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Degradation of PCBs in sewage sludge during methane fermentation process concerning environmental management

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ABSTRACT

The aim of the investigation was degradation of polychlorinated biphenyls (PCBs) in sewage sludge and supernatants during the methane fermentation process. The mixture of municipal sewage sludge and industrial sewage sludge was incubated for 20 d at 37°C in the dark. The quantification of the PCBs was carried out simultaneously in both the solid and supernatant phases, the latter separated from the sludge during centrifugation. The prepared samples of sewage sludge and supernatants were subjected to extraction with the application of the organic solvents mixture. The qualitative–quantitative analysis of PCBs was done using the GC–MS system. After 20 d, the solid phase was observed to have its PCBs content reduced by 58% in the solid phase and 71% in supernatants. The percentage removal of PCBs was 49 and 75% in solid phase and in supernatants mixture of municipal and industrial sewage sludge, respectively.

Keywords: PCBs; GC–MS; Fermentation; Sewage sludge; Supernatants

1. Introduction

Polychlorinated biphenyls (PCBs) are hydrophobic compounds that poorly dissolve in water, but are well soluble in organic solvents and oils. The solubility of the PCB is in the range 0.4–640 μg/L. PCBs, bioaccumulate and bioconcentrate, are biodegradable. Compounds with greater solubility can be more easily decomposed by micro-organisms than the other ones. PCBs are resistant to chemical agents such as strong acids and to high temperature, and the boiling temperature is relatively high (337–414°C). PCBs were widely used in industrial production, mainly due to very good dielectric properties. They are characterized by low electrical conductivity and high thermal conductivity. They were used as components of insulating oils, in transformers, as dielectric materials in capacitors, and some other electrical equipment. PCBs have a toxic effect on organisms, penetrate into the

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bloodstream, and accumulate in tissues. PCB toxicity depends on the position of the chlorine atom in the biphenyl molecule [1,2].

Although the use of PCBs has been severely limited or eliminated, the presence of PCBs in the sewage sludge isolated from municipal wastewater in the literature sources was confirmed. The presence of PCBs in sewage sludge is related to the presence of these compounds in wastewater and depends on their type. A large role in the amount of PCBs in the municipal wastewater plays the type and quantity of industrial wastewater, which is mixed with municipal wastewater and treated together. During mechanical treatment processes, the sedimentation process, these compounds are adsorbed on particulates. Sewage sludge in sewage treatment plants are subjected to digestion processes (biological or chemical stabilization, dewatering, drying, and incineration). During the sewage sludge digestion processes, mineralization of organic compounds takes place as well as reduction of sludge volume, inactivation of pathogenic micro-organisms, and methane production [3–8].

According to Polish legislation, the use of sludge in agriculture is limited with regard to heavy metals such as: cadmium, copper, nickel, lead, zinc, mercury, chrome, and some pathogenic organisms. The concentrations of other toxic compounds found in the sewage sludge are not normalized [9]. However, the studies concerning the identification of organic compounds in the sewage sludge, conducted up to now, have shown that other toxic contaminants are present. Among them are not only PCBs, but also polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), organic halogens (AOX), sulfonates (LAS), phthalate (DEPH), and nonylphenol ethoxylate (NPE). The proposed amendment of the directive related to sludge suggests that more control should be applied regarding the sewage sludge for agricultural utilization of those organic pollutants. In the case of PCBs, the total content of seven compounds, such as: 28, 52, 101, 118, 138, 153, and 180, should not exceed 0.8 mg/kg [10]. PCBs are also specified in the Stockholm Convention and Polish legislation on substances which are persistent in the environment. Given the need to reduce the amount of toxic compounds, including the PCBs released into the environment, it is important to ensure the conditions for their degradation in sludge treatment processes that are conducted in wastewater treatment plants [11,12].

The literature describes the findings of the studies that confirm that the biochemical processes, such as aerobic stabilization or anaerobic fermentation, allow for the degradation of these micropollutants [13–15]. It has been shown that the course of the anaerobic biodegradation consists in the gradual dechlorination of PCB. Dehalogenation of PCBs comprises dechlorination from meta position or ortho position, leading to the formation of lower chlorinated ortho chlorinated biphenyls. In the case of biphenyls having an increased number of chlorine atoms in the molecule, the chlorine is detached to the tetrachlorobiphenyl, then to the trichlorobiphenyl as far as to the dichlorobiphenyl. Fig. 1 shows an example of a path of biodegradation of PCBs.

Efficiency and the biodegradation rate of PCB depend not only on the structure of the chemical compounds but also on the environmental conditions, that is pH, temperature, the presence of micro-organisms capable of degrading these compounds, the availability of carbon sources, and the presence or absence of electron acceptors and inhibitors of microbial metabolism. These factors affect the composition of micro-organisms and their activity. The micro-organisms capable of degrading PCB anaerobically may include: *Desulfomonile tiedjei, Desulfitobacterium, Dehalobacter restrictus, Dehalospirillum mulitivorans, Desulforomonas chloroethenica, Dehalococcoides ethenogenes,* and facultative bacteria *Enterobacter* MS1 and *Enterobacter agglomerans* [17–20].

