Water Science & Technology

Photodegradation of chlorpyrifos in water by UV/H$_2$O$_2$ treatment: toxicity evaluation

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ABSTRACT

Chlorpyrifos (CP) is an organophosphorus pesticide widely used in agriculture. Due to its toxicity, it has been necessary to develop a treatment to eliminate the environmental wastes generated by this substance. The combination of UV radiation and hydrogen peroxide seemed an interesting option to reduce the concentration of CP in water, as it has proved to be a simple and effective method to degrade other similar pesticides. The purpose of this work is to study the effect of different initial concentrations of H$_2$O$_2$ on the degradation of commercial CP in water using UV/H$_2$O$_2$. Conversions of 93% were achieved in 20 min with 450 mg L^{-1} of H$_2$O$_2$ initial concentration (0.16 mg of CP degraded per mg of H$_2$O$_2$ consumed). The total organic carbon analysis showed interesting mineralization values, reaching a 70% conversion after 4 h of reaction. In addition, this degradation procedure leads to a clear reduction of the toxicity of the reaction mixture over *Vibrio fischeri*.

Key words | chlorpyrifos, toxicity, UV/H$_2$O$_2$

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INTRODUCTION

Chlorpyrifos (CP, *O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate) is an organophosphate pesticide with low solubility in water (1.39 mg L^{-1} at 25 °C (Giesy *et al.* 1999)). This pesticide is commercially available dissolved in organic solvents, which contain emulsifying additives. Emulsifiable concentrated formulations have been very popular for many years and nowadays they represent the biggest volume of all pesticide formulations supplied worldwide (Knowles 2008; Kundu *et al.* 2012). They are used for insect control in several crops such as cotton, corn and alfalfa. CP is moderately persistent in soils, with a half-life of less than 1 day to 240 days, depending on the soil type (Pino & Peñuela 2011). As for most of the organophosphates, if this pesticide is excessively or inadequately used, it can cause significant environmental damage and could cause adverse effects on the growth and reproduction of animals and humans.

Among the processes to remove organic pollutants, biological degradation is a process commonly used because it is inexpensive and causes little collateral destruction in indigenous organisms. In particular, several species of bacteria and fungi have been reported to degrade organophosphate pesticides in liquid media and soil (Briceño *et al.* 2012; Chishti *et al.* 2012; Lu *et al.* 2013). Other methods for the degradation of organophosphorus have been presented in recent papers. Zhang *et al.* (2011) reported ultrasonic irradiation as an attractive technique for the degradation of CP and diazinon in aqueous medium. A number of studies have shown that dissolved metal ions can play an important role in the catalysis of organophosphorus pesticides. Sarkouhi *et al.* (in press) researched the catalytic effect of Ag$^+$ ions on the hydrolysis of CP and phoxim. Kundu *et al.* (2012) reported the degradation of CP emulsified in water and the reduction of toxicity by hydrogen peroxide catalytically activated by the tetra-amido macrocyclic ligand (TAML) activator.

Among the different technologies to degrade pesticides, advanced oxidation processes (AOPs) are an interesting option for this type of pollutants. AOPs are based on the generation of highly oxidizing transient species (especially the hydroxyl radical, HO$^\bullet$) and include technologies such as Fenton, photo-Fenton, O$_3$/H$_2$O$_2$, O$_3$/UV, UV/H$_2$O$_2$, and heterogeneous photocatalytic processes.

There are several papers on the removal of organophosphorus pesticides in water by AOPs (Shemer & Linden 2006; Wu & Linden 2010), but few of them deal specifically with the removal of CP using these methods. Murillo *et al.* (2010) studied CP degradation (analytical-reagent grade)

using photo-Fenton, TiO$_2$, TiO$_2$/H$_2$O$_2$, O$_3$ and O$_3$/H$_2$O$_2$ processes and compared the effectiveness of each treatment, while Samet *et al.* (2012) used Fenton and solar photo-Fenton processes. Chioma Affam *et al.* (2012) evaluated the effect of various operating conditions of the solar photo-Fenton process on a solution of CP, cypermethrin and chlorothalonil. Gomathi Devi *et al.* (2009) studied the photocatalytic activity of polycrystalline TiO$_2$ doped with different transition metals, under UV/solar light, using CP as the probe molecule. Kanmoni *et al.* (2012) studied the photodegradation of CP in an aqueous suspension of ZnO and TiO$_2$ nanocrystals.

