PCDD/PCDF DECHLORINATION AND "*DE NOVO*" FORMATION THROUGH CONDENSATION OF 2,3-CHLOROPHENOLS DURING LOW TEMPERATURE PYROLYSIS OF SEWAGE SLUDGE

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Introduction

The fate of municipal wastes and sewage sludge in large cities, commonly found in Brazil, is one of the major environmental problems that remains without satisfactory solution until now. Considering sludge disposal, classical end use methods such as soil conditioner, landfillling and biocompost can be use, but these methods must be taken with reserve,because sludge can carry chemical pollutants. The thermal treatment of urban solid wastes is the main management method used in developed countries [1]. Incineration is the most often applied method although pyrolysis had shown promising results in the last two decades [2,3]. On the other hand, the possible formation of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) must be taken into consideration whenever thermal treatment of urban solid wastes is applied [4]. In this work the balance of PCDD/F, resulting from low temperature pyrolysis of two brazilians sewage sludge was determined and explained and the findings are discussed.

Materials and methods

The sludge samples were collected from 2 different sewage sludge treatment facilities. For the pyrolsis bench-scale study, a batch reactor basically composed by a Hearaus R/O 100 oven, with a temperature controller, and glassware, for the accomodation of the raw material and the recovering of the products (oil, char, water and non condensable gases) was applied. System operation conditions were: T: 400ºC/ T_R= 180 min/Carrier gas= N_2/ P= 1,0 Atm. All the glassware in contact with the raw material and pyrolysis products was weighted, for mass balance calculations.
For PCDD/F balance, the sludge samples as well as the oil and the char produced from sludges, were submitted to PCDD/F analysis. The extraction and clean-up methods prior to analysis are described elsewhere [5,6]. Identification and quantification of each PCDD/PCDF congener was carried out using the isotope dilution method. Samples were spiked with each $^{13}C_{12}$ 2,3,7,8-substituted PCDD/F (Standard mix 99%puriss. Promochem GmbH) and extracted with toluen during 24 h. PCDD/F absolute concentrations used were TCDD/F-HxCDD/F=25 ng.mL^{-1}, HpCDD/F=50 ng.mL^{-1}, OCDD=80 ng.mL^{-1}.and OCDF= 50 ng.mL^{-}. The recovery of the Standards after extraction and clean-up procedures were situated between 70-85%. For identification and quantification of PCDD/F a HRGC/HRMS (Mega Series 5160 Carlo Erba® coupled to a VGA Autospec Ultima) and a Quartz capillary column DB-Dioxin (J & W Scientific®) were used for separation and isomeric-specific analysis.

Results and Discussion

Table 1 presents the result of mass balance concerning oil prodution, total PCDD/F contents, their respective I-TEQ values as well as the PCDD/F balance in the studied samples. The balance of PCDD/F for the oil is made calculating the theoretical PCDD/F contents in oil (Values target with a * signal) based on oil production (%wt) versus the PCDD/F contents found in the corresponding sludge sample. Figure 1 shows the isomeric-specific pattern within the TCDD and HpCDF groups found for the oil samples in comparision to those found during the pyrolysis of chlorophenols substitutted in the 2,3-position. PCDD/F are not detected in the char. Possible explanation for this absence could be the catalitical destruction promoted by the ashes found in the char [7].

Table 1. PCDD/F contents, corresponding toxic equivalent concentrations (I-TEQ) found and PCDD/F balance for the sludge samples and their corresponding oil samples.

	Sludge L1	**Sludge L3**
ΣTCDD-OCDD (ng kg^{-1})	3730	1110
Σ TCDF-OCDF(ng kg^{-1})	230	210
Σ2,3,7,8-PCDD/F (ng kg^{-1})	720	130
OCCDD (ng kg^{-1})	2870	950
OCCDF (ng kg^{-1})	160	120
I-TEQ (ng kg^{-1})	**26,0**	**3,0**
oil produced (%)	**28,2**	**7,7**
	Oil L1	**Oil L3**
ΣTCDD-OCDD (ng kg^{-1})	22516,5	37925,8
ΣTCDD-OCDD***** (ng kg^{-1})	14360,0	12400,0
Δ Σ TCDD-OCDD(%)	**(+)36,2%**	**(+)67,3%**
Σ TCDF-OCDF (ng kg^{-1})	1180,0	2970,0
ΣTCDF-OCDF* (ng kg^{-1})	2680,0	840,0
Δ Σ TCDF-OCDF(%)	**(-) 127,1%**	**(+) 71,7%**
Σ2,3,7,8-PCDD/F (ng kg^{-1})	6210,0	5730,0
Σ2,3,7,8-PCDD/F* (ng kg^{-1})	2550,0	1690,0
Δ Σ 2,3,7,8-PCDD/F(%)	**(+) 58,9%**	**(+) 70,5%**
OCDD (ng kg^{-1})	4326,2	3282,7
OCDD * (ng kg^{-1})	10160,0	12400,0
ΔOCDD (%)	**(-)57,4**	**(-)73,5**
OCDF (ng kg^{-1})	273,5	537,8
OCDF *	520,0	1510,0
ΔOCDF (%)	**(-)47,4**	**(-)64,4**
I-TEQ oil (ng kg^{-1})	**2411,0**	**2048,0**
Ratio I-TEQoil/I-TEQsludge	**92,7**	**682,7**

