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Degradation of chlordecone and beta-hexachlorocyclohexane by photolysis, (photo-)fenton oxidation and ozonation

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ABSTRACT

Intensive use of chlorinated pesticides from the 1960s to the 1990s has resulted in a diffuse contamination of soils and surface waters in the banana-producing areas of the French West Indies. The purpose of this research was, for the first time, to examine the degradation of two of these persistent pollutants – chlordecone (CLD) and beta-hexachlorocyclohexane (β -HCH) in 1 mg L⁻¹ synthetic aqueous solutions by means of photolysis, (photo-) Fenton oxidation and ozonation processes. Fenton oxidation is not efficient for CLD and yields less than 15% reduction of β -HCH concentration in 5 h. Conversely, both molecules can be quantitatively converted under UV-Vis irradiation reaching 100% of degradation in 5 h, while combination with hydrogen peroxide and ferrous iron does not show any significant improvement except in high wavelength range (>280 nm). Ozonation exhibits comparable but lower degradation rates than UV processes. Preliminary identification of degradation products indicated that hydrochlordecone was formed during photo-Fenton oxidation of CLD, while for β -HCH the major product peak exhibited C₃H₃Cl₂ as most abundant fragment.

Introduction

Banana and sugarcane have been the main agricultural products of the French Antilles (Guadeloupe and Martinique) since the 1960s. To prevent crop damages from the banana weevil, chlorinated pesticides, such as chlordecone (CLD, C₁₀Cl₁₀O, CAS-number: 143-50-0), β -hexachlorocyclohexane (β -HCH, C₆Cl₆H₆, CAS-number: 319-85-7) and dieldrine were extensively used until the beginning of the 1990s, resulting in the contamination of both the soil and the surface waters.^[1,2] It was not until 2009, when they were listed as persistent organic pollutants under the Stockholm Convention,^[3] that the production and agricultural use of the first two pesticides was prohibited worldwide.^[3]

Chlordecone has a low solubility in water (2.7 mg L⁻¹ at 25  C^[4]) and its vapor tension is less than 3 \times 10⁻⁷ mmHg at 25  C.^[1] It has a strong affinity for lipids, accumulates in the food chain^[5,6] and is known for its endocrine-disrupting character^[7] and carcinogenic potential.^[8,10] Used since 1972, it was banned in 1993 in the French West Indies. Nonetheless, pollution surveys conducted in 2001 by the French Department of Health still revealed the presence of chlordecone in soils, rivers, springs and drinking water of Antilles, as well as in food crop products such as root vegetables.^[1] More recent studies in the

same area measured concentrations of chlordecone between 0.1 and 37.4 mg kg⁻¹ in soils.^[4]

HCH was spread on the form of technical HCH consisting of eight isomers whose water solubility varies between 5 (for β -HCH) and 20 mg L⁻¹ and vapor tension between 3.54 \times 10⁻⁵ (for β -HCH) and 0.003 Pa at 20  C.^[11] Mainly four of them are found in technical grade products, β -HCH (accounting for 5 to 12% of technical HCH) being considered as the most recalcitrant.^[12] Available toxicity data for this isomer are limited, especially concerning human health, because exposure mainly occurs with HCH mixture or pesticidally active lindane (γ -HCH). Neurotoxic effects were reported from animal studies and it is classified as possibly human carcinogenic.^[11] Technical HCH was mainly used in the 1960s and 1970s in the Antilles (before CLD was introduced), with amount as high as 350 kg ha⁻¹ year⁻¹.^[12] Such extensive application should explain why β -HCH is still the pesticide the most frequently detected in surface waters of Martinique after CLD.^[13]