The AOP that combines ultraviolet radiation with hydrogen peroxide (UV/H$_2$O$_2$) provides simplicity of operation and requires a minimal investment. This technique has been applied in many studies on pesticide and herbicide degradation (Abramovic *et al.* 2010; Autin *et al.* 2012; Tizaoui *et al.* 2011). Ikehata & Gamal El-Din (2006) presented a review of the published literature on H$_2$O$_2$-based AOPs. They deal with UV/H$_2$O$_2$ and various Fenton-type processes to degrade pesticides in aqueous medium. They showed information about degradation degrees, reaction kinetics, identity and characteristics of oxidation by-products, and possible degradation pathways. However, to the best of our knowledge, the degradation of CP by UV/H$_2$O$_2$ has not been so widely studied.

Measurement of the contaminant disappearance in the AOPs is not enough, because the treatment could produce a variety of organic intermediate compounds, which can be more toxic than the parent compound. For this reason, toxicity measurements are very important in AOPs. Ecotoxicity tests usually provide important information about the potential hazard of a substance in representative organisms, especially the aquatic ones such as the luminescent marine bacterium *Vibrio fischeri*, the water flea *Daphnia*, or the alga *Zooglea* (Boluda *et al.* 2002). The Microtox® Acute Toxicity Test with *V. fischeri* has been widely used for assessing the toxicity of environmental samples (Kralj *et al.* 2007; Šojic *et al.* 2012). This bioluminescence inhibition assay is often chosen as the first test in a battery of tests because it can be done quickly and inexpensively.

In this work, the degradation of commercial CP in water using the UV/H$_2$O$_2$ process was studied. The feasibility and efficiency of the process were compared with other technologies, and the toxicity of the photodegradation products was evaluated by the Microtox Acute Toxicity Test. This treatment could be applied to water used for rinsing commercial containers of CP, which need to be washed to recycle them or just to dispose of them in landfills as not dangerous waste.

MATERIALS AND METHODS

Chemicals

CP Pestanal (Riedel-de-Haën) was used as chromatographic standard. The commercial emulsifiable concentrate of CP, 48% w/v (active ingredient), was provided by Red Surcos (Santa Fe, Argentina); bovine liver catalase (>2,000 units/mg, 1 unit decomposes 1 mmol H$_2$O$_2$ per minute at pH 7.0 and 25 °C) was supplied by Fluka; and hydrogen peroxide was Ciccarelli (30%).

Experimental set-ups and procedures

The photodegradation of the CP emulsion was carried out in an annular reactor ($V_{reactor} = 1,200$ mL). The inner tube was made of quartz to allow the passage of UV radiation from a lamp (BTE Model 6,169 KV, $\lambda = 253.7$ nm, 20 W) placed concentrically. This reactor was operated in a batch system with recirculation through a centrifugal pump (SIMES) and a feed tank (Figure 1). Also, the system had a device that allowed sampling at the bottom of the feed tank.

In order to set the initial concentration of CP in the water to be treated, samples were obtained by rinsing an empty container of commercial CP three times. Each rinsing was made using a distilled water volume of three-quarters of the total volume of the container. The water of each rinsing was analyzed by total organic carbon (TOC) measurements (Table 1). The TOC initial concentration used in the degradation assays was that corresponding to the third rinsing.

The working emulsion was obtained by appropriate dilutions of the commercial concentrate of CP in distilled water (TOC initial concentration of 20 mg L^{-1}
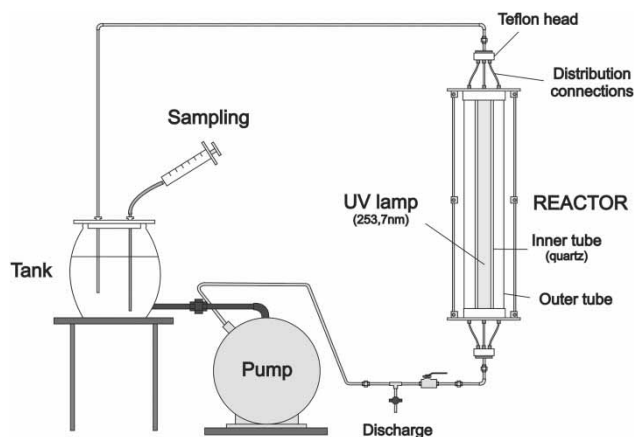

Figure 1 | Schematic representation of the experimental set-up.

