



## RESEARCH NOTE

DEGRADATION OF ORGANOCHLORIDE COMPOUNDS BY  
 $O_3$  and  $O_3/H_2O_2$ P. ORMAD\*<sup>1</sup>, S. CORTÉS<sup>1</sup>, A. PUIG<sup>2</sup> and J. L. OVELLEIRO<sup>1</sup><sup>1</sup>Department of Chemical Engineering and Environmental Technology, Science Faculty, University of Zaragoza, Pza. San Francisco, s/n 50009-Zaragoza, Spain and<sup>2</sup>Confederación Hidrográfica del Ebro. Pa. Sagasta, 28.50006-Zaragoza, Spain

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**Abstract**—This paper presents the results obtained from oxidation with  $O_3$  and  $O_3/H_2O_2$  of a residual water coming from the production of dicofol and tetradifon pesticides, where chlorobenzenes, DDTs and its metabolites and other organochloride compounds were found. The oxidation processes were carried out using ozone ( $O_3$ ) in basic medium (pH 9.4) at low dosage ( $0-1.5 \text{ g } O_3 \text{ g}^{-1}$  initial TOC) and in the presence of hydrogen peroxide ( $H_2O_2$ ), with a  $0.5 \text{ H}_2O_2/O_3$  molar ratio. During the treatment, many compounds were removed (dichlorobenzophenone, tetradifon, chlorobenzene, trichlorobenzene) and their change in concentration at different ozonation contact time was monitored. Other compounds like DDE remained practically invariable. This study investigated the formation of first ozonation by-products (FOBPs) in the wastewater, specifically chlorophenols, by means of gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD) analysis in terms of the amount of time the  $O_3$  has been in contact with the processed sample. *o*-Chlorophenol, *p*-chlorophenol, benzenemethanol, *n*-chlorohydroxybenzaldehyde, *n*-chlorobenzenemethanol, chlorobenzoic acid, etc., were formed during the treatment, due to the mechanism of fast and non-selective oxidation which ozone has through OH radicals, formed by the decomposition of the  $O_3$  molecule and accelerated by the presence of  $H_2O_2$  in water. © 1997 Elsevier Science Ltd

**Key words**—organochloride compounds, pesticides, ozone, hydrogen peroxide, chlorobenzenes, dicofol, tetradifon, by-products, wastewater.

## INTRODUCTION

Pesticide-synthesis industries generate spillages which contain many toxic and non-biodegradable compounds that remain in the environment even after the waste products have been subjected to a conventional processing system. The production of the pesticides dicofol and tetradifon generates waste effluents that contain many different organochloride compounds like the complete series of chlorobenzenes, DDTs and its metabolites, chlorobenzaldehyde, chlorobenzoic acid, etc., substances usually detected in industrial waste spillages, many of which are included in List I of the European Council Directive 76/464/EEC as future candidates for regulation (EC, 1976). The maximum contaminant levels for total trichlorobenzene, hexachlorobenzene and DDTs and its metabolites have been stipulated by the EU for wastewater and surface water (EC, 1986, 1988, 1990).

For reasons such as these, many studies have been made in order to remove these pollutants in drinking and wastewater treatments (Beltran and Beltran, 1986). Studies of the last few years have shown that the effective removal of some of these organochloride compounds from the aqueous medium is achieved by using advanced oxidation processes (Ormad *et al.*, 1994), with ozone ( $O_3$ ) at high pH or  $O_3$  combined with hydrogen peroxide ( $H_2O_2$ ), where OH radicals are formed in the decomposition of  $O_3$  in the aqueous medium (Glaze *et al.*, 1987).

Ozonation of organic matter can lead to the production of by-products (Andrews *et al.*, 1993) which are suspected to be public health concerns, like aldehydes, phenols, aromatic acids, etc. Organic compounds present in the wastewater react with ozone in both molecular form and as hydroxyl radicals to form oxygenated first ozonation by-products (FOBPs) (Legube *et al.*, 1981). This study investigated the formation of FOBPs in the wastewater, specifically chlorophenols, during the ozonation processes.

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## MATERIALS AND METHODS

### Sample

The wastewater used in this study has been taken from a factory which produces the organochloride pesticides dicofol and tetradifon. (Fig. 1).

