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RECOVERY OF VOLATILE FATTY ACIDS DURING THE PROCESS OF ANAEROBIC STABILIZATION OF SEWAGE SLUDGE COMING FROM THE FOOD INDUSTRY

POZYSKIWANIE LOTNYCH KWASÓW TŁUSZCZOWYCH W PROCESIE STABILIZACJI BEZTLENOWEJ OSADÓW POCHODZĄCYCH Z PRZEMYSŁU SPOŻYWCZEGO

Abstract: The conventional process of oxygen-free stabilization is time-consuming and has low effectiveness. The literature review made, as well as the original studies carried out suggest that the ultrasonic conditioning provides a new way of shortening the duration and increasing the effectiveness of the process of oxygen-free stabilization of sludges forming in the process of treatment of both domestic sewage and industrial liquid wastes. Achieving the considerable increase in the degree of digestion during the oxygen-free stabilization of sludge conditioned with the *ultrasonic* (US) field compared with the reduction of organic matter noted during the oxygen-free stabilization of non-conditioned sludge results from the combined action of both biological hydrolysis, being the first stage of the process, and the phenomenon of sonochemical hydrolysis taking place during the treatment process. Subjecting sludge to conditioning by the method investigated contributes to a considerable intensification of the hydrolysis phase, as reflected by the increase in the production rate and concentration of volatile fatty acids noted in the successive days of conducting the oxygen-free stabilization process, which determines directly the increase of digestion effectiveness, *ie* the degree of sludge digestion and the unit production of biogas. Excessive active sludge formed as a result of the treatment of a mixture of domestic sewage and industrial liquid wastes generated in a plant manufacturing juices and beverages was subjected to oxygen-free stabilization under static conditions. The process was conducted both in laboratory flasks, constituting fermentation chamber models, as well as in a sludge fermentation chamber by Applicon.

Keywords: oxygen-free stabilization, volatile fatty acids, active action of ultrasonic field, biogas

1. Introduction

The Act on Waste of 27 April, 2001, introduces the concept of municipal sewage sludge to refer to the sludge originating from a sewage treatment plant's digestion chambers and other installations used for the treatment of municipal sewage and other

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wastewater with composition similar to that of municipal sewage, which include wastewater coming, *inter alia*, from [1]: the processing of milk and fruits and vegetables; the production and bottling of soft drinks and alcoholic liquors; meat processing; the production of animal feed from vegetable raw materials; the production of gelatine and glues from animal skin and bones; malt-houses; fish processing; the production of vegetable and animal fats; and sugar factories.

The disposal of sewage sludge on a landfill or its natural utilization should be preceded by transformation processes that will eliminate the noxiousness resulting from their decay, and will prevent the microbial decomposition [2]. The most commonly used process of biochemical sewage sludge stabilization is the methane fermentation process [3]. The methane fermentation process involves the decomposition of macromolecular organic substances by different groups of bacteria into simple compounds, mainly methane and carbon dioxide [3]. The use of methane fermentation results in changes in the composition of the sludge and the gaseous phase [4]. A reduction in organic compounds by approx. 50 % and a decrease in the amount of noxious biological matter have been observed in the methane fermentation process [2]. An important factor in the energy aspect is the amount of energy recovered in the form of volatile fatty acids [5]. The neutralization of sludge by the methane fermentation method is a process that is very advantageous in terms of energy, as it does not require large energy inputs, and the product of reactions occurring in this process is a high-energy biogas [6]. A drawback of this process is a low rate of degradation of organic compounds contained in the sludge [7]. Therefore, the sludge must be subjected to the process of conditioning that enhances directly its susceptibility to biodegradation. A phase limiting the fermentation process is the hydrolytic phase. Increasing the degree of sewage sludge disintegration before the methane fermentation process contributes to the intensification of the hydrolysis process, which results in an increase in the concentration and the rate of increment of volatile fatty acids that form a fermentation semi-product and a substrate for methanogenic bacteria.

2. Experimental

2.1. Testing substrate

The subject of the tests was excessive active sludge coming from the waste treatment plant functioning at the Jurajska Spoldzielnia Pracy works in Myszkow. The tests were conducted on a mixture of excessive and digested sewage sludges that were subjected to mesophyllic methane fermentation, which was periodical in character. The excessive sludge constituted 90 % of the mixture, while the remaining 10 % were made up of digested sludge playing the role of an inoculant.

