Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23830

148 (2019) 329–337
April

Photocatalytic degradation of monocrotophos using TiO_2 photocatalyst: identification of intermediates by chromatographic techniques and reaction pathway

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Received 12 June 2018; Accepted 21 January 2019

ABSTRACT

The present study deals with photocatalytic degradation of monocrotophos (Organophosphate pesticide), the identification of intermediates formed during the photocatalytic degradation, and reaction pathway involved during the process. Chromatographic techniques [gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/ mass spectrometry (LC/MS)] have been used for identification of intermediates. The degradation of monocrotophos was carried out in the presence of TiO_2 and UV light in the aqueous solution. The rate of degradation was estimated from residual concentration spectrophotometrically. The effect of various parameters on the degradation of the pesticide has also been assessed. Nine intermediates have been identified on the basis of LC/MS and GC/MS analysis and the mechanistic pathway for photocatalytic degradation of monocrotophos has been proposed. The degradation of monocrotophos proceeds via cleavage of C-O bond, attack of $^{\bullet}OH$ radical at various positions and dealkylation of dimethyl phosphate moiety of the pesticide.

Keywords: Monocrotophos; Photocatalysis; P25; Mechanism; LC/MS; GC/MS

1. Introduction

Monocrotophos (dimethyl [(E)-4-(methylamino)-4-oxobut-2-en-2-yl] phosphate) is most popular and widely used organophosphate (OP) pesticide. Monocrotophos is highly toxic, broad spectrum, fast acting cholinesterase inhibiting insecticide with both systemic and residual contact action. The EPA (Environmental Protection Agency) classified monocrotophos as class I (highly toxic) compound. However, due to its low cost and high efficiency in controlling a large variety of pests it is continuously used in the pest controlling purposes in agriculture of developing countries primarily due to lack of alternative replacements [1]. There have been several studies on the sorption and degradation of monocrotophos in soils [2,3]. Due to high toxicity, persistence and extensive usage of monocrotophos, there is a need for the investigation of environmentally acceptable treatment of polluted waters from industrial effluents or agricultural runoff containing trace amounts of monocrotophos. Advanced oxidation techniques (AOPs) offer the advantage of destroying pollutants because these oxidize the organic pollutants into mineral salts and non-toxic compounds under normal temperature and pressure [4,5]. Among AOPs, heterogeneous photocatalysis using TiO_2 as photocatalyst is the emerging destructive technology that lead to complete mineralization of organic carbon into CO_2 [6–9].

Although studies concerned, in particular, the photocatalytic treatment of aqueous streams containing monocrotophos [10–17] have been carried out shows promising results. However, these studies mainly discussed the disappearance of the initial pollutants by specific analysis or in

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combination with the mineralization studies. These studies are not sufficient in case of real waters or with commercial formulations of pesticides as by products/intermediates formed may be more toxic compounds than the parent pesticide. The LC/MS technique offers the opportunity for (i) the identification of highly polar, less volatile and thermal labile compounds (ii) direct analysis of the water samples (iii) avoiding the possibility of escape of polar by-products or modification of relative concentration, as an effect of extraction procedure applied [18]. The GC/MS technique helps in the identification of non-polar compounds. The products/intermediates of organophosphate pesticides (azinphos-methyl, phosphamidon, methathion and methyl parathion), azo dye and metsulfuron methyl formed during the photocatalytic degradation have been successfully identified by LC/MS [19–23]. GC/MS studies have been used for the identification of intermediates and mechanistic details of photocatalytic degradation of chlorpyrifos [24], phorate [25], dimethoate [26], quinalphos [27] and CI reactive blue [28]. The identification of photocatalytic degradation products of pirimiphos-methyl was done by using powerful techniques such as HPLC, GC/MS, LC/MS and TOC analysis by Hermann et al. [29].

The reports related to high persistence of monocrotophos and its transformed products encourage us to carry research on the photocatalytic degradation of monocrotophos. Few reaction intermediates have been identified for the sonophotocatalytic degradation of monocrotophos without any mechanistic detail [30]. Further the complete mineralization of the pesticide without formation of any stable intermediates/by products is the prime requirement for designing the water treatment systems employing advance oxidation processes. The present study focuses on the photocatalytic degradation of monocrotophos, the identification of the reaction intermediates formed during the photocatalytic degradation by LC/MS and GC/MS techniques, and thereby establishing the reaction pathway for the process.

2. Experiment

2.1. Materials

Commercial sample of technical grade of monocrotophos (72%) was obtained from the Crops Chemical Limited, Kotkupura, Punjab (India) and used in the present study. Titania P-25 having 85% anatase and 15% rutile phase (surface area 50 m^2/g) was obtained from Degussa. All other chemicals used were of analytical grade. Millipore water was used for preparation of various solutions. The pH of the solutions was adjusted with 1 M HCl or 1 M NaOH. The chemical structure and the complete spectra [31] of monocrotophos is given in Fig. 1.

