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Desorption of PAHs from solid phase into liquid phase during co-fermentation of municipal and coke sewage sludge

Bartłomiej Macherzyński*, Maria Włodarczyk-Makuła, Anna Nowacka

Department of Chemistry, Water and Wastewater Technology, Częstochowa University of Technology, Częstochowa, Poland
Email: bmacherzynski@is.pcz.czest.pl

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ABSTRACT

The work presents the results of the study that determined the changes in the concentration of polycyclic aromatic hydrocarbons (PAHs) in the sewage sludge and supernatants during the co-fermentation of municipal and coke sewage sludge. The municipal sewage sludge served as a control sample, and the mixture of municipal and coke sewage sludge was used as a test sample. The sewage sludge was incubated for 20 d at 37°C in the dark. The quantification of the PAHs was carried out simultaneously in both the solid and supernatant phases, the latter separated from the sludge during centrifugation. After 20 d, the solid phase was observed to have its PAHs content reduced by 60% in the control sample and 64% in the analyzed one, respectively. The decline in the solid phase PAHs content was accompanied by a significant quantitative increase of the PAHs in the liquid phase, which proves the desorption of solid particles. The control supernatants showed the total concentration of 16 PAHs of 1.1 μg/L prior to the treatment, and reaching 20.5 μg/L after 20 d of incubation, while for the supernatants separated from the mixture of municipal and coke sewage sludge, a 13-fold higher total concentration of the analyzed PAHs was determined

Keywords: PAHs; GC–MS; Desorption; Co-fermentation; Sewage sludge; Supernatants

1. Introduction

The sewage sludge is a dispersion system with diversified composition, which causes problems as far as its treatment is concerned. Biological or chemical stabilization, drying and incineration are commonly used processes of sludge neutralization. During the sewage sludge treatment, decomposition of organic compounds takes place as well as the reduction of sludge volume, preparation to subsequent treatment, and utilization or waste management [1–3].

Biological stabilization is conducted in oxygen and anaerobic conditions. The following stages are singled out in an anaerobic process: hydrolysis, acidogenesis, acetogenesis, and methanegenesis. In comparison with oxygen stabilization, the advantage of the anaerobic process is that there is reduced formation of biogas,

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*Corresponding author.

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Faculty of Environmental Engineering and Biotechnology, Czestochowa University of Technology

which is utilized as an energy carrier. Mineralized biomass with a high content of biogenic compounds is obtained in the process [4–6]. Pursuant to the Polish legal regulations in force, restrictions concerning an application of sewage sludge for nature purposes involve the occurrence of heavy metals such as: cadmium, copper, nickel, lead, zinc, mercury, chromium, and some pathogenic organisms. The concentrations of other toxic compounds found in the sewage sludge are not normalized. These pollutants include: polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, the sum of organic halogens adsorbing one another, linear alkylbenzene sulfonates, bis (2-ethylhexyl) phthalate, and substances of nonylophenol and nonylophenolthoxylate with 1 or 2 groups of ethoxy. 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 case of PAHs, the total content of 11 compounds such as: acenaphthene, phenanthrene, fluorine, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, and indeno (1,2,3,c,d)pyrene should not exceed 6 mg/kg [7].

The compounds with hydrophobic properties, for example, PAHs tend to be slightly soluble; however, they are characterized by greater solubility in fats, oils, and organic solvents. Solubility in water can increase in the presence of organic compounds such as surface active substances or purines. PAHs are characterized by high values of distribution coefficient logarithm—octanol/water, and that is why they usually occur in an adsorbed form [8,9]. In Table 1, the selected physical and chemical properties of 16 PAHs according to the list of EPA are shown.

The presence of PAHs in the sewage sludge isolated from municipal wastewater was confirmed in the literature sources. On the basis of some tests performed by different authors, the sum of PAHs concentrations in the sewage sludge is believed to range: from 0.1 to 87.5 mg/kg, and in supernatants: from 402 to 863 μg/L [14–19]. The tests focused on sewage sludge from municipal sewage treatment plants, into which the mixture of household and industrial sewage of diversified composition is introduced. However, only a few tests regarding industrial sewage sludge were made. The occurrence of these compounds in the coke deposits and in supernatants was also confirmed in various preceding tests performed. The marked concentrations were diversified and ranged from several micrograms to several hundreds of milligrams with respect to the kilogram of dry matter. The total concentration of 16 PAHs in the solid phase was 740 mg/kg_{dw} and in the liquid one it was 17 μg/L [20]. In tests performed by Zhang and others, the PAHs concentration in the isolated sewage sludge during the treatment of coking wastewater reached 4,490 mg/kg [21].

