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Photocatalytic degradation of diazinon in aqueous solution by platinized TiO_2

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ABSTRACT

The photocatalytic degradation of diazinon, which is one of phosphorothiate insecticides, was carried out in the presence of platinized TiO_2 photocatalyst. The degradation rate was strongly influenced by the pH, catalyst dosage and light intensity. In addition, platinization was found to increase the rate of diazinon degradation. When 0.5 wt% of platinum was deposited onto the surface of TiO_2, an initial diazinon concentration of 30 mg L^{-1} was completely degraded after 30 min. Furthermore, the first-order rate constant for diazinon degradation by Pt-TiO_2 was 2.5 times higher than P-25 TiO_2. The decrease of TOC as a result of mineralization of diazinon was observed during the photocatalytic process. The degree of diazinon mineralization was about 88% under UV irradiation after 30 h. The formations of sulfate, phosphate, nitrate and ammonium ions as end-products were observed during the photocatalytic system. The decomposition of diazinon gave six kinds of intermediate products. The degradation mechanism of diazinon was proposed on the base of the evidence of the identified intermediates. Based on these results, the photocatalytic reaction by Pt-TiO_2 could be useful technology for the treatment of wastewater containing diazinon.

Keywords: Diazinon; Photocatalyst; Titanium dioxide; Platinum; Mineralization

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1. Introduction

Diazinon [*O,O*-diethyl *O*-(2-isopropyl-6-methylpyrimidin-4-yl) thiophosphate] is an organophosphorus insecticide with widespread agricultural and non-agricultural uses. The primary environmental concerns associated with its use are bird kills, contamination of surface water, and impacts on aquatic species. Diazinon and its metabolites have been encountered during monitoring studies in various aquatic systems all over the world [1–3]. Additionally, high diazinon residues have been found in urban waterways and effluents from sewage treatment plants [4,5].

Toxic effects of diazinon are due to the inhibition of acetylcholinesterase. Metabolic studies in animals have shown that the main route of metabolism is oxidation, and several metabolites with higher acetylcholinesterase inhibition activity have been identified [6]. Because of the great risk that it poses to human health and the environment, diazinon use has been reviewed by many European environmental agencies in the past decade. Recently the U.S. Environmental Protection Agency announced a three-year phase-out of diazinon for indoor use, because it is one of the leading causes of acute insecticide poisoning of humans and wildlife [7]. Since diazinon can also affect the nervous system of humans, concern about its use arises from the large amount applied and the production of rinse water from

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containers and application equipment. Therefore, the rapid and simple wastewater treatment of diazinon is now required urgently.

The oxidation of diazinon by ozone [8] and aqueous chlorine [9] has been reported. A specific ozone generator is needed for ozonation treatment, and aqueous chlorine treatment is suspected of yielding some hazardous chlorinated organic compounds during the process [10]. Compared with these two treatment technologies, the Fenton [11] and TiO_2 [12] treatments may be simpler and safer. Especially, photocatalytic method (TiO_2) is highly promising because it can operate at ambient temperature and pressure with low energy photons, and does not require expensive catalyst. Previously, the photocatalytic degradation of diazinon has been reported by other researchers [12–15]. However, its wide band-gap energy (3.0 eV for rutile and 3.2 eV for anatase) means that only 5% of solar spectrum can be used. Moreover, TiO_2 presents a relatively high electron-hole recombination rate, which is detrimental to its photocatalytic activity. In order to solve these problems, one of the approaches is that noble metals are doped onto TiO_2 surface. Many investigators have demonstrated that the photocatalytic activity may be enhanced by impregnating the surface of titanium dioxide with noble metals [16–19].

In the present study, we have investigated the degradation and mineralization of diazinon in water using of platinized TiO_2. The many factors, such as Pt doping concentration, catalyst dosage, pH value, and light intensity, affected on the photocatalytic degradation were evaluated. The progress of mineralization of diazinon was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the intermediate products of diazinon during this photocatalytic process have been identified by gas chromatography–mass spectrometry (GC/MS). The degradation pathway was proposed on the basis of intermediates formed.

2. Experimental

2.1. Reagents

Diazinon was supplied by Wako Pure Chemical Industries (Osaka, Japan) and was used as received. The solubility of diazinon in water is 60 mg L^{-1}. TiO_2 powder from Degussa (P-25) was used throughout the experiments. Dihydrogen hexachloroplatinate hexahydrate (Wako Pure Chemical Industries, Osaka, Japan) was used as the platinum precursor. All other chemicals and solvents were of the purest grade commercially available and were used without further purification. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity > 18 MΩcm.

2.2. Preparation of Pt-TiO_2

Platinized TiO_2 catalysts were prepared by impregnation method. The required amount of dihydrogen hexachloroplatinate (VI) hexahydrate solution for doping was added to the calculated amount of TiO_2 (P-25) in such a way that they wet the catalyst completely. The slurry was stirred for 1 h at 90 °C in the presence of H_2PO_3 and dried overnight in an air oven at 110 °C. The dried powder was subjected to calcination in air atmosphere at 500 °C for 5 h and then cooled to room temperature. This preparation method was also described in the previous report [20].