### Ozonation

Ozonation was carried out using a closed reactor (Fischer Model 501) to which 4 litres of residual water was added. The raw water (pH 9.4; conductivity 13 mS; TOC 1150 mg litre<sup>-1</sup>; COD 3920 mg litre<sup>-1</sup>; TOX 606 mg litre<sup>-1</sup>; Cl<sup>-</sup> 5815 mg litre<sup>-1</sup> and EC<sub>50</sub> 370.000 mg litre<sup>-1</sup>) was treated with O<sub>3</sub> and O<sub>3</sub> combined with H<sub>2</sub>O<sub>2</sub> in a H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratio of 0.5 (Bellamy *et al.*, 1991).

In the experiments, the total contact time was 60 min and the O<sub>3</sub> dosage used was 0–1.5 g litre<sup>-1</sup> (0–1.3 g g<sup>-1</sup> TOC). The non-consumed O<sub>3</sub> was determined by bubbling the gas through a 2% KI solution that was titrated with sodium thiosulphate and starch as indicator (Kolthoff and Belchor, 1957). The residual O<sub>3</sub> in the aqueous phase was measured by the Indigo colorimetric method (4500-O<sub>3</sub> B Standard Method (Cleresci *et al.*, 1989).

### Parameter measurements

Organic compounds present in aqueous samples collected during the experiments at different ozonation dosages were analysed by means of GC/ECD and GC/MS (US EPA method 625). The chromatography conditions were as follows: mass spectrometer, ITD Finnigan Mat 800; gas chromatograph, HP 5890 and Varian 3300; detector, electron capture detector; column, DB-5; splitless, 0.8 min; injection temperature, 250°C; detection temperature, 350°C; temperature program, 60(1)-4-280(10).

Other chemical parameters were also measured: chloride (Standard Method 4500B, Cleresci *et al.*, 1989); TOC (Standard Method 5310B, Cleresci *et al.*, 1989); COD (Standard Method 5220B, Cleresci *et al.*, 1989); TOX (Standard Method 5320, Cleresci *et al.*, 1989); EC<sub>50</sub> (Bioluminescence test photobacterium phosphoreum; BOE, 1989).

## RESULTS AND DISCUSSIONS

The wastewater coming from the production of dicofol and tetradifon pesticides was treated at high pH with O<sub>3</sub> and O<sub>3</sub> plus H<sub>2</sub>O<sub>2</sub>, and the results were compared.

The majority of compounds present in the wastewater were determined by using GC/MS analyses (Fig. 2) and they were quantified by GC/ECD (the concentration of these compounds was below the maximum levels established by the European legislation). The degradation of some of these compounds using O<sub>3</sub> has been studied by many authors: chlorobenzene and nitrobenzene by Lykins *et al.* (1986), benzaldehyde and chlorobenzene by

Legube *et al.* (1983), trichlorobenzene by Masten *et al.*, 1993), etc. Rate constants of reaction of O<sub>3</sub> with chlorobenzenes, nitrobenzene, benzaldehyde, benzoic acid, etc., have been determined by Hoigné and Bader (1983a,b). These organochloride compounds exhibit low reaction rate constants ( $K_{O_3} < 10 \text{ M}^{-1} \text{ s}^{-1}$ ), but their degradation can be effective when ozonation is performed in the range of very high pH or in the presence of H<sub>2</sub>O<sub>2</sub>.

Table 1 shows the variation in concentration of four different solutes (M) during the treatment with ozone or ozone combined with H<sub>2</sub>O<sub>2</sub>. Approximately 80% of initial chlorobenzene ( $M_0 = 33.4 \text{ mg l}^{-1}$  in wastewater), the raw material of dicofol, was degraded after consumption of 0.23 g O<sub>3</sub> l<sup>-1</sup> in both treatments. A total disappearance was achieved by using O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> after dosage of 1.51 g O<sub>3</sub> l<sup>-1</sup>.

1,2,4-Trichlorobenzene (1,2,4-TCB), the raw material of tetradifon, with an initial concentration of  $M_0 = 0.7 \text{ mg l}^{-1}$  in the wastewater, exhibited lower reactivity towards O<sub>3</sub> than chlorobenzene. Using a dosage of 0.23 g O<sub>3</sub> litre<sup>-1</sup>, the elimination of 50 and 62% of 1,2,4-TCB was achieved in the treatment of O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, respectively. Table 1 shows that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was more effective than O<sub>3</sub> alone to remove 1,2,4-TCB from wastewater. At the end of the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment only 7% of initial 1,2,4-TCB remained after the consumption of 1.51 g O<sub>3</sub> litre<sup>-1</sup>.

