Degradation and by-product formation of diazinon in water during UV and UV/H₂O₂ treatment

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Abstract

Kinetics and degradation products resulting from the application of UV and UV/H₂O₂ to the US EPA Contaminant Candidate List pesticide diazinon were studied. Batch experiments were conducted with both monochromatic (low pressure [LP] UV 253.7 nm) and polychromatic (medium pressure [MP] UV 200–300 nm) UV sources alone or in the presence of up to 50 mg l^{-1} H₂O₂, in a quasi-collimated beam apparatus. Degradation of diazinon by both UV and UV/H₂O₂ exhibited pseudo first order reaction kinetics, and quantum yield of 8.6×10^{-2} and 5.8×10^{-2} mol E^{-1} for LP and MP lamps respectively. Photolysis studies under MP UV lamp showed 2-isopropyl-6-methyl-pyrimidin-4-ol (IMP) to be the main degradation product of diazinon at aqueous solution pH values of 4, 7 and 10. Trace levels up to 1.8×10^{-3} μM of diazinon oxygen analogue diethyl 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon) were detected only during the UV/H₂O₂ reaction. Decay of both products was observed, as the UV/H₂O₂ reaction prolonged, yet no mineralization was achieved over the UV fluence levels examined. Photolysis kinetics, quantum yield and UV/H₂O₂ degradation of the reaction product IMP was determined using MP UV lamp at pH values of 4, 7 and 10.
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1. Introduction

Diazinon (*O,O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) is an organophosphorus insecticide 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^{-1} [1], with an LC$_{50}$ in killifish (48 h) of 4.4 mg l^{-1} [2]. Fetal human doses were found to be in the range from 90 to 444 mg kg^{-1} [1]. Toxic effects of diazinon are attributed to its inhibition of the enzyme acetylcholinesterase.

Over 13 million lbs of diazinon are applied annually in the United States [3]. Diazinon is relatively water soluble (40 mg l^{-1} at 25 °C) [4], 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. However, vaporization of diazinon from water of up to 50% of applied mass was reported [5].

Diazinon and its metabolites have been detected in aquatic systems worldwide [6,7,1]. Its sediment-water partition coefficient is small indicating minor adsorption of the substance on sediments [1]. Contamination of water by pesticides is mainly due to runoff, usually within a few weeks after application. Once in the environment, its fate depends on volatilization, hydrolysis, and photolysis [8]. Diazinon undergoes fast hydrolysis at acidic and basic conditions, with half lives of 0.5, 171, and 6 days at pH 3.1, 7.3, and 10.4 (at 20–21 °C), respectively [9,2].

2-Isopropyl-6-methyl-4-pyrimidinol (IMP) was reported as a major degradation product of diazinon in compost, soil and water [1]. IMP is regarded as less toxic compared to its parent compound. When diazinon was irradiated at λ < 290 nm in water/soil suspension, it was isomerized to a product containing a S–(P=O)– group rather than O–(P=O)– group. Other products were diazoxon and hydroxyl diazinon [9]. Diazoxon was also identified as the oxidation product of diazinon during ozonation [10]. Ku et al. [11] concluded that pH, temperature and

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buffer capacity of aqueous solution did not affect the efficiency of ozonation of diazinon. These results contradict most reported results that showed that the degradation rate of organic pollutants by ozone increases with increasing of the solution pH. Zhang et al. [2] identified only diazoxon as the product of oxidation of diazinon with aqueous chlorine. Diazoxon can also be formed by enzymatic reaction in birds, fish, insects and mammals. It is regarded as more toxic than diazinon due to it being a stronger cholinesterase inhibitor with an LC_{50} in killifish (48 h) of $0.22 \, mg \, l^{-1}$ [2]. Primarily hydroxyl derivatives of diazinon were identified in titanium dioxide aqueous suspensions irradiated at 300–400 nm. The pathway of degradation was assumed to be substitution of sulfur by oxygen on the P=S bond, cleavage of the pyrimidine ester bond, and oxidation of the isopropyl group [12].

