of diazinon molecules to intermediates while increasing the nano-TiO_2 concentration which can effectively mineralize the pollutants by reactions like hydroxylation, oxidation, and decarboxylation [28].

The best condition for COD removal (65.7%) was determined in neutral pH and nano-TiO_2 concentration (0.51 g/L) with irradiation time of 92 min under UV irradiation and aeration, while other study found out that the degree of diazinon mineralization was about 88% under UV irradiation after 3 h [33].

The degradation efficiency and COD removal increased rapidly with presence of UV light and O_2 in aeration [33]. As effects of operational parameters on photocatalytic degradation of diazinon are shown in Fig. 8, the condition of maximum degradation is due to presence of UV light, aeration, and catalyst.

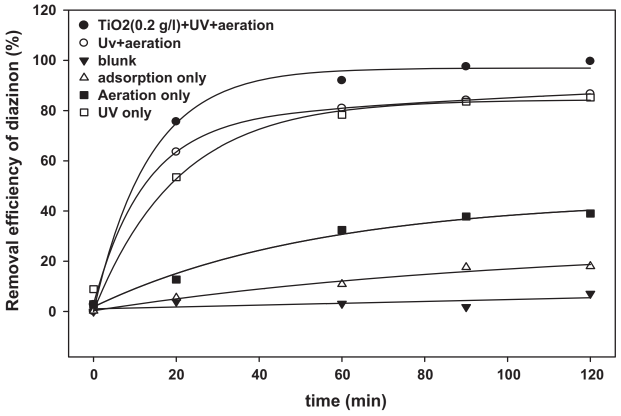


Fig. 8. Effect of various conditions of photocatalytic degradation of diazinon ($C_0 = 40$ mg/L) in the presence of UV lamp (125 W) and aeration (3.5 L/min) and pH 6.

4. Conclusions

Photocatalytic degradation of aqueous diazinon solution have been tested by using nano-TiO_2 as a photocatalyst, focusing on the influence of some parameters such as presence of UV irradiation, aeration, pH, nano-TiO_2 concentration, and time of reaction.

In this study, we have evaluated the photocatalytic degradation of diazinon using commercial P-25 nano-TiO_2. The rate of degradation and overall mineralization (COD) were used as the quantifying factors in determining the order of degradation of this pesticide.

The results of photocatalytic removal efficiency of diazinon were obviously affected by the aeration, irradiation time, and nano-TiO_2 dosage. The addition of electron acceptors, as aeration, enhanced the photodegradation rate of the pollutants. From the ANOVA test using Design Expert software version 7.0.0.1, variables (irradiation time, aeration, and UV light) had significant effect on diazinon degradation, however, presence of UV light was the most strong factor that could affect the removal efficiency of diazinon and the optimum conditions for diazinon degradation (100%) were found out, as dose of nano-TiO_2 0.55 g/L, with irradiation time of 95 min under UV irradiation and aeration. Degradation efficiency of COD removal were significantly affected by the time of reaction, dosage of nano-TiO_2, presence of UV light, aeration, however, presence of UV light was the most strong factor that could affect the COD removal efficiency. The best condition for COD removal (65.7%) was determined in neutral pH and nano-TiO_2 concentration (0.51 g/L) with irradiation time of 92 min under UV irradiation and aeration.

Acknowledgment

This study was financially supported by Vice-chancellor for Research Affairs of Tehran University of Medical Sciences (Project No. 12063). Authors highly appreciated of Mr M.R. Gholami and Mrs S. Ghasemi (Department of Chemistry, Sharif University of Technology, Iran) for their scientific assistance.

References

[1] Y. Nakaoka, H. Katsumata, S. Kaneco, T. Suzuki, K. Ohta, Photocatalytic degradation of diazinon in aqueous solution by platinized TiO_2, Desalin. Water Treat. 13 (2010) 427–436.

[2] M. Pirsaheb, A. Dargahi, S. Hazrati, M. Fazlzadehdavil, Removal of diazinon and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions by granular-activated carbon, Desalin. Water Treat. (2013) 1–6, doi: 10.1080/19443994.2013.801787.

[3] H. Shemer, K.G. Linden, Degradation and by-product formation of diazinon in water during UV and UV/H_2O_2 treatment, J. Hazard. Mater. 136 (2006) 553–559.

[4] N. Daneshvar, S. Aber, M.S.S. Dorraji, A.R. Khataee, M.H. Rasoulifard, Preparation and investigation of photocatalytic properties of ZnO nanocrystals: Effect of operational parameters and kinetic study, Int. J. Chem. Biomol. Eng. 1 (2008) 66–71.

[5] P.C.H. Li, E.J. Swanson, F.A.P.C. Gobas, Diazinon and its degradation products in agricultural water courses in British Columbia, Canada, Bull. Environ. Contam. Toxicol. 69 (2002) 59–65.

[6] M. Bavcon, P. Trebse, L. Zupancic-Kralj, Investigations of the determination and transformations of diazinon and malathion under environmental conditions using gas chromatography coupled with a flame ionisation detector, Chemosphere 50 (2003) 595–601.

[7] N. Daneshvar, S. Aber, M.S. Seyed Dorraji, A.R. Khataee, M.H. Rasoulifard, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light, Sep. Purif. Technol. 58 (2007) 91–98.

[8] M.B. Colovic, D.Z. Krstic, G.S. Uscumlic, V.M. Vasic, Single and simultaneous exposure of acetylcholinesterase to diazinon, chlorpyrifos and their photodegradation products, Pestic. Biochem. Physiol. 100 (2011) 16–22.

