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Effect of peracetic acid disintegration on the acceleration of hydrolysis process

Iwona Zawieja*, Mariusz Barański

Faculty of Environmental Engineering and Biotechnology, Institute of Environmental Engineering, Czestochowa University of Technology, Brzeznicka 60a, 42-200 Czestochowa, Poland Email: izawieja@is.pcz.czest.pl

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ABSTRACT

Excess sludge is difficult to be processed and it is hydrolytically degraded under both anaerobic and aerobic conditions, since a high proportion of the sludge comprise living micro-organisms. The key phenomenon that occurs during the process of disintegration of sewage sludge is destruction of cell walls in micro-organisms caused by physical, chemical or biological factors. Consequently, sludge is fragmented and some intracellular components are released into the surrounding liquid. In order to determine the best parameters of acid disintegration of excess sludge, the study examined the effectiveness of oxidizing treatment with peracetic acid. STERIDIAL W 15 solution, which is a mixture of PAA (15%), hydrogen peroxide (10%), acetic acid (36%) and water (39%) was used in the study. Pre-treatment in the ambient temperature prior to the period of 1 and 24 h was conducted. The doses of peracetic acid of 0.1-5 mL of STERIDIAL/L of excess sludge were used (as for the organic dry matter content corresponds to the about 0.01–0.66 mL of STERIDIAL/g $dm_{org.}$). The volatile fatty acid and COD levels obtained after acid pre-treatment of excess sludge were corrected by taking into account the value of those parameters originating during the PAA hydrolysis in the water surrounding. For non-pre-treatment and undergoing chemical modifications of the sludge, the organic dry matter content was 7.56 g/dm^3 . In the case of non-pre-treatment sludge, the value of volatile fatty acids 51 mg CH₃COOH/L was recorded. During the chemical disintegration lasting 24 h, volatile fatty acids content of 171 mg CH₃COOH/L and 5734 mg CH₃COOH/L was obtained, respectively, for the low dose i.e. 0.1 mL of STERI-DIAL/L of sludge and the highest dose i.e. 5 mL of STERIDIAL/L of sludge. The value of chemical oxygen demand (COD) for non-pre-treatment and chemically conditioned sludge after using the above doses amounted, respectively, to 102, 222 and $5432 \text{ mg O}_2/\text{L}$. The content of volatile fatty acids correlated with the observed level of COD.

Keywords: Excess sludge; Pre-treatment; Peracetic acid; Volatile fatty acids; Chemical oxygen demand

*Corresponding author.

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1. Introduction

Treatment of sewage sludge represents a serious sanitary threat. Using new or technologically advanced methods imposed by legal conditions (i.e. Resolution No. 217 of the Council of Ministers of 24 December 2010 on the "National Waste Management Plan 2014") concerning limitation in their storage is both a required and necessary solution. The need for implementation of disintegration technologies in sewage sludge processes is connected with observed in recent years' deterioration of sludge susceptibility to anaerobic stabilization [1].

This phenomenon is particularly unfavourable in huge wastewater treatment plants where a dominant method of stabilization is methane fermentation which leads to stabilization of the sludge and generation of biogas. Biogas is particularly desirable since it allows for partial recovery of costs of fermentation. Decrease in the susceptibility of excess sludge to biochemical decomposition is primarily due to using highly effective methods of wastewater treatment in the process of removing biogenic compounds using the method of activated sludge. Another reason is a high degree of thickening of the sludge obtained in mechanical equipment. Various methods have been used to intensify the process of biomass distribution under anaerobic conditions, for example, hybrid disintegration conducted using a homogenizing mixer and sonication. As a result of hybrid disintegration, the effect of cell lysis was obtained five times higher than in the case of the same ultrasonic disintegration. For 3-min homogenization of 6.7 min of sonication in disintegration OL-Myl, the most beneficial effect of disintegration was achieved, defined in relation to expended specific energy is about 0.3 kWh/kg dm of sludge [2]. The use of chemical processing before anaerobic stabilization positively affects hydrolysis. The increase in sewage sludge susceptibility to biochemical decomposition under anaerobic conditions leads to intensification of the biogas generation. The biogas can be utilized for generation of energy and allows for partial recovery of the energy used for processing the sludge.

