

Heterogeneous photocatalytic degradation of diazinon in water using nano-TiO₂: Modeling and intermediates

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ABSTRACT

In this study, photocatalytic degradation of diazinon was investigated using commercial nano-TiO₂ as a photocatalyst. The operational parameters such as adsorption, aeration, pH and nano-TiO₂ dosage were investigated. Dispersive liquid-liquid microextraction (DLLME) technique was used to extract and pre-concentration of residual diazinon and by-products from the liquid samples and the analysis was applied by gas chromatography with flame ionization detector. The amount of diazinon mineralization was quantified by chemical oxygen demand (COD) experiment. The intermediates formed during the photocatalytic treatment were identified by using gas chromatography with mass spectrometric detection (GC/MS). Based on models and the related constraint conditions, numerical optimization with the help of Design Expert software version 7.0.0.1 considering each value of response, the best condition for diazinon photodegradation (100%) was achieved on pH value of 6 and nano-TiO₂ concentration (0.55 g/L) with irradiation time of 95 min under UV irradiation and aeration and the best condition for COD removal (65.7%) was determined in pH value of 6 and nano-TiO₂ concentration (0.51 g/L) with irradiation time of 92 min under UV irradiation and aeration. Maximum removal of diazinon and COD were due to UV irradiation (71%, 41%), exposure time (16%, 39%), aeration (7%, 4%) and increase concentration of nano-TiO₂ (0.4%, 2%) respectively. The main by-products, which were identified during diazinon photo-oxidation, were 2-isopropyl-6-methyl-pyrimidin-4-ol (IMP), 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon) and hydroxydiazinon, which some of them were less toxic than its parent compound. Generally, based on the results, the photocatalytic degradation could be useful method for the removal, mineralization and detoxification of wastewaters containing diazinon.

Keywords: Photocatalyst, Intermediates, Diazinon, TiO₂, DLLME

INTRODUCTION

Diazinon is an organophosphorus pesticide (OP) used to control a variety of insects in agriculture and household environment [1] and classified by the World Health Organization (WHO) as “moderately hazardous” Class II. It was associated with toxicity to aquatic organisms at concentration of 350 ng/L, and the fetal human doses were found to be in the range from 90 to 444 mg/kg [2]. They have replaced Organochlorine pesticides because of the low persistence and accumulation of OPs in the environment situations. Organophosphorus pesticides do not accumulate in organism bodies and they could be destructed easily in the environment [3]. Diazinon is relatively water soluble

(40 mg/L at 25 °C), 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 °C, and Henry's law constant of 1.4×10^{-6} atm m^3 mol $^{-1}$ which would indicate that it would not easily volatilize from soil or water [2, 4]. Like other OPs, the main toxic effect of diazinon is inhibition of acetyl cholinesterase activity by phosphorylation of the serine hydroxyl group in the substrate-binding domain of the enzyme which results in accumulation of acetylcholine and associated neurotoxicity [5]. In addition, researches have demonstrated that diazinon has immunotoxic, cytotoxic and genotoxic effects [6]. More recent researches have focused on new methods such as ultrasonic technique [6], biodegradation [7], Photodegradation[8], ozonation[9], Radiolytic degradation [10], Fenton treatment [11], UV/H₂O₂ treatment [2] and photocatalytic degradation [12]. When the nano- TiO₂ is irradiated with UV lamp, valence band holes (h_{vb}) and conduction band electrons (e_{cb}) are generated. OH radicals generated through water oxidation by photo-generated valence band holes, are known to be the most oxidizing species [13]. OH radicals react with diazinon molecules leading to the generation of numerous oxidation byproducts. In the presence of air, other species, such as H₂O₂ or even superoxide radicals, might contribute to the oxidation of the diazinon molecules. However, the dissipation of diazinon in aqueous solutions by nanophotocatalytic processes has rarely been studied which is effective technique to removal of recalcitrant contaminants. Therefore, in the present study, the photodegradation of diazinon in aqueous solution under UV irradiation and suspension of nano-TiO₂ was investigated. The effect of factors including initial concentration of nano-TiO₂, pH of solution and initial concentration of pesticide on the degradation of diazinon was investigated in a bench-scale photoreactor. In addition, degradation products of diazinon were identified by GC/MS instrument.

