

DEGRADATION OF PAHS IN SEWAGE SLUDGE DURING FERMENTATION PROCESS

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In this study, the changes of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge and supernatants during anaerobic digestion under sulphate-reducing conditions were investigated. Na_2SO_4 were added to the mixed sludge in order to obtain sulphate reduction conditions. Abiotic losses of PAHs were observed simultaneously. PAHs concentration was determined before incubation and after 21 days. PAHs were determined both in sewage sludge and in supernatants pararely. Quantification of 16 PAHs (EPA) was carried out by GC-MS. The initial concentration of 16PAHs in sewage sludge was $2221\mu\text{g}/\text{kg.s.m}$. In supernatants the initial concentration was $4.8\mu\text{g}/\text{L}$. The concentration of 16 PAHs in sewage sludge was reduced by 43% and in supernatants by 38% on average under sulphate-reducing conditions.

Keywords: sewage sludge, supernatants, 16 PAHs, sulphate reducing condition.

1. INTRODUCTION

Effectiveness of the degradation depends on the presence of proper microorganisms and environment conditions (temperature, redox potential, pH). In the wastewater treatment plant PAHs mainly absorb onto solid particles (sewage sludge) [1,5,13]. The presence of PAHs is also confirmed in the raw sewage sludges as well as in the digested sludges [3,6,9,11]. The available investigations into removal of PAHs from sewage sludges in the process of digestion are not completed [1,8,10]. The results of investigations described in the literature are not unambiguous and Heterogeneity of sewage sludge makes difficulties in comparison of the results. Therefore, not only the results in which

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the increase of efficiency degradation of PAHs in the presence of sulphates was obtained are available but the studies with diverse results as well. It was proved in the former investigations that supernatants may contain the significant load of PAHs [14]. Therefore, it is necessary to determine simultaneously concentration of PAHs in solid and in liquid phase. The aim of the investigations was to compare the changes in the concentration of PAHs in sewage sludges and supernatants during fermentation process conducted under sulphate-reducing conditions. At the same time, the experiment was carried out with keeping sewage sludge samples without biological activity of the microorganisms.

2. MATERIALS AND METHODS

2.1. Materials

The experiment were carried out using sludges originating from a municipal treatment plant. Two portions of sewage sludge were used in the studies: digested sludge coming from the closed digestion chamber (inoculums) and raw sludge originating from a primary settling tank. The samples of raw sludge and digested sludge were mixed (1:8 v/v). The mixture of sewage sludges was primary analyzed by determining physical-chemical properties and used for fermentation process. Level of mineralization of organic compounds was followed by determining: solid residue in the sewage sludge and volatile fatty acids content, alkalinity, acidity, pH in the supernatants. Sludge samples were centrifuged in order to separate solid phase from liquid phase (supernatants). The analyses were performed according to applied procedure [12]. Measurements were carried out at the beginning of sewage sludge incubation and after 21 days of digestion. Before fermentation process in raw and digested mixture of sewage sludge concentration of total suspended solids TSS were 40 mg L⁻¹. After fermentation process stabilized sludge had high water contents of 98% (concentration of total suspended solids was 20 mg L⁻¹) and low contents of organic substrate matter (40%). The pH was in the range of 7.5 - 7.8. The decrease in the content of volatile fatty acids 150 mg L⁻¹ was observed. Redox potential was in the range of 260-285mV after fermentation process.

2.2. Experimental procedure

The following samples were prepared for the investigations into degradation of PAHs in sewage sludges:

- the control sewage sludge (biotic samples)
- sludge sample with added sodium sulphate (Na₂SO₄) in the amount of 4g/L (required to reduction of sulphates – intensification of growing of microorganisms),

- sludge with sodium azide (NaN_3) [4,8] in order to deactivate the microorganisms (abiotic samples),

The process of digestion was carried out in bioreactors. Bioreactors were kept in thermostat at 37°C for 21 days. The pressure of biogas produced during digestion of biotic sewage sludges was measured every day. Every-day control of biogas production is typical measurement of profile of fermentation process. The PAHs determination were carried out at the beginning of experiment and after 21 days. PAHs were determined in sludge samples as well as supernatants parallelly.

