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IMPACT OF ORGANIC ADDITIVES ON BIOGAS EFFICIENCY OF SEWAGE SLUDGE[1]

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ABSTRACT

Methane fermentation, which constitutes at the same time a precious biogas source, is the most frequently applied stabilization method of sewage sludge. Municipal or industrial sewage does not, however, provide for the effective biogas production, mainly on account of their chemical composition. The objective of the paper was to verify susceptibility to the methanation process of the selected organic substrates (refined glycerine, beet molasses, whey) with sewage sludge. The scope of the research covered initial analysis of the raw material (pH, dry mass, dry organic mass), methane fermentation of the suitably prepared samples of fermentation mixtures and the assessment of biogas and methane efficiency. The highest concentration of methane was obtained from the mixture of sewage sludge with refined glycerine (63.10%), whereas the lowest – from the mixture with whey (49.8%).

Introduction

Sewage sludge is a product of sewage treatment and its processing and disabling constitute an essential element of technological processes of sewage treatment.

Sewage which is formed in the municipal sewage treatment plants tends to decaying, which is related to secretion of unpleasant odours. It is also characterized with high hydration, which impedes the process of their management. Whereas sludge from industrial sewage treatment plants is characterized with the increased content of heavy metals and toxic components (Magrel, 2002; Pierścieniak and Bartkiewicz, 2011).

During the last few years, sludge production in the European Union has been constantly increasing, presently even to several tonnes of dry mass of sewage annually. Sludge handling, and in particular the use of sewage sludge, which is formed in the sewage treatment plants, must comply to the environmental requirements. The provisions included in the

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Council Directive 91/271/EEC (CEC, 1991) impose construction of new sewage treatment plants and optimization of work – of those existing. Construction of a higher number of sewage treatment plants and also the use of more and more effective processes of urban sewage treatment plants causes the increase of production of the amount of sewage sludge. Additionally taking into consideration the number of sludge that has been already stored and very limited perspectives of its storage, these facts constitute a serious problem.

Sewage that is formed during sewage sludge treatment is subjected to the dehydration and stabilization processes. The most frequently, biological processes are applied: aerobic, anaerobic, chemical and thermal processes of stabilization of sewage sludge (Miodoński and Iskra, 2011). Methane fermentation is a popular technology, which improves the quality of the sewage sludge in the aspect of usage in agriculture, being at the same time a precious biogas source. However, both municipal sewage as well as industrial ensures effective biogas production, due to their chemical composition, which is mainly characterized with carbon deficiency. Issues related to the improvement of biogas efficiency of sewage sludge, constitute a present research problem of the known scientific centres around the world. In the selected works, various, interesting solutions have been suggested, which aim at the increase of biogas production, at optimally conducted methane fermentation of the sewage sludge. Anaerobic decomposition of this substrate with organic waste is one of the proposals. Due to the fact that the most favourable relation C:N is 20:30 (Parkin and Owen, 1986; Fugol and Prask, 2011) and the sewage sludge has 6:16, co-fermentation (fermentation in the multi-component system) with organic waste of any type which has high C:N, may effectively improve balance of nutritious components and cause the increase of the carbon amount, and consequently raise biogas production (Sosnowski et al. 2007). Among other advantages of carrying out the process of co-fermentation, the fact of balancing mineral components should be mentioned: Na, K, Mg, Mn, dilution of toxic substances, optimal use of the volume of fermentation chamber, reduction of retention time (HRT), increase of the degree of re-digestion of substrates and general decrease of costs.

In the literature, the use of sewage sludge in the process of methane digestion with organic additives is reported in the form of: pigs and poultry manure (in the first case the increase of biogas yield was by 40% Borowski et al., 2014) of beet pulp (Montańés et al., 2013) and grease waste, in case of their use, a considerable improvement of biogas productivity was obtained , even to 60% (Noutsopoulos et al., 2013; Silvestre et al., 2011; 2013). These solutions mainly give a high biogas potential including methane. During execution of the process, however, it is hard to avoid potential operational problems, the most frequently related to: inhibition of methanogenesis, caused by release of ammonia (for example at the use of poultry droppings, Borowski et al., 2014), accumulation of LCFA (long chain fatty acids), unfavourable decrease of pH of the system (Shin et al., 2003; Silvestre et al., 2014) as well as low-effective reduction impact of digestion - towards pathogens (the most frequently E.coli), included in added animal droppings (Borowski et al., 2014; Scaglia et al., 2014). Moreover, high load of a digestion chamber may cause difficulties (Montańés et al., 2013), formation of digestion foam (Kabouris et al., 2008) or issues related to the transport of substrates (Pereira et al., 2004). In numerous research, attempts to solve the mentioned problems are made on account of decisive prevail of advantages: pro-environmental, economic, social, which result from handling of sewage sludge in co-fermentation with organic waste.