Table 1 │ TOC measurements

Wastewater	1st rinsing	2nd rinsing	3rd rinsing	Commercial chlorpyrifos
TOC (mg L^{-1})	1,502	28	20	488,100

corresponding to CP initial concentration of 15 mg L^{-1}). Then, the required amount of H$_2$O$_2$ was added. The preparation was intensely stirred before loading it into the feed tank, which is really important when working with emulsions. During the course of each experiment, samples of 20 mL were taken at fixed times. Measurements of the spectral fluence rate at the reactor window ($E_{P,0,W}^{\lambda}$)were made with potassium ferrioxalate actinometry (Murov *et al.* 1993). Table 2 summarizes the experimental conditions applied to the system. The molar ratio between the H$_2$O$_2$ initial concentration and the TOC initial concentration for the working emulsion was defined as $r = C_{H_2O_2}^0 / C_{TOC}^0$.

In this work, we studied the effect of different H$_2$O$_2$ initial concentrations on the CP emulsion degradation rate by keeping the remaining parameters constant (Table 2). The molar ratio range was chosen taking into account previous works (Zalazar *et al.* 2007; Mariani *et al.* 2010; Manassero *et al.* 2010). Thus, *r* values were initially set between 2 and 8. This range was modified during the optimization of the degradation rate of emulsified CP. The final range was 0–16.

Analytical methods

CP was analyzed by high-pressure liquid chromatography (Waters 1525 Binary HPLC Pump) with a UV detector (Waters 2489 UV/Visible Detector), on a C18 reverse phase analytical column (SUPELCOSIL^{TM}LC-18–4.6 × 250 mm). A solution of acetonitrile–water was used as

Table 2 │ Experimental conditions

Variable	Value
CP initial concentration	15 mg L^{-1}
TOC initial concentration	20 mg L^{-1}
H$_2$O$_2$ initial concentration	0–910 mg L^{-1} ($r = 0$–16)
Spectral fluence rate at the reactor window, $E_{P,0,W}^{\lambda=253.7}$	1.21×10^{-8} einstein cm^{-2} s^{-1}
Reaction time	4 h
Total volume	4 L
Flow rate of the recirculation pump	3.5 L min^{-1}

mobile phase (ratio 4:1). The flow rate was 1 mL min^{-1}, at 30 °C, and an injection volume of 20 μL was used. The UV detector was set at the wavelength of 300 nm. The technique was adapted from the one described in WHO/SIT/21.R3 (1999). Under these conditions, the retention time for CP was 4.5 min.

Hydrogen peroxide was analyzed using a colorimetric method, according to the techniques of Allen (1952), and employing a Cary 100 Bio UV visible spectrophotometer with detection at 350 nm.

TOC was analyzed to quantify the mineralization degree of the samples. The instrument used was a Vario TOC Elementar.

The pH was monitored using an Orion Expandable Ion Analyzer EA 940.

Bioassay test

For the Microtox Acute Toxicity Test, a specially selected freeze-dried strain of the marine bacterium *V. fischeri* was used. The bioassays were performed using a Model 500 Analyzer (Strategic Diagnostics Inc.) according to the ASTM Standard Method D 5660-96 (2004).

The hydrogen peroxide was removed from the samples using catalase from bovine liver. The removal was performed before the toxicity analysis and after adjusting the sample pH to between 6 and 8.

The toxicity of the samples was tested with the Microtox 81.9% screening test protocol. The percentage of inhibition of light emission was determined after 5 and 15 min of incubation.

RESULTS AND DISCUSSION

Control assays

After having established the optimal range of H$_2$O$_2$ (see next section), two types of run were carried out to study the possible effect of UV radiation and H$_2$O$_2$ separately.

