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Biogas Generation from Sonicated Excess Sludge

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Received: 6 September 2019; Accepted: 10 October 2019; Published: 14 October 2019

Abstract: The article presents an analysis of the possibilities of biogas production in the process of methane fermentation of sonicated excess sludge. The greater the percentage of methane in biogas, the higher its calorific value. In order to increase the intensity of biogas production containing approximately 70% of methane, sewage sludge is disintegrated. In particular, excess sludge formed as a result of advanced wastewater treatment by the activated sludge method shows low biodegradability. The study aim was to examine the effect of the ultrasonic field disintegration of excess sludge on biogas production. As a result of subjecting the sludge to disintegration by ultrasonic field, there was an increase in the digestion degree of sewage sludge. In the methane fermentation process of modified sludge, an increase of the biogas yield was noted, which confirmed the supportive action of ultrasonic field on the excess sludge biodegradation. In the case of disintegration of excess sludge by ultrasonic field, for the ultrasonic field intensity value of 4.3 W cm^{-2} and a sonication time equal to 300 s, the highest values of soluble chemical oxygen demand (SCOD), total organic carbon (TOC), and volatile fatty acids (VFAs) concentrations were obtained. In the process of conventional methane fermentation, biogas yield value was 0.303 L g VSS^{-1}, while in the process of methane fermentation of sonicated excess sludge, the value 0.645 L g VSS^{-1}.

Keywords: ultrasonic field disintegration; methane fermentation; biogas yield; digestion degree

1. Introduction

As part of the activated sludge stream, excess sludge is directed in the technological process of wastewater treatment to separate closed fermentation chambers. This sludge is formed as a result of the growth of microorganisms during the removal of dissolved and colloidal pollutants from sewage. Depending on the applied treatment methods, excess sludge contains about 97% of the water and from 30% to 50% mineral substances obtained during the removal process [1,2]. In addition, they are characterized by a large number of facultative bacteria, which affects their low susceptibility to degradation under anaerobic conditions. In order to accelerate the degradation of macromolecular compounds before the process of methane fermentation, excess sludge is subjected to preliminary disintegration processes, during which the walls and membranes of microorganisms cells are destroyed and organic compounds are released [3,4].

The problem of sewage sludge disintegration is currently the subject of research conducted by many scientists, which results from the need to implement disintegration technologies in the sewage treatment sequence, especially in large sewage treatment plants, where methane fermentation is the predominant method of sludge stabilization [2]. Iglesias and others have shown that subjecting sewage sludge to physical disintegration increases the production of volatile fatty acids (VFA) generated in the methane fermentation process. About 45% sludge acidification was achieved [5]. Moreover in the methane fermentation process, an environmentally safe product is obtained, while biogas is also a valuable source of energy [2].

In order to increase the efficiency of the methane fermentation process, in terms of energy, a number of tests aimed at increasing the production of biogas have been conducted. For example, Alibardi et al. [6] proposed carbon dioxide (CO_2) injection in anaerobic digestion to boost methane (CH_4) recovery from sludge and organic waste by converting a greenhouse gas into a renewable resource. Ultrasonic disintegration is a method that influences the increase in the efficiency of the methane fermentation process, and therefore requires further research [7].

Ultrasounds are elastic waves with frequencies above 16 kHz. Ultrasonic wave energy is used to generate and detect ultrasonic waves. The most frequently used sources of ultrasonic waves are mechanical vibrating systems immersed in or adjacent to a material medium. The energy of mechanical vibrations in the system is excited by means of another type of energy, e.g., electricity, and is converted into acoustic wave energy. The sound wave passing through the center is suppressed or weakened. The attenuation of acoustic waves in the medium is caused, among other factors, by the conversion of wave energy into heat and friction between particles [8,9]. Ultrasonic waves are determined by analyzing parameters such as frequency, pulsation, speed, wavelength, vibration period, acoustic impedance, power, and intensity.

The introduction of high acoustic energy into the liquid system affects the occurrence of factors that can significantly modify the nature of the substances present in the solution. Such reactions are the result of the formation and contraction of cavitation bubbles, which may eventually disappear in the implosion cycle. During the implosion of bubbles in the gaseous phase, very high temperatures of about 5000 K and high pressure of about 500 bars occur. These conditions lead to the formation of sonochemical reactions associated with chemical transformations of organic compounds and the formation of radicals, hydrogen peroxide, as well as ozone according to the following reaction [10,11]:

$$H_2O \rightarrow H + HO \tag{1}$$

$$O_2 \rightarrow 2O \tag{2}$$

$$HO + O \rightarrow HOO \tag{3}$$

$$O_2 + O \rightarrow O_3 \tag{4}$$

$$2\ HO \rightarrow H_2O_2 \tag{5}$$

Sonochemical reactions occur mainly inside the cavitation vesicles and at the interfaces. Research indicates that sonochemical phenomena do not occur only at low frequencies, but also between 100–1000 kHz. However, the optimal frequency is substrate-specific [10].

The effectiveness of the sonication process is determined by the frequency of ultrasonic field vibrations, as well as by the ultrasonic field surge in the temperature of the modifiable medium. Ultrasound field has the strongest disintegrating action in the low frequency range of the ultrasonic wave of 20–22 kHz [11,12]. High efficiency of disintegration of sewage sludge is achieved by using ultrasound with low frequency (20 kHz) and sufficiently high power [13].

