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EFFECT OF PRELIMINARY THERMAL CONDITIONING OF SEWAGE SLUDGE ON THE CONCENTRATION OF PAHs

The paper reports how preliminary thermal conditioning of sewage sludge at 70 °C for 6, 12 and 24 hours affected the changes of physical and chemical properties of the sludge and concentration of 16 EPA-PAHs. Thermal conditioning of sewage sludge improved hydrolysis, brought about an increase in acidity and content of volatile fatty acids as well as a decrease in pH; in the sludge conditioned for 24 hours, a decrease in organic matter content was also observed. Thermal conditioning for 6 hours brought about a decrease in the concentration of total PAHs and carcinogenic compounds, whereas conditioning for 12 and 24 hours resulted in an increase in total PAH concentrations.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are environmentally hazardous compounds because of their mutagenic and carcinogenic properties. Sixteen of these compounds are therefore included in EPA list of environmental priority pollutants. PAHs consist of two or more fused benzene rings and originate due to anthropogenic inputs (mainly coke plants' outputs, incomplete combustion of fossil fuels and their transportation or storage). Natural sources of PAHs include fires, sediment diagenesis, biological conversion or synthesis, etc. [9]. Because of non-polar properties and slight solubility in water PAHs in the environment are mainly attached to particles [16]. During wastewater treatment PAHs are transferred from the aqueous phase to the sludge [8]. Total concentrations of 16 EPA-PAH up to 300 $mg \cdot kg_{d.m}^{-1}$ have been found in various types of sewage sludge, however usually these concentrations are much lower and do not exceed a few to several mg PAHs/$kg_{d.m}$ [7], [8]. PAHs content in sludge is strongly affected by the type of sewerage system and quantities of industrial wastewater.

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It has been shown that PAHs may undergo biological and chemical oxidation, volatilisation and photolysis, although they are quite stable in the environment. PAHs may also be accumulated in microbial cells. The environmental persistence as well as hydrophobic and carcinogenic properties increase along with an increase in the number of rings in PAH molecule [9], [16]. Some selected physicochemical and toxicological properties of 16 EPA-PAHs are listed in table 1.

Table 1

Selected physicochemical and toxicological properties of EPA-PAHs [12], [15]

No.	Compound	Number of rings	Water solubility [$\mu g \cdot dm^{-3}$]	Henry's law constant [$Pa \cdot m^3/mol$]	Mutagenicity/ carcinogenicity
1	naphthalene	2	31700	43.01	–/–
2	acenaphtylene	3	3470	n.d.	–/–
3	acenaphthene	3	3930	12,17	–/–
4	fluorene	3	1980	7.87	–/–
5	anthracene	3	73	3.96	–/–
6	phenanthrene	3	1290	3.24	–/–
7	pyrene	4	135	0.92	–/–
8	fluoranthene	4	260	1.04	+/–
9	benzo(a)anthracene	4	14	0.58	++/+
10	chrysene	4	2	$1.22 \cdot 10^{-2}$	++/+
11	benzo(k)fluoranthene	5	0.55	n.d.	++/+
12	benzo(b)fluoranthene	5	1.2	n.d.	++/+++
13	benzo(a)pyrene	5	3.8	$4.6 \cdot 10^{-2}$	++++/++++
14	dibenzo(a,h)anthracene	5	0.5	$1.7 \cdot 10^{-4}$	++/++
15	benzo(g,h,i)perylene	6	0.26	n.d.	+++/++++
16	indeno(1,2,3-cd)pyrene	6	62	n.d.	+/+

n.d. – no data available.
– – no mutagenic or carcinogenic activity.
+ – slight mutagenic or carcinogenic activity.
++ – average mutagenic or carcinogenic activity.
+++ – strong mutagenic or carcinogenic activity.
++++ – very strong mutagenic or carcinogenic activity.

Actually a number of biological and chemical pretreatment and treatment technologies in sewage sludge management are used, including anaerobic digestion, aerobic stabilisation, chemical and thermal conditioning or dewatering processes. The pretreatment technologies are usually applied to speed up hydrolysis of organic substrates before their further biological processing. They may be used for disinfection of sewage sludge as well as to improve draining [4]. Further biological processing results in transformation of sewage sludge to easily dewatered substance and in generation of methane and carbon dioxide in the case of anaerobic conditions. Consequently, the volume of solids is reduced [11].