One of the final products of the chemical industry, the pesticide tetradifon ( $M_0 = 0.15 \text{ mg litre}^{-1}$ ), was totally removed (>98%) with a dosage of 0.23 g O<sub>3</sub> litre<sup>-1</sup> in both treatments.

Also, dichlorobenzophenone ( $M_0 = 0.16 \text{ mg litre}^{-1}$ ), the biodegradation by-product of dicofol, was degraded by the two oxidation processes. An elimination level of 80 and 85% was achieved with a dosage of 0.35 g O<sub>3</sub> litre<sup>-1</sup> with O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, respectively. Other compounds, like DDTs and their metabolites, were not oxidized under these experimental conditions.

After the two treatments, with an O<sub>3</sub> dosage of 1.3 g g<sup>-1</sup> TOC, the TOC, COD, TOX and chloride concentration remained practically invariable (similar results were achieved by Andrews *et al.*, 1993). The low elimination of TOC, COD and TOX after treatments (<10%) shows that the compounds have been degraded only partially to CO<sub>2</sub>. So, by means of GC/MS analysis, many FOBPs were identified: benzenemethanol, chlorobenzenemethanol, benzoic

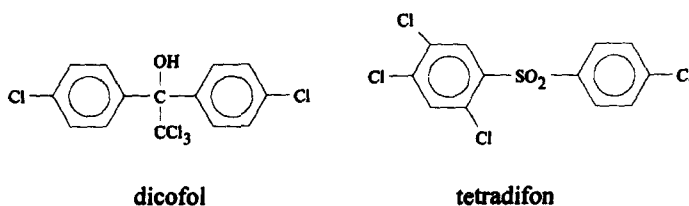


Fig. 1. Dicofol and tetradifon.

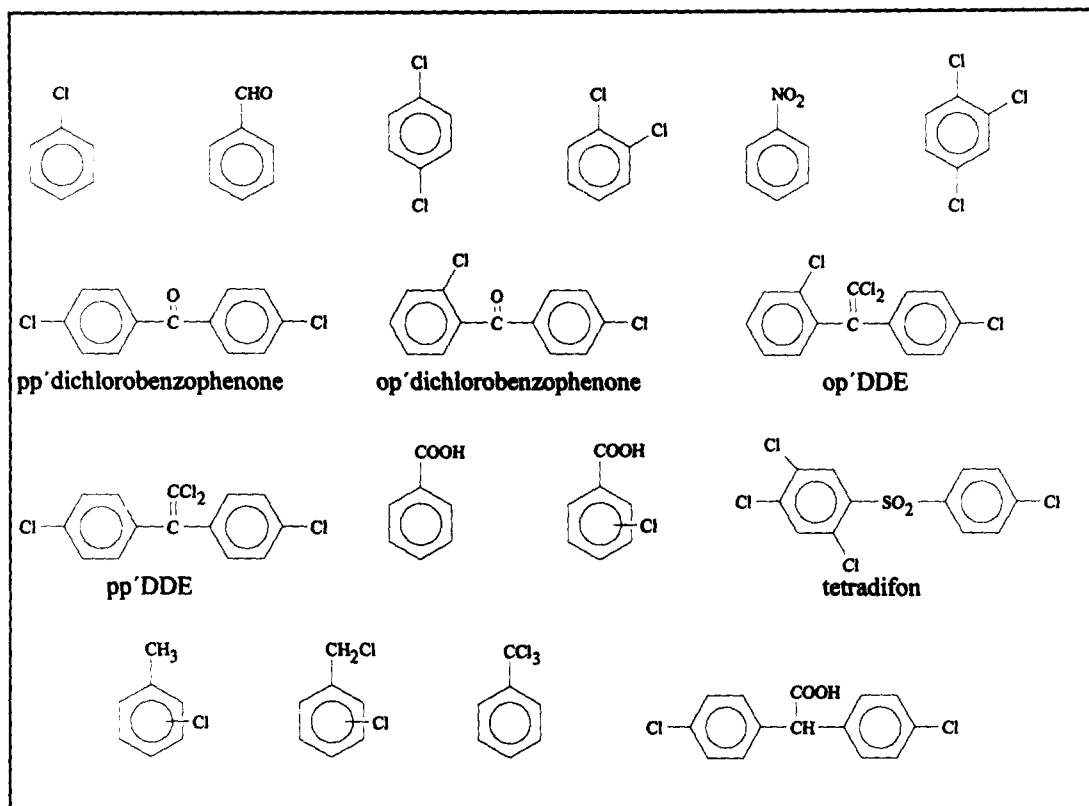


Fig. 2. Majority of compounds present in the wastewater.

acid (detected by Legube *et al.* (1983) in the oxidation of benzaldehyde), chlorobenzoic acid, dichlorobenzoic acid, nitrobenzaldehyde, chlorohydroxybenzaldehyde, chlorophenol and trichlorophenol (Fig. 3).