2.2. Instruments

The experiments were carried out in specially designed reaction vessels (diameter 0.08 m and volume 500 mL) in the photo reactor equipped with 4 UV tubes each of 30W (Philips). The intensity of UV light was 2.4×10^{-6} Einstein/min measured by chemical method, i.e. potassium ferrioxalate actinometry [32]. The experimental setup used for photodegradation experiment was reported earlier [33]. Constant stirring of the solution has been ensured by using magnetic stirrers and aeration was done with the help of aquarium aerator. UV–vis spectrophotometer (Shimadzu UV1800) was used for analysis and pH meter (Thermo Orion 920A) to adjust the pH of the solution.

2.3. Photocatalytic degradation experiments

The aqueous suspension of the pesticide solution and photocatalyst (TiO_2 Degussa) was subjected to irradiation under artificial UV light. The suspension was magnetically stirred and aerated throughout the experiment. At different time intervals, an aliquot was taken out with the help of syringe and then filtered through a millipore syringe filter of 0.45 µm. The complete absorption spectrum was recorded and λ_{max} was found at 216 nm. The rate of degradation was studied in terms of changes in the absorption spectra. The degradation efficiency (%) has been calculated as follows:

$$\text{Degradation efficiency (\%)} = [(C_0 - C)]/C_0 \times 100$$

where C_0 is the initial concentration of pesticide, and C is the concentration of pesticide after photoirradiation. Similar experiments were carried out by varying the pH of the solution and dose of photocatalyst.

2.4. LC/MS analysis

The samples were analyzed by LC/MS (Water Alliance 2795 LC) for the identification of degradation products. A column Terra C-18 (5 µm×100 mm length) was used for separation of intermediate products. The mobile phase was a mixture of acetonitrile–water (20/80, v/v) and samples were filtered through millipore syringe filter of 0.22 µm. The flow rate of eluent was 1.4 mL/min and the injection volume was 10 µL. The eluent from the chromatography column successively enter the UV–vis diode array detector, the ESI interface and the quadruple ion trap mass analyzer. MS analysis in the positive ion mode was performed on a mass spectrometer equipped with an ESI ion source. The ESI probe tip and capillary potentials were set at 2.5 kV and 25 V, respectively. The mass range was 50–400 m/z. The heated capillary was set to 200°C.

2.5. GC/MS analysis

Metabolites and degradation products of monocrotophos were identified with gas chromatograph interfaced with a mass selective detector. The samples for GC/MS analysis were prepared by extraction of part (20 mL) of irradiated solution (after the removal of TiO_2 particles) with dichloromethane (40 mL). The extracts were dried with anhydrous sodium sulphate overnight. The finished samples were concentrated under reduced pressure to 1 mL and then analyzed by GC/MS. The GC (Polaris Q Thermo Electron Corporation) is equipped with a DB-1MS capillary column. Helium was used as both the carrier (1 mL min^{-1}) and make-up gas (40 mL min^{-1}). A split/splitless injector in the splitless mode at 250°C was used. The transfer line

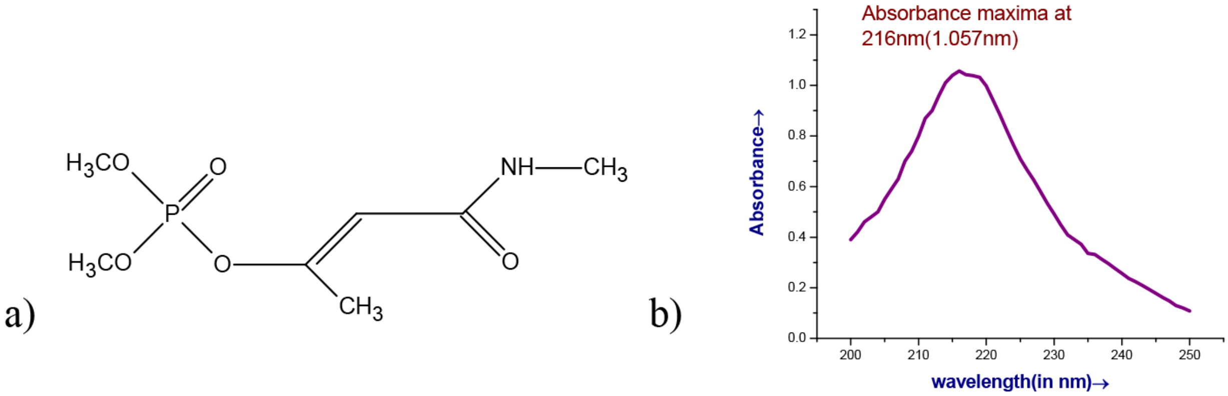


Fig. 1. Monocrotophos (a) structure and (b) UV-vis spectra.

temperature was set at 280°C and oven temperature was programmed from 60°C (2 min hold) to 300°C at the rate of 10°C min^{-1} (5 min hold). The injected volume and scan time was 2 L and 0.2 s, respectively. Chromatographic data were acquired by recording the full scan mass spectra in the range m/z 50–500.

