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Improvement of Phosphorus Removal from Wastewater Through Fermentation of Low-Concentrated Wastewater Sludge and Increased Production of Volatile Fatty Acids

Elena Gogina [1], Nikolay Makisha [2,*], Igor Gulshin [2] and Anna Reshetova [1]

[1] Laboratory of Water Purification and Wastewater Treatment, Research Institute of Building Physics, Russian Academy of Architecture and Construction Sciences, 21, Lokomotivny Drive, 127238 Moscow, Russia; gogina-es@yandex.ru (E.G.); reshetova.anny@yandex.ru (A.R.)

[2] Research and Education Centre "Water Supply and Wastewater Treatment", Moscow State University of Civil Engineering, 26, Yaroslaskoye Highway, 129337 Moscow, Russia; gulshinia@mgsu.ru

* Correspondence: makishana@mgsu.ru

Abstract: This article presents the results of a two-stage study: the first stage involved assessing the dependence of the increase or decrease in the concentration of volatile fatty acids (VFAs) on external factors and then assessing the relationship between the VFA concentration in the supernatant after fermentation and the processing characteristics (temperature, mixing mode, alkalinity, pH, nitrogen and phosphorus content). The greatest increase in VFAs (content up to 285 mg/L in the supernatant) was achieved at a temperature in the range of 28 to 38 °C with constant mixing of the sludge. Based on the results of the second stage, a conclusion was made on the efficiency of using a particular substrate depending on the concentration of phosphorus phosphates in the incoming wastewater. The study results showed that 7.54 mg/L of phosphorus can be removed with a given probability (for activated sludge, raw sludge and wastewater). It is recommended to compensate for the excess of this concentration by dosing the acetic acid solution at a rate of 3800 meq/L of VFA per 1 mg/L of phosphorus phosphates. The literature does not contain any results of parallel studies of the operation of a controlled bioreactor with artificial external feeding and acidified VFA. The results of the study can be applied in planning sludge acidification systems in the technological scheme of wastewater treatment and sludge processing.

Keywords: wastewater treatment; phosphorus removal; prefermentation; easily oxidizable organic matter; volatile fatty acids

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1. Introduction

Eutrophication is a predominantly anthropogenic phenomenon that affects aquatic biodiversity worldwide. Eutrophication is caused by a significant increase in nutrients (mostly nitrogen and phosphorus), which results in an increase in the productivity of aquatic ecosystems due to the intensive growth of microorganisms, mainly blue-green algae. The limiting factor of the development of algal blooms in water bodies is the concentration of soluble phosphorus. This means that the intensity of the eutrophication can be controlled by the efficient removal of phosphorus (P-removal) [1,2]. However, stable and efficient P-removal, as a rule, requires high costs.

Phosphorus (P) can be removed from wastewater by means of chemical treatment, biological treatment or a combination of biological and chemical methods.

Chemical P-removal considers the application of aluminum and iron salts as reagents. The use of lime increases the pH of the effluent water, which goes beyond the permissible limits, so it does not have frequent implementation. The chemicals can be input at several points of treatment sequence: before the primary sedimentation (pre-sedimentation); within the secondary treatment; before the tertiary treatment facilities (post-sedimentation); and to the return flows from the sludge treatment facilities [3].

P-removal has a strong link to the activity of polyphosphate-accumulating organisms (PAOs). Under anaerobic conditions, these bacteria consume acetate and propionate, storing them in the form of polyhydroxyalkanoates (PHAs).

At the same time, the formation of orthophosphates occurs because of the accumulation of reserve substances due to the energy released during the decomposition of polyphosphates. Under aerobic conditions, PAOs use energy in the form of PHAs and grow by consuming phosphates. As a result, the polyphosphate accumulated in the cells is being removed with excessive activated sludge from the treatment facilities. The aerobic and anaerobic zones should be separated within the aerobic sludge reactor (ASR) to implement biological P-removal. The anaerobic zone is often called the phosphorus removal zone; however, it is aimed at the release of phosphates into wastewater. To this end, a ratio of at least 15 g of biological oxygen demand (BOD) per 1 g of phosphorus (P) should be provided in the influent wastewater. In this regard, technological schemes with biological P-removal may have different modifications.

The biological and chemical methods of P-removal mean a combination of technological solutions inherent in the biological removal process in the ASR and the introduction of appropriate methods in cases of low organic matter concentration. In other words, it means that the BOD value is the limiting factor, which directly affects the stability of the biological P-removal.

In recent years, a large number of studies have been conducted and new technologies have been proposed for improved wastewater treatment from phosphorus compounds. The study in [4] proposes a method for combined wastewater treatment from phosphorus compounds and denitrification using a new type of sulfur–siderite composite ReF (SSCReF). By using SSCReF to construct packed-bed reactors, the highest denitrification and dephosphorization rates reached 829.70 $gN/m^3/d$ (25 wt % siderite) and 36.70 $gP/m^3/d$ (75 wt % siderite), respectively.

Paper [5] reports on the use of a new anode membrane (defective UiO-66 (D-UiO-66)/Graphite/Polyvinylidene fluoride (PVDF)) with zirconium, which enables one to achieve high efficiency in wastewater treatment, including removal of difficult-to-remove micropollutants such as antibiotics and phosphate-containing organic pollutants. A recent study [6] is devoted to the same issue. An electroactive metal–organic framework/carbon nanotube membrane has been developed that can retain most common antibiotics (tetracycline, norfloxacin, sulfamethoxazole, sulfamethazine) with an efficiency of up to 99.3%.

In cases of low BOD in the influent wastewater, the following measures can be taken: the introduction of an external carbon source [7], excluding primary sedimentation from the treatment sequence, or the acidification of raw sludge.

The introduction of an external carbon source, however, inevitably leads to an increase in operating costs for secondary treatment and requires the installation of special chemical facilities operating with hazardous compounds (acetic acid, methanol, etc.). Wastewater treatment without preliminary sedimentation leads to a decrease in the sludge retention time (SRT) and its excessive growth. It also requires additional oxidation of organic matter and nitrogen compounds, which results in higher operation costs for aeration [8].

Thus, the most promising method to increase the BOD value is the use of metabolic products from the first stage of the anaerobic digestion of sludge [9,10]. Within this study, improvement of the efficiency and stability of biological P-removal by means of raw sludge acidification will be considered [11–14]. The research will be focused on VFA formation, which can significantly increase the efficiency of phosphate-accumulating bacteria, with the following comparison to the introduction of pure acetic acid into the ASR.