2.3. Photocatalytic degradation procedure

Photocatalytic experiments were conducted in a 50 ml Pyrex glass cell. 30 mL of diazinon solution and the precise amounts of platinized TiO_2 catalysts were added into the reaction cell. The pH of the sample solution was adjusted with HCl and/or NaOH solution. The initial concentration of diazinon in all experiments was 30 mg L^{-1} (1×10^{-4} mol L^{-1}). Reaction temperature was kept at 25 ± 1 °C with a water bath. In all the studies, diazinon solution containing the appropriate quantity of the photocatalyst powder was magnetically stirred before and during irradiation. The sample solution was irradiated with a Xe lamp (990 W, Ushio Electronics Co.). The beam was parallel and the distance between lamp and the reactor wall was 10 cm. The lamp was warmed up for 10 min to reach constant output. In this case, the short UV radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The intensity of the light was measured by a UV radio meter (UVR-400, Iuchi Co.) with a sensor of 320–410 nm wavelength. The radio meter was set up at the same position as the reactor.

2.4. Analyses

After irradiation, Pt-TiO_2 was separated through the 0.45-μm Advantec membrane filter. The progress in the degradation of diazinon was followed with a HPLC (GL Science Co., Tokyo, Japan) equipped with a GL-7450 UV detector (GL Science Co.) and a Inertsil ODS-2 separation column (150 mm × 4.6 mm i.d., GL Science Co.). The elution was monitored at 250 nm. The mobile phase was a mixture of acetonitrile and water

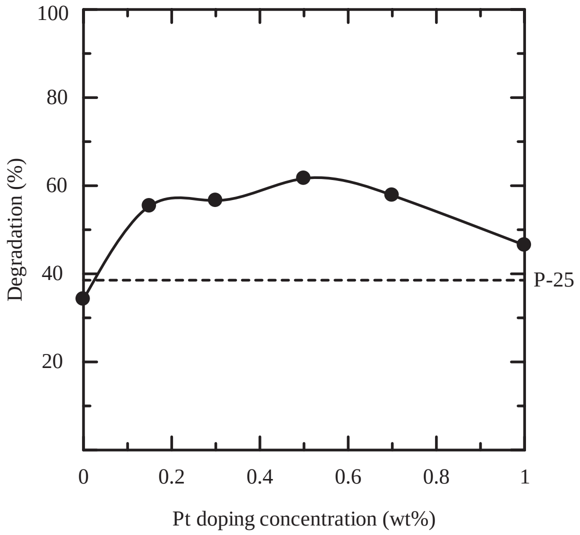


Fig. 1. Effect of platinum doping concentration on the photocatalytic degradation of diazinon. (Catalyst dosage: 10 mg; pH: 4.3; light intensity: 1.5 mW cm^{-2}; irradiation time: 10 min).

(10/90, v/v), and was pumped at a flow rate of 1.0 mL min^{-1}.

The progress of mineralization of diazinon was monitored by measuring the TOC. TOC of the sample solution was measured with a Shimadzu TOC analyzer (TOC-V$_E$) based on CO_2 quantification by non-dispersive infrared analysis after high-temperature catalytic combustion. The formations of anions and cations were analyzed by ionic chromatography using a Metrohm Compact IC 7611 equipped with a Shodex anionic (IC SI-90 4E) and a Shodex cationic (IC YK-421) columns, respectively.

XRD were collected using a RINT 2000/PC X-ray diffractometer (Rigaku Co.), with a diffraction angle range $2\theta = 10–80°$ using Cu Kα radiation. The mass fraction of rutile (X_R) in the calcined samples was calculated by Spurr formula (Eq. (1)) which is the relationship between integrated intensities of anatase (1 0 1) and rutile (1 1 0) peaks where I_A and I_R are the integrated peak intensities of anatase and rutile peaks, respectively.

$$X_R = 1/1 + 0.8(I_A/I_R) \tag{1}$$

Particle size was determined by the Scherrer equation which calculates crystalline size using the expression $(0.9\lambda/(\beta \cos\theta))$, where λ is the X-ray wavelength, θ is the Bragg angle and β is the line broadening.

The photo-products during the photocatalytic degradation of diazinon were extracted with dichloromethane (2 mL × 3). The combined organic fraction was dried by Na_2SO_4, and concentrated under N_2 flow. A GC/MS (Shimadzu GC-MS 5050A) was used for separation and detection of the intermediate products. The GC was equipped with a HP-5 capillary column (30 m × 0.25 mm i.d.) in helium carrier gas (1.5 mL min^{-1}) and with splitless injection system. The GC oven temperature was programmed to hold 40 °C for initial 3 min, to increase from 40 to 200 °C at a rate of 5 °C min^{-1}, to 210 °C at a rate of 1 °C min^{-1} (2 min) and to 270 °C at a rate of 20 °C min^{-1} (3 min). The injector and interface temperatures were kept at 250 and 280 °C, respectively. Mass spectra were obtained by the electron-impact (EI) mode at 70 eV using the full scan mode.