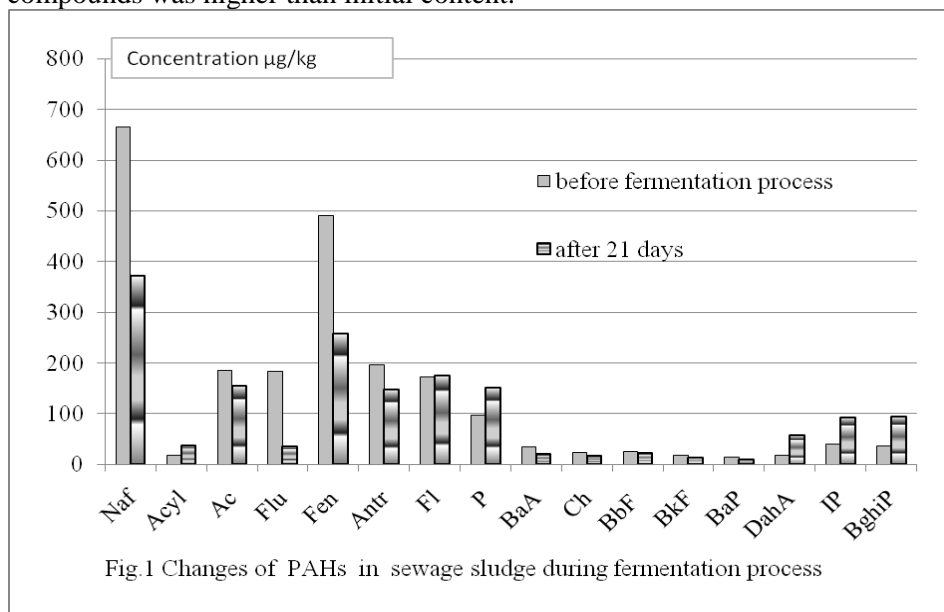
2.3. PAHs analysis

PAHs were determined using gas chromatography - mass spectrometry. Preparation of samples consisted of the extraction by the mixture of solvents [7,14,15]. Extraction process for solid phase with cyclohexane and chloromethane mixture (in the ratio 5: 1 (v/v)) as a solvents was carried out in ultrasonic bath. The extraction process for liquid phase with methanol, cyclohexane and dichloromethane mixture (in the ratio 25:5:1 (v/v)) as a solvents was carried out in horizontal shaker. Prepared extracts (from solid and liquid samples) were concentrated under nitrogen steam and were purified using SPE columns packed with silica gel under vacuum conditions. Subsequently extracts were concentrated again and then analyzed using gas chromatography method. Qualitative and quantitative analysis was done using Fisons gas chromatograph (model CGC8000/MS800). 16 PAHs were determined. In order to verify the applied procedure of preparation of sludge samples and supernatants the recovery of standard mixture was also made. Average PAHs recoveries from solid phase (sewage sludge) ranged from 47 to 94%. The recoveries of analyzed organic compounds from liquid phase (supernatants) were in the range of 46 to 108%. The recoveries obtained in the study correspond to data found in literature (0–128%) for complex organic matrixes [9,15].