MATERIALS AND METHODS

In this study thenano-TiO₂ powder (P-25, mainly in anatase form) were purchased from Degussa. Table 1 shows specifications of nano-TiO₂ powder. High-Purity of diazinon was purchased from Sigma–Aldrich that its chemical characteristics are listed in Table 2. In order to prepare the standard solution, 250 mg of pure diazinon was added to 5mL of absolute methanol and prepared 16×10^{-2} M solution and ten standard dilutions were then prepared by distilled and deionized water (DDW). Standard solutions were protected from light, and stored at 4 °C. Calibration of GC/FID prepared from 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. Chlorobenzene, Sulfuric acid, Sodium Hydroxide, (KCr₂O₇), (Ag₂SO₄), (HgSO₄) (Analytical grade), methanol and Acetone (HPLC grade) were Obtained from Merck Co.(Germany). Photocatalytic experiments were carried out in a 3 L cylindrical stainless steel reactor which improve 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.

<i>Parameters</i>	<i>Description</i>
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[25]	6.3
Crystalline phase	Anatase: 80% Rutile: 20%

<i>Parameters</i>	<i>Description</i>
Molecular formula	C ₁₂ H ₂₁ N ₂ O ₃ PS
Mw (g/mol)	304.3
Density (g/ml) (20 °C)	1.11
Solubility (mg/L) (20 °C)	40
WHO class	II
LD ₅₀ (Daphnia) (mg/kg)	1.4

The UV exposure source (Fig. 1-a) was provided by OSRAM (125W) high-pressure (HP) UV lamp (310-450 nm) installed inside the inner quartz tube in the reactor. Photocatalytic degradation studies of diazinon were performed in the batch reactor (Fig. 1-b). Oxygen was introduced to the reactor from an air pump at regulate flow rate of 3.5 L/min. Solutions with the desired diazinon concentration and nano-TiO₂ loading were fed into the reactor and the initial pH was adjusted by addition of either NaOH or HCl solutions (1M). 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 of that 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 [14].

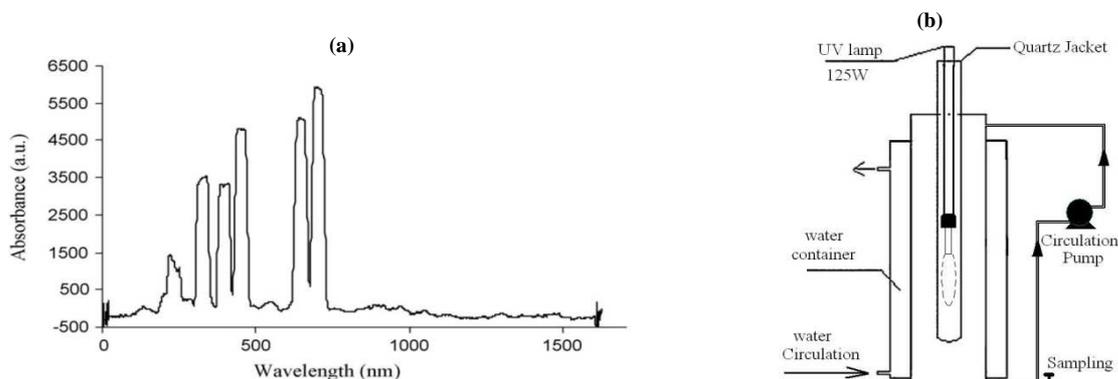


Fig 1: (a) Spectrum distribution of the UV irradiation source provided by OSRAM (125W) lamp, (b) Scheme of Cylindrical photocatalytic reactor

The concentration of diazinon and COD in each degraded sample was determined by using calibration curve (Fig. 2). The degradation of pesticide have been investigated under variable conditions: (pH, Diazinon dosage, nano-TiO₂ dosage, time, Presence or absence of UV and aeration). Sampling was carried out from 0 to 120 min in time intervals of 20 min. To eliminate the nano-TiO₂ particles, Samples (ca. 12 mL) were filtered by 0.22- μm pore polytetrafluoroethylene syringe filters (PTFE) and centrifuged in 5000 RPM for 10 min.

