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The course of the methane fermentation process of dry ice modified excess sludge

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Abstract: The essence of the methane fermentation course is the phase nature of changes taking place during the process. The biodegradation degree of sewage sludge is determined by the effectiveness of the hydrolysis phase. Excess sludge, in the form of a flocculent suspension of microorganisms, subjected to the methane fermentation process show limited susceptibility to the biodegradation. Excess sludge is characterized by a significant content of volatile suspended solids equal about 65 ÷ 75%. Promising technological solution in terms of increasing the efficiency of fermentation process is the application of thermal modification of sludge with the use of dry ice. As a result of excess sludge disintegration by dry ice, denaturation of microbial cells with a mechanical support occurs. The crystallization process takes place and microorganisms of excess sludge undergo the so-called "thermal shock". The aim of the study was to determine the effect of dry ice disintegration on the course of the methane fermentation process of the modified excess sludge. In the case of dry ice modification reagent in a granular form with a grain diameter of 0.6 mm was used. Dry ice was mixed with excess sludge in a volume ratio of 0.15/1, 0.25/1, 0.35/1, 0.45/1, 0.55/1, 0.65/1, 0.75/1, respectively. The methane fermentation process lasting for 8 and 28 days, respectively, was carried out in mesophilic conditions at 37°C. In the first series untreated sludge was used, and for the second and third series the following treatment parameters were applied: the dose of dry ice in a volume ratio to excess sludge equal 0.55/1, pretreatment time 12 hours. The increase of the excess sludge disintegration degree, as well as the increase of the digestion degree and biogas yield, was a confirmation of the supporting operation of the applied modification. The mixture of reactant and excess sludge in a volume ratio of 0.55/1 was considered the most favorable combination. In relation to not prepared sludge for the selected most favorable conditions of excess sludge modification, about 2.7 and 3-fold increase of TOC and SCOD values and a 2.8-fold increase in VFAs concentration were obtained respectively.

In relation to the effects of the methane fermentation of non-prepared sludge, for modified sludge, about 33 percentage increase of the sludge digestion degree and about 31 percentage increase of the biogas yield was noticed.

Introduction

It should be emphasized that the choice of an appropriate sewage sludge management strategy should be preceded by an analysis of the final product market taking into account the ecological and economic assessment of the proposed solution. Therefore efficiency and long-term nature of the applied solution should be an idea for good managing of this type of waste (Wolski and Zawieja 2012, Wolski and Zawieja 2014, Wolski and Małkowski 2014, Neczaj et al. 2013, Grosser et al. 2012). The costs of construction and operation of sewage treatment plant equipment are very high, therefore economic conditions force the operators of the plant to treat sludge as raw material with a certain fertilizing value, especially energy, which may be the basis for partial reimbursement. A promising solution in terms of technology is the dry ice disintegration of sludge, which is a method that does not cause secondary pollution of the sludge stream.

Most of the organic matter of the activate sludge are compartmentalized within microbial cell membranes (Weemaes and Verstraete 1998).

As a result of the introduction of the sludge processing into the technological line, before the methane fermentation process, the freezing treatment of sewage sludge follows the release of the soluble organic matter, nutrients and intracellular substance to the sludge liquid. Due to the low operation temperatures, the freezing/thawing (F/T) process has the advantage of low corrosion of treatment facilities and low odor generation (Gao 2011). Based on the research carried out by Jean et al. (Jean et al. 2001) it was shown that dry ice freezing/thawing can sufficiently condition the sludge and is an economically reasonable alternative for sludge conditioning. It should be emphasized that the pre-treatment increases the amount of biogas produced, which can be used in the cogeneration process for the production of heat and power generation, which amortizes part of the costs incurred to carry out the process of disintegration of sludge (Vinay Kumar Tyagi, Shang-Lien Lo 2011).