The identification of photodegradation products was done by interpretation of mass spectra and fragmentation pattern corresponding to chromatographic peaks.

2.6. Determination of Chemical Oxygen Demand (COD)

COD measurement was carried out with Thermo Orion Aqua Fast II AQ 2040 COD meter.

Preparation of reagents for COD: standard potassium dichromate digestion solution (0.01667 M) and sulphuric acid reagent were prepared according to the method given by Clesceri and Greenberg [34].

Procedure: Test solution (2 mL) was placed in culture tubes and 1.2 mL of the digestion solution was added. Sulphuric acid reagent (2.8 mL) was carefully run down so an acid layer is formed under sample-digestion solution layer. Tubes were tightly capped and solution was mixed thoroughly to prevent local heating of tubes before applying heat. Tubes were placed in a block digester preheated to 150°C and refluxed for 2 h behind a protective shield. Then colored solution was cooled and absorbance was measured against blank sample.

3. Result and discussion

3.1. Photocatalytic degradation of pesticide

The photocatalytic degradation of monocrotophos was carried out by using TiO_2 as a photocatalyst in the presence of UV light. The preliminary experiment was performed by taking 0.1 g photocatalyst in 100 mL solution of monocrotophos. Monocrotophos shows characteristic absorption peak at 216 nm. The rate of degradation of monocrotophos was recorded with respect to the change in intensity of absorption peak at 216 nm using UV-vis spectrophotometer. The absorption peaks corresponding to monocrotophos diminished during the photocatalytic reaction, which confirms degradation of pesticides with time. It has been observed that about 60% of monocrotophos was degraded with TiO_2 within four hours of irradiation. To confirm the result, analysis of samples was also done by HPLC as shown in Fig. 2. Retention time of monocrotophos is 3.3 min. It was observed that after four hours peak area of the peak due to monocrotophos decreased and calculated degradation of monocrotophos was 58.96%.

The effect of catalyst dose (TiO_2) was observed by varying the catalyst dose from 0.5 to 2.5 g/L for pesticide solutions. The results revealed that efficiency of degradation increases up to concentration 2.0 g/L and after that the rate of degradation decreases (Fig. 3). This is in accordance with the previous studies [35] and has been explained on the basis of optimum catalyst loading which depends on initial solute concentration. The increase of catalyst dose increases the total active surface area [36] but at the same time, increases turbidity of the suspension which leads to decrease in the penetration of UV light. Hence the photo activated volume of suspension decreases [37].

pH of the solution plays a key role in the photocatalytic oxidation of pollutants. To study the effect of pH on degradation, the experiments were carried out by varying pH from 2 to10. The maximum degradation was obtained at pH 4 for the monocrotophos while sharp decrease occurred at both high and low pH (Fig. 4). The interpretation of pH effect depends on a number of factors i.e. adsorption of the organic molecules on TiO_2 surface and acid-base properties of TiO_2 i.e. pzc. The zero-point charge (pzc) reported for Degussa P25 TiO_2 is 6.3 [38]. The surface of catalyst is positively charged below pzc (pH < 6.3) and at above pzc (pH > 6.3) it is negatively charged [39]. At high pH columbic repulsion between the negatively charged surface of photocatalyst and the hydroxide anions may prevent the formation of $^{\bullet}OH$ and the organic molecule i.e. pesticide also gets deprotonated which results in decrease in adsorption of the pesticide on negatively charged surface of TiO_2 thus decreases the photoxidation. At pH 4, there is interaction between lone pair of alkylated amide group of pesticide and positively charged surface of TiO_2 hence degradation increases. Minimization of electron–hole recombination is also an important factor in the enhanced degradation; hence the degradation rate increases with decrease in pH. However, with further decrease in pH, the pesticide also gets protonated resulting in decrease of adsorption on the surface of the catalyst thus degradation decreases at very low pH. It was also reported that TiO_2 particles tend to agglomerate under acidic condition and thereby

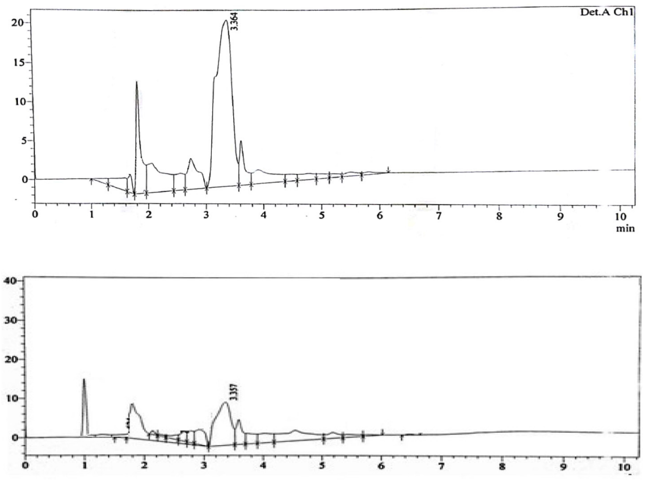


Fig. 2. HPLC chromatograms of extracts of irradiated solutions of monocrotophos after (a) 0 h (b) 4 h.