3. Results and discussion

3.1. *Effect of variables on the photocatalytic degradation of diazinon*

Effect of Pt doping concentration on the degradation of diazinon was examined in the range of 0–1.0 wt%. The results are shown in Fig. 1. The degradation percentage of diazinon gradually increased with increasing Pt doping concentration up to 0.5 wt%. Although TiO_2 samples platinized over the range of 0.7–1.0 wt% Pt enhanced the photocatalytic activity for P-25 TiO_2, the degradation percentage was lower than 0.5 wt% Pt sample. It was therefore concluded that the optimum platinum doping in this study for diazinon degradation was 0.5 wt%.

The X-ray diffraction patterns of P-25 TiO_2 and Pt-TiO_2 are shown in Fig. 2. The diffraction patterns of Pt-TiO_2 samples almost were in agreement with that of P-25 TiO_2 showing no diffraction peaks due to Pt suggesting that the Pt particles were well dispersed on TiO_2 surface. In addition, the crystal sizes of anatase and rutile phases calculated from the XRD patterns are presented in Table 1, together with the mass fractions of anatase and rutile phases. As can be seen Fig. 2 and Table 1, there are no diffraction patterns characteristics of the doped samples in the XRD patterns. Therefore, these parameters of TiO_2 were not changed by doping Pt.

On the other hand, the improved photocatalytic activity of TiO_2 for the degradation of organic compounds in aqueous systems by platinization has also been reported by other researchers [21–26]. The observed increase in photocatalytic activity of TiO_2 by platinization was attributed to the enhanced separation of electron-hole pairs within TiO_2. When platinum species are deposited onto the surface of TiO_2, a Schottky junction at the platinum–TiO_2 interface is formed [27]. As a result, electrons are transferred from the conduction band of TiO_2 to platinum and became

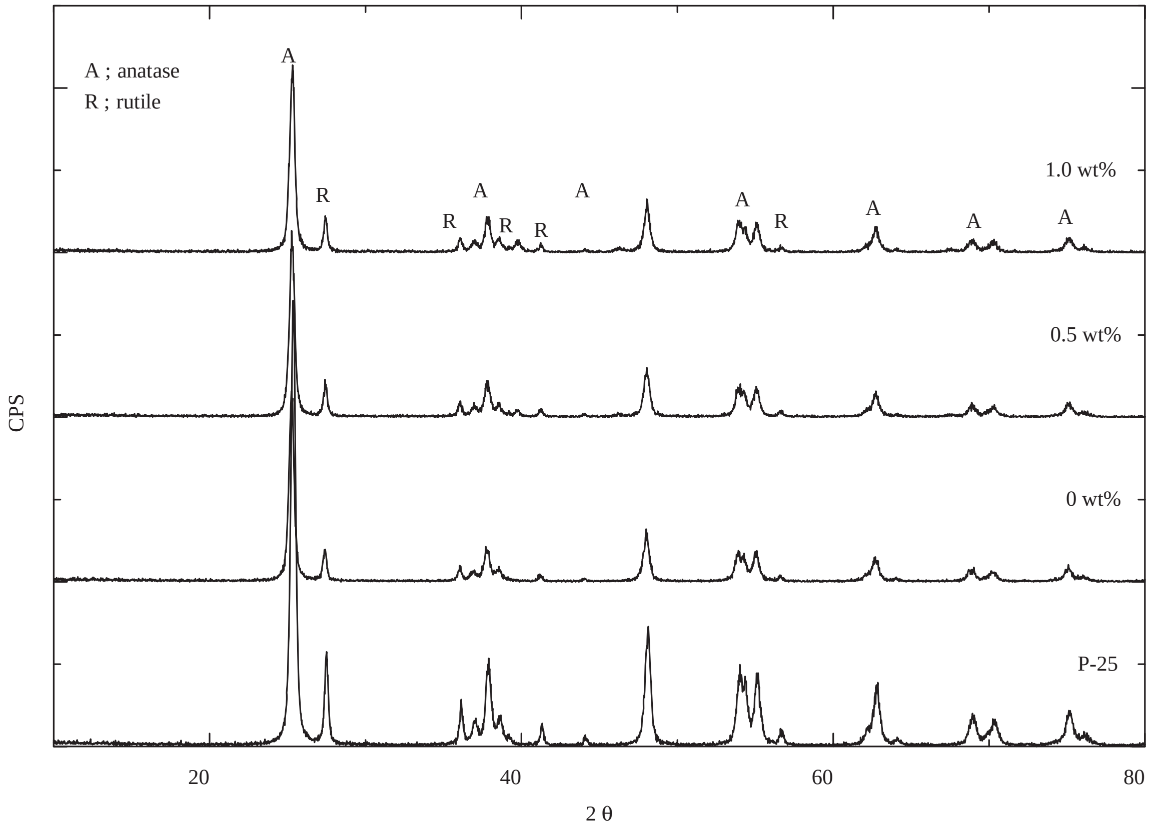


Fig. 2. XRD patterns of TiO_2 containing various platinum contents. A: anatase; R: rutile.

trapped there. This trapping mechanism slows down the recombination reaction of electron-hole pairs and allows a more efficient charge separation. Consequently, the transfer of trapped electrons to dissolved oxygen in the system become faster and more holes and hydroxyl radicals are available for the oxidation of the target organic pollutants on the catalyst surface as well as in the solution phase. However, when the doping of the platinum was increased, platinum deposits could block the surface of TiO_2 and decrease the absorption of UV photons. This was evidenced by the lower photocatalytic activity for the degradation over the range of 0.7–1.0 wt% Pt in this study.

