

## Effect of hydrogen peroxide on nitrogen forms in sewage sludge subjected to the anaerobic stabilization

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#### ABSTRACT

Changes in the forms of nitrogen in sewage sludge depend on the value of pH, process temperature and its amount in the substrate used for biodegradation. These forms have a significant effect on methane fermentation processes. In the water environment, ammonium nitrogen contained in organic compounds is subjected to ammonification and transformed into the mineral form of ammonium nitrogen. The aim of this study was to determine the effect of chemical modification of excess sewage sludge with an oxidative reactant on the value of Kjeldahl nitrogen and ammonium nitrogen observed during anaerobic stabilization. After the process of 8 and 25 d anaerobic stabilization of non-conditioned and chemically disintegrated excess sludge, the proposed sludge modification was found to have an effect on the increase in Kjeldahl nitrogen and ammonium nitrogen levels. The doses of sludge reactants were equal to 1.0 and 5.0 mL H,O,/L, and time of contact with sludge was 2 h. In the case of methane fermentation of sludge subjected to chemical disintegration using hydrogen peroxide, on the 8th day of the methane fermentation, the values of Kjeldahl nitrogen and ammonium nitrogen were equal to 322 N/L and 314 mg N-NH<sub>4</sub>/L, respectively, for dose 1 mL/L of sewage sludge, and equal to 344 N/L and 342 mg  $N-NH_4/L$  for dose 5 mL/L of sewage sludge. In addition, on the 25th day of methane fermentation, the values of Kjeldahl and ammonium nitrogen were 567 N/L and 551 mg N-NH4/L, respectively, for dose 1 mL/L of sewage sludge, and were 598 N/L and 586 mg N-NH<sub>4</sub>/L for dose 5 mL/L of sewage sludge.

*Keywords:* Excess sewage sludge; Chemical disintegration; Hydrogen peroxide; Methane fermentation; Kjeldahl nitrogen; Ammonium nitrogen

#### 1. Introduction

The physical and chemical properties as well as structural characteristics of sewage sludge are determined by the type of treated wastewater, the methods of their purification and the unit processes used for their treatment. Depending on the technological conditions of biological sludge treatment, excess sludge demonstrates different susceptibility to the process of biological decomposition under anaerobic conditions and, consequently, different susceptibility to the dewatering process [1–6].

Excess sludge represents a heterogeneous mixture composed of the suspension of living and dead microorganisms and their sporulated forms [7]. In order to release biologically bound compounds present in living organisms, excess sludge has been subjected to disintegration processes. The hydrogen peroxide disintegration increased the accessibility of sludge to the anaerobic microorganisms. Solubilization facilitates the usage of soluble compounds with low molecular weights by the microorganisms, which increasing biodegradability of modified sludge [8]. Hydrogen peroxide is an environmentally friendly oxidative reactant since its decomposition products include water and oxygen [9]. The increase in the hydrogen peroxide dose improves the efficiency of contaminants oxidation [10–13].

According to Wong et al. [14], the ammonia concentration in sludge supernatant is found to be very sensitive to

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hydrogen peroxide concentration. During hydrogen peroxide disintegration, it is likely that the organic nitrogen present in the sludge is being converted to soluble nitrogen, in either ammonia or nitrate and (or) nitrite forms. During the research conducted by Eskicioglu et al. [15], the concentration of ammonium nitrogen in the supernatant of excess sludge after hydrogen peroxide disintegration increase over the initial control value. In the case of disintegration, a dose of 1 g  $H_2O_2/g$  total solids (TS) was used. The initial value of ammonium nitrogen was 106 mg N-NH<sub>4</sub>/L and for modified sewage sludge by hydrogen peroxide equal 284 mg N-NH<sub>4</sub>/L.

As reported by Yin et al. [16], initial sludge concentration and hydrogen peroxide dosage are the most important factors, which control nutrient solubilization.