2.2. Testing methodology

The purpose of the tests was to examined the process of hydrolysis in the oxygen-free stabilization of sewage sludge and to determine the effectiveness of the methane fermentation process. The tests were conducted in a laboratory scale under mesophyllic conditions in ten glass flasks constituting fermentation chamber models. At the same time, tests for the assessment of methane fermentation effectiveness were conducted in a bioreactor by Applicon.

At the first stage, a mixture of digested sludge and non-conditioned excessive sludge, designated as Mixture I, was subjected to 10 days' stabilization. The next stage consisted of the process of stabilization of a mixture of digested sludge and excessive sludge that had been subjected to the active action of an ultrasonic field. In order to determine the best parameters of sludge conditioning, the most advantageous vibration amplitude and sonification time were selected. The criterion for the selection of the parameters sought for was the increase in the concentration of organic matter in the supernatant water of the excessive sludge after sonification, expressed as the COD of the supernatant water. A VC-750 type ultrasonic disintegrator was used for the tests. The following vibration amplitudes were used in the tests: 15.3 μm; 21.4 μm; 30.5 μm; and 36.6 μm; whose action was examined for the sonification time of 30–360 s. At the second stage of tests, based on the performed optimization of the ultrasonic field parameters, Mixture II, *ie* the excessive sludge conditioned with the ultrasonic field of an amplitude of 36.6 μm and an exposure time of 240 s, was subjected to oxygen-free stabilization.

The following physicochemical parameters were determined: pH value using a pH-meter, Model 59002-00, by Cole-Parmer Instrument Company – according to the standard PN-91/C-04540/05 [8]; dry matter, dry organic matter, and dry mineral matter – by the direct gravimetric method according to the standard PN-EN-12879 [9]; *volatile fatty acids* (VFA) – according to the standard PN-75/C-04616/04 [10]; basicity – according to the standard PN-74/C-04540/00 [11]; acidity – according to the standard PN-74/C-04540/00 [12]; *chemical oxygen demand* (COD – Cr), as determined by the chromate method – according to the standard PN-74/C-04578/03) [13]; ammonium nitrogen – according to the standard PN-ISO 5664:2002 [14]; and total nitrogen – according to the standard PN-73/C-04576/14 [15].

3. Test results

A mixture of non-conditioned excessive sludge and digested sludge, playing the role of an inoculant (Mixture I), was subjected to subjected to oxygen-free stabilization. Abrupt changes in the values of selected physicochemical parameters were observed during the tests. Those changes might result from the inhomogeneous structure of the sludges. Excessive sewage sludge is fairly hard to undergo biochemical decomposition under oxygen-free conditions. This is indicated by the degree of sludge fermentation achieved on the tenth day of conducting the process of stabilization of Mixture I. Therefore, on the basis of the performed tests it was found it necessary to subject the sludges to the process of pre-conditioning with the active action of the US field in order to increase the effectiveness of the process.

During the process of methane fermentation of Mixture I conducted in fermentation flasks, an approx. 35 % degree of sludge fermentation was noted. The concentration of volatile fatty acids kept increasing until the sixth day of running the process, when it achieved a value of 805 $mgCH_3COOH/dm^3$. From the sevenths day on, the VFA concentration steadily decreased down to a value of 102 $mgCH_3COOH/dm^3$ on the tenth day of the process. During the oxygen-free stabilization process conducted in the bioreactor, an approx. 43 % degree of sludge fermentation was achieved after 25 days of the process. The analysis of the sludges after 25 days showed that the VFA concentration on the last day of fermentation amounted to 445 $mgCH_3COOH/dm^3$.

At the next stage, excessive sludge conditioned with the ultrasonic field with a vibration amplitude of 36.6 μm and a sonification time of 240 s (Mixture II) was subjected to the process of methane fermentation. In the case of Mixture II, an approx. 40 % degree of sludge fermentation was noted after a period of 10 days' stabilization. The concentration of volatile fatty acids before the oxygen-free stabilization process was 943 $mgCH_3COOH/dm^3$. On the second day of the process, the value of VFA concentration reached its maximum of 171 $mgCH_3COOH/dm^3$. Ultimately, the VFA concentration on the tenth day amounted to 658 $mgCH_3COOH/dm^3$.
In the case of the process conducted in the fermentation chamber for Mixture II, an approx. 56 % degree of sludge fermentation was achieved after 25 days of the process. The concentration of volatile fatty acids on the 25th day of stabilization was 702 $mgCH_3COOH/dm^3$.

