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Applying ultrasonic in the PAHs degradation in sewage sludge

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ABSTRACT

The article presents experiments and research results whose purpose was to establish the effectiveness of ultrasonic disintegration of various types of sewage sludge. The research material contained sewage sludge sampled from three wastewater treatment plants located in Podlaskie Voivodeship. The sewage sludge under examination was collected from a patch with earthworms (vermicompost) and a reed bed (dewatered and stabilized sludge) at Municipal Wastewater Treatment Plant in Zambrów, Autothermal Thermophilic Aerobic Digestion (ATAD) stabilized sludge from Municipal Wastewater Treatment Plant in Wysokie Mazowieckie and digested sludge from Dairy Wastewater Treatment Plant Mlekovita in Wysokie Mazowieckie. Based on the research, it was proven that applying ultrasounds shaped the final content of the examined indicators and polycyclic aromatic hydrocarbons (PAHs) in sludge in an individual manner. In own research, in one type of treated sewage sludge, the sum of 16 PAHs concentration exceeded the value permitted by EPA and 10 PAHs according to WD2000 in sewage sludge used in farming 6 mg/kg of dry mass (6,000 μg/kg of dry mass). The conducted research proves that the total content of 16 PAHs in the examined sewage sludge varied within a wide range from minimum content of 1,161 μg/kg DM to a maximum value of 7,103 μg/kg DM.

Keywords: Ultrasonic disintegration; Polycyclic aromatic hydrocarbons; Sewage sludge

1. Introduction

The research on applying the ultrasounds technique for sewage sludge treatment showed a great potential of this disintegration method based on cavitation phenomenon, mainly in intensifying the process of anaerobic fermentation. The ultrasounds wave frequency range is between 20 kHz and 1 GHz. [1,2]. Ultrasonic interaction leads to processes which usually cause irreversible macroscopic changes in the core. Primary mechanisms of this interaction are cavitation, radiation pressure, and acoustic pressure. These processes cause secondary phenomena, such as dispersion, ultrasonic coagulation, depolymerization, heat phenomena, oxidation, reduction, degassing, and others [3]. Most researchers claim that ultrasonic cavitation is mostly responsible for the disintegrating character of the ultrasonic wave. This phenomenon is based on the occurrence of empty spaces (cavities) in liquids and their disappearance, as well as resonant vibration of gas vesicles [4].

Sewage sludge might also be a source of mineral and organic pollutants. Research on organic pollutants has been given exceptional attention in recent years. In sewage sludge, 516 substances have been identified, which have been classified into 15 classes. They include polycyclic aromatic hydrocarbons (PAHs) [5,6].

The Polish legislation does not provide any regulations on the maximum PAHs content in sewage sludge designed for use in agriculture. There is also no uniform procedure of analytic analysis of PAHs in sludge. Determination of micro-contaminations in sewage sludge is one of the most complicated analytical tasks connected with the heterogeneity of these materials and with differentiated PAH concentrations [7]. The concentrations of PAHs in sewage sludge are different. There are many articles available in literature. Their

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content in various sewage sludge ranges from several hundred to several thousand µg/kg DM [8–10].

Although in Poland PAHs content in sediments used in agriculture is not subject to any norms, these substances are taken into account in the draft of alterations/amendments to the UE Directive 75/442/EWG, according to which a permissible summary concentration of 11 aromatic compounds (acenaphthene [ACE], phenathrene, fluorine [FLU], fluoranthene [FLA], pyrene [PYR], benzo[b]fluoranthene [B[b]FLA], benzo[j]fluoranthene [B[j]FLA], benzo[k]fluoranthene [B[k]FLA], benzo[a]pyrene [B[a]PYR], benzo[g,h,i]perylene [B[g,h,i]PER], indeno[1,2,3-cd]pyrene [Ind[1,2,3-c,d]P]) should be 6 $mg \cdot kg^{-1}$ (converted to dry mass).

From the ecological point of view, PAHs collection and transformation within individual ecosystems are more important. Because nearly 90% of the PAHs contained there come from soil, specific actions and means should be implemented to protect these ecosystems. Moreover, studies have so far demonstrated differences in the degree and speed of PAHs transformation in soil, which proves their long life and the possibility of bioaccumulation in this environment. PAHs (and other organic compounds) occur also in plants, thus being a great concern as the mechanism of absorbing PAHs and other organic compounds are yet not fully understood [11]. It is assumed that it is possible due to accumulation of harmful substances on the surfaces of leafs during atmospheric precipitation or due to contamination with soil particles. Irrespective of that, in many countries studies are being conducted in order to determine the limit values for organic substance content in sewage sludge, composts, and potable water. In Europe, when sewage sludge is used in agriculture, limits on the content of PAHs in naturally used municipal sewage sludge have been proposed [12,13]. Some of the European Union (EU) countries have introduced an internal limitation of PAHs contents in sewage sludge intended for agricultural use [14,15]. In Germany, there are no binding regulations concerning the PAHs content in sludge, however, a designation of nine PAH is recommended, the sum of which should not exceed 6,000 µg/kg DM. In the proposed amendment to the Sludge Directive, the sum of 11 hydrocarbons should not exceed 6,000 µg/kg DM.

Applying ultrasounds in PAHs degradation for various sewage sludge is broadly described in literature [16] as an autonomous process or joined with another one, for example, Fenton process. In research conducted by Lin et al. [17], 16 PAHs degradation in sludge from textile industry was achieved at 41%–45%. Sonification is very often treated as a phase preceding the anaerobic sewage sludge stabilization process. In this research, a significant influence of ultrasounds on subsequent PAHs degradation during sewage sludge fermentation is pointed out. Research conducted by Zhou et al. [18] showed degradation of selected PAHs in sonicated sludge to have been higher by several percents. The majority of literature data concern the influence of ultrasounds on PAHs degradation in unprocessed (raw) sludge. The novelty of the conducted research was examining the influence of ultrasounds on PAHs degradation in sewage sludge stabilized with various methods.