Nitrogen contained in sewage sludge occurs in large amounts in the form of easily available compounds. These forms of nitrogen account for 30%-50% of total content of this compound. Nitrogen occurs mainly in the ammonium form, whereas its remaining part is contained in organic connections. Kjeldahl nitrogen and ammonium nitrogen are important indicators determined in the methane fermentation process of excess sludge. Kjeldahl nitrogen contains ammonium nitrogen and organic nitrogen. In the process of anaerobic decomposition of organic substances, organic nitrogen is transformed into ammonium nitrogen. The efficiency of ammonium nitrogen formation depends on the load of the fermentation chamber in which the process takes place. During the breakdown of proteins during fermentation, organic nitrogen in 75%-90% turns into ammonium nitrogen (anaerobic ammonification). According to the information provided by Jędrczak [17], the presence of nitrogen in the raw material is necessary for two reasons: (1) it is an important component for the synthesis of amino acids, proteins and nucleic acids, and (2) it is converted to ammonia, which neutralizes volatile acids produced by fermentation bacteria, thus enabling the maintenance of the neutral reaction of the environment necessary for their growth.

In the process of anaerobic stabilization, organic nitrogen is transformed to ammonium nitrogen, whereas its part is integrated into biomass. Binding organic nitrogen in biomass depends on the C:N ratio in substrates. The optimal value for the C:N ratio is 10:1-25:1. If the maximal value is exceeded, methanogenic bacteria use nitrogen, leading to the decrease in the amount of the produced biogas. Furthermore, if the lowest value is exceeded, nitrogen is released in the form of ammonia, resulting in higher pH in the environment, which has a negative effect on the state of nitrogen equilibrium and methanogenic bacteria. The efficiency of ammonium nitrogen generation depends on process temperature and load to the fermentation chamber with organic substances. The increase in the content of ammonium nitrogen is caused by the ammonification process [17,18]. With methane fermentation, organic compounds that contain nitrogen and phosphorus undergo hydrolysis and decomposition, which leads to the release of biogenic compounds to supernatant water. In wastewater treatment plants, these waters are returned to bioreactors in order to continue treatment. The generation of soluble chemical oxygen demand (SCOD) from excess sludge during partial oxidation is a good carbon source for a denitrification. Many researchers connect the solubilization with a reusing of sewage sludge

for a biological denitrification. However, high concentration of biogenic substances in post-fermentation waters can lead to the overload of activated sludge and consequently result in reduced efficiency of removing biogenic compounds and higher treatment costs [19–23].

Chemical modification, increasing the disintegration degree of sludge, affects the intensification of metabolic processes occurring during anaerobic stabilization. As a result of these changes, the value of ammonium and Kjeldahl nitrogen increases, which may be toxic to methanogenic microorganisms.

The aim of this study was to determine the effect of chemical modification of excess sewage sludge with an oxidative reactant on the value of Kjeldahl and ammonium nitrogen observed during anaerobic stabilization.

#### 2. Experimental part

#### 2.1. Substrate

The substrate for the experiment was excess sludge (90%) and fermented sludge (10%) used as inoculum. The sludge was sampled from municipal wastewater treatment plant with a capacity of about 45,000 m<sup>3</sup>/d (314 835 PE), which is a mechanical and biological treatment plant with increased biogenic compounds removal [24]. Due to the nature of the conducted research, sediments from the installation of a large wastewater treatment plant were selected for laboratory experiments. Sludge treatment technology operating in this plant allows for the potential and effective implementation of the disintegration process. Selected samples were subjected to analysis and technological research on the day of collection. All determinations were made using a three-point repetition.

Sewage sludge used for the examinations was sampled directly before mechanical thickening. Table 1 presents a general characterization of the substrate used in the study.

#### 2.2. Methodology

During the first stage of the research, the evaluation of the effects of chemical disintegration method on excess sludge were performed by means of conditioning process using a solution of hydrogen peroxide at 3% concentration. Six reactant doses were used in the examinations, that is: 0.5, 0.75, 1.0, 5.0, 7.5 and 9 mL of hydrogen peroxide solution per 1 L of sludge (0.03, 0.04, 0.06, 0.28, 0.42 and 0.5 mL of hydrogen

Table 1

General characteristic of the substrate used in the study

TS, g/L	$21.34\pm0.9$
VSS, g/L	$17.94 \pm 1.5$
SCOD, mg O <sub>2</sub> /L	$140 \pm 7.2$
Alkalinity, mg CaCO <sub>3</sub> /L	$240\pm11.5$
Kjeldahl nitrogen, mg N-NH+/L	$42 \pm 2.1$
Ammonium nitrogen, mg N/L	$25 \pm 1.1$
pH	$7.2 \pm 0.02$

TS – total solids; VSS – volatile suspended solids; SCOD – soluble chemical oxygen demand.

peroxide solution per 1 g VSS), whereas the time when the specific doses were in contact with excess sludge used in the study was 2 h. Chemical disintegration consisted in adding of the previously specified doses of hydrogen peroxide solution to the samples with excess sludge, mixing them and leaving for a set time at room temperature. The volume of each sample was 0.5 L.

