DYNAMICS OF CHANGES IN COPLANAR AND INDICATOR PCB IN SEWAGE SLUDGE DURING MESOPHILIC METHANE DIGESTION

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ABSTRACT

Research was conducted, which aim was to evaluate the influence of mesophilic methane digestion on degradation of coplanar and indicator PCB in sewage sludge, and on dynamics of changes of these congeners during the process. For the research, mixtures of sewage sludge from a municipal, mechanical-biological wastewater treatment plant were used. Mesophilic digestion was conducted in the temperature of 36°C±1°C. PCB analytics was based on separation of these compounds through extraction, and then on chromatographic separation.

Results of the analyses indicated, that the anaerobic stabilization processes of sewage sludge occurred correctly. Biodegradation of organic compounds in sewage sludge was confirmed by the decrease in total solids and volatile solids. The reduction of organic substance content during the digestion of analyzed sewage sludge was equal to 36%.

Prior to the mesophilic digestion process, coplanar PCB with code 169 was dominant in sewage sludge, which concentration amounted from 8.2 to 23.4 µg kg^{-1} d.m. Concentration of indicator PCB was between 1.0 and 12.7 µg kg^{-1} d.m. Up to the 3^{rd} day of the digestion process no statistically significant differences in concentration of both coplanar and indicator PCB was observed. During the following days of the process, an increase in lower chlorinated PCB concentration was demonstrated, which represented tri- and tetrachlorobiphenyls, and a decrease in concentration of higher chlorinated congeners, which belong to penta-, hexa, and heptachlorobiphenyls. After the digestion, a decrease in higher chlorinated congener concentration was found. Significant degradation was demonstrated for coplanar PCB 169 (from 77.8 to 80.5%), and indicator PCB 180 (from 57.1 to 90.3%) and PCB 153 (from 60.4 to 79.2%).

Keywords: mesophilic methane digestion, polychlorinated biphenyls, sewage sludge

1. Introduction

Because of the presence in sewage sludge of contaminations like heavy metals, pathogens and harmful organic compounds, including PCBs, the effective processes, resulting in reduction of hazardous sewage sludge impact on the environment, are developed (Lyberatos and Skiadas, 1999). For neutralization and removal of PCB from sewage sludge, the processes of aerobic and anaerobic digestion are usually applied (Patureau and Trably, 2006, Field and Sierra-Alvarez, 2008). During mentioned processes, the changes of PCB resulted in decrease of their content in sludge. According to earlier reported data, under anaerobic conditions, the reductive dechlorination of highly chlorinated PCB occurs forming lightly chlorinated PCB (Borja *et al*., 2005).

According to the United States Environmental Protection Agency in the environment 7 indicator congeners should be identified, with codes: 28, 52, 101, 118, 138, 153, and 180, also the Working Document on Sludge states permissible value of total concentration of seven above mentioned PCB congeners in sewage sludge destined for agricultural purposes (Working Document on Sludge, 2000). However the Working Document on Sludge does not consider coplanar PCB with codes 77, 126, and 169, which are the most toxic and biochemically active among all PCB (Eljarrat *et al*., 2003). Therefore it is justified to conduct complete studies determining to what extent polychlorinated biphenyls (with paying attention to the most toxic ones with coplanar structure) are eliminated during mesophilic methane digestion.

The aim of this work was to evaluate the influence of mesophilic methane digestion on changes dynamics of coplanar and indicator PCB congeners in sewage sludge. The research results should complement the knowledge of how methane digestion conducted in mesophilic conditions will contribute to minimizing or elimination of potentially hazardous PCB in sewage sludge, so that sludge quality will meet current legal regulations.

2. Methods

2.1. Materials and mesophilic digestion

In the study sewage sludge from a municipal, mechanical–biological wastewater treatment plant of Silesian province (Poland) was used. The wastewater inflowing to the treatment plant contains approximately 20% of industrial wastewater.

The methane digestion process was carried out in two parallel bioreactors with different sewage sludge samples. Samples marked as (S_1) contained a mixture of primary and excess sludge inoculated with fermenting sludge at the volumetric ratio 1:2. Samples marked as (S_2) contained primary sludge inoculated with fermenting sludge at the ratio 1:2 (vol.). The samples were subjected to methane digestion process at the temperature of 36°C±1°C for 15 days, in 10 bioreactors filled with 1L of analyzed sludge.