Sludge disintegration is one of the processes of conditioning. It consists in destruction of the structure of the sludge through application of external forces. The aim of this process, in the case of excess sludge, is to release components in cells in order to ensure faster and more intensive sludge stabilization. This leads to changes in the structure and deactivation of micro-organisms contained in the sludge. This causes a reduction in the size of sludge particles. The organic components contained in the sludge are also released as a result of destruction of cell membranes with the conditioning medium [3]. Intensification occurs in particular in the first hydrolytic phase of fermentation, causing shortening of its duration and acceleration of the growth of bacteria of the acid and methane phases. A criterion for the evaluation of the obtained effects of disintegration is usually an increase in biogas recovery due to the opportunities for using it for energy purposes. Another important factor is increased mineralization of the sludge and the related improvement in sludge dewatering capacity [4–6]. Other benefits derived from disintegration include changes in rheological properties of sludge and therefore reduction in the costs of transport, mixing and heat exchange in the systems of the fermentation chamber [2].

It is essential that before choosing a method, both technological and economic analysis should be carried out in consideration of such factors as installation capacity, expected effects of disintegration, operating costs of disintegration equipment, balance of utility costs and the costs connected with sludge processing [7].

Chemical methods of disintegration can be divided into the methods of advanced oxidation based on Fenton's reaction, hydrogen peroxide and ozone, and the ones using a strong acid or alkali in the amount that causes pH reaching close to extreme values [8,9]. For example, during some tests conducted by Jeongsika et al. [10] alkaline conditioning performed the following reagents: NaOH, KOH, Mg (OH)₂, Ca(OH)₂. At a constant ambient temperature, the degree of disintegration of the organic substances after the process of conditioning, amounted, respectively, to said alkali: 39.8, 36.6, 10.8 and 15.3%. In the dose range of 7–21 g NaOH/dm³, there was a slight increase in the disintegration of organic matter in conditioned sludge.

Penaund et al. [11] found that a significant increase in the concentration of organic substances in dissolved form obtained at a dose of 5g NaOH/L during the process at ambient temperature, i.e. the degree of disintegration of organic material was 65%. Takumura et al. [12] applied a similar advanced oxidation method of photo-Fenton reaction to WAS in a batch photo reactor for disintegration purpose. The soluble chemical oxygen demand (SCOD) was achieved at the highest level in the presence of 4 g H_2O_2/L , 40 mg Fe (II)/L and 3,000 mg MLSS/L, pH 3 for 6 h reaction time and effective disintegration was obtained. At a longer than 6 h retention time, COD decreased and mineralization occurred. While Nevens et al. [13] applied Fenton process to thickened sludge and they noted an optimum activity in the presence of 25 g H₂O₂/kg DS, and 1.67 g Fe(II)/kg DS, pH 3 and at ambient temperature and pressure. In these conditions, Fenton process resulted in a considerable reduction of dried solid (DS) and volatile solid (VS) contents in the filter cake of approximately 20%, an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase in the cake DScontent when compared with the untreated sludge sample PAA disinfection has already been utilized in some WWTPs and US EPA has included PAA among five disinfectants recommended for use on combined sewer overflows [14].

Due to its chemical properties, peracetic acid belongs to the group of reactive microbicidal compounds. The substances belonging to this group, including aldehydes, undergo some chemical transformation due to the substances contained in the cell or/ and cell membrane.

Therefore, their mechanism is non-specific, which limits the opportunities of developing immunity [15].

It can be noted based on the changes in physical and chemical properties of the chemically stabilized sludge that peracetic acid causes oxidation of some part of organic suspensions of sludge while deactivating sludge micro-organisms [16].

