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Influence of ultrasonic field on methane fermentation process: Review

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Abstract
One important aspect of the process of anaerobic stabilisation of sewage sludge in medium and large sewage treatment plants, in addition to sludge mineralisation, is the acquisition of a valuable source of energy, which is biogas. There are well-known methods of intensifying the process of methane fermentation by subjecting sludge to disintegration using physical factors, i.e. ultrasonic field. Acetate production is the rate-limiting step in the acetate consumption pathway and affects the efficiency of the anaerobic stabilisation process. The product of the first stage of the process is also the substrate for the next stage. Therefore, it is advisable to subject sewage sludge to disintegration, which increases its susceptibility to biodegradation. Sludge modification with the above-mentioned method causes a significant increase in the concentration of organic substances in the supernatant liquid. The reflection of the physical and chemical transformations of sludge in the disintegration processes is the change in their structure expressed by the increase in the degree of particle dispersion. The disintegration of sludge using sonolysis is an effective process solution, both in terms of technology and energy, in terms of obtaining biogas, which is a valuable source of energy.

Keywords
ultrasonic field, hydrolysis proces, methane fermentation, biogas.

1. INTRODUCTION

As a result of biological wastewater treatment using the activated sludge method, excess sludge is formed, characterised by a flocculent structure containing significant amounts of microorganisms. Excess sludge shows a certain susceptibility to the anaerobic stabilisation process. In order to increase its susceptibility to biochemical decomposition taking place in anaerobic conditions, excess sludge is subjected to the process of disintegration using physical, chemical and biological factors, as well as combined disintegration, using a mixture of independent methods. After the disintegration process, excess sludge is more susceptible to biodegradation. As a result, the process of anaerobic stabilisation is more intensive, the time of the hydrolytic phase is shortened and unit biogas production increases. Based on a review of literature data (Alagöz et al., 2018), it was shown that subjecting excess sludge to disintegration with the ultrasonic field increases the efficiency of methane fermentation. Sludge disintegration prior to the methane fermentation process shortens the hydrolysis phase and intensifies the processes occurring in the methanogenic phase, leading to an increase of sludge digestion as well as unit biogas production. Acetates are an important intermediate product of the methane fermentation process: according to literature data, the rate-limiting step (RLS) for the pathway of acetate consumption was acetate production. Therefore, in order to increase methane production, pre-treatment of the substrate (by disintegration methods), the use of an acid-forming reactor or the identification of inhibitory agents is used. According to Wu et al. (2016) and Tsigkou et al. (2022) and others, not only does RLS depend on the substrate itself and its susceptibility to biodegradation but also on many dependencies in the substrate-inoculum-reactor system.

In addition, due to its time-consuming nature and sensitivity to process conditions, the effectiveness of the methane fermentation process of sewage sludge is influenced by such parameters as: pH, temperature, C/N ratio and organic load index (*OLR*). However, due to the benefits resulting from stabilisation of sludge in anaerobic conditions, i.e. reducing the volume of sludge, improving susceptibility to drainage, converting organic substances into a valuable source of energy, biogas, methane fermentation is considered a technologically and economically advantageous solution (Azarmanesh et al., 2023).

Therefore, the purpose of this review is to bring together the data on the application of ultrasonic intensification that can enhance the generation efficiency of desired products of methane fermentation, i.e. volatile fatty acids (VFAs) and biogas. Considering a number of methods affecting the efficiency of excess sludge biodegradation and the existence of many challenges related to the methods of process intensification, the scope of the review is focused on two important processes: conventional methane fermentation and sonication technology and its impact on the biodegradation process.

2. ANAEROBIC STABILIZATION OF SLUDGE

Anaerobic stabilisation is the basic process of sewage sludge treatment, which reduces the content of easily decomposable organic substances and deprives the sludge of its natural tendency to putrefy and release volatile components with an unpleasant odour. Sludge stabilisation is carried out by biological, chemical and thermal methods. One commonly used method of sludge stabilisation is methane fermentation, a set of biochemical processes taking place in anaerobic conditions, in which high-molecular organic substances, mainly carbohydrates, proteins and fats, are broken down by bacteria into alcohols or lower organic acids and into gaseous products. Methane fermentation is aimed at transforming sewage sludge into a mass that does not putrefy, easily dehydrates and does not pose a potential source of health hazard (Rak and Wieczysty, 1997). Methane fermentation, which is a complex biochemical process involving the decomposition of fragmented organic matter, is a multi-stage process. Reactions occurring during the process are classified as the following steps: a) hydrolysis; b) acidogenesis; c) acetogenesis; d) methanogenesis; these run serially and in parallel (Tandukar and Pavlostathis, 2022). The effect of methane fermentation of sewage sludge is the generation of biogas consisting mainly of methane (approx. 70% by volume) and carbon dioxide (approx. 30% by volume). It is a technology commonly used in large wastewater treatment plants, characterised by ecological and economic efficiency, requiring low energy expenditure related to the use of biogas generated in the cogeneration process as a source of electricity and heat (Macarie, 2000).

As a result of biochemical transformations, the decomposition processes of organic substances take place, which are reduced to the form of, acetic, propionic and butyric acids, for example. Substances that cannot be converted to acids are retained in the sludge. These substances are primarily cellulose, hemicellulose and lignin as well as inorganic solids. Free fats and proteins are very well degradable. During the methane fermentation process, the concentration of carbon, nitrogen and phosphorus, which are transported with the sludge liquid to the beginning of the sewage treatment process, also changes (Vítezová et al., 2020).

Extracellular enzymes of fermentation bacteria are responsible for the decomposition of complex biopolymers into monomers during the hydrolysis process, which are available for direct processing in the cell in subsequent stages of the process. Then, at the stage of acidogenesis, with the participation of bacteria that are mostly absolute anaerobes, the monomers are transformed into lower volatile fatty acids, alcohol, lactic acid, molecular hydrogen and carbon dioxide. Research on the influence of molecular hydrogen on the methane fermentation process was initiated by Zhao et al. (2021). It has been shown that carbon dioxide and hydrogen can also be a source of acetate formation by omoacetogenesis. In addition, it has been shown (Zouagri et al., 2020) that there is a possibility of anaerobic oxidation of alcohol, propionate and longer-chain fatty acids as well as aromatic acids to acetate or acetate and CO_2 by a group of H_2-producing acetic bacteria. During methanogenesis, methane is produced by three pathways: acetoclastic, hydrogenotrophic and methylotrophic. It should be emphasised that as a result of establishing the process equilibrium, all reactions occurring during the methane fermentation process take place in parallel (Merlin and Boileau, 2013; Nwokolo et al., 2020).

According to Myszorgaj and Płuciennik-Koropczuk (2023), methane fermentation is the optimal method for municipal sludge characterised by a significant content of carbon, nutrients, and trace elements:

- not containing significant amounts of toxic additives,
- not showing significant quantitative and qualitative changes during the day.

Compared to excess sludge, primary sludge is characterised by a higher content of organic matter susceptible to biodegradation. Therefore, it is estimated that the methane fermentation process of primary sludge will be more effective, both in terms of energy capacity and unit biogas production (Sakaveli et al. 2021).

Excess sludge, with low biodegradability during the period after pre-treatment, shows an increased degree of liquefaction, a higher degree of fermentation and an increase in the efficiency of methane production than primary sludge, more susceptible to biodegradation (Liu et al., 2021).

Digested sludge takes up much less volume than raw sludge; it contains approx. 80–90% of water, does not rot easily and dries quickly. Stabilised sludge after methane fermentation is characterized by a much lower degree of hydration, but at the same time it contains more overlying water than non-digested sludge.

Sewage sludge is a valuable source of organic matter that is susceptible to biochemical decomposition in oxygen conditions. The measurable effect of the methane fermentation process is (Zhao et al., 2021; Zouagi and Mameri, 2020):

- obtaining an increase in the degree of sludge digestion, expressed by the degree of reduction of organic substances contained in them; removal of pathogenic microorganisms and helmite eggs,
- improvement of rheological parameters of sludge
- increased susceptibility to dehydration.

The main product of methane fermentation is biogas, while the by-product is fermentate, which can, for example, be used in the reclamation of degraded areas as a valuable source of carbon and biogenic elements. The resulting biogas is a gas mixture consisting mainly of methane (CH_4) and carbon dioxide (CO_2), with traces of carbon monoxide (CO), hydrogen

(H_2), hydrogen sulphide (H_2S), oxygen (O_2), nitrogen (N_2) and ammonia (NH_3) (Nwokolo et al., 2020).

The goal of fermentation is achieved when 40 to 50% of the organic matter in the sludge has been decomposed. The decomposition of 50% of organic substances is considered the technical limit of the process (Malina and Pohland, 1992).

The essence of methane fermentation is the path of transformation of complex organic substances in an anaerobic environment into small gaseous molecules such as methane and carbon dioxide, involving hydrolysing and fermenting bacteria or hydrogen-producing acetogenic bacteria and methanogenic bacteria (Park et al., 2018; Yang et al., 2013).

Methane fermentation is a competitive technology for biological disposal of sludge in accordance with the ideas of sustainable development which, in relation to the process of aerobic degradation, is characterised by highly efficient decomposition of organic compounds, energy recovery in the form of biogas and low operating costs (Parawira et al., 2005).

2.1. Mechanism of methane fermentation of sewage sludge

Methane fermentation proceeds successively in four phases of molecular decomposition of organic substrates with the participation of various groups of microorganisms, each of which requires appropriate environmental conditions.

According to Tian et al. (2017), in the case of anaerobic methanogenesis, three stages can be distinguished: hydrolytic fermentation, production of hydrogen and acetic acid, and generation of methane. During the hydrolysis step, extracellular bacterial enzymes break down high-molecular organic compounds (e.g. cellulose, starch, protein, fat) into small molecules (e.g. monosaccharides, disaccharides, polypeptides, long-chain fatty acids, etc.) In addition, H_2 and CO_2 are produced at this stage; as a result of biochemical reactions, they are finally converted by fermentacin bacteria into final products using intermediate products, which are volatile fatty acids (VFA). The volatile fatty acids produced in the previous stage are used by hydrogen-producing acetic bacteria to generate products such as acetic acid, hydrogen and carbon dioxide, which can be a source of biogas through transformation. It should be emphasised that there are two ways of obtaining biogas by methanogenic bacteria, i.e. by reducing hydrogen with carbonic acid anhydride and producing methane from acetic acid (Baek et al., 2018; Roopnarain et al., 2021).

The methane fermentation phases are as follows (Nagarajan et al., 2022):

- Phase I – high-molecular polymers i.e.: carbohydrates, proteins and lipids are degraded by hydrolytic bacteria into monomers (respectively monoamides, amino acids and fatty acids),
- Phase II – decomposition of hydrolysed substances into organic acids – acidogenesis,
- Phase III – decomposition of organic acids to acetic acid – acetateogenesis,
- Phase IV – decomposition of acetates and acetic acid into methane and carbon dioxide – methanogenesis.