At high intensity of ultrasound, irreversible damage to the cells of microorganisms occurs. This is related to the formation and collapse (annihilation) of the cavitation bubble, and thus with the simultaneous increase in pressure. Therefore, it is believed that the use of an ultrasound field with a sufficiently high intensity can be a bactericidal factor [11]. Low-intensity waves can accelerate cell metabolism by improving the penetration of various substrates through cell membranes and increase the rate of substrate transfer to the active enzyme center. Ultrasonic waves of higher intensity, on the other hand, denature and destroy the activity of biocatalysts, change the charge on the surface of cells, and break and fragment the cell membrane [14]. The amount and type of microorganisms present in sewage sludge has a decisive influence on the final stage of hygienization. Inactivation of microorganisms with different properties, structure, and morphology proceeds to varying degrees [15].

Tiehm et al. [8] conducting studies on the total costs of applying ultrasounds in sewage treatment plants showed that the processes using them can be implemented in a way that ensures a positive effect both in technology and economics. They concluded that biogas obtained in stabilization processes can be converted into electricity and thus used to cover the operating costs of treatment plants. In addition, they found that from an ecological point of view when using ultrasounds, no additional environmental pollution is created [16].

The paper presents the results of research on obtaining methane in the process of conventional methane fermentation of excess sludge and in the process of methane fermentation of excess sludge disintegrated by an ultrasonic field. The methane production efficiency was evaluated in a methane fermentation process of non-processed sludge and modified with an ultrasonic field, and analysis of the possibility of using hydrogen extracted from methane in the reforming process using fuel cell technology was performed.

2. Materials and Methods

2.1. Characterization of Test Substrates

The basic substrate used in the methane fermentation process was excess sludge, which was collected from the urban municipal wastewater treatment plant with a capacity of 90,000 m^3 d^{-1} (314 835 PE). In order to initiate the process, excess sludge was inoculated with digested sludge, acting as an *inoculum* and sludge mixture was created in a volume ratio of 0.75 L to 0.25 L, respectively. Due to the nature of the proposed energy technology for the use of methane generated in the methane fermentation process, sludge was collected from the installation of a large wastewater treatment plant with high energy potential. The sampling of sludge was carried out once and repeated physico-chemical parameters were carried out three times, which made it possible to determine standard deviations. The general physico-chemical characteristics of the sludge used in the studies are shown in Table 1.

Table 1. General physico-chemical parameters of sludge used in research.

Physico-Chemical Parameters	The Type of Sludge Used in the Research	
	Excess Sludge	Digested Sludge (*inoculum*)
Total solids (TS)	12.4 ÷ 15.3 g L^{-1}	17.0 ÷ 19.6, mg L^{-1}
Volatile Suspended Solids (VSS)	8.1 ÷ 10.15 g L^{-1}	10.8 ÷ 13.2 g L^{-1}
Soluble Chemical Oxygen Demand (SCOD)	142 ÷ 164 mg O_2 L^{-1}	1056 ÷ 1278 mg O_2 L^{-1}
Total Organic Carbon (TOC)	43 ÷ 58 mg C L^{-1}	324 ÷ 467 mg C L^{-1}
Volatile Fatty Acids (VFAs)	74 ÷ 97 mg CH_3COOH L^{-1}	487 ÷ 675 mg CH_3COOH L^{-1}
Alkalinity	780 ÷ 960 mg $CaCO_3$ L^{-1}	2700 mg ÷ 3450 $CaCO_3$ L^{-1}
Kjeldahl Nitrogen	87 ÷ 143 mg N L^{-1}	612 ÷ 876 mg N L^{-1}
Ammonium Nitrogen	68 ÷ 124 mg N-NH_4^+ L^{-1}	585 ÷ 815 mg N-NH_4^+ L^{-1}
pH	7.2 ÷ 7.4	7.3 ÷ 7.6

The methane fermentation process was subjected to unprepared excess sludge and disintegrated with an ultrasonic field using the most favorable modification conditions, i.e., field strength of ultrasonic field 4.3 W cm^{-2} and sonication time 300 s. Methane fermentation was subjected to raw excess sludge and digested sludge, forming an *inoculum* (Mixture I), mixture of excess sludge disintegrated with an ultrasonic field with an ultrasonic wave intensity of 4.3 W cm^{-2}, sonication time of 300 s, and digested sludge forming an *inoculum* (Mixture II).

2.2. Selected Physico-Chemical Parameters of Sewage Sludge

In the case of conducted tests, the following physico-chemical parameters were determined:

- total solids (TS), volatile suspended solids (VSS) according to PN-EN-12879 [17];
- pH, alkalinity according to PN-91/C-04540/05 [18];

- soluble chemical oxygen demand (SCOD) the dichromate method using the company's spectrophotometer tests HACH 2I00N IS according to ISO 7027 [19];
- volatile fatty acids (VFAs) calculated as acetic acid by steam distillation according to PN-75/C-04616/04 [20];
- total organic carbon (TOC) by spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena);
- ammonium nitrogen according to PN-73/C-04576/02 [21];
- Kjeldahl nitrogen according to PN-73/C-04576/10 [22].

2.3. Conditions of Disintegration of Excess Sludge by Ultrasonic Field

In the case of ultrasonic disintegration, the excess sludge was subjected to a high intensity generator, i.e., a VC-1500 ultrasonic disintegrator (1500 W acoustic power), an American company Sonics. The sludge was subjected to an ultrasonic field with intensity of 1.9, 2.8, 3.1, 3.8, and 4.3 W cm^{-2} and sonication time from 60 to 600 s, respectively.

The ultrasonic field intensity was calculated from the following relationship [23]:

$$I_a = \frac{E_a}{S \times t} \tag{6}$$

where

I_a—ultrasonic wave intensity, W cm^{-2};
E_a—the amount of energy supplied, J;
S—cross-sectional area of the vessel inside which the sonicated sample has been placed, cm^2;
t—sonification time, s.