Dosing suitable chemical reactants in excess sludge causes a rise or reduction in pH and causes some changes in ionization of protein components and consequently leads to the loss of activity in enzymes and some decline in biological activity [17]. One of the benefits of PAA disinfection is that it does not produce any significant amounts of toxic or mutagenic DBPs or chemical residues into effluents [18,19].

The oxidation of organic compounds by peracetic acid takes place through formation of hydroxyl radicals. These radicals further react with the organics according to the following reaction: $RH + OH^* \rightarrow H_2O + R^*$. The organic radical produced will, in its turn, further react with other components. Peracetic acid degrades into water and acetic acid, the latter being highly biodegradable [20].

The aim of the study was to determine the effect of initial processing of excess sludge which was submitted to chemical pre-treatment with the use of peracetic acid on the acceleration of the hydrolysis process i.e. intensification of volatile fatty acids (VFAs) generation and chemical oxygen demand (COD) value.

2. Experimental

2.1. Characterization of the substrate in the study

The sludge was sampled from Warta Sewage Treatment Plant in Czestochowa, Poland. Excess activated sludge samples used for the investigations were taken immediately before mechanical densification. Due to following consecutive stages of research, sludge was taken regularly at about three-week intervals in between, which had an impact on the scale of differences concerning its physical and chemical parameters.

During the first stage of research, the most favourable parameters of chemical disintegration process were determined with the use of peracetic acid basic substrate being excess sludge with the following physical and chemical parameters: dry matter 11,67 g/L, organic dry matter 8.94 g/L, mineral dry matter 2.73 g/L, volatile fatty acids 152 mg O_2/L and chemical oxygen demand 102 mg O_2/L .

During the next stage of research, sludge was subjected to eight-day anaerobic stabilization. There were four processes of methane fermentation of excess sludge subjected to different methods of preparation, inoculated to initiate the process of sludge digesting. The substrate in the second stage of study was excess activated sludge (90% of mixture) and fermented sludge (10% of mixture) which represented the *inoculum*. In the case of the process carried out, each one of the eight flasks, each day a support sludge sample was used in order to assess the effectiveness of the stabilization process.

The process of methane fermentation was carried out in eight glass laboratory flasks, which performed the role of fermentation chambers. The laboratory flasks with the volume of 0.5 dm³ were protected from air access with plugs with diameter of 33 mm and glass liquid-column gauges, which allowed the generated biogas to discharge. They were placed in a laboratory thermostat at the temperature of 37 °C. The flasks were mixed manually, once a day, in order to mix the whole volume of the sludge and prevent generation of the skin on the surface and creation of the areas overloaded with contaminants.

Table 1 presents some characteristics of physical and chemical parameters used for examinations of excess sludge before pre-treatment and fermented sludge which were the components for mixtures AD.

The following mixtures of sludge were subjected to methane fermentation:

- Mixture A—non-pre-treatment excess sludge + fermented sludge;
- (2) Mixture B—chemical pre-treatment excess sludge with the reactant's dose equal 0.1 mL of STERIDIAL/L of sludge (0.02 mL of STERI-DIAL/g dm_{org}.) + digested sludge;
- (3) Mixture C—chemical pre-treatment excess sludge with the reactant's dose equal 0.5 mL of STERIDIAL/L of sludge (0.07 mL of STERI-DIAL/g dm_{org}.) + digested sludge; and

Parameters mixture	Dry mass	Min. dry matter	Org. dry matter	VFAs	COD		
Mixture A	Digested sludge (inoculum)						
	g/Ľ	Ğg∕L	g/L	mg CH ₃ COOH/L	mg O_2/L		
	18.03	6.38	11.65	822.86	1357.50		
	Non-pre-treatment excess sludge						
	8.98	1.99	6.99	102.86	65.00		
Mixture B	Digested sludge (inoculum)						
	15.30	5.01	10.29	720.00	1125.00		
	Non-pre-treatment excess sludge						
	8.35	2.16	6.19	162.86	86.00		
Mixture C	Digested sludge (inoculum)						
	17.84	5.41	12.43	205.71	1004.00		
	Non-pre-treatment excess sludge						
	10.96	3.29	7.68	120.00	89.00		
Mixture D	Digested sludge (inoculum)						
	10.74	3.49	7.26	257.14	1051.00		
	Non-pre-treatment excess sludge						
	10.97	3.29	7.68	120.00	96.00		