The purpose of the study reported herein was to determine kinetics and degradation products resulting from the application of UV photolysis and UV/H_2O_2 advanced oxidation to the US EPA Contaminant Candidate List (CCL) pesticide diazinon. Photolysis kinetics of the by-product of diazinon photodegradation, IMP, was then determined using a polychromatic UV source (medium pressure Hg vapor UV lamp) at pH values 4, 7 and 10.

2. Methods and materials

2.1. Materials

Diazinon (99% purity) was purchased from Supelco, PA, USA; hydrogen peroxide (30% w/w) and HPLC grade acetonitrile from Fisher, NJ, USA; HPLC grade water from Acros, NJ, USA; IMP from Aldrich, MO, USA; diazoxon from AccuStandard, CT, USA. All chemicals were used as received. All solutions were prepared with de-ionized (DI) water.

2.2. Photolysis experiments

Two common UV sources were studied for the degradation of diazinon, low pressure mercury (LP) vapor germicidal lamps (ozone-free, General Electric No. G15T8) and medium pressure mercury (MP) arc lamps (Hanovia Co., Union, NJ). The former emits essentially monochromatic light at 253.7 nm, while the latter has various outputs ranging from about 205 nm to above 500 nm (Fig. 1b). Photolysis was carried out in a quasi-collimated beam (QCB) apparatus. Diazinon, at initial concentration of 3 μM, was exposed in batches to average UV fluences of up to $2000 \, mJ \, cm^{-2}$, at ambient temperature. The UV fluence was defined as the energy over the 200–300 nm range and 254 nm for the MP and LP lamps, respectively.

Experiments were carried out in a $70 \times 50 \, mm$ crystallization dish with surface area of $34.2 \, cm^2$ open to the atmosphere. A 100 ml aqueous solution was gently stirred to maintain homogeneity. Direct diazinon photolysis and hydrogen peroxide assisted degradation were studied in DI water solution at pH 4, 7 and 10, using the MP UV lamp. pH was adjusted using 0.1N H_2SO_4 and 0.1N NaOH. Hydrogen peroxide assisted UV degradation was conducted using 25 and $50 \, mg \, l^{-1} \, H_2O_2$, from a 30%

stock solution. The same procedure was applied to examine the degradation kinetics of IMP using UV MP lamp alone and combined with $25 \, mg \, l^{-1}$ hydrogen peroxide in DI water solution at pH 4, 7 and 10. All experiments were performed in duplicate.

No loss of diazinon due to volatilization or/and hydrolysis was observed in unexposed stirred samples, which is consistent with its high water solubility and Henry's law constant.

2.3. Analysis

Quantification of diazinon and its intermediates (IMP and diazoxon) was performed on a Varian Prostar Liquid Chromatograph (Varian, Inc., Palo Alto, CA) with C-18 $7.5 \times 150 \, mm$ column (Varian). Diazinon concentration was determined with mobile phase of 65% CH_3CN in water with flow rate of $1.5 \, ml \, min^{-1}$ and absorbance detection at 210 nm.

Due to its high polarity IMP was analyzed using an elute gradient from 15% CH_3CN to 55% in water and flow rate gradient from 1.0 to $1.3 \, ml \, min^{-1}$, and absorbance detection at 234 nm. Both elute and flow rate gradients were achieved within 4 min. An additional 10 min were required to re-establish the initial conditions. The same method was used for diazoxon. Calibration was made by using aqueous dilutions of analytical standards dissolved in methanol. Identification of IMP and diazoxon, during photolysis experiments, were based on HPLC retention times determined using reagent grade standards.

Anions concentrations in the reaction mixture were measured with DX-120 Dionex ion chromatograph equipped with an AS 14A column.