Commonly used parameter to evaluate the effectiveness of disintegration is soluble chemical oxygen demand (SCOD) (Neumann et al. 2016). As reported by Bougrier et al. (Bougrier et al. 2006) there is a relationship between COD solubilization and biodegradation. In addition, there is a relationship between an increase in the SCOD value and the VFAs concentration. However, as reported by Nazari et al. and Sapkaite et al. (Nazari et al. 2016, Sapkaite et al. 2017) higher SCOD value, due to the excessive increase in the charge of dissolved organics, did not result in higher biogas production.

The freezing/thawing technique is considered a method contributing to the release of extracellular polymers and the disruption of sludge cells (Gao 2011).

The freeze/thaw (F/T) treatment could facilitate mass transfer from the solid phase into the aqueous phase (Kai Hu et al. 2011). As reported by Kai Hu et al. (Kai Hu et al. 2011) freeze/thaw (F/T) treatment is an efficient pretreatment method of excess sludge, increasing their biodegradability. According to Parker and Collins (Parker and Collins 1997) curing is a storage process of frozen sludge under subfreezing temperature.

During the freezing process, the term "curing stage" is called the process during which bulk sludge is frozen and tiny unfrozen regimes in the ice matrix are continuously dehydrated by surrounding ice fronts. Therefore, the F/T treatment could enhance sludge organic matter solubilization. The curing process contributes to a limited growth of SCOD and ammonium nitrogen release. The crystallization of intraaggregate is responsible for the destruction of cell membranes and release of intracellular substances to the sludge liquid (Parker and Collins 1997).

In the case of the freeze/thaw method, the formation of intracellular and extracellular ice crystals is responsible for the lysis process. The ongoing process of destroying cell walls of microorganisms and the release of intracellular substances has a mechanical basis and occurs as a result of the so-called thermal shock (Gao 2011, El-Kest et al. 1992).

Figure 1 shows the process of freezing/thawing of sludge (Parker and Collins 1997).

Thermal shock of bacteria occurs usually under specific conditions such as rapid freezing and in the case of the log phase of cell growth. The occurrence of thermal shock is conditioned by the cells concentration and the nature of the medium in which they are undergoing freezing. Changes are usually not evident immediately after chilling but appear to an increasing degree with extended storage near 0°C. Microbes undergo the so-called thermal shock and are injured when the ambient temperature drops sharply. During this process, frozen cells can be injured mechanically by intra- and extracellular ice crystals. During the thawing the growth of ice crystals which occurs can physically affect cells (El-Kest and Marth 1992). Freeze-thaw pretreatment increases significantly the concentrations of proteins, carbohydrates, and cations in the sludge liquid, what is the consequence of cell disruption and releases intracellular substances (Örmeni and Vesilind 2001).

The aim of the study was to determine the effect of dry ice disintegration on the course of the methane fermentation process of modified excess sludge.

Experimental part

Substrate

The basic substrate used in the studies was excessive activated sludge. In the case of anaerobic stabilization processes of the sludge, a fermented sludge was used, which served as the "seed". The sludge was collected from the wastewater treatment plant with a capacity of about 90,000 m^3/d , which is a mechanical and biological treatment plant with increased biogen removal. Due to the nature of the conducted research, sludge from the installation of a large wastewater treatment plant was selected for laboratory experiments. Sludge treatment technology operating in this treatment plant allows for the potential and effective implementation of disintegration processes. Samples taken at random were subjected to analysis and technological research on the day of collection. The sampling of sludge was carried out only once. Three-fold analysis of selected physico--chemical indicators was carried out. The general physico--chemical characteristics of the sludge used in the studies are presented in Table 1.