Nagarajan et al. (2022) presented the biochemical distribution of individual groups of organic compounds during methane fermentation as follows (Fig. 1).

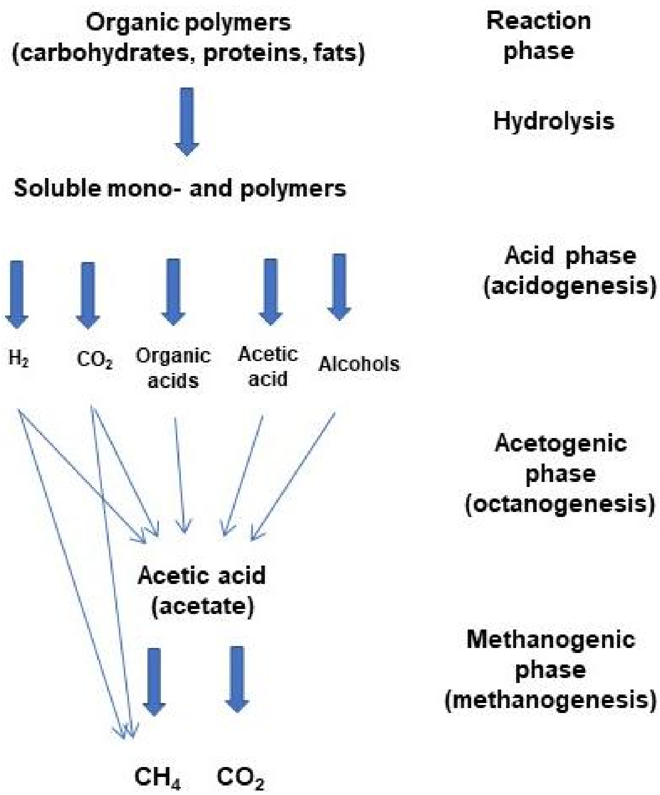

Figure 1. Decomposition of individual groups of organic compounds in biochemical processes (Nagarajan et al., 2022).

In the first phase, high-molecular weight polymers, often insoluble, are decomposed into simpler compounds by the enzymes of hydrolytic bacteria. These processes are a source of energy for saprophytic (non-methane) microorganisms. In the acidic phase, acetate bacteria break down hydrolysed substances into organic acids, alcohols, aldehydes, H_2 and CO_2. This phase is characterised by a clear decrease in the pH value to approx. 5.0. There is no visible reduction of COD or BOD_5, because the amount of organic substances remains basically unchanged. In this phase there is no stabilisation of organic compounds, and the outflow from this phase is characterised by an intense odour (Nagarajan et al., 2022). According to Sadecka (2002), as early as this phase, methanogenic compounds are formed, e.g. formic acid, acetic acid, methanol, CO_2 and H_2. They can be directly used by methane bacteria and processed into energetically attractive end products of fermentation, i.e. methane (CH_4). The formation of methane from gaseous products, resulting from the reduction of carbon dioxide with hydrogen, reduces the partial pressure of this gas. This is beneficial for the proper development of bacteria involved in the next, third phase of the process, which require a sufficiently low hydrogen pressure ($<10^{-4}$ atm). The hydrolysis and acidic phases are closely related and are often collectively referred to as the acidic phase, which is related to the intermediate products formed during their course, such as: CH_4, CO_2 and volatile acids. In the bioenergy industry, volatile fatty acids (VFAs) and their derivatives have value-added applications and are considered an important intermediate product of methane fermentation, prior to obtaining biogas. The most common volatile acids during methane fermentation are (Zhang et al., 2022):

- HCOOH formic acid,
- acetic acid CH_3COOH,
- propionic acid CH_3CH_2COOH,
- butyric acid $CH_3CH_2CH_2COOH$,
- valeric acid $CH_3CH_2CH_2CH_2COOH$,
- isovaleric acid $(CH_3)_2CHCH_2COOH$,
- caproic acid $CH_3CH_2CH_2CH_2CH_2COOH$.

In the next phase, the acetate phase, organic acids, alcohols and aldehydes are converted into acetic acid. Acetate bacteria convert the products of the acidic phase into substances that can be used by methane bacteria (acetic acid, H_2, CO_2). During the decomposition of fatty acids, alcohols and organic acids, acetate bacteria produce hydrogen. Since these bacteria can only exist with low concentrations of hydrogen, they require symbiosis with hydrogen-consuming methane bacteria. In addition, an appropriate amount of energy generated in methane formation reactions must be supplied for the course of the metabolic reaction (Merlin and Boileau, 2013; Nwokolo et al. 2020; Vítezová et al., 2020).

The products of hydrolysis are fermented using acid-forming bacteria, which are responsible for the production of volatile fatty acids and hydrogen. According to Krupp and Widmann (2009), acidogenesis in turn proceeds via the acetic acid paths according to reaction (1) and butyric acid according to reaction (3), where the by-product of the ongoing processes is hydrogen. It should be emphasised that the process of using biohydrogen occurs during the production of propionic acid; this is a common VFAs generated in the process of methane fermentation of sewage sludge according to reaction (2).

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \tag{1}$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \tag{2}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow C_3H_7COOH + 2H_2 + 2CO_2 \tag{3}$$

Under standard conditions, the above reactions are thermodynamically feasible if hydrogen is removed from the system and its partial pressure is kept low from 6 to 400 Pa. Octanogenesis can therefore only proceed in the symbiosis of acetate-producing bacteria with hydrogen-consuming methanogenic bacteria. Hydrogen can be consumed in the formation of acetic acid from carbon dioxide and hydrogen:

$$\begin{aligned} &2HCO_3^- + H^+ + 4H_2 \rightarrow CH_3COO^- + H_2O \\ &\Delta G_0 = -104.6\ \text{kJ/mol} \end{aligned} \tag{4}$$

or in the methanogenesis phase.

Octanogenesis determines the efficiency of biogas production. The transformations of higher organic acids taking place in this phase are the source of approx. 25% of the amount of acetates and 11% of hydrogen. The last phase is the methane phase, in which methane bacteria form methane from acetic acid, hydrogen and carbon dioxide. There is then a significant reduction in the amount of organic matter and an increase in the amount of released biogas.

In a stable methane fermentation process, the rate of formation of intermediate products in a given phase is equal to the rate of their decomposition in the next phase. As a result, almost all biodegradable organic substances are converted into final products, i.e. methane, carbon dioxide, ammonia and hydrogen sulphide. Stages I and II are closely related: they are called "acid fermentation" stages due to the fact that the products formed during their course are acids. Similarly, stages III and IV, directly responsible for the production of methane, are closely related to each other and are referred to as "methane fermentation" stages (Miksch, 1995).

During the acid phase, bacteria break down complex organic substances into volatile acids. Among these acids, acetic and propionic acids predominate, with lesser amounts of butyric and valeric acids. Acetic acid accounts for as much as 72% of all intermediate compounds formed during the acid phase of fermentation (Enebe et al., 2023).

2.2. Decomposition of organic compounds occurring in the process of methane fermentation of sewage sludge

Fats and oils are natural components of sewage. Although they occur in small amounts, they are easily sorbed on flocs of secondary sludge. In secondary sludge, the share of lipids reaches 6–12% TS, while in digested sludge it is approx. 7% TS. Fats in the aqueous environment of sludge undergo slow, partial or complete hydrolysis, leading to the formation of free fatty acids and glycerol, as well as its poly- and monoester derivatives. As a result of anaerobic decomposition, glycerol is converted to glyceraldehyde phosphate, which is converted back to pyruvic acid for further oxidation or reduction (Macarie, 2000; Vítezová et al., 2020).

Proteins break down into simpler compounds so that they can penetrate cell membranes. The hydrolysis of amino acids depends on the environmental conditions and the type of organisms involved in the process. In an oxygen-free environment, products with an unpleasant odour are formed, such as mercaptans, amines or ammonia. Protein is the dominant component, accounting for 50% of the total escess sludge organic matter.On the other hand, digested sludge proteins are present in amounts lower than 15% TS. The degradation of protein has a major impact on sludge digestion (Shao et al. 2013; Yan et al., 2022).

As a result of methane fermentation, carbohydrates are broken down into simpler sugars, mono- and disaccharides as, in this form, they can penetrate cell membranes. It is possible to decompose glucose to pyruvic acid, which in turn is a common link in the metabolic transformations of carbohydrates and proteins.

2.3. Anaerobic microorganisms

Three groups of microorganisms are involved in the process of anaerobic conversion of organic substances into biogas: acid-forming bacteria, acetate bacteria and methanogenic bacteria. The group of microorganisms involved in methane fermentation includes different types of microorganisms in terms of food, but synergistically they dependent on each other. Organic polymers are broken down into simple compounds, and these are substrates for fermentation bacteria that produce hydrogen, alcohols and volatile fatty acids (VFAs). VFAs are consumed by syntrophic bacteria to form acetate and hydrogen. Acetate can also be produced from H_2 and CO_2 by some homoacetogenic bacteria, sulhate-reducing bacteria and other anaerobic microorganisms (Shao et al. 2013; Yan et al., 2022).

Both obligatory anaerobes (*Bacillus, Pseudomonas, Clostridium, Bifidobacterium*) and optional anaerobes (*Streptococcus, Enterobacterium*) dominate in both the hydrolysis phase and the acidic phase. Some of the acid-forming bacteria are obligatory anaerobes (*Aerobacter, Alcaligenes, Clostridium, Escherichia, Lactobacillus, Mikrococcus, Flavobacterium*). Acid phase microorganisms are relatively tolerant of changes in pH and temperature. The growth rate for bacteria of both phases depends on the type and concentration of the substrate (Bhatia and Yang, 2017; Feng et al., 2018).

The longest time of bacterial development in both phases occurs during the decomposition of fats; bacterial growth in the presence of carbohydrates last approx. five hours. For a mixed substrate, the development time is nine hours. During metabolism, facultative bacteria may consume oxygen accidentally introduced into the system during the addition of the substrate, thus creating a conducive environment for obligate anaerobes (Choromański and Łebkowska, 2008; Heidrich and Niścier, 1999).

