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DEFINING INDICATORS FOR THE ANAEROBIC FERMENTATION PROCESS OF AQUACULTURE WASTEWATER SEDIMENTS

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The object of this study is the process of anaerobic fermentation of wastewater sludge from aquaculture. It was established that the exponential dependence adequately describes the experimental data on the change in the level of decomposition of dry organic matter (DOM) and the specific yield of biomethane per unit of decomposed DOM of aquaculture wastewater sediment depending on the time of anaerobic fermentation. The maximum level of DOM decomposition during anaerobic fermentation achieved in 38 days was 0.74 relative units at a process speed of 0.108 relative units per day. The integrated level of DOM decomposition over 21 days of anaerobic fermentation can reach only 0.43 relative units, and the integrated level of DOM decomposition is set at the level of 0.033 relative units per day. The output of biogas and biomethane during anaerobic fermentation over 21 days of anaerobic fermentation reached 4.083 and 2.627 l, respectively. At the same time, the concentration of biomethane in biogas on day 7 of fermentation reached 74–75 % and remained at this level until day 21. The maximum level of specific yield of biomethane during anaerobic fermentation reached on day 38 was 803.936 ml in terms of normal conditions per gram of decomposed DOM with a rate of change of the specific yield of biomethane of 0.207 ml in terms of normal conditions per gram of decomposed DOM per day. The integrated specific yield of biomethane over 21 days of anaerobic fermentation could reach 580–590 ml in terms of normal conditions per gram of decomposed DOM. With a fermentation time of 21 days, the specific output of biomethane has an optimal value depending on the periodicity of loading the reactor, which is 1.48–1.49 m^3 of biomethane per one m^3 of biomass in the reactor in one day with a periodicity of loading the reactor once per time from 4.5 to 6 days. The research results could be used to determine the volume of biomethane production and electricity based on it during the anaerobic fermentation of aquaculture wastewater sludge

Keywords: anaerobic fermentation of sediment, specific yield of biomethane, recirculation system of aquaculture, biomethane

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1. Introduction

Fisheries provide humans with a significant amount of high-quality protein, significantly contributing to global food and nutrition security. The high demand for fishery products is the reason for the stable growth of its production [1].

Fish products are made by using recirculating aquaculture systems (RASs). These are systems in which water, having passed through stages of mechanical and biological purification, is reused in the technological process of making aquaculture products. The application of such systems has a low negative impact on the environment and significantly reduces water and energy needs. It should also be noted that the process of aquaculture production is accompanied by significantly lower greenhouse gas emissions compared to meat production in animal husbandry. This means that breeding and consuming protein derived from fish can contribute to mitigating the effects of climate change [2]. However, such systems have a significant drawback, namely, the need to dispose of contaminated wastewater, which is formed during washing of the nets of mechanical filters intended for the purification of recirculation water [3].

It is common knowledge that sedimentation with subsequent use of sediment and settled wastewater is the simplest and most economically feasible wastewater treatment technique. However, the sediment formed during settling also needs further disposal [4].

Sedimentation of wastewater involves the use of settling tanks in the form of mesh mechanical filters with rotating microscreens, which are designed to treat the main flow of recirculation water. Particles retained on the grid are washed into the collection chute and removed from the recirculation system. The volume of wastewater from mesh mechanical filters is less than 1 % of the recirculation flow, so it is considered that sedimentation is an effective sediment concentration technique [5]. Anaerobic fermentation with subsequent production of biogas and biomethane is an economically and ecologically feasible technique for disposing of concentrated sewage sludge [6].

The technology for disposing of concentrated aquaculture wastewater sludge by anaerobic fermentation is relatively new. Therefore, in view of the above, the issues of determining the volumes of biomethane and electricity production during the anaerobic fermentation of these wastewaters, as well as ways to increase the efficiency of this process, remain relevant. Solving this issue requires the development of appropriate technical means and justification of the technical and technological parameters of the process.

2. Literature review and problem statement

The scientific literature related to the technologies of sedimentation of sewage sludge and subsequent fermentation of this sludge for the purpose of biogas production can be conditionally divided into two main directions. The first is sedimentation and anaerobic fermentation of thickened sewage sludge from freshwater aquaculture, the second is sedimentation and anaerobic fermentation of thickened saline sludge from marine aquaculture wastewater. Technologies of sedimentation and processing of thickened sediment of freshwater aquaculture for the purpose of producing biogas (biomethane) for electricity generation are described in [7–9].

Work [7] reports innovative technologies for sedimentation of sewage sludge, which are based on reducing the biochemical and chemical oxygen demand of freshwater aquaculture, as well as reducing its resistance to antibiotics. The authors analyzed known methods of wastewater treatment, each of which was evaluated according to energy consumption and the degree of negative impact on the environment. The study gives practical solutions for increasing the efficiency of wastewater treatment with the subsequent utilization of the extracted sediment. But the issues of ensuring the given composition of sewage sludge and determining the optimal duration of anaerobic fermentation in order to increase the efficiency of this process remained unresolved.

The solution to this scientific problem is given in study [8]. The authors fermented salmon sediment in a continuous reactor for 55...60 days at a temperature of 35 °C with a content of dry organic matter (DOM) of 6.3...12.3 %. As a result of fermentation, the processed sludge contained 3.4...6.8 kg/ton of nitrogen and 1.2...2.4 kg/ton of phosphorus. The chemical composition of the sediment and the duration of its fermentation ensured an increase in the efficiency of biomethane production by 11.7 %, the output of which reached 0.14...0.154 l/h (DOM). The high concentration of organic fatty acids in the precipitate (≈28 g/l) made it impossible to achieve higher efficiency indicators, which slowed down the process. The solution was to adjust the volume of the container and the fermentation time, which ensured a pH of 7.4...7.55 throughout the entire process. Therefore, a high concentration of organic fatty acids under production conditions significantly reduces the efficiency of anaerobic sludge treatment. This gives reason to claim that research should be conducted to establish methods for reducing the concentration of organic fatty acids in the sediment.

Such a study is reported in [9]. The authors evaluated the effect of adding macrophyte to RAS sediment with a high content of organic fatty acids. Additional pretreatment of sludge with steam accelerated the hydrolysis process and increased the efficiency of anaerobic digestion from 9–19 % (without treatment) to 38–48 %. At the same time, the yield of methane increased from 108±31 to 200±36 ml/g (DOM). However, the addition of macrophyte to the sludge and its steam treatment contributed to the increase in the concentration of undissolved lignin and phenolic compounds in the digestate, which destabilized the anaerobic fermentation process. A partial solution was the continuous removal of byproducts from the reactor. Although the problem of chemical-thermal decomposition of fatty acids was solved, the question of researching the efficiency of biomethane production depending on the content of lignin in the mixture remained unresolved.

Studies that consider methods for increasing the efficiency of the process of biomethane fermentation of sediments of marine RAS are described in [10–12].

The authors of work [10] investigated the dependence of the efficiency of biomethane fermentation of filtered and thickened sediment of marine RAS at different ratios DOM in the sediment to the inoculum (i) and at different fermentation times. The highest efficiency of the process corresponded to the highest ratio (i)/(DOM) and was characterized by a long lag phase (5.5...14 days). In the absence of inoculum, the fermentation efficiency was low and barely reached 62.2 nml CH_4/g DOM. Therefore, using (i) and achieving a lag phase duration of 5.5...14 days increases the efficiency of the fermentation process of saline sewage sludge and could be a viable option for waste management in the aquaculture sector. However, the degree of influence of (i) on fermentation efficiency and specific methanogenic and phosphatase activity of the sediment should be substantiated based on the content of salt, potassium, and iron chloride in the sediment, which the authors did not investigate.