3. Results

3.1. Photolysis of diazinon

Diazinon absorbs light in the wavelength range 200–280 nm, as shown in Fig. 1a. Its absorption spectrum displays a strong transition centered at 245 nm and increased absorption from 200 to 227 nm. Hence, diazinon has the potential to be photolyzed by any wavelengths below 280 nm.

Plotting $\ln([diazinon]/[diazinon_0])$ versus UV fluence (UV dose) resulted in a linear relationship indicating pseudo first order degradation kinetics (Fig. 2). The slope of Fig. 2 gives the pseudo first order rate constant (k'_d). The decay performance of the respective UV sources were directly compared via the UV fluence-based rate constants, which is a more accurate basis for comparing photochemical reactions than time based kinetics [13]. Table 1 summarizes the direct photolysis rate constants, and quantum yield (Φ) of diazinon using both lamps, at pH 7. Diazinon undergoes slow direct photolysis by both LP and MP UV lamps, as indicated by the fluence-based rate constants on the order of 10^{-4} (Table 1). The diazinon direct photolysis rate constant was two times higher under the LP lamp as compared to the MP lamp with rates of 4.61×10^{-4} and $2.48 \times 10^{-4} \, cm^2 \, mJ^{-1}$, respectively. Consequently, a higher quantum yield, $0.086 \, mol \, E^{-1}$, was established using the low pressure UV lamp as compared to Φ of $0.058 \, mol \, E^{-1}$ obtained using the MP lamp. The calculation method for the quantum
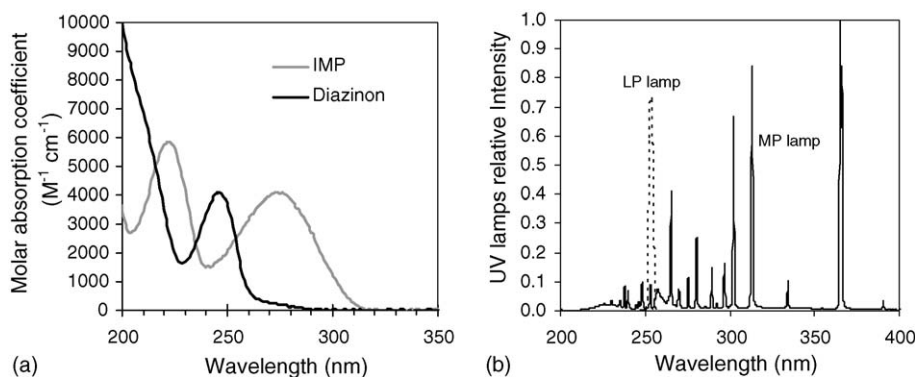
Fig. 1. Molar absorption spectrum of diazinon and 2-isopropyl-6-methyl-4-pyrimidinol (IMP) (a) and UV emission spectra of LP (dashed line) and MP (solid line) lamps (b).
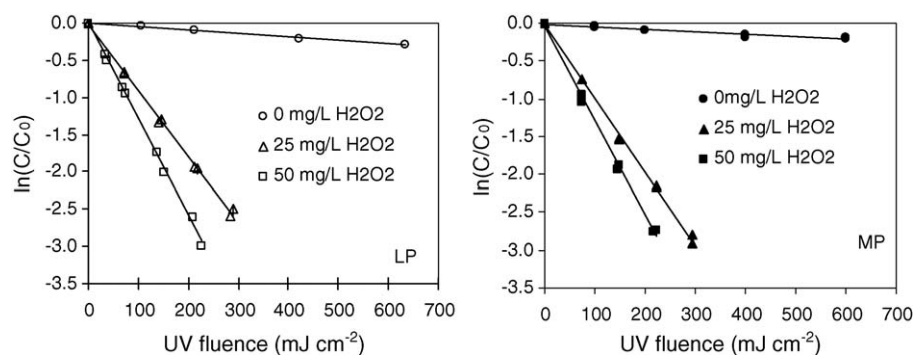