In the acetate phase, the decomposition of organic acids with bacteria requires the cooperation of different bacterial species. Valeric acid is broken down to acetic and propionic acid by Mbact. Suboxydans, while Mbact.propionicum is responsible for further decomposition of propionates to acetates, CO_2 and CH_4. Acetate bacteria (*Syntrophomonas sp.* and *Syntrophobacter sp.*) convert acid phase products (butyric acid, propionic acid, alcohols) into acetates and hydrogen, which can be used by methanogenic bacteria. These may grow when hydrogen is consumed by hydrogenotrophs. Hydrogen can also be removed from the environment by homoacetogenic bacteria in the process of creating acetates from CO_2 and H_2. However, under typical fermentation conditions, this process does not occur for thermodynamic reasons (Heidrich and Niścier, 1999).

According to Amin et. al. (2021) and Vanwonterghem (2016) up to 72% of the methane production is driven by the activity of acetoclastic methanogens, while through hydrogenotrophic methanogenesis (ancestral pathway of methane formation) up to 28% of methane content is generated in the anaerobic system.

The syntrophy between organisms producing and consuming hydrogen enables the growth and activity of these microorganisms and can transfer H_2. Additionally, it may also be accompanied by the removal of toxic compounds (Teng et al., 2019). Acetogenic phase bacteria are characterised by a long generation time depending on the type of available substrate. Hydrogen is produced by fermentation of butyric acid, mixed acidfermentation and bacterial ethanol fermentation in various pyruvate metabolic pathways. The generation time for butyric acid-using bacteria is 71 hours; for fatty acid-using bacteria, it is 131 hours (Fang et al., 2006; Teng et al. 2019).

Methanogenic bacteria classified as Archaeobacteriales are obligate anaerobes. In the event of the appearance of oxygen (even in the amount of 0.01 mg/L), methanobacteria are immediately inhibited, which leads to an increase in the concentration of organic acids and a decrease in the pH of the environment. Methanogenic bacteria are morphologically diverse and, at the same time, adapted to the assimilation and processing of specific types of substrates. Methanogenic bacteria occur in the form of rods (Methanobacterium), spirals (*Methanospirillum*) or cocci (*Methanococcus, Methanosarcina*). Methanobacteriales, Methanomicrobiales, and Methanosarcinales are the most frequent orders detected in the anaerobic digesters, while methanococcales are rarely found . The simplest organic compound that can be converted by methane fermentation bacteria is acetic acid. However, all volatile acids can be a substrate for certain types of bacteria. The generation time of methanogenic bacteria ranges from 15 to 85 hours, depending on the type of substrate and reaction temperature (Chmiel, 1998; Harirchi et al. 2022; Heidrich and Niścier, 1999).

Acid fermentation products can also be used by other groups of microorganisms, e.g. bacteria that reduce sulphates or nitrates. The involvement of reducing bacteria leads to the appearance of hydrogen sulphide, which is highly toxic to all organisms, in the reaction environment and in the biogas. Hydrogen sulphide with a pH above 6 is hydrolysed and occurs in the form of HS^- or S^{2-} ions. Sulphate-reducing bacteria may have a negative impact on the course of methane fermentation, inhibiting the process of methanogenesis. In order to reduce sulphates, these microorganisms compete with methanogens to obtain hydrogen and acetate, substrates used by these two groups of microorganisms. Two groups of sulphate-reducing bacteria can be distinguished, i.e. oxidising substrates to acetate and oxidising organic acids, including acetate to CO_2. Sulphate-reducing bacteria can form a syntrophic association with hydrogenotrophic methanogens to degrade propionate or butyrate, or function independently in anaerobic digesters and compete with methanogens. Sulphate-reducing bacteria include: *Desulfovibrio, Desulfomotaculum, Desulfobacter*. These are obligate anaerobes and do not oxidise organic substrates to CO_2, but to acetic acid (Demirel and Yenigün, 2002; Gerardi, 2003).

Nitrate-reducing bacteria, are optional anaerobes and can switch to aerobic respiration in the presence of oxygen and utilise nitrate, nitrite, as an electron acceptor when placed in an oxygen-deficient environment. In nitrate respiration, nitrates are used as an energetically favourable electron acceptor in the electron transport chain. Nitrates, on the other hand, are reduced to nitrites, which are eventually converted to molecular nitrogen. These include bacteria of the genus *Propionibacterium, Velionella*. Predominance of sulphate- and nitrate-reducing bacteria can lead to hydrogen accumulation, except when other hydrogen acceptors are present in the environment (Duarte et al., 2020; Simon, 2013).

2.4. Kinetics of the process of methane fermentation of sewage sludge

Amongst other things, the rate of methane fermentation depends, on on the temperature of the process, the intensity of mixing the content of the fermentation chamber and the phase of decomposition of organic compounds.

Kinetic models for the mehane fermentation process, which are a mathematical representation of the reactions taking place during the process, make it possible to understand them and find correlations between the parameters tested. These models also enable conducted experiments to be simulated on an industrial scale, which is an important aspect of research (Rodriguez Leon et al., 2018).

In order to describe the kinetics of methane fermentation, different models are used, based on the rate-limiting approach, or of a complex, structured nature, i.e. steady-state models or dynamic models (Tandukar and Pavlostathis, 2022).

It is possible to evaluate the kinetics of the methane fermentation process on the basis of the intensity of the released biogas.

The volume of the generated biogas can be calculated from the relationship described in the following equation (Marcinkowski, 2010):

$$V_g = V_{g\,\max}(1 - e^{-kt}),\ \mathrm{m}^3 \tag{5}$$

where: V_g – amount of biogas produced, m^3; $V_{g\,\max}$ – practically achievable amount of biogas, m^3; k – reaction rate constant, d^{-1}; t – fermentation time, d.

For mesophilic methane fermentation can be adopted $k = 0.25$ d^{-1} (Wierzbicki, 1996).

The correct course of the methane fermentation process is affected by the retention time of sludge in fermentation chambers, which is closely related to the process temperature. With a known load of organic substances in the sludge, the approximate fermentation time can be determined in Table 1.

Table 1. Fermentation time at different temperatures (Imhoff, 1996; Podedworna and Umiejewska, 2008).

Temperature [°C]	8	10	20	30	32	42	50	55	60
Time [day]	120	75	44	26	24	30	15	14	13

The amount of biogas produced in the process of methane fermentation is directly proportional to the degree of decomposition of organic substances. During the first ten days of the process, it is possible to obtain a decrease in the content of organic compounds, measured as dry organic matter, from 7 to 50%. As the process continues, the rate of decomposition decreases and after 20, 25 days 30 to 60% of decomposition is observed.

The kinetics of biogas production for a non-flow system depends on decomposition phase of organic compounds. The volume of released biogas, in the case of methane fermentation of lower organic acids and cultivation of methanogenic bacteria, is proportional to the amount of decomposed acid and the reaction efficiency factor.

In the first phase of methane fermentation, the amount of biogas produced per unit of time is constantly increasing. This phase is called the "logarithmic growth phase". The reaction rate of this stage is proportional to the amount of biogas produced and is described by the Equation (6) (Magrel, 2004).

$$\frac{\mathrm{d}G}{\mathrm{d}\tau_1} = k_1 \cdot G \tag{6}$$

where: G – volume of biogas obtained for time τ_1, m^3/d; τ_1 – the duration of the first phase of biochemical decomposition, d; k_1 – reaction rate coefficient in the first phase of methane fermentation, d^{-1}.

After reaching the inflection point, the rate of biogas production begins to decrease steadily. The total amount of biogas produced is approaching the G_e limit value. The speed of the second phase exhaustion is proportional to the difference between the practically achievable amount of biogas and the amount obtained at a given moment, as shown in the following equation:

$$\frac{\mathrm{d}G}{\mathrm{d}\tau_2} = -k_2 \cdot (G_e - G) \tag{7}$$

where: G_e – practically achievable amount of biogas, m^3/d; τ_2 – the duration of the second phase of biochemical decomposition, d; k_2 – reaction rate coefficient in the second phase of methane fermentation, d^{-1}; G – volume of biogas obtained for time, τ_1.

To predict biogas yield, the modified Gompertz model (Eq. 8), logistic model (Eq. 9) as well as the Richards model (Eq. 10) can be used. The input parameters of the Gompertz model and the logistic model include: potential methane production, specifc rate of methane production, phase delay time and final digestion time. The Richards model is based on the same input parameters as the above models with the addition of a fourth parameter (constant form) to fit the methane accumulation curve more precisely.

However, the main limitation of the modified Gompertz model and logistic model is their unsuitabilityt for complex substrates. On the other hand, the Richards model is more difficult to implement due to the greater number of input parameters.

To describe biogas production in bioreactors, it is possible to use the modified Gompertz equation (Zhu et al., 2009):

$$M(t) = R_{\max} \cdot \exp\left\{-\exp\left[\frac{K \cdot e}{M_{\max}}(\lambda - t) + 1\right]\right\} \tag{8}$$

where: $R_{\max}$ – maximum biogas production determined experimentally, mL; K – rate of biogas production in the intensive growth phase of a mixed population of microorganisms, mL/d; t – fermentation time, d; λ – lag phase in biogas production – lag phase, d; e – constant 2.718.

The logistic model (Ware, and Power, 2017) is given by

$$y = A/\{1 + \exp[4R_{\max} \cdot (\lambda - t)/A + 2]\} \tag{9}$$

where: A is the maximum cumulative methane yields, mL/g·TS, $R_{\max}$ is the maximum methane production rate, mL/g·TS/d, λ is the lag phase time, d.

The modified Richards model ([]Zwietering et al., 1990) with the fourth parameter v is given by

$$y = A \cdot \{1 + v \cdot \exp(1 + v) \cdot \exp[R_{\max} \cdot (1 + v) \cdot (1 + 1/v) \cdot (\lambda - t)/A]\}(-1/v) \tag{10}$$

where A, $R_{\max}$, and λ have the same meaning as above, v is the shape coefficient.

2.5. Factors affecting the process of methane fermentation of sewage sludge

According to literature data (Chen et al., 2008), the main factors influencing the process of methane fermentation are:

- process temperature,
- pH and buffering capacity of sludge,
- substrate composition,
- mixing the contents of the chamber,
- amount and frequency of sludge supply,
- process duration,
- presence of toxic substances.

Mixing the content of digesters ensures homogeneity of the fermenting mass throughout the volume. The mixing of raw and fermenting sludge is an important condition for the stable course of the methane fermentation process. Inaccurate mixing or no mixing causes the occurrence of overheated and underheated places, and as a consequence, the metabolism of anaerobic bacteria is disturbed. Circulation in fermentation chambers accelerates and intensifies the processes of biological decomposition, prevents the formation of a scum formed on the surface of sludge and prevents the formation of zones in the chamber with unequal concentrations of metabolic products.

The higher the temperature, the greater the mixing intensity should be (Bień et al., 1999; Dymaczewski et al., 1995). In a properly mixed digester, the difference between the sludge dry matter content at different depths of the chamber should not exceed 5 kg TS/m^3.