The formation of the two isomers of chlorophenol may be explained by the electrophilic attack of OH radicals in the *ortho* and *para* positions of chlorobenzene. Chlorophenols have high reaction rate constants (Hoigné and Bader, 1983b; Haag and Yao, 1992). Their degradation by  $O_3$  has also been studied by Yu-Hwa Yu and Szu-Tsong Hu (1993). During the present experiments, chlorophenol is formed;  $O_3$  reacts with it simultaneously, destroying it (Figs 4 and 5). The initial concentration in the raw water of the *ortho* and *para* isomers was 4.2 and 7.6  $\mu\text{g litre}^{-1}$ , respectively. The *para* isomer was formed faster than the *ortho* isomer. Approximately 2.0  $\text{mg litre}^{-1}$  of *p*-chlorophenol was detected in the

treatment with  $O_3$  at a dosage of 1.19  $\text{g O}_3 \text{ litre}^{-1}$ , and 3.7  $\text{mg litre}^{-1}$  was detected in the  $O_3/H_2O_2$  treatment at a dosage of 0.83  $\text{g O}_3 \text{ litre}^{-1}$ . The maximum concentration of *o*-chlorophenol detected during both treatments was 9.6  $\mu\text{g litre}^{-1}$  in the  $O_3$  oxidation processes. Trichlorophenol only was detected during treatment with  $O_3/H_2O_2$  at trace levels.

The biotoxicity (measured as  $EC_{50}$ ) increased during the ozonation processes by about 60%.

#### CONCLUSIONS

The results presented in this paper and those obtained previously show the following in the treatment by  $O_3$  of wastewater containing organochloride compounds:

1. The elimination of TOC, COD and TOX was very limited (<10%), using low  $O_3$  dosages.
2. DDTs and their metabolites remained practi-

Table 1. Degradation of compounds during ozonation (M/M<sub>0</sub>)

Compound	Ozone				Ozone + H <sub>2</sub> O <sub>2</sub>				
	O <sub>3</sub> /TOC (g g <sup>-1</sup> )				O <sub>3</sub> /TOC (g g <sup>-1</sup> )				
	0	0.2	0.6	1.0	0	0.25	0.4	0.7	1.3
(Mono)chlorobenzene	1.00	0.20	0.15	0.15	1.00	0.03	0.02	0.02	0.01
1,2,4-TCB	1.00	0.50	0.46	0.38	1.00	0.35	0.20	0.12	0.07
Tetradifon	1.00	0.02	0.01	0.00	1.00	0.02	0.01	0.00	0.00
Dichlorobenzophenone	1.00	0.35	0.18	0.02	1.00	0.29	0.14	0.07	0.00

