

HEAVY METALS AND PCBs IN SEWAGE SLUDGE DURING  
THERMOPHILIC DIGESTION PROCESS

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**Keywords:** Heavy metals, polychlorinated biphenyls, sewage sludge, thermophilic digestion.

**Abstract:** The investigations were carried out in order to assess the effect of thermophilic fermentation on changes in concentration of seven congeners with codes: 28, 52, 101, 118, 138, 153 and 180 in sewage sludge. The total concentration of PCBs was the highest before the process of thermophilic fermentation. On the tenth day of the process of fermentation it was found that the total concentration of LCB doubled the previous level, whereas in higher chlorinated PCBs this value decreased twice. After the process of thermophilic digestion, all the determined congeners of PCBs were still present. However, their total concentration was reduced by 84% on the fourteenth day of the process. Low concentration of heavy metal ions in the liquid phase of sewage sludge was observed. The metal ions precipitated and remained bound throughout the stabilization process. Metal speciation analysis was performed, and revealed some changes in the chemical forms of the metals during the stabilization process of sludge. The highest increase of zinc, copper, nickel, cadmium, and chromium concentration was observed in the organic-sulfide fraction, whereas the highest increase of lead was found in the residual fraction. Thermophilic methane fermentation did not cause the accumulation of heavy metals in the mobile fractions of sludge.

## INTRODUCTION

This wide use of PCBs in products with long periods of their practical utilization has led to deposition of these compounds in all the components of human natural environment, i.e.: in water, air, soil, sludge, waste and even in living organisms [7, 9, 20]. Trace PCBs have also been discovered in far regions of the Arctic and Antarctica [18, 25]. It is claimed that chlorinated biphenyls are the contaminants which are spreading around the globe.

The source of PCBs in sewage sludge include: liquid waste, e.g. transformer oil, dielectric fluids and flushing from municipal catchment which contain organic substances created as a result of burning processes [8, 12, 16]. Due to poor solubility, PCBs are removed from sewage in the process of sedimentation. This process generates sewage sludge [15]. It has been demonstrated that PCBs concentrations might vary within a wide range from trace amounts to 10 mg/kg d.m.

An increasing tendency has been reported in Poland in terms of the mass of sewage sludge created in municipal waste treatment plants. Managing sludge requires rational strategy. It is known that a part of the biochemically stabilized sludge is used for non-in-

dustrial purposes, including agricultural applications being one of the most fundamental ways to manage the sludge. Therefore, it is essential to point to the method of processing of sewage sludge which would allow for obtaining a high level of removal of polychlorinated biphenyls [2, 4, 23]. One of the promising methods is the process of anaerobic methane fermentation [24].

The investigations were carried out in order to assess the effect of thermophilic fermentation on changes in concentration of seven congeners with codes: 28, 52, 101, 118, 138, 153 and 180 in sewage sludge. The investigations will provide explanation whether the use of advanced method of sewage sludge procession (thermophilic fermentation) will contribute to minimization of PCB concentration.

During fermentation, the decomposition of the organic substances results in the increase of heavy metals concentrations in the dry matter of stabilized sewage sludge. It is crucial, however, not only to determine the total heavy metal concentrations in stabilized sludges but most of all to determine their chemical forms of occurrence; since their forms determine their mobility and bioavailability [13, 31].

In order to determine the forms of heavy metals in the sewage sludge the speciation analysis is performed. The analysis is based on the sequential extraction of metals with increasingly aggressive solvents. Reagents for each step are chosen in such a way to extract metal groups with known properties [14, 27]. So far, there has been no research done on the determination of chemical forms of occurrence of heavy metals in sewage sludge during thermophilic methane fermentation. The research on the subject is then considered to be justified.

## EXPERIMENTAL PROCEDURE

### *Substrate*

Sewage sludge was sampled from municipal, mechanical-biological treatment plant of communal wastewaters 20% of which were industrial wastewaters. The treatment process was performed with the use of the activated sludge method, which takes into account nitrification, denitrification, and chemical/biological removal of phosphorus. Stabilization of sludges was a two stage process, combining both mesophilic and psychrophilic methane fermentation. For the study randomly chosen two single sludge samples were collected: from the primary clarifier (raw sludge) and from closed fermentation chamber CFC (digested sludge). Before the sludge was introduced to bioreactors, it was first sieved through 3 mm sieve to facilitate uniformity of the studied material.