2.2. Analysis procedure

Before, during (on the 3rd, 7th and 10th day) as well as after the methane digestion process, the following parameters of the sludge were determined: hydration, total solids, volatile solids and ignition losses. Sludge supernatants were analyzed for pH, alkalinity, acidity, volatile fatty acids (VFA) and total organic carbon (TOC). The analyses were repeated triply according to the standard procedures (Standard Methods, 1998).

The content of three coplanar PCB: 3,3',4,4'-tetrachlorobiphenyl (PCB 77), 3,3',4,4',5-pentachlorobiphenyl (PCB 126), 3,3',4,4',5,5'-hexachlorobiphenyl (PCB 169) was detected in sludge. Preparation of sewage sludge samples for coplanar PCB analysis was conducted according to the procedure described in the literature (Rosińska, 2014).

Indicator PCB marked with codes: 28, 52, 101, 118, 138, 153, and 180 were evaluated before, during, and after the methane digestion process, according to the procedure described elsewhere (Dąbrowska and Rosińska, 2012), with the use of PCB separation from sludge with hexane and sonication as an extraction method. Qualitative and quantitative analysis of determined PCB congeners was performed by means of CGC-MS.

Changes in concentration of indicator and coplanar PCB in sewage sludge during the process of methane digestion was calculated based on conducted quality control of the results and statistical analysis, assuming that variation in concentration of given PCB congener over 25% was statistically significant.

3. Results

3.1. Coplanar PCB

The presence and content of PCB 126 in sewage sludge was the indicating parameter for determination of toxicity changes (Toxicity Equivalent Quantity according to WHO recommendations from 1998 - WHO_{98} -TEQ_{PCB}). Toxicity Equivalent Factor (TEF) value of that congener equals 0.1. In comparison, TEF value of PCB 169 equals 0.01 and PCB 77 – 0.0001.
Before the process of mesophilic methane digestion, PCB with code 169 was dominant in both sludge. Its content was 23.4 and 8.2 µg kg^{-1}. Concentration of PCB 126 was on the level of 11 µg kg^{-1} in sludge S_1. Much lower concentration, on the level of 1.8 µg kg^{-1} was detected for congener with code 77 (Fig. 1a). The value of toxicity equivalent was equal to 1.36 ng g^{-1}. Concentration of PCB 126 in sludge S_2 was on the level of 4.7 µg kg^{-1} and PCB 77 above 1 µg kg^{-1} (Fig. 1b). The toxicity of sludge given as WHO_{98} -TEQ_{PCB} was equal to 0.55 ng g^{-1}. Up to the 3rd day of the process no statistically significant differences in PCB content were discovered.

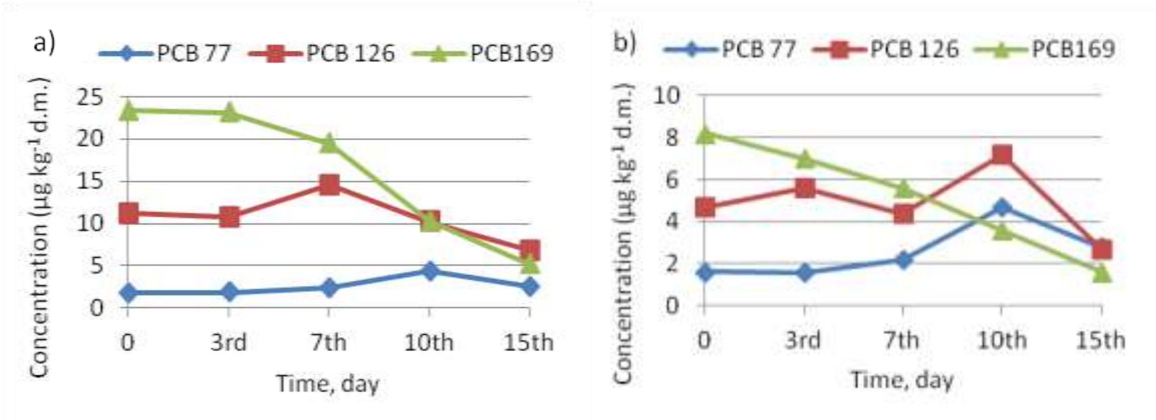

Figure 1: Dynamics of changes in coplanar PCB in sewage sludge during mesophilic methane digestion a) sludge S_1, b) sludge S_2.

On the seventh day of the process, in (S_1) sludge, the concentration of PCB 126 increased by 23%, what caused the toxicity level to be the highest and was determined on the level of 1.64 ng g^{-1} (Fig. 1a). In sludge (S_2), the content of PCB 169 was decreased by 32%. At the same time the content of PCB 77 increased by 29%. The content of PCB 126 was similar to the initial concentration (Fig. 1b). Toxicity level of sludge was equal to 0.49 ng g^{-1}.