Thus, there is growing political and social pressure to find remediation solutions for CLD and β -HCH problem in the French West Indies. Physical treatments applied for the removal of pesticides from contaminated wastewater, such as coagulation, flocculation,

membrane separation or adsorption on activated carbon, only operate a transfer of the pollutants which still have to be destroyed. Biological solutions are under development,^[14,15] but they are limited by slow degradation kinetics or use of anoxic conditions. On the other hand, advanced oxidation processes like (photo-)Fenton oxidation or ozonation have been applied for the degradation of several classes of pesticides and refractory compounds such as thiamethoxam,^[16] lindane,^[17–20] parathion and dichlorvos,^[18] endosulfan,^[19] linuron,^[21] bromoxynil and trifluralin,^[22] monuron,^[23] 2,4-dichlorophenoxyacetic acid.^[24] Except one patent for CLD,^[25] only very recent works investigated chemical processes for the remediation of CLD^[26] and β -HCH.^[27,29] The purpose of this work is, for the first time, to examine the degradation of CLD and β -HCH in synthetic aqueous solutions by means of photolysis, (photo-)Fenton oxidation and ozonation.

Materials and methods

Chemicals

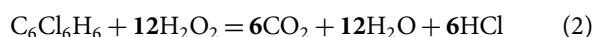
CLD and β -HCH were supplied by Sigma-Aldrich with a purity $\geq 99.0\%$. 700 mL of pesticide solutions with an initial concentration of 1 mg L⁻¹ (corresponding to 2.0 μ mol L⁻¹ for CLD and 3.4 μ mol L⁻¹ for β -HCH) were treated by photo-mediated processes. For ozonation experiments only 250 mL were used. All the samples were prepared by diluting a stock solution (0.5 g L⁻¹ of pesticide in acetone) into demineralized water. For Fenton and photo-Fenton experiments they were then acidified to pH 2.6 using 10% H₂SO₄ (95–97%, Sigma Aldrich).

Hydrogen peroxide (Ph Eur, 30% w/w solution, Sigma-Aldrich) and Fe₂SO₄·7H₂O (99.5%, Sigma-Aldrich) were applied as Fenton's reagents. Methanol (99%, Scharlau Chemie) was used to quench homogeneous Fenton reaction by scavenging hydroxyl radicals.^[30]

Experimental setups

Photolysis and (photo-)Fenton experiments were conducted in a 1 L stirred Pyrex reactor, equipped with a jacket to maintain the temperature of the solution at 30°C. It included a medium-pressure mercury vapor lamp (MP Hg, 450 W Hanovia PC451.050 lamp, arc length 4.8 cm) or a low-pressure mercury vapor lamp (LP Hg, 10 W Heraeus GPH212T5L/4 lamp) placed in either a jacketed quartz or borosilicate glass immersion well. The solution was agitated by a magnetic stirrer rotated at 350 rpm and by gentle bubbling of air. It was checked from blank experiments that no stripping or adsorption of the CLD or β -HCH occurred during the reaction time (5 h). 7 mL aliquots were sampled at selected time intervals, treated with methanol (using 1:1 w/w mixture of sample and MeOH) and centrifuged when Fenton's reagent was present.

The stoichiometric amount of H₂O₂ required for the mineralization of the pesticides was calculated based on the following equations, for (1) CLD and (2) β -HCH:



A H₂O₂ dosage equivalent to 20 times the stoichiometric amount and a molar ratio of H₂O₂ to Fe²⁺ equal to 2 were used

for the Fenton experiments. It corresponded to the following concentrations of the Fenton's reagent: 0.6 mmol L⁻¹ of H₂O₂ and 0.3 mmol L⁻¹ of Fe(II) for CLD; 0.8 mmol L⁻¹ of H₂O₂ and 0.4 mmol L⁻¹ of Fe(II) for β -HCH. The Fenton reaction was initiated by the addition of H₂O₂.