One run was performed without UV radiation (not shown) with initial concentrations of CP and H$_2$O$_2$ of 15 mg L^{-1} and 681 mg L^{-1} ($r = 12$) respectively. In these conditions, after 2 h of recirculation, no degradation was observed.

A similar run was carried out without H$_2$O$_2$ and using the UV lamp for 2 h ($r = 0$). Even though direct photolysis was observed for CP, this conversion was clearly lower

than the results obtained using UV radiation combined with H_2O_2 (Figure 2).

Effects of initial H₂O₂ concentration

In the UV/H_2O_2 process, there exists a range of H_2O_2 concentrations in which the decomposition rate of the contaminant reaches maximum values (Stefan et al. 1996; Mariani et al. 2010). Thus, it is important to establish experimentally this operating range for each particular pollutant, unless it is available in the literature under similar conditions.

Figure 2 shows the relative concentrations of CP, C_{CP}/C_{CP}^0, versus reaction time, for different molar ratios r, between 0 and 16. C_{CP}^0 is the initial concentration of CP, working at the natural pH of the system, i.e., pH 6.

The results show that the reaction rate rises when r increases, i.e., when the initial concentration of H_2O_2 increases. It could be assumed that, under the conditions assayed, the optimal r values are between 8 and 16 (H_2O_2 concentrations between 450 and 910 mg L^{-1}), since the reaction rate does not increase significantly for r values higher than 8. Despite this, it is not necessary to perform the degradation over $r = 8$ because a high excess of H_2O_2 is unfavorable for the economy of the whole process. The reaction rate with $r = 0$ (corresponding to the direct photolysis of CP) is very much lower than the reaction rate with other molar ratios (using the UV/H_2O_2 process). The hydrogen peroxide absorptivity coefficient at 254 nm is 36.8 M^{-1} cm^{-1} (Zalazar et al. 2007) and the CP absorptivity coefficient at 254 nm is near to 2.0 M^{-1} cm^{-1} (Slotkin et al. 2009). These values would indicate that the radiation is preferably absorbed by H_2O_2 to give hydroxyl radicals.
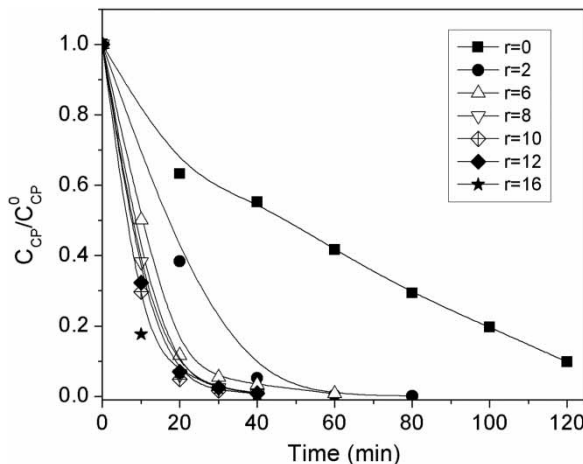
Figure 3 shows conversion values of CP after 20 min of reaction for different values of r. Conversions obtained with $r = 0$ reached 37%, while those obtained above $r = 8$ reached almost 93%, which represents a 2.5-fold increase.

Figure 4 compares runs with two different molar ratios, $r = 2$ and $r = 12$. Results of CP and H_2O_2 concentration and pH as a function of reaction time are shown. Despite the big difference between the molar ratios, CP is reduced to a negligible concentration before the first hour in both cases. In general, within the studied range, when H_2O_2 is applied, the concentration of CP is reduced to less than 1 mg L^{-1} within the first 40 min of reaction. For $r = 0$, these values are reached only after 2 h.