Preliminary thermal conditioning of sewage sludge is usually applied as a pretreatment process. In order to inactivate pathogenic microorganisms, the sludge is heated at 70–150 °C for more than 30 min. To promote hydrolysis of organic matter the temperature is kept at 135–220 °C for 0.5–60 min. [4]–[6], [10], [19]. The studies mentioned above were undertaken to determine the optimal thermal pretreatment and its effect on the sludge suitability for filtration, improvement of settling properties and decomposition of complex polymers into smaller ones whose biodegradation is easier. However, little is still known about the fate of PAHs during thermal conditioning of sewage sludge. NICHOLLS at al. [14] suggest that thermal pretreatment of sewage sludge has no significant effect on the concentration of most 4-, 5- and 6-ring PAHs in sewage sludge at 180–200 °C (heating for 20–60 min.). The reason was that thermal conditioning might bring about desorption of lower-molecular weight PAHs from the sludge.

This paper reports the effects of preliminary thermal conditioning of sewage sludge at 70 °C for 6, 12 and 24 hours on the changes in physicochemical properties and composition of selected PAHs.

2. EXPERIMENTAL

2.1. THE SLUDGE AND ITS PROCESSING

The raw sludge samples used in the study were collected from a primary settler of the municipal sewage treatment plant in Częstochowa, Poland. Before further processing the samples were homogenised by mixing and passing through a thick sieve, Ø 2 mm. The homogenised sludge was packed into 800 cm^3 glass vessels and conditioned at 70 °C for 6, 12 and 24 hours. During processing the sludge was continuously mixed.

The raw and conditioned sludges were analysed for a number of physical and chemical properties, including pH, volatile fatty acids, acidity, alkalinity and dry matter.

2.2. PAHs ANALYSIS

Cyclohexane (60 cm^3) was used to extract the sludge (40 g) in a glass vessel (250 cm^3) placed in the ultrasonic bath (model UD-20, TECHPAN) at room temperature for 7 min. After settling supernatant was carefully removed from the vessels (as not to disturb the particles at the bottom), evaporated at 60 °C and redissolved in 2 cm^3 of cyclohexane. Extracts were then purified in a separation column BAKERBOND spe PAH Soil (500 mg of cyano/1000 mg of silica gel). The column was rinsed with 12 cm^3 of petroleum ether before use. The extracts were transferred to the column and eluted with 9 cm^3 of 3/1 acetonitryle–toluene mixture. Cleaned extracts (2 μl of sample solution) were analysed for 16 EPA-PAHs by gas chromatography–mass spectrometry with Fisons GC 8000/MS 800 gas chromatograph. The gas chromatographic separation was performed in DB-5 column (30 m length, 0.25 mm diameter and 1 μm film). Helium was used as carrier gas (the flow rate of 0.5 cm^3/min). The oven was kept at 40 °C for 1 min, heated with 5 °C min^{-1} to 120 °C and finally the temperature of 280 °C was kept for 60 min. Retention times of EPA-PAHs (minutes) were as follows: naphthalene, 9.95; acenaphthalene, 16.72; acenaphthene, 17.60; fluorene, 20.09; phenanthrene, 25.00; anthracene, 25.23; fluoranthene, 31.46; pyrene, 32.46; benzo(a)anthracene, 39.89; chrysene, 40.24; benzo(b)fluoranthene, 51.77; benzo(k)fluoranthene, 52.07; benzo(a)pyrene, 56.60; indeno(1,2,3-cd)pyrene, 80.89; dibenzo(a,h)anthracene, 81.90; benzo(ghi)perylene, 88.10.

2.3. SPIKING AND RECOVERY

Recoveries were determined by adding standard mixture of PAHs in methylene chloride into sewage sludge. Then the samples were carefully mixed, extracted and analysed for PAHs as briefly described above. Average PAHs recoveries ranged from 10 to 45% (relative standard deviation (RSD) ranged from 4 to 38%). The recovery values depended on PAH molecular weight and Henry's law constant. The recoveries obtained in this study were comparable with the values obtained by KIRK and LESTER [8] and BARTULEWICZ et al. [1] for the matrices with high water content. The authors reported the values of recovery were 0–128% (mean value: 65%) and 38–56% (mean value: 48%), respectively [1], [7], [8].

3. RESULTS AND DISCUSSION

Physicochemical characteristics of raw as well as conditioned sludge are listed in table 2. Thermal conditioning of sewage sludge for 6 h and longer brought about a decrease of pH and an increase of volatile fatty acids and acidity. The content of volatile fatty acids increased as the time of sludge thermal treatment was lenghtened. Thermal conditioning of sludge for 6, 12 and 24 h improved hydrolysis. An increase of dry matter content in the sludge was observed. An increase of dry matter concentration as well as pH decrease during sludge thermal heating are typical of this process [14].

