



Concentration of Hydrocarbons in Reject Waters During Aerobic Stabilization of Sewage Sludge

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1. Introduction

Along with the construction of new and modernization of existing sewage treatment plants and the application of highly effective methods of treatment, the amount of produced sewage sludge is gradually increasing (GUS 2018). According to the current legislation, it is required to apply sludge treatment processes leading to highly efficient decomposition of organic substances (Dz. U. Nr 134 poz. 1140, 2002). In order to meet these requirements, excluding process of fermentation, especially in smaller wastewater treatment plants, aerobic stabilization is used. In addition to the easily decomposable and biodegradable compounds, both municipal and industrial sewage sludge contains organic and inorganic contaminants classified as non-easily decomposable and toxic (Włodarczyk-Makuła et. al 2003, Lim et. al 2003, Lawal 2017). Among the organic pollutants polycyclic aromatic hydrocarbons (PAHs) are mentioned. Their presence in sewage sludge has been confirmed in literature and previous ones (Włodarczyk-Makuła et. al 2003, Lawal 2017, Abdel-Shafy 2016). In most publications, PAHs content is determined and converted into a unit of dry matter. The content of these compounds in reject waters was neglected. This problem was taken into account in previous co-authorship studies (Włodarczyk-Makuła 2008, Macherzyński et. al 2014). It has been shown that, despite the fact that a significant number of PAHs present in wastewater is accumulated in sewage sludge, these compounds are also found in reject waters. This is related to the desorption of solid particles, but also to the presence of other organic compounds in wastewater, which increase the solubility of PAHs. Therefore, despite the high affinity and sorption on the surface of solid particles, these compounds are also present in the liquid phase released from the sewage sludge. In addition, they also appear in the film of oils and fats that surround the sewage sludge particles (Dat et. al 2017, Park et. al 2018). The presence of these pollutants in sewage sludge

may prevent the use of sewage sludge in agriculture or for natural purposes (Sadecka et.al 2011). In contrast, high concentrations in liquids can enrich the raw sewage stream with an additional amount of these toxic compounds. Although the applicable legal acts do not specify the permissible PAH content in sewage sludge intended for agricultural use, it is proposed to amend Directive 1986/278/EEC. It will determine the permissible content of PAH (acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b)-fluoranthene, benzo(j)-fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene) at the level of 6 mg/kg of dry mass of sludge when using sewage sludge for soil fertilization (1986/278/EEC). Therefore, processes of processing sewage sludge in which these compounds can be effectively removed are an important research issue. The research described in the literature usually focuses on determining the possibility of degradation of these compounds under anaerobic conditions and in municipal sewage sludge (Lim et. al 2003, Dat et. al 2017, Włodarczyk-Makula 2010, Włodarczyk-Makula et. al 2018). In the literature one can find information that the loss of PAH under aerobic conditions is faster than under anaerobic conditions and the process of biodegradation occurs with greater efficiency (Lim et. al 2003, Petersen et. al 2003). Other studies prove the superiority of sorption over the PAH biodegradation process in biochemical processes (Lim et. al 2003). Usually, however, the studies were carried out using single hydrocarbons or their mixtures added in a known amount to the samples free of PAH. Research on environmental matrices is conducted much less frequently. Investigation into the possibility of removing these compounds from industrial sewage sludge under aerobic processes is also limited. Also previous studies of co-authors concerned the determination of changes in PAH concentrations in sewage sludge and liquids during methane fermentation, under conditions reducing sulphates or nitrates (Macherzyński et. al 2014, Włodarczyk-Makula 2011). The transformations of PAHs in municipal wastewater stabilized chemically and in wastewater in the presence of strong chemical oxidants were also studied (Włodarczyk-Makula 2010b, Kozak et. al 2018, Włodarczyk-Makula et. al 2016). Initial investigations of co-authors in this field were focused on the determination of PAH levels in stabilized sewage sludge from small wastewater treatment plants and in sewage sludge intended for soil fertilization (Włodarczyk-Makula 2010, Włodarczyk-Makula 2010b). The concentrations of low-molecular PAHs in reject water fluids from sewage sludge under aerobic stabilization were also studied (Kozak et. al 2019). The aim of the studies was to follow carcinogenic PAH concentrations in reject water during aerobic stabilization of municipal and industrial sewage sludge.