In biochemical changes, the temperature should not exceed 55 °C; only a few bacterial populations survive above 60 °C. The thermal resistance of bacteria depends on the water content in the cell: the lower the water content in the cell structure, the higher the temperature which the organism can survive.

As the temperature increases, the rate of chemical reactions increases. An increase in the temperature in the system increases the rate of enzymatic reactions. Regardless of the type of methane fermentation to which sewage sludge is subjected, it is important for the temperature of the process to be stable and for fluctuations not to exceed from 2 to 3 °C. A stable temperature is essential for the growth of the microorganisms that are involved in this process. With high stability, methane bacteria develop better, which results in the release of more fermentation gas (Jędrczak, 2008; Zouagri et al., 2020).

Rapid changes in temperature (above 10 °C) during the day cause a thermal shock to methane bacteria with little effect on other bacteria (hydrolytic, acidic). The consequence is an increase in the concentration of volatile acids in the chamber and the associated rapid decrease in alkalinity and pH (Bień et al., 1999). On the other hand, Jędrczak (2008) gives ±1 °C/h as an acceptable temperature fluctuation that does not interfere with the course of the mesophilic stabilisation process. According to Imhoff (1996), the temperature also significantly affects the degree of decomposition of organic substances as well as the amount and composition of the released biogas.

According to literature data (Jędrczak, 2008; Malina and Pohland, 1992), one very important factor affecting the stability of the methane formation process is the reaction. The reaction is the result of weak acids (carbonic acid, phosphoric acid, volatile organic acids, hydrogen sulphide) and weak bases, e.g. ammonium hydroxide. These compounds shape the buffer capacity of the system and allow the pH to be maintained within a range from 6.8 to 7.4. The reaction affects the solubility and forms of occurrence of both organic and inorganic compounds. It also determines the proper development of microorganisms that cause fermentation, especially methanogens. The acidification phase and methanogenesis require different pH values to ensure the proper course of the transformations that occur. The optimum pH value for bacteria that hydrolyse and convert monomers to simple organic acids is within a range from 5.2 to 6.3. Excessive production of acids and their dissociation causes a reversal of the dissociation of carbonic acid with a simultaneous increase in the content of carbon dioxide in the system.

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \tag{11}$$

$$H^+ + HCO_3^- \rightarrow H_2CO_{3(aq)} \rightarrow H_2O + CO_2 \tag{12}$$

The consequence of this process is a decrease in the pH of the environment to 5.0. Lowering the pH shifts the balance between dissociated and undissociated forms of volatile acids towards undissociated forms. At a pH of 4.5 to 4.8, the buffer system of the bacteria starts to work. Further lowering the pH leads to the inhibition of the production of volatile acids. Methanogenic bacteria therefore require neutral conditions, pH should be in the range from 6.8 to 7.2. Below pH 6.6, the growth rate of methanogens decreases. An excessive increase in pH may, in turn, lead to an increase in the concentration of ammonia in the sludge and to the inhibition of methane fermentation. Methane bacteria show activity at different pH values: acetate-degrading methanogens were detected in an environment with a pH of approx. 5, while methylotrophic and hydrogen-oxidising methanogens were found in a strongly alkaline environment. In a properly proceeding process of methane fermentation, the pH of the overlying liquid should be slightly alkaline (from 7.0 to 7.5). The optimum production of biogas occurs at a pH from 7.0 to 7.2. A high proportion of biogas can also be obtained at a pH of 6.6 to 7.0 and 7.2 to 7.6. According to Magrel (2004), the reaction of the overlying liquid should be from 7.0 to 7.2. The pH limits should be between 6.5 and 8.5.

The regulation of pH is related to the alkalinity of the system and the presence of volatile fatty acids. In a properly proceeding methane fermentation, the value of VFA concentration ranges from 100 to 500 mg CH_3COOH/L with alkalinity not lower than 500 mg $CaCO_3$/L and for the pH of the supernatant liquid from 7.0 to 7.2. Limit values of VFA concentration should not exceed 2000 CH_3COOH/L (Heidrich, 1999; Magrel, 2004).

According to Sadecka (2002), the optimal value of VFA concentration at pH from 6.8 to 7.4 is from 50 to 500 mg CH_3COOH/L, and the alkalinity should be within a range from 1500 to 3000 mg $CaCO_3$/L.

Control of the content of organic acids, alkalinity and reaction enable the correctness of the process to be assessed. The ratio of volatile acids to alkalinity is an indicator of the proper course of the fermentation process. The increase in the value of volatile fatty acids/alkalinity (VFAs/A) is preceded by a rapid decrease in pH. Podedworna and Umiejewska (2008) believe that it is beneficial for its value to be stable, as low as possible and maintained at a value of 0.01 during the correct operation of the chambers. The danger level for VFAs/A is 0.3; if this value is exceeded, then corrective action must be taken.

The microorganisms responsible for the methane fermentation process are very sensitive to chemical substances that may be supplied in fermented raw materials or be formed as intermediate products in the process of their decomposition. These substances are called inhibitors, and the effect of their presence may be a significant reduction in daily biogas production or a complete collapse of biochemical changes occurring during methane fermentation.

The simultaneous presence of several different toxic substances in the system may lead to the enhancement of their toxic effect, which means that the total effect of the action is greater than the sum of the separate actions. This is the so-called synergistic effect. The toxicity of various pollutants also depends on the antagonism with other pollutants, which reduces the toxic effect (Magrel, 2004).

Some heavy metals are toxic to anaerobic organisms. The most harmful metals include cadmium, lead, mercury, arsenic, selenium, molybdenum, copper, zinc, as well as nickel. Heavy metals adversely affect the activity of bacteria responsible for biochemical sludge processing. High concentrations of heavy metals are also an important factor limiting the use of natural, including agricultural, sludge (Jędrczak, 2008). The range of concentrations of metals that are toxic or inhibiting the process of anaerobic stabilisation of sludge is presented in Table 3.

The limits to concentrations of inhibitory and toxic heavy metals given in the literature vary. This is due to the fact that ionic forms have a toxic effect, the share of which depends on the oxidation-reduction potential, pH, salinity of the environment and the degree of binding of metals into complexes or insoluble forms.

Table 2. Synergistic and antagonistic combinations of cations (Krull et al., 2000).

Toxic cation	Synergistic cations (increase in toxicity)	Antagonist cations (reduction of toxicity)
NH_4^+	Ca^{2+}, Mg^{2+}, K^+	Na^+
Ca^{2+}	NH_4^+, Mg^{2+}	K^+, Na^+
Mg^{2+}	NH_4^+, Ca^{2+}	K^+, Na^+, NH_4^+, Ca^{2+}
Na^+	NH_4^+, Mg^{2+}, Ca^{2+}	K^+

Table 3. Inhibitory and toxic concentration of various metals in the supernatant liquid (Krull et al., 2000).

Cation type	Concentration range [mg/L]
Cr^{3+}	28–200
Ni^{2+}	50–200
Cu^{2+}	5–100
Zn^{2+}	3–100
Cd^{2+}	70
Pb^{2+}	8-30

Numerous organic compounds, including detergents and pesticides, have an inhibitory effect on the processes of anaerobic decomposition. Products formed as a result of transformations of organic compounds inside the fermentation chamber may also have a toxic effect. These may include:

- organic acids (especially propionic) as a product of the acidic phase;
- ammonia as a mineralisation product of organic nitrogen compounds;
- hydrogen sulphide as a reduction product of sulphates, sulphites and organic sulfur compounds;
- metabolites of transformations of various compounds in the conditions of methane fermentation.

The high adaptive capacity of the biocenosis enables it to adapt, at least under favourable conditions, to the presence of a constant concentration of toxic substances in the environment (Jędrczak, 2008).

2.6. Characteristics of biogas generated in the process of methane fermentation of sewage sludge

The product of methane fermentation of organic compounds is biogas, which is a mixture of gases (methane, carbon dioxide) and admixtures of hydrogen sulphide, hydrogen, carbon monoxide, water vapour and other gases in trace amounts.

In the anaerobic condtions, through hydrogenotrophic methanogenesis, ancestral paths of methane formation, up to 28% of methane content is produced. Moreover, up to 72% of the methane production is obtained by the activity of acetoclastic methanogens (Amin et al., 2021; Vanwonterghem et al., 2016).

The biogas formation reaction is presented according to the equation (Lewandowski, 2007)

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CO_2 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CH_4 \tag{13}$$

$$C_nH_aO_bN_d + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3d}{4}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} - \frac{3d}{8}\right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} - \frac{3d}{8}\right) CO_2 + dNH_3 \tag{14}$$

where: C, H, O, N – chemical symbols of the elements, sequentially carbon, hydrogen, oxygen, nitrogen; n, a, b, d – number of atoms, successively carbon, hydrogen, oxygen, nitrogen.

According to literature data, from 1 kg of sewage sludge, under optimal conditions, approx. 0.32÷0.57 m^3 of biogas can be obtained (Buraczewski, 1989; Lewandowski, 2007). Depending on the type of stabilised sludge, the amount of biogas production varies; for primary sludge it is approx. 0.5÷0.6 m^3/kg TS, while for excess sludge it is from 0.2 to 0.4 m^3/kg TS (Nellenschulte and Kayser, 1997).The amount of biogas produced and the content of individual gases in it also depends on the type of substrate subjected to fermentation. The largest volume of biogas (from 1.125 to 1.515 m^3/kg) can be obtained from fats, a smaller one (from 0.5 to 0.75 m^3/kg) from proteins or carbohydrates. The volume and composition of biogas depends on many factors, including the content of organic compounds, temperature, and time of the process (Janosz-Rajczyk, 2008).

Examples of the amount of biogas produced and its composition depending on the substrates of the methane fermentation process are shown in Table 4.

Table 4. Volume and composition of biogas resulting from the decomposition of various groups of organic compounds (Podedworna and Umiejewska, 2008).

Type of organic substrate	Volume of generated biogas [L/kg *VSS*]	Percentage composition of biogas
Carbohydrates	790	50% CH_4 50% CO_2
Fats	1250	68% CH_4 32% CO_2
Proteins	700	71% CH_4 29% CO_2

To ensure that the methane fermentation process is successful, the methane content in biogas is in the range of 65÷70%. Biogas is produced by biological decomposition of acetic acid (approx. 72%) and by reducing carbon dioxide with hydrogen (approx. 28%) Apart methane content, biogas contains 26÷36% of carbon dioxide, 1÷10% of nitrogen, 0.1÷7% of oxygen, 0÷1% of hydrogen and 0÷1% of hydrogen sulphide (Graczyk and Sadecka, 1993; Hartmann, 1996; Janosz-Rajczyk, 2008).

