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Comparison of the efficiency of organic compounds decomposition in sewage sludge using selected physical, chemical and biological methods

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ABSTRACT

Sewage sludge, commonly used in the process of municipal wastewater treatment, is characterized by high organic load and therefore is a valuable substrate in the process of methane fermentation. However, their biodegradability may be limited by the presence of microorganisms, which show limited susceptibility to decomposition in anaerobic conditions. The aim of the conducted research was to compare the efficiency of decomposition of organic compounds in excess sludge by various methods before sending the sludge to fermentation. The paper refers to selected physical (ultrasound field, microwave radiation, low-temperature modification up to 100°C, modification with dry ice), chemical (hydrogen peroxide, Fenton's reagent, peracetic acid) and biological (enzymatic biopreparations) method of sludge disintegration garbage. Excess sludge from a mechanical–biological sewage treatment plant with the use of a highly effective method of removing biogenic substances was used as the research substrate. As a result of the use of selected physical, chemical, and biological methods of sludge disintegration, an increase in potential susceptibility to biodegradation was observed already at the stage of modification, which was confirmed by methane fermentation in the next stage and the biogas yield recorded. The highest process efficiency in terms of biogas production was recorded for sludge modified with the peracetic acid method, that is, 0.85 L/g·VSS, while the lowest increase in unit biogas production was obtained for sludge modified with dry ice 0.44 L/g·VSS.

Keywords: Excess sludge; Disintegration; Anaerobic stabilization; Biogas yield; Digestion degree

1. Introduction

Sewage sludge is a by-product of the wastewater treatment process, is characterized by high organic load and therefore is a valuable substrate in the process of methane fermentation [1]. Implementation of the European Directive Concerning Urban Wastewater Treatment (Council Directive 91/271/EEC) [2] influenced the development of new wastewater treatment technologies and sludge treatment. As a result of the use of highly effective wastewater treatment methods with an increased level of biogenic removal, larger amounts of sludge are generated, which also show limited susceptibility to biochemical decomposition in anaerobic conditions. According to the literature data [3] in 2020, Germany, one of the main producers of sewage sludge in Europe, generated and disposed of approximately 1.8 million metric tons of sludge, while in Poland this value is almost 570,000 metric tons of sewage sludge. Therefore, it is reasonable to subject the sludge to the disintegration process, which will increase the efficiency of the anaerobic stabilization of the modified sludge, that is, the degree of the digestion plant, biogas production, susceptibility to dewatering.

However, excess sludge biodegradability may be limited by the presence of microorganisms, which show limited susceptibility to decomposition in anaerobic conditions

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[4]. According to Wu et al. [5] and Czatzkowska et al. [6], another factor inhibiting biodegradation is the presence of substances resistant to biodegradation, such as cellulose or lignocellulose, or the presence of substances toxic to microorganisms responsible for the course of acidic and methane fermentation. According to literature data [7], maintaining optimal living conditions for microorganisms responsible for the methane fermentation process is determined by such factors as pH and carbon, carbon-to-nitrogen ratio (C/N), temperature, hydraulic retention time (HRT), solids retention time (SRT), and organic loading rate (OLR).

In order to increase the effectiveness of methane fermentation, excess sludge, showing limited susceptibility to biochemical decomposition in oxygen-free conditions, is subjected to different disintegration methods. The idea of excess sludge disintegration, considered a stage of the so-called pre-treatment, is to destroy the structure of the sludge flocs by forced solubilization and initiation of processes leading to the lysis of the cells of microorganisms living in the sludge [8]. There are disintegration methods that aim to reduce the mass of sludge, but there are also methods to increase the susceptibility of sludge to biodegradation. The sludge technology uses physical, chemical, and biological methods as well as hybrid methods, which are a combination of independent methods [9,10]. Solubilization of excess sludge is used as a pre-treatment step as it is implemented to increase the fraction of biodegradable sludge and reduce the fraction of refractory compounds by converting particulate organic matter into soluble organic matter.

The structure of excess sludge flocs is a compilation of elements embedded in a common matrix made of extracellular polymeric substances which are the binding material. Taking into account the spatial distribution in the floc structure, one can distinguish (Fig. 1) soluble extracellular polymeric substances, loosely bound extracellular polymeric substances, and tightly bound substances that surround the bacterial biomass [8].

The structure of excess sludge can be described as partially loose, which is related to the porosity of the sludge, and a tight spatial distribution, indicating a compact structure [7]. Disintegration led to a breakdown of the high-molecular structure of sludge flocs, followed by the release of organic matter from the inside of the cells of microorganisms (Fig. 1).

The decrease in the content of organic matter with a high molecular weight that builds aggregates of sludge flocs occurs as a result of the release of internal components of the flocs. According to the literature data, the increased bioavailability of sludge results from the migration of extracellular proteins, polysaccharides, and enzymes from the inner layers of sludge flocs to the outer layers [11–14]. This is also conducive to the cell lysis of microorganisms in the disintegrated sludge. The consequence is the intensification of fermentation of pre-modified sludge with the use of selected disintegration methods and an increase in the unit value of biogas production [11,15]. Therefore, the content of inorganic matter in digested sludge tends to increase while improving sludge dewaterability [16,17].

The methods of thermal preparation based on the methane fermentation process were the earliest to be used in the technology of sludge processing, as a technological system of variable-temperature fermentation. However, the effects of fermentation can be intensified by selecting the most favorable conditions for the disintegration of selected physical, chemical or biological methods of preparation, and on this basis, selecting the most advantageous method from among those tested, which is a novelty of the conducted research.

The conditions for the preparation of excess sludge using different methods and their impact on the effectiveness of methane fermentation, determined by the researchers, expressed by the degree of fermentation and the intensity of biogas production, are presented in Tables 1–3.