The aim of the research was to determine the influence of ultrasounds on changes in characteristics and parameters of digested sewage sludge, most importantly changes in 16 PAHs and changes in organic substance and carbon content.

2. Materials and methods

2.1. Materials

The examined sewage sludge was collected from a patch with earthworms (vermicompost) and a reed bed (dewatered and stabilized sludge) at Municipal Wastewater Treatment Plant in Zambrów, ATAD stabilized sludge from Municipal Wastewater Treatment Plant in Wysokie Mazowieckie and digested sludge from Dairy Wastewater Treatment Plant Mlekovita in Wysokie Mazowieckie.

2.2. Experimental procedure

Sewage sludge disintegration process was conducted with the use of ultrasonic atomizer Sonics VCR-130 (USA) with the frequency of 20 kHz. Sewage sludge was exposed to ultrasounds of 20 kHz frequency in four periods of 5, 10, 15, and 20 min, with maximum vibration power and amplitude equal to 88% of the rated amplitude.

In order to determine the effectiveness of ultrasonic disintegration, such parameters as pH, dry mass, organic dry mass, total carbon (TC), organic carbon, non-organic carbon, 16 PAHs, and their sum were measured in the samples before and after sonification.

2.3. Analytical methods

Dry matter, organic matter, total organic carbon (TOC), and TC were determined using standard methods [19].

In the study of PAHs content in sewage sludge, gas chromatography coupled with mass spectrometry detection (GC-MS) was applied. In purified and concentrated extracts from sewage sludge, 16 PAHs were identified (according to US EPA): naphthalene (NAPH), acenaphthylene, ACE, FLU, phenanthrene, anthracene [ANT], FLA, PYR, benzo[a]anthracene [B[a]ANT], chrysene [CHR], B[b]FLA, B[k]FLA, B[a]PYR, dibenzo[a,h]anthracene [D[a,h]ANT], Ind[1,2,3-c,d]P, B[g,h,i]PER, as well as their sum [19].

2.3.1. Extraction procedure

A total of 20 g of sludge sample with a field moisture content was weighed and placed in a conical flask of 200 mL capacity. Then 50 mL of acetone was added, the flask was sealed and subjected to extraction on a shaker for 1 h. A volume of 50 mL of petroleum ether was added and agitated again for 1 h. The supernatant was decanted and shaken with another 50 mL petroleum ether portion. The supernatant liquid was decanted. The extracts were combined, and acetone and other polar compounds were removed by shaking twice with 400 mL of water. The water was discarded. The organic layer was dried over anhydrous sodium sulfate (VI) and then filtered through a filter. The dried extract was transferred to a concentrating device, 100 µL of isooctane as a stabilizer was added and concentrated to the volume of about 2 mL. The resulting solution was analyzed by means of GC-MS. Determination of the content of PAHs was conducted through GC-MS.

2.3.2. Calibration

Five solutions containing calibration standard mixture and the test sample matrix were analyzed. The calibration function was calculated by linear regression of the corrected peak areas. The current sensitivity of the method was estimated from the calculated regression function. Calibration was performed on the measurement day. Also, determination of a certified reference material was carried out in order to investigate the recoveries of PAHs. Values of PAHs recoveries ranged between 85% and 110%, which is permissible for chromatographic methods [20]. The limit of detection was 10 ng kg^{-1} in dry mass. Precision expressed as relative standard deviation was below 12%.

Determinations of the test samples were performed in triplicate. Mathematical and statistical calculations presented in the paper were made using a common computer software and spreadsheets. To study the relationship between quantitative parameters and to describe the strength of the correlation in the case of a small number of observations, Spearman's rank correlation coefficient was applied [21]. In order to verify whether there was a statistically significant change, analysis of variance (ANOVA) rank Kruskal—Wallis (K–W) test was used for each pair of observations [22].

2.4. Statistical analysis

To determine any interdependencies within the parameters group and to describe the intensity of their intercorrelations, correlation matrixes were built. Spearman correlation matrix was constructed for the parameters group. The results were explored graphically [23]. A selection of suitable criteria allowed to determine a small number of parameters behaving in a similar way in each of the sewage sludge stabilization processes. After the grouping process, a certain number of variables groups were graphically labeled according to the following criteria:

- The number of variables groups must be the smallest possible (which means maximizing the number of variables in each group).
- In each group, there can only be variables with Spearman correlation coefficient greater than 0.
- If statistically unimportant correlation coefficients appear in a group, their number should be the smallest possible (not bigger than 30%).
- Despite the possibility of manual selection of variables in a group, the task was performed by an algorithm in order to obtain results' independency of possible mistakes in interpretation. An assessment of how one parameter from a group behaved in time allowed to predict how the other parameters from that group will behave.

Statistical analysis was conducted in statistical environment R (3.3.0 version called "Supposedly Educational"), with the use of basic package and additional packages spearman (version 0.3-0) and corrplot (version 0.77) [24–26].

