Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27322

232 (2021) 216–224
August

Methane fermentation of the excess sludge sonicated and oxidized with Fenton's reagent

Iwona Zawieja*, Małgorzata Worwąg, Kinga Brzeska

Czestochowa University of Technology, Faculty of Infrastructure and Environment, Institute of Environmental Engineering, Brzeznicka 60a, 42-200 Czestochowa, Poland, emails: iwona.zawieja@pcz.pl (I. Zawieja), malgorzata.worwag@pcz.pl (M. Worwąg), kinga.brzeska@gmail.com (K. Brzeska)

Received 20 January 2021; Accepted 12 April 2021

ABSTRACT

To increase the susceptibility of excess sludge to biochemical decomposition occurring in anaerobic conditions, it has been disintegrated using physical, chemical and biological methods, or subjected to combined disintegration based on the application of several independent techniques. Consequently, anaerobic stabilization becomes more intensive, the duration of the hydrolytic phase is reduced, and the biogas yield increases. The study aims to demonstrate that compared to the conventional method, the use of a hybrid excess sludge disintegration, that is, combined sonic disintegration and advanced oxidation with Fenton's reagent improves the efficiency of methane fermentation. The hybrid method was found the most effective since for the most favorable conditions of modification, the higher increases in soluble chemical oxygen demand (SCOD) and volatile fatty acids (VFAs) concentrations were reported compared to the non-disintegrated sludge. The dose of iron ions of 0.04 g Fe^{2+}/g TS, the molar ratio Fe^{2+}:H_2O_2 of 1:3, the amplitude of ultrasonic field vibration of 16 μm, and sonication time of 360 s were found to be the most favorable conditions of the hybrid disintegration process. Similar effectiveness of disintegration was obtained for excess sludge disintegration with the hybrid method with doses of iron ions ranging from 0.06 to 0.12 g Fe^{2+}/g TS. During methane fermentation of excess sludge disintegrated using the exposure to the ultrasonic field, Fenton's reagent and combined disintegration, higher levels of SCOD and VFAs concentrations were recorded for the hybrid method with the iron ion dose of 0.04 g Fe^{2+}/g TS while maintaining the Fe^{2+}:H_2O_2 ratio at 1:3. For the above initial conditions, the digestion degree was 63% and the biogas yield was 0.54 L/g VSS.

Keywords: Anaerobic stabilization; Excess sludge; Ultrasonic field; Fenton's reagent; Volatile fatty acids; Biogas yield; Digestion degree

1. Introduction

Sustainable management of waste, including sewage sludge, is an important element in the implementation of measures for the circular economy in the EU (and/or in the world). It should be emphasized that with the upward trend observed for the production of sewage sludge, it becomes necessary to promote sustainable sludge management. The proposed technological solution, which is aimed at improving sewage sludge biodegradation through disintegration with simultaneous acquisition of biogas as a valuable source of energy, is consistent with the concept of the circular economy [1].

Increasing the efficiency of sewage sludge disintegration by using oxidative methods is an important research issue that requires further exploration. Therefore, the most favorable conditions are sought to disintegrate sewage sludge using hybrid methods that combine independent techniques. These usually involve the application of complex oxidation methods or supporting oxidation with

* Corresponding author.

Presented at the 1st International Conference Strategies toward Green Deal Implementation — Water and Raw Materials (ICGreenDeal2020), 14–16 December 2020, held online by the Mineral and Energy Economy Research Institute, Polish Academy of Sciences

1944-3994/1944-3986

electrochemical processes, UV irradiation, or ultrasound exposure. The purpose of combining methods is to generate additional hydroxyl radicals to improve the effectiveness of the oxidation process. With the combination of oxidation with Fenton's reagent and ultrasonic wave propagation, the production of hydroxyl radicals increases, thus reducing the time of final degradation of hardly degradable organic pollutants [2–5]. According to Chen et al. [6], the Fenton method has been widely investigated for the treatment of organic wastewater. The Fenton method has been proposed as an environmentally friendly approach to sewage sludge conditioning.

It is possible to improve sewage sludge disintegration through sonication [7,8], oxidation with Fenton's reagent [9], and the method combining ultrasonic disintegration with in-depth oxidation and to increase the efficiency of the anaerobic stabilization of hybrid pretreated sludge.

Dewil et al. [10] explored the problems of hazardous substances and found that alkaline thermal hydrolysis and Fenton's reagent utilization can reduce the heavy metal content in excess sludge by degrading the extracellular polymeric substances. The combination of bioleaching and the Fenton method, that is, the catalyst reaction of Fe^{2+} by iron-oxidized bacteria and an optimal H_2O_2 dose of 5 g/L, yielded the removal of Cu, Zn, Pb, and Cd of 75.3%, 72.6%, 34.5%, and 65.4%, respectively [11]. According to Wen et al. [12], at an initial pH of 2.5–3.0, a molar ratio of Fe^{2+}/H_2O_2 of 0.1–0.4, and an H_2O_2 dose of 20 mmol/L, radical-induced Fe nanoparticles contained in the sewage sludge can be used as a catalyst to degrade the Eriochrome Black T in textiles. Chen et al. [6] reported that the application of the Fenton method has seldom been investigated to evaluate changes in the concentration of organic substances in sewage sludge.

According to literature data [13–15], the effectiveness of conventionally used disintegration methods, that is, treatment of sludge only with ultrasound exposure or the Fenton method is much less effective compared to using the combined method. The effectiveness of oxidation with Fenton's reagent combined with ultrasonic wave propagation depends on many factors, including the frequency and power of the ultrasonic wave, the volume of the reagents, and process duration.