Fig. 2. Destruction of diazinon under LP and MP UV sources, without and with 25 and 50 mg l^{-1} H$_2$O$_2$ addition.

yield is described in detail elsewhere [13]. These results indicate that the quantum yield for diazinon photolysis is dependent upon wavelength in the UVC region. The higher efficiency of photolysis of diazinon by the LP lamp can be explained by the substantial overlap of the emission of this UV source (253.7 nm) with the high-energy absorption band of diazinon centered at 245 nm. Similar results were reported by Ku et al. [14] who found slower degradation rates of diazinon by simulated solar irradiation system as compared to the monochromatic UV source emitting at 254 nm.

3.2. Hydrogen peroxide assisted degradation

Addition of H$_2$O$_2$ leads to an increase in removal rates of diazinon (Fig. 2), as expected because photolysis of hydrogen peroxide leads to the formation of the very strong oxidizing species, hydroxyl radicals Eq. (1). Hence, oxidation by free radicals Eq. (2) can be determined as the dominant degradation mechanism of diazinon in the UV/H$_2$O$_2$ system, as compared to its direct photolysis.

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \qquad (1)$$

$$HO^{\bullet} + diazinon \rightarrow products \qquad (2)$$

The high hydroxyl radical reactivity of diazinon was reflected by a second order hydroxyl radical (k_{OH}) rate constant value of $(9.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1}. This rate constant was measured using a competition kinetics approach [15] with nitrobenzene (NB) as a reference compound because its hydroxyl radical rate constant is well established (3.9×10^9 M^{-1} s^{-1}, [16]), and it does not undergo significant direct photolysis. Degradation rates of diazinon and NB (2 µM each in a mixture) were determined in the UV/H$_2$O$_2$ system. A plot of ln([diazinion]/[diazinon$_0$]) versus ln([NB]/[NB$_0$]) (Fig. 3) results in a straight line passing through the origin and whose slope represents the ratio of rate constants $K_{diazinon}/k_{NB}$. The diazinon k_{OH} was then calculated by multiplying this ratio by the known k_{OH} value of NB. Feigenbrugel et al. [8] estimated the k_{OH} value for diazinon, at 8.2×10^9 M^{-1} s^{-1}, based on its calculated rate of reaction with $^{\bullet}$OH in a gas phase, which is in close agreement with k_{OH} obtained in this research in water.

The LP and MP lamps have virtually similar efficiencies for the removal of diazinon in the presence of hydrogen peroxide, as indicated by the pseudo first order rate constants (Table 1).

Table 1
Direct and hydrogen peroxide assisted photodegradation rate constants, and quantum yield of diazinon using LP and MP UV lamps at pH 7

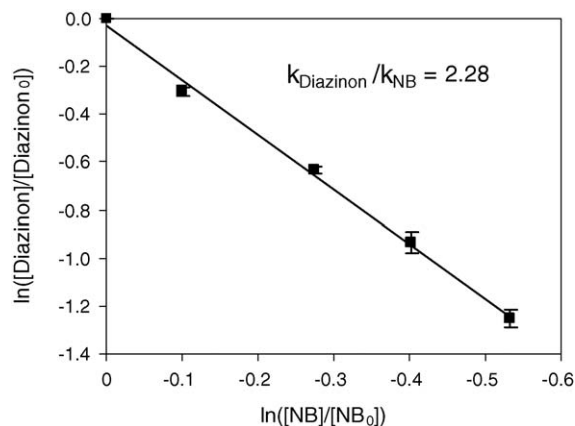| UV lamp	H$_2$O$_2$ (mg l^{-1})	k'_d (cm^2 mJ^{-1})	Φ (mol E^{-1})
LP	0	4.61×10^{-4}	0.086
	25	9.19×10^{-3}	
	50	1.30×10^{-2}	
MP	0	2.48×10^{-4}	0.058
	25	8.96×10^{-3}	
	50	1.24×10^{-2}	

Fig. 3. Relative decay rate of diazinon vs. nitrobenzene (NB) under medium pressure UV lamp exposure in the presence of $25 \, mg \, l^{-1} \, H_2O_2$.