### *Inoculum*

In order to develop the growth of thermophilic anaerobic microorganisms, the 550 cm<sup>3</sup> standard glass bioreactors were filled with 350 cm<sup>3</sup> of sludge collected from CFC. Bioreactors (sealed with butyl rubber stoppers, tightened with aluminum nuts adjusted for multisampling of biogas) were placed in a thermostat at 55 ± 1°C. Starting from the fifth day of the incubation 1 cm<sup>3</sup> of the growth medium (advised for fermentation microorganisms [10]) was fed every 48 hours into the culture. In addition 200 g/dm<sup>3</sup> of glucose was added into the medium. Incubation was carried out for 30 days.

### ***Thermophilic methane fermentation***

First inoculum was mixed with the sludge from CFC in the volumetric ratio of 1:10. The used volumetric ratios were to facilitate the growth of thermophilic microorganism culture. Next the sludge was mixed with the raw sludge in the volumetric ratio of 2:1. The purpose of the digested sludge addition was to insert microorganisms, which would carry out fermentation [17, 22]. Bioreactors (used previously for the growth of inoculum) were then filled with 350 cm<sup>3</sup> of the obtained sludge mixture. Incubation lasted for 14 days.

The control of the process consisted in manometric measurement of the amount of biogas and, at defined time intervals, analysis of composition of biogas. Before and in the specified intervals for the sludge the following parameters were determined: hydration, total solids, volatile and non-volatile solids, pH, alkalinity, volatile fatty acids VFA, total organic carbon TOC, additionally heavy metals (Zn, Cu, Ni, Cd, Pb, Cr) and PCBs.

### ***Analytical methods***

The composition of biogas (the content of CH<sub>4</sub> and CO<sub>2</sub>) was measured with the use of gas chromatography (gas chromatograph with TCD detector, model Agilent GC 6890 made by Agilent Technology). Separation was performed on Hayesep column. During the analyses the temperature was risen from 50°C to 100°C at 20°C/min during 5 min. Split/splitless injection and the standard mixture of the following CH<sub>4</sub> – 70%, CO<sub>2</sub> – 28.2%, CO – 0.37%, O<sub>2</sub> – 0.89%, H<sub>2</sub> – 0.54% were used. The inert gas flow N<sub>2</sub> was 19.2 cm<sup>3</sup>/min.

The determination of physicochemical properties of the sludges was performed with three repetitions and with commonly accepted methodology, TOC by infrared spectrometry (carbon analyzer multi N-C, Analytik Jena). The concentration of heavy metals was determined by means of atomic absorption spectrometry (AAS) method [11] (spectrometer novAA 400, Analytik Jena).

### ***PCB analysis***

Methodology of sample preparation was described elsewhere [17, 29]. The extract was compacted in vacuum and then subjected to qualitative and quantitative analysis by means of gas CGC chromatography. Separation was made on a DB-5 column (30 m x 32 mm x 1 µm). A quadrupole mass spectrometer MS 800, working in a selective mode of ion monitoring was used for detection. Determination was performed for each sample and each of the four injections of the obtained extract. In order to check the procedure for determination of PCBs in sewage sludge, the recovery values were also determined. Sewage sludge was enriched with Ehrenstorfer's PCB MIX3 at the concentration of 10 ng/µl. Then biphenyls determination was carried out using the abovementioned procedure. The obtained values of recovery ranged from 65 to 87% and were within the range typical of the references [3, 17]. The precision of the determination was expressed by means of the values of standard deviation.

### ***Fractionation of heavy metals***

Before and after fermentation the overall content of heavy metals (Zn, Cu, Ni, Cd, Pb, Cr) in the sludge was determined but also their concentration in the particular chemical fractions of the sludge was analyzed. Preparation of the sludges required centrifugation of the samples in the laboratory centrifuge (rotary speed – 6000 rpm, duration – 10 min), evaporation in a heated bath and drying in a laboratory dryer at 105°C. Dried sludges were

ground with the use of a porcelain mortar and sieved on a 0.4 mm stainless steel sieve. Three different samples of the same sludge were prepared for the analyses.

For the sequential extraction analysis of the metals from the sludge, the method suggested by BCR was applied. A general scheme of the procedure is shown in Table 1.