Physical and chemical properties of the sludge used in the study during second stage of research (mixture AD)

(4) Mixture D—chemical pre-treatment excess sludge with the reactant's dose equal 2.5 mL of STERIDIAL/L of sludge (0.33 mL of STERI-DIAL/g dm_{org}.) + digested sludge.

2.2. Conditions of acid disintegration of excess sludge

The aim of the research work was to settle the most important conditions of chemical pre-treatment. It was a commercial STERIDIAL W—15 preparation, which is a concentrate containing 15% solution of peracetic acid, hydrogen peroxide, acetic acid and water in an equilibrium mixture. The preparation is caustic and exhibits strong oxidative properties. It is used as a disinfectant, bleach and as an oxidant in chemical preparation [21].

In order to determine the most favourable conditions, the effect of peracetic acid (CH₃COOOH) was verified for the doses of 0.1 mL of STERIDIAL/L of sludge 5 mL of STERIDIAL/L of sludge. The authors carried out 1 and 24-h processes of sludge conditioning with peracetic acid in the liquid form. The choice of the most advantageous dose was made based on the increase in concentration of organic compounds in sludge liquor, conditioned excess sludge, expressed in COD and VFA.

The chemical modification was carried out at ambient temperature in sealed bottles whose contents were stirred by hand.

Obtained after the process of chemical disintegration, values of VFA and COD were adjusted by the value of these parameters derived from deposits placed on the dose of peracetic acid and acetic acid contained in the applied formulation. It was assumed that the peracetic acid in aqueous media is completely decomposed to acetic acid. An additional COD value derived from the incorporated dose of reagent can be calculated from the relation 1.07 g O₂/g CH₃COOH. [20]. The adjustment carried out in further incorporates the percentage of peracetic acid and acetic acid in the preparation and its density.

In order to determine the efficiency of the disintegration process using peracetic acid, the authors determined the degree of sludge disintegration.

According to Thiem et al. [22] the degree of disintegration was determined from the relationship:

$$DD_{COD} = [(COD_{dis.} - COD_0) : (COD_a - COD_0)] \times 100\%$$
(1)

where DD_{COD} —degree of disintegration, %; $COD_{dis.}$ and COD_0 —COD in disintegrated and raw sludge liquors, respectively, mg O₂/L; COD_a —COD in referential sludge sample subjected to chemical disintegration by means of 1 M solution of NaOH with the ratio of 1:1, at the temperature of 90 °C for 10 min, mg O₂/L.

2.3. Conditions of methane fermentation of excess sludge

The laboratory tests were aimed at determination of the efficiency of hydrolysis process of sewage sludge during methane fermentation after disintegration by means of the acid method. The process of

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Table 1

methane fermentation was carried out in eight glass laboratory flasks which performed the role of fermentation chambers. Before the process was started, laboratory flasks with volume of 0.5 L had been protected from the access of air with plugs with diameter of 33 mm and glass liquid-column gauges, which prevented the flow of oxygen. The content of the flasks, placed in a laboratory thermostat at the temperature of 37°C, was mixed once a day manually in order to mix the whole volume of the sludge and prevent the formation of the scum and the areas overloaded with contaminants.

The following physical and chemical determinations were carried out:

- (1) pH using pH metre (Cole Palmer 59002-00), according to PN-9/C-04540/05 standard [23],
- (2) dry matter, organic dry matter and mineral dry matter (PN-EN-12879) [24],
- (3) volatile fatty acids (VFA) by means of distillation with water vapour (PN-75/C-04616/04) [25], and
- (4) chemical oxygen demand (COD) by means of the dichromate method (PN-74/C-04578/03) [26].

