DOI: 10.2428/ecea.2014.21(2)17 ECOL CHEM ENG A. 2014;21(2):211-219

Ewelina NOWICKA[1*], Alicja MACHNICKA[1]
and Klaudiusz GRÜBEL[1]

IMPROVING OF ANAEROBIC DIGESTION BY DRY ICE DISINTEGRATION OF ACTIVATED SLUDGE

DEZINTEGRACJA OSADU CZYNNEGO SUCHYM LODEM W CELU INTENSYFIKACJI FERMENTACJI METANOWEJ

Abstract: Disintegration by dry ice has a positive effect on the degree and rate of surplus activated sludge anaerobic digestion. By applying thermal disintegration the lysis of cells occurs in minutes instead of days. The intracellular and extracellular components are set free and are immediately available for biological degradation which leads to an improvement of the subsequent anaerobic process. Thermal disintegration by dry ice of the surplus activated sludge results in organic matter and a polymer transfer from the solid phase to the liquid. During the disintegration process, soluble chemical oxygen demand (SCOD) value and proteins concentration increase about 583 mg/dm^3 and 265 mg/dm^3, respectively. At the same time the concentration of carbohydrates increase about 53 mg/dm^3. In addition the degree of thermal disintegration changed from 13 % for the volume ratio of dry ice to surplus activated sludge 0.25:1 to 49 % for the volume ratio of dry ice to sludge 1:1.

The addition of thermal disintegrated sludge (30 %SASDI of volume) to the digestion process leads to increased biogas production about 49 %.

Keywords: dry ice, soluble chemical oxygen demand, proteins, carbohydrates, anaerobic digestion, biogas

Introduction

The aim of wastewater treatment is to mineralise organic matter and enhance nutrient removal. Anaerobic digestion is a common method for surplus activated sludge stabilization resulting in the reduction of sludge volatile matter and the production of biogas. Anaerobic degradation of biomass is considered to follow a sequence of four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The slow degradation rate of surplus activated sludge in the anaerobic digestion process is due to the

[1] Department of Environmental Microbiology and Envirenmental Biotechnology, Institute of Environmental Protection and Engineering, University of Bielsko-Biala, 43–309 Bielsko-Biała, ul. Willowa 2, Poland, phone: +48 33 827 91 57.

* Corresponding author: enowicka@ath.bielsko.pl

rate-limiting step of sludge hydrolysis. Therefore, the disintegration pretreatment of a surplus activated sludge process using physics (thermal) [1, 2], chemical (using *eg* acids) [3], mechanical (ball mill, ultrasonic) [4–6], oxidation (ozone and hydrogen peroxide) [7, 8], or biological (using enzymes) [9–11] and thermal (heat treatment, freezing/thawing) [12–14] treatment processes, can improve the subsequent anaerobic digestion. Although the methods are different, the aim of all of them is partial or complete bacterial cell rupture, *ie* destruction of the cell wall and release of organic substances present inside the cells to the liquid phase. Thermal disintegration by dry ice has a positive effect on the degree and rate of sludge anaerobic digestion.

The freeze/thaw frequently found in nature, which leads to changes in soil. This process is used in the municipal wastewater treatment for dewatering of sewage sludge. Sludge dewatering by freezing is done by separating the solid and liquid fractions during the formation of ice crystals. It was also found that the refrigeration mechanism is conducive to converting the form of flocs in a more compact, dense [15].

Freezing/thawing using by dry ice is an effective technique for dewatering, sewage sludge and its attention was already 1990 by Vesilind and Martel [16]. Dry ice transforms the structure of flocs into larger agglomerates and reducing water-related because the process of freeze/thaw by dry ice is becoming more and more popular [17–21].

Basic mechanisms of freeze/thaw sludge used as a method of conditioning of sludge prior to anaerobic stabilization are increasing interest due to the reduction of pathogenic bacteria, reduce sediment and increase the biomass production of biogas [22, 23].

Dry ice is a completely natural product. It is produced in the form of granules for compressing gaseous carbon dioxide to liquid form, removing the heat generated by compression, and then rapid expansion. This expansion and rapid evaporation of carbon dioxide gas remaining fluid which cooled to the melting point and freezing in the CO_2 "snow", which takes the form of beads or prills. The dry ice sublimes at –78.5 ^oC and a pressure of 1013.25 hPa. Its heat of sublimation is 573 kJ, which means that it is approximately 3.3 times more effective coolant than water ice (with the same volume). Its specific gravity comprises in the range from 1.2 kg/dm^3 to 1.6 kg/dm^3, and its hardness on the Mohs scale is 2, which corresponds to the hardness of gypsum. It is anhydrous, non-flammable, non-toxic and has no smell or taste. It is intended as a catering, refrigeration, to clean all types of machines and laboratories to slow exothermic reactions [24, 25].

The new concept described in this paper is based on the combined process of surplus activated sludge disintegration by dry ice prior to anaerobic digestion. Thermal disintegration by dry ice can activate the biological hydrolysis process and therefore significantly increase the biogas production in anaerobic stabilization.

Materials and methods

Experimental material was surplus activated sludge taken from the municipal wastewater treatment plant in the south of Poland, working according to the Enhanced Biological Nutrient Removal (EBNR). The plant was designed for a flow of 120 000

m^3/d. At present the amount of treated wastewater is about 90 000 m^3/d. Solid retention time (SRT) is about 14 days and concentration of mixed liquid suspended solids (MLSS) 4.3–4.7 g/dm^3.