Comparable values of the percentage share of gaseous components of biogas produced during methane fermentation of sewage sludge are given by Łomotowski and Szpindor (1999). Methane constitutes 55÷70% of the total biogas volume, carbon dioxide 27÷44%, hydrogen 0.2÷1%, and hydrogen sulphide 0.2÷3.0%.

The methane content in biogas is an important indicator of process stability. A decrease in methane content in biogas indicates an imbalance in the system and lower activity of methanogens (Jędrczak, 2008).

The biogas generated in the process of methane fermentation is colourless, it is a mixture of flammable and non-flammable gases, after desulphurisation, under normal conditions, it burns with a blue flame. Biogas with a high methane content is lighter than air, with a methane content of 80%, its density is 0.97 kg/m^3 under normal conditions, while with increasing CO_2 content, its density increases and for biogas with, for example, 60% CH_4, it is 1.13 kg/m^3 (Buraczewski, 1990).

According to literature data (Lewandowski, 2007; Łomotowski and Szpindor, 1999), an important parameter of biogas is the calorific value, which predisposes it to be used as a full-fledged energy carrier. The calorific value is directly dependent on the biogas calorific value, i.e. the percentage of methane in the biogas. From 1 kg of organic matter, biogas with a calorific value of 16.8–23 MJ/m^3 is obtained. In the case of separation of CO_2 from biogas, the calorific value of biogas increases to 35.7 MJ/m^3. According to Stier and Fischer (1998), biogas has a higher calorific value than municipal gas by 30%, but lower than the calorific value of high-methane natural gas.

2.7. Use of biogas

The use of biogas combines the energy effect with the ecological one. Producing biogas from organic waste brings a double benefit, as it eliminates environmental pollution while producing energy. When burning biogas, less harmful nitrogen oxides are produced than when burning fossil fuels. Another important benefit is the reduction of carbon dioxide and methane emissions into the atmosphere, which in turn contributes to the reduction of the greenhouse effect. For this reason, the continuous development of this renewable energy sector is observed in the European Union countries. More and more investment is being made in creating numerous installations for methane recovery. In addition, the use of biogas for energy purposes reduces the consumption of non-renewable raw materials for energy production (coal, oil and gas) (Dudek and Zaleska-Bartosz, 2010; Zawieja et al., 2010).

The best effects of biogas production are obtained in biological treatment plants, which at the same time have a high demand for heat and electricity. As a result of combustion, biogas is converted into electricity or heat in cogeneration systems. The heat obtained at the treatment plant is used for technological purposes such as heating sludge in separate closed fermentation chambers (winter, summer), heating buildings, heating utility water, and ventilation of facilities. The biogas produced can also be a source of energy for sludge drying (Dymaczewski et al., 1995). However, the technological process of obtaining biogas must take into account its dehydration and purification. Biogas purification in such installations comes down to the removal of hydrogen sulphide and water vapour, not only to prevent the emission of sulphur dioxide into the atmosphere but also to prevent the corrosive effect of the H_2S condensate with water vapour (Jędrczak, 2008). Biogas generated in sewage treatment plants can also be used to generate mechanical energy in gas engines, as well as to generate electricity in gas engines or turbines. Cleaned and treated biogas with a methane content of over 95% can be used as fuel in fuel cells and microturbines. After technological approval, biomethane can be injected into the publicly available gas pipeline network in the form of a biocomponent added to natural gas (Appels et al., 2008).

2.8. Intensification of anaerobic stabilisation of sewage sludge

The rate of decomposition in organic substances during methane fermentation is limited by the rate of the first phase of this process, called hydrolysis, during which organic compounds are liquefied. Cells of activated sludge microorganisms agglomerated with biopolymers and polymers become inaccessible in stabilisation processes. Due to the complex molecular structure of biological sludge, the bioenzymes present in the sludge cannot fully hydrolyse the interior of such structures. The introduction of the technique of sludge disintegration prior to the stabilisation process contributes to the loosening of intermolecular bonds and to the change of sludge structure properties. In addition, the use of a properly selected disintegration technique prior to the stabilisation process contributes to the destruction of the sludge structure, the disintegration of the cell membranes of microorganisms and the release of intracellular substances into the overlying liquid, hence the initiation and increase of the degree of biological degradation (Zhang et al., 2007). As a result of this process, the organic components of the cell become potentially available as a substrate for the living heterotrophic mass. The released organic compounds contained in the sludge are more easily subjected to anaerobic stabilisation processes. This shortens the hydrolytic phase of methane fermentation and accelerates and intensifies the processes occurring in subsequent phases. The introduction of disintegration techniques also increases the degree of reduction of dry organic matter, and also affects the intensification of biogas production during methane fermentation (Bień et al., 2005; Wójtowicz, 2006).

The main goal of the research according to Penaud et al. (1999) is to determine the optimal pre-treatment methods that can ensure the highest proportion of COD dissolved in the total COD of the substrate. However, under certain conditions, complex compounds that are difficult to decompose can be formed. As a consequence, the optimal conditions determined for obtaining the maximum share of dissolved COD may be different from those that are appropriate to achieve the highest biodegradability of the substrate.

The criterion for the effectiveness of disintegration may be, among others, an increase in the content of organic substances in the supernatant liquid, expressed by the dissolved COD value and the degree of sludge disintegration. The consequence of effective disintegration is the intensification of the acid fermentation phase, manifested by an increase in the concentration and rate of increase of volatile fatty acids. Therefore, the use of disintegration methods prior to the methane fermentation process contributes to an increase in the amount of hydrolysates rich in soluble fractions of COD and VFAs (Iglesias-Iglesias et al., 2019; Zawieja et al., 2019).

It was found that the VFAs concentration values for individual vibration amplitudes increase to a certain limit value, and the extension of the disintegration time does not or only slightly increases the value of this indicator. A similar relationship between sonication time and VFA and COD concentrations was obtained by Zielewicz (2010). The research results provided by the author indicate that extending the sonication time above a certain value does not significantly improve the efficiency of the process. According to Cichowicz (2007), extending the time and increasing the amplitude of vibrations during disintegration above certain limit values reduces the effectiveness of the process.

The most favourable conditions for sludge preparation by the ultrasonic method and the effectiveness of methane fermentation are presented in Table 5.

For pre-treatment of sludge prior to methane fermentation, disintegration techniques are used, which, depending on the type of energy supplied to the system, can be divided into four groups: chemical, thermal, mechanical and biological methods. In order to increase the effectiveness of these techniques, combined methods are also used, forming the so-called hybrid systems. The best-known combinations are thermal-mechanical methods, e.g. thermal-ultrasound, and

Table 5. Influence of ultrasonic disintegration conditions on the effectiveness of methane fermentation of excess sludge (own elaboration).

Ultrasonic disintegration conditions			Efficiency of methane fermentation ultrasonically modified excess sludge		Author
Field strength of ultrasonic field or energy acoustic	Requency vibrations of the ultrasonic field [kHz]	Time of sonication [min]	Sludge digestion degree [%]	Increase production biogas [%]	
8 Wcm^{-2}	31	1.5	42.4	30	Neis et al. (2008)
48 Wcm^{-2}	24		–	37	Pérez-Elvira et al. (2009)
1 Wcm^{-2}	–	1	–	6.3	Şahinkaya and Sevimli (2013)
18 Wcm^{-2}	–	1.6	about 31% increase for the sample control	14	Erden and Filibeli (2010)
14547 $kJ\cdot kg^{-1}$ TS	–	–	–	60	Wang et al. (2010)
4 000–4 300 $kJ\cdot kg^{-1}$ TS	20	–	–	20	Gianico et al. (2013)
$\sim$ 23000 $kJ\cdot kg^{-1}$ TS	200	–	–	50	
10 Wcm^{-2}	–	–	about 30% increase for the sample control	11	Wang et al. (1999)
4.3 Wcm^{-2}	20	300 s	about 57% increase for the sample control	50	Shirgaonkar and Pandit (1997)
9 690 $kJ\cdot kg^{-1}$ TS	20		–	44	Cheung and Kurup (1994)
0.33 $W\cdot mL^{-1}$	20	20	–	104	Zhen et al. (2017)

Table 5 continued

Ultrasonic disintegration conditions			Efficiency of methane fermentation ultrasonically modified excess sludge		Author
Field strength of ultrasonic field or energy acoustic	Requency vibrations of the ultrasonic field [kHz]	Time of sonication [min]	Sludge digestion degree [%]	Increase production biogas [%]	
200 W	20	–	–	6.3	Lizama et al. (2017)
12 400 kJ·kg^{-1} TS	–	–	–	40	Donoso-Bravo et al. (2010)
96 kJ·kg^{-1}		8	–	27	Houtmeyers et al. (2014)
15 000 kJ·kg^{-1} TS	20	10	–	8.6	Sahinkaya (2015)
35 000 kJ·kg^{-1} TS				31.4	

thermal-chemical methods, including the method of oxidation under elevated pressure and temperature (Iskra and Miodoński, 2014; Wolski et al., 2012; Zielewicz-Madej and Fukas-Płonka, 2002).

2.9. Disintegration of sewage sludge with ultrasonic field

A widely used method of mechanical treatment of sewage sludge is the technology related to the use of ultrasounds. The impact of ultrasonic waves disturbs the equilibrium in the system, leads to a better spatial packing of particles, changing the structure of sewage sludge and its properties. The ultrasonic field can intensify the dewatering and thickening processes of sewage sludge (Bień et al. 2023). The advantage of sewage sludge preparation with the ultrasonic field is the release of organic substances from inside the cells of microorganisms, which are a source of easily assimilable organic carbon in the process of denitrification and dephosphatation, in the case of its deficiency in the inflowing sewage. The ultrasonic technique is also used to reduce the activated sludge index and improve the volumetric index, as well as to reduce foaming and sludge swelling in wastewater treatment processes by eliminating filamentous bacteria (Wolny et al., 2004; Tomczak-Wandzel et al., 2009).

According to Wolny and Kamizela (2003), the use of ultrasonic technology in the process of anaerobic stabilisation of sewage sludge leads to:

- improvement of the sedimentation properties of the fermentation blanket,
- increasing the activity of enzymes,
- intensification of metabolism,
- increased breakdown of organic substances,
- increased production of biogas.

According to literature data (Kidak et al., 2009; Nanzai et al., 2009), the use of ultrasonic techniques in wastewater management requires the optimization of operational parameters such as: frequency, vibration amplitude, wave intensity, input energy and impact time. The volume and geometry of the tank in which the process takes place are also important elements of ultrasonic technology. The susceptibility of sludge to the impact of the ultrasonic field is related to the properties that depend on the type of wastewater treatment process, type of substrate, sludge dry matter concentration and particle structure. Therefore, the mechanical disintegration of sludge from different treatment plants can proceed in different ways. This is connected with the necessity, prior to making a decision to include disintegration processes in the sludge treatment process, to conduct tests determining the susceptibility of sludge to disintegration. In addition, the technological and economic effects of the proposed solution should be estimated.

