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Comparison of parameters co-fermentation process of municipal sewage sludge with excess sewage sludge from treated coking wastewater

Porównanie parametrów procesu kofermentacji mieszaniny osadów komunalnych z nadmiernymi osadami z oczyszczania ścieków koksowniczych

Abstract
The study presents results concerning changes of physicochemical properties and biogas production during the co-digestion process. The sample constituted a mixture of raw and excess sludge that was inoculated and fermented. The sample is the abovementioned mixture with an addition of excess sewage. In the assumed test, the conditions of technological parameters of sewage sludge fermentation and its mixtures with sewage sludge coke did not differ from each other by more than 25%. Therefore, excess sewage sludge from treated coking wastewater can be neutralized in the process of fermentation along with municipal sewage sludge provided a constant quality-quantitative control of sewage sludge and procedural parameters.

Keywords: biogas, co-fermentation, sewage sludge, sewage sludge from treated coking wastewater

Streszczenie
W pracy przedstawiono wyniki badań dotyczące zmian właściwości fizyczno-chemicznych oraz produkcji biogazu podczas procesu kofermentacji. Próbką kontrolną stanowiły osady komunalne zaszczerbione przefermentowanymi. Próbka badana to mieszanina komunalnych z dodatkiem nadmiernych osadów koksowniczych. W przyjętych warunkach badań wartości parametrów technologicznych fermentacji osadów komunalnych oraz ich mieszaniny z osadami koksowniczymi nie różniły się od siebie więcej niż o 25%. Zatem osady koksownicze mogą być unieszkodliwiane w procesie fermentacji wraz z osadami komunalnymi pod warunkiem stałej kontroli jakościowo-ilościowej osadów i parametrów technologicznych.

Słowa kluczowe: biogaz, kofermentacja, osady ściekowe, osady ze ścieków koksowniczych
1. Introduction

The anaerobic biological stabilization is currently the most common process of neutralizing sewage sludge in large wastewater treatment plants. Mineralization of biodegradable organic substrates is followed by an improvement of the drainage efficiency and a decrease of pathogenic organisms. The composition of fermented substrate depends on the quantity of the produced biogas and its composition. The content of methane in biogas varies from 50 up to 80% and depends on the content of proteins, carbohydrates and fats in sewage sludge subjected to the fermentation. In addition to the type of substrate, the fermentation process also depends on temperature, pH, process duration, presence of toxic substances, substratum load chambers, concentration of easily digestible components for micro-organisms and appropriate conditions of their development [1, 2]. Combustion of biogas allows for energy recovery. Therefore, produced biogas is used above all for the needs of covering demand for thermal energy and electricity. It is used for the needs of sewage treatment plants, such as heating digesters or powering devices for mixing and aerating [3, 4]. Taking into account the need to develop effective treatment methods of excess sewage sludge from treated coking wastewater, studies on the co-fermentation of this sewage sludge with municipal sewage sludge were conducted. An aim of these studies was to assess the effect of excess sewage sludge from treated coking wastewater on the technological parameters of fermentation, mineralization degree of organic compounds and biogas production.

2. Experimental procedure

2.1. Fermentation process

Sewage sludge coming from municipal sewage treatment plant and sewage sludge from coking sewer plant were used in the study. Primary sewage sludge and excess sewage sludge as well as the fermented sewage sludge were collected. Primary sewage sludge and excess sewage sludge from a primary and a secondary settle tank were collected, respectively. Fermented sewage sludge was collected from the fermentation chamber. The samples were collected as temporary. In the coking wastewater treatment plant, the sewage treatment is performed by the processes of denitrification and nitrification. The sewage flows through a gravel filter, tar separator, and desorption column before it is fed to the biological part of the treatment plant and is directed to the averaging tank. The excess sewage sludge with treatment wastewater coking was sampled as temporary (from recycled tank of sewage sludge). The anaerobic digestion (fermentation) tests were conducted in bioreactors fitted with nozzles intended for measuring biogas pressure. The following mixtures were prepared for the fermentation studies:

▶ municipal sewage sludge (mixture of primary sewage sludge and excess sewage sludge with the addition of fermented sewage sludge (1:1.5 v/v) as an inoculum) – control sample (K);
▶ municipal sewage sludge amended with excess sewage sludge from treated coking wastewater (10:1 v/v) – sample (B).
The sewage sludge mixtures were incubated for 16 days with no access to light in a thermostat at a constant temperature of 37 ± 2°C. The fermentation process was carried out in glass reactors with a volume of 1 L with a single power supply. The volume of sewage sludge was 0.7 L. The process was carried out in 6 reactors with the same mixture of sewage sludge. After 4, 8, 12 and 16 days, one reactor was eliminated and a necessary analysis was conducted. The process was completed in 16 days because the amount of secreted biogas was difficult to measure with a manometer.

2.2. Analytical methodology

In order to determine the follow of the digestion process, the selected physical-chemical properties of the sewage sludge were determined. The total suspended solids (TSS) and fixed suspended solids (FSS) of the sewage sludge before and after 4, 8, 12 and 16 days of incubation were analyzed. In the supernatants, the pH, alkalinity, chemical oxygen demand (DCOD) and volatile fatty acids (VFA) were determined. The above mentioned analyze were carried out before of the digestion process and after 4, 8, 12 and 16 days of samples incubation. The determinations were made in accordance with the methodology specified by Hermanowicz [5].

During the process, the atmospheric pressure and biogas pressure using the manometer in 24-hour intervals were monitored. The daily biogas volume using the Boyle-Mariott was calculated. The methane and carbon dioxide contents in biogas were determined four times. The analysis of biogas composition was performed using a gas chromatograph with a thermal-conduction detector (GC-TCD) (model Agilent GC 6890).

3. Results and discussion

3.1. Changes in the physico-chemical properties of sewage sludge during the fermentation process

The results of the physical-chemical analysis of sewage sludge during 16 days of stabilization are shown in Table 1.

In test sludge (K), there was a decrease in the contents of the total suspended solids by 21%. The share of organic matter in sludge after 16 days of incubation constituted 54% of the dry mass. Decomposition degree of organic matter was 29%. The contents of organic compounds determined as DCOD in supernatants from municipal sewage sludge (K) decreased by 88%.

In a mixture of municipal sewage sludge with industrial, the contents of dry matter before co-digestion process was 18.4 g/L. After the co-digestion process, there was a decrease in dry matter content by 18% (Table 2). Percentage of organic matter in fermented sludge was 54%. Decomposition degree of organic matter was 23%. The loss of organic compounds expressed with DCOD in supernatants was at a level of 81%.
Table 1. Changes in the physico-chemical properties of sewage sludge during the fermentation process – control sample

| Ratio                          | Unit         | Process time, day |
|--------------------------------|--------------|-------------------|
|                                |              | 0                 | 4     | 8     | 12    | 16    |
| pH                             | –            | 7                 | 7.6   | 7.6   | 7.7   | 7.8   |
| DCOD (mg O₂/L)                 |              | 970               | 660   | 320   | 241   | 110   |
| Total suspended solids (TSS)    | g/L          | 18.9              | 17.6  | 16.9  | 16.2  | 15.0  |
| Fixed suspended solids (FSS)    | g/L          | 7.5               | 7.2   | 7.1   | 7.1   | 6.9   |
|                                | %            | 40                | 41    | 42    | 44    | 46    |
| Volatile suspended solids (VSS) | g/L          | 11.4              | 10.4  | 9.7   | 9.1   | 8.1   |
|                                | %            | 60                | 59    | 58    | 56    | 54    |