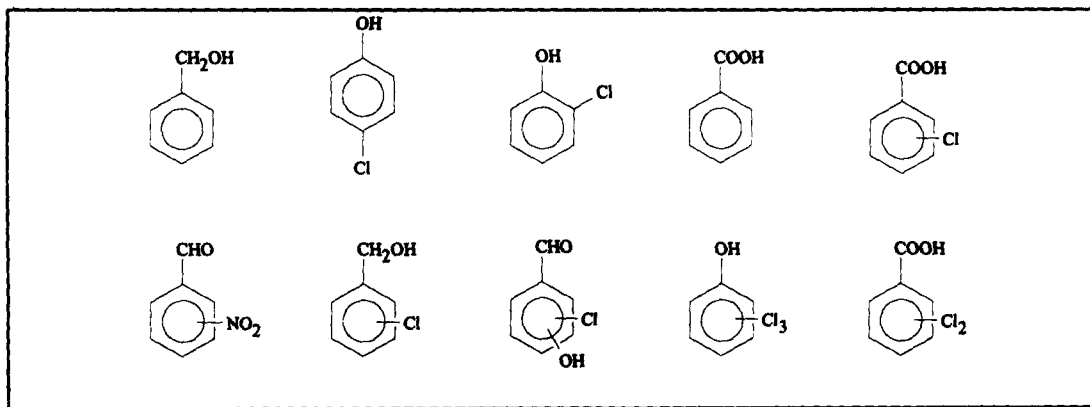
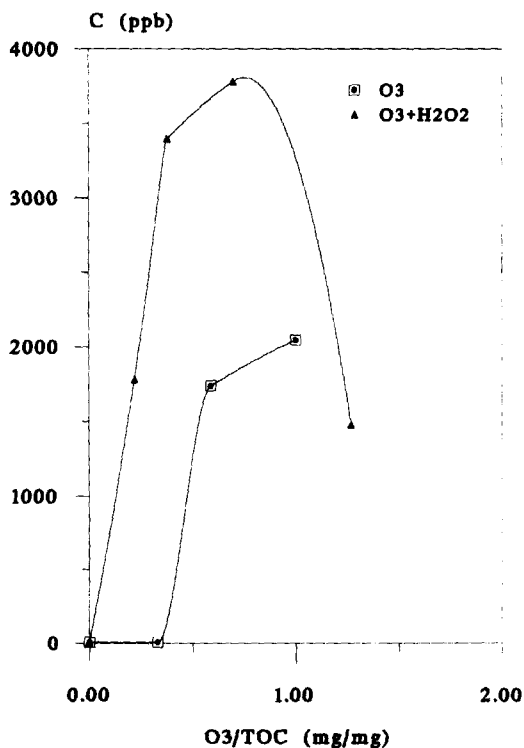
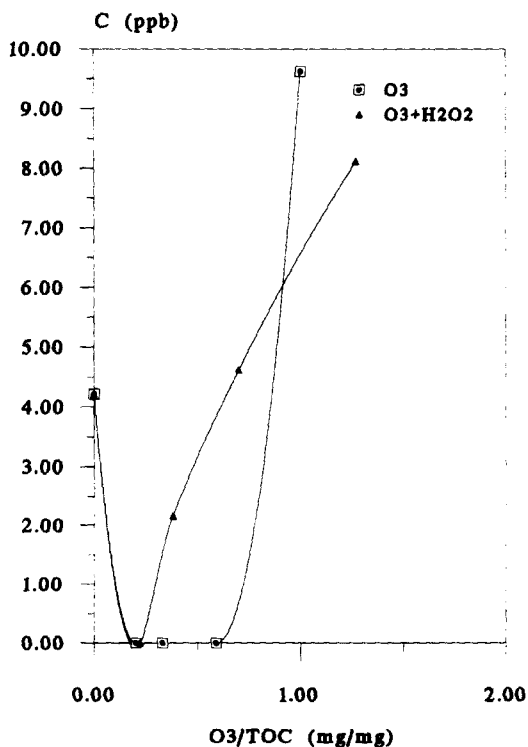


Fig. 3. FOBPs identified during treatment.

- cally invariable under these laboratory conditions.
- Chlorobenzene exhibited higher reactivity towards  $O_3$  than 1,2,4-TCB.
  - The  $O_3/H_2O_2$  system appears to be more efficient than the  $O_3$ /high-pH system to remove chlorobenzenic compounds under these experimental conditions.
  - Tetradifon and dichlorobenzophenone were totally oxidized by  $O_3/H_2O_2$  and  $O_3$ /high-pH.
  - Hydroxylated FOBPs (*o*-chlorophenol, *p*-chlorophenol, benzenemethanol, *n*-chloro-

droxybenzaldehyde, *n*-chlorobenzenemethanol, chlorobenzoic acid, etc.) were formed during the treatment, due to the mechanism of fast and non-selective oxidation which  $O_3$  has through OH radicals, formed by the decomposition of the  $O_3$  molecule and accelerated by the presence of  $H_2O_2$  in water. The results of this study have shown that the intermediates in the reaction are highly reactive themselves. The concentration of chlorophenol was decreased at the end of the oxidation with  $O_3/H_2O_2$ . In a first step,  $O_3$  attacks

Fig. 4. Formation and degradation of *p*-chlorophenol during treatment with  $O_3$  and  $O_3/H_2O_2$ .Fig. 5. Formation and degradation of *o*-chlorophenol during treatment with  $O_3$  and  $O_3/H_2O_2$ .

chloroaromatic compounds and chlorophenol is formed; in a second step,  $O_3$  attacks the chlorophenol molecule, destroying it.

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