Further evidence of biodegradability of the POP chlordecone under methanogenic conditions

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HIGHLIGHTS

Measurement of chlordecone at the entrance, exit and in the sludge of anaerobic digesters treating contaminated rum vinasses confirms the capacity of such environments to eliminate it, suggesting that methanogenic sludges could be used as microbial agents in the remediation of impacted environments.

Keywords

chlordecone; chlordecone-5b-hydro; organochlorine; remediation, French West Indies

INTRODUCTION

Chlordecone ($C_{10}Cl_{10}O$; CLD) (Fig. 1) is an organochlorine insecticide that sorbs strongly to soils, is poorly soluble in water, and highly persistent in the environment. It accumulates in food chains, has potent chronic and acute toxicity, and is a proven carcinogen. CLD is now banned under The Stockholm Convention on Persistent Organic Pollutants (POPs) (Dolfing et al., 2012).

Figure 1. Chlordecone and chlordecone-5b-hydro structures (carbons numbered according to IUPAC)

It has been intensively used on the French West Indies (FWI) islands of Martinique and Guadeloupe between 1972 and 1993 against the banana weevil *Cosmopolites sordidus*. This has resulted in a long-term pollution of the banana field soils, causing a diffuse contamination of water and food resources (crops, livestock, fishes, crustacean) that are responsible nowadays of a sanitary and social crisis. A final solution to the problem would consist to destroy the CLD stock still presents in soils through bioremediation. Until now, however, due to its cage structure and above-mentioned characteristics, CLD is considered as practically non-biodegradable, a feeling reinforced by the apparent absence of natural attenuation of this compound in FWI soils (Cabidoche et al., 2009). Old literature suggests however that anaerobic (Schrauzer and Katz, 1978) and particularly methanogenic conditions (Jablonski et al., 1996) would be favourable to achieve important chemical transformations of CLD or compounds with similar bishomocubane structure (e.g., mirex; Andrade et al., 1975). FWI islands are important rum producers where anaerobic systems are often used to treat the vinasses resulting from this activity. Since the distilleries may use sugarcanes cultivated on polluted soils, their vinasses may also potentially contain CLD and so their anaerobic treatment plants appear as good models to study if methanogenic conditions really favour CLD degradation. In this poster we report the following of the concentrations of CLD and of CLD-5b-hydro, the only derivate (Fig. 1) for which an analytical standard is available, at the entrance, exit and in the sludge of the anaerobic treatment plants of two FWI distilleries.

MATERIAL & METHODS

The 2 sampled anaerobic systems where of the UASB and downflow filter (DAF) types. The samples were analysed by two different laboratories (LDA26, Brgm) accredited for CLD analysis. CLD was determined both on the vinasse TSS (Total Suspended Solids) separated by filtration and the filtered liquid. In the case of TSS, ASE was used for extraction while liquid/liquid extraction was used for the aqueous phase. Identification and quantification of both compounds were done by LC/MS or GC/MSMS. The sludge samples were lyophilized before analysis and treated as the TSS.

RESULTS & DISCUSSION

The anaerobic systems were sampled during the 2010 and 2011 distillery campaigns. Despite of the high dispersion of the concentrations provided by the two analytical laboratories, the results obtained (Table 1) showed that 53 to 91% of the CLD detected at the entrance of both digesters were not detected at their exit. Similar results were found for CLD-5b-hydro. A mass balance done for both compounds taking into account (1) their removal, (2) the volume of vinasse treated in a campaign and (3) the mass of sludge generated during the same time showed that the concentrations found in the sludge were well below those that should be measured (Table 1) if all the CLD and CLD-5b-hydro that disappeared would be retained by simple adsorption on the sludge due to their high hydrophobicity and resulting preferential partition to the organic insoluble compartment.

Table 1. FWI anaerobic digester operating conditions and mass balance for CLD and CLD-5b-hydro

Parameter	Anaerobic system	
	DAF	UASB
Reactor operating conditions and performances		
[COD] entrance (g/l)	20	29
Hydraulic retention time (days)	5.7	2.4-3.2
Volumetric organic loading rate (kg COD/$m^3_{reactor}$.day)	3.5	9-12
Specific organic loading rate (kg COD/kg TSS.day)	0.12	0.45-0.76
Recycling flow rate / vinasse flow rate	10	12
COD removal efficiency (%)	92.5	78
CLD and CLD-5b-hydro fate		
[CLD] entrance (µg/l)	0.77 - 7.5	0.29 – 0.99
[CLD] exit (µg/l)	0.28 – 0.77	0.04 – 0.29
CLD removed (%)	62 – 89.8	53.6 – 91.4
[CLD] sludge measured (µg/kg TSS)	48 - 362	< 10 - 158
[CLD] sludge theoretical without degradation (µg/kg TSS)	103 – 1640	86 - 1287
[CLD-5b-hydro] entrance (µg/l)	0.07 – 0.34	0.018 - <0.225
[CLD-5b-hydro] exit (µg/l)	< QL – 0.01	< QL*
CLD-5b-hydro removal (%)	≥ 61.6 - 86.7	≥ 23.2
[CLD-5b-hydro] sludge measured (µg/kg TSS)	< QL	< QL
[CLD-5b-hydro] sludge theoretical without degradation (µg/kg TSS)	12 - 73	≤ 11 - 416

**QL: Quantification Limit*

Vinasse being a very complex matrix (e.g. it contains ≥ 20 g COD/l), it generates a huge background during MS analysis that did not allow the search of eventual CLD degradation intermediates.

PERSPECTIVES

In order to definitively confirm the degradation of CLD under methanogenic conditions, a lab scale UASB reactor has been set up. It will be fed with a defined synthetic culture medium that will

allow to make an accurate mass balance on chlordecone and to follow the formation of potential degradation products including chloride.

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