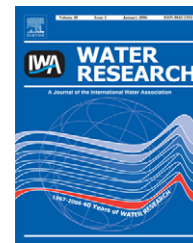


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# Oxidation of chlorfenvinphos in ultrapure and natural waters by ozonation and photochemical processes

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## ABSTRACT

The chemical oxidation of the organophosphorus insecticide chlorfenvinphos, a priority pollutant in aquatic environments, has been conducted in ultrapure water, by means of single degradation agents (ozone and UV radiation), and by the Advanced Oxidation Processes constituted by combinations of these oxidants ( $O_3/H_2O_2$  and  $UV/H_2O_2$ ). The influence of the operating variables was discussed, and the degradation rates were evaluated by determining the rate constants for the reactions with ozone ( $k_{O_3} = 3.7 \pm 0.2 \text{ L mol}^{-1} \text{ s}^{-1}$ ) and OH radicals ( $k_{OH} = (3.2 \pm 0.2) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ), as well as the quantum yield for the photodegradation (around  $0.1 \text{ mol E}^{-1}$ , depending on the pH). Additionally, the ozonation of chlorfenvinphos in a natural water system (a surface water from a reservoir) was studied. The influence of the operating conditions on the insecticide removal efficiency was established, and the  $R_{ct}$  parameter was evaluated. A kinetic model was proposed for the prediction of the elimination rate of chlorfenvinphos in the ozonation process and the results obtained reveal a good agreement between experimental results and predicted values.

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## 1. Introduction

Indiscriminate usage of synthetic agrochemicals or pesticides is considered to be detrimental to sustainable development, due to their persistence and toxic nature. As a consequence, the EU has set pesticide standards for drinking water at a maximum permissible concentration for any particular pesticide of 0.1, and  $0.5 \mu\text{g L}^{-1}$  for the sum of all pesticides, including their degradation products (Directive 98/83/EC of the Council).

More specifically, organophosphorus pesticides (chlorpyrifos, chlorfenvinphos, diazinon, malathion, parathion, etc.) are amongst the pesticides which have been found in a major extent in water supplies. Because of their high solubility and their rapid decomposition in aquatic systems, they are frequently used as substitute of the more persistent organochlorine compounds which are suspected to be bioaccumu-

lated in the food chain (Lartiges and Garrigues, 1995). At the same time, organophosphorus pesticides follow different physical, chemical, and biological processes in waters, which constitute serious environmental problems concerning the fate and behavior of these compounds and their metabolites or decomposition products in the aquatic systems. As inhibitors of cholinesterase activity, organophosphorus insecticides in general produce overstimulation of cholinergic neurotransmission, both centrally and peripherally, producing symptoms such as increased salivation, sweating, changes in blood pressure and heart rate, nausea, diarrhea, headache, muscle tremor, and, in high-dose situations, breathing difficulty, convulsions and death (Padilla et al., 2005).

The removal from water and wastewaters of hazardous organic pollutants is frequently performed by using single oxidants, such as chlorine, ozone, UV radiation, hydrogen peroxide, etc. In other cases, when these pollutants are

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especially refractory to the oxidants, or are present at high concentrations, more effective treatments have been applied, like some systems based on the generation of very reactive and oxidizing free radicals. These systems are called “Advanced Oxidation Processes” (AOPs) (Hoigné, 1998), which mainly produce hydroxyl radicals by combining two or more degradation agents (ozone, hydrogen peroxide, and UV radiation) (Meunier et al., 2006), as well as the combination of hydrogen peroxide with ferrous ions in the Fenton’s reagent (Walling, 1975), or the combination of that Fenton’s reagent with UV radiation in the photo-Fenton system (Chu et al., 2005). Previous studies focused on the ozonation of organophosphorus pesticides reported that these compounds are generally reactive towards ozone, phosphate derivatives being more resistant to ozonation than thiophosphate derivatives (Ikehata and Gamal El-Din, 2005). Similarly, chlorination is a feasible option for the removal of organophosphorus pesticides with thiophosphate group, but not for the elimination of pesticides with phosphate moiety (Acero et al., 2008). Therefore, the oxidation of organophosphorus pesticides with phosphate moiety must be carried out with AOPs (Ikehata and Gamal El-Din, 2005, 2006).