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Fig. 1. The idea of freezing/thawing process of sewage sludge (Parker and Collins 1997)

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Table 1. General physico-chemical characteristics of the excess and digested sludge

	The sludge used in the research				
Physico-chemical indicators	Excess sludge	Digested sludge (<i>inoculum</i>)			
Total Solids	15.24 g/L±0.26	12,6 mg/L±0.15			
Volatile Suspended Solids	9.9 g/L±0.56	7,4 g/L±0.72			
Total Organic Carbon (TOC)	42 mg C/L±0.17	421 mg/L±0.7			
Soluble Chemical Oxygen Deman (SCOD)	132 mg O ₂ /L±3.1	1165 mg O ₂ /±L1±14.3			
Volatile Fatty Acids (VFAs)	85 mg $CH_{3}COOH/L\pm 2.5$	684 mg CH ₃ COOH/L±2.8			
Alkalinity	860 mg CaCO ₃ /L±8.13	3120 CaCO ₃ /L±11.23			
Kjeldahl Nitogen	67 mg N/L±0.34	845 mg N/L±1.16			
Ammonium Nitrogen	42 mg N-NH ₄ /L±3.5	794 mg N-NH ₄ +±/L±2.3			
рН	7.2±0.13	7.7±0.04			

Methodology

During the research the following physico – chemical indicators were made:

- ✓ pH (PN-9/C-04540/05),
- ✓ the volatile suspended solids (VSS) (PN-EN-12879),
- ✓ volatile fatty acids (VFAs) by steam distillation (PN-75/C-04616/04),
- ✓ alkalinity (PN-91 C-04540/05),
- ✓ soluble chemical oxygen demand (SCOD) by dichromate method, using a colorimetric spectrophotometer Hach Dr 400 (PN-EN ISO 7027),
- ✓ Kjeldahl nitrogen (PN-73/C-04576/10),
- ✓ ammonium nitrogen (PN-73/C-04576/02),
- ✓ total organic carbon (TOC) by spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena).

In the case of dry ice modification reagent in a granular form with a grain diameter of 0.6 mm was used. Dry ice was mixed with excess sludge in a volume ratio of 0.15/1, 0.25/1, 0.35/1, 0.45/1, 0.55/1, 0.65/1, 0.75/1, respectively. Disintegration was carried out at ambient temperature. The time of the modification process, i.e. freezing and thawing, was equal 12h and the volume of sludge subjected to modification was 1L.

In addition, microscopic observations of the structure of sludge were carried out. The formulations were fixed by drying at ambient temperature. The observation of the structure of sludge was carried out using an Olympus BX 41 microscope with photo equipment. Observations of sludge structure and microphotographs were made using 100x magnification.

The process of mesophilic methane fermentation was carried out in eight models of fermentation chambers, placed in temperature of 37°C in a laboratory thermostat. The sludge was placed in laboratory flasks with an active volume of 0.5 L, air-protected glass stopper with a manometric tube allowing for the outflow of biogas produced. The contents of the flasks were mixed using magnetic stirrers, ensuring a continuous mixing throughout the day, preventing the formation of the skin and preventing the creation of areas overloaded with pollutants. The anaerobic stabilization process was subjected to modified dry ice excess sludge in the dose, which in the preliminary tests in terms of the disintegration degree obtained, the VFAs

concentration, TOC values and pH was considered the most favorable. Excess sludge, in order to initiate the methane fermentation process, was inoculated with digested sludge, assuming a volume ratio of excess to digested sludge of 10:1, respectively. Anaerobic stabilization was subjected to:

- non pretreatment excess sludge,
- excess sludge disintegrated with dry ice in a dose i.e. volume ratio dry ice to excess sludge equal 0.55/1.

Based on the selection of the most beneficial doses of reagent made in the first stage of research, i.e. dry ice in the next stage of research, the effectiveness of applied sludge modification was verified. During the research the course of the first days of methane fermentation was analyzed, as well as the effects of 28-day methane fermentation were assessed, i.e. the digestion degree of sewage sludge and the biogas yield.

Biogas yield was obtained from the formula (2) (Zawieja and Wolny 2013):

$$b.y. = V/\Delta VSS$$
(2)

b.y. - biogas yield, L g⁻¹ VSS;

- V total of biogas volume released throughout the process of fermentation, L;
- ΔVSS decrement of dry organic mass in the sludge, g VSS.