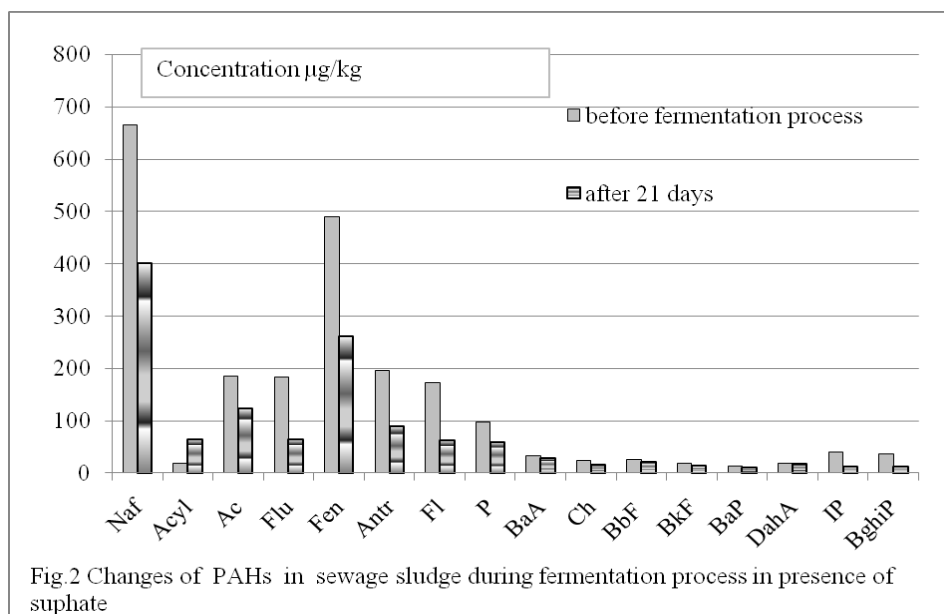
3. RESULTS

The initial concentration of total 16 PAHs in sludge was equal to $2221\mu\text{g}/\text{kg}$ d.m. The concentration of 3-ring hydrocarbons was the highest and these compounds amounted to 48% of the total contents of PAHs ($1074\mu\text{g}/\text{kg}$ of dry mass). Changes in the individual concentration of hydrocarbons in sludges in biotic control samples before digestion and after 21 days are presented in Figure 1. The concentration of 4-, 5-, and 6-rings of hydrocarbons in the control sludge samples increased. In the former studies the higher concentrations of PAHs in the primary phase of digestion were already found especially [14]. In the final

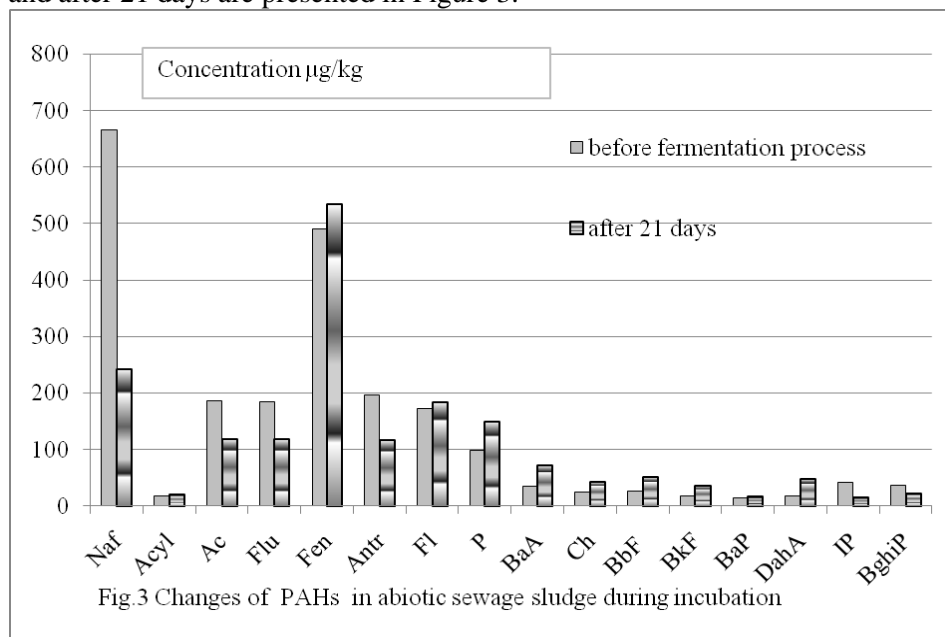
step of the investigations the total concentrations of 16 PAHs decreased to the amount of $1665\mu\text{g}/\text{kg.d.m}$ (75% of initial content). The significant decrease occurred in naphthalene and 3-rings of hydrocarbons. Concentration of other compounds was higher than initial content.



Changes in the total concentration of hydrocarbons in sludges amended with sodium sulphate before digestion and after 21 days are given in Figure 2.



In sludge samples with added Na_2SO_4 as an acceptor of electrons the degradation of PAHs was also observed. After 21 days of incubation the total concentration was lower than the initial contents of 43%. Changes in the total concentration of hydrocarbons in sludges in abiotic samples before digestion and after 21 days are presented in Figure 3.



In the sludge samples with the inhibited activity of microorganisms the final total concentration of 16 PAHs was equal to $1781\mu\text{g}/\text{kg.d.m.}$ and was lower than the initial content. The abiotic losses may be related to the evaporation, sorption as well as reactions with other compounds of sewage sludges.

The initial concentration of 16 PAHs in supernatants was $4.8\mu\text{g}/\text{L}$ on average. The concentration of naphthalene and 3-rings of PAHs were the highest and these compounds amounted to 60% of the 16 compounds. Changes in the concentration of hydrocarbons in supernatants during the process of sludge digestion are given in Figure 4. In the control sample (biotic sample) almost 1.6-times higher concentration of hydrocarbons was found after 21 days of incubation. As it was proved in the former studies hydrocarbons may have released to the water phase during fermentation process. It was due to the fact of both decomposition of complex polymers and bacteriolysis. Changes in the concentration of hydrocarbons in supernatants in the presence of sodium sulphate during the process of sludge fermentation are given in Figure 5.