The synergistic effect of the Fenton reaction and ultrasound exposure has a significant effect on the decomposition of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. The study [16] analyzed the process of PAH degradation at different doses of Fenton's reagent (20, 70 and 140 mmol/L), variable ultrasonic power (0.36, 0.90 and 1.80 W/L), and different sonication times. The results confirmed the effectiveness of PAH removal in sewage sludge. The tests performed by Sun et al. [13] also demonstrated the high efficiency of the process manifested in improved degradation and mineralization of organic compounds contained in sewage sludge. The study conducted by Qiu et al. [17] found higher efficiency of reduction and better dewaterability of the sludge disintegrated using the hybrid method compared to that using the ultrasonic field alone.

The exposure to the ultrasonic field leads to the formation of cavitation bubbles which are a source of highly reactive –OH and –OOH radicals [18]. These radicals react with the substances present in the solution. The additional source of radical production increases the reaction efficiency and speed.

According to Mahamuni and Adewuyi [19] Neppolian et al. [20], several reactions can occur in solutions oxidized with Fenton's reagent and sonicated using the exposure to the ultrasonic field:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} \tag{2}$$

$$Fe\text{-}OOH^{2+} +))))^* \rightarrow Fe^{2+} + HO^2 \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \tag{4}$$

*)))) – ultrasound wave exposure.

Kavitha et al. [21] performed a comparative analysis of energy consumption between independently conducted ultrasonic disintegration and ultrasonic disintegration combined with oxidation with Fenton's reagent. During the experiment, an increase in soluble chemical oxygen demand (SCOD), changes in dry matter content in the sludge, and the volume of biogas were evaluated. The results showed a positive effect of the hybrid method. The organic fraction expressed as the value of SCOD in the sonicated sludge and sludge oxidized with Fenton's reagent increased by ca. 34.4% compared to SCOD in the sludge exposed only to ultrasonic disintegration. It has been proved that the combination of ultrasonic disintegration of excess sludge using oxidation with Fenton's reagent reduces the amount of energy needed for the disintegration process, thus reducing its costs. According to Bagal and Gogate [22], combining advanced oxidation using Fenton's reagent with the exposure to the ultrasonic field while optimizing process conditions results in higher energy efficiency compared to the standalone methods.

Due to the simplicity of the process, the lack of requirements for specialized equipment, and the low cost of reagents, the use of a combination of ultrasonic exposure with Fenton's reaction offers a promising disintegration method that can be successfully used in sludge treatment [23,24].

An important research issue that needs further exploration is to identify universal and optimal conditions for conducting hybrid disintegration that combines sonication with advanced oxidation.

The study aimed to show that compared to conventional methods, the use of a combined method of excess sludge disintegration improves the effectiveness of anaerobic stabilization of sewage sludge.

2. Experimental part

2.1. Substrate

The basic excess sludge was the main research substrate. The sludge was sampled from the mechanical–biological municipal wastewater treatment plant with a daily capacity of about 90,000 m^3. Household wastewater flowing into the treatment plant is treated mechanically and then supplied to the activated sludge chambers, where organic matter is decomposed biologically. The wastewater treated using this method is supplied to secondary settling tanks in which the sedimentation of suspensions occurs. Part of the activated sludge is returned through biological pipelines to biological chambers. The intensity of the recirculation of the activated sludge to the biological chambers is controlled automatically, consequently allowing for even loading. The excess of activated sludge is subjected to mechanical thickening followed by a methane fermentation at 37°C in separate closed fermentation chambers. Excess sludge was sampled from the pipeline supplying the sludge to a mechanical thickener. Digested sludge was sampled from the pipeline transporting sludge from the separate closed fermentation chambers to separate open fermentation chambers. Sampling was carried out randomly and once, and the samples were subjected to the analysis and technological tests on the day of collection. The characteristics of the sludge tested are presented in Table 1.

In the case of anaerobic stabilization, excess sludge was mixed with digested sludge to initiate the process at a volumetric ratio of 10 to 1, respectively.

Anaerobic stabilization was carried out for:

- unmodified excess sludge;
- excess sludge disintegrated by the exposure to the ultrasonic field with a vibration amplitude of 16 μm (wave intensity of 2.93 W/cm^2) and sonication time of 300 s;
- excess sludge disintegrated with Fenton's reagent, iron mass 0.04 g Fe^{2+}/g TS, and the Fe^{2+}:H_2O_2 molar ratio of 1:3;
- excess sludge disintegrated using the hybrid method, that is, the combination of an ultrasonic field with a vibration amplitude of 16 μm and sonication time of 300 s with Fenton's reagent with an iron ion mass of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3.

2.2. Methodology

Hybrid disintegration of excess sludge was carried out using a method combining the exposure to the ultrasonic field with chemical disintegration with a strong oxidizing agent (Fenton's reagent). In the first stage, excess sludge was modified with an ultrasonic field with an amplitude of 16 μm and a sonication time of 300 s. The ultrasonic disintegration of excess sludge was conducted with the use of an ultrasonic generator with a sandwich-type immersing concentrator. The ultrasonic generator was characterized by the maximum output power of 180 W and generated frequencies of ca. 22 kHz at a constant field intensity. The choice of the most favorable conditions of disintegration using ultrasonic field was based on the results of the author's previous research [25]. The ultrasonic pretreatment was performed in the non-flow system and the volume of the pretreated sample was 0.5 L. Next, the sonicated excess sludge was subjected to the oxidation with hydrogen peroxide in the presence of iron ions in the mass range of iron ions of 0.02–012 g Fe^{2+}/g TS Fe^{2+}/g TS while maintaining the Fe^{2+}:H_2O_2 molar ratio of 1:1–1:10.

