Advanced oxidation processes for the treatment of chlorpyrifos, dimethoate and phorate in aqueous solution
Kavita Gandhi, Summaya Lari, Dhananjay Tripathi and Gajanan Kanade

ABSTRACT
Photo-chemical-transformations of organophosphate pesticides, chlorpyrifos, dimethoate and phorate, using advanced oxidation processes (AOPs) namely UV photolysis, UV/H₂O₂, UV/Fenton and Fenton systems in aqueous solution were investigated in this work. A laboratory set-up was designed to evaluate and select the optimal oxidation process. Results show that addition of hydrogen peroxide/Fenton’s reagent increased the UV degradation rates of all pesticides, and data were simulated through kinetic modeling. Kinetic results evidence pseudo first-order degradation, with the rate constant of reaction as 3.3 × 10⁻⁴, 2.07 × 10⁻² and 1.88 × 10⁻² for chlorpyrifos, dimethoate and phorate, respectively. Furthermore treatment efficiencies obtained for the studied AOPs indicate that UV/Fenton was most efficient for chlorpyrifos (50.3% degradation) and UV/H₂O₂ for dimethoate (96.9%) and phorate (89.6%). Finally, the identification of degradation products indicated that the UV/H₂O₂ technique results in the formation of fewer end products, with low toxicity. However, UV irradiation of phorate results in formation of more toxic degradation end products such as phorateoxonsulfone.

Key words | AOPs, Fenton’s reagent, H₂O₂, organophosphate pesticides, UV

INTRODUCTION
Pesticides are substances, or mixture of substances, which are used for pest control, including vectors of human or animal disease, nuisance pests, unwanted species of plants or animals causing harm (Hajslova 1999). Organophosphorus pesticides (OPPs) are one of the most widely used classes of agricultural pesticides and were introduced in the 1970s. Recent studies have demonstrated that OPPs have endocrine-disrupting effects (Kitamura et al. 2003), cytotoxicity (Jacobsen et al. 2004), mutagenicity (Okamura et al. 2005), and immunosuppressive effects (Neishabouri et al. 2004). Properties of organophosphate compounds employed for the study are shown in Table 1 and Figure 1.

Pesticides contaminations in a water matrix of chlorpyrifos (Marino & Ronco 2005; Leong et al. 2007; Kumari et al. 2008), Dimethoate (Cerejeira 2003; Singh et al. 2004; Gao et al. 2009; Jurado 2012) and Phorate (Mourkidou et al. 2004; Maloschik et al. 2007; Lari et al. 2014) are reported in several studies across India and worldwide. Among the multiple factors responsible for the significantly higher observed prevalence of cancer cases in Punjab were the presence of phorate in drinking water and vegetables in regions of Punjab, India (Thakur et al. 2008). A prospective study of a cohort evaluating the incidence of cancer among pesticide applicators in an agricultural health study, in the USA, suggested the incidence of lung cancer was statistically significantly associated with chlorpyrifos lifetime exposure (Lee et al. 2004). A study investigating the cytotoxic effects of dimethoate in human peripheral blood lymphocytes reported that dimethoate caused a significant increase in malondialdehyde levels, a significant decrease in thiol levels, as well as a significant increase in superoxide dismutase, and catalase activities in lymphocytes at different concentrations (Gargouri et al. 2011).