These results can be explained by the excess in the concentration of H_2O_2 added to the aqueous solution, which compensates for the differences in emission spectra of the lamps. As seen in Fig. 2, an increase of the hydrogen peroxide concentration from 25 to $50 \, mg \, l^{-1}$ resulted in only a slight enhanced degradation of diazinon, due to the increased efficiency of hydroxyl radicals production in the aqueous solution. The relatively minor increase of the degradation rate observed between 25 and $50 \, mg \, l^{-1}$ H_2O_2 in both lamps used suggests that hydrogen peroxide concentrations greater than $25 \, mg \, l^{-1}$ may scavenge the generated hydroxyl radicals, forming the less reactive $HO_2^{\bullet}$ Eq. (3), thus making the UV/H_2O_2 process less effective at high hydrogen peroxide concentrations.

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$
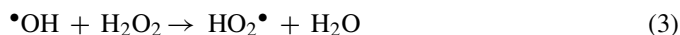
3.3. pH effect

Acidic natural and alkaline pH values of 4, 7, and 10 were selected to study the effect of pH on the oxidation rate of diazinon using a medium pressure mercury UV lamp. The photolysis of diazinon by UV irradiation was found to be sensitive to pH. Direct photolysis of diazinon was slower at acidic pH of 4, while no significant effect was observed between neutral and alkaline pH values of 7 and 10, as shown in Fig. 4a. Similar results were reported by Ku et al. [14] who proposed that protonation of diazinon occurs by addition of hydrogen to the sulfur atom. In acidic solution, the protonated form of diazinon dominates

$(pK_a \, 2.4)$ whereas its deprotonated form dominates at neutral and alkaline solution. These results suggest that the protonated form of the diazinon is less reactive under UV irradiation as compared to its deprotonated form.

In the UV/H_2O_2 AOP process the degradation rate of diazinon was comparatively inhibited at alkaline pH of 10. No difference was observed between pH values of 4 and 7, as shown in Fig. 4b. Chu [17] showed that photolysis of hydrogen peroxide to hydroxyl radicals, at 254 nm, was slightly pH dependent, with higher degradation rate of H_2O_2 at pH 10 as compared to 2.5 and 7. Nevertheless, hydrogen peroxide undergoes self-decomposition (to oxygen and water) at neutral to high pH with rate constants of 2.3×10^{-2} and $7.4 \times 10^{-2} \, min^{-1}$ at pH 7.0 and 10.5, respectively [17]. Combination of these effects, self decomposition and photodegradation into hydroxyl radicals at pH 10 might explain the inhibition in the degradation of diazinon at the alkaline pH as compared to pH values of 4 and 7.

A reduction of the aqueous solution pH was observed at the end of the reactions, because no buffer was added to the DI water solution. Up to 0.4 pH units reduction were measured at the neutral pH (7), while only 0.1 difference was observed at acidic and alkaline pH values of 4 and 10.