However, the authors of work [11] investigated the effect of the content of salt, potassium, iron chloride, and microorganisms adapted to salty conditions on the specific methanogenic and phosphatase activity of the sediment, the degree of release of phosphate and extracellular substances. The efficiency of reducing chemical oxygen consumption and decomposition of dry organic matter was 39.7–62.1 % and 45.2–70.9 %, respectively. At the same time, the percentage of methane in biogas was 46.1–65.6 %, which is 7.6–12.4 % higher than the data given in [10]. However, the authors failed to achieve higher values of biomethane production. The reason for this is the objective difficulties associated with the fundamental difficulty of achieving stable operation of the reactor. An option to overcome the difficulties could be the use of chemical solvents that accelerate the release of organic fatty acids and phosphates.

The authors of paper [11] achieved stable operation of the reactor and obtained higher rates of biomethane production during anaerobic fermentation of the salty sediment of marine RAS than those given in works [7–10]. It was also confirmed that an increase in the salinity of the sediment reduces the activity of a specific methanogen, the release of organic fatty acids and phosphates, and worsens the production of exopolysaccharides, as stated in paper [10]. The solution was the use of two compatible solvents (betaine and trehalose), which accelerated the release of these substances. However, the study is incomplete and requires further valuable experiments on the effect of other types of solvents on the efficiency of biomethane production in order to generalize the results and make them suitable for use in other studies.

Work [12] also investigated the effect of the salt content in the sediment of marine RAS and the duration of anaerobic fermentation on the specific yield of biomethane. It is noted that the specific yield of biomethane during the fermentation of saline sediments of PCH is low due to the high level of sodium cations in these sediments. The authors proposed technical solutions for enhancing specific meta genic activity, substantiated the parameters of sediment thickening of marine RAS and the fermentation time to increase biomethane production, provided recommendations on the design and technological parameters of anaerobic digestion plants.

High efficiency indicators of biomethane production (57–86 % of the total biomethane potential) were achieved in work [13] during anaerobic fermentation of a mixture of marine and freshwater sediments of RAS. The addition of ferrous iron in concentrations of 100 mg/l and 1000 mg/l to such mixtures increased the salt resistance of methanogenic bacteria and, as a result, the concentration of methane in biogas increased. The addition of iron also stabilized the pH and accelerated the utilization of organic fatty acids. At the same time, the output of biomethane was in the range from 0.1 to 0.4 l in terms of normal conditions CH_4/g DOM. Therefore, adding ferrous iron to the sediment mixture and optimizing the duration of fermentation is one of the effective methods for increasing the efficiency of the biomethane production process.

The shortcoming of works [10–13] is the lack of generalization of the results (their universalization), which requires conducting new studies every time the input parameters change: physical and chemical properties of the sediment, reactor design, fermentation technology, inoculum composition, solvent characteristics, etc.

In recent years, scientific studies on the intersectoral synergy of aquaculture and agricultural production have been reported. An example is paper [14]. The authors combined the production of biogas from agricultural raw materials with the production of microbial proteins (MB) and performed an economic evaluation of the proposed solutions. The liquid phase, rich in organic fatty acids, was obtained by fermentation of agricultural raw materials and was further used for the production of MB in a continuous reactor. The highest productivity of MB production was 1.21 g/l per day dover 2–3 days of hydraulic retention. The resulting MBs were rich in proteins, polyhydroxyalkanoates, and essential amino acids, which can be used as feed ingredients in aquaculture. Production of 590 t/y of MB provided a break-even MB price of EUR 1,300/t, taking into account the investment in technology and additional operating costs. The study confirms the competitiveness of the existence of the combined plant and emphasizes the promising prospect of the synergy of aquaculture and agricultural production.

In [15], a pilot platform for the bioprocessing of agricultural waste and RAS sludge for the production of H_2, CH_4, and organic fatty acids was studied. The processing system is a two-stage anaerobic process where H_2 and organic fatty acids were produced in the first phase (fermentation) and methane in the second (degradation). The study confirmed the possibility of producing biogas consisting of 10 % H_2 and 55 % CH_4 by reducing organic fatty acids.

It follows from studies [14, 15] that ensuring the energy autonomy of objects opens a promising direction in the design of equipment for both agricultural production and aquaculture enterprises. The level of use of renewable energy sources is increasing, and we have scientific and technical progress in this area [16]. Thus, the integration of agricultural production and aquaculture with anaerobic fermentation of sediments is a method of production of both fish products and energy [17]. However, the results reported in [14, 15] also have local application and are adequate for similar research conditions.

In [7–15], much attention is paid to the evaluation of biogas production from RAS sediments with different properties and parameters of the anaerobic processing process. The influence of the duration of the decomposition of substrates, additives (iron, betaine, trehalose) on the stabilization of the pH level and utilization of organic fatty acids was studied. The research results and methodology could be used in the future for studying the conditions and parameters for the fermentation process of RAS sediments. The question of the influence of anaerobic fermentation time on the level and rate of decomposition DOM, the output of biogas, biomethane, and the concentration of biomethane in biogas remained unresolved. There are also no studies on the effect of the duration of anaerobic fermentation on the specific yield of biomethane and on the specific yield of biomethane per unit mass of sediment in the reactor. Establishing these dependences will make it possible to increase the efficiency of the process of anaerobic fermentation of aquaculture wastewater sludge and to determine the volumes of biomethane and electricity production based on it. Therefore, despite the difficulty of taking into account all the parameters for the process of fermentation of aquaculture sewage sludge, conducting such studies is necessary. This could ensure an increase in the level of energy autonomy of aquaculture enterprises.

3. The aim and objectives of the study

The purpose of our study is to determine the indicators of the process of anaerobic fermentation of wastewater sludge from aquaculture. This will make it possible to determine the volume of production of biomethane and electricity based on it during the anaerobic fermentation of wastewater sludge from aquaculture.

To achieve the goal, the following tasks were set:

– to determine the influence of anaerobic fermentation time on the level and rate of decomposition of dry organic matter;

– to determine the influence of anaerobic fermentation time on the output of biogas, biomethane, and the concentration of biomethane in biogas;

– to determine the influence of anaerobic fermentation time on the specific yield of biomethane;

– to determine the influence of anaerobic fermentation time on the specific output of biomethane per unit of sediment biomass in the reactor.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our study is the process of anaerobic fermentation of aquaculture sewage sludge, obtained by sedimentation of sewage water in RAS during the cultivation of Nile clary catfish (*Clarias gariepinus*).

The hypothesis of the study assumes existence of an estimated quantitative dependence between the volumes of biogas and biomethane production during the operation of biogas reactors with periodic loading based on the experimental dependences of the level of decomposition of dry organic matter and the specific yield of biomethane per unit mass of decomposed dry organic raw materials from the time of fermentation.

When determining parameters for anaerobic fermentation, the adopted assumption was the existence of several portions of biomass in the biogas reactor, which are at different stages of the level of decomposition of DOM. Experimental data were treated using exponential approximation.