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Therefore, it is important to explore a practical approach to eliminate these pesticide pollutants. Various technologies have been proposed for the removal of pesticides from water. Conventional techniques, such as physical methods of mass transfer (flocculation, filtration, precipitation, adsorption onto active charcoal, etc.), incineration, or the biological pathway, are either ineffective in the face of the extent of this pollution, result in crippling costs, or are a source of secondary pollution (sludge formation); hence there is a need to seek better alternatives (Youssef et al. 2015). Organic compounds can be removed from polluted water by conventional treatment methods or alternative destruction processes, e.g. advanced oxidation processes (AOPs) (Ismail et al. 2016, 2013). Advanced oxidation processes are technologies with significant importance in environmental restoration applications (Anipsitakis & Dionysiou 2003). Irradiation of aqueous solutions by ionizing radiation produces three primary transient species: the oxidizing hydroxyl radicals (OH), reducing hydrated electrons (e\textsuperscript{-aq}) and hydrogen atoms (H\textsuperscript{+}) that can oxidize or reduce contaminants simultaneously. When using ionizing radiation as an AOP, pollutants can be degraded in most cases to less toxic and in some cases to more biodegradable compounds that do not pose adverse environmental consequences. Several studies have reported the use of AOPs for degradation of various contaminants including pesticides and organic pollutants (Liu et al. 2005; Basfar et al. 2007, 2009; Zhang et al. 2011). Generated radicals are able to oxidize organic pollutants mainly by hydrogen abstraction (Equation (1)) or by electrophilic addition to double bonds to generate organic free radicals (R') which can react with oxygen molecules, forming peroxy radicals, and initiate oxidative degradation chain reactions that may lead to the complete mineralization of the organics, as proposed in Equation (1) (Blanco & Malato 2003):

\[
RH + HO^\bullet (or \text{SO}_4^\bullet) \rightarrow HR^\bullet + H_2O
\]  

(1)

To evaluate the application of AOPs it is necessary to obtain fundamental data on degradation and formation of reaction end products.

The present work investigates the degradation of chlorpyrifos, dimethoate and phorate using UV photolysis, H\textsubscript{2}O\textsubscript{2}, UV/H\textsubscript{2}O\textsubscript{2}, UV/Fenton and Fenton systems. An attempt has been made to study the applicability of AOPs for the destruction of the concerned pesticides and to study their degradation kinetics and end-product formation in the water matrix.

**EXPERIMENTAL METHOD**

**Standards and reagents**

Hydrogen peroxide (30%, w/w) and ferrous sulphate hepta hydrate (FeSO\textsubscript{4}·7H\textsubscript{2}O) were purchased from E. Merck, India. Certified reference standards of chlorpyrifos (96.0%), dimethoate (98.5%) and phorate (96.0%) were procured

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**Table 1** Physico-chemical properties of organo-phosphorus model substances used in this study

<table>
<thead>
<tr>
<th></th>
<th>Chlorpyrifos</th>
<th>Dimethoate</th>
<th>Phorate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular formula</strong></td>
<td>C\textsubscript{9}H\textsubscript{11}Cl\textsubscript{3}NO\textsubscript{3}PS</td>
<td>C\textsubscript{5}H\textsubscript{12}NO\textsubscript{3}PS\textsubscript{2}</td>
<td>C\textsubscript{7}H\textsubscript{17}O\textsubscript{2}PS\textsubscript{3}</td>
</tr>
<tr>
<td><strong>IUPAC name</strong></td>
<td>O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate</td>
<td>O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate</td>
<td>O,O-Diethyl S-(ethylsulfanyl) methyl phosphorodithioate</td>
</tr>
<tr>
<td><strong>Molar mass (g/mol)</strong></td>
<td>350.59</td>
<td>229.26</td>
<td>260.38</td>
</tr>
<tr>
<td><strong>Density (g/cm\textsuperscript{3}) (at 43.5 °C)</strong></td>
<td>1.398</td>
<td>1.3</td>
<td>1.16</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>Acetylcholinesterase inhibitor</td>
<td>Birth defects, carcinogenic</td>
<td>Acetylcholinesterase inhibitor</td>
</tr>
</tbody>
</table>

![Chemical structure of (a) chlorpyrifos, (b) dimethoate and (c) phorate.](image)
from Dr. Ehrenstorfer, Germany. The solvents used for the extraction were obtained from Merck (HPLC grade for chromatography). Individual pesticide stock standard solutions were prepared by exact weighing of high-purity substances in 10 mL volumetric flasks and filled up with an appropriate solvent such as acetone and n-hexane. All stock standard solutions were stored in a deep freezer protected from light at \(-20\) °C. An intermediate and working standard of suitable concentration was prepared from the stock.