The findings of the studies described in the literature refer mainly to the bottom sludge, soils, and sludge separated from municipal sewage. Contamination of municipal sludge with the PCBs is dependent upon the type of sludge and ranges from 7 to 108 μg/kg dm [21–24]. The literature has discussed the research on quantitative changes of PCBs in municipal sludge under anaerobic processes [24–30]. The degree of degradation of these compounds varied. In municipal sludge mixture subjected to fermentation under thermophilic conditions, the degree of loss of PCB ranged from 47 to 84%. During fermentation under mesophilic conditions, the degree of degradation was in the range of 33–93% [24,26,30]. In the study conducted by Patureau, the degradation efficiency was lower. In the solid phase, the degree of removal of PCBs was less than 9%, and in the supernatants—14% [25]. As it has been stated, these results related to the sludge separated from municipal wastewater, while for the industrial sludge, there is no data. Some previous studies of the authors demonstrated that the PCB content in coke deposits can reach 1.23 μg/kg dm [27].

Due to the fact that, on the one hand, coke deposits are charged with organic pollutants (including PCBs), and at the same time, they are supposed to be neutralized, the co-fermentation of municipal sludge with the coke deposits was performed. During the process, quantitative PCBs changes were analyzed in both solid and liquid phases of municipal sludge

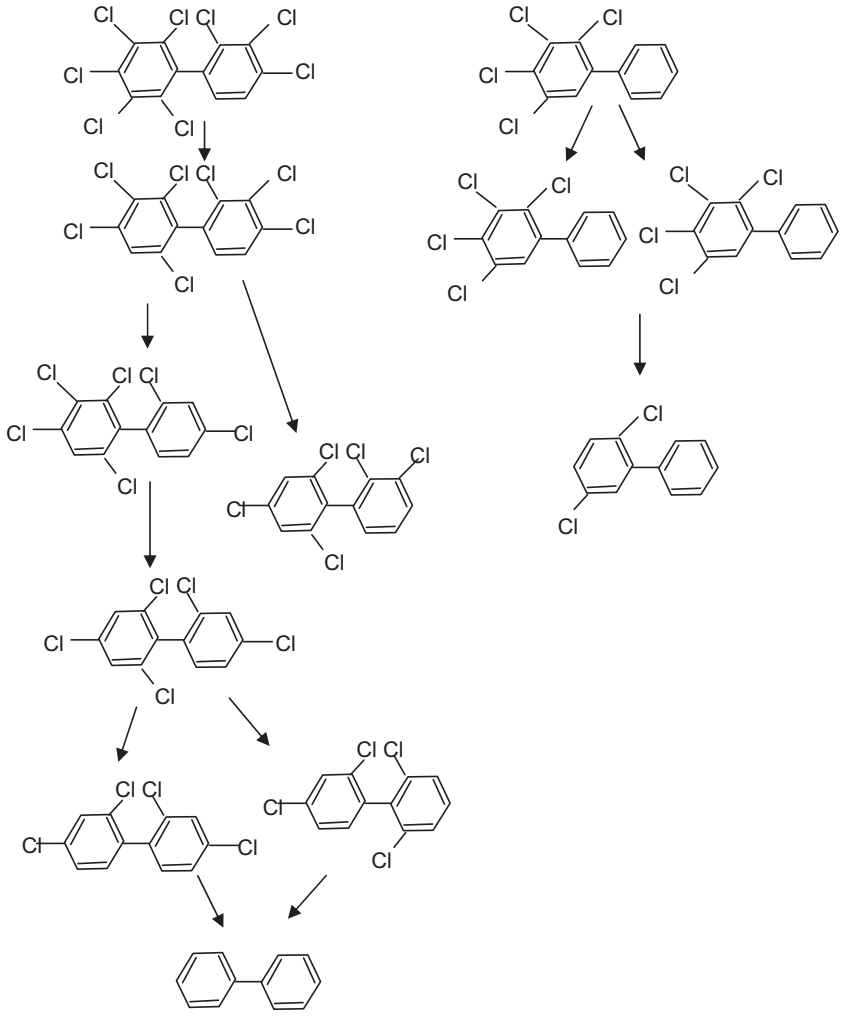

Fig. 1. Biodegradation of PCBs in anaerobic conditions [16].

mixture with the industrial one. On the basis of PCBs concentrations in the solid phase with reference to dry matter and concentrations in supernatants, the PCBs mass balance in the sewage sludge was determined.