4. 2. Description of the experimental setup

The research was carried out at the biogas production laboratory of the Institute of Technical Thermophysics, the National Academy of Sciences (NAS) of Ukraine, using the sludge from the sewage washing water of the mechanical RAS filter for the cultivation of Nile clary catfish (*Clarias gariepinus*). The general view of the experimental setup is shown in Fig. 1.

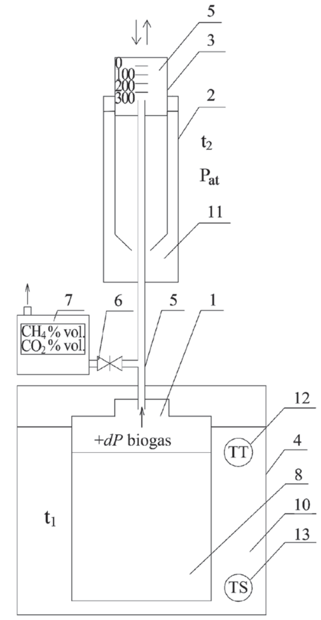

Fig. 1. Schematic diagram of the unit system of the research installation: 1 – bioreactor capacity; 2 – stationary part of the eudiometer; 3 – moving part of the eudiometer; 4 – tank with coolant; 5 – PVC pipe for biogas movement; 6 – gas shut-off valve; 7 – gas analyzer; 8 – working environment of the bioreactor; 9 – the internal space of the eudiometer with biogas; 10 – coolant (water); 11 – 5 % NaCl aqueous solution; 12 – mercury thermometer; 13 – thermostat

An experimental study on the process of anaerobic fermentation of sewage sludge was carried out taking into account the provisions set forth in the German standard VDI 4630:2016 [VDI 4630:2016. Fermentation of organic materials – Characterization of the substrate, sampling, collection of material data, fermentation tests].

4. 3. Research methods and characteristics of aquaculture wastewater sludge

The selected samples of the sediment of wastewater washing water, as well as the inoculum, were analyzed for the content of dry substances and ash content. The inoculum, which contained an active population of methanogenic bacteria and archaea, was obtained under laboratory conditions in the process of methane fermentation of organic materials of variable composition. Test mixtures were prepared on the basis of data on the content of DOM in the sediments and in the inoculum.

The main characteristics of the materials that were used in the process of anaerobic fermentation are given in Table 1, and their ratio by variants of experiments is in Table 2. The conditions for conducting experiments are given in Table 3.

After introducing the experimental mixtures into the reactors, nitrogen gas was supplied to the residual gas space of the reactors in order to displace oxygen from the air, after which each reactor was hermetically connected to the eudiometer using a flexible silicone tube. The formation of biogas in the reactor led to an increase in its partial pressure in the gas space of the eudiometer, as a result of which the moving part of the eudiometer rose to a certain height. The moving part of the eudiometer is graduated in ml. The reading of the volume of separated biogas was carried out visually.

The absolute error in the visual reading of the volume of biogas accumulated in the eudiometer was ±10 ml. The relative error of visual registration of the volume of biogas released did not exceed 2 % of the cumulative yield of biogas released over the entire period of the experiment.

The level of decomposition of DOM (E_{VS}, relative units) was determined from the following expression:

$$E_{VS}=\frac{M_{\mathrm{CH}_4}+M_{\mathrm{CO}_2}}{0.93M_{VS}},$$

where M_{CH_4} is the calculated mass of methane separated from biogas, g CH_4; M_{CO_2} – calculated mass of carbon dioxide separated from biogas, g CO_2; M_{VS} is the initial mass of DOM of sediment introduced into the reactor, g DOM; 0.93 is a coefficient that takes into account the growth of bacterial biomass in the reactor during the decomposition of sediment organic matter.

The repetition of each of the 3 experimental mixtures of experiments was threefold.

Table 1

Main indicators of the inoculum and sediment in the RAS washing water

Material	Dry matter (105 °C), %	Humidity, %	Dry organic matter (550 °C), % to DM
Inoculum	2.89	97.11	64.08
RAS washing water sediment	7.26	92.74	95.86

Table 2

Correlation between the amount of inoculant and sediment of RAS washing water based on variants of experiments

Test	Research material	Volume, ml	Mass, g	DM content, g	DOM content, g	Ratio of COP sediment and inoculum, *Rvs/as*	Ratio of the COP of the test material and the mass, *Cvs*, g DOM/kg	Content of DM in the mixture, %
1	Inoculum	750.0	780.0	22.6	14.5	0.359	16.909	3.27
	Sediment of RAS washing water	71.0	74.6	5.4	5.2		6.075	
	Mixture	821.0	854.6	28.0	19.6		22.984	
2	Inoculum	750.0	780.0	22.6	14.5	0.498	16.358	3.40
	Sediment of RAS washing water	98.5	103.4	7.5	7.2		8.146	
	Mixture	848.5	883.4	30.1	21.6		24.504	
3	Inoculum	750.0	780.0	22.6	14.5	0.631	15.862	3.52
	Sediment of RAS washing water	124.8	131.0	9.5	9.1		10.008	
	Mixture	874.8	911.0	32.1	23.6		25.870	

Table 3

Conditions for conducting experiments

Period of time from the start of the test to the current measurement of the volume of biogas, days	Ambient temperature, °C	Reactor temperature, °C	Atmospheric pressure, mm Hg
0.0	20	36	742
1.0	19		739
2.5	30.5		742
3.7	28		742
5.0	29		742
7.0	31		748
8.6	21		752
11.1	21		748
14.0	29		744
16.0	30		744
20.8	31.5		747
37.7	20		742

The temperature regime in the reactors (36±0.2 °C) was provided by means of a heating element for water environments with a thermostat. The temperature was measured using a temperature sensor installed in a container with a heat carrier (water).

The content of CH_4 and CO_2 in the selected biogas was measured using a Landtec GEM-500 portable gas analyzer.

Experimental data were processed by determining the average value of the measurement results and their confidence interval.

We determined parameters of anaerobic fermentation for the conditions when there are several portions of sediment in the biogas reactor, which are at different stages of the level of decomposition of organic matter, on the basis of [18].

5. Results of investigating indicators of the process of anaerobic fermentation of aquaculture wastewater sediment

5. 1. The effect of anaerobic fermentation time on the level and rate of decomposition of dry organic matter

After conducting the experiment and processing the experimental data, it was established (Table 1) that the current calculated value of the level of anaerobic fermentation of solid waste can be represented by the following exponential expression:

$$\alpha = \alpha_0\left[1-\exp\left(-k_F\tau_F\right)\right] = 0.74\left[1-\exp\left(-0.108\tau_F\right)\right], \qquad (1)$$

where α is the current calculated value of the level of anaerobic fermentation of DOM, relative units; $\alpha_0=0.74$ relative units – the maximum value of the level of anaerobic fermentation of DOM (according to the calculations given in Table 4); $k_F=0.108$ relative units/day – rate of anaerobic fermentation of DOM (according to the calculations given in Table 4); τ_F – time of anaerobic fermentation, days.

