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Effect of Dry Ice Modification of Excess Sludge on the Methane Fermentation Process

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1. Introduction

The essence of the methane fermentation process is its phase course. The efficiency of the process is determined by the rate of reactions taking place during the hydrolysis phase, occurring during the first days of the process. As a result of hydrolytic changes, the concentration of volatile fatty acids (VFAs) increases and correlates with it the increase in dissolved chemical oxygen demand (SCOD) and total organic carbon (TOC). Excess sludge, which are an important substrate for the methane fermentation process carried out in isolated closed fermentation chambers of sewage treatment plants, show limited susceptibility to the biochemical degradation process under anaerobic conditions. Excess sludge is an activated sludge isolated in secondary settling tanks. Excess sludge form clusters of microorganisms occurring in the form of flocks. In excess sludge live and dead organisms as well as spore forms can be observed. This sludge is characterized by a significant content of organic matter at the level of 65-75% of volatile suspended solids (VSS) (Wolski & Wolny 2011).

On the basis of our own research and literature reports, the application of thermal disintegration with dry ice as a method supporting the anaerobic stabilization process is a promising technological solution contributing to both sludge hygienization, reduction of sludge mass through the process of evaporation as well as intensification of the hydrolysis phase, phase determining the efficiency of methane fermentation (Nowicka et al. 2014, Grübel et al. 2013, Chen et al. 2014, Gao 2011).

The purpose of heat treatment of excess sludge is to facilitate biodegradation of organic substances contained in modified sludge (Elliott & Mahmood 2007, Wang 2009). Thermal disintegration acts supportively to the anaerobic stabilization process. The essence of thermal modification is the supply or removal of thermal energy to sludge, which determines the change of their structure and affects the increase in the value of indicators such as soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), as well as total organic carbon (TOC) (Stier & Fischer 1998, Zawieja & Wolski 2012). According to the literature data (Stier & Fischer 1998, Zawieja & Wolski 2012, Zawieja 2010) and the conducted own research, the effect of thermal disintegration of sludge depends not only on the temperature used, but also the processing time.

Dry ice is a natural product that does not cause secondary contamination of thermally modified sludge with its use. The property of dry ice is sublimation, i.e. the transition from the solid phase to the gas phase, omitting the liquid phase. Dry ice is carbon dioxide in the solid phase, produced, among others, in the form of granulate. Freezing point for CO_2 is -78.5°C. The sublimation temperature of dry ice is -78.5°C at 1013 hPa. Dry ice has no taste or smell, has bacteriostatic properties and removes oxygen from the surrounding air. Other important features of dry ice decisive for its wide application: it is a natural product, environmentally friendly, sublimates in a gas with no residue, has a high cooling efficiency, is non-flammable, is non-toxic (http://www.prokontech.pl/suchy_lod.html, Hu et al. 2011).

As reported Lygonie et al. (Leygonie et al. 2012) as a result of thermal modification of sludge with the use of dry ice, denaturation of microbial cells with a mechanical foundation takes place. The essence of the disintegrating effect of dry ice on sludge is the crystallization process occurring both in the case of sludge particles as well as microbial cells. This process leads to the loss of hydration water of proteins, that are a significant component of the cell walls of microorganisms and consequently the release of intracellular substances into the supernatant.

Mechanical damage to microbial cells and the occurring osmotic shock are responsible for the inactivation of excess sludge microorganisms following the destruction of biomembranes. The formation of crystals both inside the cells of microorganisms and in the environment surrounding them is responsible for the phenomenon of the release of intracellular substances into the supernatant liquid (Thammavongsa et al. 2004, Nowicka & Machnicka 2013).

According to El – Kest and Marth (El – Kest & Marth 1992) with the rapid temperature reduction, microorganisms undergo the so-called "thermal shock". Frozen cells can be damaged mechanically. The formation of intra- and extra-cellular ice crystals causes mechanical damage to frozen cells of microorganisms. The effect of the freezing process is the increase in the concentration of dissolved cells, which can lead to the dissociation of cellular lipoproteins. On the other hand, the gradual heating of frozen cells increases the size of the ice crystals formed. The use of thermal disintegration, i.e. rapid freezing and gradual thawing, causes an increase in fastidiousness and changes in cellular morphology, as well as denaturation of macromolecules.

