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STATE OF THE ART IN TECHNOLOGIES OF THE BIOGAS PRODUCTION INCREASING DURING METHANE DIGESTION OF SEWAGE SLUDGE

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A b s t r a c t

At present many WWTPs are focused on increasing quantity of biogas generated during sewage sludge processing. Various disintegration methods can be used for this purpose – thermal heating, ultrasonic disintegration, chemical treatment. The limiting step in sewage sludge digestion is hydrolysis, increasing the rate of this process allows for shortening solids retention time in digester, increasing soluble COD concentration in the reject water and as a result also biogas production. In technical scale ultrasonic and thermal disintegration are used. The most effective are ultrasounds below 100 Hz. In thermal conditioning various technological parameters are applied (from 60 – 80 °C to even 250°C, retention times from 15 min. to 2 hours). Effectiveness of the processes can be increased by using combined processes, e.g. thermal treatment and chemical stabilization. Chemical methods are at present mainly applied in laboratory scale. They include alkaline and acidic pretreatment or advanced chemical oxidation methods.

Keywords: sewage sludge, biogas, methane digestion, disintegration

1. INTRODUCTION

Treatment of wastewater, among others wastes, generates also sewage sludge. The sludge is separated from wastewater during preliminary sedimentation (primary sludge, raw sludge) and in secondary clarifiers (secondary sludge,

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excess sludge). Preliminary sludge contains more than 60% of volatile suspended solids (VSS), up to 8% of total suspended solids (TSS) and several percent of phosphorus and nitrogen (Kjeldahl Nitrogen) - Table 1.

Table 1. Characteristics of primary sewage sludge from various WWTP

Parameter	Unit	WWTP in Poland [1]	Average WWTP (European Union) [2]
pH	-	5 - 7	5 - 8
TSS	%	0.5 - 3	2 - 8
VSS	% TSS	60 - 75	60 - 80
Alkalinity	mgCaCO^3/L	500 - 1000	500 - 1500
Volatile acids	mgCH$_3$COOH/L	1800 - 3600	200 - 2000
Proteins	% TSS	-	20 - 30
Nitrogen (Kjeldahl)	% (w/w)	2 - 7	1.5 - 4
P	P_2O_5 % TSS	0.4 - 3*	0.8 - 2.8

*As P% TSS

Secondary sludge consists mainly of excess biomass of activated sludge or biofilm [3]. It contains 40 – 50% of VSS, and less TSS than raw sludge (Table 2).

Table 2. Characteristics of excess sewage sludge from various WWTP

Parameter	Unit	WWTP in Brazil [3]	WWTP in Thesaloniki, Greece [6]	WWTP according to the data given by [5]
pH	-	7.2 - 7.5	no data	6.0 - 7.0
TSS	g/L	37.9 - 56.3	no data	0.4 - 1.2
VSS	g/L	16.6 - 23.7	no data	no data
	%	no data	66.3 ± 1.57	55 - 80
Alkalinity	mgCaCO$_3$/L	442 - 781	no data	55 - 1000
Volatile acids	mgCH$_3$COOH/L	109 - 130	no data	1800 - 3600
Proteins	g/L	9.8 - 18.7	no data	no data
Nitrogen (Kjeldahl)	% (w/w)	3.3 - 3.6	no data	3 - 10
	g/kg	no data	44.7 ± 1.4*	no data
P	g/kg	6.7 - 8.1	8.0 ± 1.1	9.0

*Total N

Compared to raw sludge the excess sludge one contains higher concentrations of phosphorus (it is especially noticeable in WWTP with BNR removal). Because of relatively high organic matter content both kinds of sewage sludge are well putrescible and in WWTP undergo methane digestion. During this process biogas is generated [4]. It contains about 50 – 75% CH_4. The volume of biogas which is generated can reach 875 – 1020 L/kg d.m. [5]. At present many WWTP are focused on generation high quantities of biogas during fermentation process, because usage of this gas is important in electric power supply of the plants and allows to decrease sewage treatment costs [8]. Because of this there is a lot of interest in technologies which allow for increasing biogas production by ensuring better availability of organic compounds present in sewage sludge. These technologies are especially effective in the case of excess sludge which contains bacterial cells quite resistant to fast biodegradation. Quantities and quality of biogas which is generated during methane digestion are affected both by technological parameters of the process and by pre-treatment of the sludge.