Active research of acidification within wastewater treatment began in the 2010s, when more than 25 articles on this topic began to be published per year [15]. However, a literature review showed an insufficient number of studies carried out to date, despite the benefits of the technology. Acidification is mostly considered as part of sludge treatment. The study in [16] proposes innovative approaches to producing hydrogen fuel from sludge using acidification. As a result of sludge pre-treatment, the efficiency of obtaining free nitrous acid was increased.

Article [17] focuses on the preliminary fermentation to increase the methane yield during sludge anaerobic digestion. The polyacrylamide degradation efficiency increased from 30.6% to 80.1% under the optimal alkaline pre-fermentation condition (pH 10 for 12 d). Polyacrylamide strongly adheres to organic matter in sewage sludge (e.g., proteins) and significantly reduces the interaction between functional acidifying microorganisms and sludge substances. Alkaline fermentation breaks down long chains of polyacrylamide, segmenting them into individual short chains, which in turn affects the bonds between polyacrylamide and sludge substances, breaking them down, which increases the bioavailability of the sludge. Some recent works are devoted to the study of optimal technological parameters that increase the efficiency of preliminary fermentation [18–22]. Considering enzymes, a biocatalyst plays an important role in anaerobic digestion [23], which may also increase the VFA production and be a potential direction for future research. Another study was aimed at investigating the effect of various microorganisms on the VFA output concentration [24]. Some researchers are also considering the possibility of using this technology to increase the content of organic matter for industrial wastewater treatment [25,26]. However, the number of comprehensive studies is limited. In this regard, the current research will be aimed at studying the acidification potential and the effect of preliminary fermentation on P-removal from wastewater. The literature does not contain any results of parallel studies on the operation of a controlled bioreactor with artificial external feeding and acidified VFA.

2. Materials and Methods

The study was carried out in lab-scale conditions with wastewater and sludge samples obtained from existing wastewater treatment plants (WWTPs). The first part of the study investigates and compares acidification under variable conditions on the sludge samples from different WWTPs. Currently, researchers may perform comprehensive studies of acidification processes at WWTPs [27–30], but the results of the studies typically relate to a single type of sludge.

The current study included two stages. The purpose of the first stage of research was to study the effect of the technological parameters of the first step of the studied sludge's anaerobic digestion on the efficiency of VFA formation. For this part, four sludge samples from various WWTPs were taken. At the second stage of research, the P-removal efficiency was estimated by means of dosing a VFA solution from the sludge selected at the first stage of the study. Additionally, the study reveals the treatment efficiency when dosing a solution of acetic acid related to a constant model operating without an additional substrate.

Within the first stage of the study, laboratory experiments were carried out on the digestion of wastewater sludge (raw sludge from primary clarifiers) in plastic containers, which act as acidifiers or primary sedimentation tanks (Figure 1).

The sludge samples taken from primary clarifiers of the real WWTPs were placed in plastic containers (volume of 1 L) acting as acidifiers under variable temperature conditions from t = 14 to 30 °C. The temperature conditions of the fermented sludge were kept by means of a WTW TS 608/2-i thermostat (Xylem Analytics, San Diego, CA, USA); for heating, an AQUAEL cylindrical heater (AQUAEL, Warsaw, Poland) was used. Temperatures above 35 °C were not considered within the research since such conditions within WWTPs' operation lead to high operating costs. Also, some of the samples studied were mixed using magnetic stirrers. Based on the design features of the primary sedimentation tanks, the overlapping of tanks (acidifiers) in the upper part was not provided.

In the initial and fermented sludge, the following parameters were determined: temperature, pH, concentrations of VFA (C_{VFA}), ammonium nitrogen ($N\text{-}NH_4$), phosphorus ($P\text{-}PO_4$), and alkalinity. In the fermented sludge, measurement was carried out twice a week.

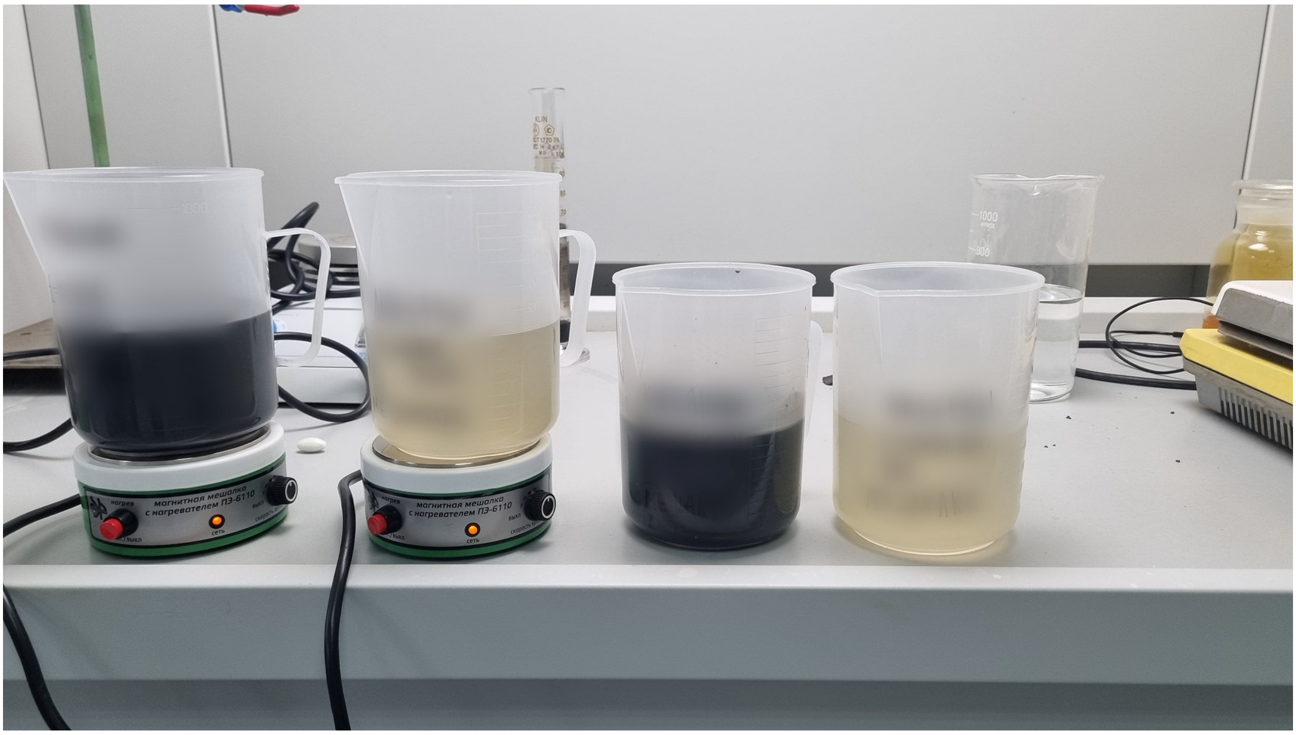


Figure 1. Tanks with test sludge from primary sedimentation tanks.