[9] N.M. Mahmoodi, M. Arami, N.Y. Limaee, K. Gharanjig, Photocatalytic degradation of agricultural N-heterocyclic organic pollutants using immobilized nanoparticles of titania, J. Hazard. Mater. 145 (2007) 65–71.

[10] J. Wu, L. Lin, T. Luan, Y.S. Chan Gilbert, C. Lan, Effects of organophosphorus pesticides and their ozonation byproducts on gap junctional intercellular communication in rat liver cell line, Food Chem. Toxicol. 45 (2007) 2057–2063.

[11] T.M. Sakellarides, D.E. Petrakis, P.J. Pomonis, T.A. Albanis, Removal of organophosphorus insecticides from aqueous solution by adsorption on microporous pillared clays and mesoporous alumina aluminum phosphates, Environ. Technol. 20 (1999) 1033–1044.

[12] Y. Zhang, W. Zhang, X. Liao, J. Zhang, Y. Hou, Z. Xiao, F. Chen, X. Hu, Degradation of diazinon in apple juice by ultrasonic treatment, Ultrason. Sonochem. 17 (2010) 662–668.

[13] M. Cycoń, M. Wójcik, Z. Piotrowska-Seget, Biodegradation of the organophosphorus insecticide diazinon by *Serratia* sp. and *Pseudomonas* sp. and their use in bioremediation of contaminated soil, Chemosphere 76 (2009) 494–501.

[14] J. Wu, C. Lan, G.Y.S. Chan, Organophosphorus pesticide ozonation and formation of oxon intermediates, Chemosphere 76 (2009) 1308–1314.

[15] K.A. Mohamed, A.A. Basfar, A.A. Al-Shahrani, Gamma-ray induced degradation of diazinon and atrazine in natural groundwaters, J. Hazard. Mater. 166 (2009) 810–814.

[16] Q. Wang, A.T. Lemley, Oxidation of diazinon by anodic Fenton treatment, Water Res. 36 (2002) 3237–3244.

[17] R. Pourata, A.R. Khataee, S. Aber, N. Daneshvar, Removal of the herbicide bentazon from contaminated water in the presence of synthesized nanocrystalline TiO_2 powders under irradiation of UV-C light, Desalination 249 (2009) 301–307.

[18] M. Farzadkia, A. Esrafili, M.A. Baghapour, Y.D. Shahamat, N. Okhovat, Degradation of metronidazole in aqueous solution by nano-ZnO/UV photocatalytic process, Desalin. Water Treat. (2013) 1–6, doi: 10.1080/19443994.2013.810322.

[19] J.K. Choi, H.S. Son, T.S. Kim, M.K. Stenstrom, K.D. Zoh, Degradation kinetics and mechanism of RDX and HMX in TiO_2 photocatalysis, Environ. Technol. 27 (2006) 219–232.

[20] S.K. Kansal, A. Hassan Ali, S. Kapoor, Photocatalytic decolorization of biebrich scarlet dye in aqueous phase using different nanophotocatalysts, Desalination 259 (2010) 147–155.

[21] C.S. Uyguner, S.A. Suphandag, A. Kerc, M. Bekbolet, Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques, Desalination 210 (2007) 183–193.

[22] APHA, Standard Methods for the Examination of Water & Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.

[23] A.V. Herrera-Herrera, M. Asensio-Ramos, J. Hernández-Borges, M.Á. Rodríguez-Delgado, Dispersive liquid–liquid microextraction for determination of organic analytes, TrAC. Trends Anal. Chem. 29 (2010) 728–751.

[24] M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, J. Chromatogr. A 1116 (2006) 1–9.

[25] M.V. Shankar, K.K. Cheralathan, B. Arabindoo, M. Palanichamy, V. Murugesan, Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by $TiO_2/H\beta$, J. Mol. Catal. A: Chem. 223 (2004) 195–200.

[26] G. Moussavi, H. Hosseini, A. Alahabadi, The investigation of diazinon pesticide removal from contaminated water by adsorption onto NH_4Cl-induced activated carbon, Chem. Eng. J. 214 (2013) 172–179.

[27] M.A. Hasnat, M.M. Uddin, A.J.F. Samed, S.S. Alam, S. Hossain, Adsorption and photocatalytic decolorization of a synthetic dye erythrosine on anatase TiO_2 and ZnO surfaces, J. Hazard. Mater. 147 (2007) 471–477.

[28] R. Vinu, S.U. Akki, G. Madras, Investigation of dye functional group on the photocatalytic degradation of dyes by nano-TiO_2, J. Hazard. Mater. 176 (2010) 765–773.

[29] M. Muneer, M. Qamar, M. Saquib, D.W. Bahnemann, Heterogeneous photocatalysed reaction of three selected pesticide derivatives, propham, propachlor and tebuthiuron in aqueous suspensions of titanium dioxide, Chemosphere 61 (2005) 457–468.

[30] H. Kawaguchi, Dependence of photocatalytic reaction rate on titanium dioxide concentration in aqueous suspensions, Environ. Technol. 15 (1994) 183–188.

[31] P. Kaur, D. Sud, Photocatalytic degradation of quinalphos in aqueous TiO_2 suspension: Reaction pathway and identification of intermediates by GC/MS, J. Mol. Catal. A: Chem. 365 (2012) 32–38.

[32] D. Klauson, M. Krichevskaya, M. Borissova, S. Preis, Aqueous photocatalytic oxidation of sulfamethizole, Environ. Technol. 31 (2010) 1547–1555.

[33] L. Liu, F. Chen, F. Yang, Y. Chen, J. Crittenden, Photocatalytic degradation of 2,4-dichlorophenol using nanoscale Fe/TiO_2, Chem. Eng. J. 181–182 (2012) 189–195.