2. EFFECT OF TECHNOLOGICAL PARAMETERS ON BIOGAS PRODUCTION

Main technological parameters having an effect on biogas generation are composition of the sludge (including among others fineness of the sludge solids) and temperature [9,10].

2.1. Composition of sewage sludge

During methane digestion of sewage sludge quality and quantities of biogas generated is strongly connected with content and composition of organic substrates in solids. Percent share of methane in biogas increases as protein content in the sludge increases however the volume of biogas generated during fermentation of proteins is equal to 0.5 – 0.75 m^3/g. Biogas yield is the highest (1.125 – 1.515 m^3/kg) when fats are present in substratum being fermented. Carbohydrates generates at average 0.42 m^3 of biogas/kg. When proteins are a source of organic carbon methane content in the sludge reaches 71 – 84% of CH_4. Proteins and fats are more valuable sources of CH_4 reach biogas than carbohydrates. Biogas generated during methane digestion of mixed substratum (e.g. sewage sludge) usually contains 65 – 70% of methane [11]. Research work on the effect of grease on the biogas generation during methane digestion was carried out by Neczaj et al. [12]. They digested mixture of sewage sludge and grease from the fat trap. Grease trap sludge accounted for 20, 22, 24, 26, 28 and 30% of the mixture (on VSS basis). Digestion was performed for 10 days. Significantly important increase in methane production was stated during the research work. Similar results (increase of biogas and methane yield in methane digestion process of fat reach substratum) were obtained by Davidsson et al. [13] and Luostarinen et al. [14]. In the studies by Davidsson et al. [13] it was stated that addition of grease trap fats into sewage sludge allowed for increasing methane yield by 9 – 27% when 10 – 30% of the fats were added into the sludge. The authors have also observed that amendment of grease trap fats increased methane yield but not increased the sludge production. Luostarinen et al. [14] added 46% of grease from the trap to the digester. They stated that 16 day digestion of fat reach substratum at organic loading rate 3.46 kgVSS/m^{3}d significantly increased biogas production; no effect of fats amendment on characteristics of digested sludge was observed. Also the results obtained by Martinez et al. [15] indicate that addition of fats to the sewage sludge increases biogas production. Under thermophilic conditions problem with poor quality of supernatant occurs because of high volatile fatty acids content and high COD. Another problem during anaerobic digestion of the sludge with fats is that lipid components adsorb onto the biomass which disturb complete degradation of substrate. The results of the research works done so far indicate that co-digestion of sewage sludge with fats is an effective method of increasing biogas production, it is however necessary to uphold the optimal process parameters, mainly volatile fatty acids concentration.

2.2. Temperature

Generation of biogas during methane fermentation starts at temperature above 0°C, and increases as process temperature increases. Nowdays two temperature ranges: 25 - 45°C (mesophilic conditions) and 45 - 60°C (thermophilic conditions) are the most frequently applied in WWTPs [4]. Thermophilic methane digestion allows to generate higher quantities of biogas with higher methane content (Table 3).

Table 3. Mesophilic vs. thermophilic fermentation taking into consideration biogas production [10]

Parameter	Unit	Mesophilic digestion	Thermophilic digestion
Optimal temperature range	°C	35 - 40	55 - 60
Temperature variations tolerated by microorganisms	°C	3 - 5	1 - 2
TSS reduction	%	45 - 55	55 - 70
Biogas production	Nm^3/tone of organic material dry mass	920 - 980	950 - 1000
Methane content in biogas	%	60 - 70	70 - 85

Thermophilic digestion has a lot of advantages but it is less frequently used in WWTP as a process of sludge utilization than mesophilic one. This is because of the fact that thermophilic process needs more energy to heat the digester and it is more sensitive to temperature fluctuations as well as to toxic substances [10]. The problem during the thermophilic process is also mentioned in chapter 2.1. poorer quality of the supernatant. Research work carried out by Kardos et al.

indicate, however, that the production of biogas during thermophilic process is enough high to equalize the larger energy consumption [10].