The aim of the conducted research was to compare the efficiency of decomposition of organic compounds in excess sludge by various methods before sending the sludge to fermentation. At the modification stage, an increase in the potential susceptibility to biodegradation was found due to an increase in the soluble chemical oxygen demand/total chemical oxygen demand (SCOD/TCOD) value and the concentration of volatile fatty acids (VFAs), which was further confirmed in the next stage of the research by

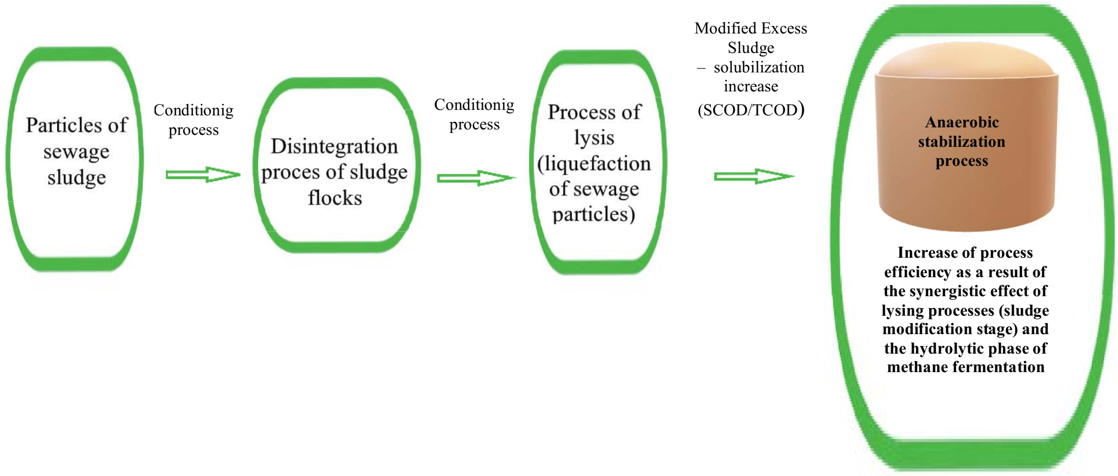

Fig. 1. Idea of the sewage sludge disintegration process (own elaboration on the base of [7]).

Table 1
Influence of the conditions of selected chemical methods of excess sludge disintegration on the efficiency of methane fermentation (own elaboration)

Most favorable conditions chemical disintegration			COD value or degree disintegration	Sludge digestion degree	Intensity biogas production	References
Reagent	pH or dose	Period h				
NaOH	9.0	2	–	increase for the sample control, %: 8.6	about 6% increase of biogas production	[18]
NaOH	0.4 g/g·d.m.	24	increase COD value ok. 72%	–	–	[19]
CH_3COOOH	25 g/kg·d.m.	–	–	–	about 21% increase of biogas production	[20]
NaOH	pH = 8	24	–	for untreated sludge approx. 32% for modified sludge approx. 36%	about 19% increase of biogas production	[21]
O_3	0.1 g·O_3/g·COD	–	–	approx. 26% increase of the digestion degree of	about 2.2-fold increase of biogas production	[22]
CH_3COOOH	0.011%	12	–	–	about 72% increase of biogas production	[23]

Table 2
Influence of thermal disintegration conditions on the effectiveness of methane fermentation of modified excess sludge (own elaboration)

Most favorable conditions thermal disintegration		COD value or degree disintegration period h	Sludge digestion degree	Intensity biogas production	References
Temperature, °C	Period, h				
60 80	1	–	Increase for the sample control 7.4 16.7	Increase for the sample control 10.1 13.3	[18]
175	2	About 54% increase of value	–	–	[19]
160–170, pressure 6 bar	0.3÷0.5	Disintegration degree: from 51%–66%	–	–	[24]
90	3	About 75% disintegration degree	–	–	[25]
70–121 160–180	–	–	–	From 20%–48% increase of biogas production From 40%–100% increase of biogas production	[26]
75	7	35-fold increase COD value	–	About 50% increase of biogas production	[27]

conducting methane fermentation and noting a significant increase in biogas yield.

2. Material and methods

2.1. Experimental design

The conducted research concerned the course of conventional methane fermentation assisted by different methods of disintegration.

In the first stage of the research, the following processes of disintegration of excess sludge were carried out:

- physical (ultrasound field, microwave radiation, low-temperature modification up to 100°C, modification with dry ice),
- chemical (hydrogen peroxide, Fenton's reagent, peracetic acid),
- biological (enzymatic biopreparations).

Table 3
Influence of ultrasonic disintegration conditions on the effectiveness of methane fermentation of excess sludge (own elaboration)

Ultrasonic disintegration conditions			Efficiency of methane fermentation ultrasonically modified excess sludge		References
Field strength of ultrasonic field or energy acoustic	Frequency vibrations of the ultrasonic field kHz	Time of sonication min	Sludge digestion degree %	Increase production biogas %	
0.5 W·cm^{-2}	20 kHz	80	–	50	[28]
1.8 W·cm^{-2}	–	7.5–150	5.6–56.7	16–42	[29]
5–18 W·cm^{-2}	–	1.6	About 31% increase for the sample control	14	[30]
660–14,547 kJ/kg·d.m.	–	–	–	13–60	[31]
10 W·cm^{-2}	–	–	About 30% increase for the sample control	11	[32]
4.3 W·cm^{-2}	20 kHz	300 s	About 57% increase for the sample control	50	[33]
9,690 kJ/kg·d.m.	20		–	44	[34]
–	30	120	About 43% increase for the sample control	82	[18]

The results were used to determine the most favorable modification conditions in the case of which the highest value of the ratio of the dissolved SCOD to the TCOD and the highest increase in the concentration of VFAs were obtained.

The selected physical (ultrasound field, microwave radiation, low-temperature modification up to 100°C, modification with dry ice), chemical (hydrogen peroxide, Fenton's reagent, peracetic acid, sodium hydroxide), and biological (enzymatic biopreparations) methods of sludge disintegration were used.