In order to optimize Pt-TiO_2 suspension concentration, effect of the photocatalyst dosage on the degradation of diazinon in aqueous solution was investigated as presented in Fig. 3. The degradation efficiency increased with increasing the dosage up to 20 mg, and then the efficiency became nearly flat. When the suspension concentration of Pt-TiO_2 increased above the limiting value of 20 mg, the number of active sites on the Pt-TiO_2 surface may become almost constant because of the decreased light penetration, the

Table 1
Characteristics of TiO_2 containing various platinum contents

Platinum content (wt%)	Anatase		Rutile		Diazinon degradation after 10 min (%)
	Cristal size, $D_{(101)}$ (nm)	X_A (%)	Cristal size, $D_{(110)}$ (nm)	X_R (%)	
[P-25]	23	84	30	16	39
0	22	87	28	13	34
0.5	22	86	29	14	61
1.0	23	86	34	14	46

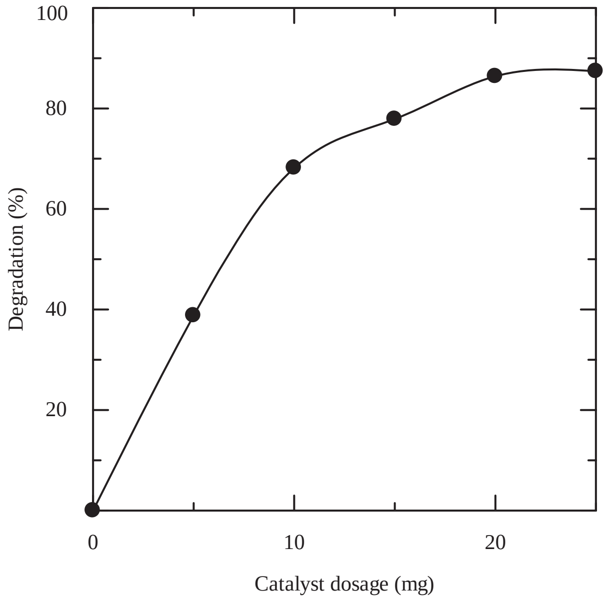


Fig. 3. Effect of catalyst dosage on the photocatalytic degradation of diazinon. (pH: 4.3; light intensity: 1.5 mW cm^{-2}; irradiation time: 10 min).

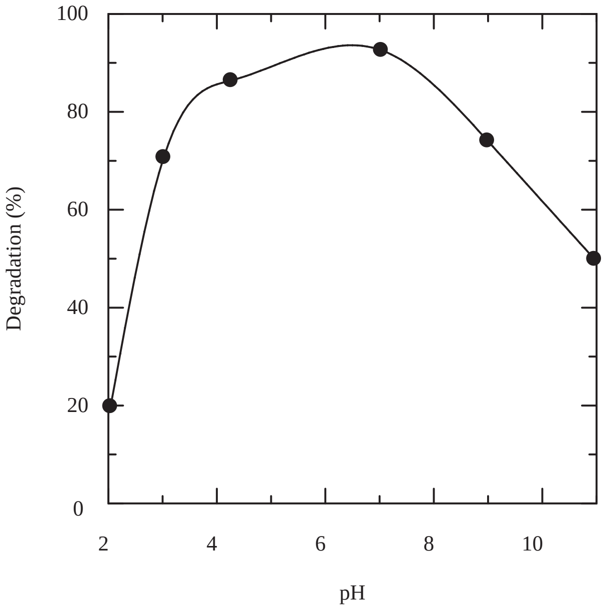


Fig. 4. Effect of pH on the photocatalytic degradation of diazinon. (Catalyst dosage: 20 mg; light intensity: 1.5 mW cm^{-2}; irradiation time: 10 min).

increased light scattering and the loss in surface area occasioned by agglomeration (particle–particle interactions) at high solid concentration [28]. Therefore, 20 mg of Pt-TiO$_2$ was selected as the optimal amounts of photocatalyst for the sequential experiment.