In the presented paper, refined glycerine, beet molasses and whey were used as organic additives to sludge. The most favourable results were reported for a sample of sewage sludge with glycerine.

The objective and the scope of research

The objective of the research was verification of susceptibility of the mixture of sewage sludge with specific organic additives on the methanation process and determination of biogas efficiency of substrate. The scope of the research covered initial analysis of the raw material (pH, dry mass, dry organic mass), methane digestion of suitably prepared samples of digestion mixtures and assessment of biogas and methane efficiency according to proper analytic procedures.

Research methodology

pH Measurement

pH measurement of particular substrates was carried out according to the specific procedure. Firstly, to two beakers with the volume of 250 ml for 20 g of material was collected, which was then diluted with demineralized water. A pH-meter electrode (Elmetron CP215) was kept in the mixture for stabilization of pH value. Measurement was repeated three times, and results were averaged.

Determination of dry mass

Fresh material,which was collected from a bioreactor to two aluminium forms was weighed (RADWAG precision to 0.01 g) and then dried for approximately 12 h in temperature 105ºC to the moment of obtaining solid mass.

Percentage content of dry mass is calculated with the following equation:

$$s.m. = \frac{(m_2 - m_3)}{m_1} \cdot 100 \tag{1}$$

where:

s.m. – dry mass (%),
m_1 – mass of a sample before drying (g),
m_2 – mass of a sample after drying (g),
m_3 – average mass of an aluminium form≈ 6.02 g

Moisture, which is calculated according to the following formula, is a reverse of the dry mass content of output material (fresh mass):

$$ś.s. = 100 - s.m. \tag{2}$$

where:

ś.s. – moisture (fresh mass) (%),
s.m. – dry mass (%),

Determination of organic substance content

Method of determination of organic substance content consists in weight determination of losses at combustion of samples in the temperature of 520ºC to the moment of obtaining solid mass. As a result of roasting we obtain ash (mineral matter) whereas organic compounds included in the mixture, in the set temperature of roasting (520ºC) – transfer into volatile state.

Organic substances content in the investigated sample should be calculated in percentages in relation to dry mass samples according to the equation:

$$S_{org} = \frac{m_1 - m_2}{m_1} \cdot 100 \tag{3}$$

where:

S_{org} – organic substance content (%),
m_1 – mass of a sample before roasting (g),
m_2 – mass of a sample after roasting (g).

Preparation of samples

Preparation of digestion mixtures was carried out based on the pH value of substrates so that it was approximately 7. It is a reaction characteristic for a batch in fermentors of really working biogas plants as well as optimal for anaerobic bacteria.

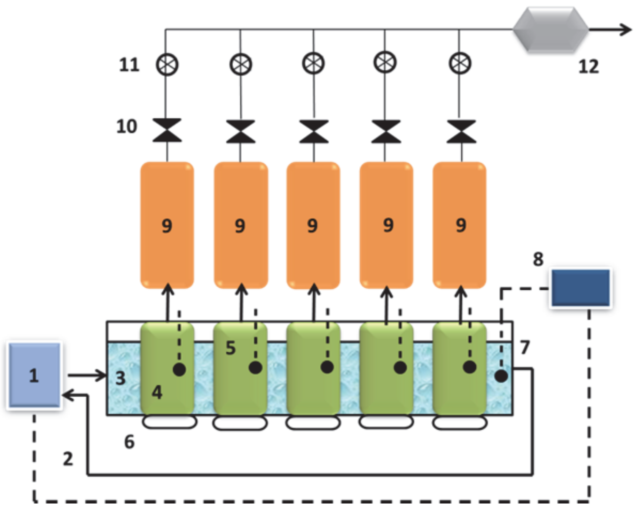
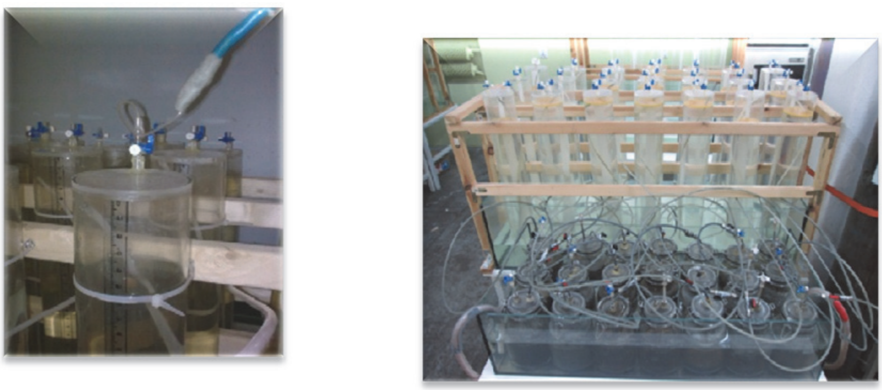