**Sample preparation**

Studies were performed in the aqueous matrix containing 1 mg/L of individual pesticides (chlorpyrifos, dimethoate and phorate). The required amount of \(\text{H}_2\text{O}_2\) and iron \((\text{FeSO}_4 \cdot 7\text{H}_2\text{O})\) was added to the pesticide aqueous media to make the concentration of additives to 100 mg/L and 5 mg/L respectively.

**Experimental procedure**

Five AOP techniques: (1) \(\text{H}_2\text{O}_2\) (2) \(\text{H}_2\text{O}_2/\text{Fe}^{2+}\) (3) UV irradiation alone (4) UV/\(\text{H}_2\text{O}_2\) and (5) UV/\(\text{H}_2\text{O}_2/\text{Fe}^{2+}\) were used for degradation of selected pesticides. The first two AOP techniques were carried out for 240 min in the dark and the last three for time intervals of 30, 60, 120 and 240 min. The concentration of pesticides in each experiment was maintained to 1 mg/L of individual pesticides. Batch experiments were carried out in a Pyrex reactor with 500 mL of the pesticide aqueous solution. The pH of the solution was in the range of 3.5–6.5, for all the experiments performed. The mixture was irradiated by a UV lamp having a 400 W medium pressure mercury lamp (MVL 4 supplied by SAIC, India), which emits radiation at various outputs ranging from 200 to 400 nm. The lamp produces more than \(5 \times 10^{19}\) photons/sec, which was measured by ferrioxalate–actinometry in a quartz well. The cylindrical photochemical reactor was provided with a water circulation arrangement (with chillers) to maintain the temperature at \(25 \pm 1\) °C. For the dark processes, the reaction time started when the solution was injected with hydrogen peroxide. For light photo-processes, the time at which the UV lamp was turned on was considered time zero.

After the experimental procedure, liquid–liquid extraction was performed for the sample with 100 mL of dichloromethane (50:25:25). The combined organic phase was dried by passing it through anhydrous \(\text{Na}_2\text{SO}_4\). The organic phase was concentrated to 3–5 mL in a vacuum rotary evaporator (Heidolph) and further dried under a gentle stream of nitrogen in a Turbomax (Caliper Science) low volume concentrator. The sample was reconstituted to 1 mL by n-hexane, and 1 µL of the aliquot was analyzed by GC–ECD (gas chromatography–electron capture detector) and GC–MS (gas chromatography–mass spectroscopy).

**Analytical methodology**

**GC system and conditions**

The pesticide residues were analyzed by GC using a Perkin-Elmer Autosystem XL gas chromatograph, equipped with an ECD and Turbochrom software (Clarus 500). The analysis was conducted on a fused silica capillary column of 30 m length, 0.32 mm id., and 0.25 µm film thickness. Nitrogen was used as the carrier gas and makeup gas, and the injection technique was in the split mode with a 3:1 ratio. The oven temperature was programmed from an initial temperature of 150 °C (1 min hold) to 225 °C at a rate of 5 °C min\(^{-1}\) and was maintained at 225 °C for 10 min. Injector and detector temperatures were maintained at 220 °C and 270 °C, respectively. Nitrogen was used as a carrier gas at a flow rate of 0.87 mL/min. The peak was quantified by comparing the sample retention time value with those of the corresponding pure standard.

**GC-MS analysis**

A Varian Saturn 2200 gas chromatograph mass spectrometer was used for qualitative confirmation of pesticide and intermediates analysis. The injection port temperature was set at 250 °C, and a liner with a plug of glass wool was installed. An amount of 1 µL of the concentrated extracts was injected in split mode (1:5). Helium was used as the carrier gas at a flow rate of 0.94 mL/min. The pesticides were separated with a 50.10 min run time, and the oven temperature program was set at an initial temperature.
of 40 °C (hold 2 min), increasing at 25 °C min⁻¹ to 130 °C (hold 0 min), increasing at 12 °C min⁻¹ to 180 °C (hold 0 min) and finally increasing at 3 °C min⁻¹ to 280 °C (hold 7 min). The mass spectrometer was operated in the electron impact (70 eV) selected ion monitoring (SIM) mode. The temperature of the injector and interface were 200 °C and 250 °C, respectively.