The results of studies on the effectiveness of selected disintegration methods were used to determine the most favorable processing conditions, for which the highest value of SCOD relative to TCOD and the highest increase in the concentration of VFAs was obtained.

Ultrasonic disintegration of excess sludge was carried out using a high-power generator, which is the ultrasonic disintegrator VC-1500 (acoustic power 1500 W), manufactured by the American company Sonics. The sludge was subjected to the ultrasonic field with an intensity of 3.75 W·cm^{-2} and a sonication time of 600 s, which were found to be the most favorable in the preliminary tests.

Evaluation of the effectiveness of sludge disintegration with microwave radiation was made based on five research cycles, during which microwave radiation power was 100, 180, 300, 600, and 800 W. For each of the above-mentioned radiation power values, the disintegration time used was 60, 120, and 180 s. Physical disintegration of sludge was carried out using a SAMSUNG MG23K3575AS microwave generator with a maximum power of 2,300 W and a frequency of 2,450 MHz. The volume of each disintegrated sediment sample was 250 mL. The most favorable disintegration conditions were a power of 800 W and a heating time of 180 s.

Thermal disintegration of excess sludge was carried out in a shaking water bath, in which the sludge placed in laboratory flasks with an active volume of 0.5 L was heated for a specified time at low temperatures, that is, 65°C–95°C. The sludge was heated for 0.5–12 h. The optimal conditions for thermal modification were 80°C and 6 h of treatment.

Dry ice, present in a granular form with a grain diameter of 0.6 mm, was used as a reagent in the thermal treatment (carbon dioxide in the solid phase). Dry ice was mixed with excess sludge at a volume ratio ranging from 0.05:1 to 0.75:1. disintegration was carried out at ambient temperature. The time of the modification phases, that is, freezing and defrosting, was determined by the size of the reagent dose and was increased with the increasing doses. For the doses of reagent used, it ranged from 3 to 12 h. The combination of dry ice and excess sludge at a volume ratio of 0.35 to 1 was considered the most favorable mixture.

Chemical disintegration of excess sludge was carried out using a 30% solution of hydrogen peroxide (H_2O_2). Each sludge sample with a volume of 250 mL was acidified to pH 3.0 before being treated with hydrogen peroxide and heated to 60°C using the microwave method. Hydrogen peroxide at doses of 1, 2, 3, 5, 6, and 10 mL was added depending on the volume of sludge given above. Then, the modified sludge was stirred at a speed of 180 rpm at room temperature for 1 h. Based on preliminary research, the dose of 5 mL H_2O_2/L of excess sludge was considered the most beneficial.

The Fenton's reagent disintegration was performed in glass vessels with an active volume of 0.25 L. The tested excess sludge was acidified with a 2-molar H_2SO_4 solution to pH 3 before the oxidation process. A weighed amount of $FeSO_4·7H_2O$ in the solid state was added to the acidified sludge and a specific dose of a 30% solution of H_2O_2 was used. The disintegration using Fenton's reagent was carried out for iron ion doses ranging from 0.04 to 0.1 g·Fe^{2+}/g·TS. Hydrogen peroxide was measured at ratios of 1:1–1:10 relative to the weight of iron ions. After 60 min, the samples were alkalized with a 4-molar solution to a pH value optimal for methane fermentation. The iron ion dose of 0.06 g·Fe^{2+}/g·total solids (TS) was considered the most favorable process condition, with a Fe^{2+}:H_2O_2 ratio of 1:5.

During the disintegration of excess sludge with peracetic acid, a compound with the trade name STERIDIAL W-15 was used, which is an aqueous solution of 15% peracetic acid, 10% acetic acid, and 8% hydrogen peroxide. Selected doses of the tested reagent were used (0.5–10 mL STERIDIAL W-15/L), and the pretreatment times using the chemical method ranged from 1 to 8 h. Disintegration of sewage sludge with peracetic acid was carried out at ambient temperature. The reagent dose of 1.5 mL of STERIDIAL W-15/L, and the pretreatment time of 1 h were found to be the most favorable pretreatment conditions.

The biopreparations used in the experiments to increase the susceptibility of excess sludge to biodegradation were DBC Plus Type L and a nutrient for yeast. DBC Plus cultures are a mixture of harmless saprophytic bacterial strains originally isolated from the wild strain and use non-living organic matter as a nutrient. Saprophytic bacteria are not pathogenic, toxic, or corrosive, which makes them safe to use, and cause no harmful side effects. The cultures are harmless to both aquatic and terrestrial plants and animals and can be safely introduced into marine, freshwater, and soil areas.

In the second stage of the research, methane fermentation of unmodified and disintegrated sludge was carried out using selected methods.

The research model is shown in Fig. 2.

2.2. Research substrate

Excess sludge was the basic research substrate. The sludge was collected from a mechanical and biological sewage treatment plant using a highly effective method of removing biogenic substances. Excess sludge was collected from the pipeline supplying the sludge to the mechanical thickener. Digested sludge was collected from a pipeline transporting sludge from separate closed digesters to separate open digesters. Samples were collected randomly and once and subjected to analysis and technological tests on the day of sampling. It should be emphasized that the technological line of the sewage treatment plant from which the sludge was collected for testing allows for the potential implementation of technological processes based on disintegration methods.

The characteristics of the tested sewage sludge are presented in Table 4.