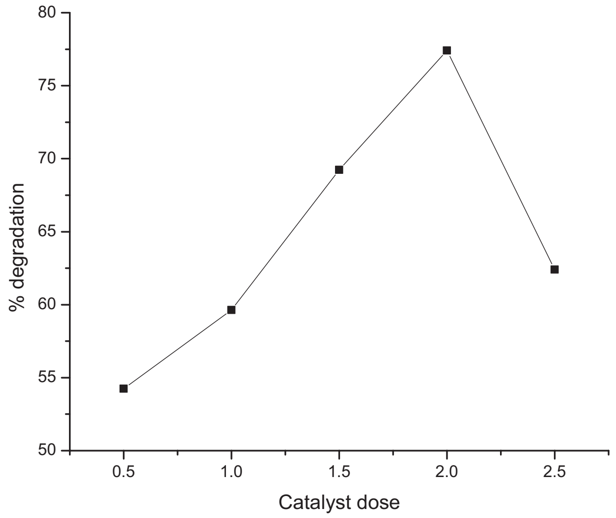


Fig. 3. Effect of photocatalyst dose on degradation rate of monocrotophos.

decreases the available surface area for pesticide adsorption and photon absorption. Hence at very low pH, degradation rate decreases [40].

The kinetic of disappearance of monocrotophos for an initial concentration 20 ppm is shown in Fig. 5. The degradation rate of photocatalytic oxidation of monocrotophos over illuminated TiO_2 fitted the Langmuir–Hinshelwood (L–H) kinetics model:

$$r = dC/dt = kKC/(1 + KC) \quad (1)$$

where r is the oxidation rate of the reactant (mg/L min), C is the concentration of the reactant (mg/L), t is the illumination time, k is the reaction rate constant (mg/L min), and K is the adsorption coefficient of the reactant (L/mg).

When the chemical concentration C_0 is a millimolar solution (C_0 is small) the equation can be simplified to an apparent first-order equation:

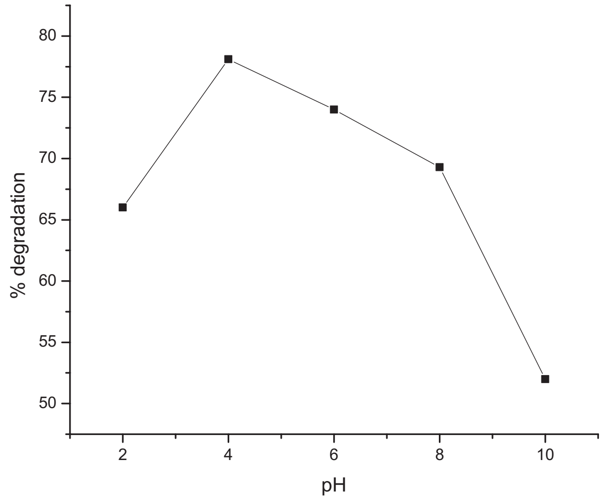


Fig. 4. Effect of pH on degradation rate of monocrotophos.

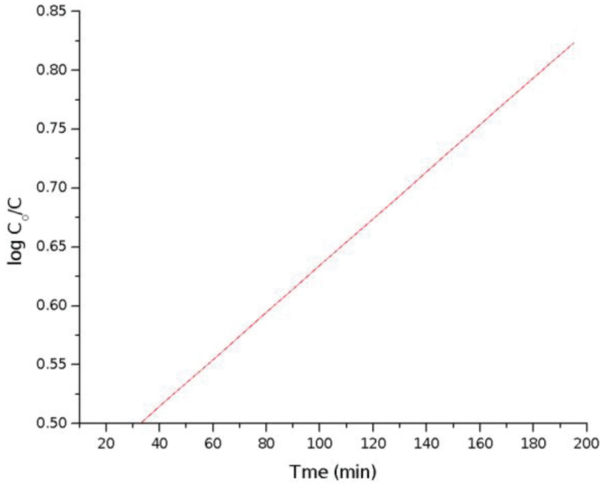


Fig. 5. Kinetic analysis of monocrotophos under conditions (TiO_2 dose – 2.0 g/L, pesticide initial concentration – 20 mg/L, pH 4).

$$ln\ (C_0/C) = kKt = k_{app}t\ or\ C_t = C_0exp(-k_{app}t) \quad (2)$$

A plot of ln C_0/C vs. time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k_{app}.