A new microextraction technique is known dispersive liquid-liquid microextraction (DLLME) was applied to extract diazinon from aqueous phase to solvent phase which is a very simple and rapid method for extraction and pre-concentration of organic pesticides from water samples^[15]. 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 are injected into the aqueous sample (10.0 mL) by syringe, rapidly. After 3 minutes 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. Diazinon was analyzed using a CP 9001 Chrompack gas chromatograph with flame ionization detector equipped with an HP-5 capillary column (30 m \times 0.32 mm \times 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. The metabolites formed during the degradation were monitored using a GC/MS supplied by Agilent, USA, and a temperature program were as follows: the temperature of the column was initially set at 50 °C for 2 min, then increased by 10 °C per min to 280 °C and maintained at this isothermal temperature for the final 5 min. Injector temperatures was set at 250. Helium was used as a carrier gas at a flow rate of 1.0 mL/min and the injections were made in the split mode with a split ratio of 1:2. The kinetic study using nano-TiO₂ (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 optimum of pH. Pseudo-first-order model expression was used to calculate the photocatalytic deradation rate using the kinetic study data. The kinetic expression is given by Eq. 1:

$$\ln(C/C_0)=kt \quad (\text{Eq. 1})$$

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 ANOVA test to statistically compare the diazinon photo-degradation efficiency in different variable parameters. In order to evaluate the effect of conditions of time reaction, nano-TiO₂ 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.

RESULTS AND DISCUSSION

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-TiO₂ 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

circulating, and then filtered after being centrifuged. The effect of pH (initially at 4, 6, 7, 8, 10) on degradation of diazinon is shown in Fig. 3. The maximum degradation of diazinon was achieved at pH 6.

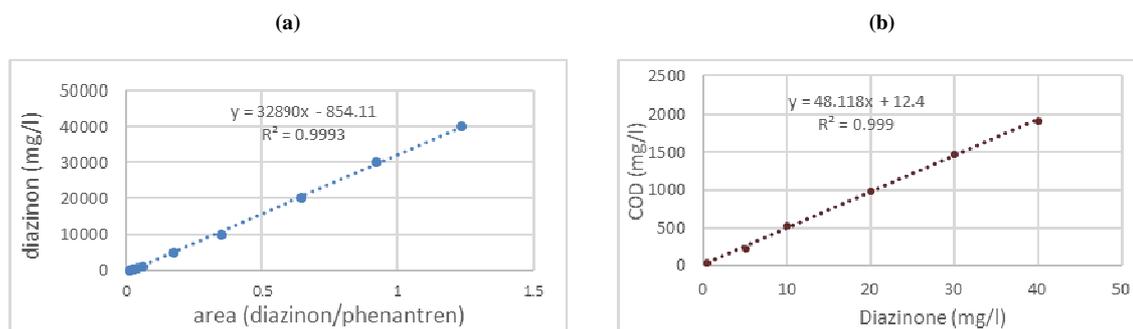


Fig 2:(a) Calibration curve for the determination of diazinon concentration in aqueous solution (b) Calibration curve for the determination of COD of various concentration of diazinon

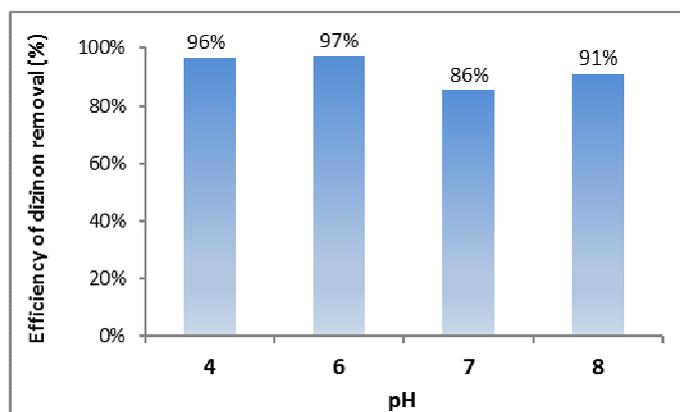


Fig 3: Effect of initial pH on photocatalytic degradation of diazinon at irradiation times of 60 min. $[\text{diazinon}]_0 = 40 \text{ mg/L}$; $[\text{nano-TiO}_2] = 400 \text{ mg/L}$