It is possible to assess and compare changes based on a unified method of determination of the degree of disintegration of excess sludge subjected to different methods of modification. The effectiveness of selected disintegration methods was evaluated using the method proposed by Müller [26], whereas the disintegration degree DD_{SCOD}, was calculated according to the following formula:

$$DD_{SCOD} = \frac{(SCOD_1 - SCOD_2)}{(SCOD_3 - SCOD_2)} \times 100 \tag{5}$$

where DD_{SCOD} – disintegration degree, %; $SCOD_1$ – SCOD level in the sludge conditioned using ultrasound exposure, mg O_2/L; $SCOD_2$ – SCOD level in the raw sludge, mg O_2/L; $SCOD_3$ – SCOD level in the sludge chemically conditioned with 1 mol NaOH at a ratio of 1:1, temp. 90°C for 10 min, mg O_2/L. The reference value of SCOD for the sludge subjected to alkaline-thermal modification was 2.652 mg O_2/L.

Methane fermentation of excess sludge was carried out under static conditions for 28 d in a fermentation chamber with an active volume of 18 L and for 10 d in models of fermentation chambers with an active volume of 0.5 L. The sludge was stabilized at a constant temperature of 37°C, characteristic for conducting the process under mesophilic conditions. Before the test, a mixture of excess sludge and digested sludge was prepared, constituting 10% of the total volume of the mixture. Fermentation chamber models were filled with the mixture to the active volume of 0.5 L and sealed with a rubber stopper with a manometric tube. The set protected the fermentation mixture against contact with the oxygen environment while allowing for the release of the produced biogas to the outside. The sludge-filled fermentation chamber models were placed in a laboratory incubator with a shaking option (37°C ± 1°C).

In the case of excess sludge disintegration, analyses were made for indicators such as SCOD and volatile fatty acids (VFAs), expressing the degree of liquefaction of the organic substances contained in the sludge. SCOD and VFAs concentration tests were carried out in the supernatant liquid obtained by sludge centrifugation using a laboratory centrifuge at a speed of 12,100 rpm and for 15 min. The results allowed for the determination of the most favorable conditions of excess sludge disintegration.

Methane fermentation of sludge was controlled based on physical and chemical analyses and examinations of the composition and volume of biogas produced. The pH of the sludge samples was determined using an Elmetron CP-411 pH meter according to PN-EN 12176 [27], whereas total solids were evaluated according to PN-75 C-04616/01 [28]. Furthermore, the total alkalinity in the supernatant liquid obtained from centrifugation was determined according to

Table 1
Selected physical and chemical parameters of sewage sludge

Indicator	Excess sludge	Digested sludge
pH	6.65 ± 0.02	7.5 ± 0.03
TS, g/L	9.18 ± 0.5	22.34 ± 0.7
VSS, g/L	7.38 ± 0.3	15.84 ± 0.6
VFAs, CH_3COOH/L	59 ± 2	856 ± 5
SCOD, mg O_2/L	143 ± 6	1,943 ± 11

TS – total solids; VSS – volatile suspended solids; VFAs – volatile fatty acids; SCOD – soluble chemical oxygen demand

PN-91/C-04540/05 [29], and volatile fatty acids were evaluated according to PN-75/C-04616/04 [30]. In the case of SCOD, supernatant liquid samples were subjected to wet mineralization using highly oxidizing mineral acids. SCOD was measured using the HACH DR/4000 HACH LANGE spectrophotometer and read at a wavelength of 620 nm.

SCOD was determined with the dichromate method using the HACH 2I00N IS spectrophotometer according to ISO 7027 [31]. The efficiency of stabilization was determined based on the sludge digestion degree [25], biogas yield [32], and biogas quality. The tests were carried out using the GA 2000 Analyser (Geotechnical Instruments), which was used to determine the percentage of methane, carbon dioxide, and oxygen in biogas.

3. Results and discussion

3.1. Combined effect of the ultrasonic field and oxidation of excess sludge with Fenton's reagent on the disintegration process

Hybrid disintegration of excess sludge was carried out using a method combining the exposure to the ultrasonic field with a vibration amplitude of 16 μm and sonication time of 300 s with chemical disintegration. A strong oxidizing agent in the form of Fenton's reagent was used in the presence of iron ions with a mass range of 0.02–012 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:–1:10. To assess the effectiveness of the combined method on disintegration, the sludge samples were analyzed for the content of organic substances in dissolved form using SCOD. Untreated sludge was characterized by total solids of 9.18 g/L. The content of volatile suspended solids (VSS) in the sludge was 7.38 g/L. SCOD obtained as a result of combined disintegration is shown in Fig. 1.

The combination of the exposure to the ultrasonic field with the oxidation of excess sludge with Fenton's reagent led to the intensification of sludge disintegration. Dosing excessive hydrogen peroxide to the sludge while maintaining constant sonication parameters yielded an increase in SCOD. An intensive increase in SCOD in the disintegrated sludge compared to its value in the unmodified sludge was observed maintaining the Fe^{2+}:H_2O_2 mass ratio of 1:1 for all doses of iron ions used. In the case of the oxidation with the Fe^{2+}:H_2O_2 molar ratio of over 1:3, a decrease or a slight increase in SCOD were observed for iron doses of 0.02, 0.04 and 0.06 g Fe^{2+}/g TS. It should, therefore, be assumed that for low Fe^{2+}:H_2O_2 molar ratios, the obtained increase in this indicator could have been mainly due to the supporting effect of the ultrasonic field. The results demonstrated a negative effect of high concentrations of chemical reagents on the disintegration of excess sludge. A decrease in SCOD in the sludge studied was observed for the use of the doses of iron ions of 0.08; 0.1 and 0.12 g Fe^{2+}/g TS and the molar ratios of Fe^{2+}:H_2O_2 of over 1:7, 1:5 and 1:7, respectively. A similar tendency was observed for the use of high concentrations of hydrogen peroxide added to excess sludge for the tested doses of iron ions. The decrease in the effectiveness of the combined method could be because hydroxyl radicals generated during sonication bind with excess hydrogen peroxide, leading to the formation of hydroperoxide radicals with lower oxidizing potential. The comparison between SCOD values of hybrid modified sludge and SCOD values of untreated sludge was made to determine the most favorable conditions for the use of the combined method. These relationships were determined for the iron ion doses used in the oxidation process and are presented in Table 2.