The experiments were conducted with the natural pH of the preparations, which showed a rapid initial decrease (from 6 to 3.5) and then, with the progress of the reaction, a slight
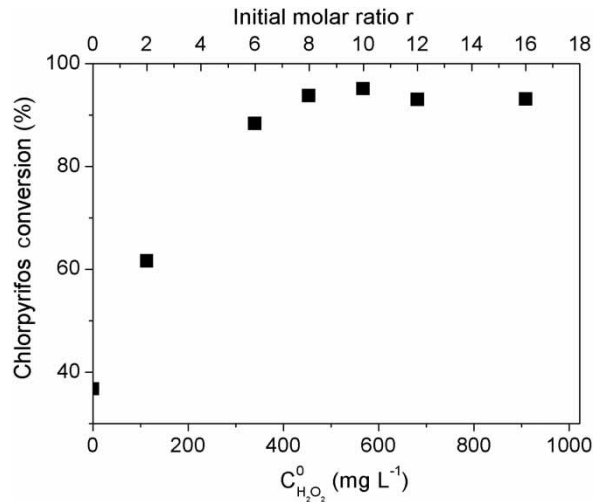
Figure 3 | CP conversion percentage vs H_2O_2 concentration (or r) for a reaction time of 20 min.

Figure 2 | Relative CP concentration as a function of time for different r. $C_{CP}^0 = 15$ mg L^{-1}.
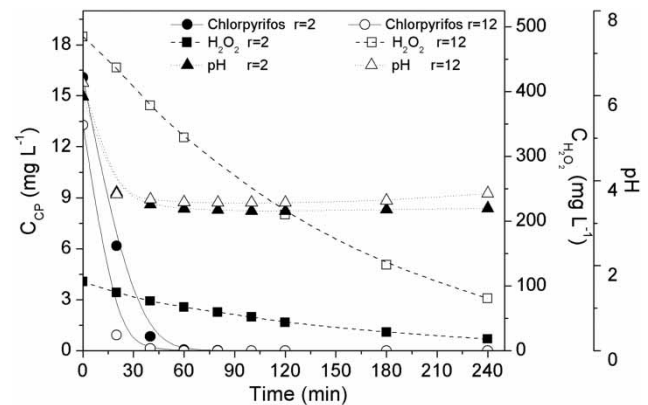
Figure 4 | CP concentration, H_2O_2 concentration and pH as a function of time for $r = 2$ and $r = 12$.

increase (Figure 4). This behavior was observed in all the experiments, and it could be associated with the formation of organic acids followed by their transformation into the final products of mineralization: inorganic acids and CO_2.

Figure 5 shows the temporal progression of the participating species concentrations for the optimum operating condition, $r = 8$. The plot of $\ln C_{CP}/C_{CP}^0$ versus time reaction shows a straight line behavior. This suggests pseudo-first-order kinetics in the decay of the CP concentration with the application of the UV/H$_2$O$_2$ process. The observed rate constant $k = 0.127 \text{ min}^{-1}$ was determined from the slope of the straight line.

Feasibility and efficiency of the process

In order to evaluate its feasibility and efficiency, the process was compared to other technologies that estimate first-order rate constants. In the work of Duirk & Collette (2006) the observed first-order rate constant, k, of CP loss in the presence of free chlorine at pH 8.75 was determined: $k = 0.108 \text{ min}^{-1}$ (CP initial concentration: 0.175 mg L^{-1}, total free chlorine concentration: 100 μM and total carbonate concentration: 10 mM).

In another study about the photodegradation of CP by TiO$_2$/UV, the first-order rate constants were calculated in two stages of the reaction: $k_1 = 0.031 \text{ min}^{-1}$ and $k_2 = 0.063 \text{ min}^{-1}$ (Gomathi Devi *et al.* 2009).

