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Effect of physical and chemical disintegration of excess sludge on the susceptibility to biodegradation

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ABSTRACT

The excess sludge formed as a result of advanced wastewater treatment processes using activated sludge methods belongs to the types of sludge characterized by low susceptibility to biodegradation. Effective methods of the disintegration of excess sludge include chemical and physical methods. The study aim was to examine the effect of the physical and chemical disintegration of excess sludge on the susceptibility of organic substances to biodegradation. The basic substrate used in the research was excess sludge formed as a result of the purification of the mixture of municipal and industrial wastewater from fibreboard production. Physical disintegration was performed using the ultrasonic field. In the case of chemical disintegration, acid disintegration with peracetic acid was used. In the next stage of the research, the process of conventional methane fermentation and methane fermentation of the modified sludge was carried out. In methane fermentation of sludge modified with the acidic reagent, the highest values of the above-mentioned parameters were recorded on the 3rd day of the process. However, during methane fermentation of the sonicated sludge, the highest values of the indices mentioned were obtained on the 4th day of the process. Values of soluble chemical oxygen demand, total organic carbon, and volatile fatty acids were 4,632 mg O_2/L, 1,915 mg C/L, and 1,923 mgCH_3COOH/L, respectively.

Keywords: Excess sludge; Disintegration; Methane fermentation; VFAs; SCOD; TOC

1. Introduction

Methane fermentation of sewage sludge is a multi-phase and spontaneous process. Disintegration has been used as a method that has an effect on the intensity of methane fermentation by increasing the concentration of organic substances in dissolved form.

The excess sludge formed in wastewater treatment plants where technologically advanced activated sludge methods are used shows significantly limited susceptibility to biochemical degradation under anaerobic conditions. Excess sludge, distinguished by a flocculating structure, is susceptible to disintegration, significantly increasing the susceptibility of modified sludge to biodegradation.

The idea of disintegration is to break the bonds between cells of microorganisms and to destroy cell membranes along with the release of organic substances into the supernatant liquid [1,2]. The disintegration process consists in the disintegration of microbial cells. Biomass increases in lysates (solutions obtained during the disintegration process), and this phenomenon is termed cryptic growth. There are two steps of the process: biodegradation (death) and lysis. The disintegration process leads to an increase in soluble chemical oxygen demand (SCOD) and production of volatile fatty acids (VFAs) [3,4].

Destruction of cell walls and membranes constituting a significant part of the volume of excess sludge contributes to their inactivation and allows for the easier release of cell contents into the supernatant liquid in the form of

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polysaccharides, proteins and enzymes. Disintegrated excess sludge shows increased susceptibility to biochemical degradation under anaerobic conditions.

Among the methods used to intensify the anaerobic stabilization of sewage sludge, chemical disintegration allows for an increase in process efficiency [5].

The methods of the disintegration of excess sludge include chemical methods consisting in the application of solutions of acids, bases, detergents, antibiotics, organic solvents, or strong oxidants that have a destructive effect on lipoproteins of cell walls in microorganisms. With a rapid change in the pH, the use of chemical reagents may cause the inactivation of microorganisms resulting from the inhibition of their metabolism [6,7].

The change in pH of sludge leads to the modification of protein ionization, mainly in the carboxyl and amino groups. Low or high pH also leads to the destruction of parasites and pathogenic microorganisms and their survival forms [8].

Chemical disintegration methods can be divided into oxidizing (oxidation and ozonation) and acid and alkaline hydrolysis. The chemicals most commonly used to conduct chemical disintegration include O_2, O_3, H_2O_2, HCl, H_2SO_4, NaOH, and NH_3. As a result of chemical hydrolysis, the walls, and cell membranes of microorganisms are destroyed, and the intracellular substances are released into the sludge liquid. The chemical reaction energy is used to disintegrate the solid organic fraction, often associated with the conditions in which the reaction occurs, such as temperature or pressure [9–13].

Peracetic acid offers an alternative to the above-mentioned reagents. In the industrial products market, it is commercially available as a solution of peracetic acid, acetic acid, and hydrogen peroxide. It is formed by the interaction of hydrogen peroxide with acetic acid. The compound is characterized by strong oxidizing and biocidal properties. It is used in the food and medical industry for disinfection. Peracetic acid oxidizes organic suspensions contained in sludge while neutralizing the effect of microorganisms [14,15].

Due to its chemical properties, peracetic acid belongs to the group of reactive microbicidal compounds. Substances from this group (which also includes aldehydes) allow for chemical conversion of substances contained in the cell and/or cell membrane. Peracetic acid acts by killing or inactivating a broad spectrum of bacteria, including mycobacteria, bacterial spores, fungi, and viruses. The high chemical reactivity of peracetic acid may also cause it to react chemically with other organic substances. With the activity of peracetic acid, radicals are also formed, reacting with the functional protein groups and leading to their irreversible damage [16].