2. Materials and methods

2.1. Research material

The investigations were conducted using excessive sludge originating from the municipal sewage treatment plant and sewage sludge coming from the coke wastewater treatment plant. Municipal sewage sludge was recycled from secondary settling tanks of the municipal sewage treatment plant of the size exceeding 200,000 PE. In the technological process in the activated sludge bioreactors, denitrification and nitrification are carried out along with the oxidation of organic pollutants. Coking sewage sludge was collected from secondary settling tanks of the biological sewage treatment plant. In the coke wastewater treatment plant PE is not specified, because the installation is not connected to an external network and coking wastewaters are not supplied outside the plant. In this case, activated sludge reactors are applied in which denitrification, nitrification and oxidation of organic compounds are carried out. Characteristics of sewage sludges applied in the experiment is included in Table 1.

Table 1. Physical-chemical properties of sewage sludges

No.	Name	Unit	Sludge-co-king waste-water	Sludge of municipal wastewater	Mixed sewage sludge 3/1(v/v)
1	pH	[-]	7.2	7.5	7.9
2	COD	[mg O ₂ /L]	1200	288	608
3	alkalinity	[mval/L]	-	1.40	2.40
4	moisture	[%]	93.2	97.1	96.1
5	dry mass of sewage sludge	[g/L]	17.54	28.72	34.95

2.2. Technological studies

Oxidation stabilization was carried out under laboratory conditions in open bioreactors with a volume of 14 L. The sewage sludges were continuously aerated ($Q = 60$ L/h to keep the constant excess of oxygen in bioreactors) using fine-bubble aquarium stones made of quartzite sand for 21 days in ambient conditions 18-22°C (average temperature 20°C). The control sample was a municipal sewage sludge, while the second bioreactor was a mixture of municipal sewage sludge and industrial sewage sludge in a 3/1 (v/v). The control of PAH concentration in the reject water samples was carried out before the stabilization process and then three times at 7 day intervals, i.e. after 7, 14 and 21 days of incubation.

2.3. Analytical methodology for PAHs determination

The reject water was separated from the sewage sludge in a laboratory centrifuge at 15,000 rpm for 10 minutes. The preliminary stage of sample preparation for PAH analysis was based on the extraction of organic substances using the liquid-liquid method. This involved adding a mixture of solvents of cyclohexane and dichloromethane in a volume of 5/1 (v/v) into the reject water. Then, samples were shaken on a laboratory shaker for 60 minutes. The separation of the extracts from the samples was carried out using a laboratory separator. The separated extracts were dried using anhydrous aluminum sulphate and purified under vacuum on silica gel. The obtained purified extract was concentrated under a stream of nitrogen to a volume of 2 ml. Subsequently, qualitative and quantitative analysis of PAHs was carried out using a GC-MS gas chromatograph-mass spectrometer. The analysis consists of the injection of 2 μ l of the extract on the DB-5 column (length 30 m, diameter 0.25 mm, thickness 0.25 μ m). The MS 800 spectrophotometer with 70 eV energy ionization was used for detection and identification. Ion selective monitoring (SIM) m/z was used, selecting three representative ions for each PAH. Helium was the carrier gas. The temperature program was 40°C/min and the final temperature was 280°C for 60 minutes. The following compounds were quantified on the chromatograph at the appropriate retention time: 5-ring: benzo(b)fluoranthene BbF, benzo(k)fluoranthene BkF, benzo(a)pyrene BaP, dibenzo(ah)anthracene DahA and 6-ring: benzo(ghi)perylene BghiP, indeno(1,2,3-c,d) pyrene IP. The analyzed hydrocarbons are on the list of priority substances of the US EPA, and according to the results of toxicological tests show a carcinogenic effect on indicator organisms.

3. Results and discussion

The total concentration of hydrocarbons studied in the reject water separated from the sewage sludge placed in the control reactor containing sewage sludge from municipal sewage (C) before the stabilization process was equal to 23 μ g/L. Whereas, in the reject water originating from the reactor containing the mixture of sewage sludge (M), the PAH concentration was on the level of 29 μ g/L. Concentration of PAHs in rejected water separated from coke wastewater was not determined.

3.1. Changes of concentration of 5-ring PAHs

Figures 1 and 2 present changes in the concentration of 5-ring hydrocarbons in the reject water during aerobic stabilization of sewage sludge.