Table 1. Operating conditions required in the BCR sequential extraction procedure

Step	Sequential extraction procedure per 1g of dry matter sludge	Forms of metals
1	40 cm <sup>3</sup> 0.11 M CH <sub>3</sub> COOH, temp. 22°C, shaking for 16 h	Exchangeable and bounded with carbonates
2	40 cm <sup>3</sup> 0.5 M NH <sub>2</sub> OH·HCl, temp. 22°C, shaking for 16 h	Bounded with Fe and Mn oxides
3	10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> , temp. 22°C, 1 h; temp. 85°C, 1 h 10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> , temp. 85°C, 1 h 50 cm <sup>3</sup> 1 M CH <sub>3</sub> COONH <sub>4</sub> , temp. 22°C, 16 h	Bounded with organic matter and sulfides
4	2 cm <sup>3</sup> 65% HNO <sub>3</sub> + 6 cm <sup>3</sup> 36% HCl, temp. 100°C, 2 h	Residue

The preparation of the necessary reagents and the extraction procedure was carried out according to [28]. The concentration of heavy metals was determined by means of AAS method.

### **Statistical analysis**

Significance test, Student t-test, was used for the difference between two means. The results of two sampling series, each with 3 repetitions were compared – heavy metals and PCBs content in the sludge before and after fermentation. Two data series were examined to determine if their mean values vary significantly. In accordance with significance Student t-test, t-value was calculated for the difference between two means.

Assuming the level of significance  $\alpha = 0.05$  for 4 degrees of freedom, critical value  $t_{0.05} = 2.776$  was taken from the Student t distribution table [19]. If the calculated value  $t > t_{0.05}$ , it means that, statistically, both mean values significantly differ from each other.

## RESULTS AND DISCUSSION

The chosen physicochemical properties of the sludges before and after thermophilic methane fermentation are shown in Table 2.

During fermentation the content of TOC in the liquid phase of sludge increased from 484 mgC/dm<sup>3</sup> (before the process) to 1160 mgC/dm<sup>3</sup> on the third day of the fermentation process, and to 1190 mgC/dm<sup>3</sup> on the 7th day. The TOC content on the 14th day of the fermentation was 1020 mgC/dm<sup>3</sup>. Dry organic matter of the sludge decreased from 17.89 to 10.78 g/dm<sup>3</sup>, which equals to 40% reduction of organic matter in the sludge during fermentation.

The biogas production obtained during thermophilic fermentation of sewage sludge is shown in Figure 1.

Table 2. The chosen physicochemical indexes of sludges before and during thermophilic methane fermentation

Indexes	Unit	Before fermentation	During fermentation of sludge			
			3 <sup>rd</sup> day	7 <sup>th</sup> day	10 <sup>th</sup> day	14 <sup>th</sup> day
pH	-	7.71	7.92	7.90	7.94	7.95
Hydration	%	97.38	97.64	97.83	98.03	98.12
Total solids	g/dm <sup>3</sup>	26.17	23.61	21.68	19.71	18.79
Volatile solids	g/dm <sup>3</sup>	17.89	15.41	13.56	11.65	10.78
	%	68.4	65.3	62.5	59.1	57.4
Non-volatile solids	g/dm <sup>3</sup>	8.28	8.20	8.12	8.06	8.01
	%	31.6	34.7	37.5	40.9	42.6
TOC	mgC/dm <sup>3</sup>	484	1160	1190	1080	1020
Alkalinity	mgCaCO <sub>3</sub> /dm <sup>3</sup>	2280	3220	3350	3510	3600
VFA	mgCH <sub>3</sub> COOH/dm <sup>3</sup>	910	1018	980	643	524