pH can be one of the most important parameters for the photocatalytic process and so it was of interest to study its influence on the photocatalytic degradation of diazinon. Therefore, the dependence of photocatalytic activity for the degradation of diazinon on initial pH was investigated in the range of 2–11. No degradation of diazinon was observed in the pH range in the absence of the photocatalyst. As shown in Fig. 4, the degree of photodegradation of diazinon increased with increasing pH up to 7, and then rapidly decreased. The zero point charge (zpc) pH$_{zpc}$ of Pt-TiO$_2$ particles is around 7 [29]. The given pK_a for diazinon is 2.6. The effect of pH on the photocatalytic activity can be explained in terms of electrostatic interaction between the catalyst surface and the target compound. Such interaction can be expected to affect the encounter probability of the generated hydroxyl radicals with the compound. It follows that the overall reaction would be enhanced or hindered depending on whether attractive or repulsive forces prevail, respectively. Diazinon is negatively charged above pH 2.6, whereas the catalysts are positively charged below pH $\approx$ 7. As expected, optimal conditions were found at $\mathrm{p}K_a{}^{\mathrm{diazinon}} < \mathrm{pH} < \mathrm{pH}^{\mathrm{Pt\text{-}Tio2}}{}_{\mathrm{ZPC}}$ at which the positively charged Pt-TiO$_2$ and negatively charged diazinon should readily attract each other. On the other hand, at high initial pH, more hydroxide ions (OH$^-$) in the solution induced the generation of hydroxyl free radicals (OH•), which came from the photooxidation of OH$^-$ by holes forming on the catalyst surface. Therefore, the pH-dependence on the degradation efficiency would be attributed to the balance between the induced generation of hydroxyl radicals and the electrostatic repulsion of diazinon molecular for the photocatalyst surface. In this study, pH 4.3 was selected for the optimum experimental condition since the original diazinon solution was this pH value indicating the unnecessary of other chemicals.

Effect of light intensity on diazinon degradation was studied in the range of 0–2.0 mW cm^{-2}. The degradation percentage increased rapidly with increasing the light intensity up to 1.0 mW cm^{-2}, and above the intensity the percentage increased gradually (Fig. 5). Since the photocatalyst powders are suspended in a stirred solution, the light intensity will affect the degree of absorption of light by the photocatalyst surface. Ollis [30] has summarized the effect of light intensity on the kinetics of photocatalysis and stated that (i) at low light intensities, the rate would increase linearly with increasing light intensity; (ii) at intermediate light intensities, the rate would depend on the square root of the light intensity; and (iii) at high light intensities, the rate is independent of light intensity. Therefore, it was found that the results obtained in this work were very reasonable.

Effect of irradiation time was investigated under the optimum conditions. The results are shown in Fig. 6.

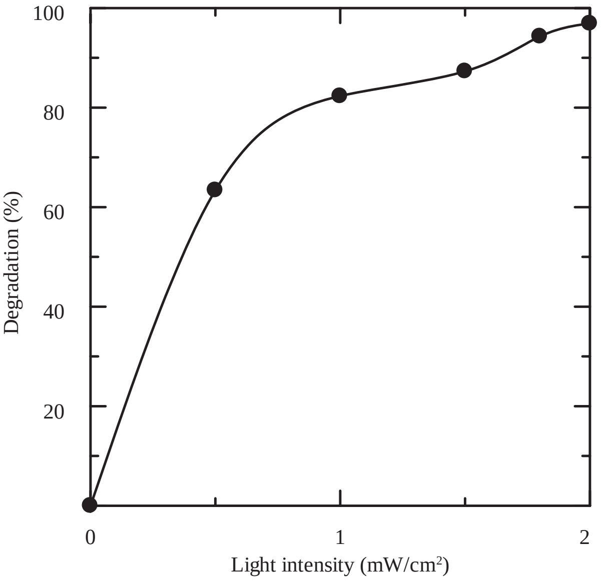


Fig. 5. Effect of light intensity on the photocatalytic degradation of diazinon. (Catalyst dosage: 20 mg; pH: 4.3; irradiation time: 10 min).

Complete photocatalytic degradation of diazinon was reached within 30 min. The primary degradation reaction is estimated to follow a pseudo first-order kinetic law. In order to confirm the speculation, $-\mathrm{Ln}(C/C_0)$ was plotted as a function of irradiation time (the insert figure in Fig. 6). Since the linear plots were observed in the insert figure as expected, the kinetics of diazinon in the Pt-TiO$_2$ suspension solution followed the first-order degradation curve. When compared to the photocatalytic activity of P-25 TiO$_2$, the pseudo first-order rate constant in Pt-TiO$_2$ photocatalytic process (0.170 min^{-1}) was about 2.5 times for P-25 (0.068 min^{-1}, data not shown).

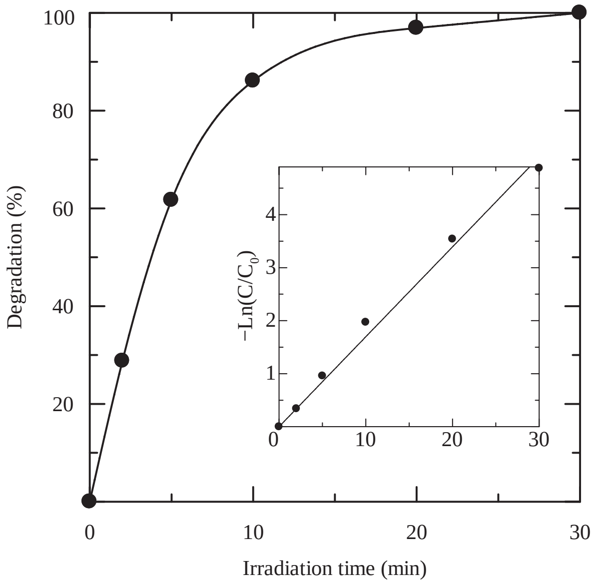


Fig. 6. Effect of irradiation time on the photocatalytic degradation of diazinon. Insert figure: plot of $-\mathrm{Ln}\ (C/C_0)$ versus irradiation time. (Catalyst dosage: 20 mg; pH: 4.3; light intensity: 1.5 mW cm^{-2}).