2. Experimental procedure

2.1. Fermentation process

The sewage sludge from the municipal sewage treatment plant and sewage sludge from coking wastewater treatment plant were used. In the municipal sewage treatment plant, the treatment of wastewater is carried out in the process of dephosphatation, denitrification, and nitrification. In technical conditions, the stabilization of sewage sludge is performed in fermentation chambers in anaerobic conditions. The preliminary sewage sludge and the digested sewage sludge from the fermentation chamber were taken. Raw sewage sludge and digested sewage sludge, as inoculum, were mixed. This mixture was the control sewage sludge. In the coking wastewater treatment plant, the sewage treatment is performed in the process of denitrification and nitrification. The sewage flows through the gravel filter, tar separator, and desorption column before it is fed into the biological part of a treatment plant and is directed to the averaging tank. The mixture of municipal sewage sludge with coke sewage sludge in the volume ratio 6:1 was prepared for further technological testing. The co-fermentation process was performed in glass bioreactors. Incubation of sewage sludge was carried on for 20 d at a temperature of 37°C with no access of light. In order to provide the right contact between biomass and the substrate, the mixture of sewage sludge was mixed once a day and the pressure of biogas was measured simultaneously. In order to specify the course of the process, the marking of selected

physical and chemical properties of sewage sludge before the process was performed, after 10 or 20 d of incubation. For sewage sludge, the following was determined: dry residue, the content of organic substances, and hydration. The following was determined in the liquid phase (supernatants) obtained from sewage sludge centrifugation: pH, alkalinity, chemical oxygen demand, and volatile fatty acids (VFAs). Both in the solid phase (spinned sewage sludge) and in the liquid phase (supernatants), PCBs were marked before the process, after 10 d of incubation and after 20 d of fermentation.

2.2. Identification of PCBs

Sewage sludge was centrifuged to obtain supernatants. Ten grams of centrifuged sewage sludge and 1,000 mL of supernatants were collected for the research. The separation of the organic substances of the sewage sludge was made via sonification using a solvent mixture of cyclohexane and dichloromethane (5:1, v/v). The obtained extracts were centrifuged for 10 min with 9,000 rpm. The separation of organic compounds in liquid samples was carried out mechanically in the liquid–liquid system with the addition of methanol, cyclohexane, and dichloromethane (20:5:1, v/v/v). In this case, the separation of extracts from samples took place in the glass separatory funnel. Silica gel was used to isolate analytes from extracts from other simultaneously extracted organic substances. Before the introduction of the extracts, columns filled with silica gel were conditioned with methanol (2 × 3 mL), and then with distilled water (2 × 3 mL). The purified extracts were concentrated in the nitrogen stream to 2 mL. Those extracts were concentrated to a volume of 0.5 mL, and then distilled water (30 mL) and methanol were introduced for obtaining a clear solution. In order to obtain further PCBs isolation, the extracts were filtered through preconditioned columns of the Bakerbond SPE octadecyl C18 type. Columns-fill with silica gel with chemically bonded octadecyl groups was conditioned with dichloromethane (2 × 6 mL) and distilled water (1 × 6 mL). Next, polychlorinated biphenyl was eluated with dichloromethane (3 × 1 mL). The received eluate was concentrated in the nitrogen stream to the volume of 1 mL. The quantitative–qualitative analysis of seven congeners of PCBs was carried out by chromatography (GC–MS). The quantitative analysis was performed using a standard mixture of seven congeners (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180) PCB MIX 3. The temperature program of column oven was as follows: 40–120˚C (heating 40˚C/min), 120–280˚C (heating 5˚C/min), and 280˚C for 15 min. Indications of PCBs were performed in duplicate. Recovery values were determined for the samples of sewage sludge and the liquid prepared in the manner described above, after the introduction of reference mixtures prior to extraction of solvents. In Table 1, both the limit of detection (LOD) and recoveries of congeners of PCBs were presented. In supernatant samples, the recoveries of individual biphenyls were in the range 9–86%. In the solid phase, the percentage of recoveries of the standard mixture of PCBs varied between 18 and 55%. The recoveries of PCB obtained in this study were within the limits published by other scientists (92–119%). It should be noted that the studies described in the literature were carried out on material sewage sludge whose chemical characteristics were different. In industrial sludge, they may occur in other compounds having similar physicochemical properties to the PCB, which is likely to have an impact on the recovery of the individual compounds in these matrices [28,29].

2.3. Kinetics of PCBs degradation

Interpreting the results of the study, it was assumed that the distribution of the PCB is in accordance with the first-order reaction. The half-life of individual congeners of PCBs according to the equation was calculated:

$$T_{1/2} = \frac{\ln 2}{k} \tag{1}$$

$$\ln \frac{C_0}{C_t} = k \cdot t \tag{2}$$

where k—reaction rate constant (d^{-1}), C_0—initial concentration of PCBs (μg/kg dm) or (ng/L), C_t—concentration of PCBs after time t (μg/kg dm), or (ng/L), t—time of incubation of sewage sludge (d).

The changes in the concentrations of PCBs and degradation of these compounds in sewage sludge and in supernatants during fermentation process were described as a mathematical function which was verified in accordance with the values of the coefficient of determination.