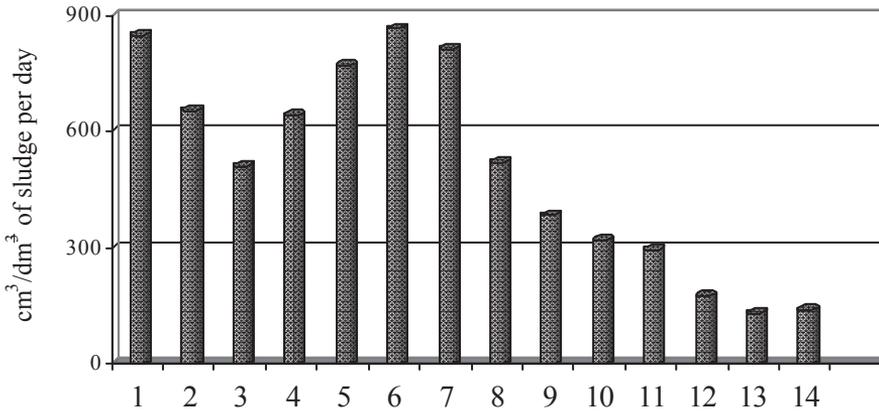


Fig. 1. The amount of biogas generated in consecutive days of thermophilic fermentation process

The amount of biogas that was generated during the first 8 days varied in the range of 866÷510 cm<sup>3</sup>/dm<sup>3</sup> sludge. The most of biogas was obtained on the sixth day. The total amount of biogas obtained after 14-day fermentation was 7060 cm<sup>3</sup>/dm<sup>3</sup> sludge (approximately 1000 cm<sup>3</sup> of gas from 1g of removed dried organic matter of sludge). The concentration of CH<sub>4</sub> in biogas, except for the first day, was in the range of 54÷57%, whereas that of CO<sub>2</sub> 38÷40% (Table 3).

Table 3. Composition of biogas in thermophilic fermentation

Component	Content in biogas, %				
	1 <sup>st</sup> day	3 <sup>rd</sup> day	7 <sup>th</sup> day	10 <sup>th</sup> day	14 <sup>th</sup> day
CH <sub>4</sub>	40.8	54.2	57.2	56.8	55.7
CO <sub>2</sub>	35.1	37.7	38.2	39.8	38.5

Despite the high content of carbon dioxide in the biogas composition no disturbances in the fermentation process were observed. No decrease of pH values for liquid phase

of sludge was recorded, neither the increase of volatile fatty acids (VFA) concentration. Moreover, VFA/alkalinity did not exceed 0.3.

Methane fermentation at low organic loading rates established favorable conditions for degradation of not readily biodegradable PCBs. Table 4 present the results of qualitative and quantitative changes of PCBs in sewage sludge during thermophilic digestion.

Table 4. Concentration of PCBs ( $\mu\text{g}/\text{kg d.m.}$ ) in sewage sludge before and during thermophilic methane fermentation

Congeners	Before fermentation	During fermentation				Student's t-test
		3 <sup>rd</sup> day	7 <sup>th</sup> day	10 <sup>th</sup> day	14 <sup>th</sup> day	
PCB 28	3.42±0.62	3.58±0.47	2.92±0.49	5.18±0.83	1.12±0.30	4.330
PCB 52	2.87±0.84	2.61±0.42	2.32±0.50	3.93±0.57	1.72±0.39	1.754*
PCB 101	5.47±0.86	5.71±0.83	4.09±0.85	2.58±0.66	3.10±0.55	3.295
PCB 118	6.73±1.20	7.30±0.82	4.75±0.93	4.12±0.51	nd <sup>1</sup>	-
PCB 138	9.76±1.44	8.83±1.85	7.01±1.63	0.80±0.51	1.50±0.43	7.784
PCB 153	8.88±1.68	7.87±1.74	6.80±1.68	3.95±0.95	0.90±0.27	8.809
PCB 180	15.21±2.52	13.46±2.6	7.90±1.84	0.83±0.14	nd <sup>1</sup>	-
$\Sigma$ PCB	52.33	49.35	35.78	21.39	8.34	

\*) the change concentration of PCBs before and after fermentation is not statistically significant