2.3. Methane fermentation of excess sludge

Methane fermentation of a mixture of excess sludge and digested sludge, acting as inoculum, was carried out in static conditions for 28 d in a fermentation chamber with an active volume of 5 L and in specially designed systems for methane fermentation, which were models of fermentation chambers with an active volume of 0.5 L. The sludge was stabilized at a constant temperature of 37°C, characteristic of the process in mesophilic conditions. Before the tests, a

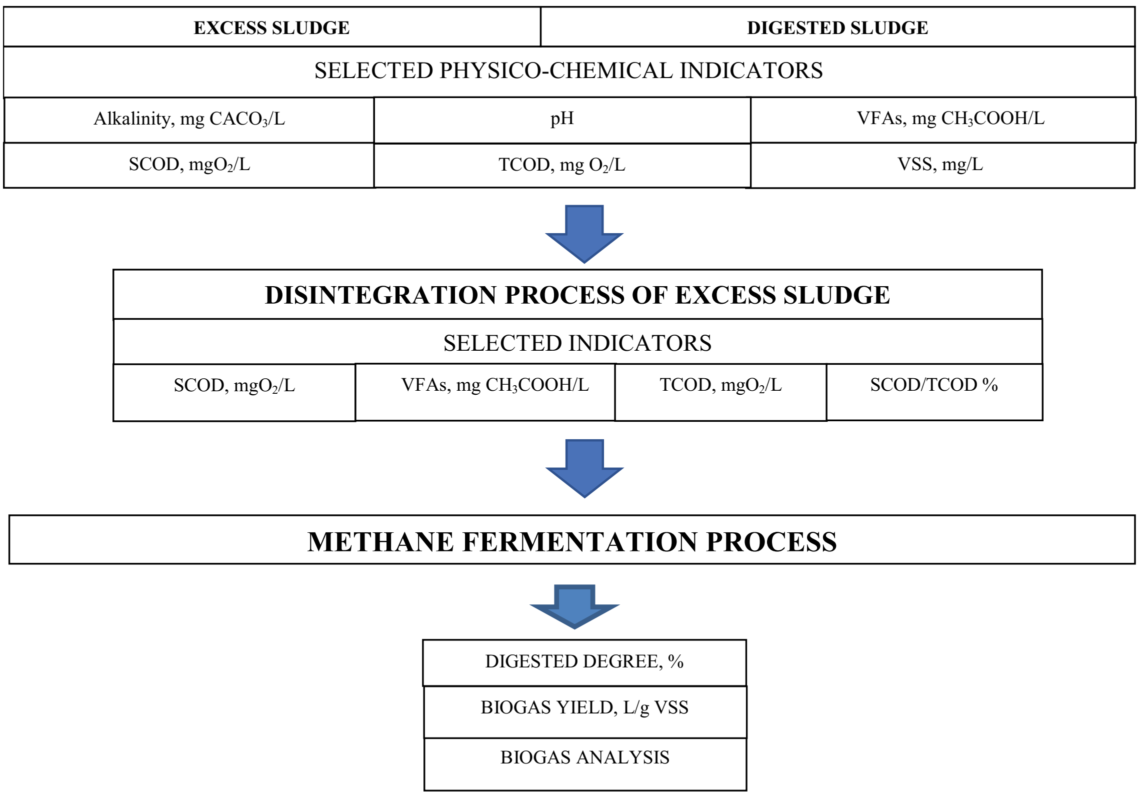

Fig. 2. Stages of the research.

Table 4
Selected physical and chemical parameters of sewage sludge

Indicator	Excess sludge	Digested sludge	Mixture of sludge
pH	6.95 ± 0.01	7.40 ± 0.02	7.04 ± 0.01
VSS, g/L	8.32 ± 0.12	6.69 ± 0.24	8.25 ± 0.17
Alkalinity, mg·$CaCO_3$/L	250 ± 20	1,950 ± 10	263 ± 7
VFAs, CH_3COOH/L	58 ± 3	878 ± 12	64 ± 9
SCOD, mg·O_2/L	171 ± 6	1,954 ± 34	182 ± 18
TCOD, mg·O_2/L	9,289 ± 12	2,794 ± 26	9,165 ± 21

VSS – volatile suspended solids,
VFAs – volatile fatty acids,
SCOD – soluble chemical oxygen demand,
TCOD – total chemical oxygen demand.

mixture consisting of the tested excess sludge and digested sludge was prepared, used as inoculation, and constituting 10% of the total volume of the mixture.

The composition of the biogas produced was monitored at 1-d intervals during methane fermentation. A GA 2000 analyzer (Geotechnical Instruments) was used to determine the percentage of methane in biogas.

2.4. Analytical methods

For selected parameters, the standard deviation was determined, with its value presented on graphs. Selected determinations were repeated three times during the research. For each value in the dataset, the deviation of this value from the mean was calculated, and the deviation is shown with the symbol ±.

The effectiveness of disintegration and methane fermentation was evaluated based on the analysis of the following physicochemical parameters of the sludge:

- volatile suspended solids, total solids according to PN-EN-12879 [35];
- SCOD, by bichromate method using tests for HACH 2I00N IS spectrophotometer according to ISO 7027 [36];
- TCOD basis of the ATV-A131 guidelines (TCOD) [37,38];
- VFAs using distillation with water vapor according to PN-75/C-04616/04 [39].

The selected determinations were repeated three times during the tests, and the standard deviation was evaluated for each parameter.

2.5. Calculation methods

Biogas yield production (BY) was calculated according to the equation [40]:

$$\text{BY} = \frac{\sum n}{\Delta u} \tag{1}$$

where BY – unit biogas production, L/g·VSS; $\sum_n$ – the sum of the volume of biogas obtained in the fermentation process brought to normal conditions, L; Δu – loss of volatile suspended solids of sludge, g VSS.

The degree of digestion of the tested sludge and the volume of biogas generated during methane fermentation converted to standard conditions were evaluated according to the Polish Standard PN-75/C-04616/07 [41].

The daily amount of biogas obtained in the process of anaerobic sludge stabilization was converted to standard conditions according to the formula [41]:

$$V_0 = \frac{V \cdot p \cdot 273}{\left(273 + T\right) \cdot 760} \tag{2}$$

where V_0 – amount of biogas converted to standard conditions, L; V – volume of measured biogas; p – atmospheric pressure, mm·Hg; T – ambient temperature, °C.