A HANNA Edge instrument with a pH sensor (Hanna Instruments, Woonsocket, RI, USA) was used to measure the temperature, °C, and pH.

C_{VFA} in the acetic acid was determined using the Hach Lange DR6000 instrument (Hach, Loveland, CO, USA). The esterification of carboxylic acids in the samples was carried out with the subsequent determination of esters by reaction with ferric hydroxamate.

N-NH_4 was determined by means of the LCK 302/LCK 303 cuvette test (Hach, Loveland, CO, USA) because of its accuracy and easy application. The essence of the method is that ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst for the formation of indophenol blue (ISO 7150-1 [31], DIN 38406E5-1 [32], UNI 11669:2017 [33]).

P-PO_4 was determined based on the orthophosphate reaction with molybdate in an acidic medium to form a mixed phosphate–molybdate complex. The ascorbic acid then reduces the complex, which gives the intense blue color of molybdenum, using Powder Pillows reagents (Hach, Loveland, CO, USA) with a measurement range of 0.02–2.5 mg/L.

Alkalinity was determined by titration of a water sample with a solution of hydrochloric acid before the color transition of the methyl orange indicator (alkalinity according to methyl orange). When titrating the water samples with a pH of 8.3 to 4.5 in the presence of an indicator providing a color transition, reactions occur between strong acid and hydrogen carbonate ions.

The second stage of the experiment was carried out on an automated laboratory unit—a bioreactor fermenter (Figure 2). The bioreactor (Yocell Biotechnology, Qingdao, China) is an 11 L borsilicate glass reaction tank with automated control of liquid, air, mixing rate, and temperature, which is also equipped with a module for analyzing the composition of the exhaust gas mixture (the module was not used in this work). The bioreactor operated in a combined mode with a separate anaerobic tank, which is similar to an anaerobic zone of an activated sludge reactor with the implemented treatment scheme of the University of Cape Town (UCT).

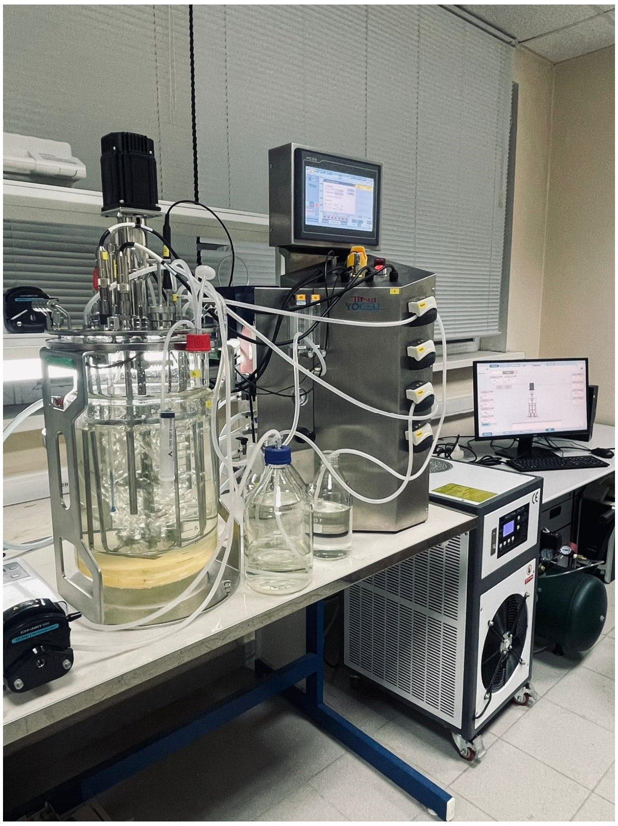


Figure 2. Laboratory reactor used in the wastewater treatment efficiency evaluation phase.

The supply and discharge of wastewater, as well as the interconnection between the reactor compartments, was carried out by means of peristaltic pumps.

The bioreactor is equipped with an automated data acquisition system for dissolved oxygen concentration (DO), liquid temperature, foam level, and pH. DO and pH were monitored using high-precision optical sensors—Hamilton VisiFerm DO and Hamilton Polilyte Plus pH ARC (Hamilton Company, Reno, NV, USA).

Concentrations of nitrogen and phosphorus compounds were measured using HACH Lange DR6000, and BOD was measured using WTW OxiTOP-IDS (Xylem Analytics, San Diego, CA, USA). The scheme of bioreactor operation is shown in Figure 3.

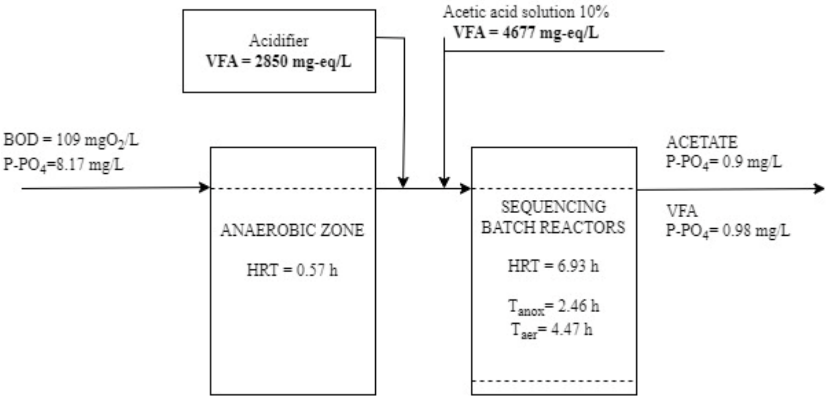


Figure 3. Scheme of laboratory bioreactor operation.

An experiment was carried out on real clarified wastewater from the existing WWTPs and synthesized wastewater prepared based on peptone with the addition of nitrogen and phosphorus salts. To verify the reproducibility of the results of the experiment on real and synthesized wastewater, a nonparametric analysis using the Monte Carlo method was performed. The experiment was carried out for 45 days, and chemical analyses were performed five times a week. The average characteristics of the incoming wastewater are presented in Table 1.

Table 1. Average characteristics of influent.

Parameter	Minimum	Medium	Maximum
BOD [mgO_2/L]	99	109	118
Suspended solids [mg/L]	77.24	94.94	109.19
P-PO_4 [mg/L]	7.7	8.17	8.61
N-NH_4 [mg/L]	18.95	25.25	29.58

A solution of acetic acid (10%) and supernatant water from the acidifier tank after sludge fermentation was used as an additional carbon substrate. Table 2 shows the average BOD and VFA content in the additional substrates.