<sup>1</sup>nd – not detected

Before the process of thermophilic digestion in the mixture of sludges, all seven congeners of PCB were determined: their total concentration was 52.33  $\mu\text{g}/\text{kg d.m.}$ , with the highest concentrations obtained for heptachlorobiphenyl with code 180 (15.21  $\mu\text{g}/\text{kg d.m.}$ ) and heksachlorbiphenyl with code 138 (9.76  $\mu\text{g}/\text{kg d.m.}$ ). Comparison of total concentrations of PCB on all the monitored days of the process of fermentation revealed that the concentration was the highest before the process. On the third day of the process of fermentation, concentrations of individual congeners were comparable. On the tenth day it was found that the total concentration of LCB doubled the previous level, whereas in higher chlorinated PCBs this value decreased twice. During next days, the content of individual congeners in the mixture of sludge was on the decrease. After the process of thermophilic digestion, all the determined congeners of PCBs were still present. However, their total concentration was reduced by 84% on the fourteen day of the process. It should be emphasized that on the tenth day of fermentation, a total concentration of LCB rose, whereas this level decreased for HCB. The sludge after fermentation showed low content of five higher chlorinated PCBs. Insignificant percentage of higher chlorinated PCBs in the studied mixture after the process of thermophilic digestion can be explained by their capability of bioaccumulation (the more chlorine atoms in biphenyl molecule the better biosorption) [5] and/or biological degradation as a result of which higher chlorinated PCBs were transformed into lower chlorinated PCBs. According to [5, 32] the kinetics of the process of dechlorination depends on the composition of a particular population of microorganisms, which are present in sewage sludge. The content of a particular culture is affected by the environmental conditions such as: availability of the sources of carbon, hydrogen and other electron donors, presence or lack of electron acceptors other than PCBs, competition with other microorganisms, presence of toxic pollutants, temperature and pH [32].

The concentrations of heavy metals ions in the sludge liquid on the chosen days of thermophilic methane fermentation are shown in Table 5.

Table 5. Concentration of heavy metals ions in sludge liquid

Metal	Unit	Concentration of heavy metals					
		Before	1 <sup>st</sup> day	3 <sup>rd</sup> day	7 <sup>th</sup> day	10 <sup>th</sup> day	14 <sup>th</sup> day
Zinc	mg/dm <sup>3</sup>	0.113	0.263	0.457	0.433	0.637	0.566
Copper	mg/dm <sup>3</sup>	0.042	0.054	0.093	0.072	0.104	0.083
Nickel	mg/dm <sup>3</sup>	0.093	0.081	0.081	0.078	0.082	0.104
Lead	mg/dm <sup>3</sup>	0.037	0.031	0.033	0.028	0.043	0.032
Cadmium	mg/dm <sup>3</sup>	0.005	0.009	0.013	0.013	0.015	0.017
Chromium	mg/dm <sup>3</sup>	0.076	0.063	0.057	0.082	0.062	0.084

During fermentation the increase of zinc, copper and cadmium in the sludge liquid was observed. In the case of zinc the concentration increased from 0.11 to 0.64 mg/dm<sup>3</sup>, and for copper from 0.04 to 0.1 mg/dm<sup>3</sup>. The concentrations of nickel, lead, and chromium in the sludge liquid varied in the range of 0.08÷0.1; 0.03÷0.04 and 0.06÷0.08 mg/dm<sup>3</sup>, respectively. It can be summarized that fermentation under thermophilic conditions did not significantly influence the release of heavy metal ions into the liquid of stabilized sludges.

The averaged concentrations of heavy metals in the sludges, before and after thermophilic fermentation process, together with standard deviations are shown in Table 6.

Student's t-test column shows calculated t values. The values in the column with an asterisk \* are smaller than critical value  $t_{0.05} = 2.776$ , which means that the change of the heavy metal concentration in the sludge before and after fermentation is not statistically significant. All other values differ significantly.

The sequential extraction revealed that the highest concentration of zinc in the sludges before fermentation was found in the fraction of hydrated oxides of iron and manganese and in the organic-sulfide fraction. After fermentation of the sludges, the significant zinc enrichment was observed in the organic-sulfide fraction and smaller in the fraction of oxides of iron and manganese. After the fermentation 45% of total zinc content was present in the organic-sulfide fraction. It is supported by other studies performed on sludges stabilized under anaerobic conditions [1, 13, 26]. Copper was bound to organic matter and sulfides (92%) before fermentation and this fraction was enriched after the fermentation process.

The highest concentration of nickel in the sludges before the stabilization was present in the exchangeable-carbonate and organic-sulfide fractions, on the other hand, the smallest concentration was found in the residual fraction. The thermophilic fermentation process resulted in nickel enrichment mainly in the organic-sulfide fraction of the sludges. The distribution of the metal over the following fractions: exchangeable-carbonate, iron and manganese oxides, organic-sulfide and residual was 36, 16, 44, and 4%, respectively. Before the stabilization of the sludge, lead was present in the organic-sulfide fraction and residual fraction. The increase of lead concentration after fermentation was observed in the residual fraction. After thermophilic fermentation, 52% of lead was present in the organic-sulfide fraction, whereas 38% in the residual fraction of the sludges.