Table 1
Properties of selected PAHs [8–13]

PAHs	Molecular weight	Melting point, ℃	Boiling point, ℃	Water solubility, μg/L	Aqueous solubility, kg/m^3	log k_{ow}
Naphthalene	128.2	80.2–81.0	217.9–218	31,700	1.16	3.36–3.37
Acenaphthalene	152.21	96	278	3,900	n.d.	3.92
Acenaphthene	154.21	96.2	265	3,900	n.d.	4.00
Fluorene	166.21	116–117	295	1980	n.d.	4.18
Phenanthrene	178.22	100–101	340	1,000–1,290	1.29	4.46–4.57
Anthracene	178.22	217	340	45–73	0.07	4,54
Fluoranthene	202.60	111	250–375	262	0.26	5.22–5.33
Pyrene	202.30	149	360	135–145	0.14	5.18–5.32
Benzo(a)anthracene	228.28	158	400–435	14	0.014	5.61–5.91
Chrysene	228.28	255	448–488	3	0.002	5.61–5.90
Benzo(b)fluoranthene	252	107–108	481	1.2	0.0012	5.80
Benzo(k)fluoranthene	252	217	481	0.55	0.00055	6.00
Benzo(a)pyrene	252	179	495	3.8	0.0038	6.04
Dibenzo(a,h)anthracene	278.36	262	524	0.50	0.0005	5.97–6.75
Indeno(1,2,3,c,d)pyrene	276.34	163	536	62	0.0003	6.58–7.23
Benzo(g,h,i)perylene	276.00	222	536–545	0.26	0.062	6.5–7.66

Note: n.d.—not detected.

During the process of anaerobic fermentation such multi-transformations of PAHs as bioaccumulation, volatilization, reactions with other constituents, adsorption, and biodegradation occur. Since these processes occur simultaneously, the tests results described in various literary sources differ. Some authors argue that the main loss of PAHs in this process is caused by a strong sorption [22] or biodegradation [23]. Others, however, determine higher concentrations in digested sewage sludge in comparison to the concentrations in raw sewage sludge [16]. This is due to different characteristics of sewage sludge tested, varied content of PAHs, and difficulties in identifying precisely the process that contributes to changes in the concentration of these compounds. The efficiency of biological degradation process depends on the presence of micro-organisms capable of decomposing PAHs and the occurrence of toxic chemical compounds affecting these micro-organisms (pesticides, heavy metals, and surface-active substances) [24].

Due to the fact that, on the one hand, coke deposits are charged with organic pollutants (including PAHs), 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 PAHs changes were analyzed in the solid and liquid phase of municipal sludge mixture with the industrial one. On the basis of PAHs concentrations in the solid phase with reference to dry matter and concentrations in supernatants, the PAHs mass balance in the sewage sludge was determined.

2. Experimental procedure

2.1. Materials

The tests were performed utilizing sewage sludge from the municipal sewage treatment plant and sewage sludge from coking wastewater treatment plant. In the municipal sewage treatment plant, the treatment of waste is carried out in the process of dephosphatation, denitrification, and nitrification. The stabilization of sewage sludge is performed in isolated fermentation chambers in anaerobic conditions. The mixture of thickened sewage sludge is fed into fermentation chambers. This mixture consists of preliminary sewage sludge and the one mixed excessively in volumetric ratio of 4:1. The preliminary and excessive sewage sludge was sampled before the fermentation chamber, and the digested sewage sludge was sampled from the pipeline discharging the sewage sludge from the closed isolated chamber of methane fermentation. In the coking wastewater treatment plant, the sewage treatment is performed by the processes of denitrification and nitrification. The sewage flows through the gravel filter, tar separator, and desorption column before it is fed to the biological part of treatment plant and is directed to the averaging tank. The coke deposit was sampled as temporary one and prepared for technological tests:

- Municipal sludge, that is, raw and excessive with inoculum (digested sludge)—the control sewage sludge (K).
- Mixture of municipal sludge with coke deposit the volume ratio of which was 6:1—the sewage sludge tested (B).

2.2. Methods

Co-fermentation was performed in glass bioreactors. Incubation of sewage sludge was carried out for 20 d at a temperature of 37°C with no access to light. In order to provide the right contact between biomass and the substrate, the reactors were mixed once a day manually measuring the pressure of biogas simultaneously. In order to specify the course of 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, content of organic substances, and hydration. The following was determined in liquids obtained from sewage sludge centrifugation: pH, basicity (Z_M), chemical oxygen demand (COD), and volatile fatty acids (VFAs). Both in the solid phase (spinned sewage sludge) and in the liquid phase (supernatants) PAHs were marked before the process and after 10 and 20 d of fermentation [20].

2.3. Identification of PAHs

In order to isolate the sewage sludge from supernatants, the sewage sludge was rotated at a speed of 9,000 rev/min for 10 min. In supernatants, the release of organic compounds was performed with the application of cyclohexane and dichloromethane (5:1 v/v; 30:6 cm^3). In order to determine PAHs in the solid phase (sludge), 10 g of spinned sewage sludge was sampled, which was then poured with the mixture of dichloromethane and cyclohexane (1:5 v/v; 4:20 cm^3). Then, the samples were subjected to the impact of ultrasounds for 25 min. The extract obtained after the process of sonification was poured into test tubes for centrifugation and placed in the centrifuge. The extract was spinned for 10 min at a speed of 9,000 rev/min. The extracts obtained both from the liquid and solid phases were cleaned on the columns with silica gel in vacuum conditions. Before the extract was introduced, the filling of column with silica gel was conditioned with the mixture of dichloromethane and cyclohexane (1:5 v/v; $3 \times 3\,\text{cm}^3$). The purified extracts were concentrated to the volume of $2\,\text{cm}^3$ in the nitrogen stream. The samples so prepared were analyzed taking into consideration their quality and quantity point of view using the GC chromatograph with the detector of mass. The chromatographic analysis was performed with the use of PAHs standard mixture—16 PAHs were mixed with benzene and dichloromethane (made by AccuStandard Inc. USA).