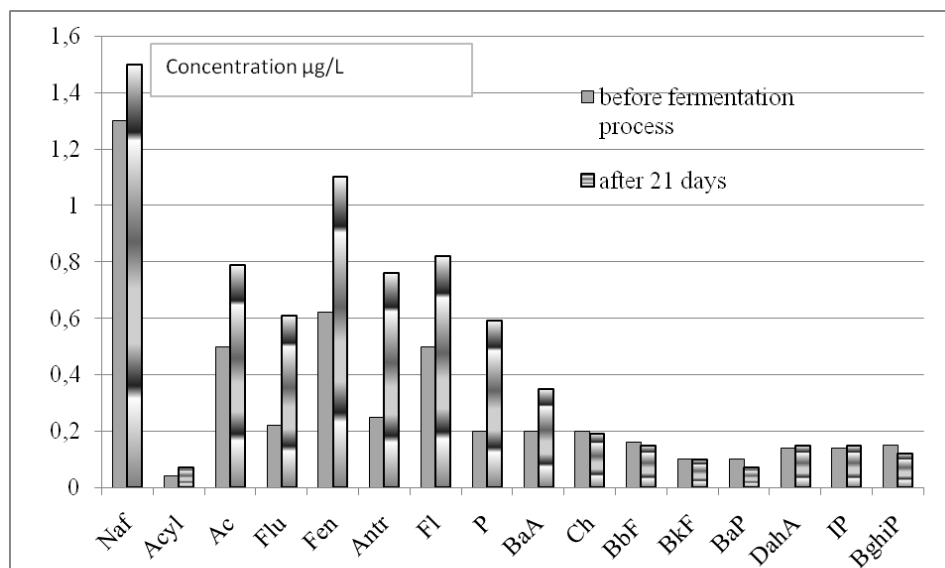


Fig.4 Changes of PAHs in supernatants during fermentation process

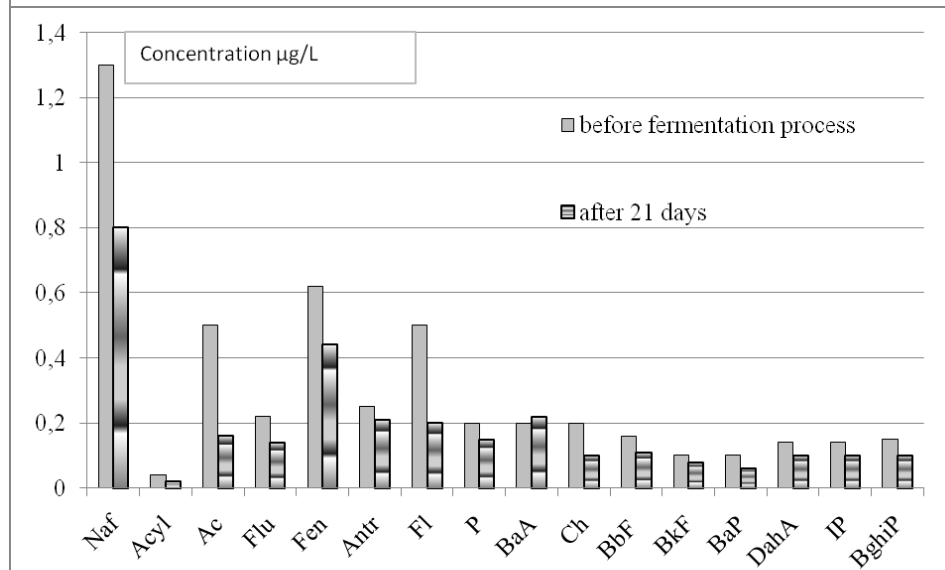
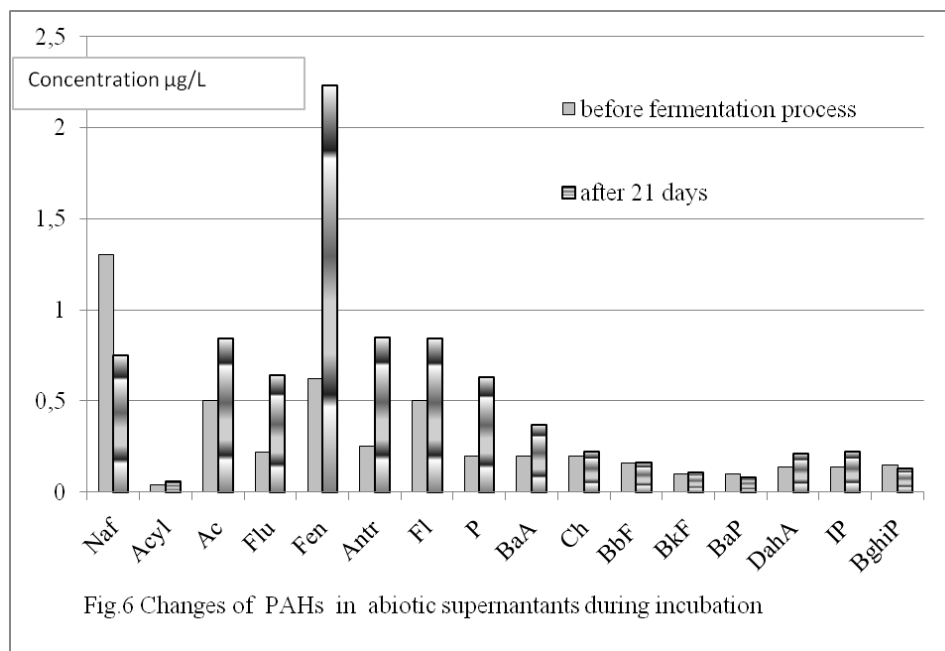