The digestion degree expressing the decomposition of organic substances under anaerobic conditions was determined in accordance with PN-EN 12879. The 28-day methane fermentation process of a seasonal nature was carried out in a fermentation chamber made of a glass cylinder with an active volume of 5 L. The closed fermentation chamber model was equipped with a biogas detection system, mixing of the chamber volume and a system of heat exchangers that ensure optimal process temperature

Results and discussion

Disintegration of excess sludge with dry ice

In order to determine the most favorable conditions for the dry ice disintegration of excess dry sludge, during the study selected doses of reagent were used, i.e. dry ice mixed with

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excess sludge in a volume ratio from 0.15: 1, to 0.75: 1 and assumed a 12-hour modification time. According to the literature data as a result of subjecting sludge to the freezing/ thawing process, there is an increase in the concentration of organic matter in the dissolved form expressed as SCOD, VFAs as well as TOC value (Chen 2014, Gao 2011, Nowicka and Machnicka 2013). This theory has been confirmed by research conducted by Hong et al. (Hong et al. 1995). The authors showed a significant increase in SCOD value of an activated sludge supernatant after freeze-thaw conditioning. A similar tendency concerning the increase of susceptibility of excess sludge to biodegradation was noted as a result of submitting the dry ice modified sludge with the usage of selected doses of reagent. Figure 2 shows changes in SCOD and TOC values of excess sludge subjected to the freezing/thawing process.

It was found that with increasing doses of dry ice an increase of TOC value was observed which correlated with the increase of SCOD value. In addition, it was observed that in the

case of the mixture of dry ice and excess sludge in a volume ratio of 0.65: 1 and 0.75: 1 respectively an increase of SCOD and TOC values was inadequate to the reagent dose, there was no significant increase in the tested indicators values. Figure 3 shows changes of VFAs concentration and pH value of excess sludge subjected to the freezing/thawing process.

For reagent doses that are the volume ratio of dry ice to excess sludge equal 0.15/1, 0.25/1, 0.35/1, 0.45/1 and 0.55/1 there was an increase in the concentration of VFAs adequate to the increase in the reagent dose. According to Montusiewicz et al. (Montusiewicz et al. 2010) the pH value of sludge is slightly reduced after F/T treatment. The decrease of pH value is probably related to the release of fatty acids from the solid phase to the liquid phase. As a result of subjecting the sludge to disintegration with dry ice, a slight decrease in the pH value correlated with the concentration of VFAs increase. Figure 4 shows changes of Kjeldahl and ammonium nitrogen values of excess sludge subjected to the freezing/thawing process.



Fig. 2. Changes of soluble chemical oxygen demand (SCOD) and total organic carbon (TOC) values of dry ice prepared excess sludge



Fig. 3. Changes of volatile fatty acids concentration (VFAs) and pH values of dry ice modified excess sludge

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Fig. 4. Changes of Kjeldahl nitrogen and ammonium nitrogen values of dry ice prepared excess sludge

Due to the fact that the next stage of the sludge treatment is the process of methane fermentation, the Kjeldahl and ammonium nitrogen value has technological signification and determines the correctness of the course of anaerobic stabilization. Small concentrations of ammonium ions (50-200 mgN L) in the fermented feed are considered to stimulate methanogenic activity. Ammonium concentrations from 200-1000 mgN/L are considered not to inhibit the process, and from 1500 mg N-NH₄/L to 3000 mg N-NH₄/L as tolerated by methanogenic bacteria. At the concentration of ammonium nitrogen around 5000 mg N-NH₄/L, the maximum growth rate of hydrogenotrophic methanogens decreases by almost 50% (Bartoszewski 1997). The increase of NH,-N concentration is due to the degradation of protein organic matter and the releasing of NH⁺ ions (Carta-Escobar et al. 2002).