2.4. Mass balance of PAHs

The balance of PAHs 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 volume of sewage sludge. The amount of PAHs 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:

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

$$L = C_1 \cdot \text{V}$$

where C_s—PAHs concentration in the solid phase (μg/kg$_{\text{dw}}$), C_1—PAHs concentration in the supernatants (μg/L), s—content of dry matter in the hydrated sludge (g/L), and V—volume of supernatants in the hydrated sludge (L/L).

2.5. Statistical test

In order to verify the importance of PAHs, changes in the solid phase and in supernatants, t-Student test was performed. The level of confidence was accepted at 0.95 level. The number specifying the degree of freedom was 3, for this parameter the theoretical value of decomposition of the t-Student t_d was 2.776.

$$t_\text{d} = \frac{|\bar{d}| \cdot \sqrt{n}}{\sqrt{\frac{n\Sigma d^2 - (\Sigma d)^2}{n(n-1)}}}$$

where n—number of results, d—difference between the results before and after the experiment $d = x_i - y_i$, x_i, y_i—value of results before and after the experiment, respectively, $\bar{d}$—average from d.

3. Results and discussion

3.1. Physico-chemical studies

COD value for the control sample in the liquid phase before the process was 2,054 mg/L and it decreased while the process was underway to 662 mg/L. The ratio of VFAs to basicity did not exceed the value of 0.3, which shows the regular course of methanogenesis. During the process, the decomposition of organic substances in percent was of 28% in the control sewage sludge and 24% in the sewage sludge tested. The pH value in supernatants changed from 7.4 to 8.2.

3.2. PAHs quantitative changes in the solid phase

In Figs. 1 and 2, the results of quality and quantity including quality determination of PAHs were presented with the breakdown into the number of rings in the solid phase during co-fermentation. The total initial content 16 PAHs in the control sewage sludge (K) was 1,300 μg/kg$_{\text{dw}}$. During the incubation of sewage sludge, the concentration of compounds tested decreased: after 10 d it was 776 μg/kg$_{\text{dw}}$, and after 20 d it was 519 μg/kg$_{\text{dw}}$. The predominant compounds in the solid phase were 3- and 4-ring hydrocarbons.

During the co-fermentation of municipal sludge with the coke deposits, the concentration of 16 PAHs before the process was 5,180 μg/kg$_{\text{dw}}$ and it decreased after 10 d to 3,476 μg/kg$_{\text{dw}}$, and after 20 d it was 1,868 μg/kg$_{\text{dw}}$. As in the case of control sewage sludge, 3- and 4-ring hydrocarbons had the greatest contribution to the total concentration of 16 PAHs. In both cases (control sewage sludge K and sewage sludge tested B), the loss of concentration in the solid phase was recorded. In control sewage sludge, the removal of PAHs was 62, 28, 62, 73, and 92%, respectively, for 2-, 3-, 4-, 5-, and 6-ring compounds. The efficiency in removing PAHs in the solid phase during co-fermentation with coke deposits was 63, 70, 57, and 59%, respectively, for 3-, 4-, 5-, and 6-ring hydrocarbons.

The results of concentration changes of individual PAHs in the control sewage sludge were presented in Figs. 3 and 4. Naphthalene (18%) had the greatest contribution to control sewage sludge. In the solid phase after 20 d, the concentration of PAHs decreased except phenanthrene, the concentration of which was higher by 38% than the initial one. The contribution of carcinogenic compounds in the total content of 16 PAHs also decreased (from 45 to 25%).

The concentrations of individual PAHs in the sewage sludge tested is presented in Figs. 5 and 6.

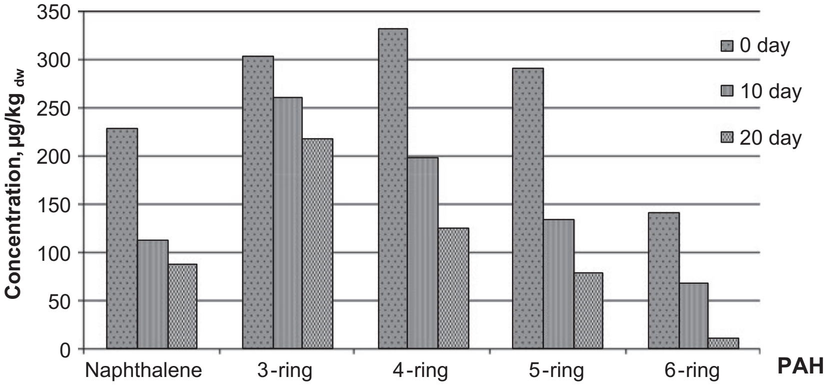

Fig. 1. Changes of PAHs concentration in control sewage sludge—K.