3. Results and Discussion

In the presented article, the criterion for selecting the most advantageous disintegration method was technological considerations, such as the increase in the concentration of organic substances in dissolved form. In preliminary studies, the most favorable preparation conditions were determined for the selected disintegration methods, for which the optimal values of SCOD, TCOD, VFAs concentration were obtained. Then, their effectiveness was assessed on the basis of their influence on the course of the methane fermentation process, by determining the value of the digestion degree and the biogas yield.

Destruction of cell walls and membranes of microorganisms living in the excess sludge was observed as a result of the lysis process. The destruction of cell walls and membranes of microorganisms living in the excess sludge was noted. There was a release of intracellular substances into the sludge liquid, the measurable effect of which was an increase in the SCOD value, VFAs concentration and the degree of disintegration of the modified sludge.

There was a release of intracellular substances into the sludge liquid, with its measurable effects being an increase in the SCOD value (Fig. 3) and concentration of VFAs (Fig. 4).

Correlations between the increase in SCOD and the concentration of VFAs were observed. The highest increase in SCOD and VFAs concentration compared to those found for unmodified sludge, amounting to 171 mg·O_2/L and 58 CH_3COOH/L, respectively, was obtained for peracetic acid-modified sludge, whereas the lowest increase was recorded for dry ice modified sludge. For the sludge subjected to the tested methods of disintegration, the following increase in the SCOD value was obtained in relation to the SCOD value of unmodified sludge (Fig. 3):

- thermal modification at a low-temperature range of up to 100°C: 13.7 times,
- modification by microwave radiation: 5.7 times,
- modification with an ultrasonic field: 16.2 times,
- dry ice modification: 5.0 times,
- modification with Fenton's reagent: 5.2 times,
- modification with peracetic acid: 18.6 times,
- hydrogen peroxide modification: 9.2 times,

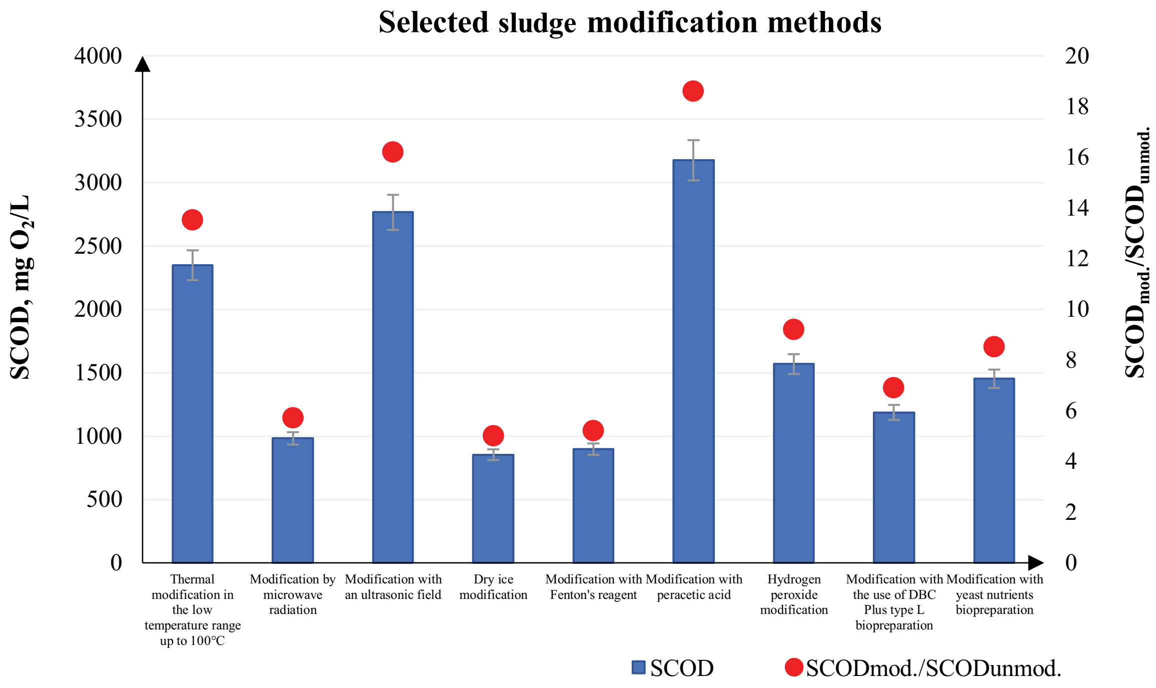

Fig. 3. SCOD value recorded for the most favorable disintegration conditions.