This theory is confirmed by the obtained results on the basis of which the increase of the Kjeldahl and ammonium nitrogen value proportional to the increase in the reagent dose was found. For the volume ratio of dry ice to excess sludge: 0.65/1, 0.75/1, no increase in the value of the nitrogen form was proportional to the increase of the reagent dose. According to Jedrczak (Jędrczak 2008), the presence of nitrogen in the raw material is necessary for two reasons: it is an important component for the synthesis of amino acids, proteins and nucleic acids and is converted into ammonia, which neutralizes volatile acids, produced by fermentation bacteria and in this way allows for maintaining the neutral reaction of the environment necessary for their growth. (Bartoszewski 1997)

Mechanical damage of the microbial cells and the occurring osmotic shock is responsible for the change in the structure of the prepared sludge and the release of intracellular substances into the supernatant liquid (Thammavongsa et al. 2004, Nowicka and Machnicka 2013). Figure 5 shows the structure of raw excess sludge, as well as modified sludge.

Disintegration with dry ice influenced the change of the sludge structure, consequently leading to the initiation of the hydrolysis process, responsible for the phenomenon of "dissolving" sludge particles. This was confirmed in Fig. $2b \div f$. The effect of liquefaction of sludge particles can be clearly seen especially in the case of a volume ratio of dry ice to sludge

equal 0.55/1, 0.65/1, 0.75/1. The structure of sludge after disintegration depends on the dose of reagent characterized by the solidification of the solid phase and the increase in the liquefaction of sludge particles. Changes in the structure of dry ice modified excess sludge correlate with the increase of the SCOD, TOC value as well as VFAs concentration and constitute an additional tool to assess the effectiveness of the proposed disintegration method.

Conventional way of conducting the methane fermentation and the process proceeded by the chosen disintegration method

During the next stage of the research unprocessed and modified by freezing/thawing excess sludge was subjected to the process of methane fermentation. The course of the methane fermentation was evaluated during the following 8 days of the process and the effects of methane fermentation after subjecting the sludge to 28 days anaerobic stabilization were evaluated. Tables 1 and 2 present values of selected physicochemical indicators of sludge subjected respectively to conventional methane fermentation and fermentation supported by the selected disintegration method.

Analyzing the course of 8-day methane fermentation of non--processed excess sludge, the highest values of SCOD and TOC as well as VFAs concentration were recorded on the 5th day of the process. Whereas during the 8-day methane fermentation of dry ice, the highest values of SCOD and TOC as well as VFAs were recorded on the 6th day of the process. The obtained values of the tested determinations indicate the intensification of the hydrolysis phase of the methane fermentation process, which, according to the literature data (Eastman and Ferguson 1981, Climent et al. 2007, Appels et al. 2010) and own research, is considered as the phase limiting the course of anaerobic stabilization.

In the case of the methane fermentation process of excess sludge disintegrated with dry ice, a digestion degree of approx. 60% and a biogas yield value of 0.62 L/gVSS were obtained. In the case of the methane fermentation process carried out in a conventional manner, the digestion degree of sludge equal about 40% was obtained, as well as the value of unitary biogas production equal to 0.43 L/gVSS. According to the results



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Fig. 5. Structure of non-prepared excess sludge (a) and chosen structure of sludge after disintegration with dry ice: the volume ratio of dry ice to excess sludge 0.35/L (b); 0.45/L (c); 0.55/L (d); 0.65/L (e); 0.75/L (f)

Time of the methane fermentation	TS	VSS	VFAs	SCOD	тос	Kjeldahl nitrogen	Ammonium nitrogen	рН	Alkalinity
d.	g/L	g/L	mg H ₃ COOH/L	mg O ₃ /L	mg C/L	mg N/L	mg N-NH ₄ /L	-	mg Ca CO₃/L
1	16.78	11.76	324	876	256	172	123	7.10	750
	±0.87	±1.02	±0.7	±2.6	±2.1	±1.5	±2.4	±0.03	±11
2	16.56	11.54	567	1245	382	255	208	7.02	990
	±0.56	±0.70	±1.4	±5.6	±1.7	±2.3	±4.7	±0.11	±23
3	16.32	11.34	789	1549	511	351	312	6.86	1740
	±0.12	±0.37	±1.4	±7.2	±1.2	±2.7	±5.2	±0.04	±8
4	16.07	11.26	923	1612	523	452	389	7.12	1950
	±0.56	±0.28	±2.8	±11.7	±2.3	±1.4	±1.8	±0.07	±23
5	16.78	11.11	956	1723	635	584	529	7.06	2480
	±0.71	±0.38	±2.3	±21.2	±3.1	±2.3	±4.9	±0.02	±25
6	15.62	10.78	876	1674	601	618	563	6.95	2150
	±1.12	±0.86	±3.7	±9.3	±3.5	±3.2	±3.2	±0.05	±42.11
7	15.38	10.54	885	1591	585	659	642	6.82	2250
	±1.67	±0.15	±4.8	±11.2	±2.7	±3.6	±5.8	±0.01	±15
8	15.21	10.32	812	1422	471	784	772	6.92	2150
	±0.65	±0.52	±5.2	±9.8	±1.2	±1.8	±3.3	±0.12	±17
28	10.89	7.05	238	561	193	965	941	7.14	3120
	±0.27	±0.75	±2.4	±3.7	±1.5	±2.5	±4.7	±0.15	±10