3. PRETREATMENT PROCESSES USED FOR INCREASING BIOGAS PRODUCTION

3.1. Ultrasonic disintegration of sewage sludge

Use of ultrasounds in sewage sludge pretreatment prior to methane digestion has been described by many authors [16 - 21]. Tiehm et al. [16] used ultrasounds at a frequency of 31 kHz and high acoustic intensity. They achieved more than 30% increase of COD in supernatant after 96 sec. of ultrasound treatment. Ultrasonic pretreatment was followed by mesophilic digestion of the sludge and allowed for achieving higher reduction of volatile solids in the sludge compared to not pretreated one. Reduction of VS was equal to 50.3% and 45.8% for pretreated and not pretreated sludge, respectively. The researchers also observed significantly higher (220%) biogas production during methane digestion of ultrasonically pretreated sludge. Methane digestion of the pretreated sludge was also more stable. The results of research works indicate that ultrasonic disintegration is especially effective as a method for disintegration of waste activated sludge. This kind of sludge contains bacterial cells which are quite persistent to biological hydrolysis because of its chemical composition. Research carried out by Appels et al. [17] with ultrasounds of 25 kHz (time of sonification was up to 250 min. with recirculation of WAS) followed by mesophilic digestion in single stage bath reactors for 8 days showed the possibility of 15 to 40% increase in biogas production. The study by Navaneethan [18] showed 57 – 81 % increase of biogas production after ultrasonic treatment of sewage sludge at constant frequency of 20 kHz. Appels et al. indicated that extra amounts of biogas generated during methane digestion of pretreated sewage sludge offset the costs of ultrasonic device application, and because of this the process is cost-efficient [17]. Ultrasonic pretreatment increases COD of supernatant and make the organic substances more available for anaerobic microorganisms. In the study by A. Davidsson et al. [19] COD in supernatant separated from sludge pretreated by 50 kHz ultrasounds was equal to 40 000 mgO_2/L (however soluble COD was only about 40% of total COD). As a result significantly higher biogas production was achieved. It was stated that by the hydromechanical shear forces generated by ultrasonic cavitation macromolecules with a molecular mass above 40,000 are effectively disrupted. The most effective seems to be ultrasounds with frequencies below 100 Hz. To obtain satisfactory effects of ultrasonic pretreatment it is necessary to supply enough energy to lyse cells of activated sludge and organic polymers [20].

Ultrasonic disintegration has been since now applied both under laboratory conditions and on pilot and full scale. Pilot scale installations were operated in Bad Bramstedt and Ahrensburg in Germany. Full scale installations were operated in Bamberg, Freising and Meldorf in Germany, and in Ergolz (Switzerland) [21]. The effects obtained in this scale are presented in Table 4.

Table 4. Effects of ultrasonic pretreatment of sludge under pilot and technical scale (according to [21])

Place	Scale	Effect on biogas generation	Effect on TSS or VS reduction	Other remarks
Bad Bramstedt	Pilot scale, 3 years of operation	Increased by factor 4	Reduction of digested sludge mass by 25%	Reduction of digestion time from 20 to 4 days, with no decrease in process efficiency in terms of VSS degradation
Ahrensburg	Pilot scale, operated for 3 months	Increase by 20%	Increase by 20%	-
Bamberg	Full scale 4 month test	Increase by 30%	Increase by 30%	-
Freising	Full scale, 4 month test	Increase by 15%	No data	Improving of sludge dewatering
Meldorf	Full scale, 3 month test	Increase by 25%	Increase by 25%	No foam and filamentous organisms in the sludge
Ergolz	Full-scale, 3 month tests	Increase by 25%	Increase by 15%	-

Biogas yield under pilot and technical scale increased et least by 15%. Increase of degradation of sludge TSS was in the range 15 and 30%. Results commented by Zafar [21] indicate that ultrasonic pretreatment has technical potential and can be used also in full scale WWTP installations.