The degree of sludge fermentation (R) expressed reducing the amount of organic compounds was calculated according to the equation [27]:

$$R = \frac{c - \frac{ab}{100 - b}}{c} \times 100\%$$
 (2)

where *R*—the degree of sludge fermentation, %; *a*—an inorganic substance in the percentage of the initial dry mass; *b*—the organic substance in the final percentage of dry mass; and *c*—the organic substance in the initial percentage of dry mass.

2.4. Results

2.4.1. Choosing the most advantageous parameters of chemical disintegration of excess sludge with peracetic acid

It was demonstrated based on the results obtained in the study that the increase in the dose of peracetic acid caused the increase in concentration of organic compounds expressed with the level of COD in the sludge liquor and VFA.

Table 2 presents the effect of the dose of peracetic acid on the increase in the value of concentration of organic compounds in sludge liquor of the disintegrated excess sludge expressed with COD. Table 2

Effect of reactant's dose on concentration of organic compounds in the excess sludge liquor conditioned with STERIDIAL for 1 h

Dose of STERIDIAL	pН	COD ₀	COD _{dis.}	COD ₀ / COD _{dis.}	DD _{COD}
mL of STERIDIAL/ L of sludge	-	mg O ₂ /L	mg O ₂ /L	-	%
0*	6.94	102	_	_	_
0.1	7.74	102	144	1/1	1.3
0.2	7.53	102	416	1/4	9.9
0.5	7.01	102	492	1/5	12.3
1.0	6.4	102	1048	1/10	29.8
1.5	5.79	102	1407	1/14	41.1
2.0	5.18	102	1872	1/18	55.7
2.5	5.07	102	2210	1/22	66.4
5.0	4.43	102	4910	1/48	151.4

Notes: 0^{*} sample of non-pre-treatment sludge, control sample. COD_{dis.}—values of COD levels obtained after acid pre-treatment corrected by taking into account the value of these parameters originating from the PAA hydrolysis in the water.

Regarding the disintegration of the sludge with peracetic acid with the dose of 0.1 mL of STERIDIAL/ L of sludge for 1 h, COD was twice higher compared to the control sample, whereas in the case of the dose of 5 mL of STERIDIAL/L of sludge, COD was 48times higher compared to the control sample (i.e. COD in the non-conditioned sludge). Furthermore, in the sludge chemically disintegrated for 24 h (Table 3) with the dose of 0.1 mL of STERIDIAL/L, COD was doubled compared to the initial level of this parameter; with the highest dose in the range studied (5 mL of STERIDIAL/L of sludge), COD was 47-times higher compared to the control sample. Increasing the dose of peracetic acid caused a considerable increase in the value of COD in the sludge liquor (Tables 2 and 3) and VFA value (Fig. 1). For the technological reasons, the time of 1-h disintegration was regarded as sufficient: a similarly real increase in the COD and VFA was obtained compared to the disintegration carried out for 24 h.

The results obtained by Xu, G. et al. [25] showed that O_3 dose and pH had a positive impact on sludge disintegration. The organic substrates were released into the liquor, which induced the increases of SCOD and turbidity in the aqueous phase.

In the case of the doses of peracetic acid as a disintegration agent i.e. 0.1 mL of STERIDIAL/L of sludge, 0.2 mL of STERIDIAL/L of sludge, 0.5 mL of STERI-DIAL/L of sludge, pH obtained after pre-treatment was optimal for the process of fermentation carried out during the next stage of the study. Regarding

Table 3

Effect of reactant's dose on concentration of organic compounds in the excess sludge liquor conditioned with STERIDIAL for 24 h $\,$

Dose of STERIDIAL	pН	COD ₀	COD _{dis.}	COD ₀ / COD _{dis.}	DD _{COD}
mL of STERIDIAL/ L of sludge	-	mg O ₂ /L	mg O ₂ /L	-	%
0*	6.94	102	_	_	_
0.1	7.48	102	209	1/2	3.4
0.2	7.37	102	318	1/3	6.8
0.5	7.05	102	569	1/6	14.7
1.0	6.12	102	1079	1/11	30.8
1.5	5.35	102	1504	1/15	44.2
2.0	4.89	102	1985	1/19	59.3
2.5	4.54	102	2425	1/24	73.2
5.0	4.06	102	4799	1/47	147.9

Notes: 0^{*} sample of non-pre-treatment sludge, control sample. COD_{dis.}—values of COD levels obtained after acid pre-treatment corrected by taking into account the value of this parameters originating from the PAA hydrolysis in the water.