Table 4

Initial data for calculating the maximum level of anaerobic fermentation of DOM and the rate of anaerobic fermentation

Time (τ) of anaerobic fermentation, days	The average level of decomposition of organic matter, relative units	Relative level of decomposition of organic matter, relative units	Estimated values			ln τ	Estimated level of decomposition of organic matter, relative units
0.0	0.000	0	–	–	–	–	0
1.0	0.073	0.098	1.109	0.103	–2.271	–0.017	0,075
2.5	0.163	0.220	1.282	0.249	–1.391	0.912	0,175
3.7	0.242	0.327	1.487	0.397	–0.925	1.307	0,244
5.0	0.316	0.427	1.745	0.557	–0.586	1.616	0,311
7.0	0.393	0.532	2.135	0.759	–0.276	1.944	0,393
8.6	0.458	0.619	2.627	0.966	–0.035	2.154	0,449
11.1	0.509	0.688	3.210	1.166	0.154	2.406	0,517
14.0	0.581	0.786	4.670	1.541	0.433	2.642	0,578
16.0	0.627	0.848	6.583	1.884	0.634	2.772	0,609
20.8	0.661	0.893	9.360	2.236	0.805	3.035	0,662
37.7	0.740		–2.223	0.108	–3.459	18.769	0.727

The plot of values of the level of anaerobic fermentation of DOM for each repetition, the average value of the level of anaerobic fermentation of DOM, and the calculated value of the level of anaerobic fermentation of DOM are shown in Fig. 2.

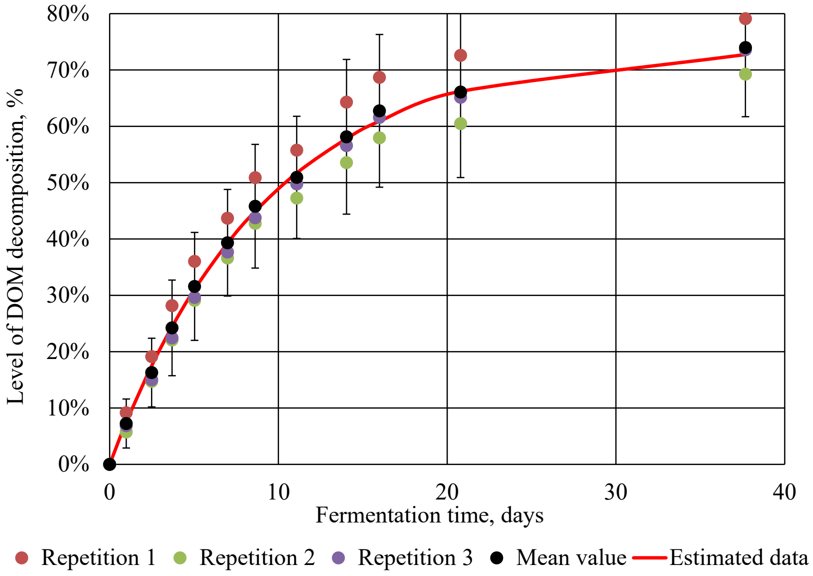

Fig. 2. Experimental dependence of the level of decomposition of dry organic matter on fermentation time

Under the real conditions of anaerobic fermentation, there are several portions of sludge in the biogas reactor, which are at different stages of the decomposition of organic matter.

In this case, the parameters of anaerobic fermentation can be determined on the basis of the calculated value of the integrated level of anaerobic fermentation of organic waste based on (1):

$$\alpha = \alpha_0 \left[\begin{array}{l} 1-\exp\left(-k_F \cdot \tau_F\right) \dfrac{\tau_L}{\tau_F+\tau_L} \times \\ \times \sum_{i=0}^{n=\frac{\tau_F}{\tau_L}} \exp\left(k_F \cdot \tau_L \cdot i\right) \end{array} \right] =$$

$$= 0.74 \left[\begin{array}{l} 1-\exp\left(-0.108 \cdot \tau_F\right) \dfrac{\tau_L}{\tau_F+\tau_L} \times \\ \times \sum_{i=0}^{n=\frac{\tau_F}{\tau_L}} \exp\left(0.108 \cdot \tau_L \cdot i\right) \end{array} \right], \qquad (2)$$

where $n=\tau_F/\tau_L$ is the number of loaded portions of biomass in the biogas reactor, units; τ_F – fermentation time (total residence time of biomass in the reactor), days; τ_L is the loading frequency of the biogas reactor, days; $i=0...n=0...\tau_F/\tau_L$ is the numbering of the biomass portions loaded into the biogas reactor.

The integrated rate of decomposition of organic biomass during anaerobic fermentation, as the differential of expression (2), will be:

$$\frac{d\alpha}{d\tau_F} = \alpha_0 k_F \exp\left(-k_F \cdot \tau_F\right) \frac{\tau_L}{\tau_F+\tau_L} \times$$

$$\times \sum_{i=0}^{n=\frac{\tau_F}{\tau_L}} \exp\left(k_F \cdot \tau_L \cdot i\right) =$$

$$= 0.74 \cdot 0.108 \cdot \exp\left(-0.108 \cdot \tau_F\right) \frac{\tau_L}{\tau_F+\tau_L} \times$$

$$\times \sum_{i=0}^{n=\frac{\tau_F}{\tau_L}} \exp\left(0.108 \cdot \tau_L \cdot i\right). \qquad (3)$$

The results of determining the integrated level and rate of anaerobic fermentation of DOM under the conditions of anaerobic fermentation, when there are several portions of sludge in the biogas reactor, according to expressions (1) and (2) are shown in Fig. 3, 4.

Our results can be used for further evaluation of the specific yield of biogas and biomethane.

5. 2. The effect of anaerobic fermentation time on the yield of biogas, biomethane, and the concentration of biomethane in biogas

The results of studies on the yield of biogas and biomethane during anaerobic fermentation are shown graphically in Fig. 5.

The experimental dependence of biomethane concentration in biogas on fermentation time is shown in Fig. 6.

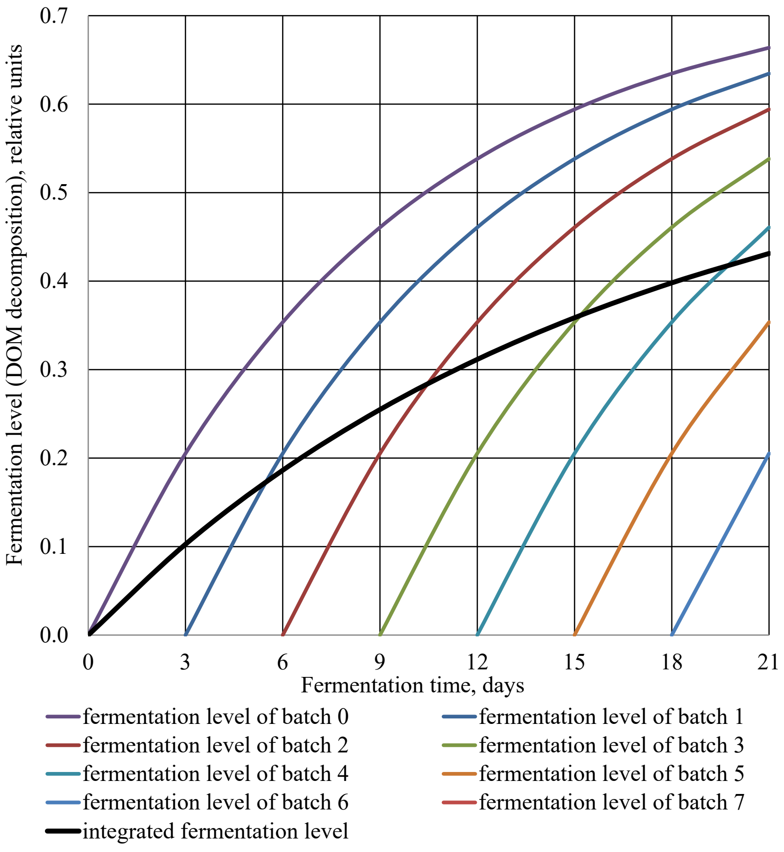

Fig. 3. The decomposition level of the organic biomass in the sediment during anaerobic fermentation with a fermentation time τ_F=21 days, the loading frequency of the biogas reactor τ_L=3 days, and the number of loaded portions in the reactor n=7 pcs.