The analysis of the results obtained from the test revealed the effect of the ultrasonic field on oxidation with Fenton's reagent. The use of the combined method led to a sevenfold increase in the concentration of organic substances in dissolved form for a dose of iron ions of 0.02 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3. An eightfold increase in SCOD for the sludge modified using the hybrid method compared to the SCOD for the untreated sludge was obtained for the dose of iron ions of 0.04 and 0.06 g Fe^{2+}/g TS while maintaining the Fe^{2+}:H_2O_2 molar ratio of 1:3. In the case of the preparation of excess sludge with doses of iron ions of 0.08, 0.10 and 0.12 g Fe^{2+}/g TS, a nine-fold increase was observed in the value of SCOD of the modified sludge compared to SCOD of the unmodified sludge using the Fe^{2+}:H_2O_2 molar ratios of 1:7, 1:5 and 1:7, respectively. The results of the tests of excess sludge disintegration using the combined method showed that the most favorable conditions for conducting the process were the doses of iron ions of 0.04 g Fe^{2+}/g TS and a molar ratio of Fe^{2+}:H_2O_2 of 1:3, for which high disintegration efficiency was obtained using small doses of chemical reagents. There was an eightfold increase in SCOD, whereas a fourfold increase in the value of this index was found for the independent oxidation method and the above iron dose. The effect of Fenton's reagent on changes in VFAs concentration was also analyzed during excess sludge disintegration using the method combining ultrasound exposure with advanced oxidation. The VFAs concentrations obtained as a result of combined disintegration are shown in Fig. 2.

In the case of the hybrid method, the effect of the doses of Fenton's reagents on changes in VFAs concentrations was also examined. The analysis of the test results revealed that as the concentration of the Fenton's reagent increased, a tendency for VFAs concentration to increase was observed compared to baseline. An approximately fourfold increase in VFAs concentrations compared to those observed in the unmodified sludge was recorded for the

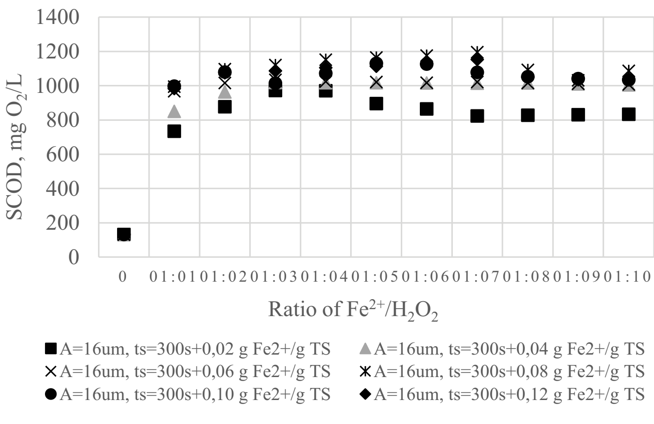

Fig. 1. The combined effect of the ultrasonic field and the Fenton's reagent on the SCOD values depending on the mass of Fe^{2+} and the Fe^{2+}:H_2O_2 molar ratio.

Table 2
Most favourable molar ratios of Fe^{2+}:H_2O_2 of Fenton's reagent for individual doses of Fe^{2+} ions based on the increase in SCOD in the sludge disintegrated using the combined method

		Most favourable Fe^{2+}:H_2O_2 ratio	$SCOD_{unmodified\ excess\ sludge}$	$SCOD_{oxidized\ excess\ sludge}$	Ratio of $SCOD_{unmodified\ excess\ sludge}$/$SCOD_{oxidized\ excess\ sludge}$
Dose of Fe^{2+} g/g TS	0.02	1:3	132	972	1/7
	0.04	1:3	132	1,019	1/8
	0.06	1:3	132	1,035	1/8
	0.08	1:7	132	1,195	1/9
	0.10	1:5	132	1,131	1/9
	0.12	1:7	132	1,153	1/9

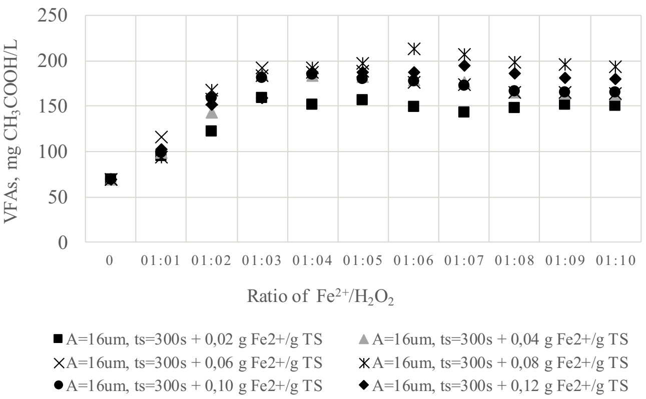

Fig. 2. Effect of the combined method on VFAs concentration depending on the doses used and the content of Fenton's reagent.