Ultrasonic disintegration is a technologically promising method of mechanical treatment of sewage sludge. The effect of ultrasonic field distorts the state of balance in the system and leads to better spatial packing of molecules, thus changing the structure of sewage sludge and its properties. Application of ultrasonic waves in the process of disintegration of excess sludge causes flocs and cells of living organisms to break down and release the organic fraction. The increased concentration of organic compounds in the hydrolysate has a supporting effect on the process of anaerobic stabilization of the modified sludge. The efficiency of the disintegration process depends on the disintegrator power used, wave frequency, dry matter content in the sludge, and sonication time [17–20]. Destruction of cell walls and membranes contributes to the inactivation of microorganisms, but it also facilitates the release of cell contents into the environment in the form of polysaccharides, proteins, and enzymes. Protein denaturation and loss of enzyme activity may cause radical reactions resulting from the effect of the ultrasonic field. This phenomenon is also caused by the formation of high stresses in the medium during cavitation. Due to cavitation, hydrogen bonds break, and weaken van der Waals interactions in polypeptides, thus leading to changes in the secondary and tertiary structure of the protein. Free radicals and the generated hydrogen peroxide also lead to the irreversible DNA damage in the cells of microorganisms. According to Bougrier [21], cavitation causes strong stresses and reactions leading to the formation of H, $OH^{\bullet}$, and $HO_2^{\bullet}$ radicals. Furthermore, chemical transformations of organic substances also occur. Strong ultrasonic interactions catalyse the course of chemical reactions and lead to the acceleration of degradation and depolymerization processes in high-molecular organic compounds.

The aim of the present research was to determine the effect of different methods of disintegration of excess sludge, that is, physical and chemical methods, on the concentration of dissolved organic substances, determined based on selected indices. Changes in the concentration of dissolved organic substances were evaluated and expressed as SCOD, VFAs, and total organic carbon (TOC). Furthermore, disintegration degree (DD) for the modified excess sludge was determined in order to estimate the effectiveness of the disintegration methods used.

2. Experimental part

2.1. Substrate

The basic substrate in the research was excess sludge obtained from a mechanical-biological wastewater treatment plant, supplied with a stream of wastewater with 77% of its volume coming from domestic wastewater, and 23% from industrial wastewater. Industrial sewage sludge was obtained from fibreboard production and contained, among others, dissolved and colloidal substances such as resins, waxes, tannins, dyes separated from wood, and products of their breakdown, carbohydrates (glucose, mannose, arabinose, xylose), and suspended compounds, that is, wood fibre. According to the literature data [22,23], cellulose and paper sewage contains compounds with high stability and low susceptibility to biological degradation; these are mainly high-molecular lignin compounds. Due to the nature of the sludge studied, it was disintegrated prior to the biochemical degradation under anaerobic conditions. There is also a potential possibility to introduce disintegration into the technological process of treatment of the sludge studied.

Samples of the sludge were subjected to analysis and technological tests on the day of collection. All determinations were made using a three-point repetition. Excess sludge used for the research was sampled directly before mechanical thickening. Table 1 presents the physicochemical characterization of the sludge used in the research.

Table 1
Selected physicochemical indices of the sludge used in the study

Indicator	Type of sludge used in the research	
	Excess sludge	Digested sludge (inoculum)
TS	16.5 g/L ± 0.7	10.2 mg/L ± 0.3
VSS	14.7 g/L ± 0.4	6.6 g/L ± 0.5
SCOD	1,033 mg O_2/L ± 7	1,418 mg O_2/L ± 12
VFAs	246 mg CH_3COOH/L ± 6	553 mg CH_3COOH/L ± 3
TOC	274 mg $CaCO_3$/L ± 0.3	480 mg C/L ± 0.8
pH	6.8 ± 0.02	7.4 ± 0.04

TS, total solids; VSS, volatile suspended solids; SCOD, soluble chemical oxygen demand; VFAs, volatile fatty acids; TOC, total organic carbon

2.2. Methodology

The process of disintegration of excess sludge with the ultrasonic field was conducted with the use of a UD-20 disintegrator manufactured by Techpan (USA), with a vibration frequency of 22 kHz and the maximum power output of 180 W. The energy of electric vibrations using a transducer was transformed in the system into the energy of mechanical vibrations, and then, using the sonotrode, transferred to the tested system in the form of the acoustic wave. Disintegration was carried out in glass vessels in a non-flow system. The active volume of the residual sludge was 0.5 L. The sonotrode in the tested sludge was placed at a depth of 2 cm from the bottom of the vessel. Examinations of the disintegration of excess sludge with ultrasonic field were carried out using the time interval of 30–720 s, the amplitude of ultrasonic field of 12, 14, and 16 μm, the ultrasonic wave intensity of 1.65, 2.24, and 2.95 W/cm^2, and acoustic power of 105, 143, and 186 W.