Figure 1. Schematic representation of a fermentor for research of biogas production: 1 – water heater with temperature controller; 2 – isolated conduits of heating liquid; 3 – water jacket; 4 – biofermentor with a batch of volume of 1.4 dm^3; 5 – pH sensors; 6 – magnetic stirrers of a batch; 7 – temperature sensors; 8 – record control room; 9 – biogas containers; 10 – cut-off valves; 11 – gas flowmeter; 12 – gas analyser (CH_4, CO_2, NH_3, H_2S, O_2)

Sewage sludge was used in the research, which came from Municipal Sewage Treatment Plant in Wolsztyn. On account of conditions required for correct course of methane fermentation, it was non-hygienized (pH=6-8). For preparation of fermentation mixtures the following were used: whey from dairy Kościan, molasses from sugar factory Opalenica and refined glycerine (Bio-Chem Sp. z o.o. Grodków). As a factor that initiates the process, pig manure from an agricutlural farm, which produces pigs, was used. Selection of the so-called graft resulted from inter alia effects of previous research, which unanimously proved that pigs manure along with glycerine gives higher biogas yield than combined with cattle manure (Pilarski et al., 2010). Proper samples were prepared using specific proportions of substrates, which were presented in table 1. Half less amount of glycerine was used on account of its high susceptibility to decomposition, which as a result was going to prevent too fast process of hydrolysis and to protect a sample against acidification in further stages of methane fermentation (Dach et al., 2009).

Realization of the methane fermentation process

The prepared raw material was subjected to fermentation in biofermentors, which were designed and performed in the Institute of Biosystems Engineering of the Poznan University of Life Sciences (fig. 1,2 a, b). 9 fermentors were used in the research. Experiment was carried out for 40 days, in temperature 38ºC (mesophile conditions), which was maintained at a constant level, due to the use of water jacket. Measurement of the amount of obtained biogas was carried out according to the standard DIN 38 414: Bestimmung das Faulverhaltens *Schlamm Und Sediment* (Beuth Verlag GmbH, Berlin, 1985), which is the most frequently used method in Europe (mainly in Germany, Austria and Holland). Batch in reactors was mixed every 24 hours for approximately 1 minute. The amount of the produced biogas was measured each day of the research with the use of a scale placed on the biogas containers (fig. 2a). Analysis of the quantity composition was carried out for the volume of the produced biogas which was 1.1 dm^3. For the research system MSMR-4/BIO by ALTER S.A. was applied (stationary analyser of gases in biogas).



a B

Figure 2. a – biogas container filled with water and marked with a scale, b – multi-chamber biofermentor

Analytic procedures related to the research on biogas and methane efficiency of substrates were developed as a part of the research projects, ordered by the Ministry of Science and Higher Education.

Discussion on the research results

In the first stage of research, analysis of basic physical and chemical parameters of the applied substrates, such as: pH, dry mass and organic dry mass, was carried out. Parameters and proportions of substrates in the prepared samples were presented in table 1.