3. Results and discussion

The sludge exposed to ultrasonic disintegration was stabilized in various ways and came from different wastewater treatment plants. Tables 1 and 2 show the results of research on sewage sludge stabilized before ultrasonic disintegration. Results analysis allows to claim that post-fermentation sludge was the most hydrated (2.18% DM), whereas vermicompost had the greatest amount of dry mass of 52.42% DM. The content of organic substance ranged from 41.27% DM in vermicompost to 61.98% DM in post-fermentation sludge. The content of TOC was on a similar level in the examined sludge that is from 234.47 g/kg DM in vermicompost to do 318.33 g/kg DM in aerobically stabilized sludge, ATAD. The content of 16 PAHs in the examined sludge was very varied. Post-fermentation dairy sludge had the lowest content of 16 PAHs which was at 1,161.01 µg/kg DM; similarly, vermicompost had a relatively low total content of 16 PAHs at 1,820.16 µg/kg DM. However,

Table 1
Physicochemical parameters in sludge before ultrasonic disintegration

The type of sludge	Physicochemical parameters in sludges					
	TC	TOC	TIC	Dry matter	Organic matter	pH in H_2O
	g/kg DM			%	% DM	–
Fermentation	330.20	255.94	74.26	2.18	61.98	8.40
STRB	332.87	284.40	48.47	25.46	57.82	5.64
ATAD	369.61	318.33	51.28	24.24	61.40	7.70
Vermicomposting	266.50	234.47	32.03	52.42	41.27	5.50

Table 2
Initial PAHs content in relation to the number of rings in sludge before ultrasonic disintegration

The type of sludge	2-Ring	3-Ring	4-Ring	5-Ring	6-Ring	The sum of 16 PAHs
	µg/kg DM					
Fermentation	62.61	511.58	334.54	123.7	128.58	1,161.01
STRB	46.77	141.63	1,481.68	2,034.9	798.26	4,503.24
ATAD	59.54	575.95	3,657.94	2,015.2	794.75	7,103.38
Vermicomposting	62.22	86.18	633.62	754.82	283.32	1,820.16

sewage sludge from long-term stabilization in sludge treatment reed beds (STRB) and aerobically stabilized sewage sludge, ATAD, had a very high content of 16 PAHs sum reaching, respectively, 4,503.24 µg/kg DM and 7,103.38 µg/kg DM. In reference to research described in literature, the claims about a much lower content of PAHs in dairy sewage sludge as compared with municipal sewage sludge were confirmed. Research on unprocessed sewage sludge conducted by Oleszczuk [27] showed the content of 16 PAHs sum according to EPA ranging from 2.83 mg/kg DM to 9.95 mg/kg DM, while Li et al. [28] demonstrated the content at a very high level from 88.81 mg/kg DM to 100.74 mg/kg DM, similarly Cai et al. [29] ranging from 64 mg/kg DM to 94 mg/kg DM. A definitely lower content was obtained in research conducted in China, from around 0.5 mg/kg DM to 3.6 mg/kg DM [30]. In research conducted in Scandinavia, a very wide range of 16 PAHs content in sewage sludge, from 1.0 mg/kg DM to 30 mg/kg DM, was observed [31].

Fig. 1 depicts the changes in the percentage share of TOC and total inorganic carbon in relation to TC with various times of ultrasonic disintegration. In reference to all sewage sludge, there is a similar tendency of increasing inorganic carbon percentage share along with the increase of sonification time. Also, short sonification time (5 min.) initially caused an insignificant increase of organic carbon percentage share. The highest increase in inorganic carbon percentage share after 20 min of sonification was observed for STRB from 13.9% to 33.2%, whereas the lowest increase occurred in post-fermentation sludge from 12.0% to 14.5%. Research conducted by Zhang et al. [32] among others, confirms that the shear force which causes organic substance disintegration occurs during sonification.

Fig. 2 presents changes in the percentage share of particular PAHs groups depending on the number of rings. The analysis of the obtained results points to individual behavior of these compounds during sonification depending on the sewage sludge type. The highest percentage share increase was observed for PAHs with four rings in post-fermentation sludge from 28.8% to 37.9%, while the greatest decrease occurred in PAHs with three rings, also in post-fermentation sludge. In reference to hydrocarbons with five and six rings, a minor drop in percentage share of 1%–3% was observed in sewage sludge exposed to ultrasounds. NAPH from two-ringed PAHs group was the most stable.

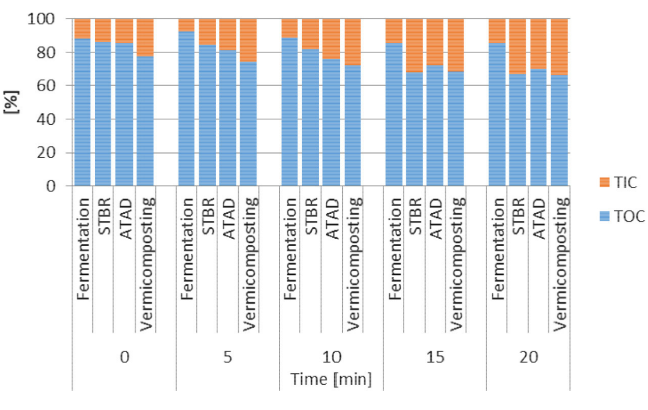

Fig. 1. The changes in percentage share of total organic carbon (TOC) and total inorganic carbon (TIC) in relation to total carbon (TC) with various times of ultrasonic disintegration.

The duration of ultrasounds interacting with sewage sludge was of significant importance for the changes in the percentage share of individual PAHs groups in sludge. Longer period of sludge decomposition on ultrasounds caused greater increase (or decrease) of percentage share of individual PAHs groups. The biggest changes were observed for ultrasound interaction duration of 15 min. The results analysis showed that the greatest changes in individual PAHs groups during ultra-sonification were recorded for fermented sludge. Aerobically stabilized sludge with the use of ATAD technology showed the smallest changes in the percentage share of ringed PAHs groups during sonification.