The results show that the photocatalytic degradation of pesticide in aqueous TiO_2 can be described by the apparent first-order kinetic model. The correlation constant for the fitted line and the rate constant for monocrotophos are 0.9758 and 0.00199 min^{-1} respectively. Similar behaviour has also been reported for photocatalytic degradation of quinoline [41].

3.2. Identification of degradation products

3.2.1. GC/MS Studies

The photocatalytic degradation experiments were carried out under optimized conditions from 1 h to 12 h, and

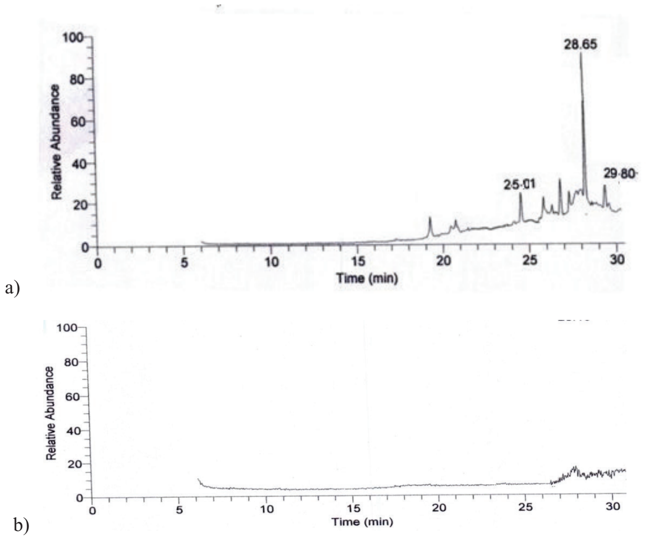


Fig. 6. GC chromatograms of extracts of irradiated solutions of monocrotophos after (a) 1 h and (b) 8 h.

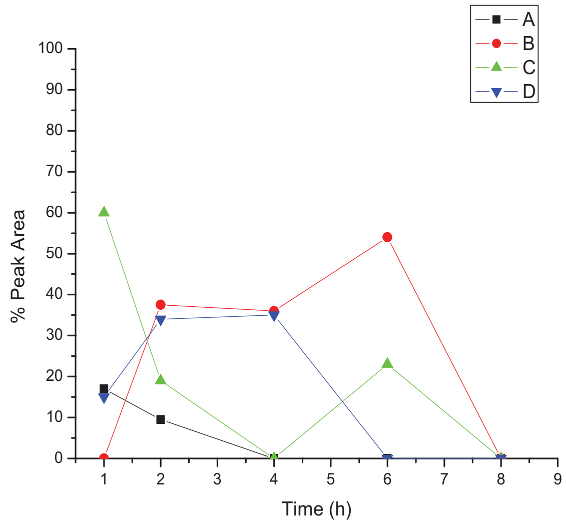


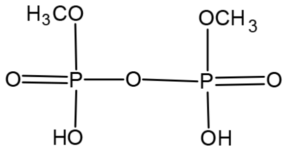
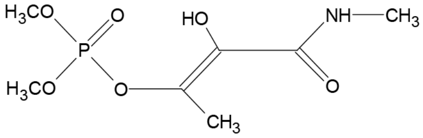
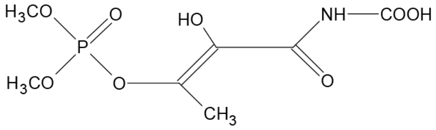
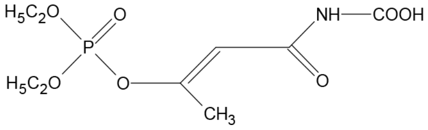
Fig. 7. GC/MS peak area (%) of the degradation products (A-D) of monocrotophos as a function of irradiation time.

degradation products formed during the photo degradation process were analyzed by GC/MS. The chromatogram obtained after 8 h of photocatalytic treatment does not contain any substantial peak (Fig. 6).

The compounds separated by GC as per their retention time were further detected by mass spectrometry. The intermediates are identified by interpretation of their fragment ions in the mass spectra. Four intermediates (A-D) were identified as photodegradation products of monocrotophos by GC/MS. The temporal evolution of these compounds and their subsequent photodegradation with time is given in Fig. 7. Moctezuma et al. also reported the temporal evolution of intermediates during photocatalytic degradation of methyl parathion [21].

