Influence of the Aerobic and Anaerobic Digestion on the Levels of Chlorinated Dibenzofurans and Dibenzodioxins in Sewage Sludge

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1.Introduction

With regard to aspects of minimisation of contaminants and keeping of limiting values in environmental related matrices the degradation and formation of polychlorinated dibenzofuranes and dibenzo-p-dioxins (PCDF/D) by microorganisms are of special interest. We have investigated aerobic and anaerobic digestion processes of sewage sludge to show the influence of microorganisms on the formation or degradation of PCDF/D compounds. In addition we have tested the accelerating or inhibiting effects on these processes for various chlorinated aromatic precursors in their actual input concentrations. Until now the function principle of precursors is not known, if their presence is really necessary or even a de-novo-synthesis can be assumed [1 - 4].
From preliminary investigations of the anaerobic digestion of sewage sludge it could be shown that the PCDF/D concentration may increase during the digestion process [5]. To confirm this result we have digested sewage sludges of different origin systematically in batch reactors applying the aerobic and anaerobic method as well [6].

2. Experimental

For the digestion experiments we have used three communal sewage sludge samples which differ in their origin and their concentrations (Tab. 1).

Sludge	A	B	C
Impact	low	moderate	high
ng/kg I-TEQ*	9	20	200
Origin characteristic	- mainly rural - middle-class industry - no heavy industry	- municipal - middle-class industry - no heavy industry	- municipal - centre of population - metal-working industry

* mean value

Table 1: Origin and impact of the used undigested sewage sludge samples.

The aerobic and anaerobic digestions of the raw sludges as mentioned were carried out in 3 L batch reactors. For this purpose the reactors were filled with 2500 g of sludge and set to 36 °C. By means of a blade stirrer the contents of the reactors were stirred for one minute with about 150 rev/min in intervals of 10 min. The PCDF/D concentrations were determined for each batch before and after the digestion. The mineralization degrees ranging between 20 and 35 % were obtained by determining the concentrations of various metal species and the ignition residue before and after the digestion.
The analytical PCDF/D determination was performed according to the EPA method 1613.

Anaerobic digestion

In a ratio of 4:1 all raw sludge samples were inoculated with digested sludge from the same sewage plant. The compounds 2,3,5-trichlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 1,2,3-trichlobenzene, 1,2,3,4-tetrachlorobenzene and 1,4-dichlorobenzene were used as precursors. The concentrations of the applied chlorophenols range between 1 and 25 ppm and those of the chlorobenzenes between 4 and 20 ppm. The volume of the digester gas and pH value were measured discontinuously within 60 days to characterize the course of the digestion. The pH measurements were carried out in argon atmosphere. The digestion process was finished after a residence time of at least 60 days and the formation of biogas stopped. The digestion batches are summarized in Table 2.

Fermentation	Origin	Number of Experiments	Precursor	Concentration in ppm
I	A	4	2,3,5-Trichlorophenol	10
II	B*	3	none	0
III	B*	5	different Chlorophenols	2,5-25
IV	B*	6	different Chlorobenzenes	4-20
V	B*	4	2,3,5-Trichlorophenol	25
VI	C	3	none	0

* taken from the sewage plant at different times

Table 2: Survey of the number of the anaerobic digestion tests, kind and amount of the used precursors

Amounts of 100 g of each sludge sample were steam stripped after the digestion to determine the precursor concentration. The steam stripping with 50 mL toluene and simultaneous back extraction in the vapour phase was carried out for two hours. The obtained extract was dried with about 20 g Na_2SO_4 and diluted up to 100 mL with toluene.

The determination of the chlorophenols and chlorobenzenes was performed by means of gas chromatography (Varian, Type 3400, equipped with electron capture detector, 350 °C). The individual compounds were separated by use of a DB5 - capillary column (Length 60 m, internal diameter 0.25 mm, film thickness 0.25 µm), carrier gas He, 4.7 bar, split 50 mL/min, injection 1 µL splitless, 80 °C, 1.5 min, 15 °C/min, 250 °C. The sample solutions were diluted up to a ratio of 1:100 depending on the concentration and the response of the analyte. The recovery of all precursors was in the range from 80 to 120 %. The quantification occurred by use of an external standard

Aerobic digestion

The aerobic stabilization was applied in case of the raw sludges B and C. The preparation of the aerobic conditions occurred by ventilation with glass tubes at the bottoms of the reactors. The air flow rate was adjusted to 100 mL/min. Precursors were not used in case of the aerobic digestion. The raw sludge remained in the batch reactor for 20 days followed by freeze drying.