3.2. Mineralization

When the total mineralization of diazinon proceeds stoichiometrically using oxygen as oxidizing agent, the mineralization reaction can be estimated as follows:

$$C_{12}H_{21}N_2O_3PS + 21O_2 \rightarrow 2HNO_3 + H_3PO_4 + H_2SO_4 + 12CO_2 + 7H_2O \quad (2)$$

It should be remarked that nitrogen released has been measured as a combination of ammonia and nitrate, but ammonia can be oxidized to nitrate after long irradiation time [31,32].

The formation of sulfate ion released from diazinon was investigated as illustrated in Fig. 7a. The conversion yield to sulfate ion quickly increased until 1 h irradiation time, and after 1 h the yield gradually increased, suggesting a very fast degradation/desulfurization stage. Finally, sulfur atoms in diazinon were stoichiometrically transformed to sulfate ion after 7.5-h treatment.

The formation of phosphate ion from the photocatalytic degradation of diazinon was also monitored (Fig. 7b). The behavior of conversion to phosphate ion was very similar to that of sulfate ion. The total amount of phosphate ion produced after 3-h irradiation time was approximately 0.1 mmol L^{-1} (ca. 100% conversion of the diazinon phosphorus content).

The formations of ammonium and nitrate ions during the photocatalytic process as a function of reaction time are presented in Fig. 7c. This photocatalytic degradation of diazinon would also yield these ions as breakdown products. Both ammonium and nitrate ions were detected in different relative concentrations. Only 72% of the initial N was detected as ammonium and nitrate ions after 30 h of irradiation time. Therefore, a part of nitrogen atoms from diazinon could be mineralized by this photocatalytic system. This incomplete nitrogen mass balance has frequently been observed in similar process [13,14] and indicates that other nitrogen-containing compounds remain adsorbed onto the photocatalyst surface or most probably, that significant quantities of N$_2$ have been produced and transferred to the gas phase. N$_2$ evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product [33].