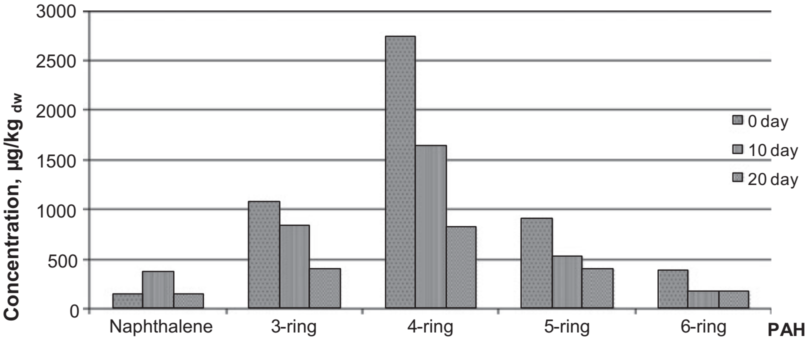

Fig. 2. Changes of PAHs concentration in examined sewage sludge—B.

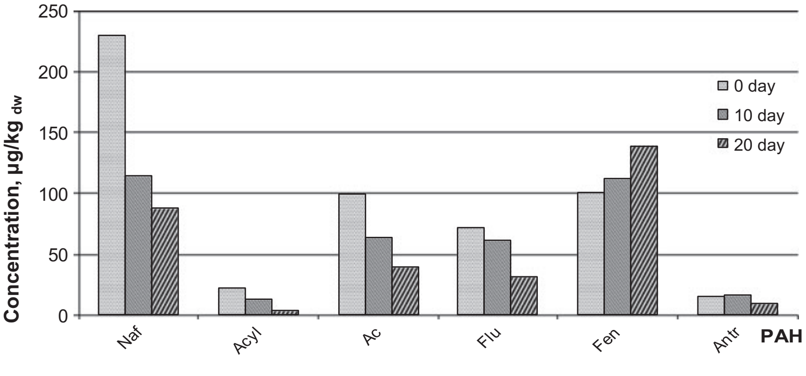

Fig. 3. Changes of 2- and 3-rings of PAHs concentrations in control sewage sludge—K.

Before co-fermentation, fluoranthene (18%) appeared in the greatest amount in the B sewage sludge tested. After 20 d of the process, the decrease in the concentration of analyzed PAHs occurred. The content of carcinogenic compounds in percent remained at the same level before the process started. Other authors obtained similar results, where the content of carcinogenic compounds before the process was 22–37% of the total quantity of PAHs, and after the incubation it ranged from 35 to 39% [25,26].

The results obtained lead to the conclusion that during the process of fermentation, concentration of PAHs changed in the solid phase. Both in the control sewage sludge and in the PAHs tested, decrease in the total concentration of 16 analyzed PAHs occurred. The process of decomposition caused by micro-organisms

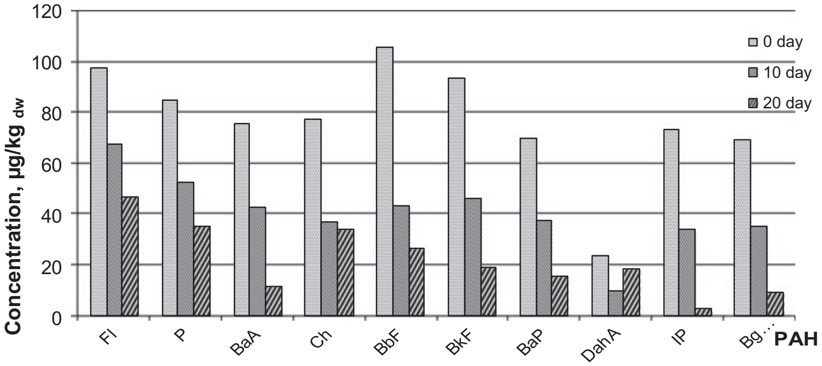

Fig. 4. Changes of 4-, 5- and 6-rings of PAHs concentrations in control sewage sludge—K.

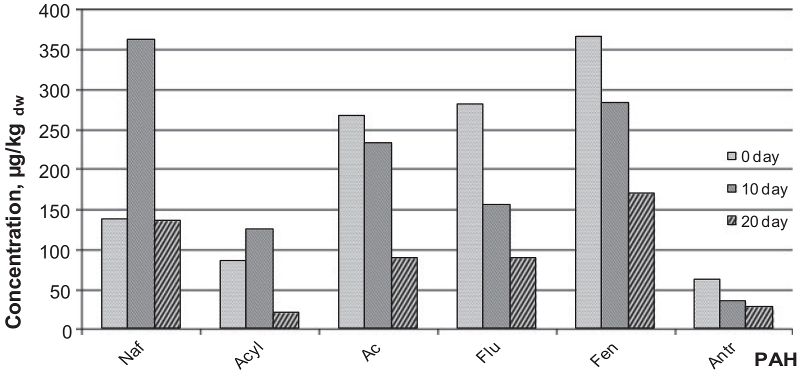

Fig. 5. Changes 2- and 3-rings of PAHs concentrations in studied sewage sludge—B.