On the tenth day of the process, in sludge (S_1), the concentration of PCB 126 and 169 decreased to the value of about 10 µg kg^{-1}. (Fig. 1a), what caused a decrease in toxicity equivalent to 1.12 ng g^{-1}. At the same time the concentration of PCB 77 increased by more than 58% in comparison to the initial value. In sludge (S_2), the content of PCB 169 was decreased by 56%, but concentration of PCB 126 increased by 35% and resulted in increasing of sludge toxicity to the value of 0.76 ng g^{-1}.

After the mesophilic digestion process, the concentration of PCB 169 in sludge (S_1) was declined by 78% in comparison to data determined before the process. Toxicity level was decreased to 0.73 ng g^{-1}. After the end of the process of sludge (S_2) digestion, a decline in concentration of coplanar PCBs 126 and 169 in sludge was detected. The most significant decrease in concentration (77.8 and 80.5%) was observed for PCB 169 and concentration of PCB 126 was reduced by 39.3 and 42.6%. Obtained results partly confirm research results from other authors. Ho and Liu (2011) performed studies of anaerobic biodegradation of three coplanar PCB with codes: 81, 126, and 169. They stated that biodegradation occurred for PCB 81 and PCB 126, which represent tetra- and pentachlorobiphenyls respectively. For PCB 169 (3,3’,4,4’,5,5’-hexachlorobiphenyl) no biodegradation was demonstrated.

3.2. Indicator PCB

In sludge (S_1) and (S_2) prior to the digestion process presence of all indicator PCB congeners was demonstrated (Fig. 2a and 2b). Total PCB concentration for this sludge amounted to 29.9 and 34.9 µg kg^{-1}. respectively. Up to the 3rd day of the process no statistically significant differences in PCB content were discovered. Concentration of particular congeners was comparable to the concentration before the digestion process.

On the 7th day of sludge S_1 digestion process significant changes of PCB 180 were indicated, which concentration decreased by over 50% down to 1.2 µg kg^{-1} (Fig. 2a). Similar changes were observed for congeners 118 and 153, which concentration decreased by approx. 31%. On the 7th day of the process for sludge S_2 increase in concentration of lower chlorinated PCB with codes 28 and 52 was demonstrated (Fig. 2b), by 30 and 52% respectively. For higher chlorinated PCB with codes 153 and 180 decrease in concentration was presented, by 30 and 41% respectively. Yet in the sludge concentration of PCB with code 118 increased by approx. 60%.

On the 10th day of sludge S_1 digestion, PCB 52 concentration went up by 52%, whereas PCB 118, 153, and 180 concentration went down by 47, 54, and 65% respectively. On this day of the process in sludge S_2, increase in PCB 52 and PCB 28 was also recorded. Obtained results confirm the pathway of PCB 180 dechlorination to PCB 28 and PCB 52, proposed by Barret *et al*. 2010. Tendencies observed in the research are consistent with the literature data, according to which under anaerobic conditions higher chlorinated biphenyls undergo degradation to lower chlorinated congeners.

After the mesophilic methane digestion process in both sludge all indicator PCB congeners were still present, however their total concentration decreased by 25 and 57%. Obtained results are consistent with the literature data (Patureau and Trably, 2006; Benabdallah *et al*., 2007). The authors obtained PCB reduction by 40 and 58% during sewage sludge anaerobic stabilization. The highest degradation was demonstrated for hexa- and heptachlorobiphenyls, i.e. PCB 153 (60.4 and 79.2%) and PCB 180 (57.1 and 90.3%). Trichlorobiphenyl (PCB 28) concentration in both sludge was comparable to the initial concentration, while tetrachlorobiphenyl (PCB 52) concentration slightly increased.