The process was carried out under static conditions, once the vessel was filled. The volume of sludge samples subjected to modification was 0.5 L. The evaluation of the effectiveness of the excess sludge disintegration process was based on the values of soluble chemical oxygen demand (SCOD), total organic carbon (TOC), and volatile fatty acids (VFAs) concentration.

2.4. Conditions of the Methane Fermentation Process Conducting

The methane fermentation process was carried out in a fermentation chamber with an active volume of 5 L for a period of 28 days in mesophilic conditions. The efficiency of the methane fermentation process was assessed on the basis of the digestion degree of sludge [24], expressed by the reduction in the amount of organic compounds in the sludge, the biogas yield [25], and the daily methane content in biogas. The assessment of the methane content in biogas was made using the analyzer type GA2000 Geotechnical Instruments.

3. Results and Discussion

3.1. Selection of the Most Favorable Conditions for the Disintegration of Excess Sludge with an Ultrasonic Field

Due to the low susceptibility of excess sludge to the methane fermentation process, excess sludge was subjected to the process of disintegration by an ultrasonic field. Figure 1 shows the changes in the soluble chemical oxygen demand (SCOD) values recorded for the tested values of the ultrasonic field strength, along with the elongation of the sonication time.

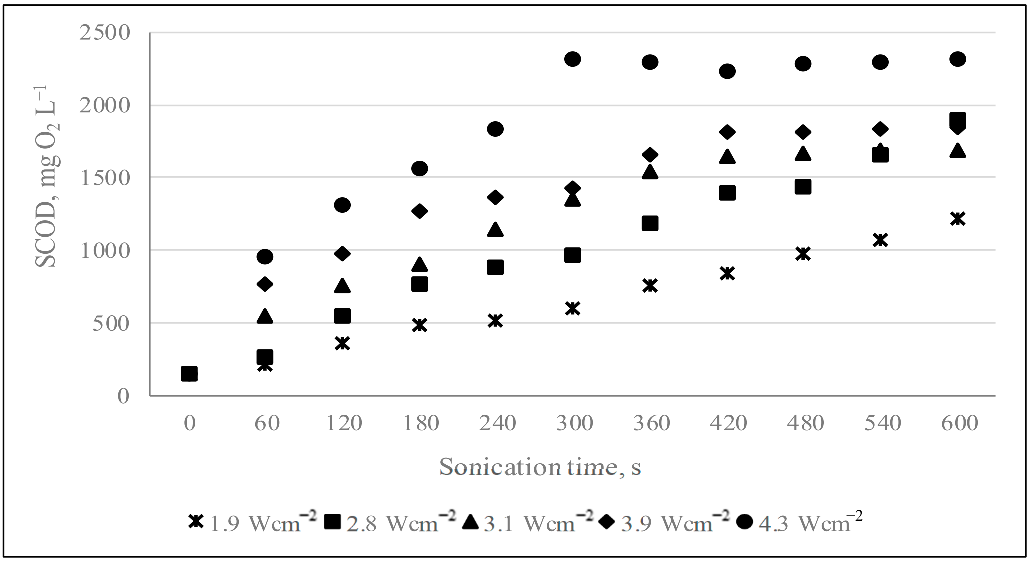

Figure 1. Changes of the SCOD value in the ultrasonic disintegration process for the tested ultrasound field intensity values depending on the sonication time.

With the increase of the ultrasonic wave intensity and the extension of the sonication time, a gradual increase in the SCOD value was noted. For each of the tested values of ultrasonic field intensity, the sonication time limit was set above which no significant increase in the value of the tested indicator was recorded. The highest SCOD value was recorded for sludge subjected to ultrasonic field strength of 4.3 W cm^{-2} and sonication time of 300 s. Wang et al. [26] using an ultrasonic density of 0.768 W/mL and oscillation frequency about 20 kHz to modify excess sludge for 5, 10, and 20 min, obtained SCOD values of 2581, 7509, and 8912 mg O_2 L^{-1}, respectively. The initial SCOD value was 52 mg O_2 L^{-1}. Meanwhile, settings of 3.6 kW ultrasonic field power, 31 kHz oscillation frequency, and 64 s sonication time obtained an increase of SCOD values of modified excess sludge from 630 to 2270 mg O_2 L^{-1} [8].

Figure 2 presents changes in the concentration of volatile fatty acids generated from excess sludge modified by ultrasonic field.