Table 2. Changes in the physico-chemical properties of sewage sludge during the co-fermentation process

| Ratio                          | Unit         | Process time, day |
|--------------------------------|--------------|-------------------|
|                                |              | 0                 | 4     | 8     | 12    | 16    |
| pH                             | –            | 7.3               | 7.6   | 7.7   | 7.8   | 7.6   |
| DCOD (mg O₂/L)                 |              | 1300              | 940   | 400   | 390   | 240   |
| Total suspended solids (TSS)    | g/L          | 18.4              | 16.4  | 16.2  | 16.0  | 15.1  |
| Fixed suspended solids (FSS)    | g/L          | 7.9               | 7.5   | 7.4   | 7.2   | 7.0   |
|                                | %            | 43                | 46    | 46    | 45    | 46    |
| Volatile suspended solids (VSS) | g/L          | 10.5              | 8.9   | 8.8   | 8.8   | 8.1   |
|                                | %            | 57                | 54    | 54    | 55    | 54    |

The VFA ratio to alkalinity was shown in Figure 1. The alkalinity after fermentation, determined in supernatants, was 3.55 and 3.50 g CaCO₃/L appropriately in the K and the B sample. The ratio of volatile fatty acids to alkalinity, decreased during the process, and after the process in test sludge, it was 0.11. In a mixture of municipal sewage sludge with excess sewage sludge from treated coking wastewater, the value of the VFA quotient to alkalinity did not exceed 0.90.

![Fig. 1. The ratio of VFA to alkalinity](image-url)
3.2. Biogas and methane production during the fermentation and co-fermentation processes

The amount of biogas produced during each day of fermentation was presented in Table 3. In municipal sewage sludge (K), the highest biogas production was achieved on the 3rd day (1.4 L), whereas in the mixture of municipal sewage sludge with excess sewage sludge from treated coking wastewater, it was achieved on the 4th day and it was 1.2 L. This might show that there is a temporary interruption of the co-digestion process (elongated lag-phase) in the presence of industrial sewage sludge. Total biogas production ranged from 0.94 L/g VSS (1.0 L) up to 1.03 L/g VSS (11.7 L) and the average methane content in biogas was between 61–69%. The amount of methane in relation to the contents of test sludge (K) was at the level of 8.1 L. About 28% less (5.9 L) compared with test sludge was received during co-digestion of mixtures of municipal sewage sludge with excess sewage sludge from treated coking wastewater.

Table 3. Daily as well as total biogas and methane production during the fermentation and co-fermentation processes

| Sewage sludge/Unit | Process time, day |
|--------------------|------------------|
|                    | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    |
| K                  | 1.3  | 2.7  | 4.1  | 5.4  | 6.4  | 7.3  | 8.2  | 8.9  |
| Σ L a)             | 1.0  | 2.0  | 3.0  | 4.0  | 4.7  | 5.3  | 5.9  | 6.4  |

| Process time, day |
|------------------|
| 9    | 10   | 11   | 12   | 13   | 14   | 15   | 16   |
| Σ L a)         | 9.5  | 10.0 | 10.6 | 10.9 | 11.1 | 11.4 | 11.6 | 11.7 |
| Σ L b)         | 6.8  | 7.1  | 7.4  | 7.6  | 7.8  | 7.9  | 8.0  | 8.1  |

| B                  | 1.0  | 2.1  | 3.2  | 4.4  | 5.3  | 6.1  | 6.8  | 7.3  |
| Σ L a)             | 0.6  | 1.2  | 1.9  | 2.6  | 3.1  | 3.5  | 3.9  | 4.3  |

| Process time, day |
|------------------|
| 9    | 10   | 11   | 12   | 13   | 14   | 15   | 16   |
| Σ L a)         | 7.8  | 8.3  | 8.8  | 9.1  | 9.3  | 9.6  | 9.8  | 10.0 |
| Σ L b)         | 4.6  | 4.9  | 5.2  | 5.4  | 5.5  | 5.6  | 5.8  | 5.9  |