Table 6. Chemical fractionation of heavy metals in sludge before and after thermophilic methane fermentation

Metal	Fraction	Content in sewage sludge				Student's t-test
		Before fermentation		After fermentation		
		mg/kg d.m.	%	mg/kg d.m.	%	
Zinc	I	397.0 ± 4	23.6	323.0 ± 4	14.2	18.045
	II	<b>653.0 ± 7</b>	38.8	<b>852.0 ± 16</b>	37.6	15.487
	III	<b>587.0 ± 11</b>	34.9	<b>1019.0 ± 21</b>	44.9	24.784
	IV	46.0 ± 3	2.7	75.0 ± 1	3.3	14.370
	Σ	1683.0	100	2269.0	100	
Copper	I	2.1 ± 0.1	1.4	0.9 ± 0.2	0.4	7.926
	II	1.8 ± 0.2	1.1	1.5 ± 0.2	0.7	1.342*
	III	<b>145.3 ± 0.5</b>	91.7	<b>204 ± 12</b>	94.3	6.636
	IV	9.2 ± 0.2	5.8	10.0 ± 0.4	4.6	2.359*
	Σ	158.4	100	216.4	100	
Nickel	I	80.5 ± 0.5	48.1	<b>79.6 ± 0.4</b>	36.0	1.939*
	II	28.7 ± 1.2	17.1	35.7 ± 0.4	16.1	7.035
	III	<b>53.9 ± 2.7</b>	32.2	<b>96.2 ± 6.8</b>	43.5	8.014
	IV	4.4 ± 0.4	2.6	9.8 ± 0.8	4.4	8.433
	Σ	167.5	100	221.3	100	
Lead	I	3.4 ± 0.2	5.9	4.6 ± 0.1	6.2	6.928
	II	1.9 ± 0.2	3.3	3.1 ± 0.1	4.2	7.589
	III	36.3 ± 3.3	63.5	<b>38.5 ± 1.5</b>	51.9	0.856*
	IV	<b>15.6 ± 2.7</b>	27.3	<b>28.0 ± 4.0</b>	37.7	3.533
	Σ	57.2	100	74.2	100	
Cadmium	I	< 0.1	-	< 0.1	-	-
	II	0.96 ± 0.22	36.5	0.92 ± 0.16	25.0	0.200*
	III	<b>1.67 ± 0.10</b>	63.5	<b>2.65 ± 0.55</b>	72.0	2.359*
	IV	< 0.1	-	0.11	3.0	-
	Σ	2.63	100	3.68	100	
Chromium	I	1.1 ± 0.3	0.7	0.4 ± 0.1	0.2	3.593
	II	0.4 ± 0.1	0.3	< 0.1	-	-
	III	<b>149.0 ± 3.1</b>	97.5	<b>202.4 ± 11</b>	93.6	6.501
	IV	2.3 ± 0.6	1.5	13.5 ± 2.8	6.2	5.600
	Σ	152.8	100	216.3	100	18.045

\*) the change of the heavy metal concentration before and after fermentation is not statistically significant (fraction: I – exchangeable and carbonates-bound, II – Fe/Mn oxides-bound, III – organic matter/sulfides-bound, IV – residual)

In the case of cadmium the increase was observed in the organic-sulfide fraction in the stabilized sludge. The distribution of cadmium in this fraction was 72%, while, 25% of total cadmium content was found together with iron and manganese oxides. Those fractions have been pointed out by several other authors to be the dominant fractions to bind cadmium in the sludges stabilized with fermentation process [6, 13]. The highest concentration of chromium was found in the organic-sulfide fraction (94%). It has been

also reported in the literature [1, 21, 30] that copper and chromium were mainly bound to organic-sulfide fraction in the sewage sludge stabilized during anaerobic treatment.