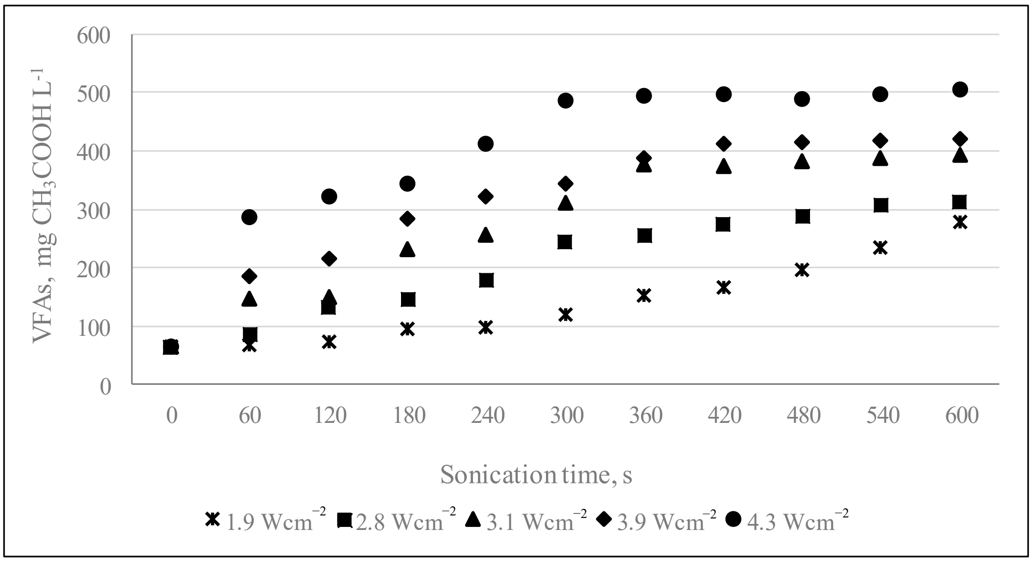

Figure 2. Changes of the VFAs concentration value in the ultrasonic disintegration process for the tested ultrasound field intensity values depending on the sonication time.

With the increase of ultrasound wave intensity and sonication time, an increase in the concentration of VFAs was noted. The highest VFAs concentration was observed for the ultrasonic wavelength of

3.78 W cm^{-2} and the sonication time of 300 s. It is observed that the increase of VFAs concentration correlated with the increase of SCOD value. The most favorable disintegration conditions were the ultrasonic field strength of 4.3 W cm^{-2} and the sonication time of 300 s resulting in an increase of SCOD and VFAs, respectively, with respect to unprepared sludge. Figure 3 presents changes of the total organic carbon values of sonicated excess sludge.

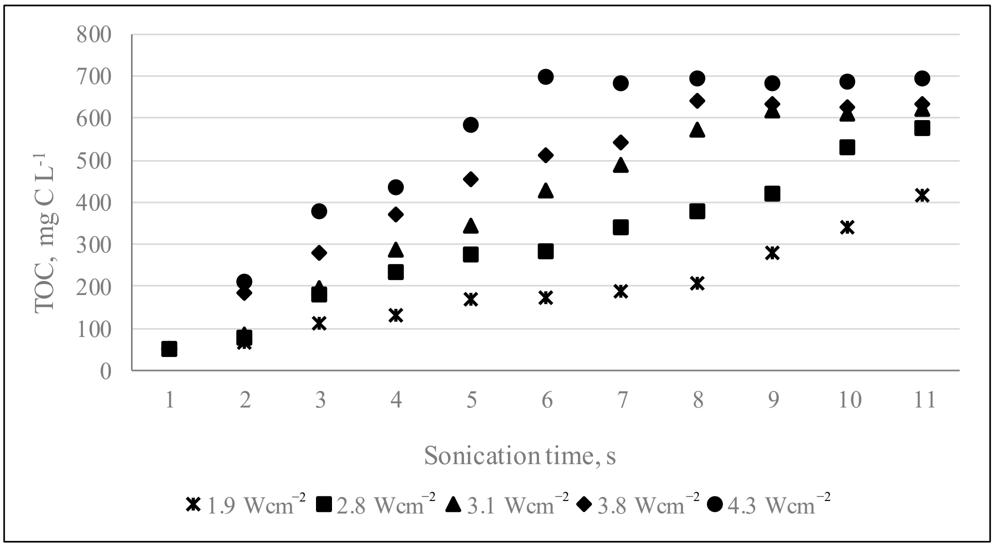

Figure 3. Changes of the TOC values in the ultrasonic disintegration process for the tested ultrasonic field intensity values depending on the sonication time.

It was observed that changes of TOC values of ultrasonic disintegrated excess sludge, depending on the ultrasonic field intensity values, correlate with changes of the SCOD values and VFAs concentration. As reported by Zawieja [27], the efficiency of conversion of organic substances contained in the excess sludge to the dissolved form is considered as an important factor limiting the process of anaerobic stabilization. As a direct effect occurring in the disintegrated sludge, the lysis process involves increasing the value of the total organic carbon (TOC), which correlates with the increase of the concentration of volatile fatty acids (VFAs). As a result of biochemical processes, any increase in the degree of decomposition of organic substances contained in the sludge decreases the value of the ratio of SCOD to TOC. With an increase in specific energy input, Simonetti et al. [28] noted changes in the structure of sludge, a reduction in their particle size, and the release of supernatant organic matter. The rapid increase of the SCOD was noticed when specific energy inputs ranged from 50 kJ/g TS to 100 kJ/g TS. For 150 kJ/g TS of specific energy input, indicator did not increased significantly. The results obtained by Feng et al. [29] indicate that the energy used for sonication strongly influences the physical–chemical characteristics of sludge.

3.2. Conventional Methane Fermentation of Excess Sludge

The process of 10-day methane fermentation was subjected to unprepared sludge. Changes of chosen physico-chemical parameters of sludge in the 10-day conventional methane fermentation process of sludge are presented in Table 2. Figure 4 shows the changes of SCOD, TOC, and VFAs values in the methane fermentation process of unprepared excess sludge.

Table 2. Changes of physico-chemical parameters of excess sludge in the 10-day methane fermentation process.