A compound with the commercial name of STERIDIAL W-15 was used for acid disintegration of the sludge. STERIDIAL W-15 is an aqueous solution of peracetic acid (15%), acetic acid (>36%) and hydrogen peroxide (18%–22%). In the process of acid disintegration, the mixtures of sludge with the appropriate dose of peracetic acid were placed in plastic bottles, with their contents mixed manually during the preparation period. The chemical modification process was carried out at ambient temperature using a 12 h modification time and the doses of 0.1–4.5 ml STERIDIAL W-15/L. The pH of excess sludge subjected to acid disintegration was chemically corrected to the value of 7.0. The values of SCOD and VFA were corrected by the value of these indices derived from the dose of peracetic and acetic acid added to the sludge. These compounds represent components of STERIDIAL W-15. Their percentage share in the solution and density were taken into account. It was assumed that peracetic acid in the aqueous environment is completely degraded to acetic acid, and its value can be calculated from the following equation: 1 gCH_3COOH = 1.07 gO_2 [24].

The following indices were analyzed in the case of the processes of disintegration of excess sludge:

- total solids and volatile suspended solids according to PN-EN-12879,
- SCOD by the dichromate method using spectrophotometer tests by HACH 2I00N, (USA) according to ISO 7027,
- VFAs according to PN-75/C-04616/04,
- the TOC by the spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena , Germany),
- pH according to PN-91/C-04540/05.

The DD, which is an indicator of the effectiveness of the disintegration methods analyzed, was determined in accordance with the equation given by Tiehm et al. [25]. The SCOD of alkaline modified excess sludge, which represents the reference value for the estimation of the DD, was 3,438 mg O_2/L. The DD expresses the degree of liquefaction of organic substances contained in the sludge.

Anaerobic stabilization of excess sludge was carried out under static conditions for 10 d in specially constructed systems constituting models of fermentation chambers with an active volume of 5 L. The sludge was stabilized in mesophilic conditions at the temperature of 37°C.

The following mixtures of sludge were subjected to methane fermentation:

- non-conditioned excess sludge + digested sludge (inoculum);
- chemically disintegrated excess sludge with peracetic acid with the dose of 2.0 ml STERIDIAL W-15/L of sludge + digested sludge (inoculum);
- excess sludge subjected to sonication with an amplitude of ultrasonic field vibration of 16 mm, ultrasound wave intensity of 2.95 W/cm^2 and sonication time of 600 s + digested sludge (inoculum).

3. Results and discussion

3.1. Determination of the conditions of chemical disintegration of excess sludge

An increase in the concentration of organic substances in dissolved form in the supernatant liquid was found following the exposure of the excess sludge to chemical disintegration. The most favorable conditions of modification were determined based on the increase in SCOD, TOC, and VFAs concentrations. Furthermore, the reaction (pH) of the modified sludge was also determined. Fig. 1 shows changes of SCOD values determined in the leachate of excess sludge subjected to acid modification, whereas Fig. 2 shows the values obtained for sludge DD.

As a result of the exposure of the excess sludge to 12 h disintegration process with STERIDIAL W-15 at doses ranging from 0.1 to 4.5 ml/L of sludge, the DD ranged from 11% to 80% (Fig. 2). The SCOD value for the leachate increased as the dose of the preparation increased, ranging from 1,956 to 7,765 mgO_2/L. For higher doses of STERIDIAL W-15, that is, 3.5, 4.0, and 4.5 ml STERIDIAL W-15/L of sludge, a decrease of the SCOD value and the respective deterioration of the DD was observed, which may have been caused by the oxidizing effect of the reagent (i.e., peracetic acid). Fig. 3 presents changes in the pH of the sludge leachate following chemical disintegration.

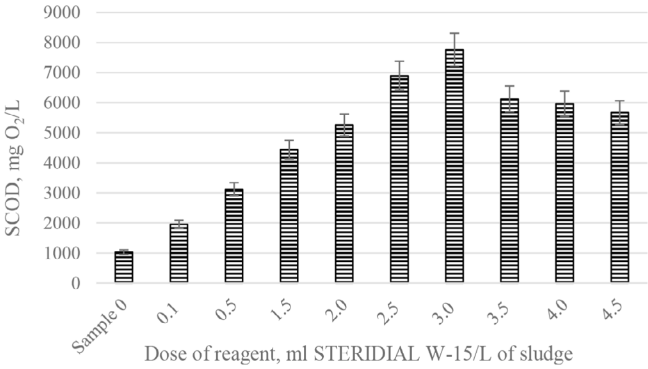

Fig. 1. Changes of SCOD values determined in the leachate of excess sludge subjected to acid disintegration for 12 h.

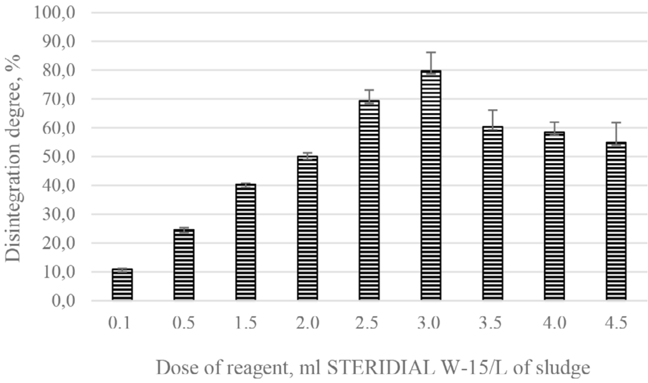

Fig. 2. Disintegration degree of excess sludge after acid modification.