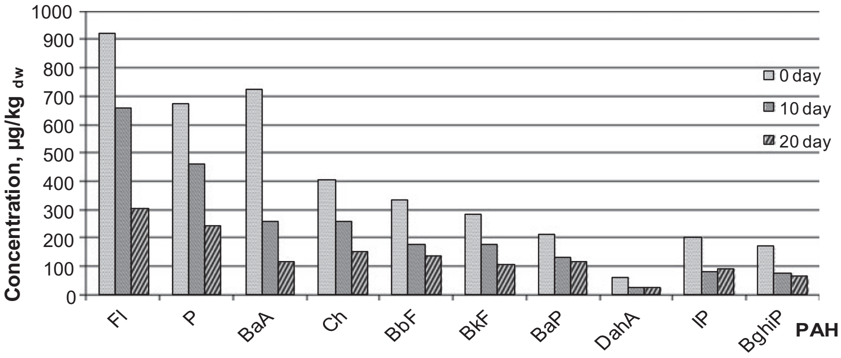

Fig. 6. Changes of 4-, 5-, and 6-rings of PAHs concentrations in studied sewage sludge—B.

and reactions with other constituents lead to the loss of PAHs, and they cause the formation of non-analyzed derivatives in these tests. Moreover, the volatilization of these compounds into biogas during the incubation at temperature increases should not be ruled out either.

As mentioned above, different contents of PAHs in the sewage sludge after the fermentation process are given in the tests described in the literature. In anaerobic conditions, the PAHs' biodegradation and the accumulation of these compounds is possible. For example, in the tests performed by Bernal-Martinez, the concentration of 13 PAHs in the sewage sludge during fermentation increased by 1.8 mg/kg, and in other tests performed by the same author, the decrease in the content of these compounds by 1.1 mg/kg was obtained.

The discrepancies are due to changeable chemical composition of sewage sludge, different conditions involved in the process, and different activity of microorganisms capable of PAHs biodegradation [16,17].

3.3. PAHs quantitative changes in the liquid phase

Changes in hydrocarbon concentrations with the breakdown into the number of rings in the liquid phase are presented in Figs. 7 and 8. The total concentration of 16 PAHs in the liquid phase isolated from K sewage sludge is 1.1 μg/L, and in the liquid phase isolated from B sewage sludge the concentration is 5.7 μg/L. In both cases, the concentration of 16 PAHs increased during fermentation and the final concentrations reached 20.5 and 74.6 μg/L, respectively. In the liquid phase (as in the solid one), the predominant compounds were 4- and 3-ring hydrocarbons. In earlier tests both before and after the process, naphthalene and 3-ring hydrocarbons appeared in the highest concentrations [27].

In K supernatants, the predominant compound before the process of co-fermentation was phenanthrene. After 20 d, the highest concentrations of fluoranthene and pyrene were determined. The concentrations of these compounds increased almost 100 times. Besides, the content of carcinogenic compounds increased from 0.4 μg/L before fermentation to 4.6 μg/L—after the completion of process. The results of concentration changes of individual PAHs in the liquid phase are presented in Figs. 9–12.

In the liquid phase, 4- and 5-ring compounds isolated from the control sewage sludge contributed, most significantly to the increase in PAHs content, and were tested. After the process of fermentation, the concentration of such compounds as chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(g,h,i)perylene was higher than the solubility in water at a temperature of 25˚C. The concentrations higher than the solubility limit in the liquid phase were confirmed in other literature sources as well as observed in earlier tests [20]. It applied to municipal sludge and supernatants, where other organic compounds such as: surface active substances or pesticides appear exerting, which exert an impact on the increase in the solubility of PAHs in water.

3.4. PAHs balance in sewage sludge

On the basis of PAHs concentrations determined, and the content of dry matter in sewage sludge, the amount of these compounds in the solid and liquid phases in the volumetric unit was calculated. In Table 2, the results of PAHs calculation balance in both phases (liquid and solid) for the control sewage sludge are listed. The total amount of PAHs in the control sewage sludge was 28.35 μg and after the fermentation process, it decreased to 28.00 μg. It turns out from the mass balance that in 16 PAHs in individual phases, that is in the solid phase, before fermentation the content of PAHs was at level 27.31 μg and after the fermentation process it was 8.31 μg. Then, the loss of hydrocarbons in the solid phase was 19.00 μg. In the liquid phase, (supernatants) the increased amount of PAHs was recorded after fermentation by 18.65 μg in comparison to the initial one. This means that during incubation in anaerobic conditions PAHs desorption occurred from solid particles into the supernatants. The discrepancy in the amount of desorbed PAHs from the solid phase with the increment of the content of these compounds in the liquid is less and it is 0.35 μg (for 16 compounds). It proves that during the incubation, physical, chemical, and biological transformations of these compounds were possible and caused the loss of PAHs. It indicates clearly which of the processes, biodegradation, volatilization, or reactions with other constituents, played the most