RESULTS AND DISCUSSION

Degradation of OPPs by H₂O₂

Degradation experiments were conducted for the OPPs (chlorpyrifos, dimethoate and phorate) using H₂O₂ (100 mg/L) in the dark for 240 minutes. The initial concentration of each OPP was kept constant at 1 mg/L. The results obtained revealed that no degradation occurred due to the action of H₂O₂ within the time limit of 240 minutes.

Degradation of OPPs by H₂O₂/Fe²⁺

Degradation of OPPs by H₂O₂/Fe²⁺ (Table 2) was carried out for 240 minutes by keeping the OPP concentration constant, and a H₂O₂ and Fe²⁺ concentration of 100 mg/L and 5 mg/L respectively.

It can be observed from the results that the degradation of dimethoate was less compared to that of the chlorpyrifos and phorate.

Degradation of OPPs by UV irradiation

UV irradiation for different time intervals of 30, 60, 120 and 240 min was done and degradation trends under photolytic conditions are shown in Figure 2. After 60 minutes of UV irradiation it was observed that phorate and dimethoate degraded to 97% and 95% respectively compared to the chlorpyrifos (37%). From the results it is clear that chlorpyrifos is more photo stable than dimethoate and phorate. Many researchers have reported that chlorpyrifos exhibits a very slow rate of direct photolysis under photo oxidation conditions. It may be due to the complex conjugated ring structures of chlorpyrifos, which makes it stable compared to the other pesticides studied.

Degradation of OPPs by UV/H₂O₂

A degradation study using UV/H₂O₂ was performed with an OPP concentration of 1 mg/L and an H₂O₂ concentration of 100 mg/L. These experiments were conducted for given intervals of time and analysed for final concentration. The trend of percentage degradation of individual pesticides is displayed in Figure 3.

The combination of UV/H₂O₂ treatment improves the degradation rates. Chlorpyrifos was degraded to 79.8%; dimethoate (99.7%) and phorate (99.4%), and all were degraded almost completely in 240 minutes.

The concentration of H₂O₂ in solution was kept to 100 mg/L because it is the optimum condition for the degradation as reported by Affam & Chaudhuri (2013a). Similar
conclusions have been reported for other organic pollutants (Chen & Cao 2002; So et al. 2002; Chu & Wong 2004; Chatzitakis et al. 2008). Pekakis et al. (2006) reported that degradation at a lower H₂O₂ concentration was presumably due to the direct photolysis of H₂O₂ by UV light, which can generate the OH radical. Another minor mechanism which may partially contribute to the rate enhancement is one in which H₂O₂ is suggested to be a better electron acceptor than oxygen. This would reduce the chances of the electron-hole pair recombination (Pekakis et al. 2006).

At higher H₂O₂ concentrations, the excess H₂O₂ molecules scavenge the valuable OH radicals generated by either direct photolysis of H₂O₂ or the photo oxidation of OH⁻ by holes, and form a much weaker oxidant HO₂⁺ (Pekakis et al. 2006) which again scavenges OH⁺ radicals as in Gerischer & Heller (1991) (Equations (2) and (3)). In addition, a higher dose of H₂O₂ might absorb and attenuate the incident UV light for photo catalysis (Muruganandham & Swaminathan 2006; Pekakis et al. 2006).

\[
\begin{align*}
H₂O₂ + OH⁺ & \rightarrow HO₂⁺ + H₂O \\
HO₂⁺ + OH⁺ & \rightarrow H₂O + O₂
\end{align*}
\]

Degradation of OPPs by UV/H₂O₂/Fe²⁺ (UV + fenton’s reaction)

Fenton’s reaction is one of the most effective methods of oxidation of pollutants, which are oxidatively degraded by the hydroxyl radical generated by H₂O₂ in the presence of Fe²⁺ as a catalyst. To determine the efficiency of Fenton’s reaction in combination with UV irradiation processes of OPP removal, experiments were conducted. The optimum ratio of [Fe²⁺]:[H₂O₂] was maintained at 0.05 (molar ratio) as described by Affam & Chaudhuri (2015b). The OPP concentration was kept constant at 1 mg/L for each pesticide, and UV exposure time varied between 60 and 240 minutes. The degradation trends are presented in Figure 4.