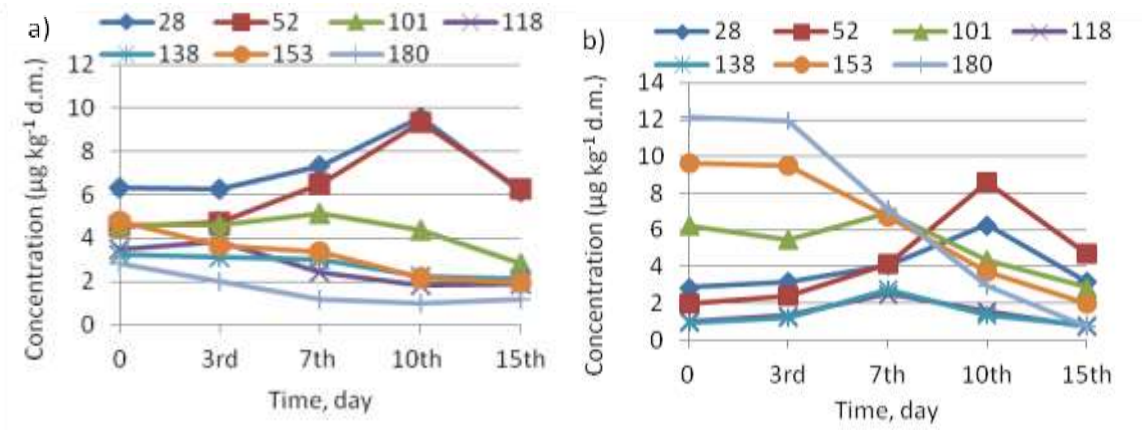

Figure 2*:* Dynamics of changes in indicator PCB in sewage sludge during mesophilic methane digestion a) sludge S_1, b) sludge S_2.

4. Conclusions

Based on the conducted experiment following conclusions can be made:

1. During the initial days of the mesophilic methane digestion process no statistically significant differences in content of both coplanar and indicator PCB in sewage sludge were demonstrated.
2. During the following days of the process, an increase in lower chlorinated PCB concentration was demonstrated, which represented tri- and tetrachlorobiphenyls, and a decrease in concentration of higher chlorinated congeners, which belong to penta-, hexa-, and heptachlorobiphenyls.
3. After the digestion, a decrease in higher chlorinated congener concentration was found. Significant degradation was demonstrated for coplanar PCB 169, indicator PCB 180 and PCB 153.
4. After the methane digestion process in sewage sludge total concentration of indicator PCB decreased by 25 and 57% respectively.
5. After the digestion process of sewage sludge WHO_{98} – TEQ_{PCB} value decreased by over 40%.
6. Mesophilic methane digestion process contributes to minimizing potentially hazardous PCB in sewage sludge.

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REFERENCES

1. Benabdallah T. El-Hadj, Dosta J., Torres R. and Mata-Alvarez J. (2007), PCB and AOX removal in mesophilic and termophilic sewage sludge digestion, Biochem. Eng. J., **36**, 281-287.
2. Barret M., Barcia C.A., Carrère G.A. and Patureau D. (2010), Influence of feed characteristics on the removalmof micropollutants during anerobic digestion of contaminated sludge, J. Hazard. Mater., **181**, 241-247.
3. Borja J., Taleon J.A., Auresenia J., Gallardo S. (2005), Polychlorinated biphenyls and their biodegradation, Process Biochem., **40**, 1999-2013.
4. Dąbrowska L. and Rosińska A. (2012), Change of PCBs and forms of heavy metals in sewage sludge during thermophilic anaerobic digestion, Chemosphere, **88**, 168-173.
5. Eljarrat E., Caixach J.and Rivera J. (2003), A comparison of TEQ contributions from PCDDs, PCDFs and dioxin-like PCBs in sewage sludges from Catalonia, Spain, Chemosphere, **51**, 595-601.
6. Field J.A. and Sierra-Alvarez R. (2008), Microbial transformation and degradation of polychlorinated biphenyls. Environ. Pollut., **155**, 1-12.
7. Ho C.H., Liu S.M. (2011), Effect of coplanar PCB concentration on dechlorinating microbal communities and dechlorination in estuarine sediments, Chemosphere, **82**, 48-55.
8. Lyberatos G. and Skiadas I.V. (1999), Modelling of anaerobic digestion - a review, Global Nest: the Int. J., **1**, 2, 63-76.
9. Patureau D. and Trably E. (2006), Impact of anaerobic and aerobic processes on polychlorobiphenyl removal in contaminated sewage sludge, Biodegradation, **17**, 9-17.
10. Rosińska A. (2014), Changes in selected dioxin-like PCB concentration and toxicity in anaerobically stabilized sewage sludge, Desalination and Water Treatment, **52**, 19-21, 3790-3797.
11. Standard Methods for the Examination of Water and Wastewater, 20th edn, American Public Health Association, Washington DC, USA, 1998.
12. Working Document on Sludge, 3rd draft, European Commission Environment ENV.E.3/LM, Brussels, 2000.