The degradation of CP by different AOPs such as photo-Fenton, TiO$_2$ and O$_3$/H$_2$O$_2$ was investigated in Murillo *et al.* (2010). From their results it is possible to estimate the first-order rate constants: 0.250 min^{-1} for photo-Fenton process and 0.090 min^{-1} for TiO$_2$ and O$_3$/H$_2$O$_2$.
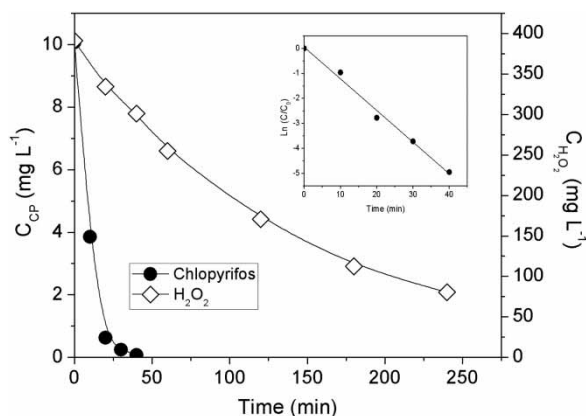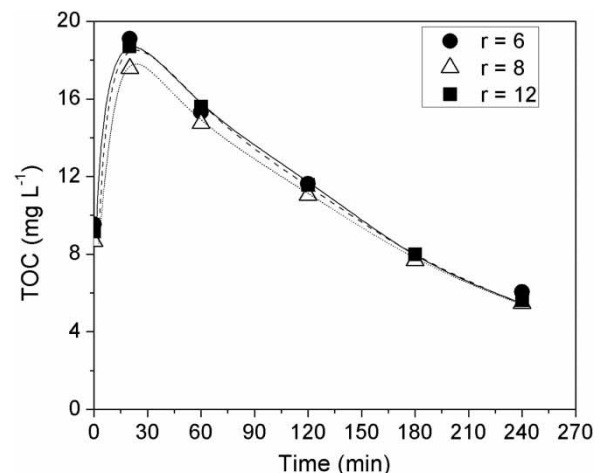
It is very difficult to compare these processes using the experimental values obtained from different studies because each study was conducted under different experimental conditions (different pH, different composition of the treated water, samples prepared with distilled water spiked with CP as active ingredient or commercial product, etc.). Nevertheless, the comparison could be useful in order to estimate and evaluate the relative feasibility and efficiency of a process.

In our study of the UV/H$_2$O$_2$ process, the pseudo rate constant is 0.127 min^{-1} and this value is in the same order as the values corresponding to the other processes cited.

TOC evolution

TOC monitoring shows the extent of mineralization of the reaction mixture, i.e., the degradation of compounds with organic carbons into inorganic compounds. For compounds such as CP it is important to achieve a high degree of mineralization, as toxicity is mostly associated with the organic compounds, to ensure that they are harmless or just to reduce their toxicity to a certain level. To achieve low toxicity may require a further treatment such as biological digestion.

The TOC measurements of the samples yielded the results shown in Figure 6, where values for different r can be seen. The initial TOC value was below the maximum TOC value. In each experiment, after around 20 min of treatment this maximum was reached and the reaction mixture changed from a murky emulsion to a clear solution. The reason for this behavior could be that CP has poor solubility and part of the emulsion adheres to the reactor walls. Accordingly, the organic carbon measurements are lower than the real ones. Then, the formation of the first soluble intermediates that still retain most of the organic carbon in their

Figure 5 | CP and H$_2$O$_2$ concentration evolution as a function of time. $C_{CP}^0 = 10.1$ mg L^{-1}; $C_{H_2O_2}^0 = 450$ mg L^{-1}. The inset illustrates the degradation kinetics of chlorpyrifos with a rate constant $k = 0.127$ min^{-1}.

Figure 6 | TOC measurements as a function of time for $r = 6$, 8 and 12.

chemical structures is a possible explanation of why the TOC values reach a maximum when the mixture becomes clear (Fallmann et al. 1999). Fallmann et al. (1999) and Huston & Pignatello (1999) observed similar results when they worked with other emulsifiable pesticides.

The conversions reached approximately 70% at 240 min in all runs (Figure 6). The behavior was independent of the initial concentration of H_2O_2 in the range studied. In the case of $r = 0$, there is no conversion (not shown); this implies that in the reaction time under study, the generated intermediates would maintain the content of total organic carbon.

The maximum TOC value of the emulsions (20 mg L^{-1}) was higher than the one assigned to the active ingredient alone (4.6 mg L^{-1} of TOC for 15 mg L^{-1} of CP, theoretical calculation). This confirms that the commercial formulate adjuvants are mostly organic. Huston & Pignatello (1999) obtained similar results when they treated an emulsifiable concentrate of pesticide.

Toxicity evaluation

Figure 7 shows the percentage of inhibition of V. fischeri for a run after 5 and 15 min of incubation. In this test, light production is directly proportional to the metabolic activity of the bacterial population, and any inhibition of enzymatic activity causes a corresponding decrease in bioluminescence. Thus, luminescence inhibition in the bacterium can effectively indicate that CP has toxic effects on higher organisms (Parvez et al. 2006).