No significant enhancement in the degradation of dimethoate and phorate is observed, while degradation of chlorpyrifos was significantly enhanced, compared to the UV/H₂O₂ processes.

A comparative plot for degradation efficiency of studied AOPs at 30 minutes (Figure 5) shows that phorate can be easily degraded, and all the AOP techniques were found to be efficient for 90% removal of phorate. The UV/H₂O₂ technique removes nearly 85% of dimethoate, while the UV + Fenton’s system is more efficient for chlorpyrifos (50% degradation).

Determination of rate constant for studied OPPs

To evaluate the kinetics of photochemical degradation of the OPPs in aqueous solutions, experiments were conducted under the optimum operating conditions. The pseudo-first order kinetics can be represented by a simple expression as in Equation (4) (Zhang et al. 2010):

\[
\ln \left( \frac{C}{C₀} \right) = -kt
\]

where \(k\) is a pseudo-first-order rate constant, \(t\) is the irradiation time in minutes; \(C₀\) is the initial concentration of the pollutant in aqueous solution and \(C\) is the residual concentration of the pollutant at time \(t\). By plotting the equation, the rate constant \((k)\) was determined from the slope of the straight line. The degradation followed pseudo-first order kinetics. Generally, first-order kinetics is
appropriate for the entire concentration range of μg/L or a few mg/L (Konstantinou & Albanis 2003).

The rate constants observed for chlorpyrifos degradation were 6.8 × 10⁻⁴, 5.6 × 10⁻³, 7.8 × 10⁻³, 3.3 × 10⁻⁴ min⁻¹ for H₂O₂/Fe²⁺, UV irradiation alone, UV/H₂O₂ and UV/H₂O₂/Fe²⁺ respectively. For dimethoate, these were 3.3 × 10⁻⁴, 2.76 × 10⁻², 2.07 × 10⁻², 1.94 × 10⁻² min⁻¹ and for phorate, these were 1.5 × 10⁻⁵, 2.01 × 10⁻², 1.88 × 10⁻², 2.08 × 10⁻² min⁻¹ for H₂O₂/Fe²⁺, UV irradiation alone, UV/H₂O₂ and UV/H₂O₂/Fe²⁺ respectively.

**Study of degradation products**

The photolytic and photochemical degradation products of chlorpyrifos was studied using GC-MS. Degradation of chlorpyrifos by 30 minute exposure of UV produces Phosphorothioic acid, o (3,6 dichloro-2 pyridinyl), 7,9 di-tert-butyl-1-oxaspiro (4,5) dione, 2 chloro [2,3,4, trimethoxy aniline] 5 nitro pyrimidine. After 240 minutes’ exposure, the degradation products detected were 7,9 di-tert-butyl-1-oxaspiro (4,5) deca- 6,9-diene-2,8-dione. UV/H₂O₂ degradation led to the formation of 7,9 di-tert-butyl-1-oxaspiro (4,5) deca- 6,9-diene-2,8-dione, Diethyl, Chlorpyrifos. Phosphorothioic acid o o Diethyl, o [3,5,6, Trichloropyridinyl] ester, diethyl [3,5,6, Trichloro 2 pyridinyl] ester, 7,9 di-tert-butyl-1-oxaspiro (4,5) deca- 6,9-diene-2,8-dione, phosphorothioic acid after 240 minutes of exposure.

UV/H₂O₂ degradation led to the formation of 7,9 di-tert-butyl-1-oxaspiro (4,5) deca- 6,9-diene-2,8-dione, Diethyl, Chlorpyrifos, Phosphorothioic acid o o Diethyl, o [3,5,6, Trichloropyridinyl] ester, diethyl [3,5,6, Trichloro 2 pyridinyl] ester, 7,9 di-tert-butyl-1-oxaspiro (4,5) deca- 6,9-diene-2,8-dione.