Ozonation was performed in a 0.5 L cylindrical glass reactor and the solution was agitated by bubbling of ozone. For all the experiments the initial pH of the solution was 5.3. Ozone was produced from pure oxygen by a WEDECO 4-HC Ozone Generator. The gas mixture containing 48 g Nm⁻³ of ozone was continuously bubbled into the solution through a porous distributor plate at a flow rate of 30 L h⁻¹. Blank runs were also performed with nitrogen only, to check for the absence of any pollutant stripping or adsorption on reactor internals. Withdrawn samples were not treated before analyses.

Analytical methods

A LC-MS/MS with external standardization was used to follow the evolution of CLD and β -HCH concentrations.

LC-MS/MS analysis

Analysis conditions: (Treated) reaction samples (50 and 80 μ L for CLD and β -HCH, respectively) were directly injected in an Agilent 1100 liquid chromatograph coupled to a triple quadrupole-linear ion trap mass spectrometer (Qtrap 2000, ABSciex). The separation column was a C18 Waters Xbridge (100 mm \times 3.0 mm I.D. and 3.5 μ m particle size) thermostated at 50°C. Mobile phases were (A) ultrapure water, with 10 mmol L⁻¹ of ammonium formate and (B) HPLC grade acetonitrile in the case of CLD samples; (A) ultrapure water and (B) HPLC grade acetonitrile in the case of β -HCH samples. They were delivered in 40/60 v/v isocratic mode of A and B, at a total flow rate of 0.5 mL min⁻¹. The mass spectrometer was used in MS/MS, negative APCI, multiple reaction monitoring (MRM) mode and the following mass transitions (m/z) were followed: 506.85–427 (CLD) and 321.8–195 (β -HCH). Declustering potential (DP) and collision energy (CE) were optimized to the following values: DP = -80 and CE = -28 for CLD, DP = -40 and CE = -18 for β -HCH. The data were recorded and treated with Analyst 1.6.2 software (AB Sciex).

Calibration method: An external standardization procedure was applied for LC-MS/MS analysis, using for each experiment a different calibration curve established in the 0.05–0.5 ppm range. In the case of (photo-)Fenton oxidation, a specific procedure was followed for its construction, so as to minimize variations in response coefficient ascribed to the presence of dissolved iron and quenching agent: the 0.5 ppm standard was prepared by mixing the pollutant solution containing ferrous iron with methanol (1:1 w/w), as for the oxidation samples. Then, a solution consisting in a 1:1 (w/w) mixture of acidic ferrous iron solution (same as previously, but without pollutant) and methanol was used to obtain the other standards by successive dilution of the first one, thereby keeping ferrous iron and MeOH concentrations unchanged. The standards were finally centrifuged as treated samples. Quantification limit was 0.05 ppm for CLD and β -HCH.

Results and discussion

Comparison of the different AOPs for CLD degradation

Photolysis (using first a large UV-Vis spectrum), (photo-)Fenton oxidation and ozonation were investigated for the removal of CLD, and their results are shown in Fig. 1. Error bars indicate the deviation from the mean of triplicate experiments.

First, it should be noticed that although hydroxyl radicals generated by AOPs are reported to be highly reactive and non-selective, Fenton oxidation did not yield any significant conversion of the contaminant in the investigated condition. As the solution also contained a significant amount of acetone which was used to help the pesticide dissolution into water (cf. § 2.1), a complementary experiment was carried out with a tenfold H_2O_2 dosage (while keeping the same H_2O_2/Fe ratio); however the degradation of CLD remained negligible. Such low reactivity might result from the high steric hindrance of the molecule. On the other hand, ozone was able to achieve 70% of pesticide removal within 2 h. In this case, both molecular and radical mechanisms should be involved, the latter being favored by high pH values.^[31] An inhibition of radical process could be then suspected.

CLD could be readily degraded by direct photolysis, to more than 95% in 3 h. Addition of the Fenton's reagent resulted in no appreciable improvement of the removal rate, and thus hydroxyl radical mechanism that should be enhanced under UV-Vis irradiation (through H_2O_2 photolysis and ferrous iron regeneration) did not seem to play any noticeable role either.