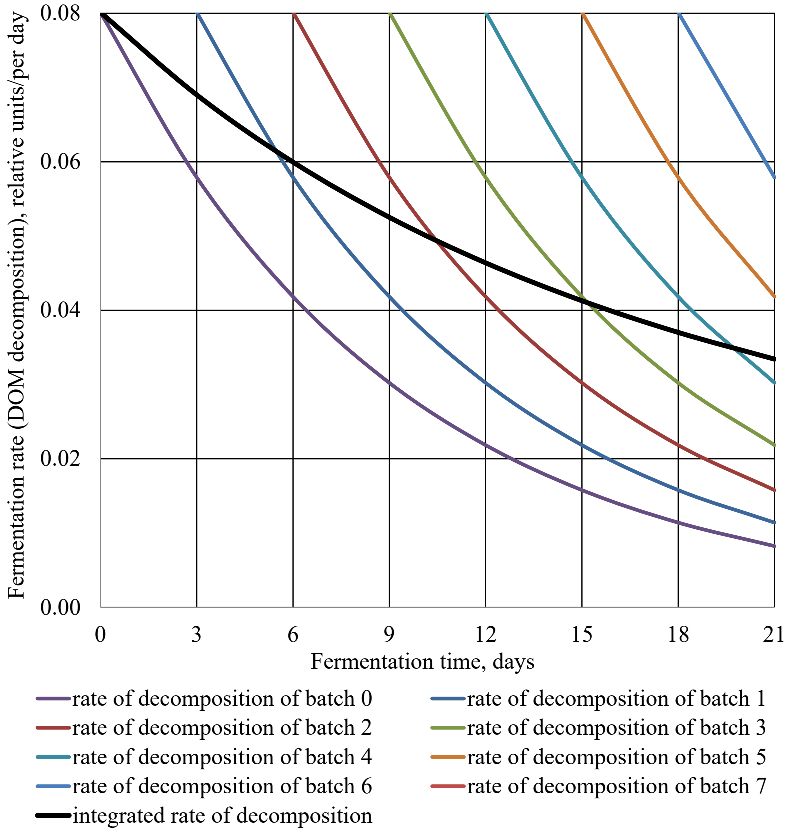

Fig. 4. The rate of decomposition of the organic biomass in the sediment during anaerobic fermentation with a fermentation time $\tau_F=21$ days, the loading frequency of the biogas reactor $\tau_L=3$ days, and the number of loaded portions in the reactor $n=7$ pcs.

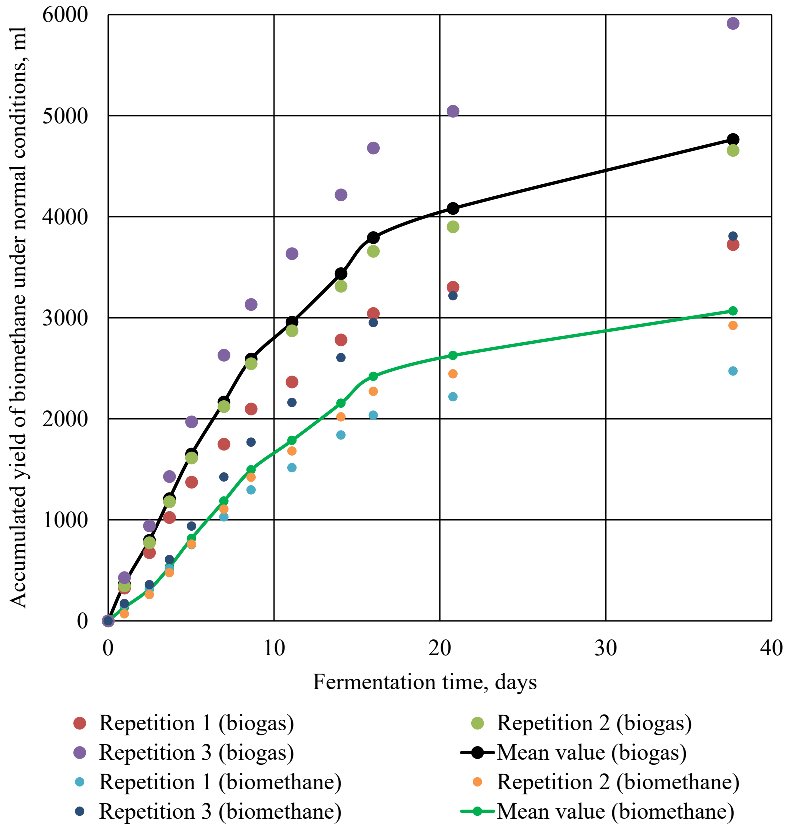

Fig. 5. Experimental dependence of the accumulated yield of biogas and biomethane funder normal conditions on fermentation time

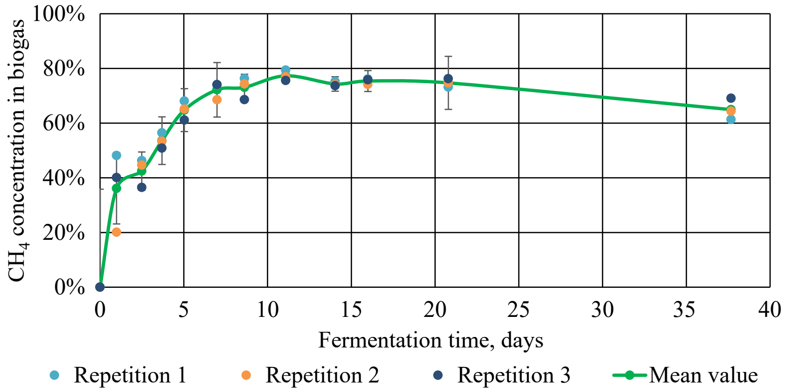

Fig. 6. Experimental dependence of biomethane concentration in biogas on fermentation time

Our results are necessary for evaluating the energy efficiency of anaerobic fermentation of aquaculture wastewater sludge.

5. 3. The effect of anaerobic fermentation time on the specific yield of biomethane

After processing the experimental data, it was also established (Table 5) that the current calculated value of the specific yield of biomethane per unit of mass of decomposed DOM can be represented by the following exponential expression:

$$\gamma=\gamma_0\left[1-\exp\left(-k_{BM}\tau_F\right)\right]=$$
$$=803.936\left[1-\exp\left(-0.207\tau_F\right)\right], \qquad (4)$$

where γ is the current calculated value of the specific yield of biomethane, ml in terms of normal conditions per gram of decomposed DOM; γ_0=803.936 ml in terms of normal conditions per gram of decomposed DOM – the maximum value of biomethane yield (according to the calculations given in Table 5); k_{BM}=0.207 ml in terms of normal conditions per gram of decomposed DOM per day – the rate of change in the specific yield of biomethane (according to the calculations given in Table 4); τ_F – time of anaerobic fermentation, days.