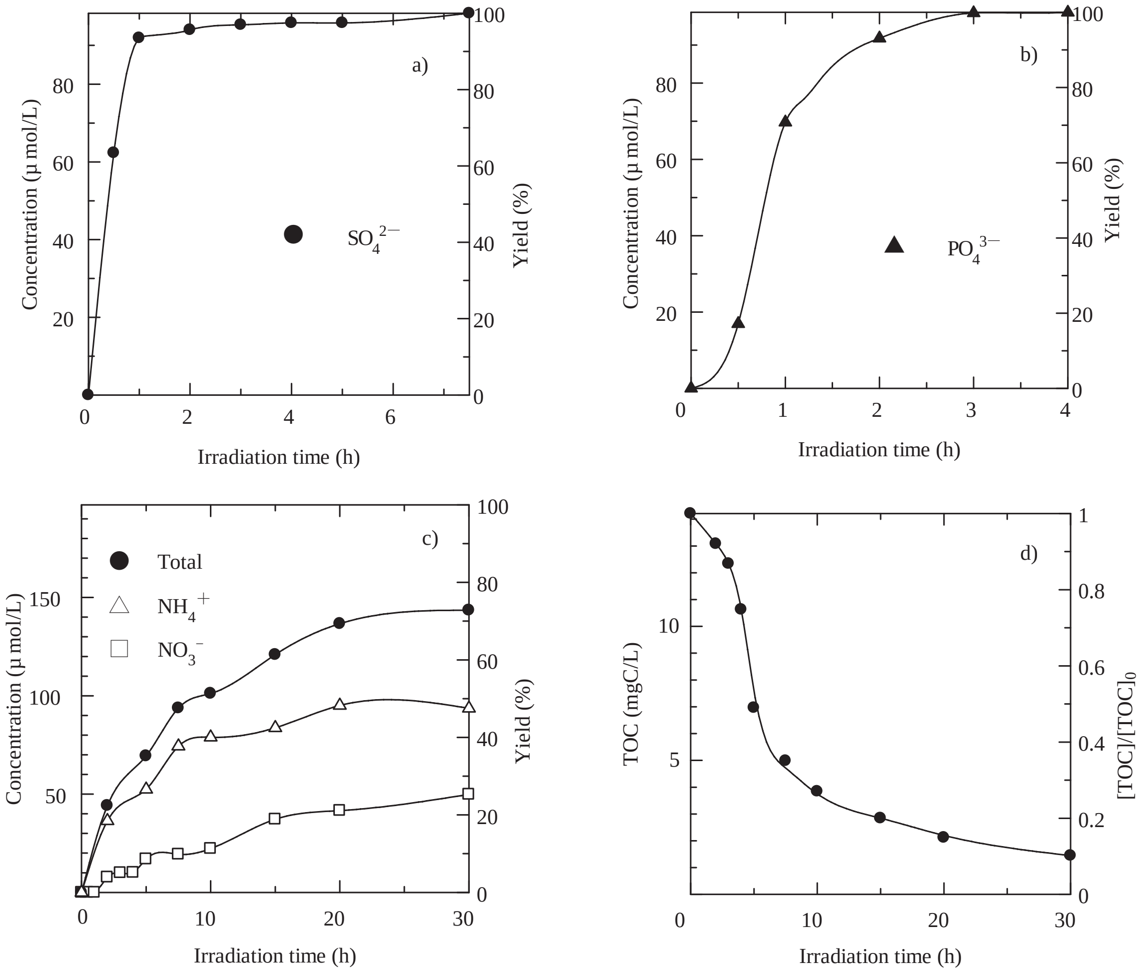


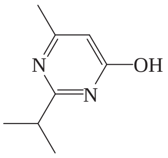
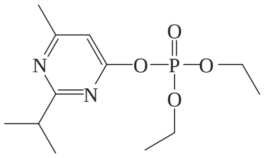
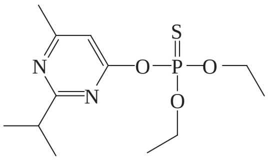
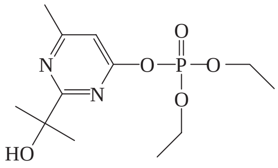
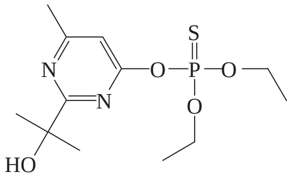
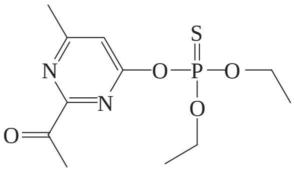
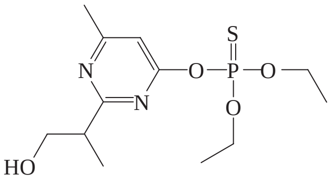
Fig. 7. Time courses of the mineralization during the photocatalytic degradation of diazinon. (a) sulfate ion; (b) phosphate ion; (c) ammonium and nitrate ions; (d) TOC.

The progress of the mineralization of the diazinon solution was monitored by measuring the TOC. As shown in Fig. 7d, the complete mineralization of diazinon was not achieved after 30 min, although diazinon was not present in the solution after the irradiation time. This difference indicates that intermediate products were produced during the photocatalytic process. The generated photoproducts are considered to be attacked in their turn by hydroxyl radicals, which are formed in a continuous manner via a heterogeneous photocatalytic process. TOC rapidly decreased with increasing the reaction time up to 10 h, and then decreased gradually. TOC remained about 1.6 mgC L^{-1} (88% mineralization) after 30 h of irradiation time. This result indicates the formation of persistent intermediate compounds which are difficult to be degraded by this photocatalytic system. Therefore, it took a long time for the mineralization of diazinon and further improvement is needed for the photocatalytic system.

3.3. Identification of photoproducts and degradation mechanism

The intermediate products formed in this photocatalytic degradation of diazinon in the aqueous solution after 2 min were investigated by GC/MS analysis. Six products were identified by the molecular ion and mass fragment ions, and also through comparison with NIST library data. The structures of the six photoproducts are represented in Table 2, together with the parent compound. The similarities of these compounds to the NIST library data were more than 85%. By interpreting the mass spectra, the product no. 1 (2-isopropyl-6-methyl-pyrimidin-4-ol, IMP) was formed from diazinon due to the cleavage of P-O (pyrimidine ring) bond. The product no. 2 (diazoxon) was found to be the product which was substituted the S atom to O atom. Further hydroxyl radical attack could yield to hydroxyl derivative of diazoxon (product no. 3). The product nos. 4 and 6 were formed due to hydroxylation of

Table 2
Identified products by GC/MS in the photocatalytic degradation of diazinon

Product No.	Rt (min)	M.W.	Characteristic ions (m/z)	Compound
1	26.1	152	137, 152, 124	
2	29.9	288	137, 151, 273	
Diazinon	30.5	304	137, 152, 179	
3	32.0	304	111,153, 289	
4	32.7	320	153, 169, 320	
5	33.7	304	153,180,199	
6	35.2	320	151,122,195	