Indicator/Unit	Methane Fermentation Time, d										
	0	1	2	3	4	5	6	7	8	9	10
Volatile Suspended Solids (VSS), g L^{-1}	8.16 ± 0.07	8.07 ± 0.12	8.01 ± 0.15	7.92 ± 0.32	7.85 ± 0.25	7.82 ± 0.18	7.73 ± 0.37	7.67 ± 0.43	7.53 ± 0.28	7.49 ± 0.37	7.41 ± 0.25
Alkalinity, mg $CaCO_3$ L^{-1}	860 ± 17.6	1020 ± 2.9	1060 ± 20.8	1080 ± 11.5	1120 ± 10.4	1180 ± 23.1	1220 ± 30.6	1270 ± 25.2	1340 ± 10.4	1360 ± 7.6	1460 ± 24.7
VFAs/Alkalinity	-	0.21	0.27	0.29	0.34	0.32	0.29	0.26	0.21	0.18	0.15

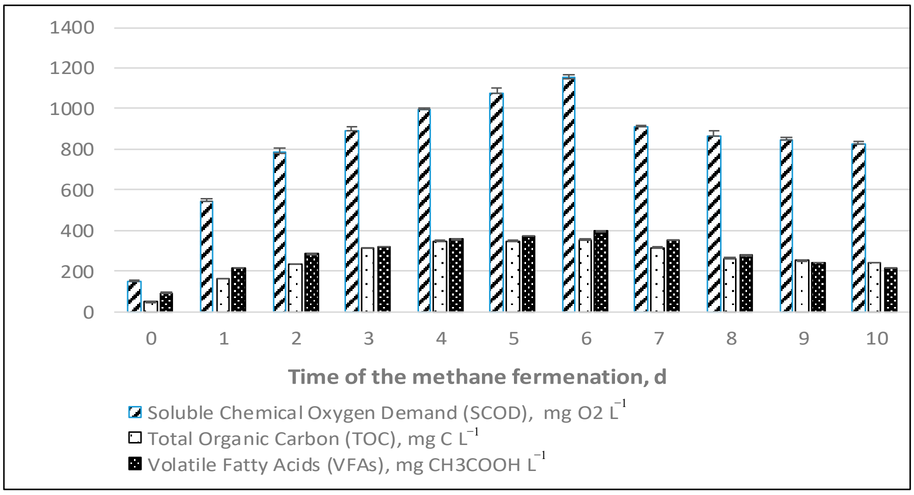

Figure 4. Changes of SCOD, TOC, and VFAs values in the methane fermentation process of unprepared excess sludge.

After the methane fermentation process, about 10% of the digestion degree was obtained, calculated by the loss of volatile suspended solids. The alkalinity increased with the extension of the stabilization time. On the 10th day of the process, it reached the value of 1460 mg $CaCO_3$ L^{-1}. The quotient VFAs/Alkalinity was in the range of 0.15 ÷ 0.34. This quotient gradually increased to the 4th day of the process, after which its gradual decrease was noted, which indicates the correctness of the methane fermentation process. During the methane fermentation process of unprepared sludge, maximum values of SCOD, TOC and VFAs amounting to 1151 mg O_2 L^{-1}, 353 mg C L^{-1} and 396 mg CH_3COOH L^{-1}, respectively, were recorded on the sixth day of the stabilization process (Figure 4). Changes of chosen physico-chemical parameters of sludge in the 25-day conventional methane fermentation process of sludge are presented in Table 3.

Table 3. Changes of physico-chemical parameters of excess sludge in a 25-day methane fermentation process.

Indicator/Unit	Methane Fermentation Time, d	
	0	25
Total Solids (TS), g L^{-1}	12.52 ± 0.54	8.69 ± 0.67
Volatile Suspended Solids (VSS), g L^{-1}	8.16 ± 0.32	5.14 ± 0.17
Alkalinity, mg $CaCO_3$ L^{-1}	860 ± 11.5	1960 ± 20.0
Soluble Chemical Oxygen Demand (SCOD), mg O_2 L^{-1}	147 ± 12.2	287 ± 17.6
Total Organic Carbon (TOC), mg C L^{-1}	48 ± 3.4	87 ± 6.2
Volatile Fatty Acids (VFAs), mg CH_3COOH L^{-1}	92 ± 8.5	112 ± 3.8
Kjeldahl Nitrogen, mg N L^{-1}	97 ± 6.3	568 ± 11.7
Ammonium Nitrogen, mg N-NH_4^+ L^{-1}	63 ± 5.4	521 ± 13.6
pH	7.4	7.3
VFAs/Alkalinity	-	0.06

After the methane fermentation process, about 37% of the digestion degree was obtained, calculated by the loss of volatile suspended solids and about 30% of the total solids reduction. Figure 5 shows the biogas production process, including methane content, in the process of anaerobic stabilization of unprepared excess sludge.

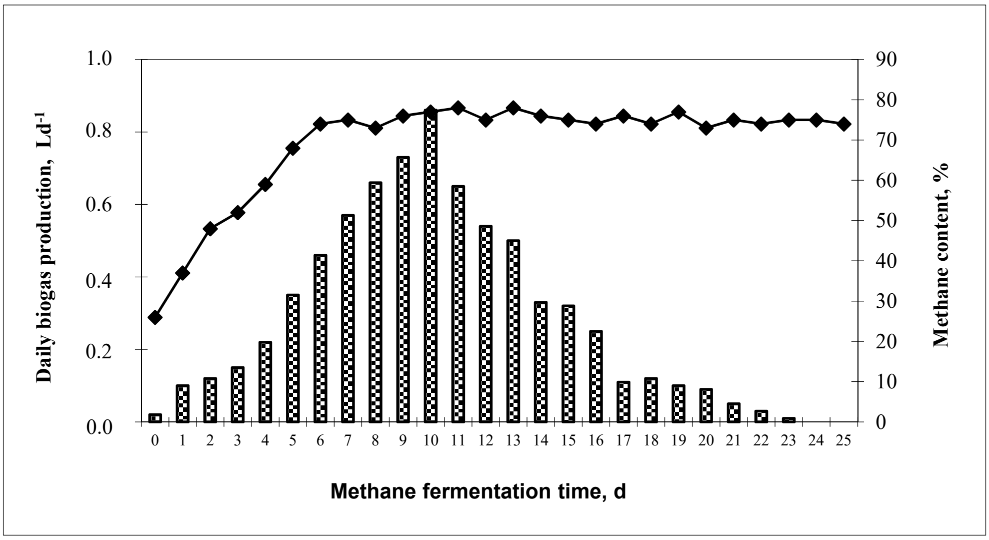

Figure 5. The biogas production process, including methane content, recorded in the process of anaerobic stabilization of unprepared excess sludge.