"Thermal shock" (a cold shock) is an effective method of cell damage caused by lowering the temperature. As reported Strange et al. (Strange et al. 1962) deactivation of microorganisms is the result of a rapid and not a gradual and slow change in the temperature value.

Freezing/thawing of excess sludge with dry ice affects the initiation of the lysis of microbial cells, resulting in an increase in the concentration of organic substances in dissolved form. With regard to mechanical or chemical methods of disintegration, thermal processes do not cause secondary sludge contamination, while with respect to mechanical methods, freezing/thawing of sludge does not require additional energy expenditure.

The process of freezing is dependent on the compartment nature of a microorganisms cellular system. Nucleation and growth of ice crystals in cells is conditioned by differences in water activity, nucleation sites, viscosity, membrane permeability, and other factors. As reported El – Kest and Marth (El – Kest & Marth 1992) most of enzymatically catalyzed reactions occur in living cells and to be effective, they must occur at the right temperature. Therefore a decrease in temperature is almost certain to disturb the balance and so modify cell function .

The aim of the study was to determine the effect of dry ice disintegration on the susceptibility of excess sludge to biodegradation. Studies have shown that thermal disintegration of excess sludge based on rapid freezing with dry ice, followed by gradual thawing at ambient temperature, compared to conventional methane fermentation, increases SCOD and TOC, as well as VFAs. Changes in the value of the indicators examined were recorded both at the stage of disintegration and during subsequent days of methane fermentation.

2. Experimental part

2.1. Substrate

Excess sludge, where the main substrate using during the research was sampled from the Central Wastewater Treatment Plant P.S.W. "Warta" in Czestochowa. Sludge was taken immediately before mechanical thickening. It is a mechanical and biological treatment plant with increased nutrients removal with a capacity of 90,000 m^3/d, 314 835 PE. Table 1 shows the main physico-chemical characteristics of the excess sludge used during the research.

Tabela 1. Fizyczno-chemiczne wskaźniki osadów nadmiernych
Table1. Physico-chemical indicators of excess sludge

Indicators	Excess sludge
Total Solids (TS)	16.32 g L^{-1}
Volatile Solubled Solids (VSS)	12.68 g L^{-1}
Chemical Oxygen Demand (COD)	110 mg O_2 L^{-1}
Volatile Fatty Acids (VFAs)	65 mg CH_3COOH L^{-1}
Alkalinity	320 mg $CaCO_3$ L^{-1}
pH	7.04 g L^{-1}
Kjeldahl Nitrogen	41 mg N L^{-1}
Ammonium Nitrogen	27 mg N-NH^+ L^{-1}
Total Organic Carbon (TOC)	26 mg C L^{-1}

2.2. Methodology

In the study 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), as well as total organic carbon (TOC) by spectrophotometric method in the infrared (carbon analyzer multi N/C manufactured by Analytik Jena).

In the case of thermal modification used reagent i.e. dry ice, which is carbon dioxide in the solid phase. Dry ice, present in a granular form with a grain diameter of 0.6 mm, was mixed with excess sludge in a volume ratio of 0.05:1, 0.1:1, 0.15:1, 0.25: 1, 0.35:1, 0.5:1 and 0.75:1, respectively. Disintegration was carried out at ambient temperature. The time of the modification phases, i.e. freezing and defrosting, was determined by the size of the reagent dose and was increased with increasing it. For the doses of reagent used it ranged from 3 to 12 hours.

The disintegration degree was estimated according to the formula 1. The sludge was conditioned by means of 1-mol solution of NaOH for 10 min., at the temperature of 90°C, with unchanged volumetric proportion of the sludge and the solution (1:1). The SCOD of chemically modified excess sludge, which is the reference value for determining of the disintegration degree, was equal 2912 mg O_2 L^{-1}.

The degree of disintegration was estimated according the following formula (Tiehm et al. 2001):

$$DD_{COD} = (SCOD_1\text{-}SCOD_2)/(SCOD_3\text{-}SCOD_2)\cdot 100 \qquad (1)$$

where:
DD_{COD} – disintegration degree,%,
$SCOD_1$ – SCOD level in the pretreatment sludge, mg O_2/l,
$SCOD_2$ – SCOD level in the non pretreatment sludge, mg O_2/l,
$SCOD_3$ – SCOD level in the sludge conditioned chemically 1-mol NaOH with ratio 1:1, temp. 90°C for 10 minutes, mg O_2/l.