To determine the interdependencies in the parameters group and to describe the intensity of their intercorrelations, Spearman correlation matrixes were built. After constructing the matrixes, hierarchical clustering algorithm of variables was applied in order to determine subgroups of variables which behave alike. As a result of applying hierarchical clustering algorithm and appropriate selection of the number of groups, the following groups of variables which behave alike were recognized. Fig. 3 presents results for all research series in the conducted experiment.

In the presented pictures, the size and color (of a circle) stand for the values of Spearman *S* correlation coefficients:

- $S = +1$
- $S = -1$

A bigger circle and more intensive color denote that Spearman correlation coefficients approach border values of +1 and –1. The X mark in the middle of the area (circle) denotes that in the Spearman correlation coefficient relevance test with Benjamini–Hochberg correction (for multiple testing), the *p*-value is larger than 0.05. The value of this coefficient is then statistically insignificant. In order to construct Spearman matrix, the examined values of organic and mineral substances, carbon and the content of PAHs grouped according to the number of rings, as well as the total content of PAHs for sewage sludge stabilized with various methods, were taken into account.

As a result of analyzing Spearman correlation matrix, the following groups of variables were obtained, which behave alike during ultrasonic disintegration of sewage sludge stabilized with various methods:

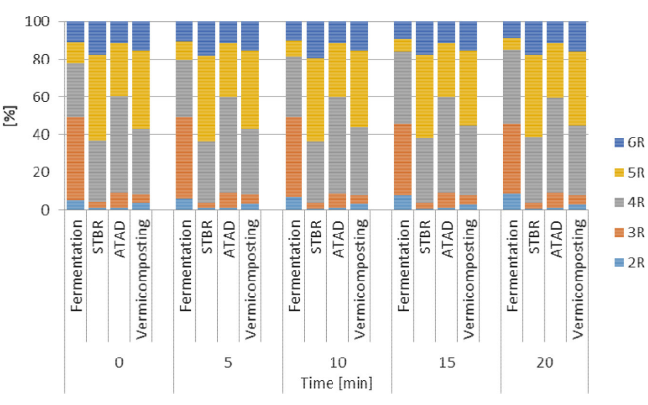

Fig. 2. Changes in the percentage share of particular PAHs groups depending on the number of rings.

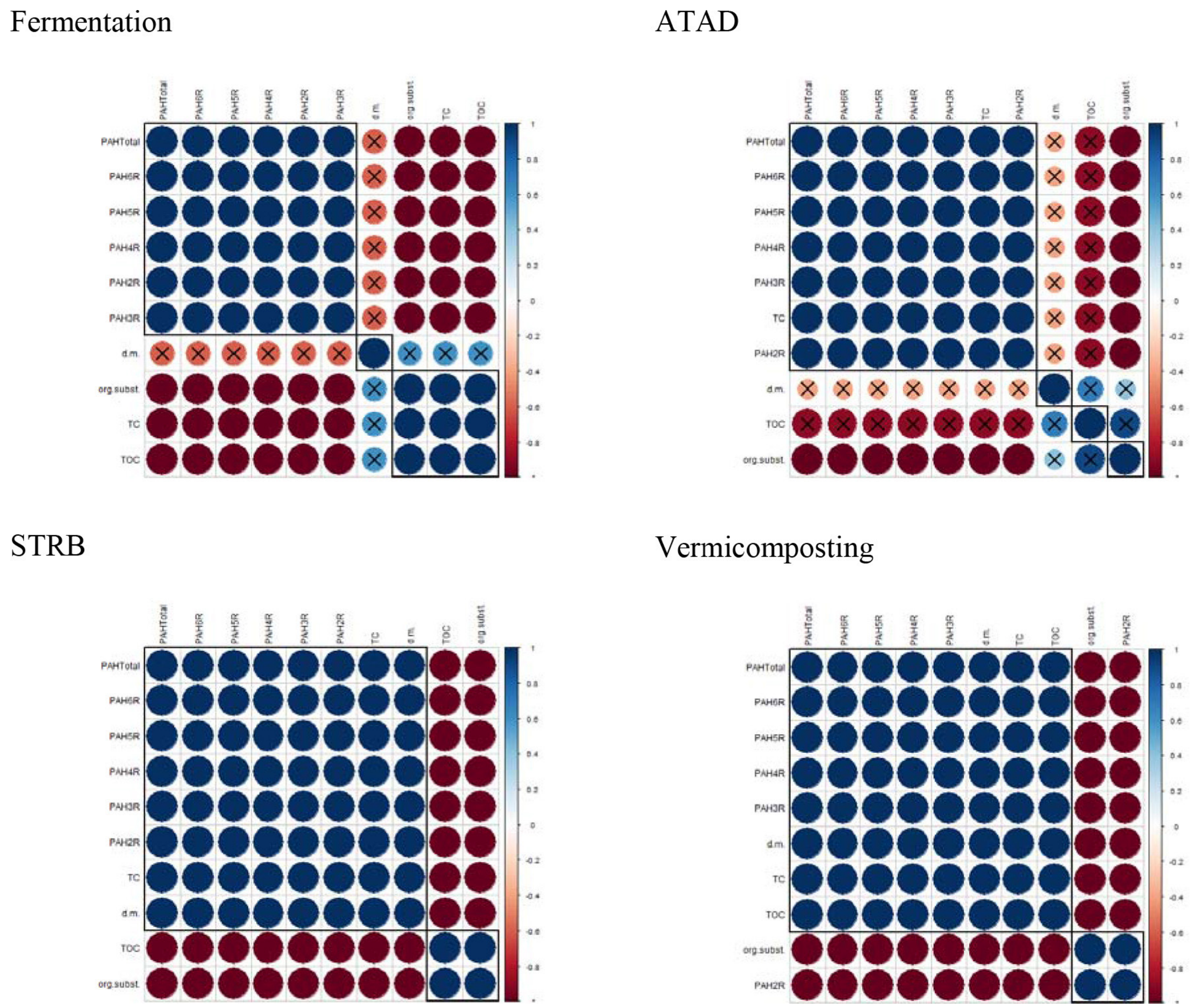

Fig. 3. Spearman correlation matrixes for all research series in the conducted experiment.