3. Results

Anaerobic digestion

The biogenic formation of PCDF/D in the aerobic stabilization of raw sludge which we have assumed could not be confirmed in an optimized test series. In nearly all digestion experiments the application of precursors did not lead to any significant changes of the PCDF/D concentrations. The increase of the PCDF/D concentrations after the digestion was effected by concentrating of the persistent contaminants due to the degradation of the biomass. Only the anaerobic digestion series II and III have shown some exceptions. The change of the impact in case of the TCDF substituted in 2,3,7,8 position was

significant. Table 3 represents the digestion series with the indication of the applied precursor and the concentration changes of 2,3,7,8-TCDF. Assessing the changes of the 2,3,7,8-TCDF concentrations the accumulation of PCDF/D caused from the mineralization was taken into account.
In all digestion processes of the digestion series III a significant concentration increase of more than 100 % of 2,3,7,8-TCDF were observed. A degradation in the range from 34 to 53 % could be determined in the digestion series IV.

Fermentation-series	Precursor	Precursor Concentration in ppm	Difference in ng/kg	Difference in %
III	2,3,5-Trichlorophenol	1	5,44	124
	2,3-Dichlorophenol	1	6,15	104
	2,4-Dichlorophenol	1	6,01	101
	2,6-Dichlorophenol	1	7,54	117
	none	0	7,52	209
IV	1,2,3,4-Tetrachlorobenzen	4	-5,43	-41
	1,2,3,4 -Tetrachlorobenzen	40	-3,81	-36
	1,2,3-Trichlorobenzen	4	-7,76	-53
	1,4-Dichlorobenzen	4	-5,1	-39
	1,4-Dichlorobenzen	40	-4,20	-35
	none	0	-3,82	-34

Table 3: Destruction and formation of 2,3,7,8-TCDF in the digestion series III and IV.

The digestion experiments in the series I, II, V and VI did not show significant concentration changes of the substituted 2,3,7,8-TCDF.

Aerobic digestion
In contrast to the anaerobic digestion of raw sludge in the aerobic digestion a significant degradation of the PCDF/D congeners could be detected. The percentual changes of the homologous isomeric PCDF/D groups in the aerobic stabilization are represented in Fig. 1.

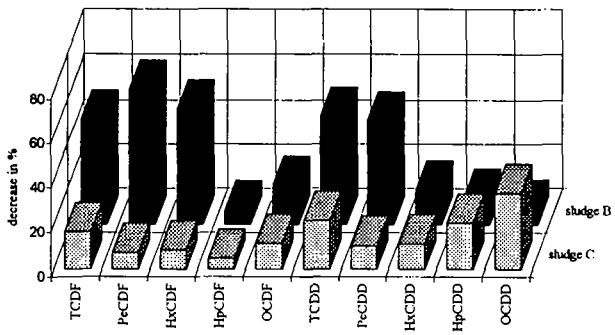

Fig. 1: Percentual decrease of the impact of different PCDF/D homologues of the aerobic stabilized sewage sludge B and C.

A comparison of both stabilized sludge samples (aerobic process) shows that all concentrations of the homologous groups decrease. It is noticeable that the concentration of the sludge sample B which is only impacted with 20 ng/kg I-TEQ decreases percentually stronger than the sludge sample C which is impacted with 200 ng/kg I-TEQ. Further experiments are planned to show how the described results indicate a non-competetive enzymatic activity or a chemical reaction course. A comparison of the homologous groups leads to another difference. Especially the compounds TCDF, PeCDF, HxCDF, TCDD and PeCD in the low impacted sludge are degraded, whereas the high impacted sludge only shows a decrease of the OCDD concentration.
Fig. 2 and 3 represents the degradation of those congeners which are degraded to more than 40 % in the aerobic stabilization.