In order to verify the effectiveness of the chosen disintegration method the sludge was subjected to eight-day anaerobic stabilization under the mesophilic condition. The process was periodic. Methane fermentation was subjected to non-processed excess sludge and thermally modified sludge using dry ice. A mixture consisting of 90% of excess sludge and 10% of digested sludge, serving as *inoculum* was prepared. The process of methane fermentation was carried out in eight models of fermentation chambers, placed in mesophilic conditions in temperature of 37°C in a laboratory thermostat. The mixture of excess sludge and digested sludge was placed in laboratory flasks with an active volume of 0.5 L, air-protected glass stopper with a manometric tube allowing 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 following mixtures of sludge i.e. excess sludge and digested sludge were subjected to anaerobic stabilization: Mixture I - non-prepared excess sludge + fermented sludge; (2) Mixture II - thermal pretreatment excess sludge with the reactant's dose equal in a volume ratio of dry ice to excess sludge 0.35/1 + digested sludge.

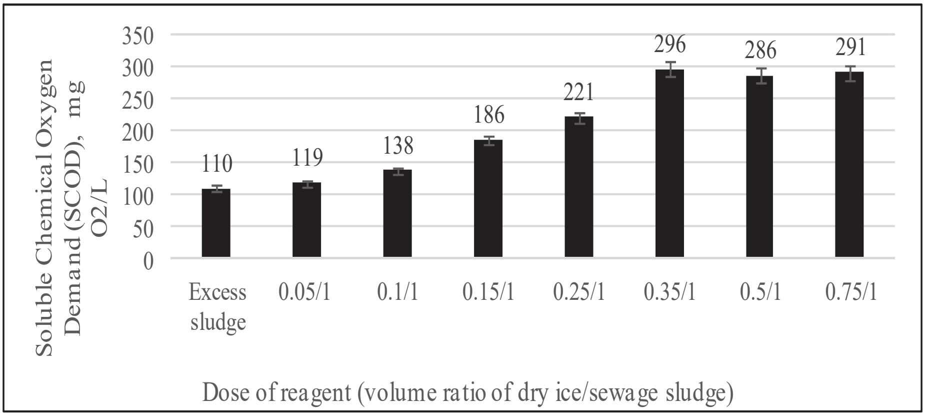
At this stage of the research, the course of the first days of methane fermentation was analyzed. Considering the phase limiting the hydrolysis proses, which is the first of the methane fermentation phases, the most favorable disintegration conditions were selected on the basis of the obtained values of the physico-chemical indicators. The selection made is the basis for conducting further research and in the next stage of optimization of biogas production.

3. Results and discussion

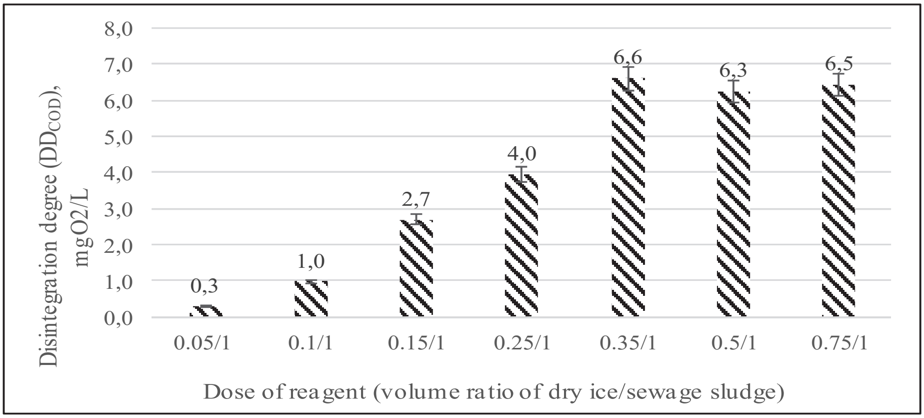
Subjecting the tested sludge to thermal modification using dry ice affect on the increase of organic compounds concentration in dissolved form, which was confirmed by the increase in the degree of disintegration of the prepared sludge. The increase of the disintegration degree of the modified dry ice excess sludge during the research conducted by Nowicka et al. and Chen et. al. (Nowicka et al. 2016, Chen et. al. 2014) was noted.