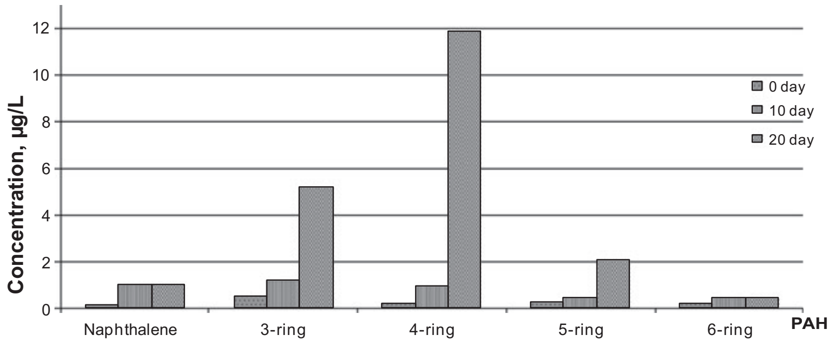

Fig. 7. Changes of PAHs concentration in supernatant—K.

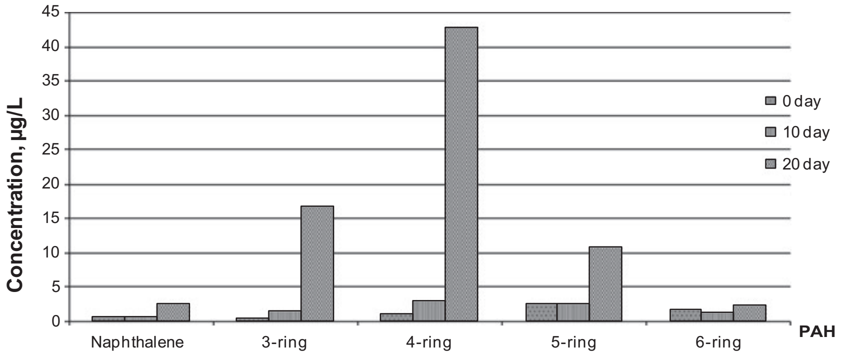

Fig. 8. Changes of PAHs concentration in supernatant—B.

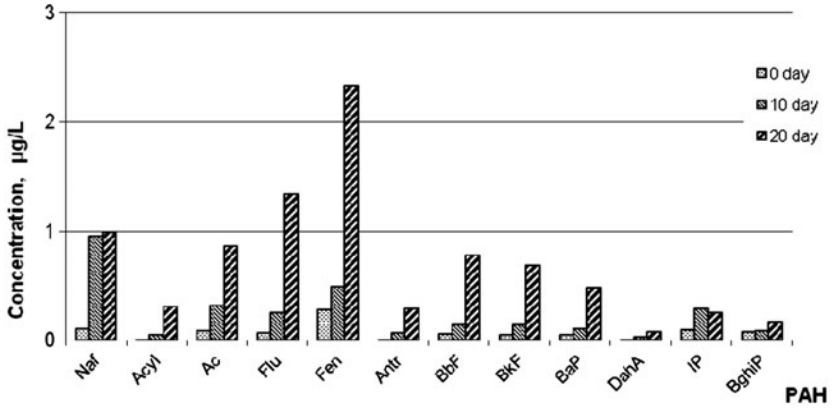

Fig. 9. Changes of individual PAHs concentrations in supernatant—K.

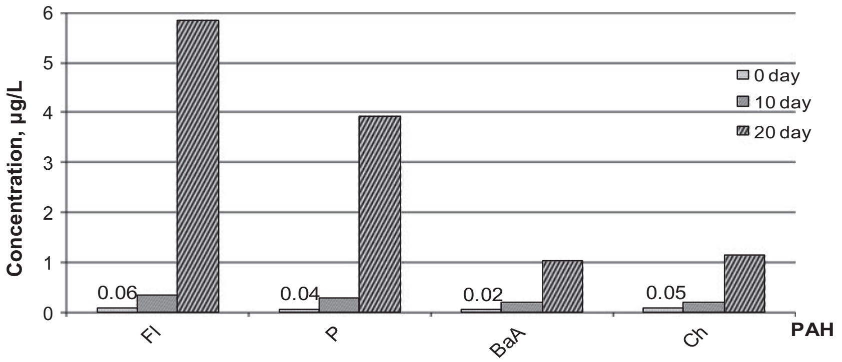

Fig. 10. Changes of fluoranthene, pyrene, benzo(a)anthracene and chrysene concentrations in supernatant—K.

important part. Analyzing the balance of individual compounds one can conclude that in the case of fluorine, fluoranthene, pyrene, phenanthrene, and anthracene, the determined amount in the liquids was greater than the loss in the solid phase. The possibility of PAHs desorption in anaerobic conditions from the solid phase to the liquid one was confirmed. The release of hydrocarbons from the cells of micro-organisms, in which they were retained earlier, is possible. It was demonstrated that PAHs can be adsorbed on the surface (biosorption), can penetrate through cell membranes, and accumulate inside the cells. When cells disintegrate, PAHs is released into the environment [28,29].