The methane fermentation process is spontaneous. The limiting phase of the process, significantly affecting the stabilization efficiency, is hydrolysis, occurring during the first days of methane fermentation. The direct effect of the hydrolysis process is the increase in the SCOD value, which indicates the increase of the concentration of organic substances in the dissolved form. This increase is observed in the first days of methane fermentation; therefore, the research results for the selected, first 8 d of fermentation were presented. Solubilization of excess sludge reveals a general indication of the extent of hydrolysis [25].

In addition, the research was supplemented by the results obtained after the completion of the fermentation process, that is, on the 25th day of the process. During the research on methane fermentation, anaerobic stabilization was continued for 8 d, in order to evaluate the effect of chemical disintegration of sewage sludge on contents of ammonium nitrogen and Kjeldahl nitrogen. The 8-h fermentation process was carried out in mesophilic conditions in 10 glass flasks, which are models of the fermentation chamber. In the next research cycle, the process of 25 d of anaerobic stabilization of sludge was carried out in the fermentation chamber made in the form of a glass cylinder with an active volume of 5 L. The content of Kjeldahl nitrogen and ammonium nitrogen in the case of 25 d stabilized sludge under anaerobic conditions were assessed.

Anaerobic stabilization was subjected to unprepared sludge and sludge prepared with hydrogen peroxide in two doses, the selection of which was made on the basis of preliminary research.

The following mixtures of sludge were subjected to methane fermentation:

- Mixture A: non-conditioned excess sludge + fermented sludge;
- Mixture B: excess sludge, chemically disintegrated using hydrogen peroxide solution with the dose of 1 mL per 1 L of sludge + fermented sludge;
- Mixture C: excess sludge, chemically disintegrated using hydrogen peroxide solution with the dose of 5 mL per 1 L of sludge + fermented sludge.

The following physicochemical determinations were made:

- volatile suspended solid according to PN-EN-12879 [26];
- pH using pH meter (59002 00, Cole Palmer, USA),
- according to PN-9/C-04540/05 [27],
- alkalinity according to PN-91/C-04540/05 [27],
- soluble chemical oxygen demand (SCOD) by means of the dichromate method according to ISO 7027 [28],
- Kjeldahl nitrogen (PN-73/C-04576/10) [29],
- ammonium nitrogen (PN-73/C-04576/02) [30].

In order to evaluate the effectiveness of the disintegration process, the degree of disintegration was determined according the following formula [31]:

$$DD_{COD} = (SCOD_1 - SCOD_2) / (SCOD_3 - SCOD_2) \times 100$$
(1)

where  $DD_{COD}$  – disintegration degree, %;  $SCOD_1$  – SCOD level in the pretreatment sludge, mg O<sub>2</sub>/L;  $SCOD_2$  – SCOD level in the non-pretreated sludge, mgO<sub>2</sub>/L;  $SCOD_3$  – SCOD level in the sludge modified chemically 1-mol NaOH with ratio 1:1, temperature 90°C for 10 min, mg O<sub>2</sub>/L.

In addition, the digestion degree of excess sludge was determined, expressing the loss of volatile suspended solids that occurs as a result of methane fermentation [32].

The SCOD of chemically modified excess sludge, which is the reference value for determining the disintegration degree, was equal to  $2,838 \text{ mg O}_2/\text{L}$ .

During the study, the method used for the onset of SCOD was colorimetric method with potassium dichromate ( $K_2Cr_2O_7$ ) as an oxidizing agent, described in Standard Methods [28]. As per the reported data,  $H_2O_2$  interferes with the COD analysis by consuming the oxidizing agent which, in the case of the method used, is  $K_2Cr_2O_7$ , which directly affects the over estimation of SCOD [33]. It should be noted that, based on literature data, 1 mg  $H_2O_2$  is equivalent to 0.25 mg  $O_2$ . Consequently, the results obtained for COD were corrected, taking into account the hydrogen peroxide content in the supernatant liquid [34].