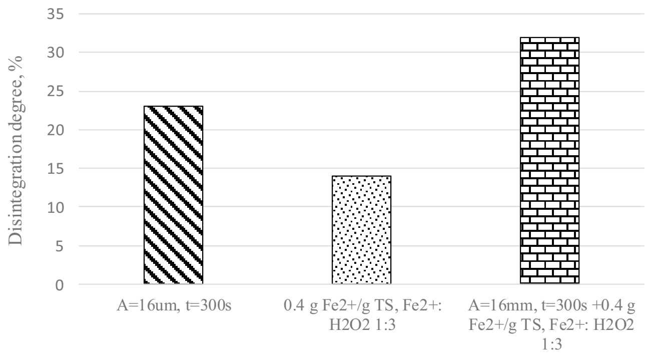

Fig. 3. Disintegration degree for the excess sludge exposed to the ultrasonic field, Fenton's reagent, and hybrid disintegration, that is, the combination of an ultrasonic field with an amplitude of vibrations of A = 16 µm and sonication time of 300 s with oxidation using Fenton's reagent.

dose of iron ions of 0.04 g Fe^{2+}/g TS and a Fe^{2+}:H_2O_2 ratio of 1:3. The results showed that the use of subsequent higher doses of Fenton's reagent does not significantly affect the effectiveness of the process. In the case of sludge disintegration using the hybrid method with the doses of iron ions of 0.06–0.12 g Fe^{2+}/g TS, the increase in VFAs was not higher than fourfold. Consequently, a dose of iron ions of 0.04 g/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3 were considered to be the most favorable parameters of excess sludge disintegration using the hybrid method.

With the synergistic effect of the oxidizing substance on sonicated excess sludge, a nearly fourfold increase in VFAs concentrations compared to those observed in unmodified sludge was found for the dose of iron ions of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3. The results showed that the use of subsequent higher doses of Fenton's reagent does not significantly affect the effectiveness of the process. For the sludge disintegrated with Fenton's reagent with the dose of iron ions of 0.04 g Fe^{2+}/g TS and the ratio of iron ions to hydrogen peroxide of 1:3, the disintegration degree was 32%. For the independent method of disintegration with Fenton's reagent at a dose of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3, the largest (18%) increase in the disintegration degree was obtained for the hybrid method combining disintegration with the exposure to the ultrasonic field and oxidation with a dose of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 ratio of 1:3. Fig. 3 shows the values of the disintegration degree of excess sludge exposed to the ultrasonic field, Fenton's reagent, and hybrid disintegration.

The exposure to the ultrasonic field with constant sonication parameters and the advanced oxidation of excess sludge led to an increase in the degree of sludge disintegration (Table 3). Analyses performed for the lowest volumes of hydrogen peroxide at a ratio of 1:1 in relation to Fe^{2+} ions over the entire range of doses of iron ions from 0.02 g Fe^{2+}/g d.m. to 0.12 g Fe^{2+}/g d.m. revealed a rapid and steady increase in SCOD. When larger volumes of Fenton's reagent were introduced into the sludge above the Fe^{2+}:H_2O_2 ratio of 1:1 in the range of iron doses used, no significant increases in SCOD were recorded. Therefore, it should be presumed that the high degree of sludge disintegration obtained for the lower concentrations is likely to have been due to the supporting effect of the ultrasonic field. An adverse effect of using highly oxidizing hydrogen peroxide was also emphasized. It was demonstrated that for the examined doses of iron ions, the addition of substantial volumes of hydrogen peroxide into the excess sludge leads to a decrease in SCOD in the sludge. The decrease in the efficiency of the combined method could have been caused by binding hydroxyl radicals generated during sonication with the excess of hydrogen peroxide, leading at the same time to the formation of hydroperoxide radicals of lower oxidizing potential. Based on the analysis of

Table 3
Digestion degree, degree of TS reduction, and total biogas production and biogas yield during 28-d methane fermentation of sludge disintegrated using conventional and hybrid methods

Disintegration methods	Unmodified excess sludge	Ultrasonic disintegration	Disintegration with Fenton's reagent	Hybrid disintegration , that is, combination of disintegration with ultrasonic field and oxidation with Fenton's reagent
Indicator		*A* = 16 mm; *t* = 300 s	0.04 g Fe^{2+}/g TS, Fe^{2+}: H_2O_2 1:3	*A* = 16 mm, *t* = 300 s, 0.04 g Fe^{2+}/g TS Fe^{2+}:H_2O_2 1:3
Digestion degree, %	25	35	44	63
Degree of TS reduction, %	16	22	30	40
Total biogas production, L	14.5	20.9	27.8	36.4
Biogas yield, L/g VSS	0.35	0.48	0.47	0.54

the relationships between the SCOD values for unmodified sludge and those of modified sludge, a positive effect of the hybrid method on the disintegration of excess sludge was observed. It was found that the efficiency of the combined method depends, among other things, on the doses of the Fenton's reagent used in the process.

3.2. Methane fermentation of unmodified excess sludge and the sludge subjected to different disintegration methods

According to literature data [33,34], the hydrolysis phase is considered to limit methane fermentation. Excess sludge disintegration with the exposure to ultrasonic field, oxidation with Fenton's reagent, and hybrid disintegration resulted in the intensification of the hydrolysis phase of methane fermentation, expressed in the increase in SCOD and VFAs concentrations in the following days of the process (Figs. 4 and 5).