Fig.5 Changes of PAHs in supernatants during fermentation process in presence of sulphate

The level of degradation of 3-ring hydrocarbons in supernatants during the process of digestion was the highest. The final concentration of these compounds was equal to 0.9 µg/L and was lower than in control samples. In Figure 6 changes of PAHs in abiotic samples of supernatants are given.



At the end of experiment the total concentration of 3- and 4-rings of hydrocarbons was higher than initial concentration. It was due to the fact of released analysed compounds during deactivate the microorganisms. At the end of fermentation process concentration of naphthalene was lower than initial content. The concentration of 5- and 6-rings of hydracarbons were in the same level compared to initial concentration.

4. CONCLUSIONS

The total concentration of 16 PAHs in sewage sludge was reduced by 43% on average under sulphate-reducing. In the control samples the final concentration of PAHs was lower than initial content of 25%. Abiotic loses of PAHs was equal 20% compared to initial content. It can be concluded that assuring conditions reducing sulphates allowed to increase the efficiency of degradation of PAHs (especially 3-rings of PAHs). The most of analysed hydrocarbons in liquid phase (supernatants) reduced under sulphate-reducing conditions. The results of these experiment indicates of the possibility of biodegradation of these compounds both in sewage sludge and in supernatant under sulphate-reducing conditions.

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DEGRADACJA WWA W OSADACH PODCZAS FERMENTACJI

Streszczenie

Określono zmiany ilościowe WWA w osadach ściekowych i cieczach nadosadowych podczas fermentacji osadów w warunkach redukcji siarczanów. Warunki te zapewniono przez dodatek Na_2SO_4 . Równolegle określono zmiany ilościowe WWA w osadach po uprzedniej dezaktywacji mikroorganizmów za pomocą azydru sodu. Wszystkie próbki były inkubowane w termostacie w temperaturze 37°C w ciemności. WWA oznaczano trzykrotnie: przed inkubacją oraz po 21 dobach. Ilościową analizę 16 WWA - EPA prowadzono z wykorzystaniem zestawu GC-MS. Oznaczano WWA równolegle w osadach (fazie stałej) oraz w cieczach nadosadowych. Zawartość początkowa WWA w osadach wynosiła $2221\mu\text{g}/\text{kg.s.m}$, natomiast w cieczach nadosadowych stężenie sumaryczne badanych węglowodorów było na poziomie $4.8\mu\text{g}/\text{L}$. Po 21 dobach fermentacji odnotowano spadek sumarycznego stężenia WWA o 43% w osadach inkubowanych w warunkach redukcji siarczanów i o 38% - w cieczach nadosadowych. W osadach kontrolnych spadek sumarycznej zawartości WWA wynosił 25%, natomiast w osadach abiotycznych - 20%. Najbardziej trwale były węglowodory 5-pierścieniowe, których ubytek nie przekraczał 15%.