In order to assess the effectiveness of the dry ice disintegration process, the value of selected indicators was evaluated, which is a direct expression of the increased susceptibility of the prepared excess sludge to biodegradation. Pretreatment carried out using selected doses of reagent received a significant increase in the sludge disintegration, value of SCOD and TOC. With increasing degree of disintegration, an increase in the concentration of VFAs was observed, which confirms initiation already at the stage of modification of the hydrolysis process of organic substances bound intracellularly to soluble forms.

Figures 1-4 show the changes in the value of selected indicators of excess sludge during freezing with selected doses reagent i.e. in a volume ratio of dry ice to excess sludge equal 0.05:1, 0.1:1, 0.15:1, 0.25:1, 0.35:1, 0.5:1 and 0.75:1.



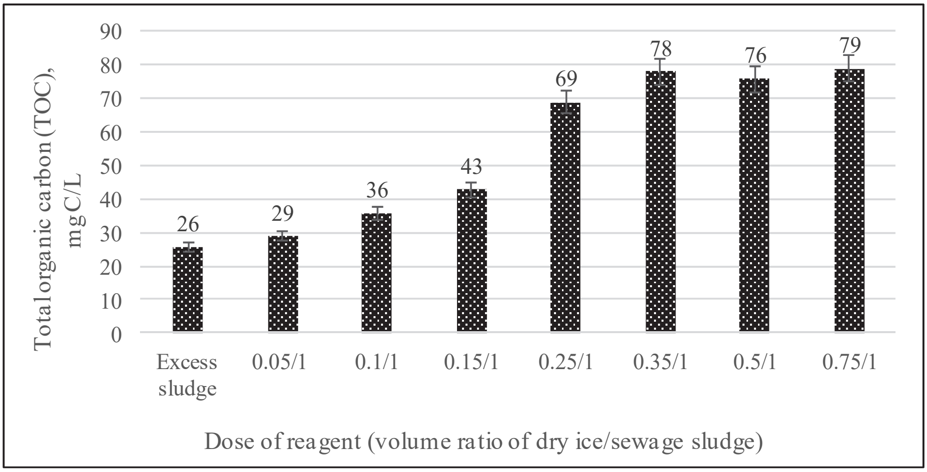
Rys. 1. Zmiany wartości chemicznego zapotrzebowania na tlen substancji rozpuszczonych w cieczy nadosadowej osadów kondycjonowanych suchym lodem
Fig. 1. Changes of soluble chemical oxygen demand (SCOD) values of pretreatment excess sludge with dry ice



Rys. 2. Wpływ dawki suchego lodu na stopień dezintegracji (DD_{COD}) osadów nadmiernych w procesie wymrażania
Fig. 2. Effect of dry ice dose on the degree of disintegration (DD_{COD}) of excess sludge in the freezing process

According to the literature data (Kanh et al 1999), SCOD is one of the basic quality parameters of sewage sludge. With increasing the dose of the reagent, for the excess sludge subjected to modification in a volume ratio of dry ice to excess sludge in the range 0.05:1-0.35/1, a gradual increase in SCOD and a correlation of the increase in the sludge disintegration degree was noted (Fig. 1, 2). The linear correlation coefficient of the dry ice dose dependence on the obtained SCOD value is 0.86. However, for the sludge modification of the reagent in a volume ratio of dry ice to sludge of 0.35/1, 0.5/1 and 0.75/1 did not show any significant increase in the value of the analyzed indicators. For the reagent doses mentioned above, a SCOD values of 298, 286, 291 and a degree of disintegration of 6.6, 6.3, 6.5 respectively were observed.

