Degradation of two chlorinated pesticides using advanced oxidation processes

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The degradation of chlordecone and beta-hexachlorocyclohexane in aqueous media is possible by means of photolysis, (photo-)Fenton oxidation and ozonation processes.

Banana and sugarcane have been the main agricultural products of the French Antilles (Guadeloupe and Martinique) since the 1960s. To prevent crop damage from the banana weevil, chlorinated pesticides, such as chlordecone (CLD, $C_{10}Cl_{10}O$, CAS-number: 143-50-0), β-hexachlorocyclohexane (β-HCH, $C_6Cl_6H_6$, (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]. It was not until 2009, when they were listed as persistent organic pollutants under the Stockholm Convention, that the production and agricultural use of the first two pesticides was prohibited worldwide.

Thus, there is growing need to find remediation solutions for CLD and β-HCH problem. The advanced oxidation processes (AOP) like (photo-)Fenton oxidation or ozonation have been applied for the degradation of several classes of pesticides and refractory compounds. This work examines the degradation of CLD and β-HCH in synthetic aqueous solutions by means of photolysis, (photo-)Fenton oxidation and ozonation [2].

Comparison of the different AOPs for CLD degradation

Photolysis, (photo-)Fenton oxidation and ozonation were investigated for the removal of CLD (Fig. 1). It should be noticed that although hydroxyl radicals generated by AOP are reported to be highly reactive and non-selective, Fenton oxidation did not yield any significant conversion of the contaminant in the investigated condition. On the other hand, ozone was able to achieve 70% of pesticide removal within 2 hours. In this case, both molecular and radical mechanisms should be involved, the latter being favoured by high pH values [3]. An inhibition of radical process could be then suspected.

CLD could be readily degraded by direct photolysis, to more than 95% in 3 hours. 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 did not seem to play any noticeable role either.

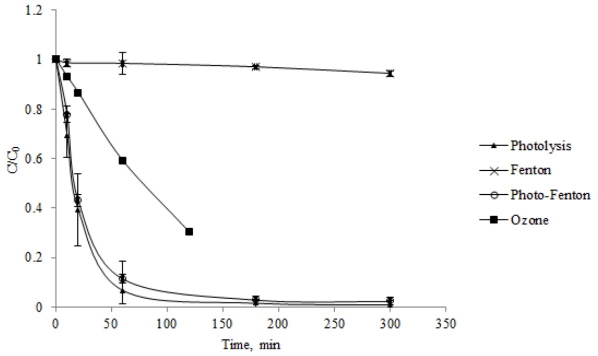

Figure 1: Degradation of CLD by photolysis, Fenton, photo-Fenton and ozonation processes. $[CLD]_0 = 2$ μmol.L^{-1}, T = 30^{o}C; 450 W MP Hg lamp and quartz lamp holder for photo-assisted processes; $[H_2O_2]_0 =$ 0.6 mmol.L^{-1}, $[Fe(II)]_0 = 0.3$ mmol.L^{-1} and $pH_0 =$ 2.6 for Fenton-based oxidation.

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 (Fig. 2).

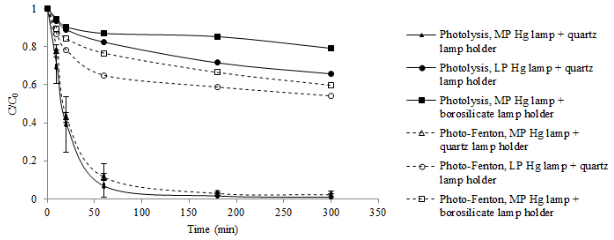

Figure 2: Effect of irradiation spectrum on the degradation of CLD by photo-assisted processes. $[CLD]_0 =$ 2 μmol.L^{-1}, T = 30^{o}C; photo-Fenton:$[H_2O_2]_0 = 0.6$ mmol.L^{-1}, $[Fe(II)]_0 = 0.3$ mmol.L^{-1}, $pH_0 = 2.6$.

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 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 $\lambda = 254$ nm than at $\lambda > 280$ 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 [4]. 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.

Comparison of the different AOPs for β-HCH degradation

The results of β-HCH degradation by AOP exhibit essentially the same features than for CLD: almost insignificant oxidation rate by Fenton's reagent and thus a photo-Fenton process mainly driven by the direct photolysis of the molecule.

Effect of lamp irradiation was also investigated (Fig. 3) and the most striking result was a still high elimination of β-HCH by photo-Fenton oxidation under UVB-Vis. Only scarce information related to the advanced oxidation of this pesticide has been reported. Ormad et al. [5] studied the degradation of a group of pesticides including β-HCH in very diluted conditions (0.5 μg.L^{-1}) by ozonation, O_3/H_2O_2, O_3/TiO_2 and $O_3/H_2O_2/TiO_2$ processes. Only $O_3/H_2O_2/TiO_2$ treatment was able to degrade β-HCH and yielded 10% conversion of the molecule with 3 mg.L^{-1} of ozone dosage, so a ratio of O_3/pollutant close to the one applied here (6 g/mg vs. 8.6 g/mg in the present study).

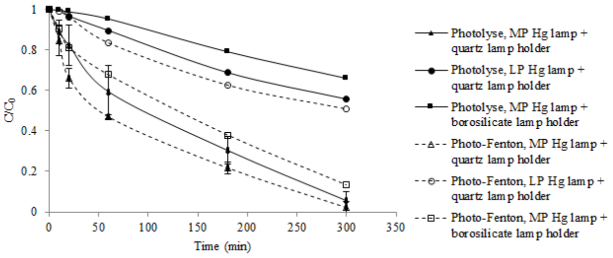

Figure 3: Effect of irradiation spectrum on the degradation of β-HCH by photo-assisted processes. $[\beta\text{-HCH}]_0 = 3.4\ \mu\text{mol.L}^{-1}$, T = 30°C; photo-Fenton:$[H_2O_2]_0 = 0.8$ mmol.L^{-1}, $[\text{Fe(II)}]_0 = 0.4$ mmol.L^{-1}, $pH_0 = 2.6$.

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 $C_3H_3Cl_2$ 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. The results show that 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 has 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 hours (against 70% for CLD).

Summarizing

In the investigated conditions, both chlordecone and beta-hexachlorocyclohexane exhibited a much lower reactivity towards Fenton's reagent (¡ 10% conversion in 2 hours) than ozone (¿ 50% conversion). Photolysis achieved almost complete removal of both pesticides within 5 hours 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 $C_3H_3Cl_2$ as most abundant fragment.

Notes

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References

[1] Y.M. Cabidoche, R. Achard, P. Cattan, C. Clermont-Dauphin, F. Massat, J. Sansoulet., *Environmental Pollution,* **157** (2009) 1697-1705

[2] G. Cruz-González, C. Julcour, H. Chaumat, S. Gaspard, U. Jáuregui-Haza., *Journal of Environmental Science and Health, Part B,* **53** 2 (2018) 121-125

[3] GA. López-López, J.S. Pic, H. Debellefontaine, *Chemosphere,* **66** (2007) 2120-2126

[4] W. Chu, S.M. Tsui, *Chemosphere* **39** (1999) 1667-1677

[5] M.P. Ormad, N. Miguel, M. Lanao, R. Mosteo, J.L. Ovelleiro., *Ozone-Science and Engineering* **32** (2010) 25-32