2.4. PCBs balance in the solid phase and in the liquid phase

The balance of PCBs mass was determined taking into consideration the concentrations of these compounds in the sewage sludge and in the supernatants, and the amount of dry matter and liquid in the unit

Table 1
Limit of detection and recoveries of PCBs [28,29]

Congeners of PCBs	LOD of PCBs (ng/L)	Recoveries of PCBs (%)]		Recoveries according to literature data (%)
		Liquid phase (Supernatants)	Solid phase (sewage sludge)	Sewage sludge
PCB 28	0.35	[a]	18.3	80–92
PCB 52	0.59	9.0	[a]	70–93
PCB 101	0.38	85.5	25.0	73–88
PCB 118	0.19	57.5	[a]	69–78
PCB 138	0.27	65.5	30.0	60–66
PCB 153	0.27	76.5	46.7	61–80
PCB 180	0.28	[a]	55.0	50–70

[a]not detected.

volume of sewage sludge. The amount of PCBs in the solid phase (S) and in the liquid phase (L) in reference to the unit volume of hydrated sewage sludge was calculated according to the formula:

$$S = C_s \quad 10^{-3} \cdot s \tag{3}$$

$$L = C_1 \quad V \tag{4}$$

where C_s—concentration of PCBs in solid phase (ng/kg d.m), C_l—concentration of PCBs in liquid phase (supernatants) (ng/L), s—content of dry matter in the hydrated sewage sludge (g/L), and V— the volume of supernatants in the aqueous sewage sludge (L/L).

2.5. Statistical test

For the statistical evaluation of the results for the addition of coke sewage sludge on the degradation of PCB *t*-Student t_d test was used. The level of confidence was accepted at 0.95 level. The number specifying the degree of freedom was 3, for this parameter, and the theoretical value of decomposition of the *t*-Student t_d was 2.776.

3. Results and discussion

3.1. Control of fermentation process

In the municipal sludge, the dry residue before the process was 21.0 g/L, and the proportion of organic material accounted for 60%. In the sewage sludge after fermentation, the dry matter content was 16.0 g/L of which 58% was the loss on ignition. The dry residue in the analyzed sewage sludge after 20 d of incubation decreased to 15.3 g/L (loss of 19%). The organic matter decomposition in the municipal sludge reached 27.6%. The analyzed sewage sludge reported a loss of organic matter of 23.8%. During the methane fermentation process, the ratio of VFAs and the basicity was not higher than 0.3, and the pH ranged from 7.4 to 8.2. Changes in the value of selected indicators were within the range specified in the literature. The fermentation process was carried out correctly reproducing the actual conditions prevailing in the sewage treatment plants. Chemical indicators indicate that the sludge after 20-d stabilization was well fermented. The organic loading rate was 0.4 g v.s./L d, and the amount of biogas formed with 1 g of dry organic matter introduced into the reactor for control sample was 0.45 L/g v.s, and in mixture of municipal sewage sludge and industrial sewage sludge, it was 0.34 L/g v.s.

3.2. Degradation of PCBs in municipal sewage sludge during fermentation process (control sample)

Changes in the concentration of PCBs in sewage sludge and in supernatants in Fig. 2 and in Fig. 3 are

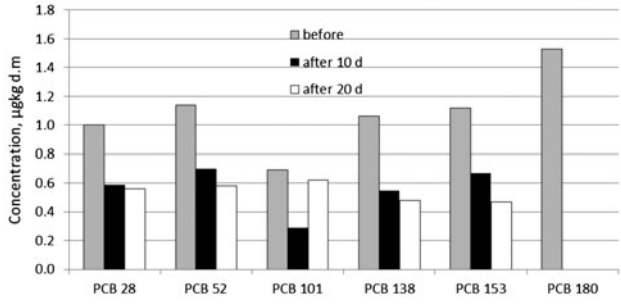

Fig. 2. Changes of PCBs concentrations in sewage sludge during fermentation process.

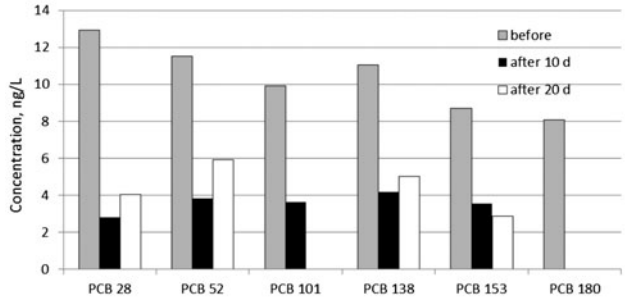

Fig. 3. Changes of PCBs concentrations in supernatants during fermentation process.

given, respectively. The total concentration of PCBs in sewage sludge reached 6.53 μg/kg dm before fermentation process. The concentration of congener PCB 118 was lower than the LOD of GC–MS system and was not detected. At the end of incubation, the concentration of PCBs was 58% lower than the initial content. The removal of PCBs was in the range of 10% (PCB 101)–100% (PCB 180). The concentration of PCBs in supernatants was 62.22 ng/L on average. At the end of the fermentation process, the total concentration of these compounds was 71% lower than the initial content. During that fermentation process, the total concentration of seven PCB congeners was reduced by 92%.

In other studies, in the solid phase, reduction was observed during the fermentation of 9%. In the case of the liquid phase, the total PCB percentage of loss reached 14% [25]. After 15 d of sewage sludge incubation, PCB 28, 118, 138, 153, and 180 were not determined. During the same time span, the concentration of PCBs 101 congener increased two times (twice). This can be explained by biological degradation, resulting in the PCBs with a high content of chlorine in the molecule, and the following changes were chlorinated PCBs [24].