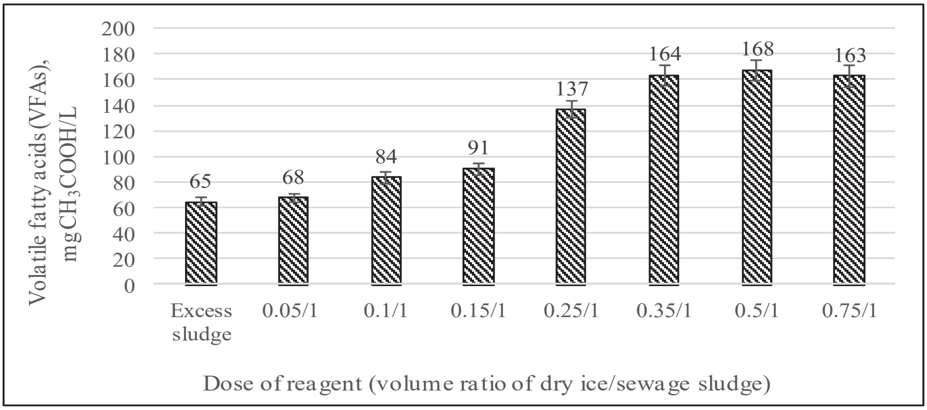
Determination of the effectiveness of disintegration of excess sludge by dry ice with total organic carbon (TOC) fully reflects the actual content of organic matter in the supernatant (Janiga & Michniewicz 2013), what was shown on the Fig. 3.



Rys. 3. Zmiany wartości ogólnego węgla organicznego (OWO) kondycjonowanych suchym lodem osadów nadmiernych
Fig. 3. Changes of total organic carbon (TOC) value of freezing excess sludge

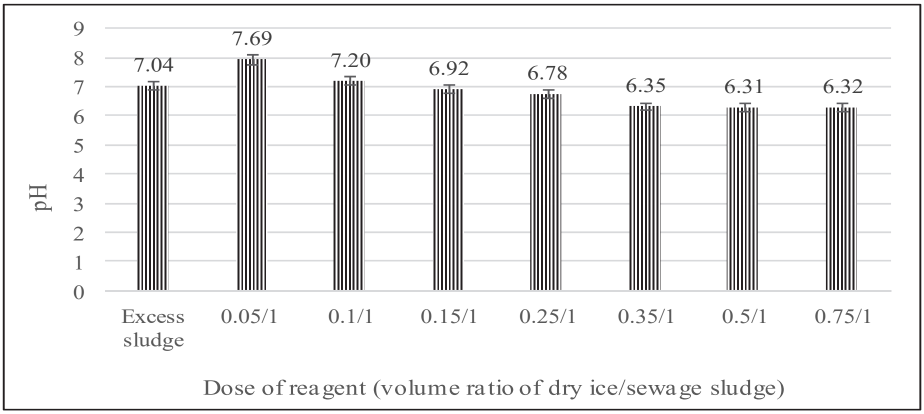
There was a gradual increase in the TOC value. However, for doses of dry ice to sludge of 0.35/1, 0.5/1 and 0.75/1 the increase in the value of the indicator was similar.

According to Hu et al. (Hu et al. 2011) in the case of sludge disintegration using freezing and thawing to the sludge supernatant of extracellular polymers are released. There was a correlation of the obtained TOC values with the SCOD values. In addition, a correlation coefficient of 0.84 was obtained for the dependence of the linear dose of dry ice on the obtained TOC value.



Rys. 4. Zmiany stężenia lotnych kwasów tłuszczowych (LKT) kondycjonowanych suchym lodem osadów nadmiernych
Fig. 4. Changes of the volatile fatty acids (VFAs) concentration of freezing excess sludge

The same tendency of gradual value increase along with an increase in the reagent dose was noted for the VFAs concentration. Changes in the VFAs concentration are indicative of lysing processes already taking place at the stage of modification and a correlation coefficient of 0.85 was obtained for the dependence of the linear dose of dry ice on the obtained VFAs value.