3.1. For post-fermentation sludge

- Group I—PAHs with two, three, four, five, six rings, and their sum.
- Group II—Organic substances, total carbon, and organic carbon.

3.2. For sludge stabilized through STRB

- Group I—PAHs with two, three, four, five, six rings, and their sum, dry mass, and total carbon.
- Group II—Organic substances and organic carbon.

3.3. For sludge stabilized with ATAD technology

- Group I—PAHs with two, three, four, five, six rings, and their sum and total carbon.

3.4. For sludge processed with vermicompost

- Group I—PAHs with two, three, four, five, six rings and their sum, dry mass, total carbon, and organic carbon.
- Group II—Organic substances and two-ringed PAHs.

Another statistical analysis of the obtained results was based on applying ANOVA K–W test. The results of the K–W test were graphically presented in the form of a diagram in Fig. 4 (frame with moustache) for the biggest correlated group of variables obtained as a result of statistical equations of Spearman correlation matrix (Fig. 4). The obtained K–W test results are statistically significant, as they have $p < 0.05$.

The obtained results of these statistical tests point to a strong similarity of most of the examined parameters in stabilized sewage sludge with sonification time, both as dependent and independent data. From Spearman correlation matrix results, it can be concluded that in all examined stabilized sewage sludge during sonification, the 16 PAHs tested and their sum are in one group of variables; therefore, their "behavior" is alike. In the case of three types of sludge (except for vermicompost), organic substances, and organic carbon content during sonification process "behaved" differently than PAHs.

Applying ANOVA K–W test allowed to state that the use of ultrasounds caused an increase of the content of 16 PAHs sum in three types of sewage sludge stabilized through vermicomposting, ATAD, and STRB. However, in the case of sewage sludge stabilized through the fermentation process, applying

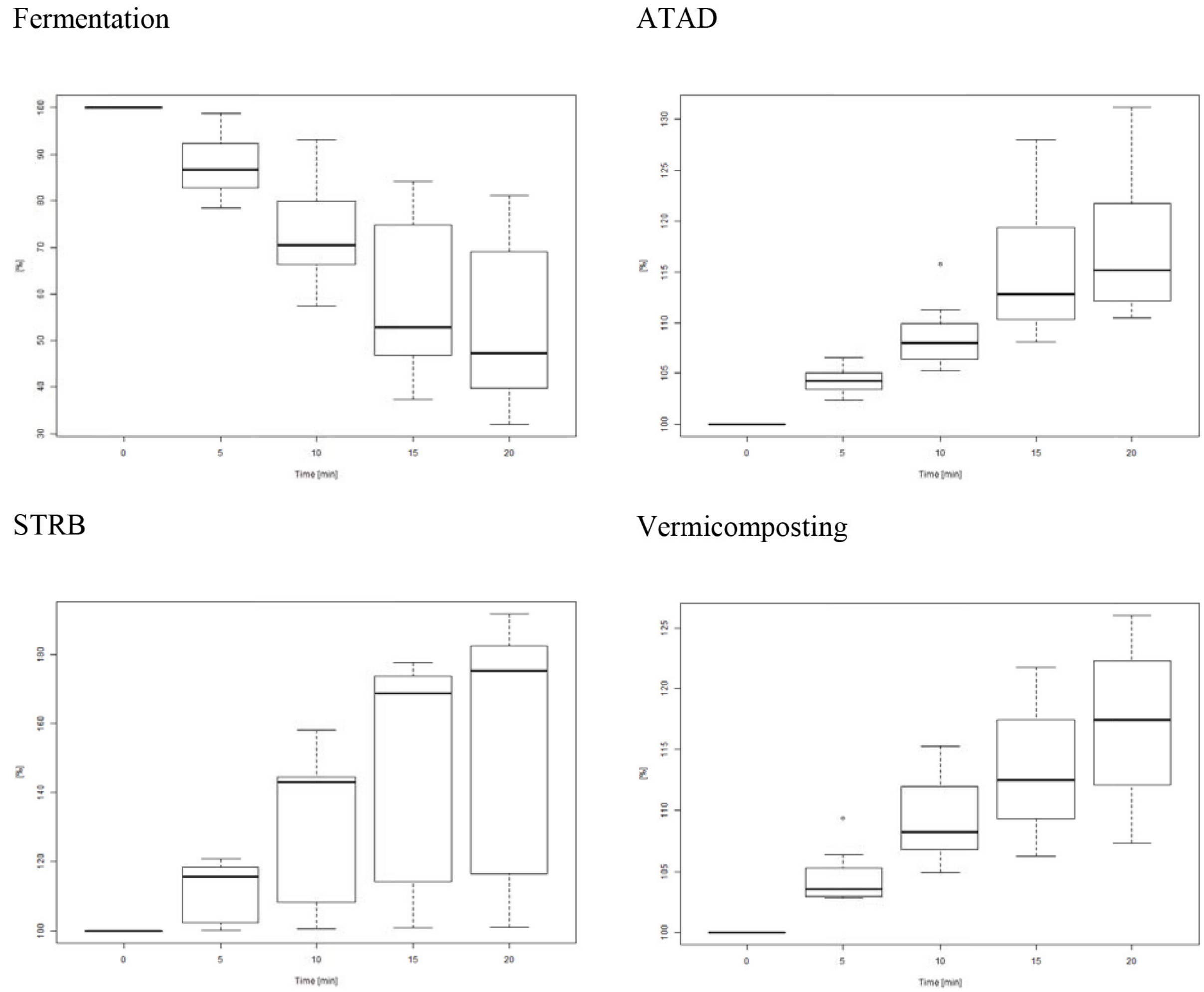

Fig. 4. Results of the ANOVA Kruskal–Wallis test.

ultrasounds caused a decrease in the content of 16 PAHs sum. Numerous research points to very various behavior of PAHs during different methods of sewage sludge stabilization.