Regarding the changes of PCBs concentration before the fermentation process and after incubation, critical values of *t*-Student t_d, test in sewage sludge and supernatants were calculated, respectively (Table 2). The results of calculations show that the changes of PCBs concentration in samples were statistically significant.

Table 3 presents the results of statistical calculations for PCBs in sewage sludge and separated supernatants as well as the difference of the average two independent samples before and after the process. In the solid phase, the additive of coke deposits had no statistically significant importance for PCB 52 before the process and PCB 101. In supernatants before the stabilization process, the introduction of coke sludge to the municipal sludge was found to be significant for PCB 138, 153, and 180; after the process of 20-d fermentation, only PCB 153 had not a statistically significant importance.

In Table 4, the results of mass balance of PCBs in the sewage sludge (solid phase) and in supernatants (liquid phase) are presented.

In the unit volume of sewage sludge, it was found that during fermentation the amount of PCBs decreased from 196.79 to 60.56 ng. In the solid phase, the content of PCBs was 137.34 ng before the process of fermentation, and the content was 43.36 ng after the process of 20 d of incubation. In the supernatants, the decrease in the amount of PCBs was 42.25 ng. (Before the process, the total content of PCBs was 59.45 ng, and after the process of fermentation—17.20 ng), the losses of PCBs 136.23 ng were noted.

3.3. Degradation of PCBs in mixture of municipal sewage sludge and industrial sewage sludge during fermentation process

Figs. 4 and 5 show the changes in concentrations of seven PCB congeners in sewage sludge and separated from them supernatants during the fermentation process. The total seven PCB concentrations in solid phase were reduced by 49%. The major compound in the sludge before the process was PCB 28, and PCB 52 (0.99 μg/kg dm) after the process. In supernatants, the total concentration of seven PCB was 62.84 ng/L, and after 20-d stabilization it was 15.6 ng/L (75% degradation). Exactly, as it was in the case of the control sample, the PCB with a code of 118 was present below the limit of quantitation.

Table 2
Values of Student-*t* distribution ($t_{d=}$2.776) for PCBs

PCBs	Sewage sludge	Supernatants	PCBs	Sewage sludge	Supernatants
PCB 28	11.867	27.594	PCB 138	7.110	18.121
PCB 52	10.287	9.328	PCB 153	17.338	19.362
PCB 101	63.375	21.457	PCB 180	28.796	28.796

Table 3
Values of Student-t distribution ($t_d = 2.776$) for PCBs for two independent samples

PCBs	Sewage sludge—before	Sewage sludge—after	PCBs	Supernatants—before	Supernatants—after
PCB 28	46.104	4.409	PCB 28	**0.829**	7.191
PCB 52	**2.459**	6.326	PCB 52	**1.905**	16.058
PCB 101	4.419	**2.692**	PCB 101	**0.818**	18.385
PCB 138	9.947	1.177	PCB 138	5.862	5.126
PCB 153	3.261	11.700	PCB 153	13.256	**2.441**
PCB 180	7.675	*	PCB 180	4.148	*
Totality	4.743	6.784	Totality	**0.309**	5.912

Notes: Bold values are not statistically significant.
*not detected.

Table 4
Mass balance of PCBs in the solid and liquid phases before and after the fermentation process

	Solid phase (ng)		Liquid phase (ng)		
PCB	Before fermentation	After fermentation	Before fermentation	After fermentation	Difference
PCB 28	21.00	8.96	12.37	3.90	+20.50
PCB 52	23.94	9.28	11.01	5.72	+19.95
PCB 101	14.49	9.92	9.49	0	+14.06
PCB 118	0	0	0	0	0
PCB 138	22.26	7.68	10.56	4.84	+20.30
PCB 153	23.52	7.52	8.32	2.75	+21.58
PCB 180	32.13	0	7.70	0	+39.83
Totality	137.34	43.36	59.45	17.20	+136.23

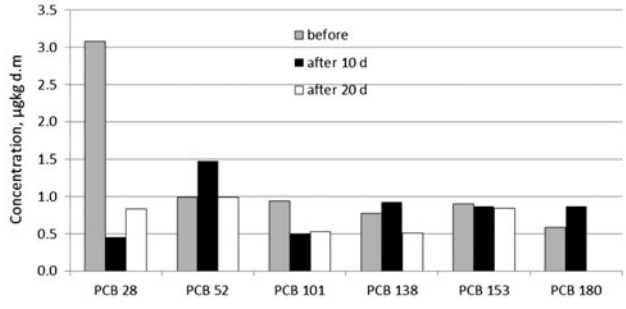

Fig. 4. Changes of PCBs concentrations in mixture of municipal sewage sludge and industrial sewage sludge during fermentation process.