Table 2. Conventional methane fermentation process



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 Table 3. Methane fermentation process aided by dry ice disintegration in the volume ratio of the reactant to excess sludge equal 0.55/1

Time of the methane fermentation	TS	VSS	VFAs	SCOD	тос	Kjeldahl nitrogen	Ammonium nitrogen	рН	Alkalinity
d.	g/L	g/L	mg CH ₃ COOH/L	mg O ₂ /L	mg C/L	mg N/L	Mg N-NH ₄ /L	-	mg Ca CO₃/L
1	16.98	11.23	418	938	321	182	154	7.12	960
	±0.65	±0.32	±1.8	±3.5	±0.7	±0.5	±3.1	±0.02	±15
2	16.43	10.81	692	1394	418	367	254	7.12	1230
	±0.56	±0.92	±2.7	±5.2	±1.1	±1.2	±4.2	±0.06	±17
3	16.01	10.53	835	1712	562	487	373	7.14	1960
	±0.37	±0.26	±2.8	±6.8	±2.3	±1.6	±1.8	±0.12	±11
4	15.20	10.12	987	1862	598	512	406	7.10	2120
	±0.78	±0.72	±1.7	±12.5	±2.7	±1.2	±4.9	±0.08	±24
5	15.07	9.76	1023	2121	693	641	538	7.12	2300
	±0.46	±0.91	±2.0	±15.1	±1.9	±2.4	±2.8	±0.05	±25
6	14.86	9.26	1338	2674	798	654	598	6.98	2380
	±0.63	±0.06	±4.8	±10.4	±1.6	±2.6	±4.7	±0.14	±15
7	13.29	8.12	1317	2422	714	728	676	6.96	2420
	±0.87	±0.15	±7.2	±16.5	±2.6	±1.5	±2.4	±0.17	±17
8	13.14	7.85	1228	1718	673	826	812	6.91	2550
	±0.52	±0.68	±5.3	±10.7	±3.1	±1.8	±1.8	±0.12	±22
28	7.94	4.55	321	761	211	995	982	6.87	3820
	±0.64	±0.41	±1.6	±7.3	±1.2	±2.7	±2.4	±0.06	±28

of own research, as well as other authors (Gao 2011, Grübel, 2013) the change of sludge structure increases the rate and intensity of volatile fatty acids generation and consequently the improvement of anaerobic stabilization. The use of disintegration of excess sludge with dry ice before the methane fermentation process increased the susceptibility of excess sludge to biodegradation, i.e. the digestion degree of sewage sludge and the value of biogas yield. On the other hand, there was no significant increase in the methane content in biogas generated from modified sludge in relation to non-processed sludge. In the period of the most intensive production of biogas, methane content was about 78% in the case of prepared sludge, while in the case of unmodified sludge about 75%.

Conclusions

Currently, technological research is carried out to minimize the amount of generated sewage sludge, its stabilization and hygienization as well as energy use. Achieving such a goal requires the combination of various unit processes, which in turn will improve the processes of sewage sludge treatment and utilization. On the basis of the analysis of the effectiveness of the methane fermentation process of excess sludge modified with dry ice, it can be concluded that the proposed modification is a solution that effectively supports the anaerobic stabilization.