The increase of PAHs content in sewage sludge during its processing with biological methods has numerous justifications in literature. According to data in literature, while assessing PAHs content it should be taken into consideration that they can penetrate into living organisms present in sludge (bacteria, fungus, protozoa, and invertebrates), undergoing various metabolic processes, as well as they can cumulate in them [33,34]. The number of PAHs undergoing this type of sorption, and later on changes, depends mainly on their solubility in water. PAHs, as multimolecular and non-polar compounds, show low solubility in water. However, this condition might change if sewage contains organic solvents or especially common, for example, in dairy sewage, detergents and flocculants. In that case, the intercell content of PAHs and the amount of their metabolic products might increase. PAHs might also occur in sludge independently, for example, during putrefaction processes, as a result of biotransformation of organic matter with varied content. Such possibility is indicated by a higher content of PAHs in fermented sewage sludge than in fresh sludge [35]. These hydrocarbons show weaker hydrophobic features than five and six-ringed PAHs, they have weaker bonds with solid molecules in sludge so they are more bioavailable. PAHs compounds with high molecular mass are absorbed by solid parts in sludge and are then characterized by low mobility [36].

Research on changes in the content of PAHs in sewage sludge stabilized and transformed in various ways by different researchers suggests the possibility of different behavior of these compounds during the process. A very high degree of 16 PAHs degradation sum ranging from 89.8% to 98.9% during the fermentation of sewage sludge in an autoclave for 60 d was received by Chang et al. [37]. Bernal-Martinez et al. [38] reported that about 50% decomposition of 16 PAHs sum occurred during fermentation of municipal sewage sludge. The use of anaerobic processes for biological decomposition of municipal sewage sludge has reduced concentrations of PAHs from 45% to 85% [39]. According to Oleszczuk and Baran [20] and Oleszczuk [27, 40], the sewage sludge compositing process with various proportions of structure-forming materials can cause some decrease in 16 PAHs sum content, even from 30% up to 70%. The authors also indicate the correlations between decomposition and degradation of individual PAHs as well as their sum vs. the type and amount of available organic matter in the biomass [41]. Other authors also report a high (about 50%) degradation of 16 PAHs during composting of sewage sludge [28,42].

Different results were achieved by Villar et al. [43], who found that composting and sludge stabilization process increased the content of PAHs sum. Decomposition of hydrocarbons can be performed both by pure bacterial strains and mixed populations, for which intermediate products are a substrate for others. Besides bacteria, bio-degradation can be carried out by fungi, actinomycetes, some cyanobacteria, and algae [44]. Due to the action mechanism, microorganisms can be divided into two groups: one uses hydrocarbons as the only source of carbon and energy (e.g., bacteria: *Pseudomonas*, *Micrococcus*, and *Alcaligens*; and fungi: *Candida*, *Fusarium*, and *Aspergillus*), the other has the ability of co-metabolic transformations [45].

For each of the examined sewage sludge types, various disintegration effects were observed in reference to particular parameters. The tested sludge samples varied in terms of dry mass content (vermicomposting, 52%; STRB, 25%; ATAD, 24%; and fermentation, 2%), which is considered to be the main factor determining disintegration effectiveness. Although the dry mass concentration recommended in publications is between 2% and 3%, it was not confirmed in the conducted tests.

The conducted research proves that the total content of 16 PAHs in the examined sewage sludge varied within a wide range from minimum content of 1,161 μg/kg DM to a maximum value of 7,103 μg/kg DM. The variation range of PAHs content in sewage sludge in four time periods of sonification was large and depended on the variety of the organic substance. In a summary of the average value of 16 PAHs content in the examined sewage sludge, four-ringed PAHs had the largest content, while NAPH and three-ringed PAHs (except for post-fermentation dairy sewage sludge) and six-ringed PAHs had the smallest content. In reference to other research, the claims about much lower PAHs content in dairy sewage sludge in comparison with municipal sewage sludge were confirmed.

The results point to the fact that there are factors (such as ultrasonic disintegration) which might influence not only the content, but more importantly the mutual composition of the PAHs group. Applying ultrasounds is a crucial factor in evaluating the toxicity and availability of PAHs in sewage sludge.

4. Conclusions

The conducted research was complex and the obtained results and experiments point to the necessity of continuation and further development of research concerning changes in the content of stabilized sewage sludge during sonification. In this aspect, the importance of recognizing the role of a varied physiochemical content of sewage sludge and degradation of PAHs should be stressed. Determining the impact of the amount of organic substance and carbon contained in sewage sludge on changes in PAHs within that sludge during sonification is of particular importance.

The permitted content of PAHs in various environmental elements is determined within the EU and in most countries in the world by suitable legal regulations [12,13,46–48]. Due to various properties of particular PAHs, different concentration values are permitted depending on the type of environmental matrix. Considered as the most toxic and cancerous, B[a]PYR is therefore used frequently as a marker of the total exposure to all PAHs.

In Poland, the content of PAHs in sewage sludge has not been determined to this day. However, there are several legal regulations in force, in which the permitted concentrations of PAHs in drinking water, subsurface water and soil and earth can be found [49–51].