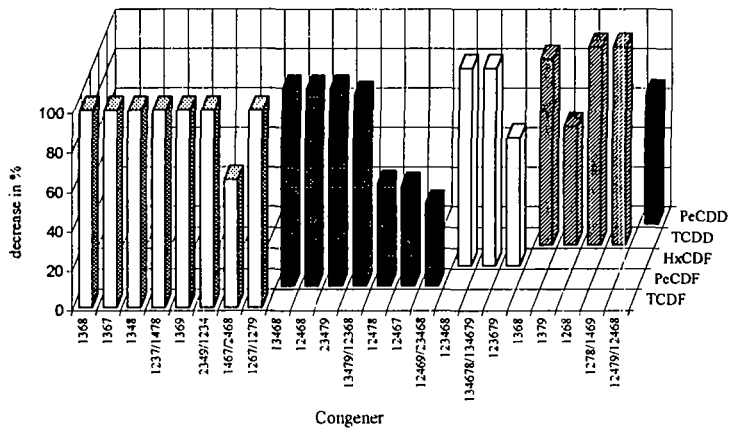

Fig. 2: Percentual decrease of the impact of different PCDF/D congeners of the aerobic stabilized sewage sludge B.

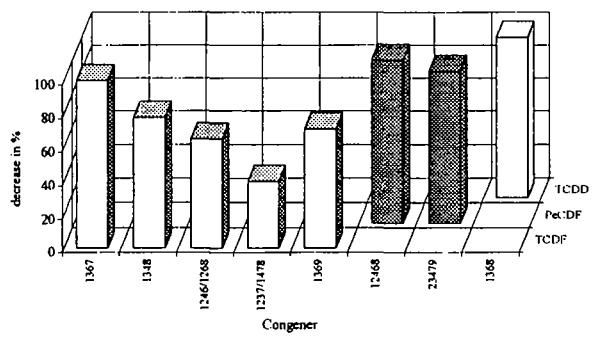

Fig. 3: Percentual decrease of the impact of different PCDF/D congeners of the aerobic stabilized sewage sludge C.

From Fig. 2 it can be shown that significantly more PCDF/D congeners are degraded in the aerobic stabilization of the lower impacted sludge. Comparing Fig. 2 with Fig. 3 results that nearly all concentration of the PCDF/D congeners which are degraded in the aerobic stabilization of the high impacted sludge are also reduced in the lower impacted sludge. From this fact we conclude that similar degradation mechanisms are effective in both sewage sludge samples. One exception is a TCDF isomer which is substituted in 1246/1268 position. This compound could not be detected in the low impacted sludge.

4. References

[1] A. Svenson, L.O. Kjeller, C. Rappe. Enzymatic chlorophenol oxidation as a means of chlorinated Dioxin and Dibenzofuran Formation.*Chemosphere* 1989, 19, 585

[2] H.C. Wagner. Biogene Bildung von polychlorierten Dibenzo-p-Dioxinen und Dibenzofuranen mittels verschiedener Peroxidasesysteme. *Diplomarbeit,Bayreuth,* 1990

[3] L.G. Öberg, C. Rappe. Biochemical formation of PCDD/Fs from chlorophenols. *Chemosphere* 1992, 25, 49

[4] L.G. Öberg, R. Anderson, C. Rappe. De novo formation of Hepta- and Octachlorodibenzo-p-dioxins from Pentachlorophenol in municipal sewage sludge. *Organohalogen Compounds* 1992, 9, 351

[5] R. Hengstmann, R. Hamann, H. Weber, A. Kettrup. Impact of sewage sludge and sewer slimes by polychlorinated Dibenzo-p-Dioxins and polychlorinated Dibenzofurans. *Organohalogen Compounds* 1990, 407

[6] H. Roediger, M. Roediger, H. Kapp. Anaerobe alkalische Schlammfaulung. *4. Auflage, Oldenbourg Verlag, München,* 1990