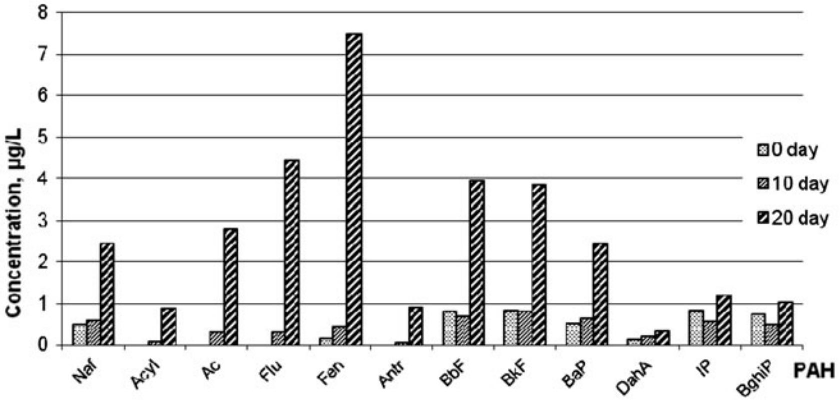

Fig. 11. Changes of individual PAHs concentrations in supernatant—B.

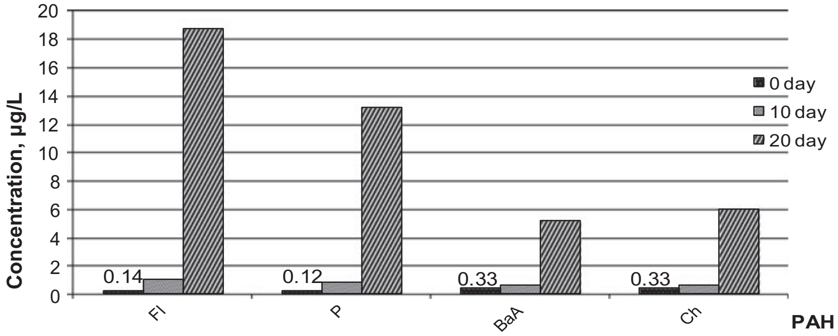

Fig. 12. Changes of fluoranthene, pyrene, benzo(a)anthracene, and chrysene concentrations in supernatant—B.

Table 2
Mass balance of PAHs in the solid and liquid phase before and after the process for control sewage sludge

	Solid phase, g		Liquid phase, g		
PAHs	Before fermentation	After fermentation	Before fermentation	After fermentation	Difference
Naf	4.83	1.40	0.10	0.95	2.58
Acyl	0.44	0.05	0.03	0.30	0.12
Ac	2.07	0.62	0.08	0.83	0.69
Flu	1.50	0.48	0.06	1.29	–0.21
Fen	2.09	2.21	0.27	2.24	–2.09
Antr	0.29	0.13	0.02	0.28	–0.10
Fl	2.04	0.74	0.05	5.63	–4.28
P	1.77	0.55	0.03	3.76	–2.51
BaA	1.58	0.17	0.02	0.96	0.46
Ch	1.62	0.54	0.05	1.08	0.05
BbF	2.22	0.42	0.06	0.75	1.10
BkF	1.96	0.29	0.05	0.66	1.05
BaP	1.45	0.24	0.05	0.46	0.80
DahA	0.49	0.29	0.02	0.08	0.15
IP	1.53	0.04	0.09	0.24	1.33
BghiP	1.44	0.14	0.07	0.17	1.21
Totality	27.31	8.31	1.05	19.70	0.35

In Table 3, the results of mass balance of PAHs in the solid and liquid phase of the mixture of municipal sludge and coke deposits (sewage sludge tested) are presented. In the unit volume of sewage sludge, it was found that during fermentation the amount of PAHs decreased from 103.88 to 100.69 μg. Before the process of co-fermentation in the solid phase, the content of 16 PAHs was 98.42 μg, and after the process of 20 d of incubation, the content was 28.59 μg. The loss of PAHs was 69.83 μg. In the liquid phase, the increase in the amount of 16 PAHs was 66.64 μg. Before the process, the total content of 16 PAHs was 5.46 μg, and after the process of co-fermentation—72.10 μg. As in the case of control sewage sludge, some slight losses of PAHs (3.19 μg) were recorded. That is why, it can be concluded that during the process of co-fermentation, the PAHs desorption from the solid to liquid phase took place. The results from the detailed balance indicate that loss in the solid phase for individual hydrocarbons corresponds to the increased amount of supernatants in most cases.