By using Eqs. (2) and (3), the pH_{pzc} of TiO_2 can be calculated as $\text{pH}_{\text{pzc}} = (\text{p}K_{a1} + \text{p}K_{a2})/2$. 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 [16]. The nano- TiO_2 catalyst surface will be charged negatively when $\text{pH} > \text{pzc}$, positively when $\text{pH} < \text{pzc}$ and neutrally when $\text{pH} \approx \text{pzc}$. 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 $\text{p}K_a$ for diazinon is 2.6 [17]. It is negatively charged above $\text{pH} 2.6$, whereas catalysts are positively charged below $\text{pH} 6.5$. As expected, optimal conditions were found at $\text{p}K_a^{\text{diazinon}} < \text{pH} < \text{pH}_{\text{pzc}}^{\text{TiO}_2}$ 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 hydrogen bonding easily and thus elevates the amount of adsorption and enhance the decomposition rate. Hasnat *et al.* reported similar findings during comparative photocatalytic studies of decolorization of an anionic and a cationic dye [18].

Effect of photocatalyst dosage

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. 4 shows the effect of catalyst loading on the decolorization of diazinon at optimum pH. It can be seen that the rate of photo-degradation 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. Because the removal efficiency of pesticide by photocatalyst loading from 0.2 to 0.6 g/L for reaction time of 120 min were 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 [13, 19]. Thus

optimum catalyst concentration has been found 0.2 g/L in order to avoid the excess of catalyst, ensure absorption of efficient photons and brought about as a result of excess photocatalyst particles [20]. As shown in Fig. 5, the removal of COD derived from diazinon content effluents is looser than the degradation trend of diazinon pollutant which may be due to the formation of smaller intermediates [13]. Applying of nano-TiO₂ (0.2 g/l) can increase the efficiency of pesticide removal significantly (13%) in compare with the case of no applying nano-particles during 90 min, 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-TiO₂ and generation of hydroxyl radicals, Although UV irradiation can effectively remove diazinon [2, 21].

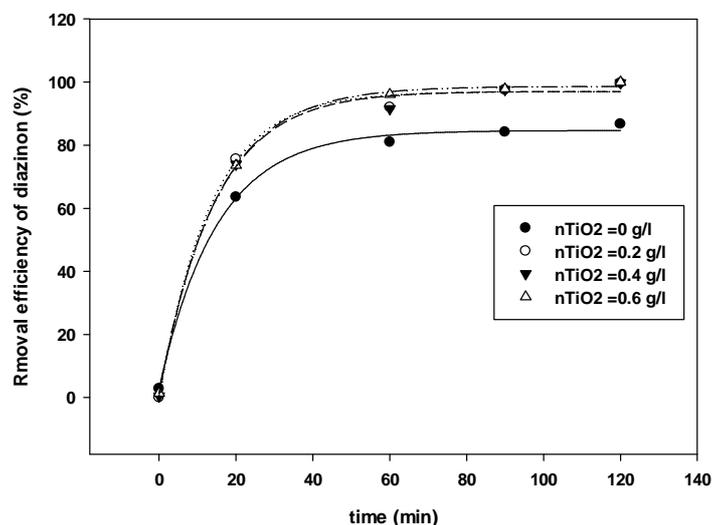


Fig 4: Effect of nano-TiO₂ dosages on photocatalytic degradation of diazinon ($C_0=40$ mg/L) in presence of UV lamp(125W) and aeration (3.5 L/min) and pH:6

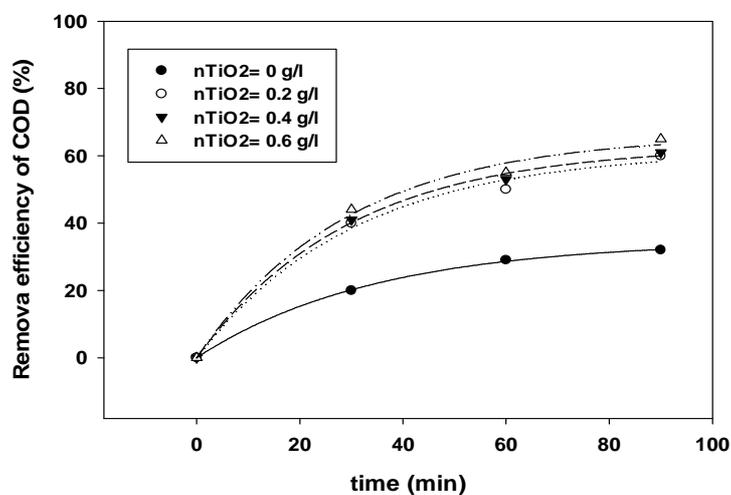


Fig 5: Effect of nano-TiO₂ dosages on COD degradation of diazinon ($C_0=40$ mg/L) in the presence of UV lamp(125W) and aeration (3.5 L/min) and pH:6