To further investigate photo-assisted processes, the applied wavelength range was varied by using the MP Hg lamp with a glass immersion well and a LP Hg lamp (with quartz lamp holder). According to the supplier, the MP Hg lamp emitted 40–48% of its energy is in the ultraviolet portion of the spectrum and 40–43% in the visible range. The glass holder should cut most of the radiation below 280 nm, about 50% of the emission at 310 nm, and showed full transmittance above 355 nm. On the other hand, the LP Hg lamp mainly exhibited a monochromatic emission at 254 nm. Results are shown in Fig. 2 for both photolysis and photo-Fenton oxidation.

For both the processes, the removal yield of CLD ranged in the order: MP Hg lamp + quartz lamp holder > LP Hg lamp + quartz lamp holder > MP Hg lamp + borosilicate lamp holder. As photolysis mechanism was shown as the dominant process, this could be explained by the absorbance spectrum of

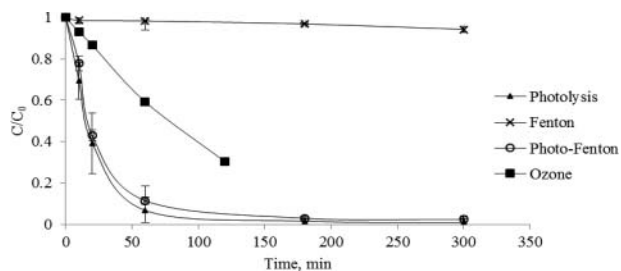


Figure 1. Degradation of CLD by photolysis, Fenton, photo-Fenton and ozonation processes. $[CLD]_0 = 2 \mu\text{mol L}^{-1}$, $T = 30^\circ\text{C}$; 450 W MP Hg lamp and quartz lamp holder for photo-assisted processes; $[H_2O_2]_0 = 0.6 \text{ mmol L}^{-1}$, $[Fe(II)]_0 = 0.3 \text{ mmol L}^{-1}$ and $\text{pH}_0 = 2.6$ for Fenton-based oxidation.

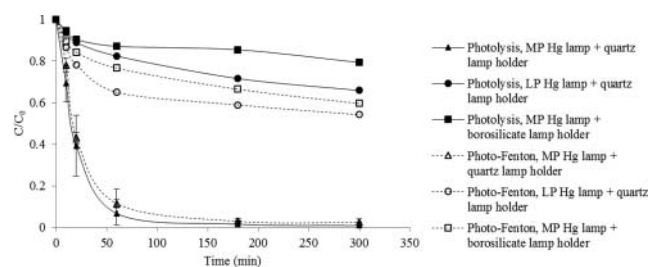


Figure 2. Effect of irradiation spectrum on the degradation of CLD by photo-assisted processes. $[CLD]_0 = 2 \mu\text{mol L}^{-1}$, $T = 30^\circ\text{C}$; photo-Fenton: $[H_2O_2]_0 = 0.6 \text{ mmol L}^{-1}$, $[Fe(II)]_0 = 0.3 \text{ mmol L}^{-1}$, $\text{pH}_0 = 2.6$.

the molecule which exhibited maxima at 210 and 320 nm and differences in lamp irradiation intensity in this wavelength range. Cutting (first) absorption maximum of CLD at 210 nm strongly reduced the molecule photodegradation. On the other hand, the higher rate observed at $\lambda = 254 \text{ nm}$ than at $\lambda > 280 \text{ nm}$ (while another absorption peak is observed at 320 nm) might be due to the presence of acetone, which was reported to act as photo-sensitizer.^[32] Moreover, when the glass lamp holder dramatically hindered photolysis, effect of Fenton's reagent addition more clearly stood out, indicating that a radical-mediated mechanism in fact contributed, but to a much lower extent.