Tables 1 and 2 summarize the results obtained from the oxygen-free stabilization conducted in laboratory flasks, while Tables 3 and 4 shows the results obtained during carrying out methane fermentation in the bioreactor for a period of 25 days.

Table 1

The selected physicochemiacal parameters of Mixture I submitted methane fermentation process (laboratory flasks 10-day process)

Indicator/Unit	Time of methane fermentation, d										
	0	1	2	3	4	5	6	7	8	9	10
Dry mass [g/dm^3]	18.3	16.4	16.3	15.8	14.9	14.2	13.5	13.7	13.8	13	12.8
Dry organic mass [g/dm^3]	17.5	15.1	14.8	14	13.2	12.6	11.4	11.6	11.8	11.4	11.1
Dry mineral mass [g/dm^3]	2.2	1.3	1.5	1.8	1.7	1.6	2.1	2.1	2.0	1.6	1.7
Acidity [$mval/dm^3$]	2.4	4.4	4.8	5.6	5.2	4.8	4.4	5.2	5.2	5.6	5.6
Alkalinity [mg $CaCO_3/dm^3$]	1660	1860	1960	2140	2160	2200	2240	2280	2260	2280	2280
COD [mg/dm^3 O_2]	834	1055	1048	1041	862	1120	718	195	181	172	164
Volatile fatty acids (VFA) [$mgCH_3COOH/dm^3$]	360	360	737	720	634	771	805	360	205	154	102
Kjeldahl nitrogen [mg N/dm^3]	302	355	406	436	431	459	464	518	478	504	498
Ammonia nitrogen [mg $N\text{-}NH_4^+/dm^3$]	20.1	280	324	364	434	439	448	452	478	503	517
pH	7.68	7.54	7.45	7.42	7.44	7.40	7.38	7.30	7.49	7.47	7.43

Table 2

The selected physicochemiacal parameters
of Mixture I submitted methane fermentation process (laboratory flasks 10-day process)

Indicator/Unit	Time of methane fermentation, d										
	0	1	2	3	4	5	6	7	8	9	10
Dry mass [g/dm^3]	20.3	18.9	18.4	18.3	18	17.1	16.3	15.7	15.6	15.5	14.65
Dry organic mass [g/dm^3]	15.9	15.7	14.6	13.8	13.4	12.9	12.5	11.7	11.0	10.5	9.6
Dry mineral mass [g/dm^3]	4.4	3.2	3.8	4.5	4.6	4.2	3.8	3.6	4.4	4.2	3.55
Acidity [mval/dm^3]	3.6	3.8	4.4	4.5	4.4	4.0	3.2	3.1	3.0	2.9	3.0
Alkalinity [mg $CaCO_3$/dm^3]	1480	1500	1760	2000	2000	2240	2400	2500	2440	2200	2160
COD [mg/dm^3 O_2]	1244	3290	3487	2825	2523	2668	1727	938	892	887	975
Volatile fatty acids (VFA) [mgCH_3COOH/dm^3]	943	1474	1714	1568	1448	1603	1311	1097	688	651	658
Kjeldahl nitrogen [mg N/dm^3]	319	319	386	439	414	428	476	504	562	586	604
Ammonia nitrogen [mg N-NH_4^+/dm^3]	213	224	224	280	336	380	397	403	408	420	420
pH	7.4	7.8	7.87	7.89	7.78	7.86	8.11	8.07	7.93	8.14	7.82

Table 3

The selected physicochemiacal parameters
of Mixture I submitted methane fermentation process (bioreactor-25-day process)

Indicator/Unit	Time of methane fermentation, d	
	0	25
Dry mass [g/dm^3]	17.5	11.5
Dry organic mass [g/dm^3]	15.3	8.7
Dry mineral mass [g/dm^3]	2.2	2.8
Acidity [mval/dm^3]	2.4	3.2
Alkalinity [mg $CaCO_3$/dm^3]	1660	2540
COD [mg/dm^3 O_2]	834	708
Volatile fatty acids (VFA) [mgCH_3COOH/dm^3]	205	445
Kjeldahl nitrogen [mg N/dm^3]	302	610
Ammonia nitro gen [mg NH_4^+/dm^3]	20.1	52.64
pH	7.68	7.7