Fig. 3. Changes of pH values determined in the leachate of excess sludge subjected to acid disintegration for 12 h.

Chemical disintegration of excess sludge with STERIDIAL W-15 and an increase in the reagent dose caused pH of the supernatant to decrease. In the range of the doses of acid reagent from 0.1 to 4.5 ml STERIDIAL W-15/L of sludge and time of 12 h, the pH of the leachate decreased from 7.2 (sample 0) to 3.9. Due to the methane fermentation process carried out in the next stage of research and the optimum pH for its course, the above dose, for which pH 6.3 was obtained, was considered technologically optimal. Changes of the TOC values in the leachate of excess sludge for 12 h chemical disintegration are shown in Fig. 4.

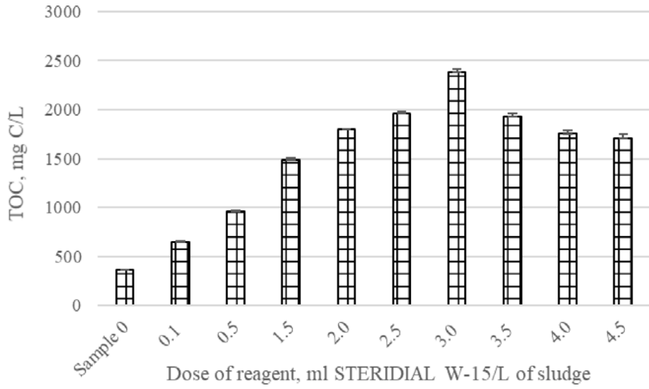

Fig. 4. Changes of TOC values determined in the leachate of excess sludge subjected to acid disintegration for 12 h.

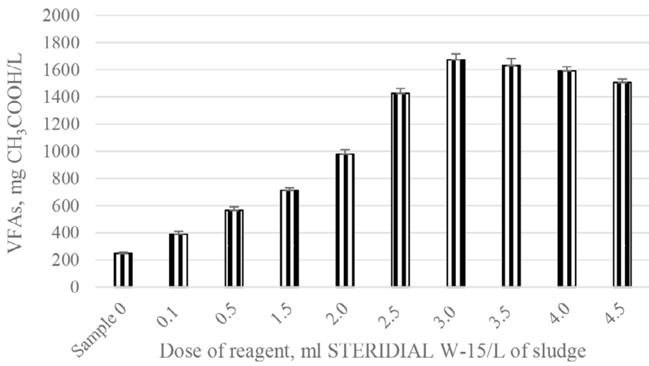

Fig. 5. Changes of VFAs concentration determined in the leachate of excess sludge subjected to acid disintegration by the period of 12 h.

Changes of TOC values recorded in the leachate of chemically modified excess sludge, depending on the reagent dose used, are correlated with changes in the SCOD value. Changes in VFAs concentration in the leachate of excess sludge for 12 h chemical disintegration are shown in Fig. 5.

A gradual increase in the concentration of VFAs was observed with the increase of the reagent dose. The highest value of VFAs concentration (1,674 mg CH_3COOH/L) was recorded for the dose of 3.0 ml STERIDIAL W-15/L of sludge. On the other hand, for the dose of 2.0 ml STERIDIAL W-15/L of sludge, considered the most effective due to the optimal methane fermentation conditions, especially the obtained pH value, the concentration of VFAs was 979 mg CH_3COOH/L. For doses of STERIDIAL W-15, that is, 3.5, 4.0, and 4.5 ml STERIDIAL W-15/L of sludge, a higher value of VFAs concentration, in relation to the dose of 2.0 ml STERIDIAL W-15/L of sludge, was obtained. However, in the case of using the above doses of reagent, an acid reaction was obtained, which would require adjustment to a pH value of about 6.5–7, optimal for the proper course of the fermentation process. Adjusting the pH of the sludge would require dosing a strong alkaline reagent, for example, sodium hydroxide, to the sludge, contributing to secondary contamination of the sludge. Table 2 shows the most favorable conditions for acid modification of excess sludge evaluated based on the increase in SCOD, DD_{SCOD}, TOC, and VFAs.

Table 2
Determination of the most favorable conditions for acid modification of excess sludge based on the increase in SCOD, DD_{SCOD}, TOC, VFAs, and the value of pH

Dose of reagent, ml STERIDIAL W-15/L of sludge	SCOD, mg O_2/L	DD_{SCOD}, %	pH	TOC, mg C/L	VFAs, mg CH_3COOH/L
0*	1.033 ± 21	–	7.2	365 ± 18	246 ± 12
2.0	5.257 ± 367	32 ± 1.4	6.3	1.794 ± 90	979 ± 49
3.0	7.765 ± 543	43 ± 1.8	5.3	2.385 ± 119	1.674 ± 84

*non-prepared excess sludge.