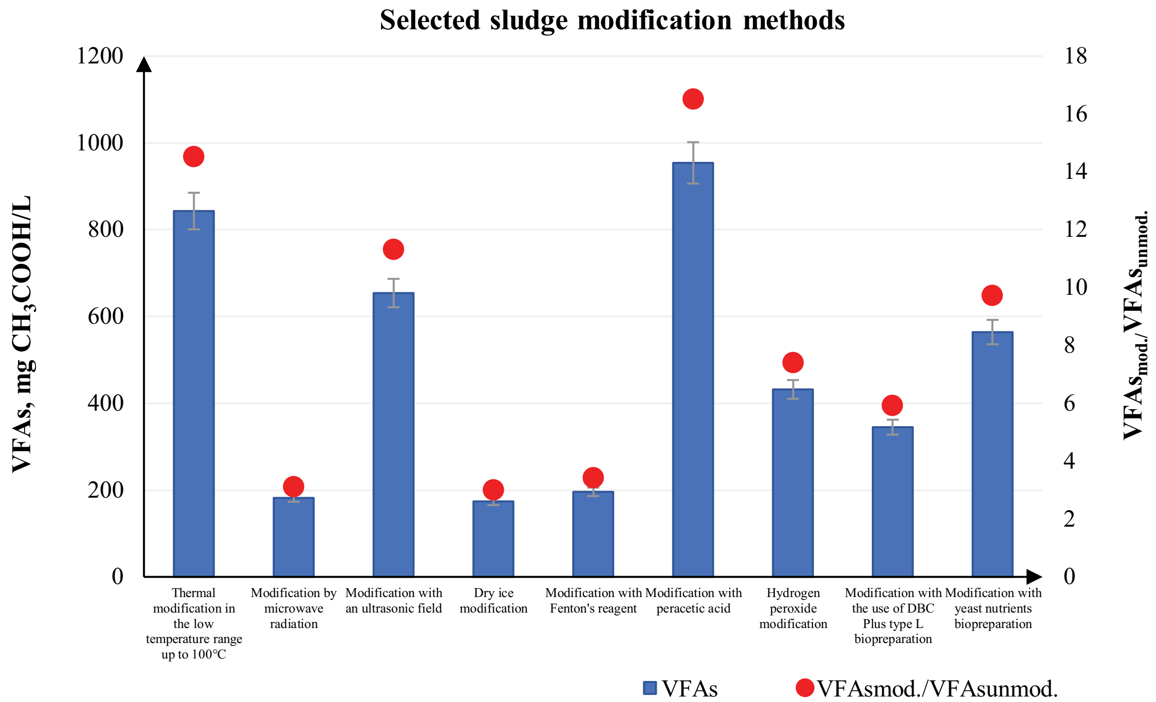

Fig. 4. Volatile fatty acids concentration recorded for the most favorable disintegration conditions.

- modification with DBC Plus type L biopreparation: 6.9 times,
- modification with yeast nutrient biopreparation: 8.5 times.

The greatest increase in the value of SCOD, in relation to the initial value of the examined parameter, was recorded for sludge modified with peracetic acid, which proves a significant degree of liquefaction of the modified sludge particles.

Moreover, for the sludge subjected to the tested methods of disintegration, the following increase in the VFA value was obtained in relation to the VFA value of unmodified sludge (Fig. 4):

- thermal modification at a low-temperature range of up to 100°C: 14.5 times,
- modification by microwave radiation: 3.1 times,
- modification with an ultrasonic field: 11.3 times,
- dry ice modification: 3 times,
- modification with Fenton's reagent: 3.4 times,
- modification with peracetic acid: 16.5 times,
- hydrogen peroxide modification: 7.4 times,
- modification with DBC Plus type L biopreparation: 5.9 times,
- modification with yeast nutrient biopreparation: 9.7 times.

On the basis of the increase in the concentration of VFAs already at the stage of excess sludge conditioning, it was found that the largest increase in the concentration of the examined indicator was recorded, similarly to the SCOD value, for sludge disintegrated with peracetic acid, which can be considered as the effect of the oxidizing effect of the reagent used.

In the case of the physical methods of excess sludge disintegration used, such as microwave radiation, dry ice modification, or low-temperature modification, the phenomenon of thermal shock was observed. However, in the case of chemical methods, the increase in the concentration of organic substances in dissolved form was due to oxidative processes and, in the case of disintegration with hydrogen peroxide, due to alkaline hydrolysis and denaturation of proteins constituting an important building material of microorganisms. According to literature data [42–49], sludge oxidation with Fenton's reagent leads to the generation of hydroxyl radicals, which are a strong oxidizing agent and therefore intensify final degradation of organic pollutants, which are difficult to decompose.

In the case of the physical methods used, such as microwave radiation, dry ice modification or low-temperature modification, the phenomenon of the so-called thermal shock.

The use of biopreparations may intensify the anaerobic biodegradation of lipids and hydrolysis of fatty acids, acting as a specific catalyzing factor. It should be emphasized that biopreparations are biodegradable and do not cause secondary environmental pollution. Moreover, no secondary pollution of the environment is observed for all physical methods, oxidation with peracetic acid, and hydrogen peroxide. In the case of oxidation with Fenton's reagent, the most favorable and at the same time the lowest doses of the tested reagent should be selected to achieve the best effects of the process.

However, in the case of chemical methods, the increase in the concentration of organic substances in dissolved form was due to oxidative processes and, in the case of disintegration with hydrogen peroxide, to alkaline hydrolysis and denaturation of proteins constituting an important building material of microorganisms.

According to literature data [50], it is possible to determine the degree of dissolution of excess particles based on the SCOD/TCOD ratio.

For sludge subjected to modification, the following increased SCOD/TCOD ratios were obtained:

- thermal modification at a low-temperature range of up to 100°C: 13.7 times,
- modification by microwave radiation: 5.9 times,
- modification with an ultrasonic field: 15 times,
- dry ice modification: 5 times,
- modification with Fenton's reagent: 5.1 times,
- modification with peracetic acid: 17.9 times,
- hydrogen peroxide modification: 9.1 times,
- modification with DBC Plus type L biopreparation: 7.2 times,
- modification with yeast nutrient biopreparation: 8.6 times.

The results showed that the highest efficiency of disintegration occurred for sludge modified with peracetic acid, and the lowest – for sludge subjected to sonication. It is possible to classify the tested methods in terms of the degree of liquefaction of the tested sludge in the following order: modification with peracetic acid > modification with an ultrasonic field > thermal modification at a low-temperature range of up to 100°C > hydrogen peroxide modification > modification with yeast nutrient biopreparation > modification with the use of DBC Plus type L biopreparation > modification by microwave radiation > modification with Fenton's reagent > dry ice modification (Fig. 5).