3.4. By-products formation

Degradation of diazinon by direct photolysis at pH values of 4, 7, and 10 indicated that its disappearance was correlated to the formation of 2-isopropyl-6-methyl-pyrimidin-4-ol (IMP). IMP formation is a result of the breakage of the P–O (pyrimidine group) bond, as illustrated in Fig. 5. IMP was reported to be much less toxic as compared to its parent compound diazinon [14]. Formation of IMP was observed upon the photodegradation of diazinon at the various aqueous solution pH levels studied. As previously explained, at pH 4 the direct photolysis degradation of diazinon was slightly lower as compared to pH values of 7 and 10 (Fig. 4a) hence, correspondingly less IMP was measured at the acidic pH. IMP was also quantified in the OH radical based UV/H_2O_2 advanced oxidation process. Because the oxidative decay of diazinon by UV with $25 \, mg \, l^{-1} \, H_2O_2$ was inhibited at pH 10, less formation of IMP was observed at this pH as compared to aqueous solution pH values of 7 and 4, as shown in Fig. 4b. In the UV/H_2O_2 process, loss of the pyrimidine group, to yield IMP, probably occurs either through oxidative desulfuration by hydroxyl radical attack on the thiono group to give
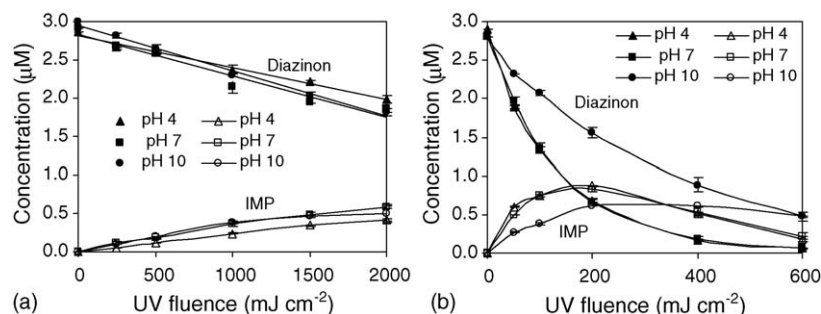

Fig. 4. Diazinon degradation and IMP formation during UV (a) and UV/H_2O_2 (b) processes at pH values of 4, 7, and 10. Diazinon $3 \, \mu M$, MP lamp, and H_2O_2 $25 \, mg \, l^{-1}$.
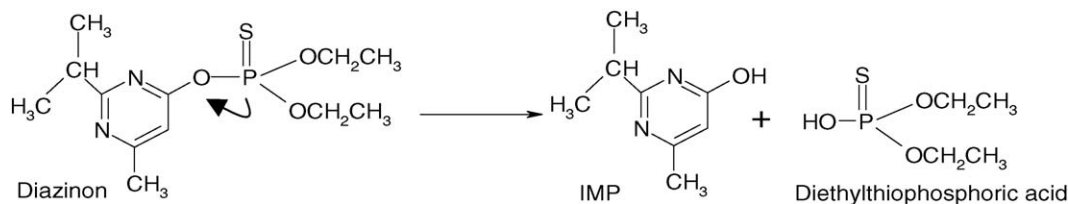
Fig. 5. Degradation of diazinon for the formation of IMP and diethylthiophosphoric acid.
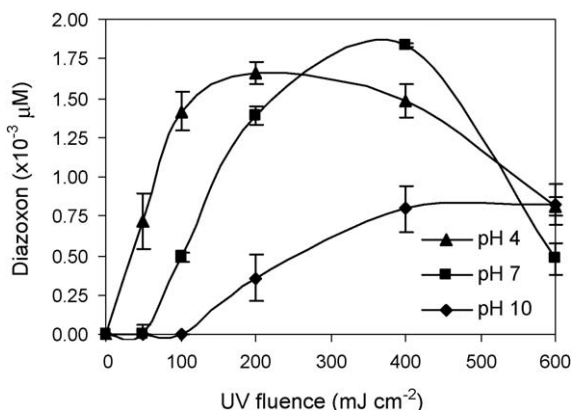

Fig. 6. Diazoxon formation during MP UV/25 mg l^{-1} H$_2$O$_2$ reaction in DI water solution at pH values of 4, 7, and 10.

diazoxon followed by hydrolysis, or through an oxidative mechanism acting directly on diazinon [12].