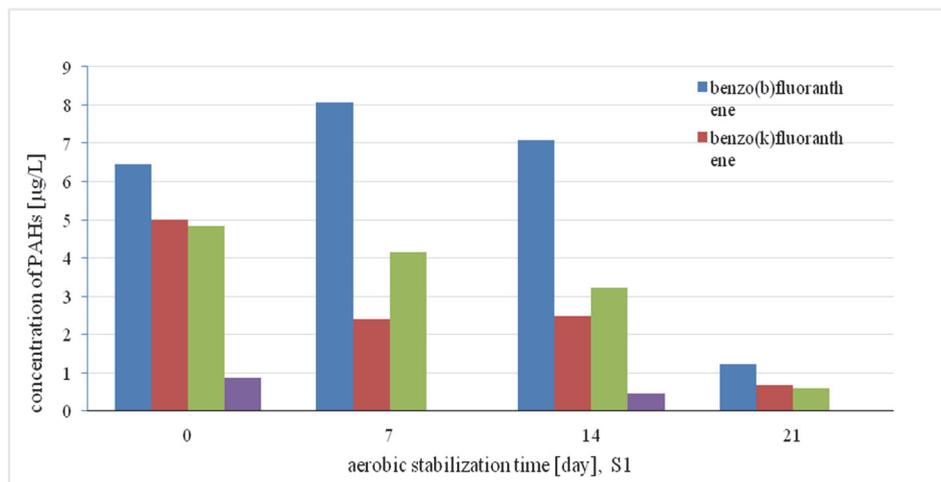


Fig. 1. Concentration of 5-ring PAHs in reject water during aerobic stabilization (C- control sample)

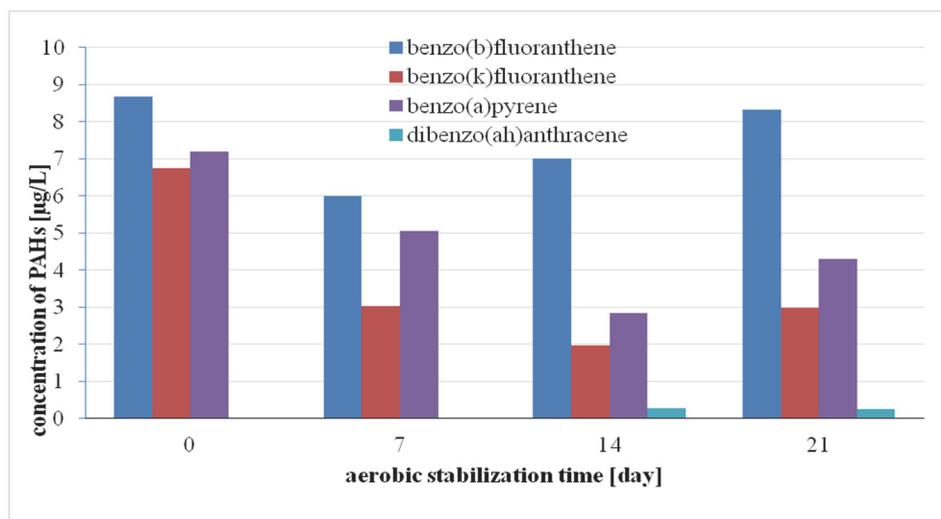


Fig. 2. Concentration of 5-ring PAHs in reject water during aerobic stabilization of mixture sewage sludge (municipal and coke sewage sludge)

The initial concentration of 5-ring hydrocarbons in the reject water coming from the municipal sludge reactor was 17.1 $\mu\text{g/L}$, and in the reject water taken from the mixed-bed reactor – 22.7 $\mu\text{g/L}$. Control of the concentration of these compounds during the process showed that PAH concentrations fluctuated, but the final values were lower than the initial ones. The effectiveness of PAH removal in the reject water from the control sludge was at the level of 73%, and in the reject water from the mixed sludge – 31%. Thus, along with the coke oven sludge, some additional PAHs were introduced into the municipal sludge, which inhibited the removal of these compounds during oxygenation. The initial concentration of PAHs in mixed sewage sludge was 33% higher than in control and the final concentration was almost 3 times higher.