Modeling and kinetic studies

Degradation rate constants (k , min^{-1}) of diazinon for the various conditions were shown in Table 3. the maximum degradation rate was in UV/ aeration/ n-TiO₂ condition (0.038 min^{-1}). Kaur and sud reported this rate for quinalphos (other organophosphate pesticide) equal to 0.00567 min^{-1} [22].

Table 3: Parameters (k and R^2) for pollutant degradation at various conditions; Nano-TiO₂ = 0.2 g/l; (diazinon)₀ = 40 mg/l; pH : 6

Conditions	Rate constant (min^{-1})	$T_{1/2}$ (min)	R^2
Adsorption only	0.001	> 11 h	0.97
Aeration only	0.005	140 min	0.98
UV/ aeration	0.025	31 min	0.91
UV/ aeration/ n-TiO ₂	0.038	19 min	0.97

Four independent variables varied at different levels were irradiation time (A), aeration (B), UV light (C), and nTiO₂ (D) concentrations and response functions are percent diazinon (Y₁) and COD (Y₂) removals. 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 [23]. However, based on F value, presence of UV light was the most strength factor that could affect the removal efficiency of diazinon (F-percent = 71%). The variations of nano-TiO₂ concentration had no significant effect on diazinon photo-degradation that it can due to limitation of penetration of UV light in the reactor by enhancement of nano-TiO₂ concentration. The best condition for diazinon photodegradation (100%) in pH value of 6 and nano-TiO₂ concentration (0.55 g/L) with irradiation time of 95 min under UV irradiation and aeration, was determined through the experimental design were 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-TiO₂, presence of UV light, aeration (P value<0.05), however, based on F value, presence of UV light was the most strength factor that could affect the COD removal efficiency (F-ratio = 672/1623). The results showed that presence of UV light can break the structure of diazinon molecules to intermediates while increasing the nano-TiO₂ concentration can effectively mineralized the pollutants by reactions like hydroxylation, oxidation and decarboxylation [21].

Table 4: Analysis of variance (ANOVA) test of various variables for diazinon removal (Y₁). pH : 6

Source	Sum of squares	df	Mean square	F-Value	p-Value
Model	100569	36	2793.6	48.6	< 0.0001
A- irradiation time (min)	39481	4	9870.2	171.7	< 0.0001
B-aeration (+/-)	3951	1	3950.7	68.7	< 0.0001
C-UV (+/-)	42704	1	42704.0	743.0	< 0.0001
D-nTiO ₂ (g/l)	742	3	247.2	4.3	0.9482
AB	1273	4	318.3	5.5	< 0.0001
AC	11291	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	2471	43	57.5		
Cor total	103041	79		1052.8	

Table 5: Results of Analysis of variance (ANOVA) test of various variables for COD removal (Y₂). pH : 6

Source	Sum of squares	df	Mean square	F-Value	p-Value
Model	19048	24	794	108	< 0.0001
A- irradiation time (min)	9433	2	4716	641	< 0.0001
B-aeration (+/-)	438	1	438	60	< 0.0001
C-UV (+/-)	4941	1	4941	672	< 0.0001
D-nTiO ₂ (g/l)	844	3	281	38	< 0.0001
AB	223	2	111	15	< 0.0001
AC	2534	2	1267	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	19217	47		1623	

The best condition for COD removal (65.7%) was determined in pH value of 6 and nano-TiO₂ concentration (0.51 g/L) with irradiation time of 92 min under UV irradiation and aeration while other study find out that the degree of diazinon mineralization was about 88% under UV irradiation after 3 h [24].