#### 3. Results and discussion

### 3.1. Determination of the conditions of excess sludge chemical disintegration

The choice of the most effective dose of hydrogen peroxide solution was made based on the examinations using the following reactant doses: 0.5, 0.75, 1.5, 7.5 and 9 mL of hydrogen peroxide solution per 1 L of sludge. Modification time was 2 h. The choice of the most advantageous conditioning parameters was made based on the value of SCOD, with reference to the value of Kjeldahl nitrogen and ammonium nitrogen levels. Table 2 presents selected physical and chemical determinations of disintegrated excess sludge.

According to Oeller et al. [35], Arslan and Balcioglu [36], and Wiśniowska [37], the process of chemical oxidation with strong oxidizing agents, that is, hydrogen peroxide contributes to the degradation of non-biodegradable organic compounds contained in sewage sludge, what determines the increase of SCOD value.

As a result of the chemical modification with hydrogen peroxide, for selected dosage of reagent, that is, 0.5, 0.75, 1.0 and 5.0 mL  $H_2O_2/L$  of sludge the SCOD as well as disintegration degree ( $DD_{COD}$ ) values increased. The Kjeldahl and ammonium nitrogen values were slightly increased. However for dosage of reagent, that is, 7.5 and 9.0 mL  $H_2O_2/L$  of sludge, the SCOD and disintegration degree ( $DD_{COD}$ ) values decreased. Moreover, it was noticed that the Kjeldahl and ammonium nitrogen values decrease. The decrease in the value of the examined indicators for the applied higher doses of hydrogen peroxide is caused by the mineralization of organic substances contained in the sludge. It should be emphasized that in addition to other staining reagents, ozone used alone as a reagent, due to less intensive degradation of carbon–carbon covalent bonds, is less effective in solubilizing

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Dose of reagent (mL $H_2O_2/L$ of sludge)	рН	SCOD (mg O <sub>2</sub> /L)	DD <sub>cod</sub> (%)	Kjeldahl nitrogen (mg N/L)	Ammonium nitrogen (mg N-NH⁺/L)
0.5	$7.34\pm0.02$	$180 \pm 12$	2.6	$43 \pm 2.1$	$26 \pm 1.4$
0.75	$7.31\pm0.03$	$206 \pm 15$	3.5	$44 \pm 1.8$	$29 \pm 1.6$
1.0	$7.25\pm0.06$	$221 \pm 18$	4.1	$49 \pm 1.4$	$39 \pm 1.8$
5.0	$7.18\pm0.03$	$872 \pm 12$	27.9	$45 \pm 2.4$	$36 \pm 0.8$
7.5	$7.03\pm0.03$	$643 \pm 23$	19.5	$42 \pm 2.6$	$28 \pm 1.1$
9.0	$6.97\pm0.04$	$312 \pm 8$	7.4	$39 \pm 1.9$	$25 \pm 1.7$

Selected physical and chemical determinations of excess sludge subjected to disintegration using hydrogen peroxide for 2 h

 Table 3

 Anaerobic stabilization of non-conditioned excess sludge (Mixture A)

Methane fermentation time (d)	TS (g/L)	VSS (g/L)	pН	Alkalinity (mg CaCO <sub>3</sub> /L)	SCOD (mg O <sub>2</sub> /L)
1	$15.87\pm0.37$	$11.76\pm0.41$	$6.48\pm0.01$	$660 \pm 11$	$218 \pm 9$
2	$15.32\pm0.49$	$11.45\pm0.63$	$6.47\pm0.03$	$820 \pm 9$	$595 \pm 12$
3	$14.43\pm0.52$	$10.69\pm0.66$	$6.66\pm0.02$	$720 \pm 14$	$813 \pm 16$
4	$13.87\pm0.82$	$9.97 \pm 0.83$	$7.00\pm0.02$	$1,080 \pm 24$	$1,042 \pm 21$
5	$13.11\pm0.73$	$9.51 \pm 0.34$	$6.74\pm0.04$	$1,100 \pm 21$	1,263 ± 1 7
6	$12.76\pm0.82$	$8.86 \pm 0.49$	$7.09 \pm 0.05$	$1,180 \pm 17$	$1,193 \pm 14$
7	$11.54\pm0.64$	$8.75\pm0.23$	$7.09 \pm 0.03$	$1,220 \pm 15$	1,116 ± 21
8	$11.07\pm0.87$	$8.69 \pm 0.74$	$7.14\pm0.02$	$1,300 \pm 14$	$1,038 \pm 24$
25	$10.54\pm0.43$	$7.23\pm0.58$	$7.06\pm0.04$	$2,150 \pm 23$	$354 \pm 15$

organic matter contained in sludge [38]. But the undisputed advantage is that hydrogen peroxide yields no noxious or polluting byproducts, its only byproducts are water and oxygen [39].