The plot of values of the specific biomethane yield per unit of mass of decomposed DOM for each repetition, the average value of specific biomethane yield, and the calculated value of specific biomethane yield are shown in Fig. 7.

Under the conditions of anaerobic fermentation, there are several portions of sediment in the biogas reactor, which are at different stages of the level of decomposition of organic matter and, accordingly, the specific yield of biomethane. In this case, the determination of the specific yield of biomethane per unit mass of decomposed organic waste can be carried out on the basis of the calculated value of the integrated specific yield of biomethane based on (4):

$$\gamma=\gamma_0\begin{bmatrix}1-\exp\left(-k_{BM}\cdot\tau_F\right)\dfrac{\tau_L}{\tau_F+\tau_L}\times\\ \times\sum_{i=0}^{n=\frac{\tau_F}{\tau_L}}\exp\left(k_{BM}\cdot\tau_L\cdot i\right)\end{bmatrix}=$$
$$=803.936\begin{bmatrix}1-\exp\left(-0.207\cdot\tau_F\right)\dfrac{\tau_L}{\tau_F+\tau_L}\times\\ \times\sum_{i=0}^{n=\frac{\tau_F}{\tau_L}}\exp\left(0.207\cdot\tau_L\cdot i\right)\end{bmatrix}. \qquad (5)$$

The results of determining the integrated level of specific yield of biomethane under the conditions of anaerobic fermentation, when there are several portions of sediment in the biogas reactor, according to expression (5), are shown in Fig. 8.

Our results are necessary for calculating the specific yield of biomethane per unit of sediment biomass in the reactor.

Table 5

Input data for calculating the maximum level of specific biomethane yield and its rate of change

Time (τ) of anaerobic fermentation, days	Average level of specific yield of CH$_4$, ml in terms of normal conditions per gram of decomposed DOM	The relative level of specific yield of CH$_4$, relative units	Estimated values			ln τ	Estimated specific yield level of CH$_4$, ml in terms of normal conditions per gram of decomposed DOM
0.0	0.000	0	–	–	–	–	0
1.0	348.395	0.433	1.765	0.568	–0.566	–0.017	148,246
2.5	373.918	0.465	1.870	0.626	–0.469	0.912	324,021
3.7	429.650	0.534	2.148	0.764	–0.269	1.307	430,192
5.0	504.759	0.628	2.687	0.988	–0.012	1.616	520,646
7.0	587.644	0.731	3.717	1.313	0.272	1.944	614,893
8.6	636.226	0.791	4.794	1.567	0.449	2.154	669,343
11.1	681.567	0.848	6.570	1.882	0.633	2.406	723,137
14.0	721.256	0.897	9.723	2.275	0.822	2.642	760,112
16.0	749.714	0.933	14.827	2.696	0.992	2.772	774,700
20.8	772.838	0.961	25.852	3.252	1.179	3.035	793,136
37.7	803.936		–1.574	0.207	3.033	18.769	803.610

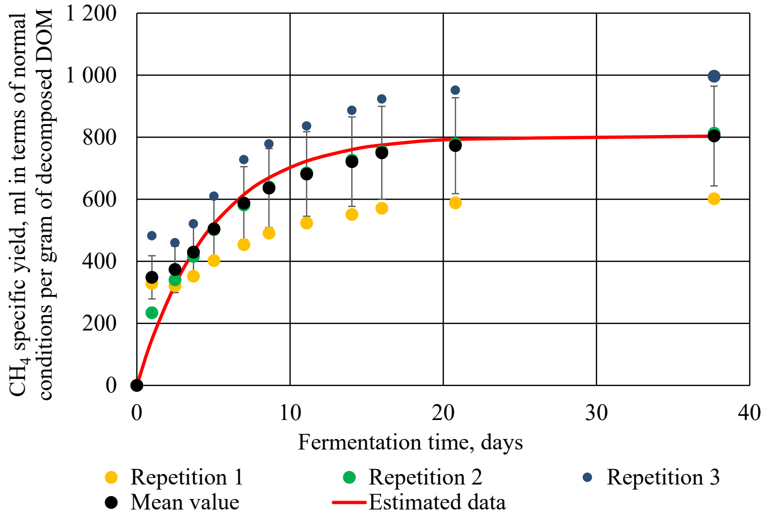

Fig. 7. Experimental dependence of the specific yield of biomethane per unit mass of decomposed dry organic raw materials on fermentation time

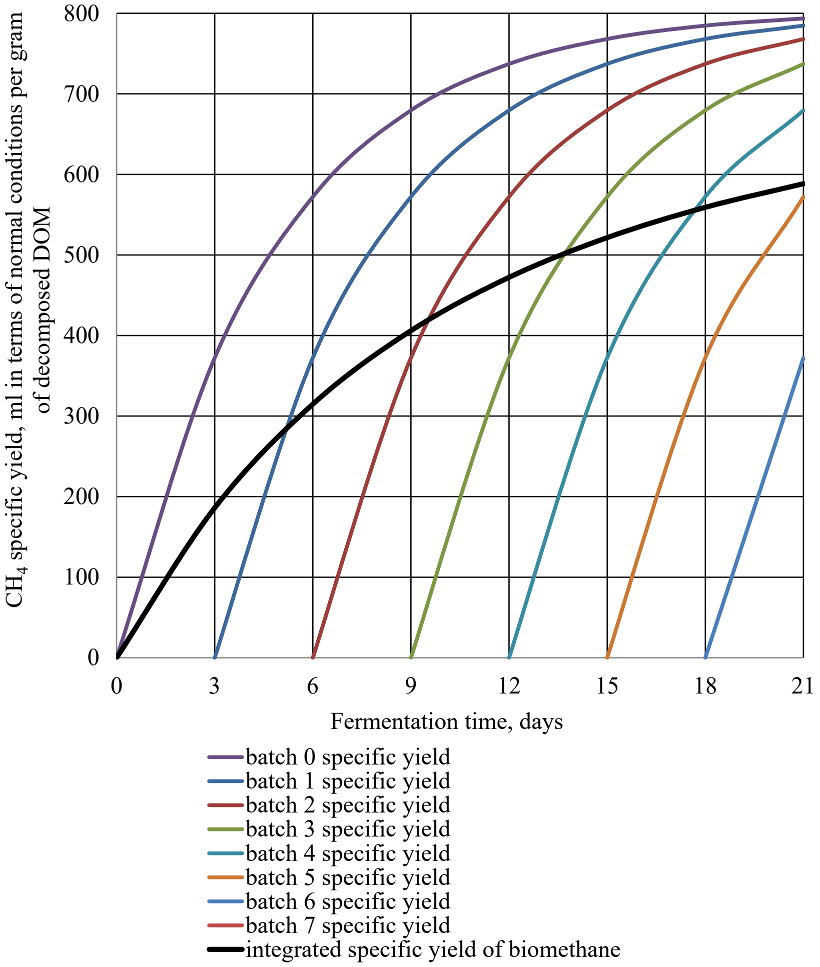

Fig. 8. The specific yield of biomethane during anaerobic fermentation with fermentation time $\tau_F=21$ days, the loading frequency of the biogas reactor $\tau_L=3$ days, and the number of loaded portions in the reactor $n=7$ units

5. 4. The effect of anaerobic fermentation time on the specific yield of biomethane per unit volume of sediment biomass in the reactor

The specific yield of biomethane per unit volume of biomass in the reactor depends on the content of organic mass in the reactor and is determined by the rate of decomposition of the organic biomass in the sediment and the specific yield of biomethane from the unit of decomposed organic biomass. This can be formalized as follows:

$$\eta=\rho\left(1-\frac{W}{100}\right)\frac{VS}{100}\frac{d\alpha}{d\tau_F}\gamma, \tag{6}$$

where η is the specific yield of biomethane per unit volume of biomass in the biogas reactor, m_3 (in terms of normal conditions)/m^3 day^{-1}; ρ – biomass density, t/m^3; W – biomass moisture, %; VS – content of dry organic matter in biomass, %; γ – specific yield of biomethane per unit of mass of decomposed DOM, m^3 in terms of normal conditions per ton of decomposed DOM.