Table 4

The selected physicochemiacal parameters
of Mixture II submitted methane fermentation process (bioreactor-25-day process)

Indicator/Unit	Time of methane fermentation, d	
	0	25
Dry mass [g/dm^3]	30.3	14.5
Dry organic mass [g/dm^3]	15.9	7.03
Dry mineral mass [g/dm^3]	13.4	5.5
Acidity [mval/dm^3]	3.6	3.9
Alkalinity [mg $CaCO_3$/dm^3]	1480	2630
COD [mg/dm^3 O_2]	1244	814
Volatile fatty acids (VFA) [mgCH_3COOH/dm^3]	943	702
Kjeldahl nitrogen [mg N/dm^3]	319	798
Ammonia nitro gen [mg N-NH_4^+/dm^3]	213	602
pH	7.4	7.37

The tests carried out confirmed the effectiveness of the sonification process as a disintegrating measure that considerably contributes to increasing the susceptibility of sludge to biodegradation. An increase in the rate of hydrolysis was achieved, as reflected by a considerable increase in the concentration of volatile fatty acids in the successive days of conducting the stabilization process, which had a direct effect of extending the time of intensive biogas production.

4. Summary

The preconditioning of excessive sludge with the ultrasonic field had the effect of enhancing the degree of its disintegration. The process of hydrolysis was intensified. An increase in the concentration of volatile fatty acids occurred in the successive days of conducting the process and, in addition, an increase in the degree of sludge fermentation and was noted that an increased biogas production was achieved. The optimal effectiveness of sludge sonification was achieved for an US field vibration amplitude of 36.6 μm and for an exposure time of 240 s. In the case of the oxygen-free stabilization of non-conditioned sludge (Mixture I), the highest value of VFA concentration was noted on the sixth day of conducting the stabilization process. In the case of sludge conditioned with the ultrasonic field with an amplitude of 36.6 μm and for an exposure duration of 240 s (Mixture II), the highest value of VFA concentration was noted already on the second day of conducting methane fermentation. For the mixtures tested, after 25 days of conducting the process, the following sludge fermentation degrees were obtained: Mixture I: 43 %, Mixture II: 56 %, and a unit biogas production of 2.43 dm^3/g d.m.$_{org}$ and 3.54 dm^3/g d.m.$_{org}$, respectively.

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Abstrakt: Konwencjonalny proces stabilizacji beztlenowej jest często czasochłonny i ma niską efektywność. Dokonany przegląd literaturowy, jak również przeprowadzone badania własne sugerują, że ultradźwiękowe kondycjonowanie stanowi nową drogę do skrócenia czasu oraz zwiększenia efektywności procesu stabilizacji beztlenowej osadów, powstających zarówno w procesie oczyszczania ścieków bytowo-gospodarczych, jak i przemysłowych. Uzyskanie znacznego wzrostu stopnia przefermentowania podczas stabilizacji beztlenowej osadów kondycjonowanych polem ultradźwiękowym (UD), w odniesieniu do redukcji substancji organicznych odnotowanych podczas stabilizacji beztlenowej osadów niepreparowanych, wynika z kombinacji działania zarówno hydrolizy biologicznej, stanowiącej pierwszy etap procesu, jak również zjawiska hydrolizy sonochemicznej, mającej miejsce podczas procesu preparowania. Poddanie osadów kondycjonowaniu badaną metodą wpływa na znaczną intensyfikację fazy hydrolizy, czego wyrazem był odnotowany w kolejnych dniach prowadzenia procesu stabilizacji beztlenowej wzrost tempa produkcji oraz stężenia lotnych kwasów tłuszczowych, warunkujący bezpośrednio zwiększenie efektywności fermentacji, tj. stopnia przefermentowania osadów oraz jednostkowej produkcji biogazu. Stabilizacji beztlenowej, w warunkach statycznych, poddano nadmierny osad czynny powstający w wyniku oczyszczania mieszaniny ścieków bytowo-gospodarczych oraz przemysłowych powstających na terenie zakładu produkującego soki oraz napoje. Proces

prowadzono zarówno w kolbach laboratoryjnych, stanowiących modele komór fermentacyjnych, jak również w komorze fermentacyjnej firmy Applicon.

Słowa kluczowe: stabilizacja beztlenowa, hydroliza, lotne kwasy tłuszczowe, kondycjonowanie, czynne działanie pola ultradźwiękowego.