#### 3.2. Anaerobic stabilization of non-conditioned excess sludge

The process of methane fermentation was used for the mixture of non-conditioned excess sludge and fermented sludge (with the latter performing the role of inoculum) with the ratio of 10:1 (Mixture A). Anaerobic stabilization of non-conditioned sludge was performed in order to achieve the results that represent the reference for the obtained values after anaerobic stabilization of chemically disintegrated sludge.

Table 3 presents the results of selected physical and chemical determinations obtained in the case of the Mixture A. The determinations were performed on each day of the methane fermentation cycle.

Fig. 1 presents changes in Kjeldahl nitrogen concentration and ammonium nitrogen concentration depending on the day of the cycle.

During the anaerobic stabilization of non-conditioned excess sludge, the highest SCOD value of 1,263 mg  $O_2/L$  was obtained in the 5th day of process, and recording 39% digestion degree in the 25th day.

Figs. 1 and 2 illustrate changes in Kjeldahl nitrogen and ammonium nitrogen recorded during anaerobic stabilization of non-conditioned sludge.



Fig. 1. Changes in Kjeldahl nitrogen of non-conditioned excess sludge on consecutive days of methane fermentation process.



Fig. 2. Changes in ammonium nitrogen of non-conditioned excess sludge on consecutive days of methane fermentation.

Table 2

The values of the contents of the indices presented on the chart were increasing on consecutive days of the process. During the 8 d of methane fermentation, the lowest values of Kjeldahl nitrogen and ammonium nitrogen of 165 mg N/L and 70 mg N-NH<sub>4</sub>/L, respectively, were found on the first day of the process. The highest levels of both nitrogen forms were observed on the 8th day of the process, reaching 288 mg N/L for Kjeldahl nitrogen and 277 mg N-NH<sub>4</sub>/L for ammonium nitrogen. During the 25th day of methane fermentation, it was observed that Kjeldahl nitrogen and ammonium nitrogen value equal to 456 mg N/L and 432 mg N-NH<sub>4</sub>/L.

# 3.3. Anaerobic stabilization of excess sludge after chemical disintegration using the hydrogen peroxide solution with the dose of 1 mL per 1 L of sludge

Anaerobic stabilization was performed for the mixture of excess sludge (90%), chemically disintegrated with the solution of hydrogen peroxide with the dose of 1 mL per 1 L used as a reactant for 24 h, and fermented sludge (10%) (Mixture B). Physicochemical determinations were performed on each day of the 8-d methane fermentation process.

Table 4 presents the results of the determinations for Mixture B.

During the anaerobic stabilization of excess sludge chemically disintegrated with the reactant dose of 1 mL of hydrogen peroxide solution per 1 L of sludge, the highest SCOD value of 1,898 mg  $O_2/L$  was obtained in the 7th day of the process, and recording 57% digestion degree in the 25th day of the process. A similar tendency of increase in the degree of solubility of sewage sludge by hydrogen peroxide oxidation was noted by Tak-Hyun Kima et al. [25].

Figs. 3 and 4 present changes in Kjeldahl nitrogen and ammonium nitrogen, which gradually increased with duration of methane fermentation process.

During the 8 d of methane fermentation, the highest value of Kjeldahl nitrogen and ammonium nitrogen was found on the 8th day of the process and reached 322 mg N/L and 314 mg N-NH<sup>+</sup>/L, respectively. The lowest values of the above contents of nitrogen forms were observed on the first day of the process and reached 151 mg N/L and 143 mg N-NH<sup>+</sup>/L, respectively. In the case of methane fermentation lasting 25 d, it was observed that the value of Kjeldahl nitrogen and ammonium nitrogen was equal to 567 mg N/L and 551 mg N-NH<sub>4</sub>/L.