The analysis of changes in the amount of PAHs in both phases shows that in the process of fermentation, the release of PAHs from sewage sludge and their accumulation in supernatants is possible, taking into consideration the fact that supernatants from sewage sludge fermentation are usually returned to the string wastewater treatment in the treatment plant, charging them with a considerable amount of PAHs and possibly influencing the increase in the concentration of pollutants in sewage. In earlier studies of authors, after 21-d fermentation the results were similar and in supernatants the increase in total concentration of PAHs by 60% took place [26]. In the studies conducted by Bernal-Martinez, the loss of PAHs in supernatants (48%) was obtained, and the increase in compounds was determined as 12.5% [16]. In the studies described in the literature, the problem of PAHs presence in supernatants is usually ignored, and the concentrations of PAHs in sewage sludge is expressed in reference to dry matter. However, the results of tests confirm the possibility of PAHs desorption from sewage sludge to supernatants in anaerobic conditions. In studies conducted both on municipal sludge (control sewage sludge) and with the addition of coke deposits, the loss of PAHs in sewage sludge was noticed together with a simultaneous increase in the content of supernatants.

3.5. Statistical calculations

In Table 4, critical values of *t*-Student t_d test were presented specifying the importance of differences in PAHs concentrations before and after the process in sewage sludge and supernatants. The results of calculations show that the recorded changes in concentration for the majority of hydrocarbons in the solid and liquid phase were statistically significant.

Table 3
PAHs mass balance in the solid and liquid phase (before and after process) for examined municipal and coke sewage sludge

	Solid phase, g		Liquid phase, g		
PAHs	Before co-fermentation	After co-fermentation	Before co-fermentation	After co-fermentation	Difference
Naf	2.57	2.07	0.49	2.37	–1.38
Acyl	1.60	0.28	0.00	0.87	0.45
Ac	5.06	1.33	0.06	2.71	1.07
Flu	5.31	1.35	0.06	4.30	–0.28
Fen	6.94	2.58	0.17	7.24	–2.72
Antr	1.15	0.41	0.00	0.89	–0.15
Fl	17.55	4.65	0.13	18.03	–5.00
P	12.82	3.69	0.12	12.61	–3.37
BaA	13.80	1.75	0.31	4.92	7.44
Ch	7.71	2.29	0.31	5.73	0.00
BbF	6.31	2.11	0.80	3.81	1.19
BkF	5.40	1.60	0.81	3.73	0.87
BaP	4.04	1.79	0.51	2.38	0.39
DahA	1.12	0.33	0.15	0.33	0.61
IP	3.82	1.40	0.82	1.17	2.07
BghiP	3.24	0.95	0.71	1.00	2.00
Totality	98.42	28.59	5.46	72.10	3.19

Table 4
Values of *t*-Student distribution ($t_{d} = 2.776$)

	Solid phase		Liquid phase	
PAHs	K	B	K	B
Naphthalene	15.884	**0.043**	75.474	56.155
Acenaphthalene	9.533	9.600	23.775	11.287
Acenaphthene	31.522	39.171	8.994	9.387
Fluorene	5.023	84.785	21.704	37.928
Phenanthrene	14.425	115.244	68.101	38.461
Anthracene	14.071	**2.454**	9.297	10.163
Fluoranthene	6.640	9.128	22.900	103.080
Pyrene	24.655	12.557	19.134	113.584
Benzo(a)anthracene	4.776	3.092	31.786	10.791
Chrysene	13.195	5.725	16.458	28.598
Benzo(b)fluoranthene	13.913	6.043	59.418	29.156
Benzo(k)fluoranthene	30.907	3.105	51.496	50.871
Benzo(a)pyrene	17.354	4.033	9.811	11.371
Dibenzo(a,h)anthracene	9.167	12.140	106.587	24.329
Indeno(1,2,3,c,d)pyrene	9.748	3.929	4.406	3.462
Benzo(g,h,i)perylene	13.515	5.727	18.327	4.666
Totality 16 PAHs	4.991	4.351	3.135	3.442

The differences between the final and initial total concentration of 16 PAHs and of most compounds were statistically significant to both in the solid and liquid phase. However, the differences in the concentration of naphthalene and anthracene in the solid phase of mixed sewage sludge for which the values calculated, t_{d}, did not exceed the characteristic values according to *t*-Student test (2.776 for confidence level 0.95 and number of freedom 3), which were quite irrelevant.

4. Conclusions

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

- During the process of fermentation, the desorption of PAHs from the solid to liquid phase occurred, due to the increase in concentration of the supernatants accompanying the decrease in concentration of these compounds in reference to dry matter of sewage sludge.
- The mass balance in the solid and liquid phase determined for hydrated sewage sludge shows minor losses of PAHs (0.35–3.19 μg) between phases (solid and liquid), which indicates that the processes of PAHs transformations leading to the loss of concentration occur simultaneously.
- The total concentration of 16 PAHs in the solid phase of sewage sludge after the process of fermentation decreased by 60 and 64%, respectively, in control and mixed sewage sludge (municipal with coke).
- The concentration of 16 PAHs in liquids after 20 d of the process of anaerobic stabilization increased 18 and 13 times, respectively, for the control and tested sewage sludge.

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