Among all the treatment techniques studied, UV/H₂O₂ leads to the formation of fewer by-products This formation is due to hydroxyl radical attack at the -P=S bond converting it to -P=O (oxon derivative), a primary characteristic product formed during the oxidation of OPPs. Similarly, Meng et al. (2009) found that the mass fragment was assigned to the daughter ions of chlorpyrifos, after losing a Cl atom during oxidation process by ozone. In addition, the fragment ions were the result of the loss of two ethylenes. Each mass spectrum was normalized to its most intense fragment, possibly TCP (3,5,6-trichloro-2-pyridinol), obtained by the loss of the side chain (Pengphol et al. 2012). The fragmentation was due to the formation of 2-hydroxy pyridine. Intermediates may react with three hydrogen radicals, eliminating all the three chloro (-Cl) groups as HCl, leading to the formation of other intermediates (Devi et al. 2009).

Many studies have examined photolysis of chlorpyrifos but only a few reports have suggested a route for photodegradation or have identified the photoproducts. Smith has studied general tranformation reaction of chlorpyrifos (Smith et al. 1967). Several studies (Mori et al. 2006; Devi et al. 2009; Meng et al. 2009; Pengphol et al. 2012) have reported 3,5,6-trichloro-2-pyridinol as a product of photodegradation. Dilling (1984) noted that 3,5,6-trichloro-2-pyridinol is more labile to photo mediated decomposition than chlorpyrifos itself.

In the experiment to measure the degradation products of dimethoate, it was observed that phosphorothioate or phosphorodithioate ester was formed in almost all the studied AOP techniques. It further shows that degradation takes place via dealkylation followed by hydrolysis to give mono- and di-methyl phosphate, phosphorothioate and phosphorodithioate ester, which are ultimately degraded to phosphate. Figure 6 describes the metabolism of dimethoate in plants.

Phorate degrades to phorate sulfoxide and phorate oxon sulfone in 30 minutes’ UV exposure, while a 240 minute exposure results in the formation of phosphorodithioic acid. UV/H₂O₂ treatment for 30 minutes gives phoratoxon and 240 minutes’ exposure gives the phosphorodithioic acid. However, a 30 minute UV/H₂O₂/Fe²⁺ reaction produces phoratoxon and o,o diethyl S (ethyl thio) methyl ester.

Robert & Hutson (1999), on phorate degradation, revealed that phorate is metabolised by an analogous route to that of disulfoton. The principal route of phorate metabolism in all media is activation via oxidation of the thioether group to the sulfoxide (rapid) and sulfone (slower). Thiether oxidation occurs preferentially to oxidative desulfuration of the P=S group to the oxon. Hong & Pehkonen studied the general breakdown products of phorate (Hong & Pehkonen 1998). Of all phorate metabolites, phosphoroxonsulfone is the most active inhibitor of acetylcholinesterase (Bowman & Casida 1957). Degradative metabolism occurs via oxidative dealkylation of the phosphorodithioate group or hydrolysis of the oxon.
CONCLUSION

Advanced oxidation processes are effective in the treatment (degradation) of chlorpyrifos, dimethoate and phorate pesticides in aqueous solution. UV/H₂O₂ was found to be one of the most effective processes for the treatment of phorate and dimethoate present in aqueous media with a percentage degradation of 96.9% and 89.6% respectively within 30 minutes. The study revealed that the persistence of chlorpyrifos is high and it is difficult to degrade in aqueous media compared to other studied OPPs, having a maximum 50.3% degradation in the UV/H₂O₂/Fe²⁺ process. The GC-MS analysis of degradation products shows that of all the studied AOPs, the UV/H₂O₂ technique leads to the formation of fewer end products and fewer toxic substances for all the pesticides studied. In the case of UV irradiation, the treatment of phorate however, causes formation of a more toxic by-product, phorateoxonsulfone (Bowman & Casida 1957).

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Figure 6 | Major pathways of dimethoate transformation in the environment (Dimethoate Residues and Dietary Risk Assessment Report Appendices).
REFERENCES