The conducted research allowed to form the following conclusions:

- Applying ultrasounds with 20 kHz frequency and four different exposure time periods shaped the final content of the examined PAHs in sewage sludge in an individual manner.
- It was observed that under the influence of ultrasounds significant changes might occur in PAHs content in previously stabilized sewage sludge.
- All applied ultrasounds duration periods caused a decrease in the content of organic carbon in sewage sludge; to the highest degree in vermicompost, while to the lowest degree in fermented dairy sewage sludge.
- Applying ultrasounds of 20 kHz frequency caused an increase of the content of 16 PAHs sum in all of the examined sewage sludge types except for post-fermentation dairy sewage sludge.

Symbols

PAH	—	Polycyclic aromatic hydrocarbons
STRB	—	Sludge treatment reed bed
ATAD	—	Autothermal thermophilic aerobic digestion of sewage sludge

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References

[1] K.Y. Show, T.H. Mao, D.J. Lee, Optimisation of sludge disruption by concation, Water Res., 41 (2007) 4741–4747.
[2] X. Feng, J.C. Deng, Q. Yu, H.L. Li, Physical and chemical characteristics of waste activated sludge treated ultrasonically, Chem. Eng. Process., 48 (2009) 187–194.
[3] C.M. Braguglia, M.C. Gagliano, S. Rossetti, High frequency ultrasound pre-treatment digestion of sludge: effect of floc structure and microbial population, Bioresour. Technol., 110 (2012) 43–49.
[4] S. Gao, Y. Hemar, M. Ashokummar, S. Paturel, G.D. Lewis, Inactivation of bacteria and yeast using high-frequency ultrasound treatment, Water Res., 60 (2014) 93–104.
[5] L. Lazzari, L. Sperni, P. Bertin, B. Pavoni, Correlation between inorganic (heavy metals) and organic (PCB and PAHs) micropollutant concentrations during sewage sludge composting processes, Chemosphere, 41 (2000) 427–435.
[6] P. Oleszczuk, Phytotoxicity of municipal sewage sludge composts related to physico-chemical properties, PAHs and heavy metals, Ecotoxicol. Environ. Saf., 69 (2008) 496–505.
[7] E. Smolik, Polycyclic Aromatic Hydrocarbons (PAHs), Institute of the Occupational Medicine and the Environmental Health Publications, 2005. Available at: https://docplayer.pl/. (In Polish).
[8] A. Rubio-Clemente, R.A. Torres-Palma, G.A. Peñuela, Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review, Sci. Tot. Environ., 478 (2014) 201–225.