Figure 1 shows the PAHs concentration in sludge being subjected to 6, 12 and 24 h conditioning. Heating of sludge for 6 hours increased the concentration of 2-ring PAHs, while the concentration of higher-molecular weight aromatic hydrocarbons decreased. Significant increase was observed for all PAHs during 12 h and 24 h thermal conditioning tests. Especially, the sludge heated for 12 hours was contaminated with PAHs. Results for the individual PAHs are presented in table 3.

Table 2

Physicochemical characteristics of the raw and conditioned sludges

Physicochemical properties	Unit	Type of sludge			
		Raw	Conditioned for 6 h	Conditioned for 12 h	Conditioned for 24 h
pH	–	5.78	5.35	5.37	5.41
Dry matter	g/dm^3	42.19	45.24	46.18	58.40
Alkalinity	$mval/dm^3$	28.40	40.00	40.00	60.00
Acidity	$mval/dm^3$	13.00	22.00	22.40	24.00
Volatile fatty acids	mg CH_3COOH/dm^3	2100	3300	3428	5743

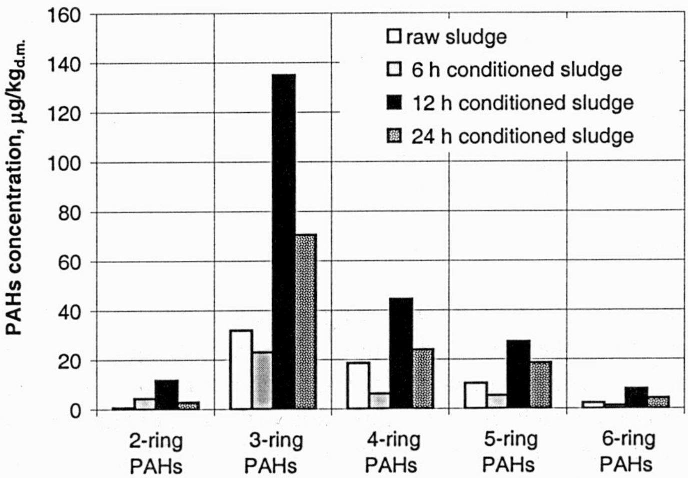

Fig. 1. Changes in the composition of PAHs during preliminary thermal conditioning of sewage sludge (6, 12, 24 h)

Except for acenaphthalene all 16 EPA-PAHs were present in raw and conditioned sludges. Total concentration of PAHs in the conditioned sludge varied from 5 $\mu g/kg_{d.m.}$ (6 h conditioned sludge) to 35 $\mu g/kg_{d.m.}$ (sludge conditioned for 12 h). Concentration of PAHs in raw sludge reached 13 $\mu g/kg_{d.m.}$. The most abundant compounds in all sludge samples were acenaphthene, fluorene and phenenthrene. This is surprising because other authors have not reported higher abundance of lower-molecular weight PAHs in raw sludge [13], [17], [18]. The occurrence of individual PAHs in the sludge depends probably not only on the type of sludge, but also on the quality of sewage influents. There are no available data which can be referred to changes in the concen-

Table 3

Changes in the concentration of individual PAHs during preliminary thermal conditioning of sewage sludge

Compound	Content of PAHs ($\mu g \cdot kg_{d.m.}^{-1}$) in the sludge			
	Raw sludge	Sludge conditioned for 6 h	Sludge conditioned for 12 h	Sludge conditioned for 24 h
Naphthalene	0.715	4.397	11.761	2.863
Acenaphtalene	n.d.	n.d.	n.d.	n.d.
Acenaphthene	5.625	10.738	61.363	28.125
Fluorene	13.806	6.647	38.352	19.943
Phenanthrene	9.715	4.500	28.125	15.340
Anthracene	2.914	1.125	7.157	7.159
Fluoranthene	5.625	2.352	15.852	8.181
Pyrene	7.670	1.789	15.340	7.670
Benzo(a)anthracene*	2.761	1.073	5.625	3.528
Chrysene*	2.556	1.073	7.670	4.704
Benzo(b)fluoranthene*	4.397	1.329	12.784	7.670
Benzo(k)fluoranthene*	3.017	0.971	8.693	4.193
Benzo(a)piren*	2.096	0.715	4.653	4.244
Indeno(1,2,3-cd)pyrene*	1.227	0.869	4.448	2.556
Dibenzo(a,h)anthracene*	0.869	2.454	1.125	2.403
Benzo(g,h,i)perylene*	1.125	0.511	3.528	1.738
∑PAHs	64.118	40.543	226.476	120.317
∑carcinogenic PAHs	18.048	8.995	48.526	31.036

* Carcinogenic PAHs.