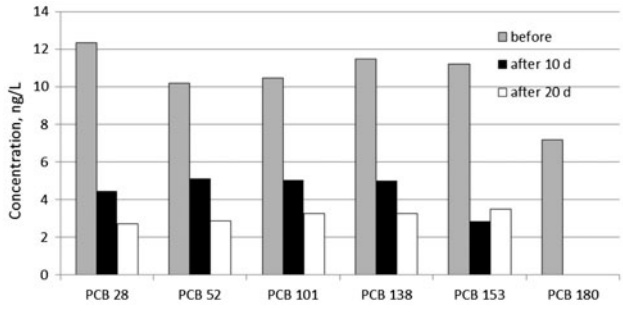

Fig. 5. Changes of PCBs concentrations in supernatants in mixture of municipal sewage sludge and industrial sewage sludge during fermentation process.

Table 5 shows the results of statistical calculations for PCBs before and after the co-fermentation process. Changes in the concentrations of most PCBs in sewage sludge and supernatants were significantly statistical ($t_d > 2.776$). Differences in the concentration of PCB 52 and PCB 153 were not statistically significant.

The mass balance of seven PCBs in the mixture of municipal sludge and coke sludge in the individual phases shows that the content of seven PCBs in the solid phase before co-fermentation was 138.13 ng. After 20-d incubation, the PCB content was 56.61 ng. The loss of PCBs was 81.52 ng which represents 59% of the initial content. In the liquid phase, on the other hand, the PCB loss during fermentation was higher and reached 75% (the initial PCB content in fluids before the process was 60.41 ng, and after the co-fermentation process – 15.08 ng). In the unitary volume of the mixed sludge (municipal and industrial

Table 5
Values of Student-t distribution ($t_d = 2.776$) for PCBs in test sample

PCBs	Sewage sludge	Supernatants	PCBs	Sewage sludge	Supernatants
PCB 28	29.375	27.594	PCB 138	18.543	12.067
PCB 52	**0.667**	9.328	PCB 153	**0.250**	47.667
PCB 101	6.669	21.457	PCB 180	14.750	48.365

Note: Bold values are not statistically significant.

sludge), the amount of seven PCBs decreased from 198.54 to 71.69 ng to sewage sludge during incubation under anaerobic conditions. That increase in the loss of PCBs in the mixed sludge stored under the same conditions as the municipal ones is likely to be caused by the introduction of an additional quantity of microorganisms capable of degrading PCBs with the industrial sludge. Table 6 shows the mass balance of PCB in both solid and liquid phases for the mixture of the municipal and industrial sludge.

3.4. Kinetics of PCBs degradation in sewage sludge during fermentation process

The mathematical description of the findings of the studies on changes in the concentrations of PCBs in sewage sludge and supernatants during fermentation uses a logarithmic function. The rate of degradation in the solid phase, both for the control sludge and municipal sludge and the coke sludge was similar and amounted to 3.682 and 3.246 t^{-1}, respectively. In the liquid phase, on the other hand, the rate in the control sample was 42,900 t^{-1} and in the mixture of municipal and coke sludge, 44,640 t^{-1}. For the individual congeners, the decomposition rate was varied: in the control sludge, it ranged from 0.119 to 1.480 t^{-1} and for the mixture with the coke sludge from 0.053 to 2.236 t^{-1}.

The control sludge showed a complete decomposition of PCB 180 congener, and for this compound the rate of biodegradation in the solid phase was the highest. Unlike in the mixed sewage sludge, where the highest rate of degradation in both the solid phase and the liquid phase were determined for PCB 28. The next step was to calculate the half-life period. Taking into account the total content of PCBs, the half-life was shorter for the control sewage sludge (16 d) compared with the mixed sewage sludge (20 d). However, for individual compounds, the half-time period was varied and amounted to 130 and 1,365 d in the solid phase of the control and mixed sewage sludge—Table 7. The highest value of $T_{1/2}$ was determined for code-52 congener whose concentration after 20 d of incubation was maintained at the same level as the initial one.

Table 8 shows the rate of biochemical degradation and the half-life period of PCBs in the supernatants. The biodegradation rates of tested PCBs were higher than in the solid phase. In the supernatants separated from the control sludge, the decomposition rate was highest for PCB 101 (9.041 t^{-1}), and for the liquids separated from the mixed sludge – for PCB 28 (9.027 t^{-1}). The half-life period was similar for both sewage sludge (from 0 to 21 d), but much shorter than in the solid phase. This indicates a much higher rate of

Table 6
Mass balance of PCBs in the solid and liquid phases before and after the fermentation process in the mixture of municipal sewage sludge and industrial sewage sludge

	Solid phase (ng)		Liquid phase (ng)		
PCB	Before fermentation	After fermentation	Before fermentation	After fermentation	Difference
PCB 28	58.52	12.70	11.86	2.63	+55.05
PCB 52	18.81	15.15	9.81	2.77	+10.70
PCB 101	17.86	8.11	10.06	3.14	+16.67
PCB 118	0	0	0	0	0
PCB 138	14.63	7.80	11.03	3.16	+14.69
PCB 153	17.10	12.85	10.76	3.37	+11.63
PCB 180	11.21	0	6.90	0	+18.11
Totality	138.13	56.61	60.41	15.08	+126.85