Tiehm et al. (2001), conducting research on the total costs of using ultrasonics in wastewater treatment plants, showed that these processes can be implemented in a way that ensures both a positive technological and economic effect. They decided that the biogas obtained in the stabilisation processes can be converted into electricity and thus used to cover the operating costs of the treatment plant facilities. In addition, they found that from an ecological point of view, when using ultrasound, no additional environmental pollution occurs.

2.10. The mechanism of action of ultrasound

Ultrasounds are elastic waves with frequencies above 16 kHz. To generate and detect ultrasonic waves, transducers converting a specific type of energy into ultrasonic wave energy are used. The most commonly used source of ultrasonic waves are mechanical vibrating systems immersed in a material medium or adjacent to it. The energy of mechanical vibrations in the system is excited by another type of energy, e.g. electricity, and is converted into the energy of an acoustic wave. The sound wave passing through the medium is attenuated, i.e. weakened. The attenuation of acoustic waves in the medium is caused by such factors as the conversion of wave energy into heat, friction between the particles of the medium, stimulation of particles to vibrate and wave scattering (Śliwiński, 2001).

Ultrasonic waves are determined by analysing parameters such as frequency, pulsation, speed, wavelength, vibration period, acoustic impedance, power and intensity. The process of interaction of elastic waves with the medium in which they propagate depends on the wavelength.

Wavelength is a quantity characteristic for a given medium and for a given type of waves. The speed of sound in a given medium depends on many factors. In the case of solids, it depends on the stresses and density of the medium, while in the case of gases and liquids, it depends on the temperature, pressure and concentration.

2.11. Active and passive ultrasonic field

Depending on the intensity of the ultrasonic wave, a passive or active ultrasonic field is created. In the case of the emission of ultrasonic waves with low energy and very small amplitude, a passive ultrasonic field is created. When emitting a high-energy wave, the influence on the medium is active. The use of an active ultrasonic field leads to the formation of processes that cause macroscopic changes in the medium, usually irreversible (Wolny, 2005). According to Śliwiński (2001), the mechanisms of the active impact of ultrasound are divided into primary and secondary phenomena (Fig. 2). Primary phenomena determine the basic parameters of the acoustic field, such as radiation pressure or variable sound pressure. At higher ultrasound intensities, cavitation and friction appear at the boundary surface. These interactions are accompanied by the release of heat. As a result of the increase in pressure and temperature, numerous secondary phenomena are initiated, most of which occur under the influence of cavitation. Figure 2 shows the phenomena accompanying the passage of the ultrasonic wave through the tested medium.

After a certain value of the ultrasonic wave intensity, called the cavitation threshold, is exceeded, the phenomenon of cavitation occurs. The phenomenon of cavitation consists in the creation of pulsating bubbles in a liquid by ultrasonic waves of high intensity, which appear as a result of local breaks in a continuous medium, under the influence of high tensile forces occurring in the rarefaction phase of the wave. In places where the medium is broken, initially microscopic caverns are formed in the shape of spherical bubbles and are filled by inward diffusion with particles of vapour of saturated liquid or gas dissolved in it. Thanks to this, they can survive

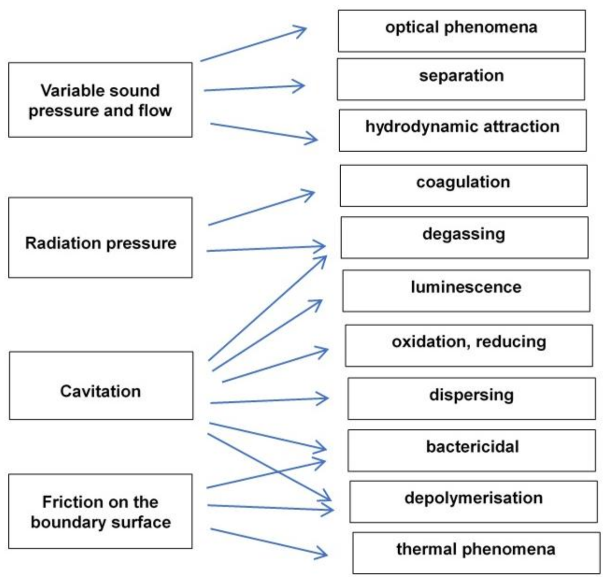

Figure 2. Phenomena accompanying the passage of an ultrasonic wave through the medium (Śliwiński, 2001).

the next phase of wave densification, and they grow and pulsate in a forced manner in the next phases of the ultrasonic wave, surviving for some time, only to suddenly collapse at some point. Such bubble collapses are sources of local shock waves that propagate through the liquid. At a constant intensity of the ultrasonic wave (greater than the cavitation threshold), a state of dynamic equilibrium is created between the emerging and collapsing bubbles (Śliwiński, 2001).

The occurrence of the cavitation phenomenon according to Cheeke (2002) and Neczaj (2010) depends on the temperature, surface tension, viscosity of the medium, degree of gas saturation or the type of gas. The phenomenon of cavitation occurs most intensively at the interface. Therefore, the presence of gas bubbles and impurities suspended in the medium (cavitation nuclei) reduces the resistance of the liquid to its occurrence. In liquids subjected to degassing or high external pressure, there is practically no cavitation.

The phenomenon of ultrasonic cavitation is used to hygienise sewage sludge. The effectiveness of ultrasonic disinfection depends on the parameters of sonication, duration of sonication, as well as the type and number of bacteria destroyed (Gonze et al., 2003). In order to achieve higher rates of sewage sludge hygienisation, methods combined with the use of other bactericidal agents, most often chemical reagents, are used (Tyagi et al., 2011).

2.12. Phenomena occurring in the active ultrasonic field

The general and thermal impact of the ultrasonic wave, which is the result of rhythmic vibrations of the particles of the medium in which it propagates, can trigger physical, physicochemical and biological processes. These can be processes of dispersion, ultrasonic coagulation, oxidation, reduction and homogenisation. The reasons for the coagulation of particles include the chaotic movements of particles and their collisions in a sonicated medium, the formation of a double electrical layer at the interface between the colloidal particle nucleus and the solution as well as intermolecular interactions. The ultrasonic field causes a change in the degree of dispersion of suspensions, increasing the fragmentation of particles, or reducing the fragmentation as a result of ultrasonic coagulation. The dispersing and coagulating effects of ultrasonic waves depend on the viscosity of the liquid, the presence of electrolytes and the temperature. The coagulating effect of ultrasonic waves also depends on the particle size of the sonicated suspension. For each size of suspended particles, there is an optimal range of vibration frequencies in which their coagulation occurs (Bień et al., 2023).

According to Śliwiński (2001), an acoustic field with frequencies up to 20 kHz appropriately selected for the size of particles is usually used for coagulation, so that hydrodynamic forces from sound pressure, radiation pressure and flow of the medium are conducive to their joining. Forces of the same type at different ratios of frequency to particle size, usually at intensities above the cavitation threshold, cause the processes of disintegration of medium particles. The high efficiency of sewage sludge disintegration using low-frequency ultrasound (20 kHz) and high-power ultrasound is also confirmed by studies conducted by other scientists (Cichowicz, 2007; Grönroos et al., 2005).

As a result of the use of ultrasonic waves in the process of disintegration of excessive sludge, flocs and cells of living organisms are broken down, releasing the organic fraction. The increased concentration of organic compounds in the hydrolysate has a supporting effect on the process of anaerobic stabilisation of modified sludge. The efficiency of the disintegration process depends on the power of the disintegrator used, the frequency of the wave, the dry matter content in the sludge, as well as the sonication time (Gallipoli and Braguglia, 2012; Nickel and Neis, 2007; Onyeche et al., 2002). According to Tiehm et al. (1997), the use of ultrasound with a frequency of 31 kHz prior to the stabilisation process contributes to shortening the duration of methane fermentation and leads to an increase in the intensity of biogas production. Zielewicz-Madej and Fukas-Płonka (2002), while conducting research in the frequency range of 10–30 kHz and with increasing ultrasound power values, noted the highest degree of disintegration for the frequency of 30 kHz. The process was most intensive in the case of low frequency values, around 20 kHz. Gonze et al. (2003) showed that the action of the ultrasonic field of low frequency and high intensity of the ultrasonic field affected the effective breakdown of sludge particles and the degradation of microorganism cells, leading to a clear modification of the sludge structure. In the initial phase of sonication, no clear changes were observed in the sludge structure. The short duration of the ultrasound action dispersed the sludge flocs without disturbing the cell structure. As a result of prolonged operation of the ultrasonic field, the cells of microorganisms contained in the sludge were permanently damaged.

Cichowicz (2007) reports that the sonication of sewage sludge in a short time with a high-power ultrasonic field results in a higher efficiency of sludge biodegradation than the use of a low-power ultrasonic field and long duration of ultrasound operation. The introduction of high acoustic energy into the liquid system affects the occurrence of factors that can significantly modify the nature of the substances present in the solution. Such reactions are the result of the formation and contraction of cavitation bubbles, which may eventually disappear in the implosion cycle. During the implosion of bubbles in the gas phase, very high temperatures of approx. 5000 K and high pressures of approx. 500 bar occur. These conditions lead to the formation of sonochemical reactions related to chemical transformations of organic compounds and the formation of radicals, hydrogen peroxide, and ozone according to the following reaction:

$$H_2O \rightarrow H^\circ + HO^\circ \tag{15}$$

$$O_2 \rightarrow 2O \tag{16}$$

$$HO^\circ + O \rightarrow HOO^\circ \tag{17}$$

$$O_2 + O \rightarrow O_3 \tag{18}$$

$$2HO^\circ \rightarrow H_2O_2 \tag{19}$$

Sonochemical reactions take place mainly inside the cavitation bubbles and at the interfaces. Studies indicate that sonochemical phenomena occur not only at low frequencies, but also between 100–1000 kHz. However, the optimal frequency is substrate-specific (Li et al., 2018).

According to Bourgrier et al. (2005), strong stresses and reactions leading to the formation of H° , OH° and $HO2^\circ$ radicals occur as a result of cavitation. In addition, chemical transformations of organic substances take place. Strong ultrasonic interactions catalyse the course of chemical reactions, lead to the acceleration of degradation and depolymerisation processes in high-molecular organic compounds. The destruction of cell walls and membranes contributes to the inactivation of microorganisms but also forms the basis for easier release of cell contents into the environment in the form of polysaccharides, proteins and enzymes. Protein denaturation and loss of enzyme activity can be caused by radical reactions as a result of ultrasound. This phenomenon is also caused by the formation of high stresses in the medium during cavitation. As a result of the course of cavitation, hydrogen bonds are broken and van der Waals interactions in polypeptides are weakened, which also affects changes in the secondary and tertiary structure of the protein. Free radicals and generated hydrogen peroxide also lead to irreversible DNA damage in microbial cells, and the action of the ultrasonic field leads to mechanical damage and changes in the biochemical and functional properties of cells. The mechanical forces generated at the point of collision of cavitation bubbles, the wave generated after their implosion, as well as the resonant vibrations of gas bubbles are the main factors responsible for the degradation of microorganism cells.