3.2. Changes of concentration of 6-ring PAHs

Figures 3 and 4 show the changes in the concentration of 6-ring hydrocarbons, during the stabilization process of the control sewage sludges and mixed sewage sludges. The initial concentration of 6-ring compounds was similar in both liquids and was 5.9 $\mu\text{g/L}$ and 6.4 $\mu\text{g/L}$ respectively from control and from mixed sewage sludges. During 21 days of incubation under aerobic conditions, a gradual decrease in the concentration of these compounds was noted, and the final contents was lower than the initial one by 90 and 64%, respectively in the case of control and mixed sludge. Summarizing the course of changes in PAH concentrations present in reject waters, it can be concluded that the loss of 6-ring compounds was greater than 5-ring ones, although they are more easily sorbed, as evidenced by the octanol/water partition coefficient and their solubility in water is lower.

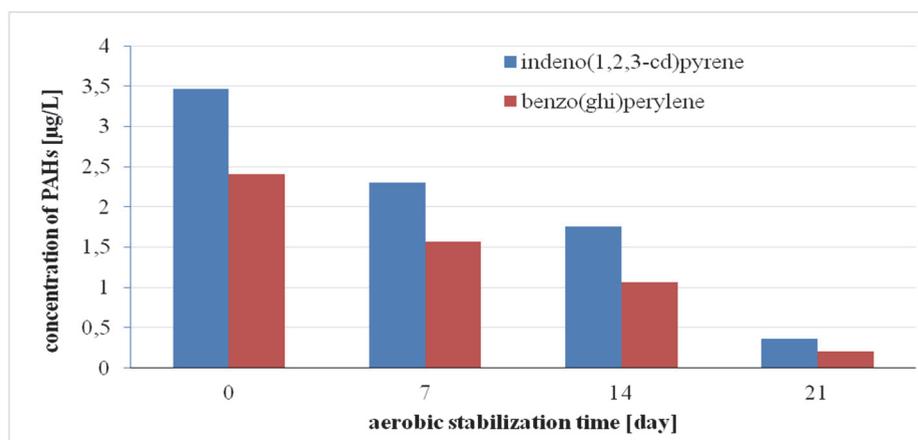


Fig. 3. Concentration of 6-ring PAHs in reject water during aerobic stabilization (C- control sample)

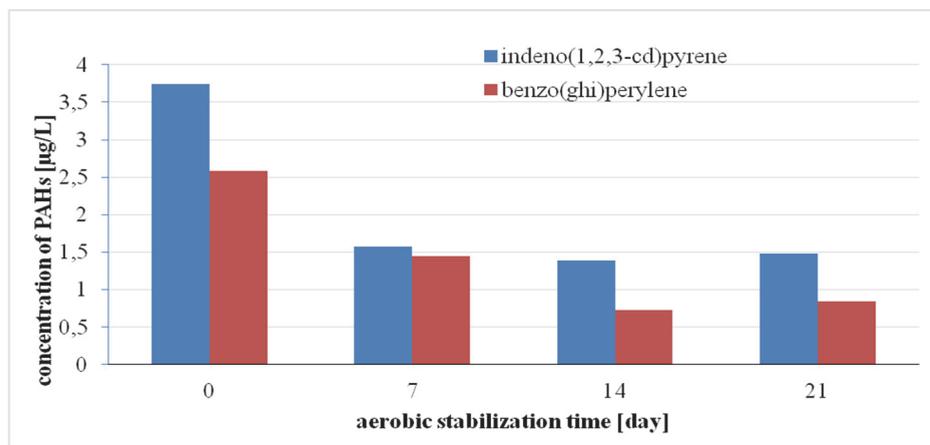


Fig. 4. Concentration of 6-ring of PAHs in reject water during aerobic stabilization of mixture sewage sludge (municipal and coke sewage sludge)

3.3. Summary

The loss of PAHs during aeration of sewage sludge consists of several processes that occur simultaneously. This applies to volatilization, sorption and desorption, reactions with other liquid components as well as biodegradation. Determining the mutual proportions between these processes is not easy and requires further research. Difficulties result from the complexity of processes and ensuring a permanent matrix composition. Sewage sludge is a heterogeneous material with a diverse composition. While compounds with high vapor pressure can escape from the liquid during intensive aeration, heavier hydrocarbons are usually permanently bound to solid particles. They may also occur in the form absorbed by the cells of microorganisms (Traczewska 2003). Literature data indicate that desorption of these compounds from the solid phase and their release into the liquid after the breakdown of cells is possible. Therefore, in monitoring studies involving concentration control, periodic variations in the concentration of PAHs during oxygenation were observed. Such fluctuations were noted in liquids from mixed sewage sludges, which may indicate the presence of microorganisms in industrial sludges containing PAHs inside cells. These sewage sludges were separated from coke wastewater, which contain much higher amounts of PAH than municipal sewage sludge. These wastewater is treated in a sewage treatment plant with activated sludge and it is possible that during this process sorption of PAHs takes place not only on the particles of sludge forming slurries, but also in the cells of microorganisms. Literature and previous studies indicate that microorganisms that were previously exposed to the presence of these compounds are able to decompose them. This ability results from the adaptation of the enzyme apparatus