At first, the toxicity was 80%, approximately. After 20 min of treatment the inhibition decreased to a 60% and then, at 40 min, it increased again to 95%, possibly due to
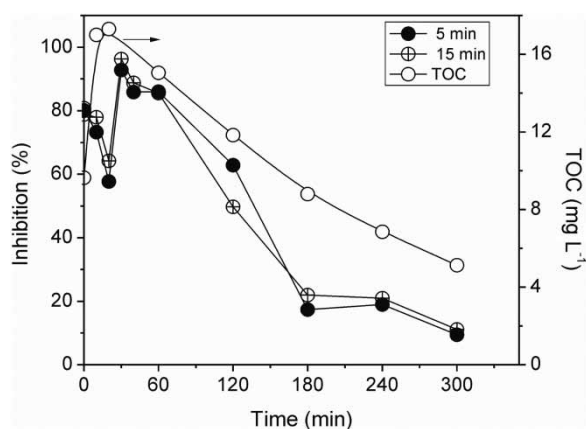

Figure 7 | Percentage of inhibition of Vibrio fischeri. Experimental conditions: $C_{CP}^0 = 12.4$ mg L^{-1}; $C_{H_2O_2}^0 = 454.4$ mg L^{-1}; initial pH = 6; $r = 10$.

the generation of more toxic intermediate products during the oxidation process.

The increased toxicity of the mixture could be explained by the possible formation of chlorpyrifos-oxon (CPO), the active metabolite of CP or other photoproducts like 3,5,6-trichloro-2-pyridinol (Kralj et al. 2007), or may be due to the interaction with the other substances that exist in commercial formulations.

After 60 min, the toxicity tends to decrease rapidly until 180 min of treatment (20% inhibition), and after that time it decreases slowly to approximately a 10% inhibition. Figure 7 shows that there is no significant difference in the inhibition achieved between the two times of exposition (5 and 15 min). It should be noted that even though more than 30% of the initial TOC content of the solution still remains, it is not necessary to complete the mineralization because the intermediate organic compounds remaining after 300 min of treatment show very low toxicity values (10% inhibition).

In Palma et al. (2008), the acute toxicity of CP, among other pesticides, was evaluated using V. fischeri. According to the toxicity categories established by the EU legislation, CP can be classified as a 'toxic' compound to this aquatic organism. The EC_{50} for 30 min is 2.84 mg L^{-1}, where the EC_{50} is the effective concentration of a chemical that causes a 50% reduction in the bioluminescence of the bacteria. CP is also classified as very toxic to other invertebrate and aquatic organisms. In a study of the acute toxicity of 11 organophosphates, CP was considered as the most toxic insecticide for two marine invertebrates, Artemia sp. and Brachionus plicatilis (Guzzella et al. 1997). Both CP and CPO are potent cholinesterase inhibitors; the cholinesterase is an enzyme vital for normal nerve function. Tahara et al. (2005) found that the acute toxicity of CPO was greater than the toxicity of CP due to its active functional group (P = O).

In Kundu et al. (2012), the CP in an emulsifiable concentrate formulation is degraded in water by hydrogen peroxide catalytically activated by TAML, leading to a significant reduction in toxicity evaluated using V. fischeri. This degradation procedure produced a 72.5-fold reduction in toxicity of the treated reaction mixture, compared to the untreated CP emulsion.

CONCLUSIONS

The combination of UV radiation and hydrogen peroxide may become a suitable and very simple process to remove commercial CP from water. In this experimental work, the

best condition found to treat 15 mg L^{-1} of CP at natural pH is a H$_2$O$_2$ concentration of 450 mg L^{-1} (total volume treated 4 L, initial CP concentration 15 mg L^{-1}). Under this condition a complete degradation of CP is achieved before 60 min of reaction. However, no significant reduction of toxicity is reached before 180 min of reaction (20% inhibition reached). At this point of the treatment, nearly 50% of the initial TOC content still remains in the solution. The results clearly show that it is possible to reduce the cost of the process by not reaching a complete mineralization.

ACKNOWLEDGEMENTS

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