Table 7
The value of the constant rate of decomposition, the half-life period, and the formulas of functions of sewage sludge

	Sewage sludge							
	Control sample				Test sample			
Congener of PCB	Function	Rate of biodegradation (t^{-1})	Rate constant (d^{-1})	Half-time (*d*)	Function	Rate of biodegradation (t^{-1})	Rate constant (d^{-1})	Half-time (*d*)
28	−0.421ln (t) + 0.968	0.421	0.029	24	−2.236ln (t) + 2.789	2.236	0.066	11
52	−0.523ln (t) + 1.119	0.523	0.034	21	−0.076ln (t) + 1.108	0.076	0.001	1,365
101	−0.119ln (t) + 0.604	0.119	0.005	130	−0.401ln (t) + 0.896	0.401	0.029	24
138	−0.550ln (t) + 1.025	0.550	0.040	17	−0.186ln (t) + 0.848	0.186	0.021	34
153	−0.598ln (t) + 1.110	0.598	0.043	16	−0.053ln (t) + 0.902	0.053	0.003	201
180	–1.480ln (t) + 1.394	1.480	0.000	0	−0.436ln (t) + 0.747	0.436	0.000	0
Totality	−3.682ln (t) + 6.212	3.682	0.044	16	−3.246ln (t) + 7.299	3.246	0.034	20

Table 8
The value of the constant rate of decomposition, the half-life period, and the formulas of functions of supernatants

	Supernatants							
	Control sample				Test sample			
Congener	Function	Rate of biodegradation (t^{-1})	Rate constant (d^{-1})	Half-time (*d*)	Function	Rate of biodegradation (t^{-1})	Rate constant (d^{-1})	Half-time (*d*)
28	−8.797ln (t) + 11.848	8.797	0.058	12	−9.027ln (t) + 11.898	9.027	0.076	9
52	−5.727ln (t) + 10.517	5.727	0.033	21	−6.746ln (t) + 10.086	6.746	0.063	11
101	−9.041ln (t) + 9.926	9.041	0.000	0	−6.700ln (t) + 10.248	6.700	0.058	12
138	−5.965ln (t) + 10.313	5.965	0.039	18	−7.662ln (t) + 11.163	7.662	0.063	11
153	−5.560ln (t) + 8.360	5.560	0.056	12	−7.550ln (t) + 10.352	7.550	0.058	12
180	−7.799ln (t) + 7.344	7.799	0.000	0	−6.947ln (t) + 6.543	6.947	0.000	0
Totality	−42.900ln (t) + 6.2125	42.900	0.062	11	−44.640ln (t) + 60.296	44.640	0.070	10

biodegradation in liquids compared with changes in the solid phase. This is consistent with the literature referring to the efficiency of biodegradation of the compounds present in a dissolved form when compared to the compounds adsorbed on the particulates [31].

3.5. Control of fermentation process in wastewater treatment plants (the technical conditions) including the environmental management

The main issue to be considered regarding the control of the fermentation process in a sewage treatment plant is to secure the most efficient decomposition of

organic material in the sewage sludge. Thus, stabilized sewage sludge is obtained, which in municipal sewage treatment plants undergoes some further digestion processes such as dewatering and drying. According to the existing legislation, there is a need for further disposal or economic use of dried sewage sludge. One possible solution is to use natural fertilizing properties of these materials. But in this case, there is a risk of soil contamination by toxic micropollutants present in sewage sludge. These substances include, among others, PCBs whose carcinogenic impact and mutagenic effects on organisms has been repeatedly confirmed in toxicological studies. The present study demonstrated that during the fermentation process, a significant loss of these organic micropollutants is observed in both sewage sludge and supernatants. It is closely related to the presence of micro-organisms capable of degrading PCBs and some process conditions (anaerobic conditions, duration, temperature, and load of organic compounds). In the research studies, favorable conditions for mineralization of organic pollutants and simultaneous degradation of tested micropollutants (PCBs) have been provided. Other products of the fermentation are supernatants that are usually (in wastewater treatment plant) mixed with raw wastewater and referred back to flow of wastewater treatment. These supernatants bring a load of micropollutants to the wastewater, so earlier effective biodegradation of these compounds in the fermentation process is important. The results of conducted technological research indicate that industrial sewage sludge can be disposed together with municipal sewage by the methane fermentation process. At the same time, highly effective biodegradation of toxic pollutants, such as PCBs, is possible.

Since PCBs are chemically stable, have good insulating properties, and do not degrade appreciably over time or with exposure to high temperatures, they are very useful in electrical devices. PCBs constitute components of many different electrical equipments, such as transformers, large capacitors, voltage regulators, switches, circuit breakers, sectionalizers, reclosers, motor starters, electromagnets, cable, lamp ballasts, and small capacitors. However, in general, common applications of PCBs include: the electricity supply industry and industrial and mining facilities using electrical appliances or generating their own power, transformers for electric trains, lighting and power capacitors in large buildings, and high-intensity lighting systems used in industry or telecommunications. Moreover, in the past, PCBs were used in a range of applications, including: dielectric fluid in transformers, capacitors, and some other electrical appliances, hydraulic and cooling fluids, heat transfer systems, clothes dryers, electric motors, ceiling fans, dishwashers, pesticides, plasticizers in plastic, paint and carbonless copy paper, fluorescent lighting, and slide mounting for microscope slides [32,33].