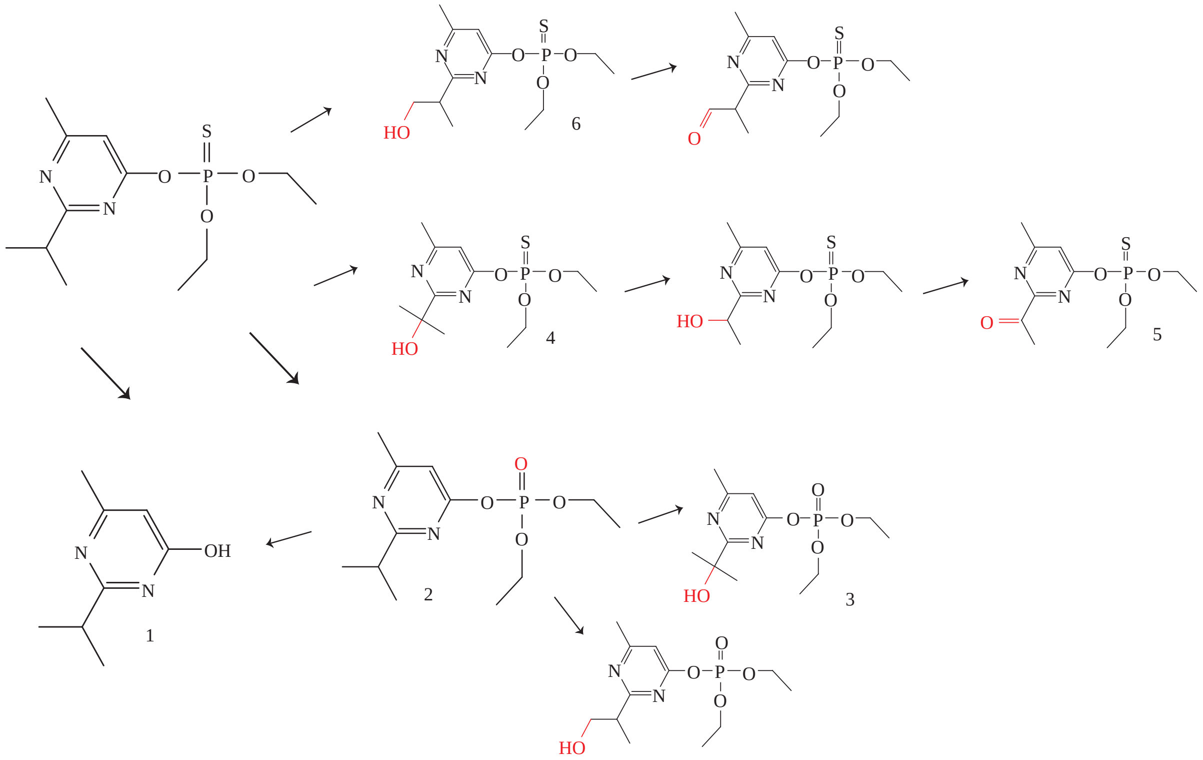


Fig. 8. Proposed degradation mechanism of diazinon by the photocatalytic system. Numbers correspond to those in Table 2.

isopropyl group on diazinon. The product no. 5 was formed by further oxidizing hydroxydiazinon (product no. 4) on the isopropanol group. In addition to these six compounds, other degradation products still possibly would exist in the photocatalytic system but were not detected because of their low concentration, extraction efficiency and limited sensitivity in GC/MS.

Based on the intermediate products listed in Table 2, as well as the literature data [12,13], the possible degradation pathway for diazinon is proposed in Fig. 8. As can be seen, two possible degradation pathways are proposed: one pathway involved the cleavage of the P-O (pyrimidine group) bond yielding IMP. In the photocatalytic process, loss of the pyrimidine group probably occurred either through oxidative desulfuration by OH radical attack [34] on the thiono group to give diazoxon followed by hydrolysis, or through an oxidation mechanism acting directly on diazinon. These oxidative mechanisms have already been observed for most thiophosphates in metabolic studies [35]. In the second pathway, the thiophosphoric moiety of diazinon was preserved. Hydroxylation of the primary or secondary carbon atoms of the isopropyl group gave hydroxydiazinon or 2-hydroxydiazinon, respectively, which after further oxidation led to diazinon aldehyde and diazinon methyl ketone. A similar transformation pathway was observed following for the oxygen analogue diazoxon formed by oxidation of the P=S bond of diazinon to a P=O bond which led to the formation of the hydroxylated derivatives.

IMP is the hydrolysis product of diazinon detected in natural waters while photochemical transformation of the parent molecule yields the production of diazoxon and hydroxydiazinon, respectively [36]. Hydroxylated metabolites of diazinon including hydroxydiazoxon have also been observed in metabolism studies [37].

4. Conclusions

The photocatalytic degradation of diazinon in aqueous solution was investigated by platinized TiO_2 catalyst. Platinization of TiO_2 photocatalyst was found to increase the photocatalytic activity for the degradation of diazinon. The degradation rate was strongly affected by many factors, such as Pt doping concentration, catalyst dosage, pH value and so on. The optimum doping Pt concentration found in this study was 0.5 wt%. Under the optimum conditions, diazinon could achieve complete degradation after 30 min. The first-order rate constant for diazinon degradation by Pt-TiO_2 was 2.5 times higher than P-25 TiO_2.

The disappearance of TOC was observed during the photocatalytic process and the remaining TOC achieved 1.6 mgC L^{-1} after 30 h (88% mineralization).

The formations of sulfate, phosphate, ammonium and nitrate ions were also observed. Therefore, we could reach the complete mineralization of the starting compound. Furthermore, we identified six kinds of intermediate products of diazinon during the photocatalytic process. The degradation pathway of diazinon was proposed based on the identified by-products under a given set of reaction conditions.

The advantages of Pt-TiO_2 photocatalytic process as an oxidative treatment are rapid degradation and simple handling. Therefore, this photocatalytic reaction would be applied to wastewater treatment works as a new developing methodology for reducing levels of other pesticides and endocrine disrupting chemicals.

Acknowledgements

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