(+/-)= formation/destruction of PCDD/F; Σ= Summe; Δ=Total variation

The sludge samples generally show a low contamination with PCDD/F (Σ TCDD/F-OCDD/F) with values ranging from 1320,0 (L3) to 3960,0 ng·kg^{-1} (L1). The equivalent concentrations, calculated from the recommendations of NATO/CCMS, range between 3,0 – 26,0 ng-I-TEQ·kg^{-1}. They also show a predominance of the high-chlorinated homologues (HpCDD/F-OCDD/F) in a typical PCP-induced pattern [8]. The oil samples produced from sludge show a high PCDD/F contamination with values of PCDD/F (ΣTCDD/F-OCDD/F) ranging from 23696,5 to 40895,5 ng kg^{-1}. The I-TEQ values lay between 2048,0-2411 ng-I-TEQ kg^{-1}. For comparison, a maximum immission level of 0,1 ng I-TEQ/Nm^3 is recommended for incinerators. These I-TEQ values found for the oil samples are within the range of those found by Weber & Sakurai (2001) [1] in the pyrolysis of plastics and above those observed by Calaminus Fiedler & Stahlberg (1997) [3] in the tar produced in the THERMOSELECT® process.

The oil samples show the predominance of the low-chlorinated congeners (TCDD/F-HxCDD/F) which constituted up to 88% of the total of PCDD/F found. The I-TEQ values found in the oil are between 93 (L1) and 683 (L3) times higher of that found to the corresponding sludge samples. This rise in the toxicity values is explained by the considerable contribution of the low chlorinated congeners, especially the 2,3,7,8-substituted isomers.

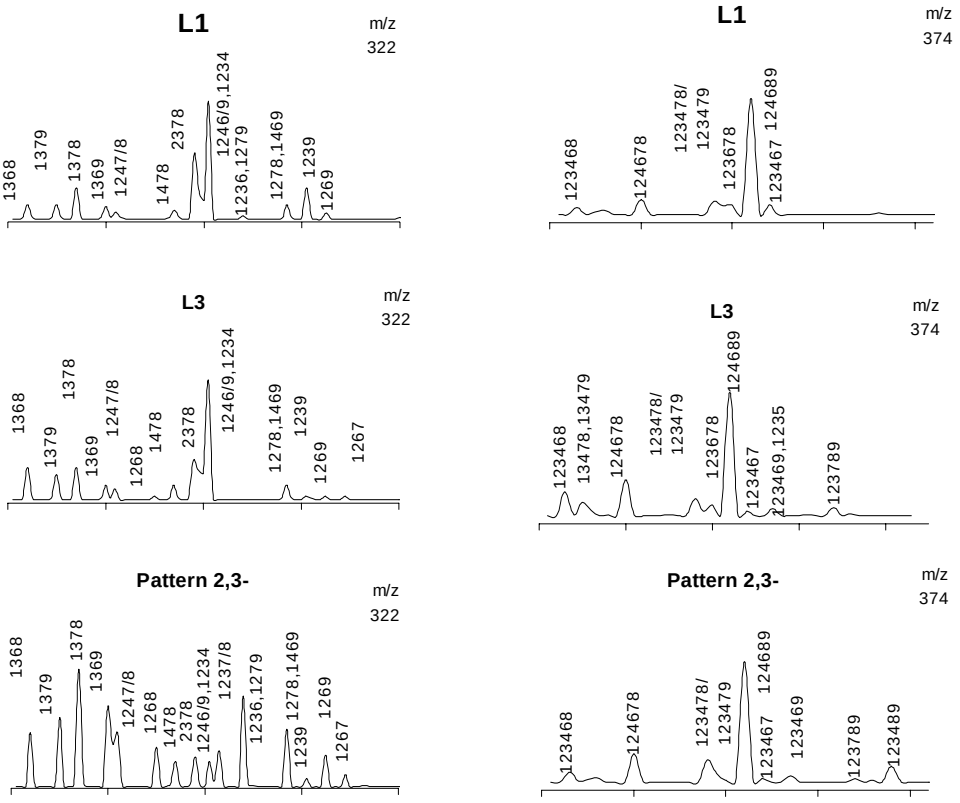

Figure 1. Isomeric-specific analysis of TCDD and HpCDF groups in the oils of this study in comparision to those found during the pyrolysis of 2,3-substitutted chlorophenols and PCP-Na contamination.

According to table 1, it seems that a dehalogenation of the high chlorinated homologues ocurred during the pyrolysis. That is pointed out by the destruction of OCDD and OCDF isomers present in the corresponding sludges L1 and L3 (Δ OCDD=57,3-73,5%; Δ OCDF=47,4-64,4%). This phenomenon was also observed by Bayer & Kutubuddin (1994) [9] during the pyrolysis of sewage sludge. At the same time, an additional formation of the low-chlorinated homologue groups can be observed, which exceed by 36-67% the total amount of PCDD/F originally found in the corresponding sludge.

From figure 1, it can be observed that TCDD group in oil shown the same 2,3- distribution found in the pirolisation of 2,3-substituted chlorophenols at 350ºC [4]. The same can be said about the HpCDF group when compared to the profile found by Hagenmaier (1985) [5] to PCP-Na contamination. The predominance of the isomers 1,2,4,6/9, 1,2,3,4-TCDD, which are considered a PCP/PCP-Na contamination marker in the TCDD Group [10] and the isomer 1,2,4,6,8,9-HpCDF in the HpCDF group [5] enforced this hypotesis.

Based on these remarks it seems that besides the catalytic dehalogenation of the high-chlorinated homologues, the mechanism of condensation of 2,3- substituted chlorophenols at 350°C already present in the sludge samples are contributting to the high PCDD/F contents found in oil.

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