The phenomenon of ultrasonic cavitation is also used for hygienising sewage sludge. The effectiveness of ultrasonic disinfection depends on the parameters of sonication, the duration of sonication as well as the type and number of bacteria destroyed. In addition, this effect is enhanced by the production of hydrogen peroxide, which is a highly bactericidal chemical agent, leading to the weakening or elimination of pathogens (Cai et al., 2018).

The idea behind using the ultrasonic field to disinfect sewage sludge is the ability of ultrasound to quickly destroy living cells of organisms. As the sonication time increases, the bacterial deactivation effect increases. When using a longer sonication time of 15 minutes and a frequency of 22 kHz, the final degree of destruction of psychrophilic bacteria is approx. 97.9% for digested sludge and approx. 98.6% for primary sludge, and the degree of destruction of mesophilic bacteria from 94.3% for primary sludge and up to 94.9% for digested sludge. Sonification is a combination of various processes of a different nature, such as chemical reactions using radicals or thermal reactions. Both the frequency of vibrations of the ultrasonic field and the increase in temperature accompanying the action of ultrasound affect the efficiency of the process. The mechanism of the process is directly conditioned by such factors as the value of the energy supplied, ultrasonic frequency and the nature of the medium subjected to sonication. Decomposition of sludge under the influence of the UD field is more effective at lower ultrasonic frequency values. The most favourable effects of sludge disintegration are obtained by using ultrasonic waves of low frequency (20 kHz) and appropriately high power, which favours the occurrence of cavitation in the modified medium, the formation of free radicals and the occurrence of other processes, e.g. mechanical and chemical (Boruszko, 2018; Bourgrier et al., 2005; Chu et al., 2001).

According to the literature (Joyce et al., 2003), high-frequency and low-power ultrasounds show a lower degree of disinfection compared to lower-frequency and high-power ultrasounds. When low ultrasound intensity is used, both in the liquid and in the cells of microorganisms, functional changes are small, acceleration of physiological processes in microorganisms is observed. The average intensity of ultrasound causes an increase in the rate of biochemical changes in bacteria and changes in the morphology of microorganism cells. Changes in the medium and cells caused by low and medium concentrations of the ultrasound field are reversible. However, at high ultrasound intensity, irreversible damage to microorganism cells occurs. This is related to the formation and collapse (annihilation) of the cavitation bubble and thus with the simultaneous increase in pressure. It is therefore believed that the use of an ultrasonic field of sufficiently high intensity can be a bactericidal factor (Bień et al., 1995).

According to Nowak (2015), low-intensity waves can accelerate cell metabolisms by improving the penetration of various substrates through cell membranes and increasing the rate of substrate transfer to the active center of the enzyme. On the other hand, ultrasonic waves of higher intensity cause denaturation and destruction of the activity of biocatalysts, changes in the charge on the cell surface, and disruption and fragmentation of the cell membrane. The amount and type of microorganisms present in sewage sludge have a decisive influence on the final stage of hygienisation. Inactivation of microorganisms with different properties, structure and morphology proceeds to varying degrees. Bacteria characterised by a spherical shape and small size show greater resistance to ultrasound than large, rod-shaped bacteria. According to literature data (Foladori et al., 2007), the group of gram-positive bacteria also shows greater resistance to ultrasonic waves compared to the group of gram-negative bacteria. Gram-negative *Escherichia coli* cells are highly sensitive to the sonication process and degradation of these cells is noted at low ultrasonic energy. Gram-positive *Enterococcus faecalis* cells showed resistance to the action of the ultrasonic field using high-energy ultrasound. Following the process of disintegration of excess sludge, the so-called latent cryptic growth on lysates is formed as a result of cell disintegration. This differs from growth based on primary organic matter. There are two stages in the process of latent growth: lysis and biodegradation. As a result of disintegration, the cells of microorganisms are lysed or die. The cell content (lysate) is released into the supernatant, causing an increase in COD. Organic substances available in dissolved form are reused by microorganisms in metabolic processes, which in turn leads to a decrease in biomass concentration (Ma et al., 2012; Low and Chase, 1999). During the sonication process of sewage sludge, most microorganisms undergo biological degradation. In order to achieve higher rates of sewage sludge hygienisation, methods combined with the use of other bactericidal agents, most often chemical reagents, are proposed (Zielewicz et al., 2008).

3. METHODS OF ASSESSING THE DEGREE OF SEWAGE SLUDGE ULTRASONIC DISINTEGRATION

The degree of disintegration can be described by the physicochemical and biological parameters of the sludge, as well as the supernatant liquid (Gonze et al., 2003; Kim et al., 2003; Müller et al., 1996; Neumann et al., 2017; Schmitz et al., 2000; Tas et al., 2018; Tiehm et al., 2001; Zhang et al., 2019; Zielewicz, 2010). As a result of the destruction of microbial cell membranes, compounds contained in the cytosol are released into the supernatant fluid, as evidenced by an increase in the concentration of protein, DNA, organic carbon (TOC) and dissolved chemical oxygen demand (SCOD) (Tyagi and Lo, 2011; Zawieja, 2015).

Depending on the process conditions of wastewater treatment using the activated sludge method, the susceptibility of microorganisms in excess sludge to the disintegration process may vary and change over time (Castro and Capote, 2007; Tiehm et al., 2001). The particle size is one of the main factors determining the speed of the biodegradation reaction. This is an indirect relationship, because the particle size reduction occurring as a result of disintegration and the associated increase in the specific surface area increase the rate of hydrolysis and the degradation proces (Almukhtar et al., 2012). Particle diameter reduction can be achieved by using e.g. ultrasound, pressure homogenization (Huan et al., 2009). The degree of disintegration depends on many factors, i.e. the composition and concentration of sludge, the content of polymers, the amount and type of energy supplied to the sludge during modification. The effectiveness of the disintegration process can be assessed on the basis of direct indicators that identify the change in the structure and physical and chemical properties of the sludge and supernatant liquid immediately after the process. These indicators include, among others, the chemical oxygen demand of dissolved substances (COD dissolved), concentration of volatile fatty acids (VFAs), protein concentration and changes in the content of dry organic matter. The size of sludge particles and the respiratory efficiency of microorganisms prior to and after the disintegration process as direct indicators (Wang and Lu, 2006).

The tools for determining the degree of sludge disintegration are also indirect (technological) indicators, which determine long-term changes resulting from the disintegration of sludge, occurring during the process of anaerobic stabilisation. With regard to methane fermentation, these include, among others, an increase in the total and unit biogas production, as well as the methane content in biogas and an increase in the degree of sludge digestion.The effectiveness of disintegration can be determined on the basis of energy indicators, i.e. the amount of energy used in relation to the disintegrated dry organic matter of sludge, its volume or in relation to the degree of liquefaction of organic substances, expressed by the SCOD value.

According to Tiehm et al. (2001), the degree of disintegration (A_{COD}) of sludge can be determined on the basis of changes in the COD value of dissolved organic compounds prior to and after the disintegration process. The method of assessing the effectiveness of disintegration is based on a comparative analysis with a reference sample (100%) subjected to alkaline hydrolysis with 0.5 M NaOH at 20 °C for 22 hours. The degree of disintegration is determined by the relationship:

$$A_{\mathrm{COD}} = \frac{\mathrm{COD}_d - \mathrm{COD}_o}{\mathrm{COD}_A - \mathrm{COD}_o} \cdot 100\% \tag{20}$$

where: A_{COD} – degree of disintegration of organic matter, %; COD_d – COD value of supernatant liquid of disintegrated sludge, mg $O_2\,L^{-1}$; COD_o – COD value of the overlying liquid of non-disintegrated sludge, mg $O_2\,L^{-1}$; COD_A – COD value of the supernatant liquid in a reference sample of sludge, subjected to chemical hydrolysis with a 0.5-mol NaOH solution at 20 °C for 22 hours, mg O_2, L^{-1}.

Gonze et al. (2003), using Eq. (20), modified the above method by extending the time of chemical hydrolysis of the reference sludge sample to 24 hours. On the other hand, Müller et al. (1996), on the basis of the above equation formula, assumes the use of a 1-molar NaOH solution at 90 °C for 10 minutes as the chemical disintegration of sludge.

According to Zawieja and Wolski (2013), to assess the degree of disintegration, tests estimating the degree of oxygen consumption by microorganisms contained in the sludge is also used. In addition, methods based on the determination of protein concentration, particle size analysis of disintegrated sludge and changes in the sedimentation and filtration capacity of sludge can be used.

However, according to Tomczak-Wandzel et al. (2009), the centrifugal test can be used to assess the impact of disintegration on sewage sludge dewatering. Changes in the efficiency level for the dewatering process can be determined using the so-called separation degree. It is a conventional value, calculated as the quotient of the volume of the centrifuged supernatant liquid to the volume of the sludge sample subjected to the centrifugation process:

$$R = \frac{V_{cn}}{V_p} \cdot 100\% \tag{21}$$

where: R – degree of separation, %; V_{cn} – volume of decanted supernatant liquid, ml; V_p – volume of the tested sludge sample prior to centrifugation, ml.

As energy density increases, more and more effective disintegration of sludge occurs. The energy used during the disintegration process affects the release efficiency of organic compounds according to the following equation (Boruszko, 2020; Garlicka and Żubrowska-Sudoł, 2017):

$$W_{\mathrm{COD}_{\varepsilon L}} = \frac{\mathrm{COD}_{\varepsilon L} - \mathrm{COD}_o}{\varepsilon L} \tag{22}$$

where: $\mathrm{COD}_{\varepsilon L}$– the COD value of the supernatant liquid in a sample of sludge subjected to the hydrodynamic disintegration process at a given energy density, mg $O_2\,L^{-1}$; COD_o – the COD value of the overlying liquid of non-disintegrated sludge, mg $O_2\,L^{-1}$; εL – value of energy density at which the disintegration process was performed, kJ L^{-1}.

4. APPLICATION AND ECONOMIC FEASIBILITY OF ANAEROBIC DIGESION OF SONICATED EXCESS SLUDGE

The issues related to the influence of the ultrasonic field on methane fermentation process and obtaining biogas as a consequence are extremely topical research areas and closely relate to the idea of a circular economy, in which the by-product of a technological process can be used as a substrate in the next unit process, becoming consequently a valuable source of energy. Energy use of biogas produced in the process of methane fermentation of sewage sludge in cogeneration systems may bring additional ecological and economic benefits to the plant implementing the proposed technological solution.