[9] B. Macherzyński, M. Włodarczyk-Makuła, A. Nowacka, Desorption of PAHs from solid phase into liquid phase during co-fermentation of municipal and coke sewage sludge, Desal. Wat. Treat., 52 (2014) 3859–3870.
[10] M. Włodarczyk-Makuła, A. Popenda, W. Sułkowski, L.W. Robertson, The influence of sewage and sludge treatment processes on concentrations of polycyclic aromatic hydrocarbons, Fresenius Environ. Bull., 12 (2003) 338–342.
[11] T. Warężak, M. Włodarczyk-Makuła, Z. Sadecka, Accumulation of PAHs in plants from vertical flow-constructed wetland, Desal. Wat. Treat., 57 (2016) 1273–1285.
[12] Working Document on Sludge, 3rd Draft, Council of the European Community, Brussels, 2000.
[13] Working Document on Sludge and Biowaste, Council of the European Community, Brussels, 2010.
[14] I. Aparicio, J.L. Santos, E. Alonso, Limitation of the concentration of organic pollutants in sewage sludge for agricultural purposes: a case study in South Spain, Waste Manage., 29 (2009) 217–228.
[15] A. Kapanen, M. Vikman, J. Rajasarkka, M. Virta, M. Itavaara, Biotest for environmental quality assessment of composed sewage sludge, Waste Manage., 33 (2013) 1451–1460.
[16] M. Sillanpää, T.-D. Pham, R.A. Shrestha, Ultrasound Technology in Green Chemistry, SpringerBriefs in Green Chemistry for Sustainability, Series: SpringerBriefs in Molecular Science, Springer, 2011.
[17] M. Lin, X.A. Ning, T. An, J. Zhang, Ch. Chen, Y. Ke, Y. Wang, Y. Zhang, J. Sun, J. Liu, Degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge with ultrasound and Fenton processes: effect of system parameters and synergistic effect study, J. Hazard. Mater., 307 (2016) 7–16.
[18] J. Zhou, W. Xu, J.W.C. Wong, X. Yong, B. Yan, X. Zhang, H. Jia, Ultrasonic and thermal pretreatments on anaerobic digestion of petrochemical sludge: dewaterability and degradation of PAHs, PLoS One, 10 (2015) 1–13.
[19] Standard Methods for the Examination of Water and Wastewater, 21th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington D.C., USA, 2005.
[20] P. Oleszczuk, S. Baran, The concentration of mild-extracted polycyclic aromatic hydrocarbons in sewage sludges, J. Environ. Sci. Health, 11 (2004) 2799–2815.
[21] M. Sobczyk, Statistica, Publishing company PWN, 2011. (In Polish).
[22] S. Siegel, Non-parametric statistics for the behavioral sciences, McGraw-Hill, New York, 1956.
[23] M. Friendly, Corrgrams: Exploratory displays for correlation matrices, Am. Stat., 56 (2002) 316–324.
[24] R.T. Core, R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, 2016. Available at: https://www.R-project.org/.
[25] P. Savicky, Spearman's Rank Correlation Test. R Package Version 0.3-0, 2014. Available at: https://CRAN.R-project.org/package=pspearman.
[26] T. Wei, V. Simko, Visualization of a Correlation Matrix. R Package Version 0.77, 2016. Available at: https://CRAN.R-project.org/package=corrplot.
[27] P. Oleszczuk, Application of three methods used for the evaluation of polycyclic aromatic hydrocarbons (PAHs) bioaccessibility for sewage sludge composting, Bioresour. Technol., 1000 (2009) 413–420.
[28] H. Li, W. Wu, Y. Liu, Y. Chen, B. Murray, Effect of composting on polycyclic aromatic hydrocarbons removal in sewage sludge, Water Air Soil Pollut., 193 (2008) 259–267.
[29] Q.-Y. Cai, C.-H. Mo, Q.-T. Wu, Q.-Y. Zeng, A. Katsoyiannis, Concentration and speciation of heavy metals in six different sewage sludge-composts, J. Hazard. Mater., 147 (2007) 1063–1072.
[30] Y. Liu, J. Shen, Z. Chen, N. Ren, Y. Li, Distribution of polycyclic aromatic hydrocarbons in surface water and sediment near a drinking water reservoir in Northeastern China, Environ. Sci. Pollut. Res., 20 (2013) 2535–2545.
[31] B. Paulsrund, A.Wien, K.T. Nedland, A Survey of Toxic Organics in Norwegian Sewage Sludge Compost and Manure, 1997, pp. 51–59. Available at: https://vannforeningen.no/wpcontent/uploads/2015/06/1999_30733.pdf.
[32] G. Zhang, P. Zhang, J. Gao, Y. Chen, Using acoustic cavitation to improve the bio-activity of activated sludge, Bioresour. Technol., 99 (2008) 1497–1502.
[33] X.-Y. Lu, T. Zhang, H.H.-P. Fang, Bacteria-mediated PAH degradation in soil and sediment, Appl. Microbiol. Biotechnol., 89 (2011) 1357–1371.
[34] T. Palanisami, M. Mallavarapu, N. Ravi, Bioremediation of high molecular weigh polyaromatic hydrocarbons co-contaminated with metals in liquid and soil slurries by metal tolerant PAHs degrading bacterial consortium, Biodegradation, 23 (2012) 823–835.
[35] H. Witte, T. Langenhol, Untersuchungen zum eintrag von organisschen schadstoffen in boden und und pflanzen durch die landwirtschaftliche klärschlammuerwerdung belastung des klärschlamms mit organische schadstoffen, Korrespondenz Abwasser, 35 (1998) 570–58.
[36] Y. Marusenko, P. Heckes, S.J. Hall, Distribution of polycyclic aromatic hydrocarbons in soils of an arid urban ecosystem, Water Air Soil Pollut., 219 (2011) 473–487.
[37] B.V. Chang, S.W. Chang, S.Y. Yuan, Anaerobic degradation of polycyclic aromatic hydrocarbon in sludge, Adv. Environ. Res., 7 (2003) 623–628.
[38] A. Bernal-Martinez, H. Carrere, D. Patureau, J.P. Delgenes, Combining anaerobic digestion and ozonation to remove PAH from urban sludge, Proc. Biochem., 40 (2005) 3244–3250.
[39] D. Boruszko, Research on the influence of anaerobic stabilization of various dairy sewage sludge on biodegradation of polycyclic aromatic hydrocarbons PAHs with the use of effective microorganisms, Environ. Res., 155 (2017) 344–352.
[40] P. Oleszczuk, Changes of polycyclic aromatic hydrocarbons during composting of sewage sludges with chosen physico-chemical properties and PAHSs content, Chemosphere, 67 (2007) 582–591.
[41] P. Oleszczuk, Influence of different bulking agents on the disappearance of PAHs during sewage sludge composting, Water Air Soil Pollut., 175 (2006) 15–32.
[42] B. Antizar-Ladislao, J.M. Lopez-Real, A.J. Beck, Bioremediation of polycyclic aromatic hydrocarbons-contaminated waste using composting approaches, Crit. Rev. Environ. Sci. Technol., 34 (2004) 249–289.
[43] P. Villar, M. Callejon, E. Alonso, J.C. Jimenez, A. Guiraum, Temporal evolution of polycyclic aromatic hydrocarbons (PAHs) in sludge from wastewater treatment plants: comparison between PAHs and Heavy metals, Chemosphere, 64 (2006) 535–541.
[44] R.A. Kanaly, S. Harayama, Biodegradation of high molecular weight polycyclic aromatic hydrocarbons by bacteria, J. Bacteriol., 182 (2000) 2059–2069.
[45] S. Pérez, M. La Farré, J.M. García, D. Barceló, Occurrence of polycyclic aromatic hydrocarbons in sewage sludge and their contribution to its toxicity in the ToxAlert® 100 bioassay, Chemosphere, 45 (2001) 705–712.
[46] Directive 86/278/EEC, Council directive on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture, Off. J. Eur. Communities, L 181 (1986) 6–12.
[47] MAFF, Review of the Rules for Sewage Sludge Application to Agricultural Land: Soil Fertility Aspects of Potentially Toxic Elements, PB1561, Her Majestry's Stationary Office, London, 1993.
[48] EPA, Environmental Guidelines: Use and Disposal of Biosolids Products, New South Wales Environment Protection Authority, Sydney, 1997.
[49] Regulation of the Minister of Environment from 9th of September 2002 on Standards of the Quality of the Soil and Standards of the Quality of the Earth (Dz.U. 2002 no 165 pos. 1359) (in Polish).
[50] Regulation of the Minister of Environment from 23th of July 2008 on Criteria and the Mode of Evaluating of the State of Underground Waters (Dz.U. 2008 no 143, pos. 896) (in Polish).
[51] Regulation of Minister of Health on the Quality of Water Intended for the Human Consumption (Dz. U. 2010 no 72, pos. 466) (in Polish).