Variability of sewage sludge makes process optimization difficult. disintegration. However, it is possible to select the most favorable disintegration conditions with regard to selected physico-chemical determinations of the tested sludge, such as the value of dissolved chemical oxygen demand, TCOD, concentration of VFAs, organic substances or the degree of disintegration.

sludge subjected to selected disintegration methods shows greater susceptibility of organic substances to biochemical decomposition by methanogenic microorganisms, which in turn leads to increased biogas production compared to biogas production from unmodified sludge, for which the biogas yield was 0.21 L/g·VSS (Fig. 6). The largest increase in the value of biogas yield in the unit value of biogas production from unmodified sludge was obtained for sludge modified with peracetic acid, that is, a 4-fold increase, and the smallest increase in the unit value of biogas production for sludge modified with dry ice, that is, a 1.8-fold increase compared to biogas yield for the unmodified sludge. In the case of the achieved degree of sludge digestion, the largest increase in value compared to the degree of digestion of unmodified sludge, amounting to 45%, was obtained for sludge modified with peracetic acid (89%), while for sewage sludge modified with dry ice, a 20% increase in digestion degree was found (Fig. 7).

The increase in the efficiency of methane fermentation results from the synergistic effect of the lysis process (sludge modification stage) and the hydrolytic phase of methane fermentation.

Depending on the applied physical force, physical disintegration methods reduce the size of sludge particles and, consequently, transform macromolecular organic compounds into smaller and soluble fractions, which provides an increased contact surface of the substrate with the

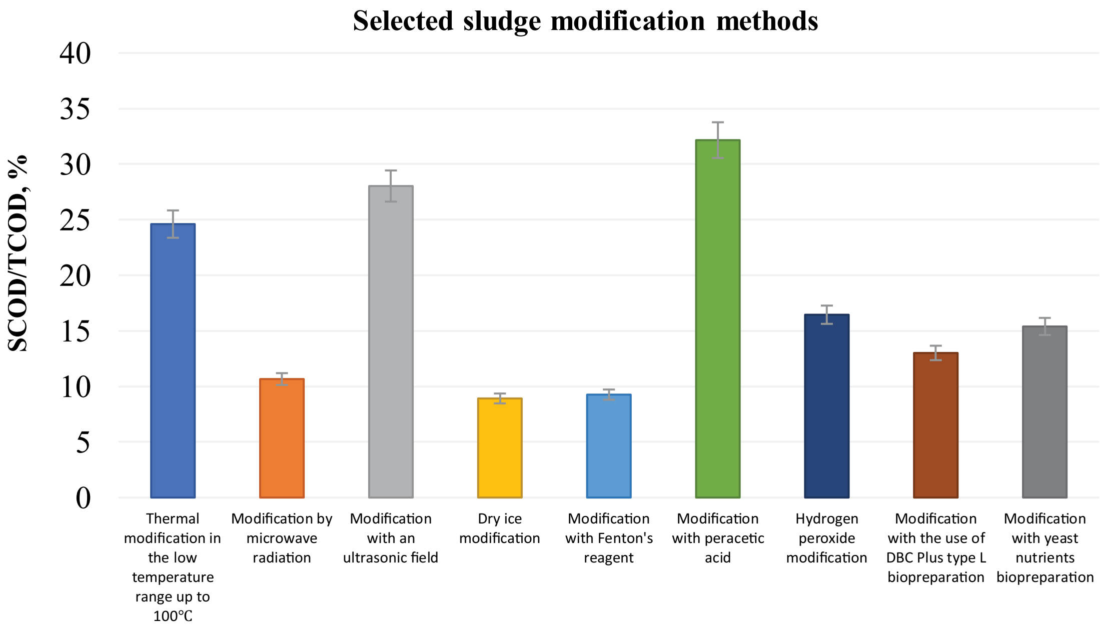

Fig. 5. SCOD/TCOD ratio recorded for the most favorable disintegration conditions.

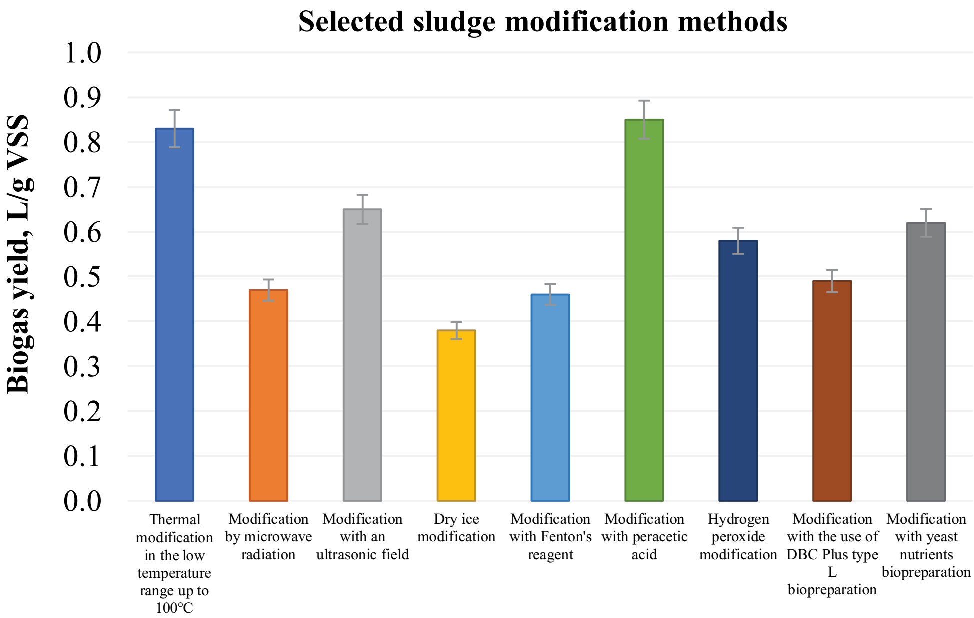

Fig. 6. Biogas yield recorded for the most favorable disintegration conditions.

consortium of microorganisms inhabiting the fermented sludge [51].