Table 2. Average content of organic matter in the additional substrate.

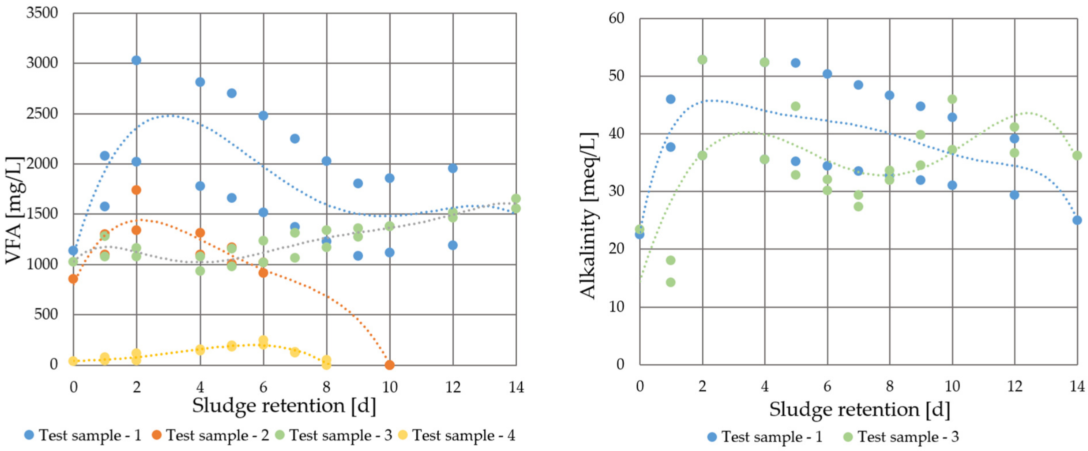
Parameter	Acidification	Acetic Acid
BOD [mgO_2/L]	432.1	860
VFA [mg/L]	2850	4677

3. Results

Figures 4–12 present the results of the preliminary fermentation study.

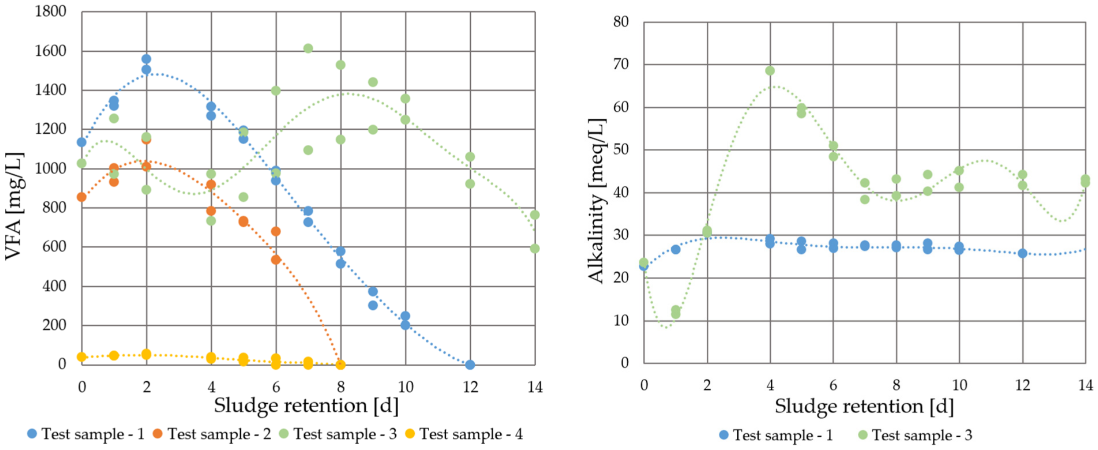
The C_{VFA} gradually decreases, reaching the initial values because the hydrogen fermentation of the sludge reaches its maximum and transforms into methane fermentation.

Within sludge retention in anaerobic conditions, alkalinity decreases to the minimum values of 14.23 meq/L (t = 14 °C), 11.38 meq/L (t = 20 ± 1 °C), and 20.87 meq/L (t = 30 °C), respectively. During the intensive VFA formation, only complex organic compounds are present in the sample, which is characterized by minimum values of HCO_3^- concentration. As a result of energy production due to the conversion of acetic acid by obligate anaerobes, which perform alkaline fermentation, an increase in the content of HCO_3^- is witnessed. During the observation, some of the samples do not show a significant change in alkalinity. This is due to slightly lower VFA concentrations compared to other samples studied, of which the fluctuations in alkalinity are more pronounced [34,35].



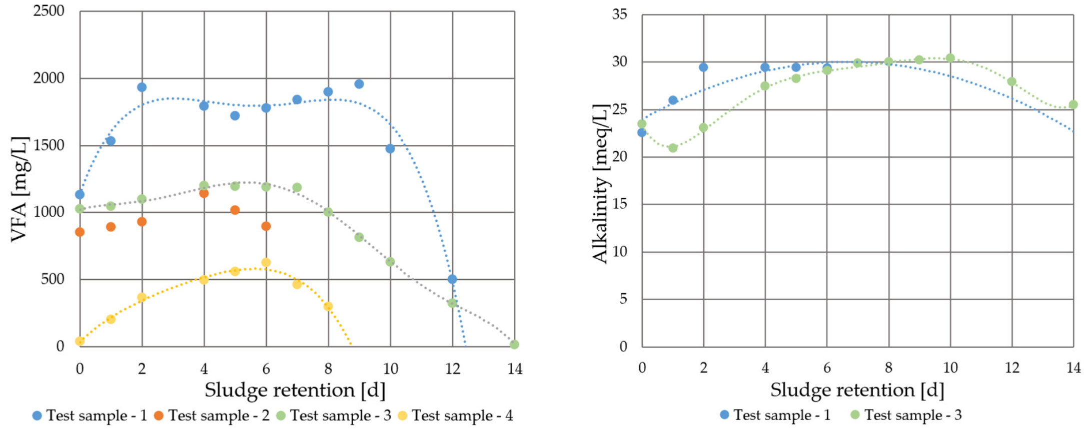
(**a**) (**b**)

Figure 4. Relation of the sludge retention under anaerobic conditions (t = 14 °C): (**a**) to C_{VFA}; (**b**) to alkalinity.