3.2. Thermal pretreatment

Thermal heating of sewage sludge is also used as a method for improving biogas yield during methane digestion. Thermal pretreatment disintegrates cell walls of microorganisms and releases water from the particles of sludge. It results in coagulation of solids and decomposition of cell mass of waste activated sludge [22]. Operating conditions of thermal pretreatment of sewage sludge are very diversified from 60 – 80 °C to even 250°C [22, 23]. Retention times for these processes range from 15 to 60 min. [22, 23]. Thermal conditioning can be supported by oxygen addition or by addition of alkali and acids [22]. Nonoxidative heat treatment usually occurs at 150 – 200 °C and under pressure from 1034 to 2068 kPa. Oxidative heat treatment is usually conducted at temperatures from 175 to 360°C (under pressure in the range 1279 – 11,377 kPa) [24]. According to Kepp et al. the highest yield of hydrolysis of waste activated sludge can be achieved at temperature between 165 and 180°C; the sludge must be keep in this temperature at least for 10 min. [25]. Some research works indicates that at temperature above 250ºC harmful by-products can be generated during disintegration, such as e.g. phenols. Research work on the effect of thermal conditioning (70°C; 1 hour) on biogas production did by Davidsson et al. [13] showed that COD of supernatant can increase to 40 200 mgO_2/L (in the case of waste activated sludge) and to 34100 mgO_2/L (for the mixture of primary and waste sludge). In the not pretreated sludge these values were equal to 40700 and 330000 mgO_2/L, respectively. It means that thermal pretreatment didn't significantly affect total COD value. It however increased soluble COD value. Soluble COD increased to 87 000 – 39 000 mgO_2/L (compared to 12000 – 17 000 mgO_2/L in not treated sludge). Thermal pretreatment increased methane production by 10 - 20% compared to not treated substratum. Studies by Kepp et al. [25] indicate that thermal pretreatment of sludge allowed to save 50% of digester volume, net electricity production in WWTP was over 20% higher than if thermal conditioning was used. Research work of Zhang et al. [26] did not increase biogas production such spectacularly by thermal pretreatment of sewage sludge (170°C, 30 min.); biogas production increased only by 7 -11%. More effective it seems to be combination of thermal and ultrasonic disintegration. Barański et al. obtained even four times higher biogas yield during methane digestion of thermally pretreated sewage sludge [27]. However under laboratory conditions Myszograj have obtained even 200 % higher production of biogas after thermal pretreatment of the sludge (2 hours, 175ºC). The findings show that thermal conditioning can be effective method of increasing biogas production, however the technological parameters of the process must be experimentally confirmed for individual cases [28].

Some technical applications of thermal pretreatment are used so far. Thermal hydrolysis under high pressure is a basis of Cambi [29]. The thickened sludge is heated at 150 – 165ºC under pressure of about 7 bars. The producer guarantees that Cambi technology enhances biogas production, allows for doubling digester capacity and improves the final sludge cake dryness.

3.3. Chemical pretreatment

Also chemical methods of sewage sludge pretreatment are used as pretreatment step of sludge processing. The most frequently used chemical agents are: Fenton's reagent, hydrogen peroxide, acids and alkali. AOPs methods are mainly applied for improvement of dewatering properties of the sludge, but also can be used for removal of organic micropollutants from sewage sludge [30, 31]. Chemical reagents can be also used to provide the efficient solubilisation of the sludge. As a result enhanced biodegradation of complex organic substratum occurs [32]. Use of chemical agents is quite simply and effective. The disadvantages of their use are corrosion and odours. The sludge after pretreatment must be in many cases neutralized [32].