In the methane fermentation of unprepared excess sludge disintegrated using independent methods and the hybrid method, a gradual increase in SCOD was observed in the first days of the process, and, after reaching the maximum, its value decreased. The highest values of SCOD were recorded for sludge subjected to hybrid disintegration with the dose of iron ions of 0.04 mg Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3.

A similar tendency for a gradual increase in the following days of methane fermentation was found for the concentration of volatile fatty acids in unprepared excess sludge disintegrated using independent methods and the hybrid method. After reaching the maximum value, the concentration of this indicator gradually decreased. The most intense generation of volatile fatty acids was recorded for the sludge subjected to hybrid disintegration with a dose of iron ions of 0.04 mg Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3. For excess sludge subjected to conventional methane fermentation, the digestion degree after 28 d of the process was 25%, while the degree of total solids reduction was about 16%. In the case of the sludge modified using independent methods of disintegration, that is, disintegration with the exposure to the ultrasonic field and oxidation with Fenton's reagent, the supporting effect of

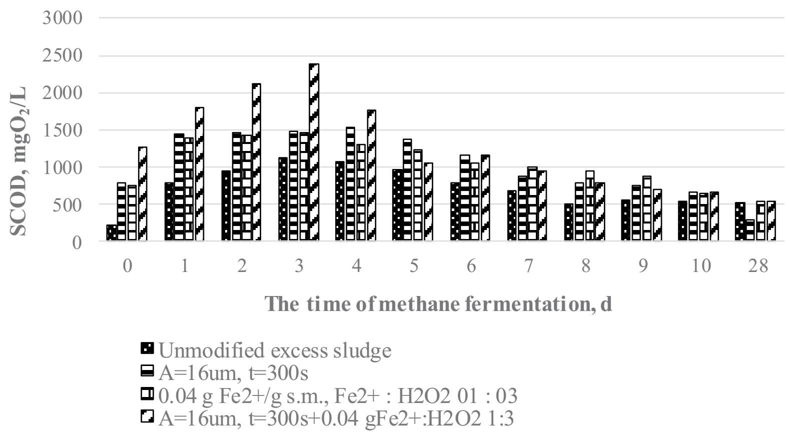

Fig. 4. Changes in soluble chemical oxygen demand (SCOD) for conventional methane fermentation of excess sludge and methane fermentation of disintegrated sludge using selected independent methods and the hybrid method.

the proposed modification on methane fermentation was observed compared to the unprepared sludge. Compared to the methane fermentation of excess sludge modified by independent methods, that is, disintegration using the exposure to the ultrasonic field, oxidation with Fenton's reagent at a dose of 0.04 mg Fe^{2+}/g TS and the correctly selected molar ratio of iron ions to hydrogen peroxide of Fe^{2+}:H_2O_2, an increase in process efficiency was observed in the case of methane fermentation of the sludge modified by hybrid method. The combination of sonolysis, advanced oxidation, and biological hydrolysis and the first methane fermentation phase yielded a high efficiency of the disintegration of excess sludge using the hybrid method.

In the case of methane fermentation of excess sludge disintegrated using the hybrid method combining the active exposure to the ultrasonic field with oxidation using Fenton's reagent at a dose of 0.04 mg Fe^{2+}/g TS, an increase in the effectiveness of the process was observed compared to the excess sludge disintegrated by independent methods, that is, ultrasonic field and Fenton's reagent at a dose of 0.04 mg Fe^{2+}/g TS, expressed as an increase in the digestion degree by ca. 28% and 19% and an increase in the reduction of total solids by ca. 18% and 10%. The effectiveness of the methane fermentation of unprepared excess sludge and the sludge subjected to different disintegration methods was evaluated based on total biogas production and biogas yield. The lowest value of biogas yield (0.35 L/g VSS) was obtained in the case of methane fermentation of untreated sludge. Furthermore, biogas yields in the case of methane fermentation of sludge disintegrated using the exposure to the ultrasonic field and oxidized with Fenton's reagent at a dose of iron ions of 0.04 mg Fe^{2+}/g TS, were 0.48 and 0.47 L/g VSS, respectively. The supportive effect of hybrid disintegration on the intensity of biogas production during methane fermentation was observed. A biogas yield of 0.54 L/g VSS was found for anaerobic stabilization of hybrid-modified sludge. For technological reasons, an increase in the efficiency of anaerobic stabilization and, as reported by Chung and Park [35], the possibility of producing biogas in energy cogeneration systems, are important determinants of both energy savings and environmental protection. In the case of methane fermentation of unmodified sludge and the sludge subjected to selected disintegration methods, a similar content of methane of ca. 72%–81% was observed in the intensive biogas production phase.

For the methane fermentation of the excess sludge disintegrated by the hybrid method combining the active exposure to the ultrasonic field with oxidation with Fenton's reagent, a supporting effect of the combination was reported compared to the excess sludge disintegrated using the independent methods, that is, the ultrasonic field and Fenton's reagent. It was found that disintegration contributes to the acceleration of biochemical decomposition of organic substances occurring during the first stage of methane fermentation, termed the acid phase. The high efficiency of the hybrid disintegration was due to the initiation of the sonolysis process occurring first, followed by the advanced oxidation process with Fenton's reagent and, finally, the biological hydrolysis, considered a phase that limits methane fermentation. Obtaining increased efficiency of methane fermentation of hybrid-modified excess sludge is the prerequisite for the development of a disintegration technology combining the exposure to the ultrasonic field with oxidation with Fenton's reagent. It is possible to implement the proposed concept in the technological process lines for sewage sludge treatment.