It was found based on the results obtained that chemical treatment using a twelve-hour modification time with the dose of 2.0 ml STERIDIAL W-15/L of sludge is a technologically advantageous solution. The pH value obtained as a result of the exposure of the sludge to chemical disintegration with the above dose is the most advantageous. It is not advisable to adjust the pH value to the optimum for anaerobic stabilization. The disintegration method with the use of STERIDIAL W-15, which is a mixture with peracetic acid as a basic ingredient being a strong oxidant can be considered effective. According to Fleck [26], in aqueous media, peracetic acid is biodegraded to acetic acid, thus not causing secondary pollution of sludge. On the other hand, the highest values of the examined indices were obtained for a dose of 3 ml STERIDIAL W-15/L. In the case of the pH value found as a result of the application of the above dose (5.3) due to the fermentation process carried out in the next stage, it is necessary to adjust the pH to the optimal value. According to Buraczewski and Bartoszek [27], the optimum growth of methanogenic bacteria occurs in the range of pH = 7 ± 0.5.

3.2. Determination of the conditions of physical disintegration of excess sludge

Current ultrasound technologies need to be continuously adapted to the chemical and physical properties of sewage sludge. The efficiency of the process is determined by the frequency of vibrations of the ultrasonic field and the temperature increase that accompanies the process. As reported by Iskra and Miodoński [28] the parameters used to obtain the optimal ultrasonic disintegration effect are low ultrasonic field frequencies (20 kHz) and correctly adjusted level of process power favouring the occurrence of the cavitation process (desirable in this case), chemical, and mechanical processes and the formation of free radicals [28]. Figs. 6, 7 show changes in SCOD and DD_{SCOD} determined in the leachate of excess sludge subjected to ultrasonic field disintegration. Table 3 shows the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in SCOD.

The data presented in Figs. 1, 2 show that the SCOD and DD of the modified excess sludge increased with the increase of the ultrasonic wave intensity and sonication time. Compared to other tested values of ultrasound wave intensity, the highest increase of SCOD (4,694 mgO_2/L) and the DD of 43% were obtained for ultrasonic disintegration at 2.95 W/cm² and the sonication time of 600 s. Furthermore,

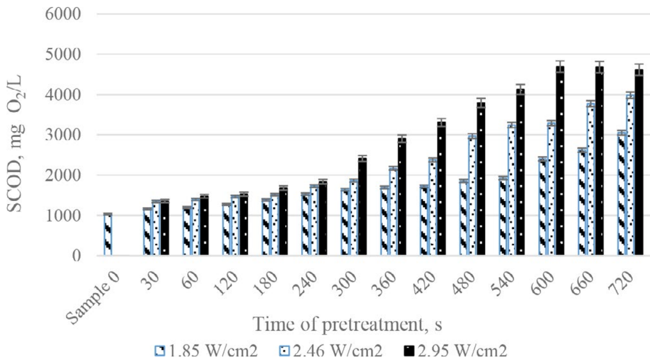

Fig. 6. Changes in SCOD values determined in the leachate of excess sludge subjected to ultrasonic field disintegration.

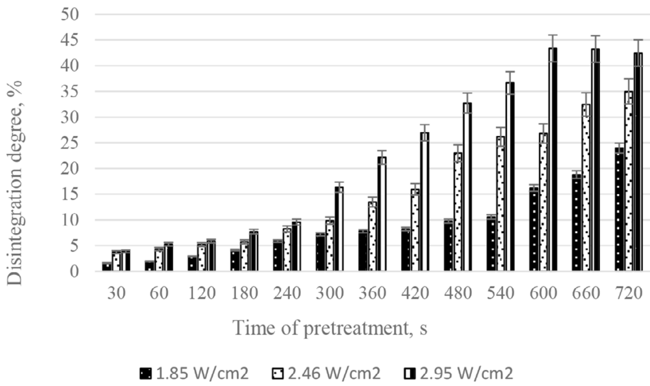

Fig. 7. Disintegration degree of excess sludge subjected to ultrasonic modification.

compared to the initial value of SCOD determined for non-modified sludge, a five-fold increase of the value of this index was obtained for the above disintegration conditions. The changes in TOC values in time for different values of ultrasonic wave intensity are shown in Fig. 8. Table 4 shows the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in TOC.