Only in the UV/H$_2$O$_2$ system was degradation of the IMP observed. A maximum concentration of IMP was obtained at a UV fluence of 200 mJ cm^{-2}, at pH 7 and 4. As long as the amount of IMP formed from the decay of diazinon is higher than the amount of IMP consumed by its own oxidation, an increase in the concentration of IMP was observed. Once the consumption rate was higher than the production rate, the IMP concentration decreased, and was almost completely removed at a UV fluence of 600 mJ cm^{-2}. At pH 10 the maximum concentration of IMP was found at a UV fluence of 400 mJ cm^{-2}. Further discussion regarding the degradation of IMP at various pH values by both UV and UV/H$_2$O$_2$ processes is presented afterward.

Unlike ozonation where diazinon oxygen analogue diethyl 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon) was identified as the main oxidation product, it was not detected during direct photolysis experiments up to a UV fluence of 2000 mJ cm^{-2}. Trace level of diazoxon were detected during UV/H$_2$O$_2$ treatment, as shown in Fig. 6. Diazoxon was measured

at a concentration of between 8.2×10^{-4} and 1.8×10^{-3} µM, which corresponds to a maximum of less than 0.1% of the original parent compound concentration. Similar to IMP, the formation of diazoxon followed the photodegradation of the parent diazinon at the various aqueous solution pH levels studied. Maximum concentration of diazoxon was observed at UV fluences of 200 and 400 mJ cm^{-2} at pH 4 and 7, respectively. Whereas, at pH 10 a maximum was not reached at UV fluences of up to 600 mJ cm^{-2} (Fig. 6) due to slower degradation of the parent compound diazinon at this pH. Diazoxon is originated probably through oxidative desulfuration by OH radical attack on the thiono group or through an oxidative mechanism acting directly on diazinon [12]. It is regarded as more toxic [2] whereas IMP is less toxic than the parent compound diazinon. The low concentrations of diazoxon and its further degradation as the reaction prolonged indicated the potential of the advanced oxidation process UV/H$_2$O$_2$ to remove diazinon without resulting in an increased toxic effect in the aquatic environment.

No anions SO$_4$$^{-2}$, PO$_4$$^{-3}$, or NO$_2$$^-$/NO$_3$$^-$ were detected by ion chromatograph measurements, indicating that mineralization was not achieved and that the pyrimidinol ring was not cleaved.

3.5. IMP photolysis

Often the fate of oxidation reaction products in aquatic systems is overlooked. Too often, the ecological or human health threat is assumed to be relieved upon degradation of the parent compound. Yet it is important to further understand the behavior of these products under the oxidation conditions applied for the degradation of their parent compound. Therefore, the degradation kinetics of the primary (mass based) UV photodegradation product of diazinon, IMP, was studied during UV and UV/H$_2$O$_2$ processes at pH 4, 7 and 10.

It was found that the direct photodegradation of IMP by the medium pressure UV source was greater at an alkaline pH of 10,
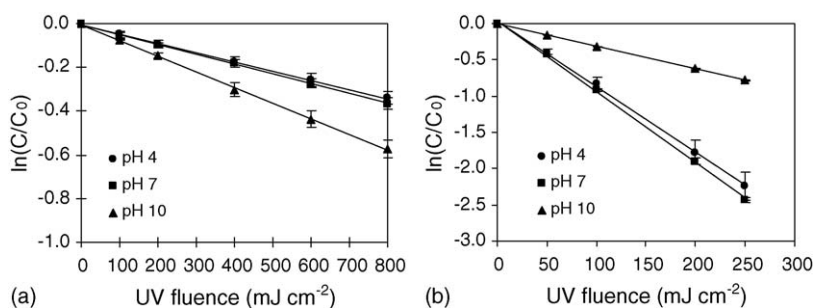

Fig. 7. Degradation of IMP by direct photolysis (a) and hydrogen peroxide assisted oxidation (b) at various pH values. IMP 2 µM, MP lamp, and H$_2$O$_2$ 25 mg l^{-1}.