a) total production of biogas
b) total production of methane
Basic co-digestion parameters of municipal sewage sludge with excess sewage sludge from treated coking wastewater were presented in Table 4. The load of digesters was in a range of 0.40–0.55 g VSS/L d. The difference between maximum methane production ($V_{\text{max}}$) and the actual obtained value after 16 days was determined during fermentation. Its value corresponded numerically to the value of methane potential, residual in sewage sludge and changed in a range from 1.0 up to 1.5 L. Favorable results were obtained during co-digestion of municipal sewage sludge, where untapped methane potential constituted 10%. In studies conducted by Montusiewicz, the untapped biogas potential in sewage sludge ranged from 11.6 up to 14.1% [6].

During the fermentation process of municipal sewage sludge, as well as with excess sewage sludge from treated coking wastewater, the constant rate of generated methane ranged from 0.111 up to 0.147 d$^{-1}$. In studies conducted by Myszograj, constant rates for excess sludge ranged from 0.179 up to 0.203 d$^{-1}$, and for bio-fraction of municipal waste, they ranged from 0.077 up to 0.137 d$^{-1}$ [7]. Both during co-digestion of municipal sewage sludge with excess sewage sludge from treated coking wastewater or with bio-fraction of municipal sewage sludge, the constant rates were on the same level.

### Table 4. Parameters and the energy balance of the co-fermentation process

| Parameters                                           | Unit   | K    | B    |
|------------------------------------------------------|--------|------|------|
| Load of organic compounds in the fermentation chambers | g VSS/L d | 0.55 | 0.40 |
| Percentage of the organic substance decomposition     | %      | 29   | 23   |
| Production of biogas during digestion process         |        |      |      |
|                                                      | L      | 11.7 | 10.0 |
|                                                      | L/g TSS | 0.62 | 0.54 |
|                                                      | L/g VSS | 1.03 | 0.94 |
| Content of methane in biogas on average               | %      | 61   | 63   |
| Production of methane during digestion process        |        |      |      |
|                                                      | L/g TSS | 0.43 | 0.39 |
|                                                      | L/g VSS | 0.71 | 0.68 |
| The maximal (theoretical) methane production ($V_{\text{max}}$) |        |      |      |
|                                                      | L      | 9.1  | 7.4  |
|                                                      | L/g TSS | 0.48 | 0.40 |
|                                                      | L/g VSS | 0.80 | 0.70 |
| The potential of methane remaining in sewage sludge   | %      | 10   | 20   |
| Constant rate of the methane production, k            | d$^{-1}$ | 0.147 | 0.111 |
| Nonlinear estimation error                            | L      | 0.14 | 0.16 |
| Coefficient of determination, $R^2$                   | –      | 0.995 | 0.975 |
In the assumed test conditions of technological parameters of sewage sludge fermentation and its mixtures with sewage sludge, cokes did not differ from each other by more than 25% (total biogas productions, decomposition degree of organic matter, changes in the content of organic compounds expressed with DCOD, loss of dry matter and methane content in biogas).

Literature data show that, during mesophilic fermentation, the VFA concentration should be in the range from 50 to 500 mg CH$_3$COOH/L; alkalinity should be from 3.00 to 5.00 g CaCO$_3$/L, while the reduction in COD should be within the limits of 65–85%, and pH value should be within the limits of 7.2–8.2 [8, 9].

Studies conducted by Fukas-Płonka et al. showed that the loss of dry matter of sewage sludge in the fermentation process was 18%, and the decomposition degree of organic matter was at the level of 22%. Total biogas production was 2.5 L, while the amount of produced biogas from 1 g VSS entered into the reactor was at the level 0.18 L/g VSS. During fermentation of excess sludge, the total quantity of biogas was 1.2 L, which, expressed in the amount of dry organic matter, was 0.07 L/g VSS. The loss of organic compounds did not exceed 15% [10]. In other studies, in which preliminary sewage sludge was the research material, the concentration of volatile fatty acids in fermented sewage sludge fluctuated from 467 to 664 mg CH$_3$COOH/L, and the alkalinity from 3.24 to 3.51 g CaCO$_3$/L. The quotient of VFA/alkalinity was in a range from 0.14 up to 0.19. The loss of dry matter ranged from 20 to 28%, and organic matter from 28 to 35% [11].