For acidic pretreatment H_2SO_4 is frequently used, for the alkaline processes mainly NaOH. According to the literature data alkali pretreatment is more effective that acid treatment [32]. Cassini et al. [33] proved that the same doses of H2SO4 and NaOH (20 mmol/L) allowed for solubilisation COD in the sludge at level 11% and 60%, respectively. Banu et al. [34] showed that optimal dose of NaOH for sludge pretreatment is 1600 mg/L (time of reaction 3 hours). Pretreatment effect was increased by simultaneous use of NaOH and lime. Myszograj et al. [28] used the doses of NaOH from 0.1 to 1.0 gNaOH/g d.m. (sludge was chemically stabilized for 24 h) to increase COD solubility. They realized that doses of NaOH in the range of 0.1 and 0.5 gNaOH/g d.m. increased COD values in supernatant. Higher doses of this alkali reduced soluble COD concentration. As a result of soluble COD increase biogas production increased after alkali treatment. Studies by Lin et al. [35] showed that optimal NaOH dose for organics solubilisation in the paper sludge was 8000 mgNaOH/100 g d.m. Under this conditions the highest methane yield was 0.32 m^3CH_4/kg of removed VS. Alkaline pretreatment was also used for pretreatment of lignocellulosic biomass [36]. Chemical processes can be also used simultaneously with e.g. ultrasonic pretreatment [37] and thermal treatment [38]. Studies by Kim et al. [37] indicated that combined (alkaline + ultrasonic) pretreatment of sewage sludge resulted in solubilisation of 70% COD. Combination of pH 9 and ultrasounds (7500 kJ/kg TS) allowed for significant increase in methane yield (from 81.9 ± 4.5 mL CH_4/g COD_{added} to 127.3 ± 5.0 mL CH_4/g COD_{added}). Penaud et al. [38] carried out experiments on simultaneous NaOH treatment (approx. 26 gNaOH/L) and thermal heating (140°C for 30 min.). It allow to obtain high COD solubilisation (over 50%).

4. CONCLUSIONS

- At present both physicochemical and chemical methods of sewage sludge pretreatment are widely researched worldwide.
- Common opinion connected with the use of these methods is that they are very flexible but expensive. Some research works performed under technical scale showed that advantages of these method cause them economically acceptable.
- Thermal disintegration and ultrasonic disintegration are at present implemented in technical scale. Pretreatment methods are especially effective in waste activated sludge pretreatment. The most effective are ultrasounds below 100 Hz. In the case of thermal pretreatment operating conditions of thermal pretreatment of sewage sludge are very diversified from 60 – 80 °C to even 250°C. Retention times for these processes range from 15 to 60 min. Effectiveness of the processes can be increased by using combined processes.
- Pretreatment methods allow for significant increase of soluble COD in the reject water and as the result increase biogas production.
- Technological parameters must be selected experimentally because of the variety of physicochemical properties of the sludge and effects which we would like to achieve.
- For chemical pretreatment acids or alkali are used. Alkali pretreatment seems to be more effective that acid treatment in sludge processing. It is also used in lignocellulitic waste treatment.

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PRZEGLĄD TECHNOLOGII INTENSYFIKACJI PRODUKCJI BIOGAZU PODCZAS FERMENTACJI METANOWEJ OSADÓW ŚCIEKOWYCH

S t r e s z c z e n i e

Obecnie wiele oczyszczalni ścieków zainteresowanych jest zwiększaniem produkcji biogazu powstającego podczas stabilizacji osadów ściekowych. W tym celu mogą być wykorzystywane różne metody dezintegracji: termiczne, ultradźwiękowe lub chemiczne. Limitującym etapem procesu fermentacji metanowej jest hydroliza. Poprzez zwiększenie szybkości hydrolizy uzyskuje się skrócenie czasu zatrzymania osadów w komorze fermentacyjnej oraz zwiększenie zawartości rozpuszczalnego ChZT w cieczy osadowej, a w rezultacie zwiększenie produkcji biogazu. W skali technicznej dotychczas były wykorzystywane ultradźwięki oraz metody termiczne. Największą efektywność uzyskuje się stosując ultradźwięki o częstotliwości poniżej 100 Hz. W przypadku dezintegracji termicznej stosowane są zróżnicowanie parametry technologiczne (od 60 - 80°C do nawet 250°C, czas obróbki od 15 min. do 2 godz.). Efektywność procesu może być zwiększona przez zastosowanie kombinacji procesów, np. termicznych i chemicznych. Metody dezintegracji chemicznej są obecnie stosowane przede wszystkim w skali laboratoryjnej. Do metod chemicznych zaliczamy obróbkę kwasami, alkaliami oraz zaawansowane procesy utleniania.

Słowa kluczowe: osady ściekowe, biogaz, fermentacja metanowa, dezintegracja

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