Kitchens^[25] investigated the removal of CLD by UV, UV/ O_3 , and UV/ H_2 in basic aqueous solution and (alkalinized) methanol using a 30W UV lamp irradiating at 254 nm. In aqueous NaOH solution, UV/ H_2 was found to be the most efficient treatment with 84% conversion of the molecule within 120 min vs. 39% and 21% for UV and UV/ O_3 , respectively. This latter result is much lower than that observed for ozonation in the present study, without irradiation and at slightly acidic pH. This is in line with a weak contribution of hydroxyl radicals in the investigated pH. With the MP Hg lamp, similar performance as the proposed UV/ H_2 process could be achieved, but this process might be more expensive and dangerous than (photo-) Fenton oxidation.

Comparison of the different AOPs for β -HCH degradation

Figure 3 provides a comparison of the same AOPs as in Fig. 1, but for the case of β -HCH. It also exhibits essentially the same features: almost insignificant oxidation rate by Fenton's reagent and thus a photo-Fenton process mainly driven by the direct photolysis of the molecule.

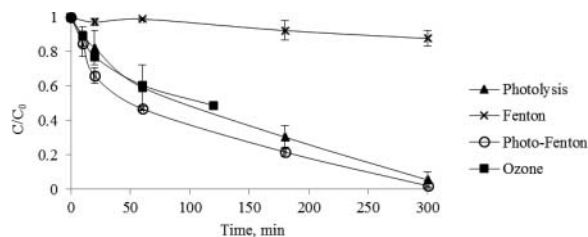


Figure 3. Degradation of β -HCH by photolysis, Fenton, UV/Fenton and ozonation processes. $[\beta\text{-HCH}]_0 = 3.4 \mu\text{mol L}^{-1}$, $T = 30^\circ\text{C}$; 450 W MP Hg lamp and quartz lamp holder for photo-assisted processes; $[H_2O_2]_0 = 0.8 \text{ mmol L}^{-1}$, $[Fe(II)]_0 = 0.4 \text{ mmol L}^{-1}$ and $\text{pH}_0 = 2.6$ for Fenton-based oxidation.

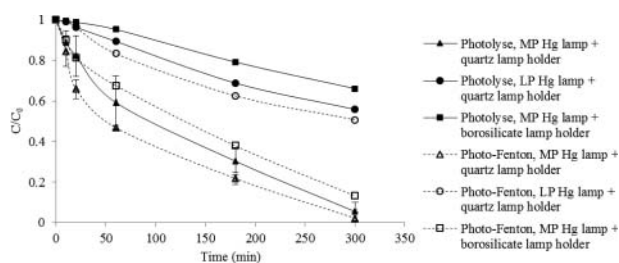


Figure 4. Effect of irradiation spectrum on the degradation of β -HCH by photo-assisted processes. $[\beta\text{-HCH}]_0 = 3.4 \mu\text{mol L}^{-1}$, $T = 30^\circ\text{C}$; photo-Fenton: $[\text{H}_2\text{O}_2]_0 = 0.8 \text{ mmol L}^{-1}$, $[\text{Fe(II)}]_0 = 0.4 \text{ mmol L}^{-1}$, $\text{pH}_0 = 2.6$.

Effect of lamp irradiation was also investigated (Fig. 4) and the most striking result was a still high elimination of β -HCH by photo-Fenton oxidation under UVB-Vis.

To our knowledge, only scarce information related to the advanced oxidation of this pesticide has been reported. The work of Usman et al. (2014) performed on contaminated soils indicated a much lower degradation of β -HCH by Fenton's reagent with respect to γ -HCH (25% vs. 90%). On the other hand, Ormad et al.^[27] studied the degradation of a group of pesticides including β -HCH in very diluted conditions ($0.5 \mu\text{g L}^{-1}$) by ozonation, $\text{O}_3/\text{H}_2\text{O}_2$, O_3/TiO_2 and $\text{O}_3/\text{H}_2\text{O}_2/\text{TiO}_2$ processes. The degradation of β -HCH was only possible when the process $\text{O}_3/\text{H}_2\text{O}_2/\text{TiO}_2$ was used with an ozone flow of 3 mgL^{-1} , for an $\text{O}_3/\text{pollutant}$ ratio close to one. In these conditions a degradation of the β -HCH of 10% was achieved.