to the metabolization or transformation of co-metabolic PAHs. In the described studies on the aerobic stabilization of coke deposits with municipal sewage, a significant loss of carcinogenic PAHs from the reject water was demonstrated. Similar results were obtained in studies on low-ring hydrocarbons. However, different results were noted in the fermentation process, where it was shown that hydrocarbons can be released into the reject water during sewage sludge incubation under anaerobic conditions. However, confirmation of the intermetallic phenomena of PAHs in sewage sludge undergoing processing requires continued testing under controlled conditions that allow comparison of results.

4. Conclusions

Based on the obtained results, the following conclusions can be formulated in the assumed experimental conditions:

- Control of hydrocarbon concentration during the aerobic stabilization process of sewage sludge showed gradual decrease of the total concentration of these compounds in reject water, which after 21 days of incubation were lower than the initial ones by 78% and 38% in control reject water sample and separated from the sewage sludge mixture, respectively.
- In the reject water originating from municipal sewage sludge, the loss of hydrocarbons grouped by the number of rings in the molecule was in the range of 73-90%, whereas in the reject water separated from the mixture of municipal sludge with coke plants from 31 to 64%.
- In the process of aerobic stabilization of industrial sewage sludge along with municipal sewage sludge, the effective removal of carcinogenic PAH from the reject water takes place.

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Abstract

The article presents the concentrations of selected polycyclic aromatic hydrocarbons (PAHs) in reject water during aerobic stabilization of sewage sludge process. The investigations were carried out in parallel for two samples i.e. for sewage sludge samples coming from a treatment of municipal wastewater treatment plant (control sample) and for mixture of municipal and industrial sludge. The aerobic stabilization process was carried out for 21 days. The concentration of 5-ring and 6-ring PAHs was determined at the beginning of the experiment (day 0) and in seven-day intervals: after 7, 14 and 21 days, respectively. The initial contents of PAHs was equal to 23 $\mu\text{g/L}$ and 29.1 $\mu\text{g/L}$ respectively in reject water from municipal and mixture sludge. During aerobic stabilization process the decrease in the concentration of studied PAHs in reject water was observed. At the end of carrying the aerobic stabilization process the decrease of the total concentration of PAHs achieved 78% in municipal reject water, whereas in coke reject water reached the value of 38%, respectively.

Keywords:

PAHs, reject water, municipal sewage sludge, coking sewage sludge, aerobic stabilization

**Stężenie WWA w cieczach nadosadowych
w procesie stabilizacji tlenowej osadów ściekowych****Streszczenie**

W artykule przedstawiono stężenia wybranych wielopierścieniowych węglodorów aromatycznych WWA w cieczach nadosadowych w procesie stabilizacji tlenowej osadów ściekowych. Badania prowadzono z wykorzystaniem osadów powstających podczas oczyszczania ścieków komunalnych oraz ścieków koksowniczych. Badania technologiczne prowadzono równolegle dla dwóch próbek, tzn. osadów komunalnych (próbka kontrolna) oraz mieszaniny osadów komunalnych z przemysłowymi. Proces stabilizacji tlenowej był prowadzony przez 21 dób. Stężenie 5- oraz 6- pierścieniowych WWA oznaczano na początku badań, dwukrotnie podczas trwania procesu stabilizacji oraz po upływie 21 dób. Początkowe stężenie WWA wynosiło 23 $\mu\text{g/L}$ i 29,1 $\mu\text{g/L}$ odpowiednio w cieczach nadosadowych z osadów komunalnych i z osadów mieszanych. Podczas stabilizacji tlenowej osadów odnotowano spadek stężenia WWA w cieczach nadosadowych. Po zakończeniu procesu stabilizacji tlenowej osadów spadek sumarycznej ilości badanych WWA był na poziomie 78% w przypadku osadów komunalnych i 38% – w przypadku osadów mieszanych.

Słowa kluczowe:

WWA, cieczy nadosadowe, osady ściekowe komunalne, osady koksownicze, stabilizacja tlenowa