With such widespread application of PCBs, mainly industrial, it is necessary that after the end of exploitation, the equipment containing PCBs ensures their safe disposal regarding natural environment protection. In this respect, environmental management concept is useful, as it supports business activities with environment-friendly techniques and technologies.

Considering business activities together with industrial performance, in which some negative impact on the natural environment is quite likely, the approach based on the functioning of the environmental management system is required. The environmental management system is the part of the overall management system used to develop and implement its environmental policy in order to cope with its environmental impact [34]. The system of environmental management as a part of general management system encompasses organizational structure, planning, duties, rules for actions, procedures, processes, and the means necessary to prepare, implement, realize, supervise, and maintain environmental policies.

Environmental management system includes such elements as: environmental aspects, goals and tasks, environmental programs, individual lists of legal acts, readiness to response in case of failures, operational control, waste management, protection of atmospheric air, water and sewage management, and noise prevention [35]. Environmental protection management should involve problems of eco-efficiency and eco-effectiveness [36]. This system is legally regulated by the ISO 14000 and is used to determine and achieve the objectives of environmental protection. The activities within the environmental management system include the organizational structure, planning activities, responsibilities, practices, procedures, processes and resources for developing, implementing, achieving, reviewing, and maintaining the environmental policy [37, 38].

According to the ISO 14000 recommendation, these elements of the environmental management system must correspond with other functions in an organization and be conducive to further development while integrating with its strategy [39]. Accepting the ISO 14000 standards gives many varied benefits from adaptation to the requirements, frequently in the form of improving the organization's image and its competitive position in the markets both domestic and foreign ones, lack of obligations concerning pollution to the environment, energy consumption and material saving, more detailed cost control, easier cooperation

with external environment in an organization, etc. [40].

The aim of environmental management, on the other hand, is a continuous reduction of a negative impact on the environment through ensuring company's activities within accepted environmental policies. The goal of this system is to ensure the methods, means, procedures, and tools necessary to reduce the failure rate and elimination of potential threats to the environment in emergency cases [41].

A fundamental principle of environmental management is continuous improvement, systematic minimization within the possible means, of a negative impact of companies' activities on the environment. Environmental management system encompasses prevention in terms of potential ecological threats in a company, developing the ecological awareness in the whole organization and forwarding the information concerning the impact on the environment [41].

Operating without damaging the environment requires a systematic approach and continuous improvement in environmental management system. The system is necessary to each company in order to determine the goals for environmental protection and then to achieve these goals as well as to operate according to the regulations of environmental protection [42].

In order to solve the natural environmental problems, early identification analysis and assessment is necessary. All the environmental aspects connected with the operation i.e. emission of gases to the atmosphere, water and sewage management, waste management, land contamination or raw material, and use of natural resources should be diagnosed [43].

The continuous improvement is the basic principle of environmental management, systematically minimizing the potential negative influence of companies on the environment. The system of environmental management includes the prevention in the field of potential environmentally friendly threats in the company, developing environmentally friendly consciousness of the whole organization and transferring the information regarding potential solutions of environmental threats. Managing the activity without prejudice requires the systematic approach and constant improvement of the system. Such system is necessary for every company to fulfill the purposes of the environmental protection, and then to reach these purposes as well as to operate in accordance with the policy of the environmental protection [44].

In terms of environmental management of industrial waste containing PCBs, there are many key activities that must be performed before the waste will be finally targeted for disposal. These actions include: the PCBs inventory, establishment of thresholds, requirements for treatment of PCBs, analyses and monitoring, education and training, storage, handling and transport, timelines, PCBs contaminated sites, and removing and replacing PCBs [38].

According to all above activities, the degradation of PCBs in industrial sewage sludge during the methane fermentation process is an activity which counteracts the negative impact of sludge on the natural environment and is in accordance with the environmental management concept.

4. Conclusions

On the basis of performed tests, the following conclusions can be drawn:

(1) During the process of fermentation, the degradation of PCBs in the solid phase and in the liquid phase occurred.
(2) A decrease in PCBs both in municipal sewage sludge and in the mixture of municipal with industrial sewage sludge was noted.
(3) The total concentration of PCBs congeners in the solid phase of sewage sludge after the process of fermentation decreased by 58 and 49% in control samples and in the mixture of sewage sludge (municipal with coke), respectively.
(4) In the liquid phase (supernatants), degradation of PCB was lower in control samples (71%) than in the mixture of municipal sewage sludge and industrial sewage sludge (75%). It proved that in coke sewage sludge, micro-organisms that adapted to PCBs degradation were present.
(5) The mass balance in the solid and liquid phases determined for hydrated sewage sludge shows high losses of PCBs (136–127 ng) between the phases (solid and liquid) which indicates that the PCBs degradation in fermentation process was possible.

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