tration of lower-molecular weight PAHs during thermal conditioning of sewage sludge. As can be seen in table 3 thermal conditioning of sewage sludge brought about desorption of PAHs absent or present in very small concentrations in raw sludge to happen. The results obtained in the study are not comparable with these obtained by NICHOLS at al. [14], because in their study a significant decrease of fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene concentration was observed as a result of thermal heating of the sewage sludge. No significant concentration changes were observed in the case of benzo(g,h,i)perylene and indeno(1,2,3c,d)pyrene. No correlation between the temperature or time of treatment and PAHs concentration was observed by NICHOLS at al. [14]. In this study, similar results were obtained. No correlation was found between dry matter content and presence of PAHs the sewage sludge (figure 2). However, the present investigation suggests that the thermal treatment of sewage sludge may lead to accumulation of PAHs on particulate matter. It is important to explain why the concentration of PAHs changes during thermal conditioning of sewage sludge. NICHOLS at al. [14] suggest that the concentration changes of fluoranthene and benzo(k)fluoranthene during thermal heating are not caused by their destruction, but by the difficulties associated with their estimation [14]. According to the BONTEN at al. [2] thermal heating of complex organic matrices increases the rate of mass transfer of hydrophobic compounds within sludge particles and increases PAHs diffusion through the pore liquid [2]. Organic matter decomposition of sludge particles brings about structure changes and facilitates PAHs desorption rate. In the untreated sludge, PAHs desorption rate is rather low because of the sludge particle structure [3] (figure 3). PAHs desorption from sewage sludge may be a reason for increase of individual PAHs concentration after 12 and 24 h of sludge heating. No evidence of PAHs formation during sludge heating was found [14].

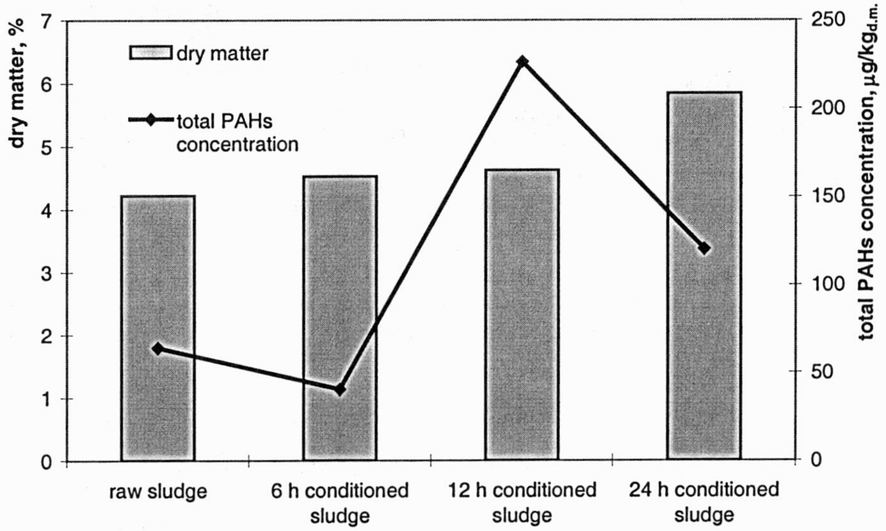

Fig. 2. Realtionship between dry matter and total concentration of PAHs during thermal conditioning of sewage sludge

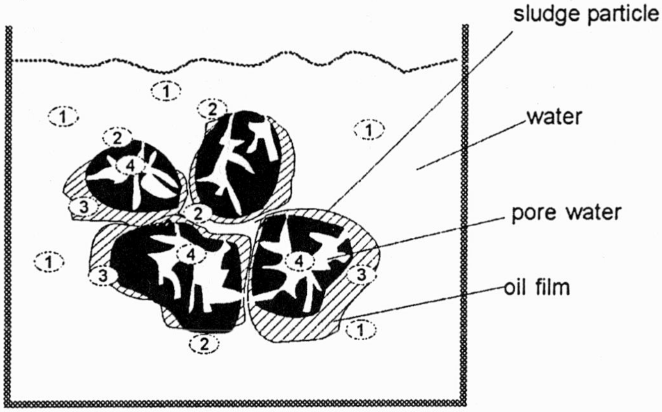

Fig. 3. Occurrence of PAHs in the sewage sludge:
1 – in the supernatant, 2 – adsorbed onto the sludge particles,
3 – in oil film, 4 – in the water phase within sludge particles