The hydroxylated product (intermediate B) formed after 1 h of irradiation and remained till 6 h with the highest

Table 1
Chemical structures of intermediates of monocrotophos identified by GC/MS analysis

Code	Chemical structure	Name	Chemical formula	Molecular weight (M/M+1)	Retention time	MS spectrum ions (m/z)
A		Dimethyl dihydrogen diphosphate	$C_2H_8O_7P_2$	207	25.01	281, 207, 192, 147, 136, 105, 73
B		(2*Z*)-3-hydroxy-4-(methylamino)-4-oxobut-2-en-2-yl dimethyl phosphate	$C_7H_{14}NO_6P$	240	26.19	270, 240, 212, 102, 58
C		{(2*Z*)-3-[(dimethoxyphosphoryl)oxy]-2-hydroxybut-2-enoyl}carbamic acid	$C_7H_{12}NO_8P$	270	28.65	270, 212, 102, 58
D		{(2*E*)-3-[(diethoxyphosphoryl)oxy]but-2-enoyl}carbamic acid	$C_9H_{16}NO_7P$	281	29.78	355, 281, 207, 147, 105, 73

relative concentration. The chemical structures of the compounds, detected by GC/MS, along with their retention time, and molecular weights are presented in Table 1. It has been observed that the compound having both carboxylic and phosphate group, have higher retention time. This fact is also supported by the retention time of the intermediates formed during degradation of pyridaben and chlorfenvinphos [42,43].

3.2.2. LC/MS Studies

The photocatalytic degradation experiments were carried out and degradation products formed during the photo degradation process from 1 h to 8 h were analyzed by LC/MS. The compounds separated by LC as per their retention time were further detected by mass spectrometry. The intermediates are identified by interpretation of their fragment ions in the mass spectra. Five intermediates (E-I) were identified as degradation products of photocatalytic destruction of monocrotophos by LC/MS. The chromatogram obtained after 8 h of photocatalytic treatment does not contain any substantial peak. The temporal evolution of these compounds and their subsequent photodegradation with time is given in Fig. 8, which shows that all the intermediates completely degraded with 8 h of irradiation. The chemical structures of the compounds, detected by LC/MS, along with retention time and molecular weights are presented in Table 2. The product E and G have also been reported for the sonophotocatalytic degradation of monocrotophos [30].

3.3. Possible mechanistic photocatalytic degradation pathway of monocrotophos under UV light

On the basis of the chromatograms derived at different irradiation time, identification of intermediates and their structures, a possible reaction pathway proposed for the photocatalytic degradation of monocrotophos is (Fig. 9) as follows:

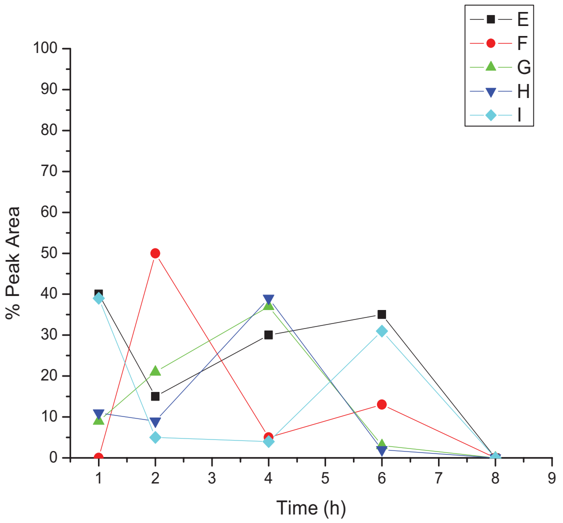
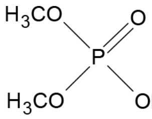
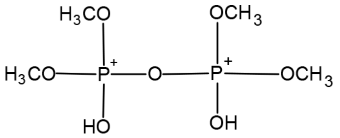
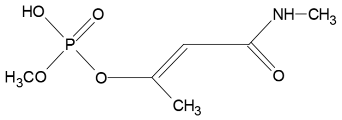
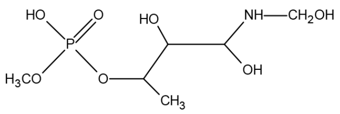
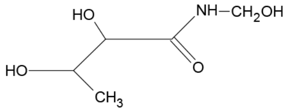


Fig. 8. LC/MS peak area (%) of the degradation products (E-I) of monocrotophos as a function of irradiation time.

Table 2
Chemical structures of intermediates of monocrotophos identified by LC/MS analysis

Code	Chemical structure	Name	Chemical formula	Molecular weight (M/M+1)	Retention time	MS spectrum ions (m/z)
E		Dimethyl hydrogen phosphate	$C_2H_7O_4P$	127	1.08	269, 246, 187, 171, 149, 127, 109, 105
F		1,3-dihydroxy-1,1,3,3-tetramethoxydiphosphoxane-1,3-diium	$C_4H_{14}O_7P_2$	237	1.91	359, 341, 246, 237, 228, 214, 205, 187, 124, 105
G		(2*E*)-4-amino-4-oxobut-2-en-2-yl dimethyl phosphate	$C_6H_{12}NO_5P$	209	4.428	249, 227, 209, 171, 149, 139, 127, 110
H		3,4-dihydroxy-4-[(hydroxymethyl)amino]butan-2-yl methyl hydrogen phosphate	$C_6H_{16}NO_7P$	246	3.13	269, 246, 223, 187, 171, 165
I		2,3-dihydroxy-*N*-(hydroxymethyl)butanamide	$C_5H_{11}NO_4$	149	2.00	249, 227, 209, 182, 149, 127, 110, 100