According to literature data [52], increased bioavailability and substrate utilization are inversely proportional to particle size. Therefore, the observed effect of the increasing SCOD value and the VFAs concentration of modified sludge determines the increase in the efficiency of methane fermentation, and thus the increase in the unit biogas production and digestion degree.

Advanced oxidation processes (AOPs) are an effective method of sludge disintegration, which shortens the hydraulic retention time and intensifies unit biogas production [46–48]. It should be emphasized that although the •OH hydroxyl radicals are slowly mobile forms, they are characterized by high reactivity. Therefore, organic matter first undergoes an advanced oxidation process (AOP). Studies conducted by Kazimierowicz et al. [49] have shown that AOPs improve the efficiency of anaerobic stabilization even of pharmaceutical sludge, both in terms of biogas/methane yield and degree of digestion.

Variability of sewage sludge makes process optimization difficult. disintegration. However, it is possible to select

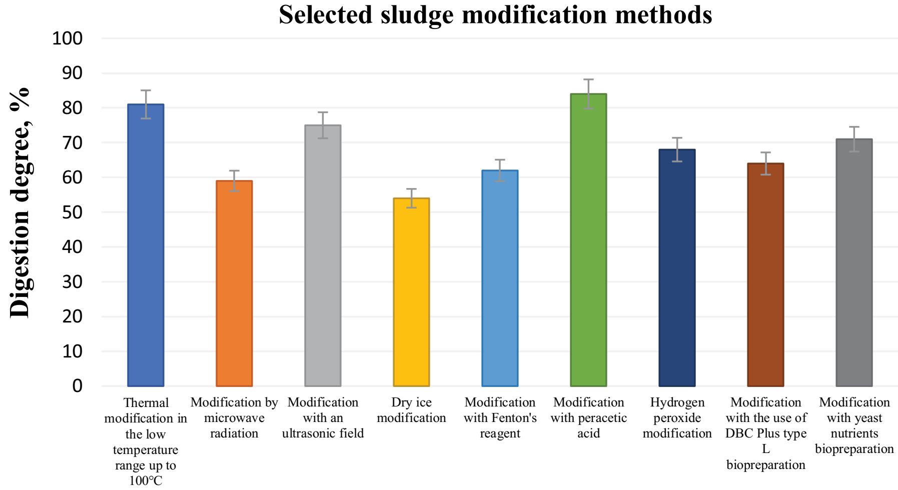

Fig. 7. Digestion degree recorded for the most favorable disintegration conditions.

the most favorable disintegration conditions with regard to selected physico-chemical determinations of the tested sludge, such as the value of dissolved chemical oxygen demand, TCOD, concentration of VFAs, organic substances or the degree of disintegration.

Subjecting excess sludge to different methods of disintegration led to the intensification of biogas production compared to conventional stabilization. For all methane fermentation processes of sludge modification, the content of methane in biogas was ca. 80%, and no statistically significant differences in biogas composition were observed compared to biogas generated from unmodified sludge.

A similar trend regarding the composition of biogas generated from modified sludge has been reported in previous studies, which found that, unlike other process variables, the methane content in biogas produced from the sludge subjected to physical modification was within the typical range of methane content [50,53].

The use of physical methods, microwave disintegration, and especially sonication generates high costs of energy consumption of the process, whereas the use of thermal modification in the low-temperature range and obtaining satisfactory efficiency of the method is associated with a long modification time. Chemical modification of excess sludge is efficient, but it requires appropriate process conditions, which in turn often entails the need to implement additional measures to obtain optimal conditions for the methane fermentation carried out in the next stage. At the same time, supporting methane fermentation by subjecting the sludge to active biopreparations increases with the constant additional costs of their purchase and the need for additional equipment [50,54].

It should be emphasized that the choice of the optimal method of disintegration is determined by technological, technical, and economic aspects.

4. Conclusions

To achieve the aim of the study, we compared the methane fermentation efficiency of physical, chemical, biological, and non-prepared excess sludge.

As a result of the decomposition of organic compounds in sewage sludge using selected physical, chemical and biological methods, an increase in the concentration of organic substances in dissolved form was noted.

As a result of the lysis process, the cell walls and cell membranes of microorganisms living in the excess sludge were destroyed. There was a release of intracellular substances into the sludge liquid, with its measurable effect being an increase in SCOD, VFAs concentration, biogas yield, and the degree of disintegration of the modified sludge.

In the case of sludge treated with the chemical method of disintegration with the use of peracetic acid, the highest SCOD value of unmodified sludge was obtained, that is, 3,176 mg·O_2/L, an approximately 18.6-fold increase in the value of the tested indicator was observed.

For the tested method, an increase in the VFAs concentration was obtained, correlating with the increase in the SCOD value, recording the highest VFAs concentration value among the tested methods, that is, 954 mg·CH_3COOH/L, obtaining an approximately 16.5-fold increase in the value of the tested indicator.

Moreover, for the tested method, the highest value of the SCOD/TCOD ratio among the tested methods was obtained, which proves a significant increase in the concentration of organic substances, potentially susceptible to biodegradation, in dissolved form.

The lowest, in relation to the SCOD and VFAs values of unmodified sludge, the SCOD values, that is, 853 mg·O_2/L and the VFAs concentration of 174 mg·CH_3COOH/L, respectively an approx. 5.0-fold increase in the SCOD value and an approx. The SCOD/TCOD ratio of 5 was obtained for the tested method, correlating with the value of SCOD and VFAs concentration and the lowest among the tested methods.

As a result of subjecting the sludge to selected physical, chemical, and biological methods of disintegration, an increase in potential susceptibility to biodegradation was found already at the stage of modification, as confirmed by the methane fermentation carried out in the next stage and the biogas yield recorded. The highest comparable efficiency of the process in terms of biogas production was recorded for sludge modified with the peracetic acid method, that is, 0.85 L/g·VSS, while the lowest increase in unit biogas production was obtained for sludge modified with dry ice 0.44 L/g·VSS.

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