Chlorfenvinphos (CVP, 2-chloro-1-(2,4-dichlorophenyl)ethenyl diethyl phosphate), an organophosphorus pesticide with phosphate moiety, is considered as a Priority Hazardous Pollutant by the EU Water Framework Directive (Decision No. 2455/2001/EC of the European Parliament and of the Council). Although some previous works have been published about the oxidation of CVP with ozone and some AOPs (Farré et al., 2005; Hincapié et al., 2005; Maldonado et al., 2006; Meijers et al., 1995), there is a general lack of kinetic data on the different oxidation reactions of chlorfenvinphos. Therefore, a research program was designed to investigate the removal of CVP in ultrapure water by single degradation agents (ozone and UV radiation) and by different AOPs ( $O_3/H_2O_2$  and  $UV/H_2O_2$ ), with the aim to provide data on the removals obtained, and to determine values of the rate constants for the reactions with ozone and OH radicals, as well as the quantum yields for the photochemical reactions. These rate constants will be used for predicting and modeling the elimination of chlorfenvinphos in a natural water during ozonation processes.

## 2. Materials and methods

### 2.1. Reagents

Chlorfenvinphos was obtained from Riedel de Haën (Seelze, Germany) at 97.2% purity (mixture of Z and E isomers). Other chemicals were of analytical grade or higher. Solutions of CVP, analytical reagents, ozone, and phosphate buffers were prepared with ultrapure water produced from a Milli-Q (Millipore) water purification system. Concentrated ozone solutions were produced by bubbling ozone-containing oxygen through a flask of Milli-Q water cooled with ice.

### 2.2. Analytical methods

The concentrations of CVP and *p*-chlorobenzoic acid (pCBA, when present as a reference or probe compound) were

assayed by HPLC in a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Nova-Pak C18 Column ( $5\mu\text{m } 150 \times 3.9\text{mm}$ ). The selected wavelengths were 245 and 238 nm for CVP and pCBA, respectively. The mobile phase was a mixture of methanol and  $10^{-2}\text{M}$  phosphoric acid in the proportion 68:32 in volume. The elution flow rate was  $1\text{mL min}^{-1}$  and the injection volume was 50–200  $\mu\text{L}$  depending on the CVP concentration. The ozone concentration in the stock solution was determined by its UV absorbance at 258 nm ( $\epsilon = 3150\text{L mol}^{-1}\text{cm}^{-1}$ ) and the ozone concentration in the reaction samples was measured by the colorimetric method proposed by Bader and Hoigné (1981).

### 2.3. Oxidation of chlorfenvinphos in ultrapure water

Ozonation experiments of CVP were conducted under pseudo-first-order conditions, where ozone was at least 30 folds in excess, with the objective of determining the rate constants of the direct reaction between CVP and ozone. These experiments were performed at  $\text{pH} = 2$  (10 mM phosphate buffer) and in the presence of *tert*-butylalcohol (t-BuOH, 0.01 M) as OH radical scavenger. The temperature was varied in the range 10–40 °C. In a typical experiment, a 100 mL volume of buffered CVP solution (around  $1\mu\text{M}$ ) was prepared in a batch reactor (serum vial of 110 mL). The experiments were started after addition of an aliquot of the ozone stock solution into the reactor while stirring (for 5 s). The initial ozone concentration ranged from  $3 \times 10^{-5}$  to  $1 \times 10^{-4}\text{M}$ . At fixed time intervals, 2 mL of sample was rapidly transferred with a syringe into an HPLC vial containing 10  $\mu\text{L}$  of potassium thiosulfate (0.1 M) to stop the reaction. The residual CVP concentrations were analyzed directly by HPLC.

The second group of ozonation experiments were carried out with the objective of determining the rate constant for the direct reactions between CVP and OH radicals. For this purpose, OH radicals were generated by using the AOP  $O_3/H_2O_2$  at high pH. These experiments were performed in 10 mL flask reactors at  $\text{pH} 9$  (10 mM phosphate buffer), 20 °C and in the presence of  $H_2O_2$  which favoured fast ozone decomposition into OH radicals. Under these conditions, OH radical was the predominant oxidant species. This rate constant was determined by competition kinetics, using pCBA as a reference compound. The experiments were started by adding different amounts (in the order of  $\mu\text{L}$ ) of the ozone stock solution (to give ozone concentrations in the reaction sample of  $(5\text{--}10) \times 10^{-5}\text{M}$ ) to aliquots of 9 mL of buffered solutions of CVP, pCBA (both  $5\mu\text{M}$ ) and  $H_2O_2$  ( $(5\text{--}10) \times 10^{-4}\text{M}$ ). The residual CVP and pCBA concentrations were analyzed after 3 h, time enough for complete ozone consumption.

The reactor used in the photochemical degradation of CVP consisted in a 500 mL cylindrical glass vessel. The radiation source was a low-pressure mercury vapor lamp (Heraeus TNN 15/32, nominal electrical power 15 W), which emitted a monochromatic radiation at 254 nm, and was placed axially within the reactor. For every experiment conducted, the reactor was filled with 350 mL of CVP ( $10\mu\text{M}$ ) solutions (plus hydrogen peroxide in the combined  $UV/H_2O_2$  experiments) at the selected pH (10 mM phosphate buffer). Samples were

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