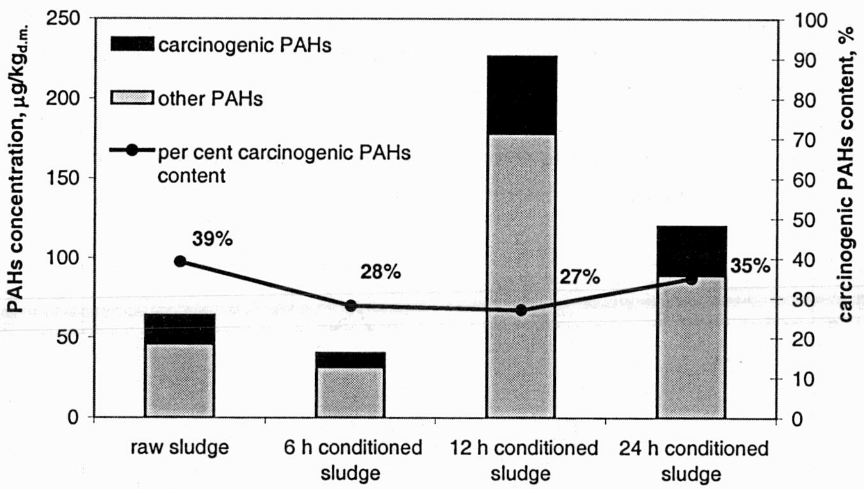

Fig. 4. Changes in the composition of carcinogenic PAHs during preliminary thermal conditioning of sewage sludge

Table 4

A comparison of PAHs concentrations in raw sludge observed in surveys carried out by different authors

Compound	Concentration ($\mu g \cdot kg^{-1}$)		
	[13]	[18]	[17]
Naphthalene	4000	113	0.5
Acenaphtalene	n.d.	91	1.51
Acenaphthene	500	96	8.30
Fluorene	400	191	9.40
Phenanthrene	2700	292	15.01
Anthracene	180	106	1.89
Fluoranthene	630	1343	1.48
Pyrene	1190	1009	0.7
Benzo(a)anthracene	130	262	n.d.
Chrysene	320	274	n.d.
Benzo(b)fluoranthene	143	82	n.d.
Benzo(k)fluoranthene	66	176	n.d.
Benzo(a)piren	140	165	n.d.
Indeno(1,2,3-cd)pyrene	73	35	n.d.
Dibenzo(a,h)anthracene	8.8	76	n.d.
Benzo(g,h,i)perylene	170	29	n.d.
∑PAHs	10650.8	4340	38.79

n.d. – not determined.

The total concentrations of carcinogenic PAHs increased after 12 and 24 h of conditioning; however, their per cent content decreased in all cases. The results for carcinogenic PAHs are presented in figure 4.

As can be seen in the table 4 the concentrations of PAHs in the raw sludge were lower than the concentrations determined by other researchers for this kind of sludge.

The European Union proposes that the sum of acenaphthene, phenenthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene should not exceed 6 $mg/kg_{d.m.}$. In our study, the concentration of EPA-PAHs was lower than 0.04 $mg/kg_{d.m.}$ and, consequently, did not exceed the standards. However, the concentration of PAHs reported by other investigators exceeds the standards. Thermal heating of the sludge may increase the risk associated with agricultural use of the sludge.

4. CONCLUSIONS

1. Thermal conditioning of sewage sludge for 6 hours brought about a decrease in the concentrations of both total PAHs and carcinogenic compounds.

2. On the contrary, for 12 and 24-hour conditioning an increased concentrations were observed.

3. No acenaphthalene was found in all samples tested.

4. Thermal conditioning of sewage for 6 hours and longer brought about better hydrolysis, an increase in both acidity and the content of volatile fatty acids and a decrease in pH of the sludge.

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WPŁYW WSTĘPNEGO TERMICZNEGO KONDYCJONOWANIA OSADÓW ŚCIEKOWYCH NA STĘŻENIE WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH

Określono, jak wstępne termiczne kondycjonowanie osadów ściekowych w temperaturze 70 °C przez 6, 12 i 24 h wpływa na ich fizyczne i chemiczne właściwości oraz na stężenie 16. wielopierścieniowych węglowodorów aromatycznych (WWA). Stwierdzono, że termiczne kondycjonowanie osadów ściekowych polepszało hydrolizę, zwiększało zarówno kwasowość, jak i zawartość lotnych kwasów tłuszczowych oraz obniżało wartość pH. W osadzie kondycjonowanym przez 24 h zaobserwowano także spadek zawartości substancji organicznej. Sześciogodzinne kondycjonowanie osadu wpłynęło na zmniejszenie całkowitego stężenia WWA i związków rakotwórczych, podczas gdy dwunasto- i dwudziestoczterogodzinne kondycjonowanie powodowało zwiększenie całkowitego stężenia WWA.