Fig. 1. Changes in VFA in the sludge liquor depending on the reactant's dose and conditioning time.

higher doses of the reactant, in order to prevent any disturbances in the process flow, the pH correction to the value of 7.0 is recommended as it is considered to be optimum in the fermentation technology.

2.4.2. Anaerobic stabilization process in the laboratory scale

In order to evaluate the effectiveness of the method of disintegration aimed at increasing the sludge susceptibility to biodegradation, the authors employed a process of eight-day anaerobic stabilization of excess sludge and sludge after chemical modification with the reactant's doses studied i.e. 0.1 mL of STERIDIAL/L of sludge, 0.5 mL of STERIDIAL/L of sludge and 2.5 mL of STERIDIAL/L of sludge, mixtures B, C and D, respectively. The fermented sludge, which was inoculum, represented 10% of the mixture. The process was controlled through determination of the values of degradation degree, volatile fatty acids and chemical oxygen demand. In the case of the mixture D, the authors used a correction of pH to the value of 7.0, using a suitable dose of sodium hydroxide solution with the ratio of 1:1 until a pH appropriate for proper process of methane fermentation was reached.

Disintegration of excess sludge before the process of anaerobic stabilization contributed to increased generation of volatile fatty acids and to distribution of organic compounds contained in the excess sludge. As it was mentioned in the theoretical part above, anaerobic stabilization necessitates destruction of cell membranes in the micro-organisms contained in the excess sludge. This effect was achieved by chemical disintegration of the excess sludge. The result of anaerobic stabilization was confirmed based on the increase in the VFA content in the sludge liquor compared to the initial level. In order to confirm that anaerobic stabilization occurred properly, VFA content was adopted as a control parameter, with its level increasing with respect to the initial value.

Regarding mixtures A, B, C and D, the content of organic dry matter before the process was 7.14; 6.54; 7.93 and 7.84 g/L, respectively.

The anaerobic stabilization of the processes yielded the following degrees of fermentation:

- (1) mixture A: 18.7%,
- (2) mixture B: 24%,
- (3) mixture C: 27.5%, and
- (4) mixture D: 34%.

Figs. 2 and 3 present changes in the content of volatile fatty acids and COD reported on the following days of anaerobic stabilization of the mixtures studied.

On the following days of the anaerobic stabilization of the sludge samples after chemical modification, the increase in content of volatile fatty acids was observed compared to stabilization of the raw sludge. The highest VFA content (771.43 mg CH₃COOH/L) in the mixture A was reported on the 3rd day of the process. Furthermore, in the case of the chemical method which used the reactant with the dose of 0.1 mL of STERIDIAL/L of sludge, (mixture B) the highest VFA content (354.29 mg CH₃COOH/L) was found on the 4th day of the process. The use of the reactant dose of 0.5 mL of STERIDIAL/L of sludge (mixture C), the content of VFA of 1302.86 mg CH₃COOH/L was found on the 4th day, whereas the highest increase in VFA compared to the initial value was observed on the 5th day of the process (1457.14 mg CH₃COOH/L)



Fig. 2. Changes in the content of volatile fatty acids reported during eight-day anaerobic stabilization of the mixtures studied (mixtures AD).



Fig. 3. Changes in the chemical oxygen demand reported during eight-day anaerobic stabilization of the mixtures studied (mixtures AD).

Regarding the obtained increase in VFA content, the most effective conditions of the process appeared during chemical disintegration with peracetic acid with the dose of 2.5 mL of STERIDIAL/L of sludge, with VFA reaching 3257.14 mg CH₃COOH/L on the 4th day of the process.