During the methane fermentation of unprepared sludge, the highest value of daily biogas production of 0.86 L was observed on the 10th day of the process, with a content of approximately 77% of methane. In the first 10 days of the process, a gradual increase in methane content was noted. In the following days of methane fermentation stabilization methane content in biogas was observed. The total and biogas yield was 7.34 L and 0.303 L g VSS^{-1}, respectively.

3.3. *Methane Fermentation of Excess Sludge Disintegrated by an Ultrasonic Field*

The process of 10-day methane fermentation was subjected to sludge modified by ultrasonic field. Changes of chosen physico-chemical parameters of sludge in the 10-day methane fermentation process of disintegrated sludge are presented in Table 4. Figure 6 shows the changes of SCOD, TOC, and VFAs values in the methane fermentation process of sonicated excess sludge.

Table 4. Changes of chosen physico-chemical parameters of disintegrated excess sludge with an ultrasonic wave intensity of 4.3 W cm^{-2} in a 10-day methane fermentation process.

Indicator/Unit	Methane Fermentation Time, d										
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Volatile Suspended Solids (VSS), g L^{-1}	9.12 ± 0.45	9.06 ± 0.21	8.78 ± 0.76	8.65 ± 0.43	8.17 ± 0.98	7.67 ± 0.58	7.34 ± 0.37	7.15 ± 0.79	6.78 ± 0.93	6.32 ± 0.54	5.76 ± 0.77
Alkalinity, mg $CaCO_3$ L^{-1}	960 ± 8.7	1320 ± 13.2	1380 ± 20.0	1420 ± 10.0	1480 ± 15.3	1670 ± 18.9	1720 ± 17.6	1840 ± 7.6	2040 ± 15.3	2270 ± 17.6	2320 ± 15.3
VFAs/Alkalinity	-	0.50	0.50	0.51	0.51	0.44	0.41	0.36	0.32	0.27	0.24

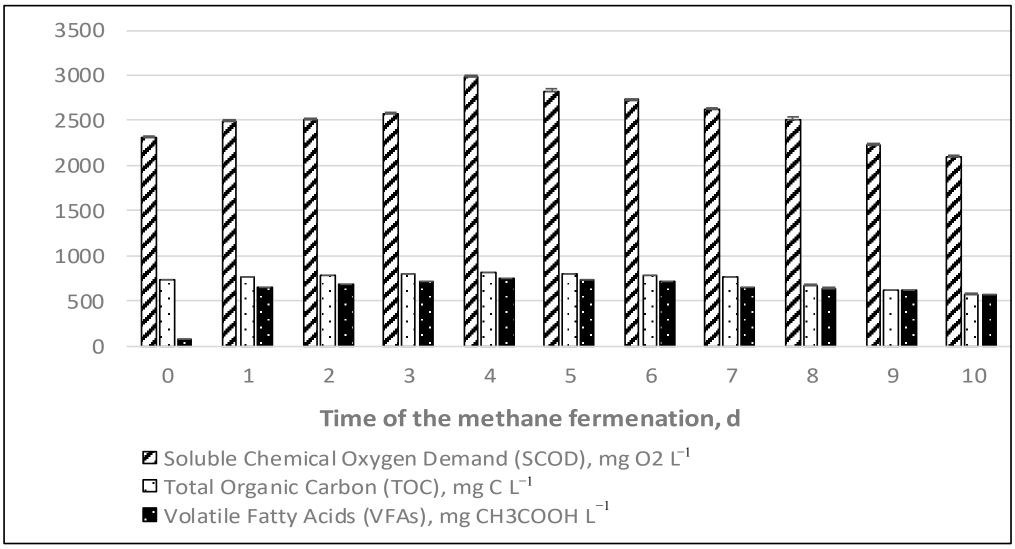

Figure 6. Changes of SCOD, TOC, and VFAs values in the methane fermentation process of sonicated excess sludge.

After the methane fermentation process, about 37% of the digestion degree was obtained, calculated by the loss of volatile suspended solids and about 24% of the total solids reduction. The alkalinity increased with the extension of the stabilization time. On the 10th day of the process, it reached the value of 2320 mg $CaCO_3$ L^{-1}. The quotient of VFAs/Alkalinity was in the range of 0.24 ÷ 0.51. In the following days of the process, a gradual decrease in the quotient was noted, obtaining a value below 0.3on the 9th and 10th days, which proves the correctness of the methane fermentation process. During the methane fermentation of sludge disintegrated by ultrasonic field, maximum values of SCOD, TOC and VFAs amounting to 2983 mg O_2 L^{-1}, 814 mg C L^{-1}, and 756 mg CH_3COOH L^{-1} was recorded on the fourth day of the stabilization process.

Both in unmodified sludge and ultrasonic modified sludge in the process of methane fermentation of excess sludge in subsequent days, the content of volatile suspended solids (VSS) decreased. There was a gradual overall increase in the basicity. In the case of VFAs and SCOD, an increase in the value of these parameters to a certain limit value was noted, followed by a drop in value, until the stabilization processes were completed.

Changes of physico-chemical parameters of sludge in the 28-day methane fermentation process of disintegrated sludge are presented in Table 5.