Depending on the ultrasonic wave intensity, changes of TOC values recorded in the leachate of sonicated excess sludge are correlated with changes of the SCOD and DD_{SCOD} values. For 2.95 W/cm² and sonication time of 600 s, compared to the tested values of ultrasound wave intensity, the

Table 3
Determination of the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in SCOD

Temperature, °C	Most favorable exposure time, s	$SCOD_{non-modified\ excess\ sludge}$, mgO_2/L	$SCOD_{sonicated\ excess\ sludge}$, mgO_2/L	DD_{SCOD}, %	Ratio of $SCOD_{sonicated\ excess\ sludge}$/ $SCOD_{non-modified\ excess\ sludge}$
1.85 W/cm² (12 μm)	720	1.033 ± 21	3.054 ± 61	24 ± 1.2	1/3
2.46 W/cm² (14 μm)	720	1.033 ± 21	3.986 ± 80	35 ± 1.75	1/4
2.95 W/cm² (16 μm)	600	1.033 ± 21	4.694 ± 141	43 ± 2.15	1/5

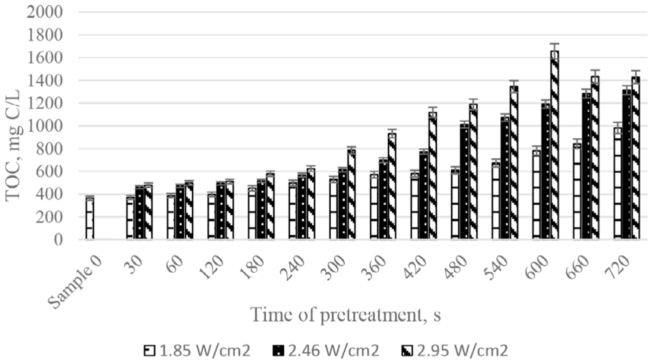

Fig. 8. Changes in TOC values determined in the leachate of excess sludge subjected to ultrasonic field disintegration.

highest value of TOC 1,656 mg C/L and a five-fold increase of the value of the index were obtained compared to the initial value. Changes of the VFAs concentration in the leachate of excess sludge for ultrasonic field disintegration are shown in Fig. 9. Table 5 shows the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in VFAs concentration.

The data presented in Fig. 9 show that the VFAs concentration in the leachate increased with the increase in ultrasound wave intensity and sonication time. The highest VFAs concentration of 954 mg CH_3COOH/L was obtained for 2.95 W/cm² and sonication time of 600 s. Sonication with these parameters resulted in a four-fold increase of the VFAs concentration compared to the VFAs in the non-prepared excess sludge. The observed increase in VFAs concentration correlated with the increase in SCOD and TOC in the leachate.

3.3. Methane fermentation of non-prepared and disintegrated excess sludge

The combination of the lysis process initiated during the disintegration process by physical and chemical factors and biological hydrolysis contributed to the increase in the value of indices determining the susceptibility of excess sludge to biodegradation. Compared to non-processed sludge, an increase in the concentration of organic substances in dissolved form was observed in the process of methane fermentation of modified sludge, expressed in the value of SCOD and TOC. Furthermore, in the following days of the methane fermentation process of the sludge disintegrated using the methods studied, an increase was observed in the concentration of VFAs compared to the conventional methane fermentation process.

Table 6 shows changes in the value of selected indices in the process of conventional methane fermentation and methane fermentation of disintegrated excess sludge.

With sludge disintegration and subsequent methane fermentation, the supportive effects of the modification methods were observed, expressed as an increase in the concentration of organic substances in dissolved form. As a result of the association of the acid hydrolysis process with biological hydrolysis, intensification of the acid phase of the methane fermentation process was observed. In the next 4 d of the process, an intensive increase in the values of the examined indicators, that is, SCOD, VFAS, and TOC, was obtained. A similar tendency of sonolysis supporting biological hydrolysis, which is the limiting phase of methane fermentation, was noted for chemical disintegration. An intensive increase in the studied indicators was recorded up to and including the 3rd day of the process. In following, fermentation days observed a decrease in the SCOD, VFAS and TOC values. Table 7 shows the values of sludge digestion degree and the maximum values of selected indices determining the efficiency of the methane fermentation process.

In the methane fermentation process used for the sludge disintegrated by chemical methods, the highest values of the analyzed indices, that is, SCOD, TOC, and VFAs concentration, were obtained on the 3rd day of the process and were 4,116 mg O_2/L, 1,511 mg C/L, and 1,745 mg CH_3COOH/L, respectively. A 36% sludge digestion degree was obtained. Similar process efficiency was obtained in the process of methane fermentation of the physically disintegrated sludge, that is, with the ultrasound field with the most favorable technological modification conditions. A slightly higher value of the tested indices was recorded for sonicated sludge on the 3rd day of the process, that is, 4,632 mg O_2/L, 1,915 mg C/L, 1,923 mg CH_3COOH/L, respectively. A 32% sludge digestion degree was obtained. Fig. 10 presents the values of the VFAs/alkalinity ratio recorded during the process of methane fermentation.