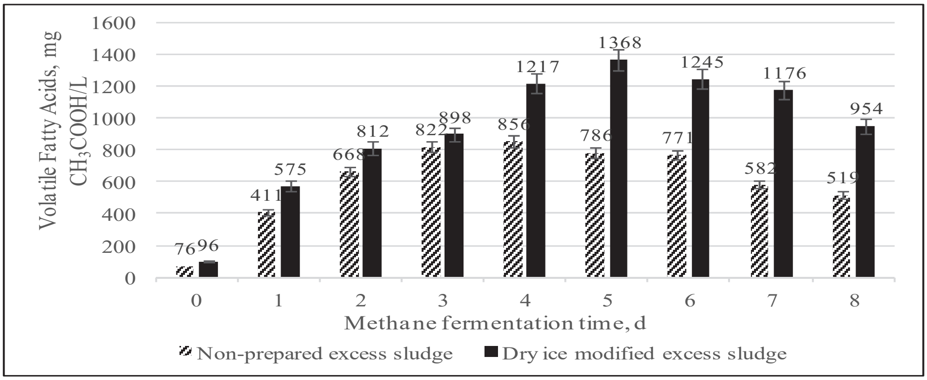


Rys. 5. Zmiany wartości pH kondycjonowanych suchym lodem osadów nadmiernych
Fig. 5. Changes of pH values of freezing excess sludge

During the disintegration of excess sludge, a gradual decrease in the pH value was noted with the increase of the reagent dose, which is conditioned by the acidifying nature of the dry ice action. The linear correlation coefficient of the dry ice dose dependence on the obtained pH value is 0.84.

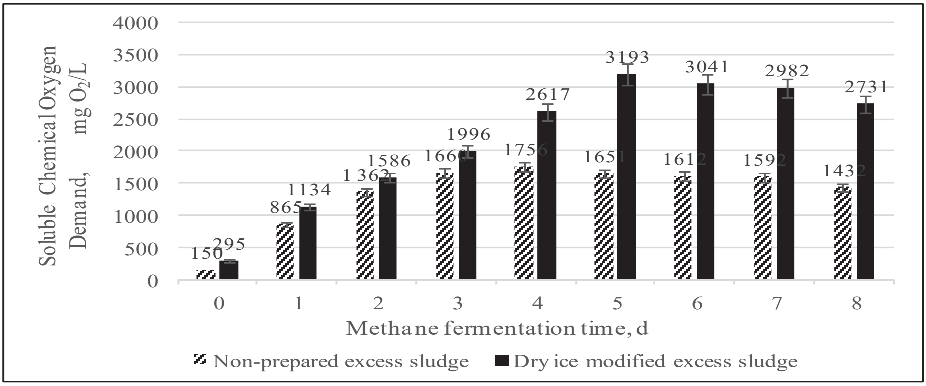
As a result of the thermal modification of the sludge and the values of selected indicators such as SCOD, DD, TOC, and VFAs carried out at this stage, the most favourable modification conditions were selected. For the best dose in terms of the proposed technological solution, for further research, the dose of dry ice to the sludge was estimated to be 0.35 /1, respectively.

Figures 6, 7 and 8 show changes in the VFAs, SCOD and TOC values determined for dry ice modified excess sludge at a dose of 0.35/1, respectively, of the reactant to sludge.



Rys. 6. Zmiany stężenia lotnych kwasów tłuszczowych (LKT) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych
Fig. 6. Changes of volatile fatty acids (VFAs) concentration during methane fermentation of non-prepared and dry ice modified excess sludge

During the methane fermentation process of modified excess sludge, in relation to the process of non-prepared sludge, intensification of the hydrolysis process was noted, the phases as reported by literature sources (Tiehm 2001, Kim 2003, Wolski & Małkowski 2014, Wolski 2016). and confirm own studies limiting anaerobic stabilization. For sludge subjected to disintegration with dry ice in the following days of the fermentation process, a gradual increase in the concentration of VFAs was noted. The highest value of the indicator equal 1368 mg CH_3COOH/L was obtained on the 5th day of the process, observing a gradual decrease in concentration in the next days. For non-prepared excess sludge, maximum VFAs concentration of 856 mg CH_3COOH/L was recorded on 4th day of the process.