Table 5. Changes of physico-chemical parameters of disintegrated excess sludge with an ultrasonic wave intensity of 4.3 W cm^{-2} in a 25-day methane fermentation process.

Indicator/Unit	Methane Fermentation Time, d	
	0	25
Total Solids (TS), g L^{-1}	11.98 ± 0.57	5.14 ± 0.24
Volatile Suspended Solids (VSS), g L^{-1}	9,12 ± 0.18	3,28 ± 0.42
Alkalinity, mg $CaCO_3$ L^{-1}	960 ± 27.8	3250 ± 45.4
Soluble Chemical Oxygen Demand (SCOD), mg O_2 L^{-1}	2316 ± 18.4	527 ± 11.7
Total Organic Carbon (TOC), mg C L^{-1}	734 ± 8.7	187 ± 4.6
Volatile Fatty Acids (VFAs), mg CH_3COOH L^{-1}	786 ± 11.7	234 ± 84.5
Kjeldahl Nitrogen, mg N L^{-1}	356 ± 11.4	765 ± 15.8
Ammonium Nitrogen, mg N-NH_4^+ L^{-1}	273 ± 5.3	715 ± 8.7
pH	7.2	7.1
VFAs/Alkalinity	-	0.07

After the methane fermentation process, about 64% of the digestion degree was obtained, calculated by the loss of volatile suspended solids and about 57% of the total solids reduction. Figure 7 shows the biogas production process, including methane content, which was recorded in the process of anaerobic stabilization of disintegrated excess sludge with an ultrasonic field of intensity 4.3 W cm^{-2}.

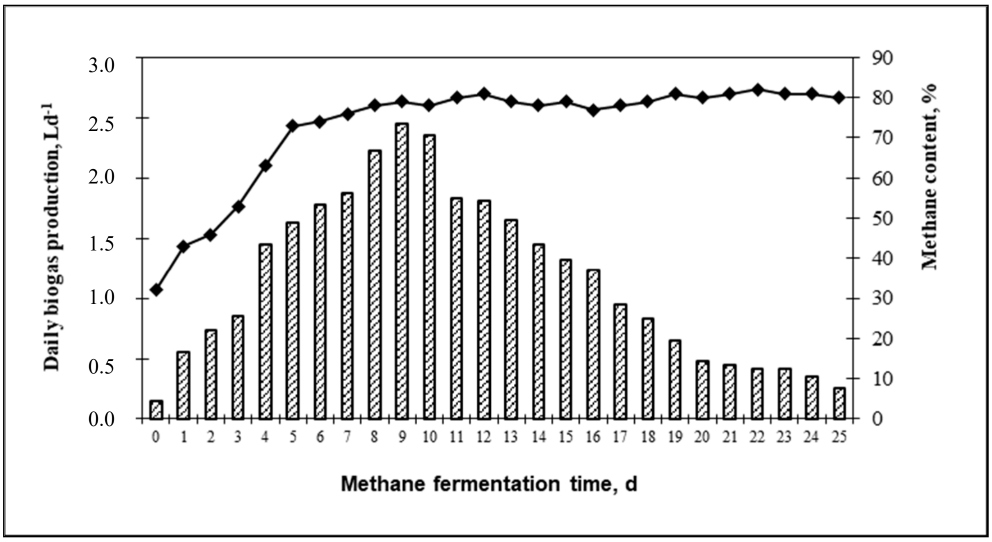

Figure 7. The biogas production process, including methane content, recorded in the process of anaerobic stabilization of disintegrated excess sludge with an ultrasonic field of intensity of 4.3 W cm^{-2}.

During the methane fermentation process, the sludge subjected to ultrasonic disintegration, the highest daily biogas production value 2.45 L was obtained on the 9th day of the process, with a content of about 79% methane. In the first 12 days of the process, a gradual increase in methane content was noted. In the following days of methane fermentation stabilization, methane content in biogas was observed. In relation to the fermentation of untreated sludge, no significant increase in methane content in biogas generated from sludge modified with ultrasonic field was noted. This theory was confirmed by research carried out by other scientists [30,31]. Total biogas production amounted to 30.14 L, and biogas yield 0.645 L g VSS^{-1}. For the excess sludge pretreatment by ultrasonic field with ultrasonic intensity equal to 2.6 W cm^{-2} and 1.9 W cm^{-2} obtained increasea of biogas production 13.0% and 19.7%, respectively, compared to the conventional methane fermentation process [30].

Ultrasonic disintegration of excess sludge prior to methane fermentation increased total biogas production (from 13.0% to 19.7%) and reduced the content of total solids (TS) from 4.1% to 8.2% and volatile suspended solids (VSS) from 5.8% to 9.5% in comparison to the conventional methane fermentation.

The association of the sonolysis process with biological hydrolysis influences the efficiency of the methane fermentation process. The technology based on the ultra-disintegration process is a promising process solution that does not cause secondary pollution of the sediment environment. As a result, there is a potential possibility of implementing the proposed technology in the sewage sludge treatment sequence.

According to Slow, higher availability of extracellular and intracellular compounds in leachate facilitates the anaerobic microbial community to biodegrade the organic matter. High kinetic results have been reported for the degradation rate of these reactions [32].

The obtained results of the research were in a good agreement with the observations of other researchers i.e., for the ultrasonic pretreatment of excess sludge at 20 kHz and power equal to 200 W, the biogas production increased by 6.3% [33], while with energy in the range of 15,000 to 35,000 kJ·kg^{-1}, TS biogas increased from 8.6% to 31.4% [34].