According to the literature data [29], the persistent value of the VFAs/alkalinity ratio of above 0.3, being borderline, demonstrates the irregularity of the process and the risk of its collapse. During the methane fermentation of non-processed sludge and the sludge disintegrated with selected methods, a gradual decrease in the value of the VFAs/alkalinity ratio was observed in the following days

Table 4
Determination of the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in TOC

Temperature, °C	Most favorable exposure time, s	$TOC_{non\text{-}modified\ excess\ sludge}$, mgO_2/L	$TOC_{sonicated\ excess\ sludge}$, mgO_2/L	Ratio of $TOC_{sonicated\ excess\ sludge}$/$TOC_{non\text{-}modified\ excess\ sludge}$
1.85 W/cm² (12 μm)	720	365 ± 18	983 ± 50	1/3
2.46 W/cm² (14 μm)	720	365 ± 18	1.314 ± 40	1/4
2.95 W/cm² (16 μm)	600	365 ± 18	1.656 ± 67	1/5

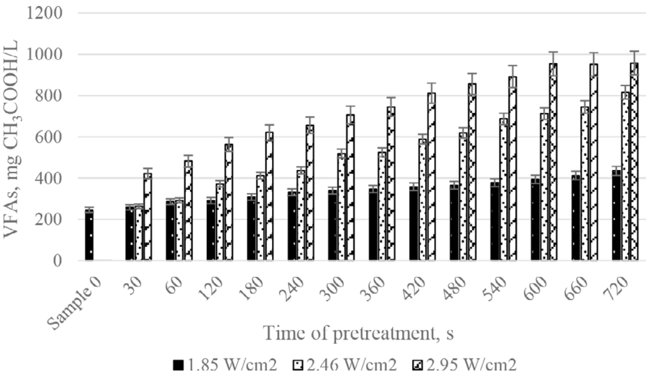

Fig. 9. Changes in VFAs concentration determined in the leachate of excess sludge subjected to ultrasonic field disintegration.

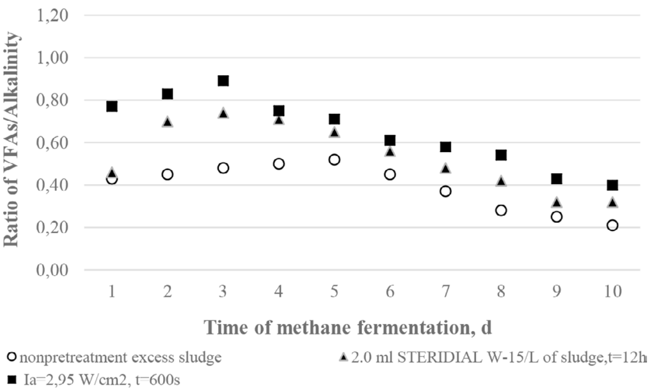

Fig. 10. Changes in the value of the VFAs/alkalinity ratio in the process of conventional methane fermentation of excess sludge and methane fermentation of sludge disintegrated with selected methods.

of the process. On the 10th day of methane fermentation of non-prepared sludge, the value of the ratio was 0.21, while in the case of the modification methods, that is, acid and ultrasonic disintegration, this value was 0.32 and 0.4, respectively. The obtained values indicate a further downward trend in the value of the indices tested and the effectiveness of the methane fermentation.

Analyzing the obtained research results regarding the operation of the disintegration methods studied, it can be stated that their technological effectiveness, that is, the obtained increase in SCOD, TOC, and VFAs concentration is similar. However, in technical terms, ultrasonic disintegration requires greater energy expenditure, which, however, can be offset by using obtained biogas as an energy source.

4. Summary and conclusions

Disintegration of sewage sludge is a dynamically developing technological issue. The supply of external energy into excess sludge leads to changes in its structure and the destruction of microorganism cells. The use of disintegration accelerates hydrolysis that determines the effectiveness of stabilization by transferring the organic load from the solid phase of the sludge to the dissolved phase.

During the research, excess sludge was subjected to physical disintegration with the use of the ultrasonic field. Furthermore, chemical disintegration method was used, that is, acid modification. The lysis processes, occurring in the sludge due to sonolysis and chemical hydrolysis, lead to an increase in the concentration of organic substances in dissolved form. The positive effect of selected disintegration methods on the increase in susceptibility of modified excess sludge to biodegradation was found.

The analysis of the results obtained in the present study leads to the following conclusions:

- In the case of chemical disintegration with STERIDIAL W-15 with selected doses of the reactant, an increase in liquefaction of excess sludge was observed compared to the non-conditioned sludge. The highest values of SCOD, DDSCOD, TOC, and VFAs concentrations were obtained for the doses of 2.0 ml STERIDIAL W-15/L of sludge. For the tested reagent dose, the pH value was 6.3.
- Modification of sludge with the ultrasonic field led to the increase in the concentration of organic substances in dissolved form compared to the values obtained for the non-conditioned sludge. Compared to the values of ultrasound wave intensity studied, the highest increase in the case of ultrasonic disintegration at 2.95 W/cm² and sonication time of 600 s was obtained for SCOD, DD_{SCOD}, TOC, and VFAs concentrations.
- 10-d anaerobic stabilization of unprepared excess sludge yielded ca. 18% digestion degree, whereas ca. 32% was obtained in the case of anaerobic stabilization of excess sludge disintegrated chemically with a dose of 2.0 ml STERIDIAL W-15/L of sludge and the DD of 36%.
- During methane fermentation of non-conditioned sludge and the sludge after acid and ultrasonic disintegration, the highest values of the indices tested were obtained on the 6th, 3rd, and 4th day of the process, which demonstrates the intensification of the hydrolysis phase limiting the stabilization process.