3.4. Anaerobic stabilization of excess sludge after chemical disintegration using the hydrogen peroxide solution with the dose of 5 mL of the solution per 1 L of sludge

Another process was conducted. It was 8 d of anaerobic stabilization of the excess sludge (90%) subjected to chemical disintegration with hydrogen peroxide solution with the dose of 5 mL per 1 L sludge for 24 h and fermented sludge (10%) (Mixture C). Selected physicochemical determinations were performed on each day of methane fermentation and are presented in Table 5.



Fig. 3. Changes in Kjeldahl nitrogen in excess sludge modified with hydrogen peroxide on consecutive days of methane fermentation process.



Fig. 4. Changes in ammonium nitrogen in excess sludge modified with hydrogen peroxide on consecutive days of methane fermentation process.

Table 4

Anaerobic stabilization of excess sludge chemically disintegrated with the reactant dose of 1 mL of hydrogen peroxide solution per 1 L of sludge (Mixture B)

Methane fermentation time (d)	TS (g/L)	VSS (g/L)	рН	Alkalinity (mg CaCO <sub>3</sub> /L)	SCOD (mg O <sub>2</sub> /L)
1	$24.87 \pm 0.67$	$19.59 \pm 0.34$	$7.29 \pm 0.02$	920 ± 12	$891 \pm 14$
2	$24.11 \pm 0.45$	$18.34\pm0.28$	$7.11\pm0.01$	$1,\!040\pm17$	$997 \pm 18$
3	$20.75\pm0.87$	$16.71\pm0.48$	$7.19\pm0.03$	$1,160 \pm 21$	$1,293 \pm 28$
4	$20.12\pm0.32$	$16.30\pm0.56$	$7.28\pm0.02$	$1,240 \pm 18$	$1,456 \pm 54$
5	$19.87\pm0.12$	$15.57\pm0.27$	$7.11 \pm 0.03$	$1,320 \pm 11$	$1,\!755\pm48$
6	$18.95\pm0.65$	$14.81 \pm 0.58$	$7.27\pm0.02$	$1,380 \pm 23$	$1,834\pm28$
7	$18.05\pm0.35$	$14.60\pm0.47$	$7.26\pm0.05$	$1,500 \pm 25$	$1,898 \pm 32$
8	$17.34\pm0.78$	$13.55\pm0.63$	$7.29\pm0.04$	$1,580 \pm 14$	$1,776 \pm 35$
25	$15.26\pm0.38$	$8.36 \pm 0.58$	$7.12\pm0.01$	$2,640 \pm 36$	$451 \pm 18$

Table 5

Anaerobic stabilization of excess sludge chemically disintegrated with the reactant dose of 5 mL of hydrogen peroxide solution per 1 L of sludge (Mixture B)

Methane fermentation time (d)	TS (g/L)	VSS (g/L)	pН	Alkalinity (mg CaCO <sub>3</sub> /L)	SCOD (mg $O_2/L$ )
1	$23.11 \pm 0.59$	$18.43 \pm 0.59$	$6.98 \pm 0.03$	$700 \pm 15$	$976 \pm 17$
2	$21.98 \pm 0.74$	$18.25\pm0.74$	$6.94\pm0.02$	$900 \pm 12$	$1,264 \pm 34$
3	$21.23 \pm 0.39$	$17.49\pm0.39$	$7.01\pm0.05$	$940 \pm 23$	1,387 ± 37
4	$20.67\pm0.65$	$16.98\pm0.65$	$6.99\pm0.04$	$1,160 \pm 31$	$1,438 \pm 25$
5	$19.78\pm0.25$	$13.79\pm0.25$	$6.96\pm0.03$	$1,300 \pm 28$	$1,646 \pm 47$
6	$16.65\pm0.58$	$12.51 \pm 0.58$	$7.03\pm0.05$	$1,480 \pm 16$	$1,854 \pm 25$
7	$15.43\pm0.76$	$11.74 \pm 0.76$	$7.04\pm0.06$	$1,580 \pm 12$	$2,154 \pm 23$
8	$14.18\pm0.47$	$11.45\pm0.47$	$7.09\pm0.03$	$1,640 \pm 18$	$2,237 \pm 43$
25	$10.56\pm0.37$	$7.21 \pm 0.37$	$7.24\pm0.05$	$3,120 \pm 21$	$418 \pm 16$



Fig. 5. Changes in Kjeldahl nitrogen in excess sludge modified with hydrogen peroxide on consecutive days of methane fermentation process.