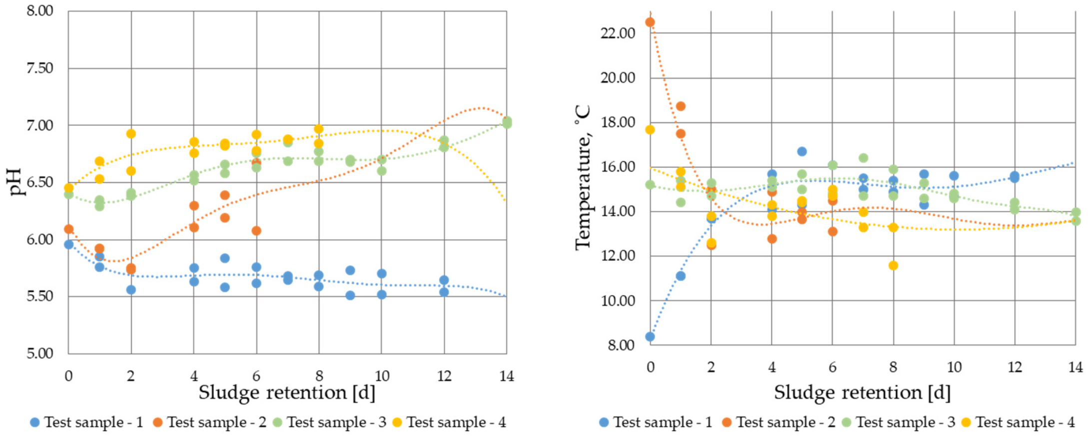
(**a**) (**b**)

Figure 5. Relation of the sludge retention under anaerobic conditions (t = 20 ± 1 °C): (**a**) to C_{VFA}; (**b**) to alkalinity.



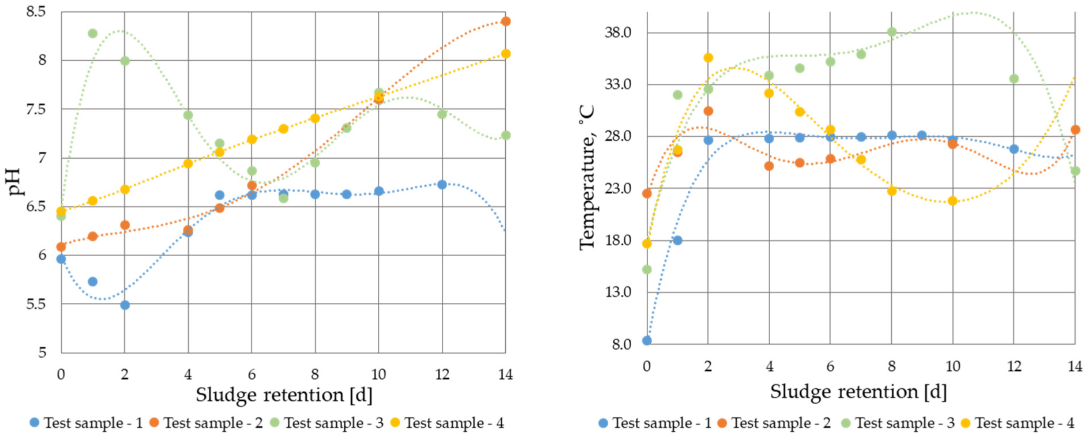
(**a**) (**b**)

Figure 6. Relation of the sludge retention under anaerobic conditions (t = 30 °C): (**a**) to C_{VFA}; (**b**) to alkalinity.



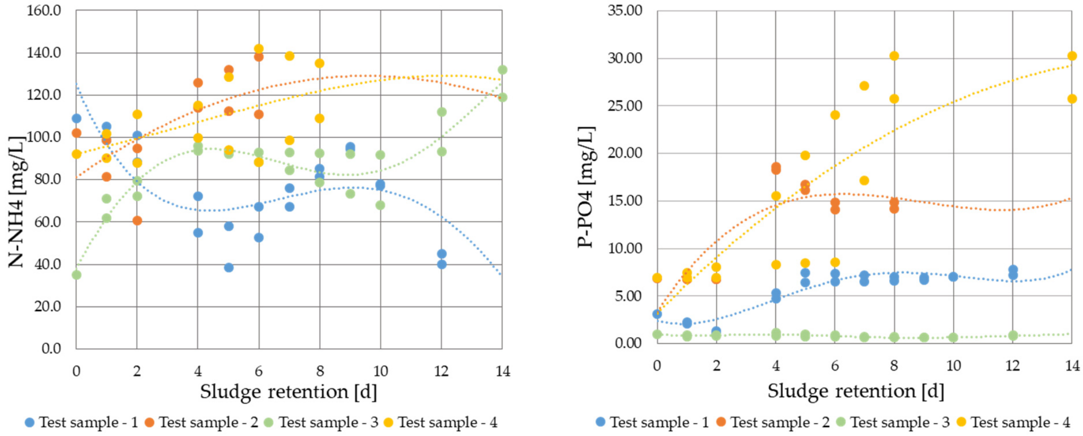
(**a**) (**b**)

Figure 7. Relation of the sludge retention under anaerobic conditions (t = 14 °C): (**a**) to pH; (**b**) to the temperature of the sludge.



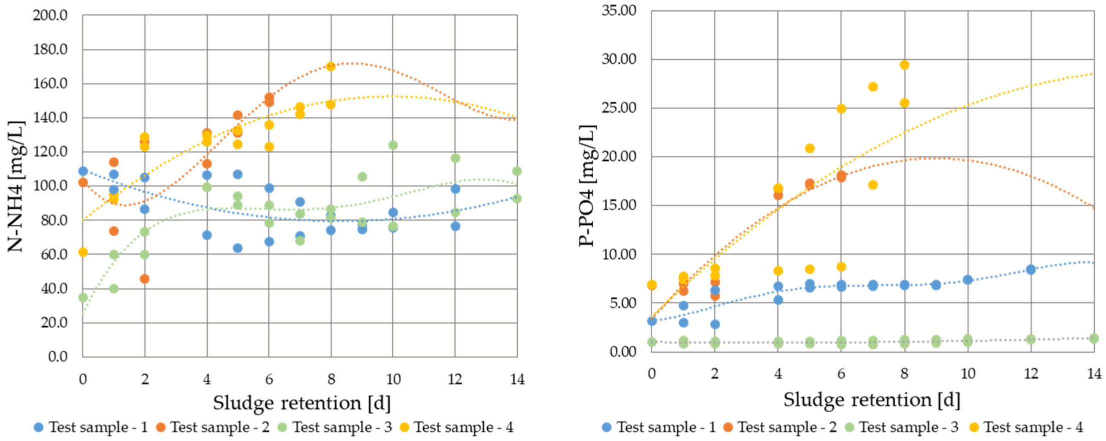
(**a**) (**b**)

Figure 8. Relation of the sludge retention under anaerobic conditions (t = 30 °C): (**a**) to pH; (**b**) to the temperature of the sludge.