4. Summary and conclusions

Due to the disintegration process, the anaerobic stabilization occurs more intensively, the time of the hydrolytic phase is reduced, and the biogas yield increases. Compared to independently conducted disintegration, the combination of the exposure to the ultrasonic field with advanced oxidation using Fenton's reagent led to an increase in the efficiency of excess sludge disintegration. The increase in SCOD obtained using the combined method was higher compared to the SCOD obtained during the sonication process using the most favourable process conditions. The observed intensive increase in the concentration of organic substances in the supernatant liquid resulted from the supporting effect of the ultrasonic field. For technological reasons to reduce the mass of iron ions added to the sludge, the most favourable conditions for conducting the disintegration process was the use of the dose of iron ions of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3. With

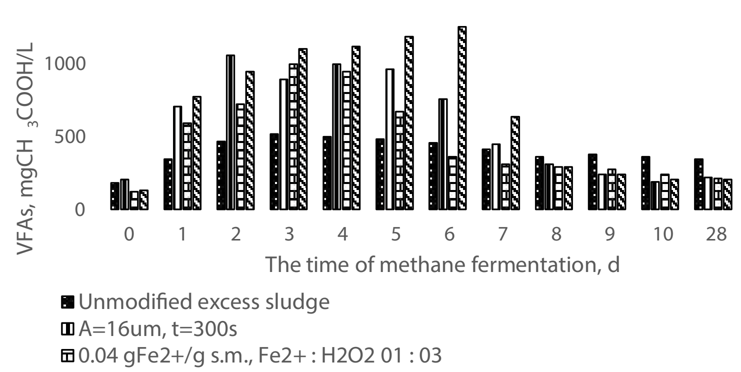

Fig. 5. Changes in volatile fatty acids (VFAs) in the conventional methane fermentation of excess sludge and methane fermentation of disintegrated sludge using selected independent methods and the hybrid method.

the low dose of iron ions and a small value of the Fe^{2+}:H_2O_2 molar ratio, the efficiency of the combined disintegration process was high. The results showed that the combination of the exposure to the ultrasonic field and the oxidation with Fenton's reagent intensifies the disintegration process.

The following conclusions were drawn based on the research results:

- The hybrid disintegration of excess sludge, which combined disintegration with the exposure to the ultrasonic field and the advanced oxidation process, improved disintegration of modified excess sludge expressed in the increase in the value of SCOD and the concentration of volatile fatty acids (VFAs).
- Modification of the combined method of excess sludge disintegration using the exposure to the ultrasonic field and the advanced oxidation led to the improved efficiency of methane fermentation, that is, the degree of sludge digestion and biogas yield, which allows for the implementation of the developed disintegration concept into sewage sludge treatment technologies.
- For technological reasons, the dose of iron ions of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3 were considered to be the most favourable for conducting the combined disintegration. A 32% sludge disintegration degree, an eightfold increase in SCOD value, and a fourfold increase in VFA concentration were obtained compared to baseline.
- During the process of 28-d methane fermentation of excess sludge disintegrated using the exposure to the ultrasonic field, Fenton's reagent, and combined disintegration, the highest value of sludge digestion degree of about 63% and biogas yield of 0.54 L/g VSS were found for the hybrid method using a dose of iron ions of 0.04 g Fe^{2+}/g TS and the Fe^{2+}:H_2O_2 molar ratio of 1:3.

Acknowledgments

The scientific research was funded by the statute subvention of Czestochowa University of Technology, Faculty of Infrastructure and Environment.