The degradation efficiency and COD removal increased rapidly with presence of UV light and O₂ in aeration [25]. As effect of treatment on parameters of photocatalytic degradation and mineralization of diazinon are shown in Fig. 6 and table 6, maximum condition of degradation is due to presence of UV light, aeration and catalyst.

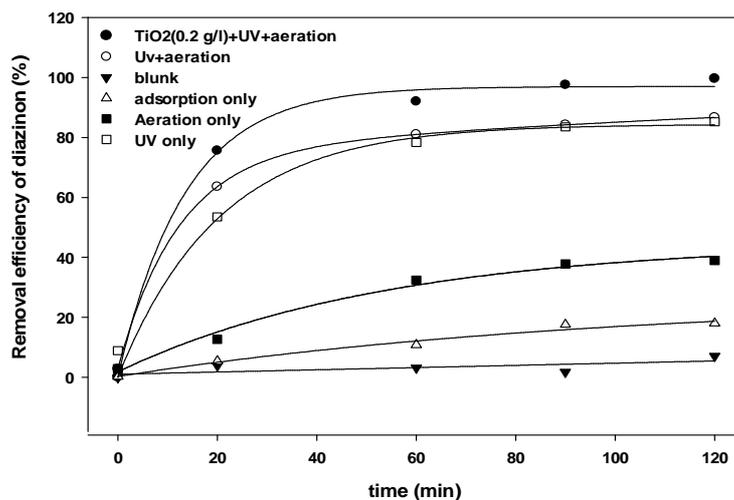


Fig 6: Effect of various conditions of photocatalytic degradation of diazinon; ($C_0=40$ mg/L) in the presence of UV lamp(125W) and aeration (3.5 L/min) and pH:6