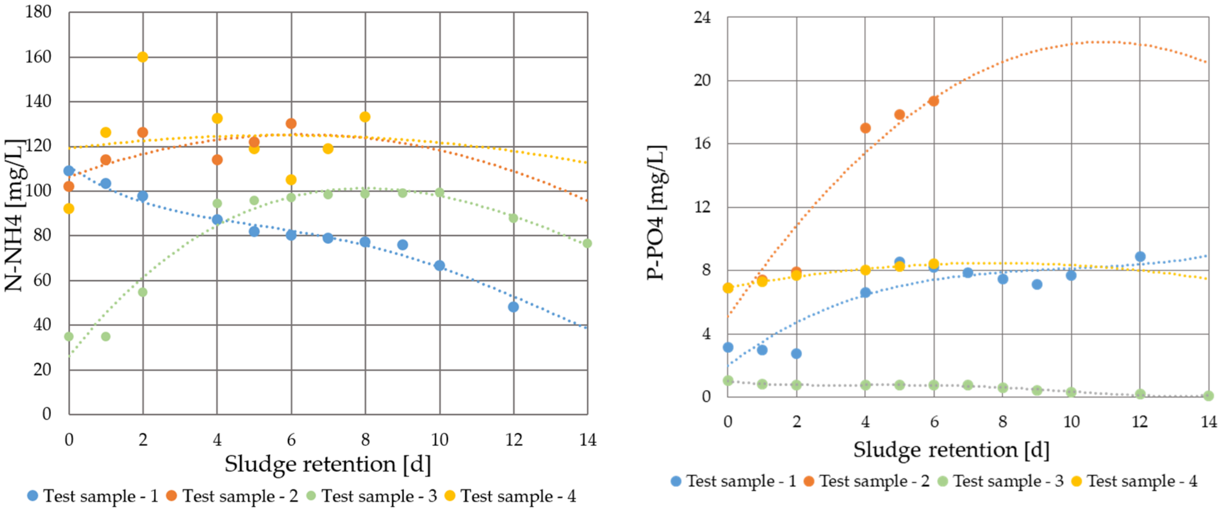
(**a**) (**b**)

Figure 9. Relation of the sludge retention under anaerobic conditions (t = 14 °C): (**a**) to N-NH$_4$; (**b**) to P-PO$_4$.



(**a**) (**b**)

Figure 10. Relation of the sludge retention under anaerobic conditions (t = 20 ± 1 °C): (**a**) to N-NH$_4$; (**b**) to P-PO$_4$.



(**a**) (**b**)

Figure 11. Relation of the sludge retention under anaerobic conditions (t = 30 °C): (**a**) to N-NH$_4$; (**b**) to P-PO$_4$.

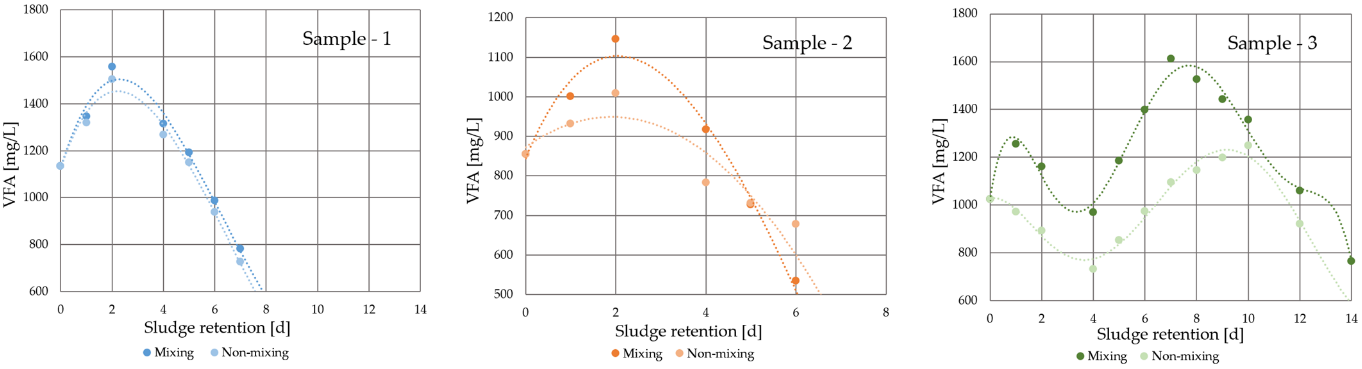


Figure 12. Impact of mixing on VFA formation.

The concentration of hydrogen ions is directly dependent on the origin of the influent wastewater. The optimal pH value is in the range of 5.5 to 7. The importance of the activity of hydrogen ions has a significant impact on the vital process of microorganisms, which are responsible for anaerobic digestion. In addition, a sharp change in the pH level has a negative impact on the rate of biochemical processes within the environment [15].

Figures 7 and 8 show a trend in the pH change in the process of anaerobic digestion of the sludge under research. The predominance of H$^+$ ions and, accordingly, a decrease in the concentration of hydrogen ions is explained by the formation of volatile fatty acids. Differences in pH dynamics during fermentation are associated with different microbial activity with different initial substrates.

The P-PO$_4$ concentration increases on average by 1.3–2 times relative to the initial values during the first five days of sludge retention in anaerobic conditions—a low background of increase in phosphorus compounds is created. Subsequently, longer sludge fermentation leads to a more intensive release of phosphorus. Considering fluctuations in the N-NH$_4$ concentration during the sludge acidification, an increase of 1.5–2 times relative to the initial values, on average, is revealed.

Mixing is another factor of influence on the concentration of the VFAs formed. To maintain the stability of the anaerobic digestion, constant mixing of raw sludge and wastewater should be provided. Mixing ensures the homogeneity of the environment, its uniform distribution throughout the volume of the tank, and prevents the formation of a crust in the upper part of the acid-forming mass. Overall, this means the best conditions for the development of bacteria and the course of the process.

Figures 13–16 reveals the research results of the P-removal. Since the lab bench operated according to a modified UCT scheme (combining plug-flow and sequenced principles of operation), phosphorus compounds and nitrogen compounds (ammonium nitrogen, nitrates, and nitrites) were considered as output parameters. However, the main interest is the efficiency of P-PO_4 removal. During the experiment, 30 chemical analyses were performed on the main parameters for three modes of operation: (1) with acetate supply; (2) with the supply of VFA solution obtained during sediment fermentation; and (3) without an additional organic substrate.