3.4. Research for the Future

An interesting technological solution may be used in the reforming process of methane obtained from methane fermentation from municipal waste. This is important because growing stacks of rubbish in the landfill are becoming a serious problem. Annually, about 130 million tons of waste are produced, and the oxidizing methane is adversely affecting the environment [35]. In addition, municipal waste is a substrate commonly available at landfills and does not contribute to the reduction of natural sources of energy. Municipal waste as a free energy source can lead to lower production costs and the use of fuel cells.

Hydrogen is obtained in the process of classical reforming:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad \Delta H = 206\ \mathrm{kJ\ mol^{-1}} \tag{7}$$

or in the process of reforming with CO_2 according to the reaction:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H = 247\ \mathrm{kJ\ mol^{-1}} \tag{8}$$

As shown by the data presented in Figure 5, the biogas production process, methane content in the process of anaerobic stabilization of unprepared excess sludge, and methane content after 7 days of the process all stabilized and amounted to approximately 75% For the biogas production process, including the methane content recorded in the process of anaerobic stabilization of disintegrated excess sludge with an ultrasonic field of intensity 3,8 W cm^{-2}, the methane content stabilized and was 80% after 6 days. On the basis of reactions 4 and 5, the volume of hydrogen was determined, which can be obtained in the process of decomposition of methane from biogas. The volume of H_2 produced as a result of the reaction (4) was about 2.268 dm^3 and that of the reaction (5) was about 1.512 dm^3 under a anaerobic stabilization process (75% methane content). When using the anaerobic stabilization process with an ultrasonic field (80% methane content), the amount of hydrogen that can be obtained is 2.394 dm^3 and 1.596 dm^3 estimated based on reaction (4) and (5), respectively.

In practice, reforming processes are tacked on with the addition of catalysts (Ru, Rh, Ni, Pd, Pt, Re, and Ir [36]) and by maintaining high temperatures (700–1000 °C), which ensures a high efficiency of the processes. Hydrogen consumption in a low-temperature fuel cells at current I = 1000 mA is about 0.007 $dm^3\ min^{-1}$ [37,38].

An important solution is to use the heat generated during hydrogen oxidation in the fuel cell to support waste treatment and support crop cultivation and processing.

Hydrogen production from biogas allows us to classify hydrogen as a renewable fuel. Currently, it is treated as unconventional fuel, hence the generator or fuel cells are expensive due to expensive hydrogen production and storage as well as poorly prepared hydrogen infrastructure.

The technologies of biogas production by methane fermentation have a high chance of development in Poland due to the demand for energy generated in the distributed system and favorable raw material conditions. Optimization of biogas production technology ensures, in contrast to wind and water technologies, continuous energy supply from waste biomass. Therefore, national legislation should support the development of biogas technology in both sewage and agricultural facilities. An important aspect of the implementation of technologies based on the use of biogas is also the promotion of these solutions for the purpose of social acceptance. Methane fermentation technology allows the generation of a source of energy in the form of biogas through the reforming of hydrogen. and as a consequence gives the opportunity for the development of a more vibrant economy. The use of hydrogen in power and communication for the production of electricity in fuel cells requires the use of an economically viable solution that guarantees continuity of energy source production.

4. Conclusions

A promising technology for obtaining biogas is methane fermentation of waste organic fractions. Production of biogas, in the process of methane fermentation, which is as an alternative source of energy, refers to the concept of sustainable development, allowing both management of hazardous waste such as sludge, and obtaining energy. Moreover the proposed technology closely refers to the idea of a closed cycle economy, in which waste is a valuable substrate for energy production. It is possible to obtain energy from biogas in the reforming process for hydrogen, which is a clear energy source and can be used for the production of electricity in fuel cells.

In order to increase the volume of biogas production, excess sludge was subjected to a disintegration process. Excess sludge formed as a result of advanced wastewater treatment by the activated sludge method shows low biodegradability. As a result of subjecting the sludge to disintegration by ultrasonic field, the intensity of the volatile fatty acids (VFAs) generation as well as the increase in the soluble chemical oxygen demand (SCOD) and total organic carbon (TOC) values were noted in subsequent days of the methane fermentation process. As a result, there was an increase in the digestion degree of sludge and an increase of the biogas yield, which confirmed the supporting action of ultrasonic field on the excess sludge susceptibility to biodegradation.

As a result the following conclusions were made:

- In the case of ultrasonic disintegration about the ultrasonic field intensity in the range from 1.9 to 4.3 W cm^{-2}, an increase of liquefaction of excess sludge was observed compared to unprepared sludge. With a value of ultrasonic field intensity of 4.3 W cm^{-2} and the sonication time equal to 300 s, the highest values of SCOD, TOC and VFAs concentrations were obtained.
- In the 10-day conventional methane fermentation process, about a 10% digestion degree was obtained, while in the case of the sonicated excess sludge methane fermentation, about a 37% digestion degree was obtained. The highest value of indicators such as SCOD and VFAs were obtained on the 6th and 4th day of the process, respectively, which indicates the increase of the efficiency of the hydrolysis phase, which is the conditioning of the methane fermentation process.
- Excess sludge is a potential source of biogas, which is a valuable energy carrier in the form of methane. Modification of conventional methane fermentation technology of excess sludge by the implementation of sonication process allows for obtaining almost the twice the increase of the biogas yield.

Author Contributions: I.Z. and R.W. conceived and designed the experiments; I.Z. performed the experiments; R.G. analysed the data; I.Z. and R.G. contributed reagents/materials/analysis tools; I.Z., R.W. and M.K. wrote the paper.

Funding: The research was funded by the project No. BS/PB-400-301/19 awarded by the Ministry of Science and Higher Education.

Conflicts of Interest: The authors declare no conflict of interest.

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