Table 2
Direct photolysis pseudo first order rate constants, and quantum yield values of diazinon and its metabolite IMP in DI water solution at pH 4, 7, and 10 using MP UV lamp

pH	Diazinon		IMP	
	Φ ($\times 10^{-2}$ mol E^{-1})	k'_d ($\times 10^{-4}$ cm^2 mJ^{-1})	Φ ($\times 10^{-2}$ mol E^{-1})	k'_d ($\times 10^{-4}$ cm^2 mJ^{-1})
4	3.97 ± 0.73	1.553 ± 0.289	4.25 ± 0.06	4.562 ± 0.038
7	3.84 ± 0.32	2.256 ± 0.131	4.86 ± 0.07	4.494 ± 0.258
10	6.97 ± 0.29	2.749 ± 0.324	7.28 ± 0.37	7.176 ± 0.559

which corresponded to higher absorbance of IMP in the range of 200–240 nm at this pH value. Protonation of IMP can occur at the NH or OH groups, resulting in a pyridinate anion light absorbing form. No significant effect of the pH was observed between 4 and 7, as shown in Fig. 7a. The error bars presented in Fig. 7a and b were derived from the standard deviation of the concentration of IMP determined experimentally in triplicates. Consequently, the quantum yield of IMP at pH 10 was found to be approximately 1.5 times higher than Φ measured at pH values of 4 and 7, as shown in Table 2.

Similar to the diazinon behavior during the UV/H$_2$O$_2$ process, the OH radical degradation rate of IMP was inhibited at an alkaline pH of 10. When the pH of an aqueous solution increases, both the fraction of radiation that hydrogen peroxide absorbs and its hydroxyl radical scavenging effect Eq. (3) become stronger. Hence, the oxidation rate is reduced as compared to acidic or neutral pH levels [18]. No significant difference in the OH radical oxidation rate of IMP was obtained between pH values of 4 and 7, as shown in Fig. 7b. A reduction of the aqueous solution pH was also observed. Aqueous solution pH decreased from 7 to 6.5 and by 0.15 units at pH 4 and 10. This was likely due to formation of acidic products.

When comparing the direct photolysis of IMP and its parent compound diazinon using the UV MP lamp, it can be seen that IMP photodecayed 2–3 times faster than diazinon at all three pH values tested, as shown in Table 2. Respectively, the quantum yields of IMP were higher than those of diazinon. These results can be explained by the difference in the absorption spectrum of these two compounds. As seen in Fig. 1a IMP absorbs light at wavelength ranged from 200 to 310 nm. Its absorption spectrum displays a strong transition centered at 220 and 270 nm, which overlap with the emission spectrum of the MP UV lamp, whereas the diazinon does not absorb much UV radiation above 260 nm, the location of the prime emission lines of the MP UV spectra.

4. Conclusions

Direct photolysis rate of diazinon at 253.7 nm under a low pressure UV lamp was higher compared to the rate measured over 200–300 nm using the medium pressure UV lamp. Consequently, a higher quantum yield was evident at 253.7 nm as compared to that over the 200–300 nm range of the MP lamp, 0.086 and 0.058 mol E^{-1}, respectively. Hydrogen peroxide assisted degradation of diazinon was found to be more efficient as compared to direct photolysis. The high reactivity of diazinon with the hydroxyl radical was reflected in its high rate constant (k_{OH})

value of $(9.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1}. Loss of the thiophosphoric moiety yields the pyrimidinol 2-isopropyl-6-methyl-pyrimidin-4-ol (IMP), by both UV and UV/H$_2$O$_2$ processes. Trace levels of diethyl 2-isopropyl-6-methylpyrimidin-4-yl phosphate (diazoxon) were detected only during UV/H$_2$O$_2$ reaction. Both products were further degraded by the UV/H$_2$O$_2$ oxidation process. Degradation of diazinon and its metabolite IMP, by both UV and UV/H$_2$O$_2$ reactions, were dependent on the aqueous solution pH. IMP was photodegraded faster than its parent compound diazinon.

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