Based on the obtained research results, the following conclusions were formulated:

✓ The mixture of reactant and excess sludge in a volume ratio of 0.55/1 was considered the most favorable conditions for the dry ice disintegration of excess sludge. In relation to not prepared sludge, about 2.7 and 3-fold increase of TOC and SCOD values and a 2.8-fold increase in VFAs concentration were obtained respectively.

- ✓ During the 8-day methane fermentation of excess sludge disintegrated with dry ice, the highest increase of TOC, SCOD and VFAs concentration was obtained on the 6th day of the process and was respectively 21, 36 and 29 percent higher in relation to the values of these indicators obtained during methane fermentation of unprepared sludge.
- ✓ The effect of 28-day methane fermentation of excess sludge subjected to dry ice disintegration was an increase in the digestion degree of sludge and biogas yield. In relation to the effects of the methane fermentation of non-prepared sludge, for modified sludge, about 26 percentage increase of the sludge digestion degree and about 27 percentage increase of the biogas yield was noticed.

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Przebieg procesu fermentacji metanowej osadów nadmiernych modyfikowanych suchym lodem

Streszczenie: Istotą przebiegu fermentacji metanowej jest fazowy charakter przemian zachodzących w trakcie procesu. Stopień biodegradacji osadów ściekowych zależy od skuteczności fazy hydrolizy. Osady nadmierne występujące w postaci kłaczkowatej zawiesiny drobnoustrojów, poddawane procesowi fermentacji metanowej, wykazuje ograniczoną podatność na biodegradację. Osady nadmierne charakteryzują się znaczną około 65 ÷ 75% zawartością substancji organicznych. Obiecującym rozwiązaniem technologicznym pod względem zwiększenia efektywności procesu fermentacji jest zastosowanie modyfikacji osadów nadmiernych suchym lodu. W wyniku dezintegracji osadów nadmiernych suchym lodem zachodzi denaturacja komórek drobnoustrojów o podłożu mechanicznym. Zachodzi proces krystalizacji, a mikroorganizmy osadu nadmiernego ulegają tak



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zwanemu "szokowi termicznemu". Celem badań było określenie wpływu dezintegracji osadów nadmiernych suchym lodem na przebieg procesu fermentacji metanowej modyfikowanych osadów. W przypadku modyfikacji suchym lodem zastosowano reagent w postaci granulatu o uziarnieniu 0,6 mm. Suchy lód zmieszano z osadem nadmiernym w stosunku objętościowym odpowiednio 0,15/1, 0,25/1, 0,35/1, 0,45/1, 0,55/1, 0,65/1, 0,75/1. Proces fermentacji metanowej trwający 8 i 28 dób prowadzono w warunkach mezofilowych w 37°C. W pierwszej serii zastosowano niepreparowane osady nadmierne, a w kolejnej mieszaninę suchego lodu i osadów nadmiernych w stosunku objętościowym wynoszącym 0,55/1, czas wstępnej obróbki 12 godzin. Uzyskany wzrost stopnia przefermentowania osadów i efektywności produkcji biogazu jest potwierdzeniem wspomagającego działania zastosowanej modyfikacji. Mieszaninę reagenta i osadów nadmiernych w stosunku objętościowym 0,55/1 uznano za najkorzystniejsze połączenie. W odniesieniu do niepreparowanych osadów nadmiernych, dla wybranych warunków dezintegracji uzyskano odpowiednio około 2,7- i 3-krotny wzrost wartości całkowitego węgla organicznego, rozpuszczonego chemicznego zapotrzebowania na tlen oraz 2,8-krotny wzrost stężenia lotnych kwasów tłuszczowych. W odniesieniu do efektów fermentacji metanowej niepreparowanych osadów nadmiernych, w przypadku osadów modyfikowanych odnotowano około 33% wzrost stopnia przefermentowania i około 31% wzrost wartości jednostkowej produkcji biogazu.