The calculation of the specific yield of biomethane per unit volume of biomass and the specific yield of biogas per unit of biomass in the biogas reactor according to expression (6) is shown in Fig. 9.

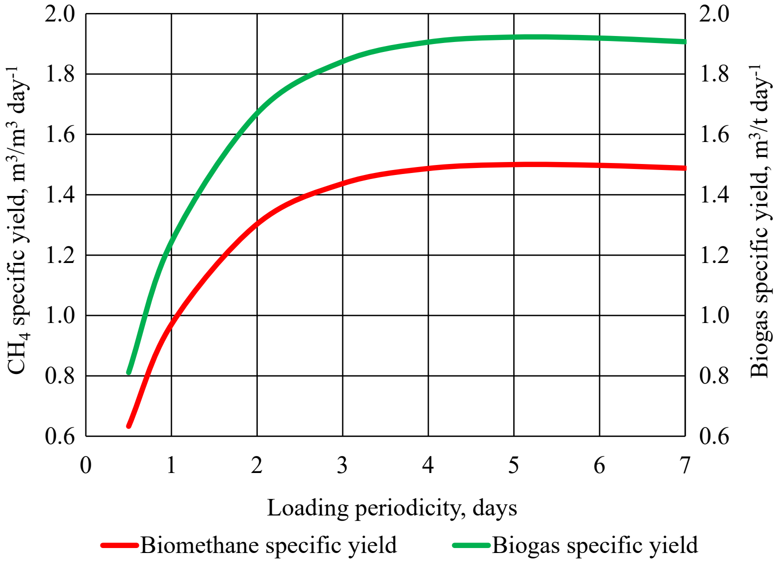

Fig. 9. Specific yield of biomethane per unit volume of biomass and specific yield of biogas per unit of biomass during anaerobic fermentation depending on the periodicity of loading the biogas reactor at fermentation time τ_F=21 days

Our data make it possible to calculate the specific yield of biomethane per unit of biomass in the biogas reactor.

6. Discussion of results of investigating the indicators of the process of anaerobic fermentation of aquaculture wastewater sludge

The results of our study shown in Fig. 1–9 make it possible to increase the efficiency of aquaculture wastewater sludge processing by anaerobic fermentation. The theoretical foundations of the proposed research method are outlined in [18]. In this study, this method has been improved to determine the specific yield of biomethane per unit of decomposed organic matter depending on the time of anaerobic fermentation. In contrast to the previously proposed method, in our study the level of DOM decomposition, the specific yield of biomethane per unit of decomposed DOM for the conditions of anaerobic fermentation of aquaculture wastewater sludge was determined. The study made it possible to propose an improved expression for determining the specific yield of biomethane per unit volume of biomass during anaerobic fermentation and to determine its optimal value depending on the periodicity of loading the biogas reactor. This became possible through determining the experimental dependences of the level of anaerobic fermentation of organic waste and the specific yield of biomethane under normal conditions and based on 1 g of decomposed DOM. The product of these values represents the specific yield of biomethane per unit of mass of decomposed DOM per day. By relating this indicator to the biomass density, it becomes possible to obtain the value of the specific yield of biomethane per unit volume of biomass during anaerobic fermentation.

It has been established that the value of the level of anaerobic fermentation of solid waste can be represented by an exponential dependence. The resulting dependence (1) is within the confidence interval of the results from experimental studies, and therefore adequately describes them. Analysis of the dependence, which determines the average value of the level of DOM decomposition (Fig. 2), revealed that the maximum level of DOM decomposition during anaerobic fermentation achieved in 38 days was 0.74 relative units. At the same time, the parameter that characterizes the rate of decomposition of DOM during anaerobic fermentation of aquaculture wastewater sediment was 0.108 relative units per day. The resulting dependence (1) was used to describe the real conditions of anaerobic fermentation, when there are several portions of sludge in the biogas reactor at different stages of the level of decomposition of organic matter. This procedure is given in full in [18]. For such conditions, dependence (2) was obtained, which determines the integrated level of DOM decomposition. This dependence is shown graphically in Fig. 3. Calculations show that the integrated level of DOM decomposition over 21 days of anaerobic fermentation can reach only 0.43 relative units. Obviously, this is due to the fact that each batch of biomass in the reactor, except for the first one, has a lower level of decomposition of DOM than the first batch.

In order to estimate the rate of DOM decomposition, expression (3) was derived as a derivative from the integrated level of DOM decomposition based on expression (2). It was established that the integrated rate of DOM decomposition is maximal at the initial moment of fermentation and on day 21 is set at the level of 0.033 relative units per day (Fig. 4). The resulting equations (2) and (3) can be used to estimate the fermentation intensity at a given fermentation time, the loading frequency of the biogas reactor, and the number of loaded portions in the reactor.

Analysis of the study results on biogas and biomethane yield during anaerobic fermentation (Fig. 5) showed that these values on day 21 of anaerobic fermentation are 4.083 and 2.627 l. At the same time, the concentration of biomethane in biogas on day 7 of fermentation reached 74–75 % and remained at this level until day 21 (Fig. 6). Later, up to day 38, the concentration of biomethane in biogas steadily decreased to 64–65 %.

It was also established that the value of the specific yield of biomethane in terms of normal conditions and based on 1 g of decomposed DOM can be represented by an exponential relationship. The resulting dependence (4) is within the confidence interval of the results from experimental studies, which allows us to draw a conclusion about its adequacy. Analysis of the dependence, which determines the average value of the specific yield of biomethane (Fig. 7), revealed that the maximum level of the specific yield of biomethane during anaerobic fermentation reached on day 38 was 803.936 ml in terms of normal conditions per gram of decomposed DOM. At the same time, the parameter that characterizes the rate of change in the specific yield of biomethane during the anaerobic fermentation of aquaculture wastewater sludge was 0.207 ml y in terms of normal conditions per gram of decomposed DOM per day. The resulting dependence (4) was used to describe the real conditions of anaerobic fermentation, when there are several portions of sludge in the biogas reactor, which are at different stages of the decomposition level of DOM. For such conditions, dependence (5) was derived, which determines the integrated specific yield of biomethane. This dependence is shown graphically in Fig. 8. Calculations show that the integrated specific yield of biomethane during 21 days of anaerobic fermentation can reach only 580–590 ml in terms of normal conditions per gram of decomposed DOM. Obviously, this is due to the fact that each batch of biomass in the reactor, except for the first, has a specific yield of biomethane lower than the first batch. Equation (4) can be used to estimate the integrated specific yield of biomethane at a given fermentation time, loading frequency of the biogas reactor, and the number of loaded portions in the reactor. For most of our research, the yield of biogas and biomethane is calculated per unit mass of organic matter added to the biogas reactor. It is obvious that it is difficult to relate the yield of biogas and biomethane to the amount of organic matter added to the biogas reactor with an unknown level of its decomposition. However, a complete set of these indicators for the conditions of biogas fermentation of various types of biomass is usually not given.