The analyses of the sludges after the thermophilic fermentation indicated low concentration of metals (except for lead) in the residual fraction (the compounds insoluble in practice), chromium 6%, for all other metals < 5%. The residual fraction is considered to be chemically stable and biologically inactive. Metals that were found in this fraction are not harmful for aquatic ecosystem. On the other hand, in the exchangeable-carbonate fraction, most mobile fraction of metals, the highest concentration of nickel (36%) was found. The presence of high concentrations of nickel in the mobile fraction indicates that when the outer conditions change, such as equilibrium in the sorption-desorption system or decrease of pH, the release of metal ions into the soil-water environment can occur. The content of zinc, copper, lead, cadmium, and chromium in the exchangeable-carbonate fraction was 14.2; 0.4; 6.2; < 0.1; 0.2%, respectively.

## CONCLUSIONS

After the process of thermophilic digestion of the mixture primary and fermenting sludge, the total concentration of seven PCBs reduced by 84%, which suggests that thermophilic digestion affects reduction in PCBs positively. On the tenth day of the process, concentration of lower chlorinated PCBs increased. Sludge after fermentation revealed low content of higher chlorinated PCBs, which can be explained with their capability of bioaccumulation (the more chlorine atoms in biphenyl molecule the better biosorption) and/or biological degradation as a result of which higher chlorinated PCBs were transformed into lower chlorinated PCBs.

Low concentration of heavy metal ions in the liquid phase of sludge was observed. The metal ions precipitated and remained bound throughout the stabilization process. The highest increase of zinc, copper, nickel, cadmium, and chromium concentration was observed in the organic-sulfide fraction, whereas the highest increase of lead was found in the residual fraction. It can be concluded that fermentation under thermophilic conditions favored the formation of stable chemical forms of heavy metals.

Undertaken research justifies the followings conclusions:

- 1) After fermentation in the studied mixture of sewage sludge, a high degree of PCBs elimination was demonstrated. Therefore, one can expect that the process of thermophilic digestion did not cause accumulation of polychlorinated biphenyls in sewage sludge.
- 2) Thermophilic methane fermentation has not caused the accumulation of heavy metals in the mobile fractions of sludge.

This work was carried out within the research project no. N N523 410635 and BS-402-301/07

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Received: March 14, 2011; accepted: June 20, 2011.

#### METALE CIĘŻKIE I PCB W OSADACH ŚCIEKOWYCH PODCZAS FERMENTACJI PROWADZONEJ W WARUNKACH TERMOFILOWYCH

Przeprowadzono badania mające na celu ocenę wpływu fermentacji termofilowej na zmianę zawartości siedmiu kongenerów o kodach: 28, 52, 101, 118, 138, 153 i 180 w osadach ściekowych oraz na przemieszczanie się metali ciężkich (Zn, Cu, Ni, Pb, Cd, Cr) pomiędzy frakcjami chemicznymi osadów. Metanowej fermentacji termofilowej poddano osad pobrany z osadnika wstępnego z miejskiej mechaniczno-biologicznej oczyszczalni ścieków. Osad przed stabilizacją zmieszano w stosunku objętościowym 1:2 z osadem przefermentowanym zaadoptowanym do warunków termofilowych. Porównując sumaryczne stężenie PCB we wszystkich monitorowanych dobach procesu fermentacji termofilowej zaobserwowano, że przed procesem było ono największe. W trzeciej dobie procesu stabilizacji stężenia poszczególnych kongenerów były porównywalne natomiast w dziesiątej dobie stwierdzono, że sumaryczne stężenie niżej chlorowanych PCB wzrosło 1,5-krotnie natomiast wyżej chlorowanych zmalało około 4-krotnie. W kolejnych dobach zawartość poszczególnych kongenerów w mieszaninie osadów zmniejszała się. Po procesie fermentacji termofilowej nie oznaczono PCB 118 oraz PCB 180. W czternastej dobie procesu sumaryczne stężenie wykrytych kongenerów zmniejszyło się o 84%. Można więc przypuszczać, że proces fermentacji termofilowej nie spowodował kumulowania się polichlorowanych bifenili w osadach ściekowych.

Stwierdzono niskie stężenia jonów metali ciężkich w cieczach osadów. Jony metali wytrąciły się i pozostały związane w osadach do końca procesu stabilizacji. Najwyższy wzrost zawartości cynku, miedzi, niklu, kadmu i chromu stwierdzono we frakcji organiczno-siarczkowej, natomiast ołowiu we frakcji pozostałościowej osadów. Tym samym przeprowadzenie fermentacji osadów w termofilowym zakresie temperatur sprzyjało powstawaniu stabilnych form chemicznych metali ciężkich.