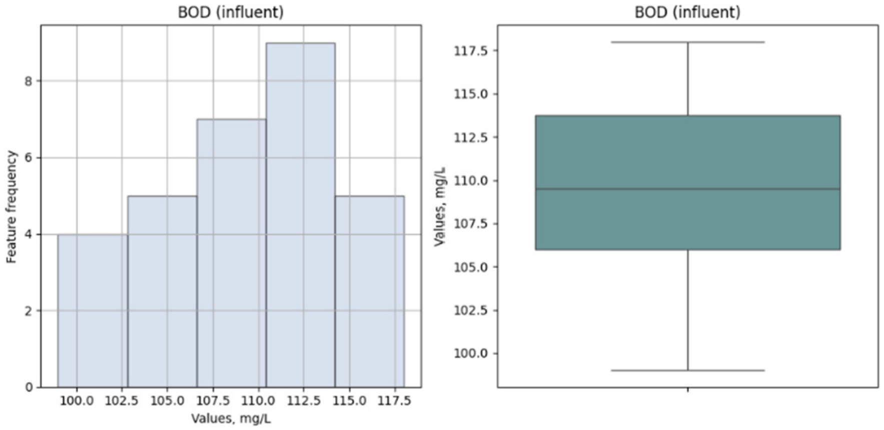


Figure 13. Boxplot and histogram of the influent—based on BOD_5.

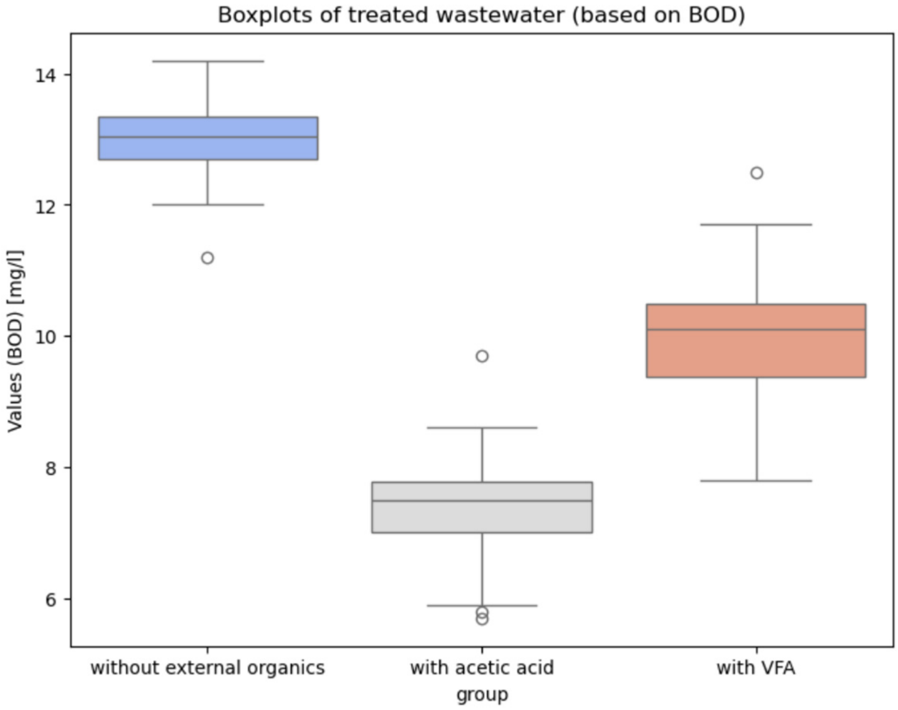


Figure 14. Boxplots of treated wastewater—based on BOD_5.

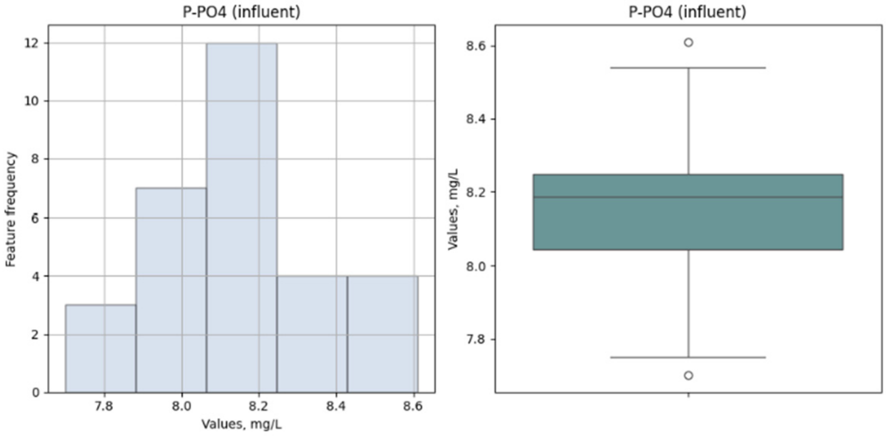


Figure 15. Histogram and boxplot for P-PO$_4$ in the influent.

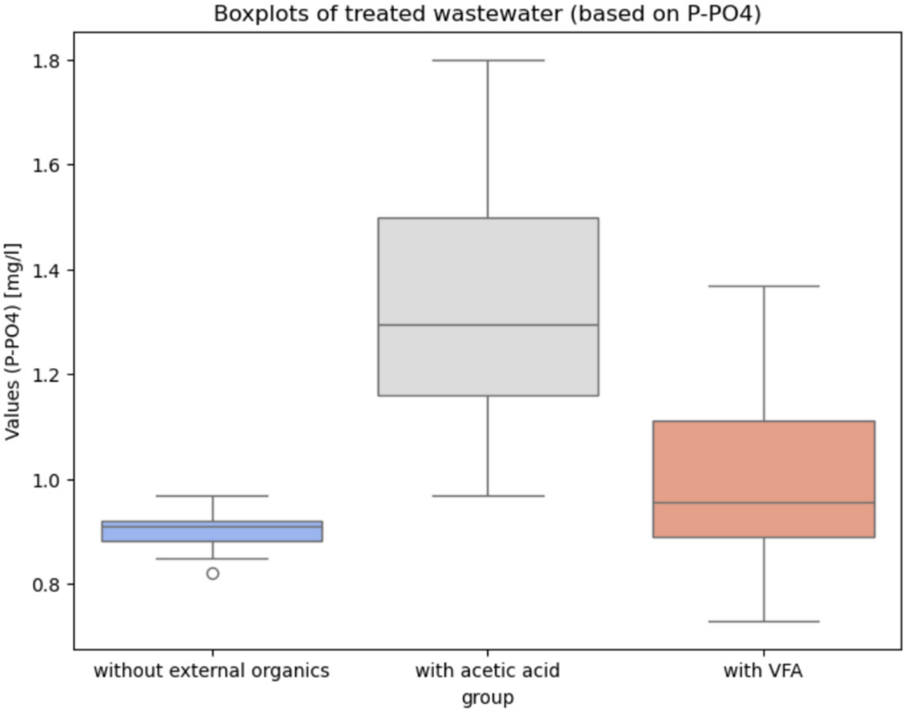


Figure 16. Boxplots of treated wastewater—based on P-PO$_4$.