Table 1
Physical and chemical properties of substrates and composition of fermentation mixtures

	Sludge Wolsztyn (without hygienization) (A)	Whey Kościan (B)	Molasses Opalenica (C)	Refined glycerine (D)	Graft (pigs manure) (E)
Dry mass* of substrates subjected to fermentation process (%)	15.88	4.88	75.68	99.60	3.80
Solid residue* of substrates subjected to fermentation process (%)	61.28	86.33	83.19	99.90	79.81
pH of the mixture at the beginning of fermentation	6.90	6.85	7.28	7.45	7.51
Amount of substrate added to fermentation (g)	200.10 (A)/ 1300.10 (E)	100.00 (B)/ 100.10 (A)/ 1300.20 (E)	100.00 (D)/ 100.10 (A)/ 1300.10 (E)	50.20 (C)/ 150.20 (A)/ 1300.15 (E)	–

*dry mass – dry mass; DOM – dry organic mass

Reaction of all used substrates is approximately neutral, which is a basic condition for correct and efficient realization of the methane fermentation process. Refined glycerine has the biggest dry organic mass and the sewage sludge has the lowest.

Sample (B) with an addition of whey (fig. 3b) fermented in the shortest time and in the least effective manner. Its initial pH which is 6.85 (table 1) was relatively low with reference to pH of the remaining substrates and requirements for correct course of the process. Slightly acid reaction of whey caused inhibition of the process in the entire methanation process and considerably lowered biogas profitability of this sample (15.80 dm^3 of biogas, table 2). Worse results in the discussed case where thus assigned to low pH of the substrate, which influenced fermentation disorders and as a result to acidification of the process environment (pH = 4.59; table 2).

Table 2
Data concerning biogas yield in the anaerobic fermentation process

Specification	Sludge Wolsztyn without hygienization (A)	Whey Kościan (B)	Molasses Opalenica (C)	Refined glycerine (D)
Amount of the obtained biogas (dm^3)	17.80	15.80	27.6	33.4
Average content of methane in biogas (%)	51.3	49.80	58.40	63.10
Amount of the obtained methane (dm^3)	9.13	7.87	16.11	21.20
pH of substrates subjected to methane fermentation	6.9	4.59	7.11	7.71
Biogas efficiency of the investigated substrates ($dm^3 \cdot kg$ ś.m.$^{-1}$)	26	6	118	338

Next sample, which was subjected to anaerobic fermentation, was a mixture with beet molasses (C). This sample was characterized with a regular methanation process (fig. 3 c). In the first 7 days a constant increase of biogas production was reported. From the 8th day of process, performance a daily decrease of biogas yield took place, which lasted regularly to the 32nd day. Total amount of the obtained biogas was 118 $dm^3 \cdot kg^{-1}$ ś.m., which is a worse result in comparison to the data included in the literature (KTBL, 2011) and indicates insufficient content of micro and macro-elements in the investigated sample. No proper quantity of elements which support the methane fermentation process causes low-effective transformation (the so-called bio-gasing) of biomass in a fermentor.

In practice, sterile substrates or disorders of conditions of the process realization put potential biogas works owners to a danger of considerable economic losses. Thus, maintaining constant monitoring of biogas works operation on account of the quantity and quality scope is important, of both produced biogas as well as input substrates and post-fermentation pulp.

According to data included in table 2, the highest biogas yield took place in case of using glycerine (sample (D); 33.4 dm^3). At the same time, from fermentation mixture with glycerine, as an organic additive, biogas, which is the richest in methane (63.10%) was obtained, which is mainly justified with chemical structure of a particle of this compound, which is characterized with relatively high amount of carbon atoms ($C_3H_8O_3$).

A plot presented in figure 3d, indicates that intensity of the methanation process of the mixture (D) in the second week of the research decreased due to the raise of pH inside a fermentor, caused by too fast rate of hydrolysis and acidogenesis. In the fourth week, according to the diagram analysis, biogas production increased followed by its extinguishing - in the 34th day. The amount of the obtained biogas is close to literature data (Dach et al., 2009).