Fig. 5 presents changes of Kjeldahl nitrogen and ammonium nitrogen depending on the day of the cycle.

Chemical disintegration of excess sludge with the reactant dose of 5 mL of hydrogen peroxide solution per 1 dm<sup>3</sup> of sludge influences on the increase of SCOD value. The greatest value of SCOD 2,237 mg O<sub>2</sub>/L noticed during the 28th day of the process, recording the 61% digestion degree during the 25th day of the methane fermentation. The increase of sludge rate on biodegradation by chemical modification using hydrogen peroxide was confirmed in the studies conducted by Wołczyński and Janosz-Rajczyk [34]. As a result of the disintegration of sewage sludge with hydrogen peroxide, the SCOD was increased, which directly influenced the efficiency of the subsequent hydrogen fermentation [34].

Figs. 5 and 6 present changes in Kjeldahl nitrogen and ammonium nitrogen during 8-d anaerobic stabilization.

The contents of studied nitrogen forms were increasing on each day of the process. In the case of methane fermentation lasting 8 d, the highest levels of Kjeldahl nitrogen and ammonium nitrogen were reached on the 8th day of methane fermentation and were 344 mg N/L and 342 mg N-NH,/L, respectively, whereas the lowest value was found in the first day of the process, and it was 136 mg N/L and 134 mg N-NH<sup>+</sup>/L, respectively. In the case of methane fermentation lasting 25 d, it was noticed that the value of Kjeldahl nitrogen and ammonium nitrogen were equal to 598 mg N/L and 586 mg N-NH<sub>4</sub>/L.

Excess sludge modified with hydrogen peroxide with the dose 5 ml/L of sludge



Fig. 6. Changes in ammonium nitrogen in excess sludge modified with hydrogen peroxide on consecutive days of methane fermentation process.

#### 4. Conclusions

The aim of the examinations was to evaluate the effect of the selected method of sewage sludge disintegration on nitrogen forms. Subjecting chemically disintegrated sewage sludge to methane fermentation resulted, compared with fermentation of non-conditioned sludge, in the increase in Kjeldahl nitrogen and ammonium nitrogen. It was found that the increase in the concentration of the examined forms of nitrogen resulted from higher rate of metabolic transitions that occur in the modified sludge.

The analysis of the results obtained in the present study led to the following conclusions:

- In the case of chemical disintegration using hydrogen peroxide for selected doses of the reactant, an increase was observed in SCOD compared with non-conditioned sludge. For the doses of 1 and 5 mL of H<sub>2</sub>O<sub>2</sub>/L of sludge, SCOD was 221, 872 mgO<sub>3</sub>/L, respectively, whereas for the non-conditioned sludge it was 140 mgO<sub>2</sub>/L;
- As a result of the 25-d anaerobic stabilization of unprepared excess sludge, about 39% digestion degree was obtained, while in the case of anaerobic stabilization of excess sludge disintegrated with hydrogen peroxide in a dose of 1.0 and 5 mL/L of sludge, approximately 57% and 61% digestion degree was obtained.
- Modification of sludge with hydrogen peroxide led to the increase in Kjeldahl nitrogen and ammonium nitrogen on

consecutive days of methane fermentation with respect to the values obtained for non-conditioned sludge;

- During anaerobic stabilization of non-conditioned sludge, the highest Kjeldahl nitrogen and ammonium nitrogen was recorded on the 8th day of the cycle, that is, 288 mg N/L and 277 mg N-NH<sup>+</sup>/L, respectively;
- During anaerobic stabilization of sludge subjected to chemical disintegration using hydrogen peroxide dose of 1 mL of H<sub>2</sub>O<sub>2</sub> per 1 dm<sup>3</sup> of sludge, the highest Kjeldahl nitrogen and ammonium nitrogen of 322 mg N/L and 314 mg N-NH<sup>+</sup>/L, respectively, was also observed on the 8th day of the process;
- In the case of methane fermentation of sludge after chemical disintegration using hydrogen peroxide with the dose of 5 mL/dm<sup>3</sup> of sewage sludge, highest values of Kjeldahl nitrogen and ammonium hydrogen (344 N/L and 342 mg N-NH<sup>4</sup>/L, respectively) were obtained on the 8th day of the process.

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