Table 5
Determination of the most favorable conditions for modification of excess sludge with ultrasonic field evaluated based on the increase in VFAs concentration

Temperature, °C	Most favorable exposure time, s	$VFAs_{non-modified\ excess\ sludge}$, mg CH_3COOH/L	$VFAs_{sonicated\ excess\ sludge}$, mg CH_3COOH/L	Ratio of $VFAs_{sonicated\ excess\ sludge}$/$VFAs_{non-modified\ excess\ sludge}$
1.85 W/cm^2 (12 μm)	720	246 ± 12	435 ± 22	1/2
2.46 W/cm^2 (14 μm)	720	246 ± 12	816 ± 33	1/3
2.95 W/cm^2 (16 μm)	600	246 ± 12	954 ± 57	1/4

Table 6
Changes in the value of selected indices in the process of conventional methane fermentation and methane fermentation of excess sludge subjected to chemical and physical disintegration using the most favorable modification conditions

Time of process, d	Conventional methane fermentation			Methane fermentation of acid disintegrated excess sludge (2.0 ml STERIDIAL W-15/L of sludge, t = 12 h)			Methane fermentation of ultrasonic disintegrated excess sludge (ultrasound intensity I = 2.95 W/cm^2, t = 600 s)		
	SCOD, mg O_2/L	VFAs, mg CH_3COOH/L	TOC, mg C/L	SCOD, mg O_2/L	VFAs, mg CH_3COOH/L	TOC, mg C/L	SCOD, mg O_2/L	VFAs, mg CH_3COOH/L	TOC, mg C/L
0	1.062 ± 14	252 ± 7	369 ± 2	3.656 ± 82	1.057 ± 28	1.102 ± 2	3.656 ± 43	1.057 ± 74	1.102 ± 11
1	1.087 ± 12	256 ± 12	386 ± 4	3.868 ± 38	1.127 ± 37	1.254 ± 4	4.294 ± 18	955 ± 72	1.338 ± 5
2	1.135 ± 8	283 ± 9	412 ± 6	3.954 ± 48	1.386 ± 52	1.359 ± 2	4.540 ± 47	1.039 ± 54	1.456 ± 9
3	1.284 ± 17	301 ± 18	426 ± 2	4.116 ± 65	1.745 ± 29	1.511 ± 3	4.600 ± 23	1.543 ± 37	1.767 ± 10
4	1.332 ± 31	394 ± 22	467 ± 3	3.898 ± 26	1.376 ± 17	1.432 ± 6	4.632 ± 51	1.923 ± 31	1.915 ± 12
5	1.487 ± 26	402 ± 34	486 ± 5	3.642 ± 24	1.287 ± 11	1.287 ± 2	4.480 ± 16	1.486 ± 22	1.887 ± 5
6	1.553 ± 43	587 ± 23	519 ± 4	3.045 ± 16	1.143 ± 9	1.098 ± 4	4.271 ± 25	1.308 ± 26	1.734 ± 3
7	1.331 ± 28	543 ± 11	478 ± 7	2.815 ± 28	1.065 ± 15	987 ± 4	3.854 ± 38	1.281 ± 14	1.668 ± 7
8	1.224 ± 32	428 ± 16	359 ± 3	2.549 ± 32	954 ± 29	905 ± 7	3.632 ± 24	1.094 ± 9	1.483 ± 11
9	1.056 ± 19	314 ± 7	283 ± 4	2.467 ± 23	916 ± 14	868 ± 4	3.410 ± 19	994 ± 11	1.287 ± 18
10	1.009 ± 25	297 ± 12	267 ± 5	2.265 ± 45	862 ± 9	853 ± 5	3.072 ± 33	838 ± 12	1.175 ± 12

Table 7
Sludge digestion degree and maximum COD, TOC, and VFAs concentrations obtained in the process of 10-day methane fermentation of non-modified and disintegrated sludge by selected methods

Conditions of methane fermentation index	Conventional methane fermentation	Methane fermentation of excess sludge subjected to disintegration with the use of the most favorable modification conditions	
		Acid disintegration	Ultrasonic disintegration
		2.0 ml STERIDIAL W-15/L of sludge, t = 12 h	I_a = 2.95 W/cm^2, t = 600 s
Digestion degree, %	18	36	32
Maximum value of SCOD, mg O_2/L	1.553 ± 43 (6 d)	4.116 ± 65 (3 d)	4.632 ± 51 (4 d)
Maximum value of TOC, mg C/L	519 ± 4 (6 d)	1,511 ± 3 (3 d)	1.915 ± 12 (4 d)
Maximum value of VFAs, mg CH_3COOH/L	587 ± 23 (6 d)	1.745 ± 29 (3 d)	1.923 ± 31 (4 d)

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