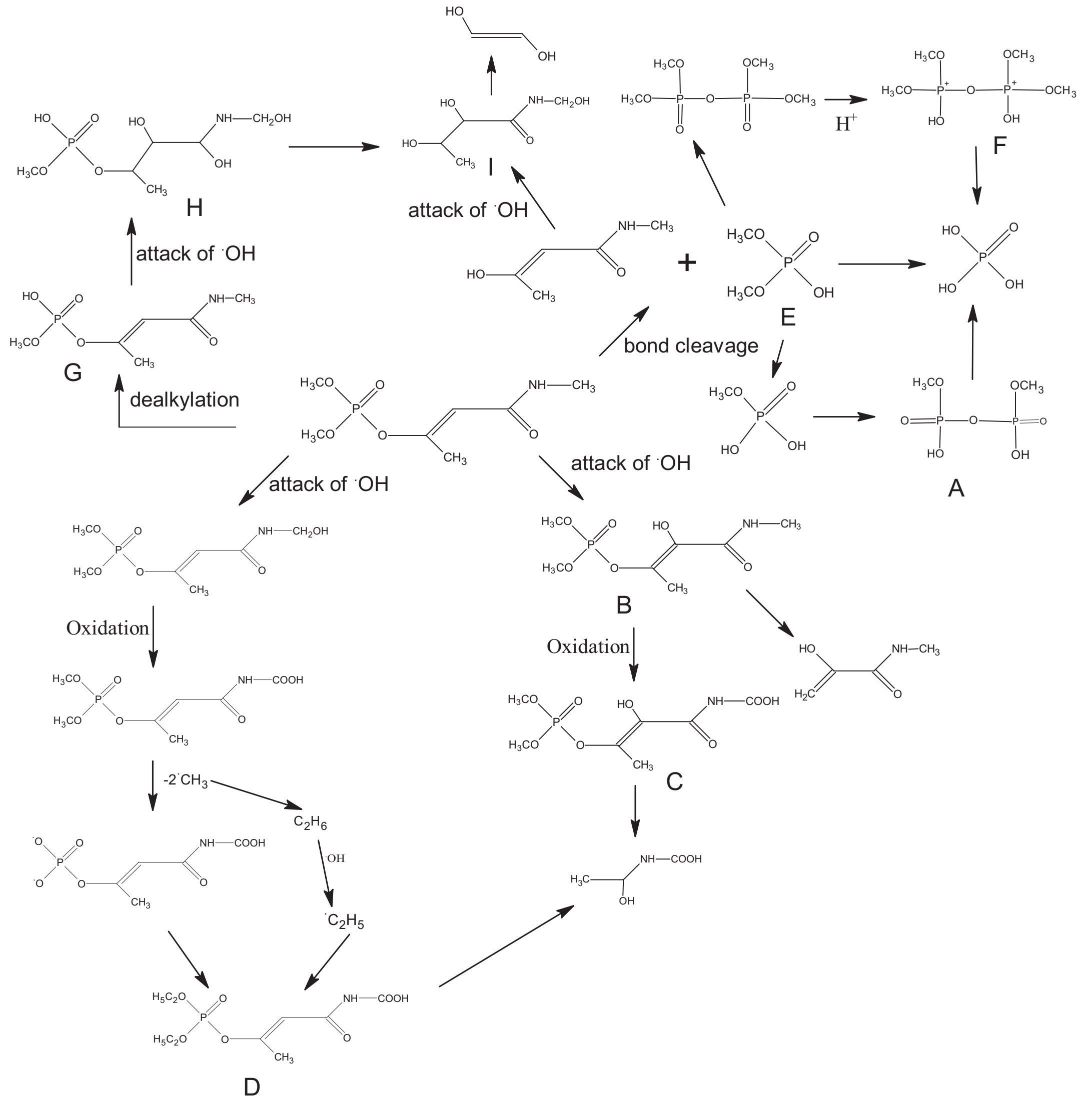


Fig. 9. Proposed degradation pathway of monocrotophos with TiO_2.

When the catalyst is exposed to UV radiation with light energy greater than its band gap energy (Eg = 3.14 eV) electrons are promoted from the valence band to the conduction band and resulted in the formation of an electron–hole pair [44,45]:

$$TiO_2 + hv\ (UV) \rightarrow TiO_2\,(e_{CB}^- + h_{VB}^+) \qquad (3)$$

where e_{CB}^- and h_{VB}^+ are the electrons in the conduction band and holes in the valence band, respectively. Further both these entities can migrate to the catalyst surface, where they can enter into a redox reaction via the formation of •OH radical [41,44]. •OH is a powerful oxidizing agent because of its high redox potential which attacks monocrotophos present at or near the surface of TiO_2 to oxidize it.