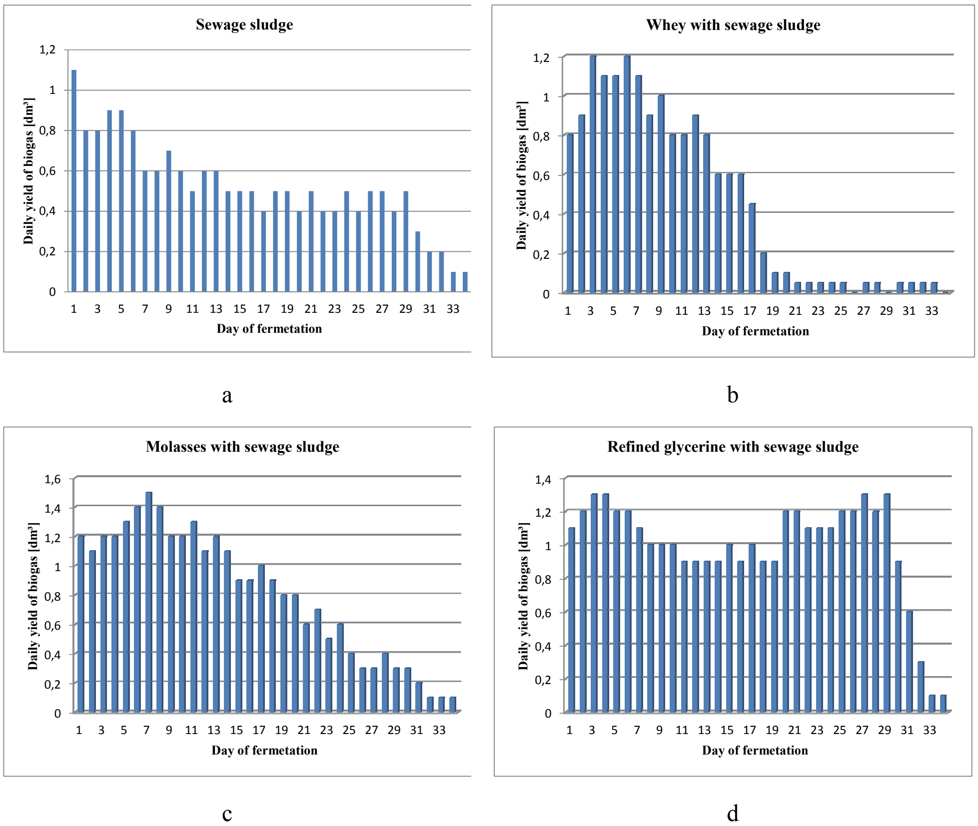


Figure 3. Daily biogas yields for:a – sewage sludge and b – whey, c – molasses, d – refined glycerine with sewage sludge

Conclusions

1. Whey as a co-substrate with sewage sludge is a low efficient additive (only 15. 8 dm^3 of the obtained biogas) and requires strict control during execution of methane fermentation.
2. Beet molasses subjected to methane fermentation with sewage sludge gave lower biogas yields (27.6 dm^3) in the research which was carried out, compared to the literature values (30-35 dm^3), which resulted the most probably from the low quality of the substrate (limited content of micro and macro-elements).
3. Biogas yield from the mixture of refined glycerine and sewage sludge was the most advantageous (33.4 dm^3). Refined glycerine as a co-substrate raises considerably the efficiency of the biogas installation.
4. Correct selection of the co-substrate for biogas works constructed at the sewage treatment plants may considerably improve their profitability.

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WPŁYW DODATKÓW ORGANICZNYCH NA WYDAJNOŚĆ BIOGAZOWĄ OSADÓW ŚCIEKOWYCH

Streszczenie. Najczęściej stosowaną metodą stabilizacji osadów ściekowych jest fermentacja metanowa, stanowiąca jedocześnie cenne źródło biogazu. Ścieki komunalne czy przemysłowe nie zapewniają jednak efektywnej produkcji biogazu, przede wszystkim ze względu na ich skład chemiczny. Celem badań było sprawdzenie podatności na proces metanizacji wybranych substratów organicznych (gliceryna rafinowana, melasa buraczana, serwatka) z osadem ściekowym. Zakres badań obejmował wstępną analizę surowca (pH, suchą masę, suchą masę organiczną), fermentację metanową odpowiednio przygotowanych próbek mieszanin fermentacyjnych oraz oszacowanie wydajności biogazowej i metanowej. Największe stężenie metanu uzyskano z mieszaniny osadu ściekowego z gliceryną rafinowaną (63,10%), natomiast najmniejsze – z mieszaniny z serwatką (49,8%).

Słowa kluczowe: stabilizacja osadu ściekowego, fermentacja metanowa, substrat, wydajność biogazowa