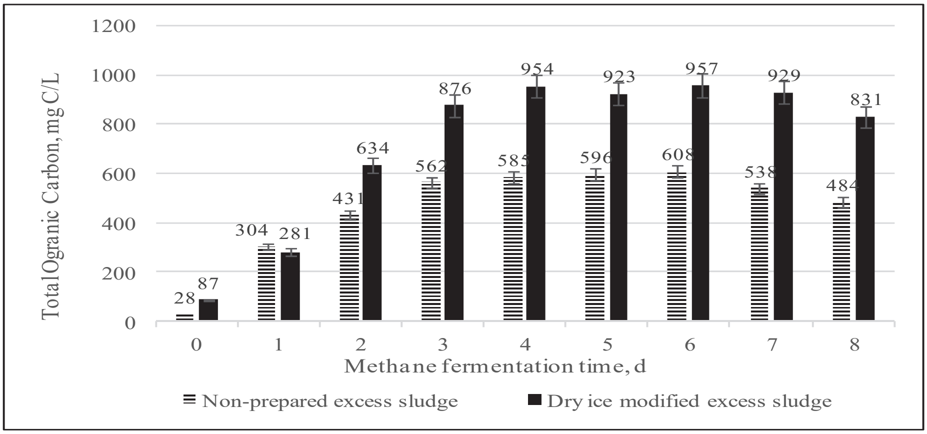


Rys. 7. Zmiany wartości rozpuszczonego chemicznego zapotrzebowania na tlen (ChZT) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych

Fig. 7. Changes of soluble chemical oxygen demand (SCOD) values during methane fermentation of non-prepared and dry ice modified excess sludge

A similar tendency of a gradual increase in value was noted in the case of the SCOD for both unprocessed and thermally modified sludge. The highest value of the SCOD equal 3193 mg O_2/L was obtained on the 5th day of the process, observing a gradual decrease of the value in the next days. For non-prepared excess sludge, maximum SCOD value of 1756 mg O_2/L was recorded on 4th day of the process. There was a close correlation between the changes in the SCOD value in relation to the VFAs concentration in subsequent days of methane fermentation.

Values of SCOD can be influenced of organic nitrogen compounds or reducing inorganic compounds. These compounds may influence on an increased demand for oxygen. Therefore the strictly defined parameter defining the content of organic substances of sludge is the total organic carbon (TOC). For sludge subjected to disintegration with dry ice in the following days of the fermentation process, a gradual increase of TOC value was noted. The highest value of the indicator equal 954 mg C/L was obtained on the 4th day of the process, observing a gradual value decrease in the next days. For non-prepared excess sludge, maximum TOC value of 608 mg C/L was recorded during the 6th day of the process.



Rys. 8. Zmiany wartości ogólnego wegla organicznego (OWO) podczas fermentacji metanowej niepreparowanych oraz modyfikowanych suchym lodem osadów nadmiernych
Fig. 8. Changes of total organic carbon (TOC) values during methane fermentation of non-prepared and dry ice modified excess sludge

4. Summary and conclusions

According to the aim of the study the comparison of methane fermentation efficiency of thermal modified excess sludge using dry ice, as well as non-prepared excess sludge was made. The conducted research has shown an increase in the susceptibility of prepared excess sludge to biochemical degradation under anaerobic conditions. Already at the modification stage, the initiation of hydrolysing processes was noted, which resulted in an increase in the value of the analyzed indicators such as: solubled chemical oxygen demand (SCOD), volatile fatty acids (VFAs), as well as total organic carbon (TOC).

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

- With increasing doses of dry ice increase of SCOD and TOC values was observed which correlated with the increase of VFAs concentration.

- In the case of mixture of dry ice and excess sludge in a volume ratio of 0.35: 1, 0.5: 1 and 0.75: 1 respectively an increase of SCOD, TOC, DD_{COD} values as well as VFAs concentration was inadequate to the dry ice dose, there was no significant increase in the indicators values.
- As a result of the dry ice modification process, the combination of dry ice and excess sludge in a volume ratio of 0.35 to 1 was considered the most favourable mixture. The choice was confirmed by the value of the disintegration degree obtained for the modified sludge equal 6.6%.
- For sludge subjected to disintegration with dry ice, using the most preferred reagent dose, in the following days of the methane fermentation process, in relation to methane fermentation of non-prepared excess sludge, increase of SCOD and TOC values as well as VFAs concentration was noted.