According to Neyens et al. [13,26] the use of Fenton pre-treatment could possibly enhance the anaerobic digestion and dewaterability of the waste activated sludge. These authors concluded that such improvement was caused by disintegration of extracellular polymeric substances and breakdown of cell walls, thus releasing intracellular water. It was also found that the amount of soluble COD and BOD in the sludge water increased considerably.

It can be concluded based on the results obtained in the study that the increase in COD depends on the reactant's dose. Application of the peracetic acid with the dose of 0.1 mL of STERIDIAL/L of sludge (mixture B) contributed to a considerable (compared to COD reported during anaerobic stabilization of unconditioned sludge—mixture A) increase in COD level. The highest value was reached on the 4th day (2360 mg O_2/L). This relationship was confirmed by the results concerning the process of stabilization of chemically disintegrated sludge with the dose of the peracetic acid of 2.5 mL of STERIDIAL/L of sludge (mixture D). The maximum value was reached on the 2nd day of fermentation (3316 mg O_2/L).

3. Conclusions

The conducted study showed that the excess sludge which was conditioned before the process of anaerobic stabilization was more susceptible to generation of volatile fatty acids. The ability of organic matter to transform is an important factor in the process of anaerobic stabilization.

The obtained effect of susceptibility of the excess sludge to biodegradation was evaluated based on COD level in the sludge liquor which was previously disintegrated chemically compared to the initial value.

- (1) A direct effect of chemical disintegration of the excess sludge was an increase in concentration of organic compounds in the sludge liquor expressed with the value of chemical oxygen demand (COD) and volatile fatty acids (VFA) content, which was observed as a result of initiation of the processes of hydrolysis of cells in micro-organisms.
- (2) Regarding acid disintegration of excess sludge, the most advantageous dose (with respect to the technological conditions of methane fermentation) was 0.5 mL of STERI-DIAL/L of sludge, which yielded for the disintegration for 1 h, a level of 12.3% disintegration of the excess sludge and a nine-time increase in the value of VFA, reported with respect to the initial value of this parameter. Furthermore, in the case of disintegration that took 24 h, a 14.7% degree of disintegration was obtained for excess sludge and 12-time increase in VFA compared to the initial level of this parameter for the proper fermentation process.
- (3) Based on the results, the study confirmed that disintegration with the duration of 24 h, compared to the degree of disintegration of the sludge and an increase in volatile fatty acids found during the process which took 1 h, showed no significant increase in the analysed values. Furthermore, in the case of the doses of peracetic acid as a disintegration agent i.e. 0.1 mL of STERIDIAL/L of sludge, 0.2 mL of STERIDIAL/L of sludge and 0.5 mL of STERI-DIAL/L of sludge, pH was optimal for the

process of fermentation carried out during the following stage of the study. Using the dose of 2.5 mL of STERIDIAL/L of sludge for the disintegration of the sludge necessitated correcting the pH value to 7.0 before the process of stabilization, which is advantageous for the growth of micro-organisms that exist in anaerobic conditions.

- (4) During the eight-day methane fermentation of raw excess sludge and the chemically disintegrated sludge it was found that the process of initial modification of the excess sludge has an essential effect on acceleration of the hydrolytic and acidogenic phases of the process. A considerable increase in the content of volatile fatty acids and accelerated loss of organic substances was observed in the sludge after disintegration.
- (5) In the case of the process of anaerobic stabilization of the chemically modified excess sludge i.e. mixtures C and D with the doses of 0.5 and 2.5 cm³ CH₃COOOH/L, respectively, the highest degree of fermentation was obtained for the mixture D (34%), which, on the 4th day of the process, exhibited VFA content of 3257.14 mg CH₃COOH/L. The process of anaerobic stabilization of the mixture C yielded the degree of sludge fermentation of 27.5% and the maximum value of VFA, recorded on the 5th day of the process (1457.14 mg CH₃COOH/L).

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