In Borowski et al. studies, the loss of organic dry substance in excess sludge was recorded in the range from 23.7 to 43.0%, and the amount of biogas per organic dry matter unit was on average 0.3 L/g VSS. During the fermentation of preliminary sludge, the decomposition degree of organic matter was 38%, and the amount of biogas in relation to 1 g VSS was 0.27 L/g VSS [12, 13].

In earlier studies of authors published in the Annual Set 'The Environment Protection' [14], a mixture of municipal sludge and excess sludge was subjected to co-digestion from coke waste treatment. Sewage sludge samples were collected in the winter season. DCOD value in supernatants decreased by 47% in fermentation of municipal sludge. Biogas production for sludge unit volume from test sludge was 4.6 L, and the amount of produced biogas per 1 g VSS was 0.47 L/g VSS. After the co-digestion process of a mixture of municipal sludge and coke, the decomposition degree of organic substances was 22%, and organic compounds expressed with DCOD rate amounted to 44%. The total amount of biogas from sludge unit volume for mixtures of municipal sludge with coke was 4.0 L, while the amount of biogas produced from 1 g VSS entered into the reactor was at the level of 0.31 L/g VSS [14].

The described studies were conducted in similar conditions, but excess coke sewage sludge was collected in the summer season in the process of modernization of the coking battery. In this case, decomposition of organic compounds, both for municipal sludge and that involving coke, expressed with the DCOD rate, was 2-fold higher than in the winter season. In addition, the amount of biogas was higher during the digestion of sewage sludge collected in the summer season. Therefore, it is possible to state that the concentration of easily biodegradable compounds was higher in sewage sludge collected in the summer season.
than the concentration of these compounds in sewage sludge collected in winter, readily biodegradable, resulting in greater amount of biogas compared to sewage sludge in the winter period. During the modernization of the coking battery, the production of coke was smaller, and simultaneously the concentration of toxic compounds was smaller, including polycyclic aromatic hydrocarbons (PAHs) in coke sewage sludge. This explains the production of a larger amount of biogas in the co-digestion process.

In studies on the fermentation of excess sludge conducted by Bohdziewicz et al., the removal degree of organic matter was 44.5%, and quotient of VFA/alkalinity – 0.1 [15]. Biogas production during fermentation of excess sludge was 0.30 L/g VSS, and the percentage of methane in biogas ranged from 51.3 to 72.0%. After the stabilization process, the biodegradation degree, determined on the basis of COD in excess sludge, was 41% [7].

Due to the loss of organic compounds, biogas production, and organic matter in fermented sludge, it is possible to state that municipal sewage sludge and mixture excess sewage sludge from treated coking wastewater were fermented well, since the values of studied sewage sludge parameters after the process were in a range given by other authors.

4. Conclusions

Based on the conducted studies, it is possible to present the following conclusions:

▶ Co-digestion of sewage sludge with excess sewage sludge from treated coking wastewater cannot exceed the mixing ratio of 10:1. While maintaining the above proportions, the technological parameters of sewage sludge fermentation and its mixtures with sewage sludge coke did not differ from each other by more than 25% (total biogas productions, decomposition degree of organic matter, changes in the content of organic compounds expressed with DCOD, loss of dry matter and methane content in biogas).

▶ Excess sewage sludge from treated coking wastewater can be neutralized in the fermentation process along with municipal sewage sludge provided that there is a constant quality-quantitative control of the sewage sludge and technological parameters. However, in order to confirm the above, it is necessary to conduct the study in a flow system.

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