References

[1] A. Gherghel, C. Teodosiu, S. De Gisi, A review on wastewater sludge valorisation and its challenges in the context of circular economy, J. Cleaner Prod., 228 (2019) 244–263.
[2] C.-Y. Chang, Y.-H. Hsieh, K.-S. Eyao, M.-C. Wei, L.-L. Hsieh, The Effect of pH on Hydroksyl Free Radical Reaction Rate in the Fenton Process, 4th International Conference on Oxidation Technologies for Water and Wastewater Treatment, Goslar, Germany, 2006, pp. 343–348.
[3] I. Ioan, S. Wilson, E. Lundanes, A. Neculai, Comparison of Fenton and sono-Fenton bisphenol A degradation, J. Hazard. Mater., 142 (2007) 559–563.
[4] A. Kwarciak-Kozłowska, R. Włodarczyk, Efficiency assessment of coke industry wastewater treatment during advanced oxidation process with biochar adsorption, Desal. Water Treat., 199 (2020) 441–450.
[5] A. Kwarciak-Kozłowska, K.L. Fijałkowski, Efficiency assessment of municipal landfill leachate treatment during advanced oxidation process (AOP) with biochar adsorption (BC), J. Environ. Manage., 287 (2021) 112309, doi: 10.1016/j.jenvman.2021.112309.
[6] Y.-J. Chen, T.-Y. Fan, L.-P. Wang, T.-W. Cheng, S.-S. Chen, M.-H. Yuan, S.K. Cheng, Application of Fenton method for the removal of organic matter in sewage sludge at room temperature, Sustainability, 12 (2020) 1518, doi: 10.3390/su12041518.
[7] L. Wolny, T. Kamizela, The technique of ultrasonic disintegration in the technology of sewage and sewage sludge, Ecol. Tech., 1 (2003) 3–7.
[8] K. Barbusiński, Advanced Oxidation in the Treatment of Selected Industrial Wastewater, Publishing House of the Silesian University of Technology, Gliwice, 2013 (in Polish).
[9] J. Yoon, Y. Lee, S. Kim, Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment, Water Sci. Technol., 44 (2001) 15–21.
[10] R. Dewil, J. Baeyens, L. Appels, Enhancing the use of waste activated sludge as bio-fuel through selectively reducing its heavy metal content, J. Hazard. Mater., 144 (2007) 703–707.
[11] Y. Zhu, G.M. Zeng, P.Y. Zhang, C. Zhang, M.M. Ren, J.C. Zhang, M. Chen, Feasibility of bioleaching combined with Fenton-like reaction to remove heavy metals from sewage sludge, Bioresour. Technol., 142 (2013) 530–534.
[12] H.F. Wen, G. Lin, H.X. Yu, X.B. Qiao, D.F. Zhang, J.F. Ye, Radical assisted iron impregnation on preparing sewage sludge derived Fe/carbon as highly stable catalyst for heterogeneous Fenton reaction, Chem. Eng. J., 352 (2018) 837–846.
[13] J.-H. Sun, S.-P. Sun, J.-Y. Sun, R.-X. Sun, L.-P. Qiao, H.-Q. Guo, M.-H. Fan, Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, Ultrason. Sonochem., 14 (2007) 761–766.
[14] J. Virkutyte, V. Vičkačkaite, A. Padarauskas, Sono-oxidation of soils: degradation of naphthalene by sono-Fenton-like process, J. Soils Sediments, 10 (2010) 526–536.
[15] J. Zhang, J.B. Li, R. Thring, L. Liu, Application of ultrasound and Fenton's reaction process for the treatment of oily sludge, Procedia Environ. Sci., 18 (2013) 686–693.
[16] Y.W. Ke, X.-A. Ning, J.Y. Liang, H.Y. Zou, J. Sun, H.L. Cai, M.Q. Lin, R.J. Li, Y.P. Zhang, Sludge treatment by integrated ultrasound-Fenton process: characterization of sludge organic matter and its impact on PAHs removal, J. Hazard. Mater., 343 (2018) 191–199.
[17] S. Qiu, M.J. Xia, Z.S. Li, Ultrasonic irradiation as pretreatment for the reduction of excess sludge by Fenton-acclimation treatment, Water Sci. Technol., 67 (2013) 1701–1707.
[18] K. Eskelinen, H. Särkkä, A.T. Kurniawan, M.E.T. Sillanpää, Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: a comparative study, Desalination, 255 (2010) 179–187.
[19] N.N. Mahamuni, Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, Ultrason. Sonochem., 17 (2010) 990–1003.
[20] B. Neppolian, H. Jung, H. Choi, J.H. Lee, J.-W. Kang, Sonolytic degradation of methyl tert-butyl ether: the role of coupled Fenton process and persulphate ion, Water Res., 36 (2002) 4699–4708.
[21] S. Kavitha, J.R. Banu, D.D. Ivin Shaju, S. Kaliappan, I.T. Yeom, Fenton mediated ultrasonic disintegration of sludge biomass: biodegradability studies, energetic assessment, and its economic viability, Bioresour. Technol., 221 (2016) 1–8.
[22] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem., 21 (2014) 1–14.
[23] T.T.H. Pham, S.K. Brar, R.D. Tyagi, R.Y. Surampalli, Influence of ultrasonication and Fenton oxidation pre-treatment on rheological characteristics of wastewater sludge, Ultrason. Sonochem., 17 (2010) 38–45.
[24] R.A. Torres, F. Abdelmalek, E. Combet, C. Pétrier, C. Pulgarin, A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters, J. Hazard. Mater., 146 (2007) 546–551.

[25] I. Zawieja, L. Wolny, P. Wolski, Influence of excessive sludge conditioning on the efficiency of anerobic stabilization process and biogas generation, Desalination, 2222 (2008) 374–381.
[26] J. Müller, Mechanischer Kläschammaufschluss, Dissertation, TU Braunschweig, Shaker-Verlag, Aachen, 1996.
[27] Polish Standards PN-EN 12176, Characteristics of Sewage Sludge, Determination of pH Value, Standardization Publisher, Warsaw.
[28] Polish Standards PN-75 C-04616/01, Water and Sewage. Special Sludge Tests, Determination of Water Content, Dry Matter, Organic Substances and Mineral Substances in Sewage Sludge, Standardization Publisher Warsaw.
[29] Polish Standards PN-91/C-04540/05, Water and Sewage. PH, Acidity and Alkalinity Tests. Determination of pH, Acidity and Mineral and General Alkalinity in Urban Sewage Sludge, Standardization Publisher, Warsaw.
[30] Polish Standards PN-75/C-04616/04, Water and Sewage. Special Sludge Tests. Determination of Volatile Fatty Acids in Sewage Sludge and Supernatant Waters by the Method of Steam Distillation, Standardization Publisher, Warsaw.
[31] International Measurements Standards ISO 7027.
[32] Ł. Fukas-Płonka, E. Zielewicz-Madej, Stabilization of excessive sludge in the methane fermentation process, Eng. Environ. Prot., 3 (2000) 37–48 (in polish).
[33] K. Grübel, M. Kuglarz, B. Mrowiec, J. Suschka, The use of initial hybrid activated sludge hydrolysis to increase the efficiency of two-stage methane fermentation, Eng. Environ. Prot., 17 (2014) 255–268.
[34] I. Zawieja, M. Barański, M. Małkowski, Obtaining biogas in the process of anaerobic stabilization of thermally modified sewage sludge, Eng. Environ. Prot., 13 (2010) 185–196 (in polish).
[35] M. Chung, H.-C. Park, Feasibility study for retrofitting biogas cogeneration systems to district heating in South Korea, Waste Manage. Res., 33 (2015) 755–766, doi: 10.1177/0734242X15592277.