The photocatalytic degradation of monocrotophos may be initiated by three possible ways (i) attack of •OH radical at various positions (ii) cleavage of C-O bond and (iii) dealkyation of dimethyl phosphate moiety of the pesticide. The product B is formed by the attack of •OH radical on carbon of C=C bond and the product oxidizes to intermediate C. Product E and the compound [(2E)-3-hydroxy-N-methylbut-2-enamide] are formed due to breakage of the C-O bond of monocrotophos. The product E subsequently undergoes dimerisation including loss of water molecules to form product A and tetramethyl diphosphate which attacked by H^+ to form product F as the degradation was carried out in acidic medium. The compound [(2E)-3-hydroxy-N-methylbut-2-enamide] attacks by •OH radical to give compound I. The •OH radical attacks at the methyl group of $–NH-CH_3$ of monocrotophos to form compound [(2E)-4-[(hydroxymethyl)amino]-4-oxobut-2-en-2-yl dimethyl phosphate], which undergoes oxidation and further methyl radicals dissociate from the compound to form biradical specie which is stable due to delocalisation. The free methyl radicals combined with each other to form ethane. As ethyl radicals are more stable than methyl radical due to hyperconjugation, therefore alkylation of biradical specie leads to the formation of D. The pesticide undergoes dealkylation to form product G. The compound G is attacked by $^{\bullet}$OH radical to form compound H.

The intermediates (A-I) undergo degradation to form smaller aliphatic compounds which further dissociate into smaller inorganic ions, carbon dioxide and water. The formation of smaller aliphatic acids and inorganic ions was also confirmed during the fragmentation pattern and Ion chromatography (761 Compact IC, Metrohm). It has been observed that monocrotophos was susceptible to oxidation and the process lead to complete mineralisation, as no peak is found in chromatograms of samples after 8 h of irradiation.

3.4. Mineralization of monocrotophos

The mineralization of monocrotophos has been measured by observing change in COD. The percentage change in COD was studied for pesticide samples (initial concentration 20 mg/L, pH 4 and 2 g/L TiO_2) subjected to photocatalytic degradation for 8 h and corresponding rate of mineralization of the pesticide is depicted in Fig. 10. The reduction in chemical oxygen demand (COD) reflects the extent of degradation or mineralization of organic species. The COD reduction is very less (23.4%) in 1h and the reduction increase up to 95.7% till 8 h of irradiation. This study further supports the complete mineralization of intermediates formed during the photocatalytic treatment of monocrotophos.

4. Conclusion

Monocrotophos, an organophosphate pesticide, could be successfully degraded by TiO_2 mediated photocatalysis at pH 4. The complete mineralization of the pesticide takes place in 8 h of irradiation, as no peak has been found in LC and GC chromatogram for 8 h photocatalytic degradation. The identification of reaction intermediates have been carried out using hyphenated techniques. Nine intermediates are formed during a reaction which subsequently degrades with time. A detailed reaction mechanism has been established. The initial photocatalytic degradation of monocrotophos proceeds by three possible ways (i) cleavage of C-O bond (ii) attack of $^{\bullet}$OH radical at various positions and (iii) dealkyation of diethyl phosphate moiety of the pesticides. The study revealed that no intermediate/transformed product has been left after 8 h, thereby confirming the applicability of the photocatalytic process for phasing out monocrotophos or its transformed products from aqueous matrix.

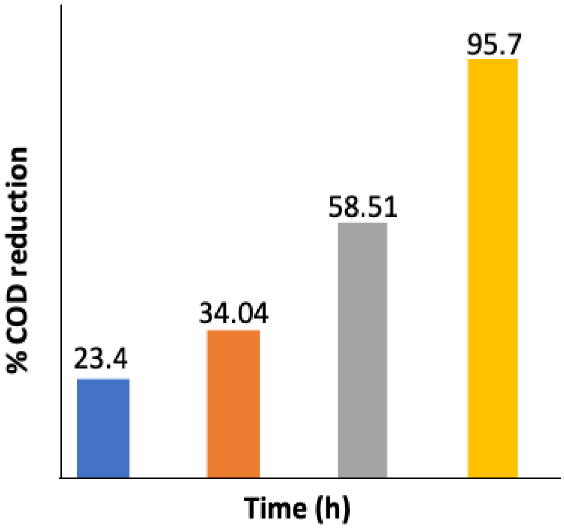


Fig. 10. Percentage COD reduction studies of monocrotophos.

Acknowledgement

Support from NIPER, Mohali and Panjab University, Chandigarh is gratefully acknowledged.

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