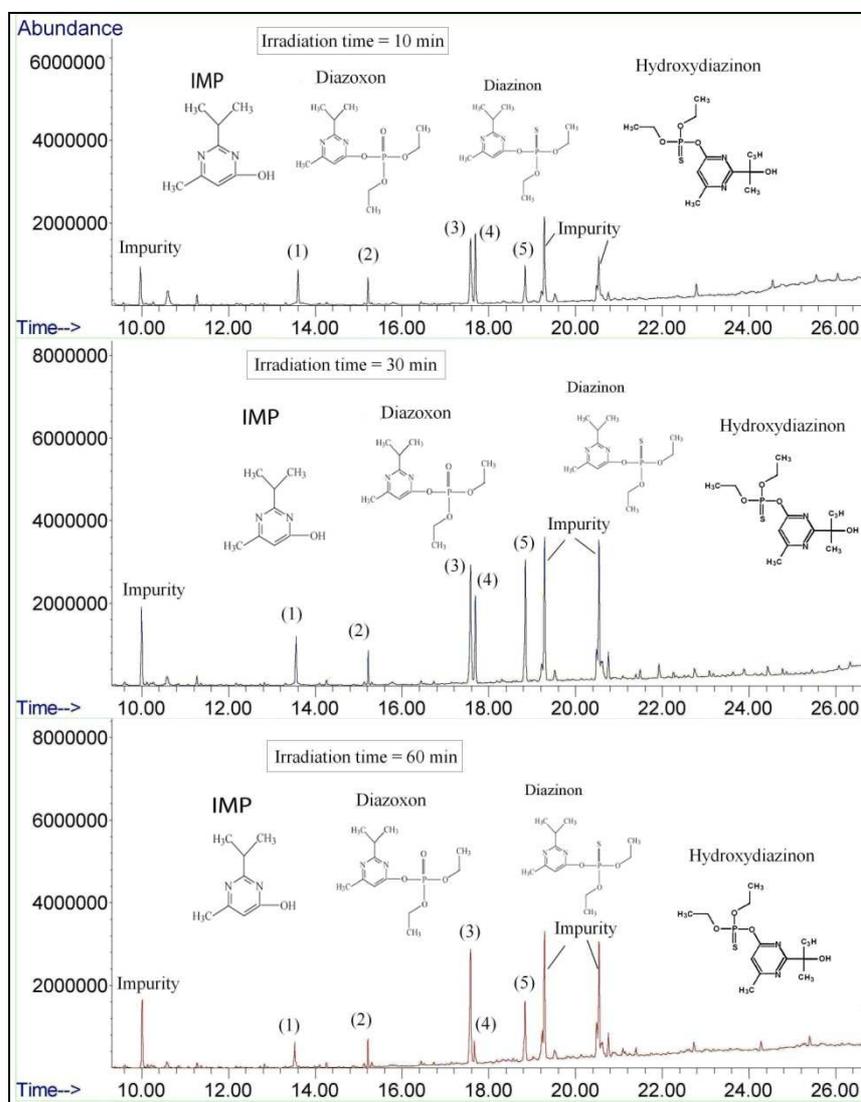


Fig 7: Mass spectrum of catalytic photo-degradation intermediates of diazinon at concentration level of 20 µg/L. [(1). 2-isopropyl-6-methyl-pyrimidin-4-ol(IMP), (2). 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon), (3). Phenanthrene (internal standard), (4). Diazinon, (5). Hydroxydiazinon]

Table 5: Effect of various conditions on diazinon mineralization; ($C_0= 40$ mg/L) in the presence of UV lamp(125W) and aeration (3.5 L/min) and pH:6

Nano-TiO ₂ +UV+air	Reaction time (min)	Nano-TiO ₂ dosage			
		0 (g/l)	0.2 (g/l)	0.4 (g/l)	0.6 (g/l)
Nano-TiO ₂ +UV+air	60	29%	50%	50%	51%
	90	38%	60%	61%	65%
only adsorption	60	2%	8%	12%	14%
	90	4%	15%	16%	17%
Nano-TiO ₂ +air	60	10%	14%	15%	17%
	90	14%	20%	21%	22%
Nano-TiO ₂ +UV	60	21%	35%	37%	40%
	90	30%	42%	45%	54%

Intermediates monitoring of diazinon

During the photocatalytic degradation of diazinon, using nano-TiO₂ as the photocatalyst, various organic intermediates were produced as the mass spectrums are shown in Fig. 7 at three irradiation time. By GC/MS analysis, the three main byproducts were identified during diazinon photo-oxidation. In this study by-products such as 2-isopropyl-6-methyl-pyrimidin-4-ol (IMP), 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon) and hydroxydiazinon were found. These intermediates have been reported in a previous study [2, 4, 26]. Diazinon is rapidly hydrolyzed at acidic pH in to (IMP) and diethyl thiophosphate as the main by-products [2, 5, 16a]. IMP is less toxic than its parent compound [2]. Most of the by-products produced during the middle of the irradiation and, as time progressed, they gradually disappeared. The photo-degradation of diazinon by nano-TiO₂ was observed to proceed mainly through a hydroxylation mechanism occurring rapidly by attack of the hydroxyl radicals. The main transformation intermediates identified were oxidation products of the isopropyl group of diazinon and its oxygen analogue diazoxon [24, 27] and the final products, as reported for other recalcitrant materials, were low chain carboxylic acids [28-30].

CONCLUSION

Photocatalytic degradation of aqueous diazinon solution have been tested by using nano-TiO₂ as a photocatalyst, focusing on the influence of some parameters such as presence of UV irradiation, aeration, pH, nano-TiO₂ concentration and time of reaction. In this study, we have evaluated the photocatalytic degradation of diazinon using commercial P-25 nano-TiO₂. The rate of degradation and overall mineralization (COD) were used as the quantifying factors in determining the order of degradation these pesticide. The results of photocatalytic removal efficiency of diazinon were obviously affected by the aeration, irradiation time and nano-TiO₂ dosage. The addition of electron acceptors, as aeration, enhanced the photo-degradation 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 strength factor that could affect the removal efficiency of diazinon and the optimum conditions for diazinon degradation(100%) were found out as dose of nano-TiO₂ 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-TiO₂, presence of UV light, aeration, however, presence of UV light was the most strength factor that could affect the COD removal efficiency. The best condition for COD removal (65.7%) was determined in pH value of 6 and nano-TiO₂ concentration (0.51 g/L) with irradiation time of 92 min under UV irradiation and aeration. Three main degradation products were identified of the photocatalytic degradation of diazinon were proposed. This analysis during the degradation process could be a useful source of information on the degradation pathways and reduced toxicity of parent pesticide. Generally, based on the results, the photocatalytic degradation could be useful method for the removal, mineralization and detoxification of wastewaters containing diazinon.

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