Sewage sludge is considered to be a by-product of the wastewater treatment process and is also an energetically valuable raw material. According to literature data (Lorenzo-Toja et al., 2016), the treatment and management of sewage sludge accounts for approx. 50% of the total operating costs of sewage treatment plants. In Europe, in terms of production capacity, approx. 10 million tons of sewage sludge are produced per year, in the United States 8 the figure is million tons, and in China 4 it is million tons per year (Qi et al., 2020). Sewage sludge is an environmental and sanitary problem. It contains contaminants such as heavy metals and toxins (Gherghel et al., 2019; Wang et al., 2020; Xu et al., 2019), and if it is not subjected to biodegradation processes, it rots and may become a source of uncontrolled methane emissions.

It was assumed that taking into account the energy properties of methane, the share of biomethane and biogas in the total share of energy in the European Union should be approx. 32%, which would significantly reduce the dependence of the energy sector on natural gas and fossil fuels. This assumption would increase the capacity of the biogas plant for electricity production to 9985 GW, with approximately 48–50 billion Nm^3 of biomethane being produced per year (Prussi et al., 2019, Scarlat et al., 2015; 2018; 2019).

Obtaining energy from waste and biomass is economically viable. However, it should be emphasised that the technology used in energy production by converting limited matter into biogas is still an open issue that requires the existing level of knowledge to be increased, especially in the fields of pre-modification of waste, liquefaction of organic substances or methane fermentation of waste showing limited susceptibility to biodegradation. An important aspect of research on the biodegradation of organic matter is the optimisation of the process in terms of biogas composition and its possible refinement, which can significantly reduce operating costs (Scarlat et al., 2015). According to Huiru et al. (2019), as a result of the economic analysis, a biogas plant with a capacity of 168 kWe is able to generate approx. 142 kW of net energy, which would guarantee a payback period of approx. 7.8 years.

By transforming the organic matter contained in the sludge, through biochemical processes, into biogas, a valuable source of green energy, the management of sludge and the use of biogas is consistent with the idea of sustainable development. Stabilised sludge can be both a substrate and a raw material for energy production, providing an alternative to conventional energy sources (Gao et al., 2020; Kacprzak et al., 2017). Due to the fact that sewage sludge is a source of valuable biochemical components used in the production of adhesives, composite materials, paints, alcohols and bioplastics (Djandja et al., 2021; Saha et al., 2017), they are an alternative to energy crops, thus limiting the negative impact of these crops on food production. Energy crops are a competition for conventional agriculture, and the use of sludge as a renewable energy source is a promising trend in the energy sector.

For example, as a result of an economic analysis of biogas production covering the territory of Bangladesh, it was revealed that the energy obtained as a result of the cogeneration process made it possible to cover approx. 10.88% of household energy demand. It has been shown that the waste-to-energy system in Saudi Arabia, when subjected to methane fermentation and gasification, makes it possible to meet the energy needs of the country, thus reducing its carbon footprint (Guo et al., 2021).

5. CONCLUSIONS AND FUTURE PERSPECTIVES

Technological research on how to intensify the course of anaerobic stabilisation of excess sludge with the ultrasonic disintegration process is still an open problem. In an age of searching for technological solutions that do not cause secondary pollution of the environment, the use of ultrasonic disintegration is a promising alternative to other methods of sludge conditioning. Ultrasound treatment of sludge initiates lysing processes. These processes, combined with biological hydrolysis, the first stage of fermentation, have a positive effect on the efficiency of the anaerobic stabilisation process. Excess sludge, characterised by a flocculent structure, made of microorganism cells agglomerated with polymers, is resistant to the biodegradation process. As a result of disintegration with the ultrasonic field, the high-molecular structure of sludge flocs is broken, and then organic matter is released from the inside of the microorganism cells. As a result of sewage sludge being subjected to the process of disintegration with the ultrasonic field, the concentration of organic substances in dissolved form increases, expressed by such factors as an increase in the COD, SCOD, VFA concentration or TOC value.

Sewage sludge is a valuable "resource" for obtaining energy and a biochemically stabilised product that can be used in agriculture, land reclamation or construction in accordance with the principles of a circular economy. The technological concept consistent with the idea of sustainable development is the creation of biorefineries, which are a technologically and economically promising solution. However, these require full optimisation on a larger scale in order to obtain a product that maximises the profitability of the installation. An important research and investment trend for the future is the creation of a biorefinery in which the implemented technology will enable biohydrogen to be obtained as the main product of the process. In addition, other promising trends include the development of technologies such as photofermentation, dark fermentation, dry fermentation, bioelectrochemical systems, the use of a mixture of volatile fatty acids to produce polyhydroxyalkanoates, two-stage digestion for biohythane production (maximising energy recovery) and intersectoral coupling to enable efficient waste management (using unconventional waste as a resource) (Cheng et al., 2020; Kumar et al., 2019; Policastro et al., 2022).

In order to achieve emission neutrality by the middle of the 21st century, a number of activities should be undertaken in many research areas by introducing innovative solutions based on innovative technologies.

Considering the development perspectives regarding the broadly understood sludge management, it should be mentioned that the disposal of sewage sludge with the use of methane fermentation requires a more holistic approach to the technology used and its optimisation in order to simultaneously eliminate environmental hazards and obtain additional energy benefits.

The intensification of the methane fermentation process by sonicating sewage sludge to obtain biogas is discussed in this review. However, there is a gap in this area that still needs more attention and adequate research.: there is a need to carry out scaled experiments on the methods of initial modification due to the heterogeneity of the raw material, which has a large impact on the productivity and efficiency of the process in terms of the final product (biogas) and the quality of digestate.

It is possible to increase the efficiency of the methane fermentation process by improving fluid dynamics and mass transfer through the selection of the bioreactor and the proper configuration of its process parameters.

The effectiveness of the sonication process and, consequently, the generation of biogas from modified sludge is mainly due to the phenomenon of ultrasonic cavitation, a phenomenon which has been described in this example. At the same time, it should be emphasised that the preliminary literature reports on the influence of the ultrasonic field on the course and effectiveness of acidogenic fermentation are encouraging for continued further research on this issue, with a view to applying the sponification technology on a larger scale (Nagarajan et al., 2021; Lanfranchi et al., 2022). In addition, there are a number of research areas based on the processes of biochemical decomposition in anaerobic conditions of sewage sludge, requiring examination and possible modifications in relation to the methane fermentation process conventionally carried out in most large sewage treatment plants.

Ultrasonic disintegration used as a method supporting the process of methane fermentation, implemented on an industrial scale, is also a current research issue. Due to the dynamic development of existing technologies, the conditions of ultrasound application still need to be adapted to the physical and chemical properties of sludge.

According to Azarmanesh et al. (2023), conventional fermentation of sewage sludge (SS) usually shows an insufficient organic substance content and a low C/N ratio. Therefore, a promising solution that eliminates the disadvantages of mono-digestion is anaerobic co-digestion (ACoD) combining biodegradable waste from various industries with sewage sludge in a joint biodegradation process.

The issues that should be addressed in future research are the use of waste and sewage sludge as co-substrates in the anaerobic co-digestion (ACoD), especially waste that is difficult to biodegrade, e.g. lignocellulosic waste.

The selection of the appropriate composition of the co-fermentation mixture affects the properties of the feed and has a synergistic effect in relation to the obtained physicochemical parameters, supporting the course of the biodegradation process, i.e. the degree of fermentation and the intensification of biogas production.

In addition, the advantages of the co-fermentation process of two different waste streams include: better supply of macro- and microelements, dilution of toxic and inhibitory substances, increased buffer capacity, reduction of greenhouse gas emissions, reduction of process costs and the option of using higher loading speeds (Borowski et al., 2018; Jain et al., 2015).

In addition, there is insufficient information on the effect of co-substrates on improving the microbial community and increasing the archaeal population as well as the effect on microbial communities living under anaerobic conditions such as changes in pH, organic load, toxic substances and inoculum source.

The methane fermentation technology is recognised as a beneficial method of sewage sludge stabilisation, and the acquisition of the main product of the process (biogas) and its valorisation is an important research issue. Based on the review of literature data on the application of the sonication process of fermented sewage sludge, a research gap can be identified, indicating that, despite the promising research results reflected in the relevant literature, the process has not yet been fully recognised and requires further experiments, focused in particular on the study of reaction mechanisms taking place in the course of the process, in order to comprehensively optimise the process.

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SYMBOLS

A	the maximum cumulative methane yields, mL/g·TS
A_{COD}	degree of disintegration of organic matter, %
COD	chemical oxygen demand, mg O_2L^{-1}
COD_d	COD value of supernatant liquid of disintegrated sludge, mg O_2L^{-1}
COD_A	COD value of the supernatant liquid in a reference sample of sludge, subjected to chemical hydrolysis with a 0.5-mol NaOH solution at 20 °C for 22 hours, mg O_2L^{-1}
$COD_{\varepsilon L}$	COD value of the supernatant liquid in a sample of sludge subjected to the hydrodynamic disintegration process at a given energy density, mgO_2L^{-1}
COD_o	COD value of the overlying liquid of non-disintegrated sludge, mg O_2L^{-1}
COD_o	the COD value of the overlying liquid of non-disintegrated sludge, mg O_2L^{-1}
e	constant, 2.718
G	volume of biogas obtained for time τ_1, m^3/d
G_e	practically achievable amount of biogas, m^3/d
K	rate of biogas production in the intensive growth phase of a mixed population of microorganisms, mL/d
k	reaction rate constant, d^{-1}
k_1	reaction rate coefficient in the first phase of methane fermentation, d^{-1}
k_2	reaction rate coefficient in the second phase of methane fermentation, d^{-1}
R	degree of separation, %
$R_{\max}$	maximum biogas production determined experimentally, mL
t	fermentation time, d
TS	total solids, mg
SCOD	dissolved chemical oxygen demand, mg O_2L^{-1}
v	the shape coefficient
V_{cn}	volume of decanted supernatant liquid, ml
V_g	amount of biogas produced, m^3
$V_{g\,\max}$	practically achievable amount of biogas, m^3
V_p	volume of the tested sludge sample prior to centrifugation, ml
VFAs	volatile fatty acids, mg CH_3COOH/L
VSS	volatile suspended solids, mgL^{-1}

Greek symbols

εL	value of energy density at which the disintegration process was performed, kJL^{-1}
λ	the lag phase time, d
τ_1	the duration of the first phase of biochemical decomposition, d
τ_2	the duration of the second phase of biochemica decomposition, d

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