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Wpływ modyfikacji osadów nadmiernych suchym lodem na proces fermentacji metanowej

Streszczenie

Specyficzna podatność osadów nadmiernych na proces fermentacji metanowej jest czynnikiem ograniczającym szybkość reakcji zachodzących w kolejnych etapach procesu. Na kinetykę przemian biochemicznych podczas zachodzących samorzutnie faz fermentacji metanowej wpływa bezpośrednio wzrost stężenia rozpuszczonych substancji organicznych dostępnych dla mikroorganizmów procesu. Modyfikacja osadów nadmiernych odmiennymi metodami dezintegracji, tj. chemicznymi, fizycznymi, hybrydowymi zwiększa efektywność procesu fermentacji metanowej. Spośród wymienionych powyżej metod modyfikacji należy podkreślić zalety metod fizycznych, zwłaszcza termicznych. Oprócz istotnej modyfikacji struktury osadów nadmiernych, nie powodują one wtórnego zanieczyszczenia preparowanych osadów i stanowią obiecujące rozwiązanie technologiczne. Celem przeprowadzonych badań było określenie wpływu dezintegracji osadów nadmiernych suchym lodem na wzrost podatność na biodegradację. Lotne kwasy tłuszczowe są ważnym produktem pośrednim fermentacji metanu, a zwiększona wydajność procesu stabilizacji zależy od ich stężenia. Ponieważ procesem limitującym fermentacje metanową jest faza hydrolizy, pierwszy etap stabilizacji, dokonano analizy wybranych oznaczeń fizyczno-chemicznych w ciągu pierwszych ośmiu dób procesu fermentacji modyfikowanych osadów Okresową fermentację metanową prowadzono w warunkach mezofilowych. Stworzono mieszaniny suchego lodu i osadów nadmiernych w stosunku objętościowym reagenta do osadów w zakresie od 0,05/1 do 0,75/1. Potwierdzeniem zwiększonej podatności dezintegrowanych osadów nadmiernych na proces fermentacji metanowej był zachodzący proces lizy osadów nadmiernych wyrażony wzrostem stopnia dezintegracji. W przypadku osadów nadmiernych poddanych dezintegracji suchym lodem, przy użyciu najkorzystniejszej dawki reagenta, w kolejnych dobach procesu fermentacji metanowej, w odniesieniu do fermentacji metanowej niepreparowanych osadów nadmiernych, odnotowano wzrost wartości rozpuszczonego chemicznego zapotrzebowania na tlen (ChZT), ogólnego węgla organicznego (OWO) oraz stężenia lotnych kwasów tłuszczowych (LKT).

Abstract

The specific susceptibility of excess sludge to the methane fermentation process is a limiting factor for the rate of reaction occurring in the subsequent stages of the process. The kinetics of biochemical changes during spontaneous methane fermentation phases is directly influenced by the increase in the concentration of dissolved organic substances available to microorganisms in the process. Excess sludge deposition by different disintegration methods, ie: chemical, physical, combined increases the efficiency of the methane fermentation process. Among the modifications mentioned above, the advantages of physical methods, especially of thermal nature, should be emphasized. In addition to the significant modification of the excess sludge structure, it does not cause secondary contamination of the prepared sludge and therefore is a promising technological solution. The aim of the study was to determine the effect of dry ice disintegration on the susceptibility of excess sludge to biodegradation. Volatile fatty acids are an important intermediate product in methane fermentation and increased effects of the stabilization process is conditioned by their concentration. Since the phase limiting process is the hydrolysis phase, the first stage of the fermentation, the detailed analysis was carried out in the first eight days of the process by performing physicochemical determinations of the modified sludge. Periodic fermentation was carried out under mesophilic conditions. Excess sludge was prepared with dry ice in a volume ratio of dry ice to excess sludge in range from $0.05L^{-1}$ to $0.75L^{-1}$. Confirmation of the increased susceptibility of the prepared excess sludge to the methane fermentation process was a modification of the sludge structure expressed by the increase of the disintegration degree. For sludge subjected to disintegration with dry ice, using the most preferred reagent dose, in the following days of the methane fermentation process, in relation to methane fermentation of non-prepared excess sludge, increase of SCOD and TOC values as well as VFAs concentration was noted.

Słowa kluczowe:
osady nadmierne, fermentacja metanowa, dezintegracja, suchy lód,
lotne kwasy tłuszczowe (LKT), chemiczne zapotrzebowanie na tlen (ChZT),
ogólny węgiel organiczny (OWO)

Keywords:
excess sludge, methane fermentation, disintegration, dry ice, volatile fatty acids (VFAs), soluble chemical oxygen demand (SCOD), total organic carbon (TOC)