Dependence (6) determines the specific yield of biomethane per unit volume of biomass in the reactor and the specific yield of biogas per unit of biomass depending on the content of organic mass in the reactor, its decomposition rate, and the specific yield of biomethane from a unit of decomposed organic biomass. This dependence is graphically illustrated in Fig. 9. It was established that with a fermentation time of 21 days, the specific yield of biomethane during anaerobic fermentation has an optimal value depending on the loading frequency of the biogas reactor. This value is 1.48–1.5 m^3 of biomethane per one m^3 of biomass in the reactor for one day, with the periodicity of loading the biogas reactor from 4.5 to 6 days. Taking into account the density of biomass at the level of 1.05 t/m^3, the concentration of biomethane in biogas at the level of 74–75 %, the value of biogas output from the reactor under normal conditions will be 1.9–1.92 m^3 per one ton of biomass in the reactor in one day. The actual yield of biogas based on the analysis of data from biogas plant studies [19–24] was: 2 m^3/t of biomass per day (fermentation temperature 40 °C, biomass moisture 96.2 %, fermentation time 5 days); 1.1 m^3/t of biomass per day (fermentation temperature 40 °C, biomass moisture 99.5 %, fermentation time 10 days); 1.2 m^3/t of biomass per day (fermentation temperature 40 °C, biomass moisture 93.7 %, fermentation time 9 days); 2.65 m^3/t of biomass per day (fermentation temperature 54 °C, biomass moisture 93.6 %, fermentation time 5 days); 1.04 m^3/t of biomass per day (fermentation temperature 38 °C, biomass moisture 94.1 %, fermentation time 16 days); 1.46 m^3/t of biomass per day (fermentation temperature 35–40 °C, biomass moisture 95.2 %, fermentation time 14 days). At the same time, such parameters as biomass density, organic mass content, maximum level and speed of organic biomass decomposition, biogas yield from decomposed organic mass under normal conditions and volume of biomethane content in biogas, as well as integrated values of the level and speed of organic biomass decomposition remained unknown, which does not allow for a more accurate assessment of the adequacy of the proposed algorithm for calculating the yield of biogas and biomethane from the reactor under normal conditions. If we average our data, we shall get a biogas output at the level of 1.58 m^3/t of biomass per day. This value differs from the calculated amount of biogas output from the reactor under normal conditions by 17 %, which indicates that with more accurate data on biomass parameters, the presence of the dependence of the level of decomposition of the organic component of biomass on the time of anaerobic fermentation and the known conditions of biomass fermentation, the proposed algorithm for calculating the specific yield of biogas during the operation of a biogas reactor in the periodic loading mode can be successfully used in scientific research and for evaluation of the process of biogas production by operating plants.

Our experimental dependences of the level of anaerobic fermentation of DOM, the results of research on the yield of biogas and biomethane are new in that they are obtained for the conditions of anaerobic fermentation of wastewater sludge from aquaculture. Dependences for determining the integrated level and speed of DOM decomposition, the integrated specific yield of biomethane, when sediment is fermented in the reactor at different stages of the DOM decomposition level, were not used in the reviewed literature. The uniqueness of our studies on defining the parameters of the aquaculture wastewater sludge processing process by anaerobic fermentation is determined by the fact that they connect the results of experimental studies with indicators that can be used in conducting a technical and economic analysis. The values of the level of DOM decomposition, the yield of biogas and biomethane, the concentration of biomethane in biogas, and the specific yield of biomethane per unit of decomposed DOM for the conditions of anaerobic fermentation of aquaculture wastewater sludge were determined experimentally. Exponential dependences of the level of anaerobic fermentation of organic waste and the specific yield of biomethane in terms of normal conditions based on 1 g of decomposed organic waste were obtained, depending on the time of anaerobic fermentation. Analytical dependences were derived that relate the integrated level and rate of decomposition of DOM depending on the fermentation time, frequency of loading, and the number of portions in the reactor for the fermentation conditions of wastewater sludge from aquaculture. An analytical dependence was derived, which relates the specific yield of biomethane in terms of normal conditions and based on 1 g of decomposed DOM, depending on the fermentation time, frequency of loading, and the number of portions in the reactor. An analytical dependence was obtained that determines the specific yield of biomethane per unit of biomass in the reactor depending on the content of organic mass in the reactor, its decomposition rate, and the specific yield of biomethane from a unit of decomposed organic biomass.

Our results (Fig. 1–9) make it possible to determine main indicators for the process of anaerobic fermentation of aquaculture wastewater sludge on the basis of experimental studies and, consequently, to conduct a technical and economic analysis of anaerobic biomass fermentation.

The limitations of our research relate to the fact that it was conducted for a specific type of aquaculture wastewater sediment, and the results are limited to the conditions of the experiment. In addition, the study was performed at a specific value of the temperature of anaerobic fermentation, namely 36 °C.

The practical significance of our results is that they can be used to determine the volumes of biomethane production and electricity based on it during the anaerobic fermentation of aquaculture wastewater sludge.

7. Conclusions

1. It has been established that the exponential dependence adequately describes the experimental data on the change in the level of decomposition of DOM in wastewater sludge from aquaculture depending on the time of anaerobic fermentation. The maximum level of DOM decomposition during anaerobic fermentation achieved in 38 days was 0.74 relative units. At the same time, the parameter that characterizes the rate of DOM decomposition during the anaerobic fermentation of aquaculture wastewater sludge was 0.108 relative units per day. At the same time, the integrated level of DOM decomposition over 21 days of anaerobic fermentation can reach only 0.43 relative units while the integrated level of DOM decomposition is set at the level of 0.033 relative units per day.

2. It has been found that the yield of biogas and biomethane during anaerobic fermentation on day 21 of anaerobic fermentation is 4.083 and 2.627 l, respectively. At the same time, the concentration of biomethane in biogas on day 7 of fermentation reached 74–75 % and remained at this level until day 21; subsequently, until day 38, the concentration of biomethane in the biogas decreased uniformly to 64–65 %.

3. We have determined that the exponential dependence adequately describes the experimental data on the change in the specific yield of biomethane per unit of decomposed organic matter depending on the time of anaerobic fermentation. The maximum level of specific yield of biomethane during anaerobic fermentation reached on day 38 was 803.936 ml in terms of normal conditions per gram of decomposed DOM. At the same time, the parameter that characterizes the rate of change in the specific yield of biomethane during the anaerobic fermentation of aquaculture wastewater sludge was 0.207 ml in terms of normal conditions per gram of decomposed DOM per day. In this case, the integrated specific yield of biomethane over 21 days of anaerobic fermentation can reach only 580–590 ml in terms of normal conditions per gram of decomposed DOM.

4. It has been revealed that with a fermentation time of 21 days, the specific yield of biomethane during anaerobic fermentation has an optimal value depending on the loading frequency of the biogas reactor. This value is 1.48–1.49 m^3 of biomethane per one m^3 of biomass in the reactor in one day, with the frequency of loading the biogas reactor once every 4.5 to 6 days.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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