Preliminary identification of degradation products indicated that hydrochlordecone was formed during photo-Fenton oxidation of CLD, while for β -HCH the major product peak exhibited $\text{C}_3\text{H}_3\text{Cl}_2$ as most abundant fragment.

In order to compare the different processes studied for the degradation of both pesticides, their kinetics constants were calculated following a pseudo-first order model (Table 1).

As we can observe for the CLD the best process was the photolysis, followed by the photo-Fenton and the ozone, all with the same order of magnitude, and the Fenton process was the less effective with 2 orders of magnitude below. In the case of β -HCH, the behavior was similar to CLD but the photolysis and photo-Fenton processes have the same rate constants.

On the other hand, β -HCH was found less sensitive to UV irradiation, its first-order photolysis rate constant being 2.10^{-4} s^{-1} , much smaller than that of CLD (8.10^{-4} s^{-1}). β -HCH also showed a slightly lower reactivity towards ozone, with about 50% conversion after 2 h (against 70% for CLD).

Finally, with the aim of comparing the efficiency of the photolytic processes a study of the electrical energy per order

Table 1. Kinetics constants of the different process studied for the pesticides degradation.

Process	Pesticide	$k \text{ (s}^{-1}\text{)}$	R^2
Photolysis	CLD	8.10^{-4}	0.99
Fenton		3.10^{-6}	0.94
Photo-Fenton		6.10^{-4}	0.99
Ozone	β -HCH	2.10^{-4}	0.99
Photolysis		2.10^{-4}	0.99
Fenton		7.10^{-6}	0.97
Photo-Fenton		2.10^{-4}	0.99
Ozone		1.10^{-4}	0.96

Table 2. Electrical energy per order for the photolytic processes.

Process	$t \text{ (h)}$	$C_0 \text{ (mg L}^{-1}\text{)}$	$C \text{ (mg L}^{-1}\text{)}$	$P \text{ (kW)}$	$V \text{ (L)}$	$\text{EE/O (kWh L}^{-1}\text{)}$
Photolysis (CLD)	5	1	0.01	0.45	0.7	1.60
Photolysis (β -HCH)	5	1	0.05	0.45	0.7	2.47
Photo-Fenton (CLD)	5	1	0.02	0.45	0.7	1.89
Photo-Fenton (β -HCH)	5	1	0.02	0.45	0.7	1.89

(EE/O) was carried out. The EE/O was calculated by the Eq. (3), proposed by Bolton and Cater.^[33]

$$\frac{EE}{O} = \frac{P \times t}{V \times \log \frac{C_0}{C}} \quad (3)$$

As we can see in Table 2, the most efficient process for CLD degradation was the photolysis, with the lowest EE/O of all the studied process. However, for the degradation of β -HCH the lowest EE/O was obtained for the photo-Fenton process. This behavior could be explained by the lowest sensibility to the UV radiation observed in this study by the β -HCH.

Conclusions

In the investigated conditions, both chlordecone and beta-hexachlorocyclohexane exhibited a much lower reactivity towards Fenton's reagent (<10% conversion in 2 h) than ozone (>50% conversion). Photolysis achieved almost complete removal of both pesticides within 5 h when using a high pressure mercury lamp, and a conversion of about 40% with a low power lamp at 254 nm. Preliminary identification of degradation products indicated that hydrochlordecone was formed during photo-Fenton oxidation of CLD, while for β -HCH the major product peak exhibited $\text{C}_3\text{H}_3\text{Cl}_2$ as most abundant fragment.

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