At the second stage of the study, the data obtained from the analysis were processed as an assessment of the presence of outliers from the boxplots for all measured indicators.

The magnitude charts show the presence of data outliers, but the magnitude is not large enough to require the exclusion of these outliers. In this case, emissions are understood as values that go beyond the boundaries of the one-and-a-half interquartile interval.

Checking the normality of distribution using the Shapiro–Wilk test is required since visually there are doubts about the characteristics of the treated water. The null hypothesis H0 of the Shapiro–Wilk test is that a random variable whose sample is known is distributed according to a normal law. An alternative hypothesis for H1 is that the distribution law is not normal. The Shapiro–Wilk analysis showed that the distributions of all samples are normal.

Figure 17 shows normalized histograms of P-PO$_4$ values in treated wastewater. A bootstrap analysis was based on the Monte Carlo method to find the limit of the feasibility of the VFA substrate.

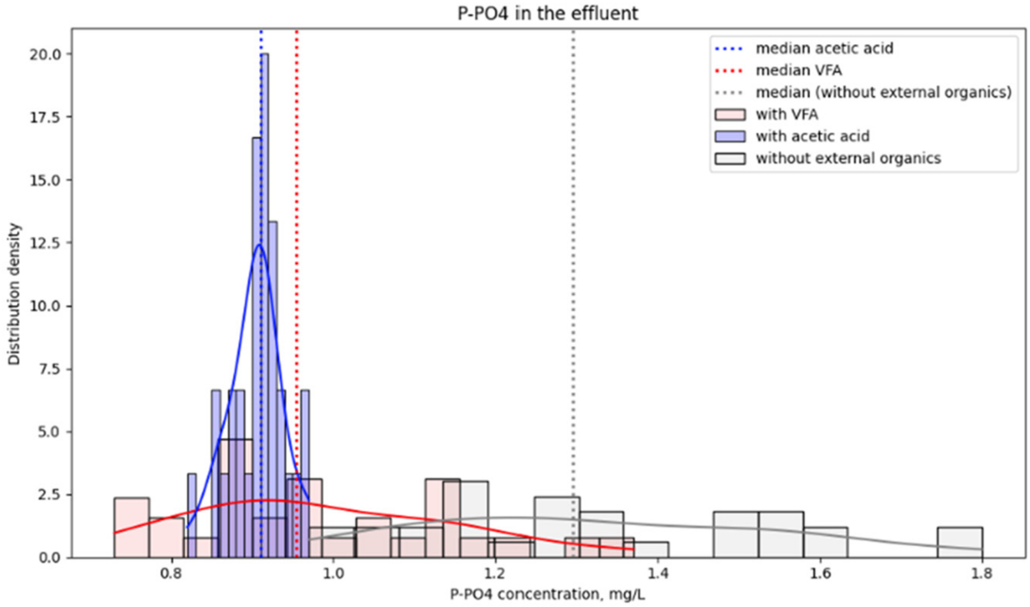


Figure 17. Histogram and boxplot for BOD in the effluent (without additional substrate).

According to the data considered, the average value of phosphates in treated wastewater with VFA is higher than in wastewater with acetate. A one-sided statistical analysis was performed according to Student's criterion, according to the results of which the null hypotheses, regarding the sample averages of the general sets of the results of the purification assays with VFA and acetate, were rejected for the values of BOD and P-PO$_4$. Thus, with a high probability, the average purification sets with VFA are still higher than with acetate. At the same time, the median value of the difference in the quality of treatment was only 0.045 mg/L with a phosphate detection limit of 0.05 mg/L (that is, the median difference is less than the detection limit).

It is important to compare the results of the study with the work carried out recently. First of all, it is interesting to compare the obtained acidification efficiency with the production tests carried out at the Kuryanovsk WWTP [27,29,30]. The characteristics of the Kuryanovsk sludge and the sludge considered in this article are similar, which indicates a possible similar acidification potential.

In studies [27,29,30], acidification in separate acidification facilities was carried out on sludge with an ash content of about 40% and enabled us to achieve an increase in VFA by more than 4 times under natural temperature conditions. This is commensurate with the results of the present study, according to which the increase reached a threefold increase with a lower acidification potential of the sludge.

This once again emphasizes the need to measure the acidification potential of the sludge each time before planning the implementation of the corresponding technology, since the economic efficiency of the measures may raise questions.

4. Conclusions

Within the research, a study of two technological processes typical for municipal WWTPs was carried out: acidification of raw sludge and subsequent biological P-removal. Based on the results of the research, the following conclusions can be drawn:

1. The largest increase in VFA in the raw sludge liquid during acidification is observed at temperatures in the range from 28 to 38 °C, while the increase relative to acidification at a normal ambient temperature (from 19 to 24 °C) is, in some cases, about 30%. At the same time, the results revealed that the maximum amount of organic matter is not always associated with an increase in the temperature of the fermented sludge. It also depends on the acidification potential of the incoming wastewater and raw sludge from the WWTP. Potential assessment is required each time it is planned

to implement sludge acidification measures, especially during the WWTP upgrade. Obviously, the need for sludge heating in most cases cannot be justified from an economic point of view; however, with an acceptable potential release of VFA at neutral temperatures, acidification will be justified. At the same time, in some cases sludge heating can be justified—such as in systems that already provide wastewater heating (for example, in the case of wastewater treatment in the northern regions). These decisions are of a single nature but should be taken into account, among other things, when calculating ASR.

2. The amount of VFAs formed during acidification is uniquely correlated with the intensity of mixing of the fermented sludge. The intensity of stirred digestion increased by more than 45% compared to non-stirring digestion. When designing sludge acidification, it is necessary to provide for the costs of installation and operation of mixing devices; the costs should also be considered in the life cycle of the WWTP.
3. The amount of $P\text{-}PO_4$ in wastewater without the introduction of an additional substrate during treatment turned out to be 35% higher than with the addition of acetate.
4. If the results of the assessment of the acidification potential of sludge and wastewater are positive, it is recommended to carry out a comparative assessment of the costs of chemical phosphorus removal. The results of the study showed that 7.54 mg/L of phosphorus (for active sludge, raw sludge, and wastewater) could be removed with a specified probability. It is recommended to compensate for the excess of this concentration by dosing acetic acid solution at a rate of 3800 meq/L of VFA per 1 mg/L of phosphorus phosphates. At the same time, the justified use of acetic acid seems to be equal to up to 7% of the capacity of treatment facilities. If it is necessary to dose a larger amount of the reagent, the chemical removal of phosphorus with a coagulant is more reasonable.

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