Thermal disintegration

The disintegration of surplus activated sludge, the following ratios by volume of dry ice to sludge, *ie*: 0.25:1; 0.5:1; 0.75:1; 1:1.

The chemical analysis

Soluble chemical oxygen demand (SCOD) and proteins value was determined for samples before and after each time of disintegration according to *Standard Methods* [26]. Carbohydrate concentration was determined according to Anthron methods [27].

The degree of disintegration

In order to obtain a quantitative measure of the effects of disintegration, Kunz and Wagner [28] have proposed a coefficient which they called the degree of disintegration (DD). Later this coefficient was modified by Müller [29]. In this paper the degree of sludge disintegration was determined according to that given by Müller [30] as follows:

$$DD = [(SCOD_1 - SCOD_2) / (SCOD_3 - SCOD_2)] \cdot 100 \text{ [\%]},$$

where: DD – the degree of disintegration;
$SCOD_1$ – the SCOD of the liquid phase of the disintegrated sample;
$SCOD_2$ – the SCOD of the original sample;
$SCOD_3$ – the value after the chemical disintegration.

Chemical disintegration was done in this case by treating the sludge samples for 10 min at 90 °C after adding NaOH, 1 M, in a ratio of 1:2. Centrifugation in all cases was done for 10 min at 30 000 g.

The fermentation experiments

The anaerobic digestion experiments were performed in six glass fermenters (3 dm^3) operated in parallel at a temperature of 35 ± 1°C. Residence time was 23 days. The volume of producing biogas was determined by the liquid displacement method ever each day. Different rates of raw and disintegrated surplus activated sludge were applied:

– **Fermenter 1** was feed with surplus activated sludge (70 % volume of fermenter; 70 %SAS) and digested sludge (30 % volume of fermenter; 30 %DS),

– **Fermenter 2** was feed with 50 %SAS and 30 %DS and with surplus activated sludge after dry ice disintegration (20 % volume of fermenter; 20 %SASDI),

– **Fermenter 3** was feed with 40 %SAS and 30 %DS and 30 %SASDI,

– **Fermenter 4** was feed with 30 %SAS and 30 %DS and 40 %SASDI,
– **Fermenter 5** was feed with 20 %SAS and 30 %DS and 50 %SASDI,
– **Fermenter 6** was feed with 30 %DS and 70 %SASDI.

The aim of carrying out the experiment of sludge digestion was to show the possibilities to improve and accelerate the anaerobic process. The investigations presented here were performed in 5 stages, and arithmetic average and standard deviation were established. The standard deviation was determined according to the estimator of the highest credibility in STATISTICA 6.0.

Results and discussions

Increase of volume of freezing water in the cytoplasm of microorganisms causes them disruption by mechanical damage of the walls and cell membranes, osmotic shock and destruction of cellular organelles. These mechanical damage is caused by the formation of ice crystals in the environment surrounding of cells as well as in their interior, which leads to changes in their properties (denaturation) [31, 32]. These crystals cause damage and changes in properties of microbial cells, which leads to release of intracellular substances into the environment.

The disintegration of surplus activated sludge by dry ice resulted in the release of organic matter (expressed as SCOD). Disrupter of flocs and microbial cells of activated sludge leads to the release of intracellular organic compounds to liquid phase. The value of SCOD in supernatant liquid of surplus sludge 63 mg/dm^3 (Fig. 1), while during the dry ice disintegration process increase:

– for the volume ratio of dry ice to sludge 0.25:1, the value of SCOD was 210 mg/dm^3 (Fig. 1),

– for the volume ratio of dry ice to sludge 0.5:1, the value of SCOD was 363 mg/dm^3 (Fig. 1),

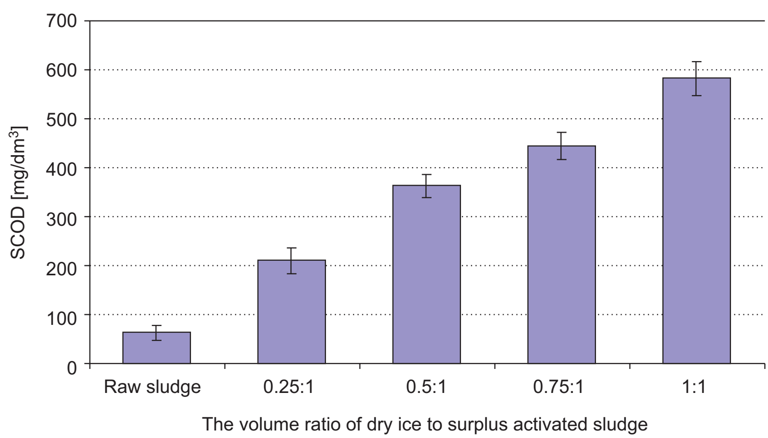

Fig. 1. Changes of SCOD value in the sludge supernatant before and after the disintegration

– for the volume ratio of dry ice to sludge 0.75:1, the value of SCOD was 445 mg/dm^3 (Fig. 1),

– for the volume ratio of dry ice to sludge 1:1, the value of SCOD was 583 mg/dm^3 (Fig. 1).

Freezing/thawing by dry ice of surplus activated sludge caused disruption of flocs structure and resulted in a different degree of disintegration (DD). The effect of dry ice (various volumes) on the sludge degree of disintegration was studied. The results of the experiments are presented in Fig. 2.

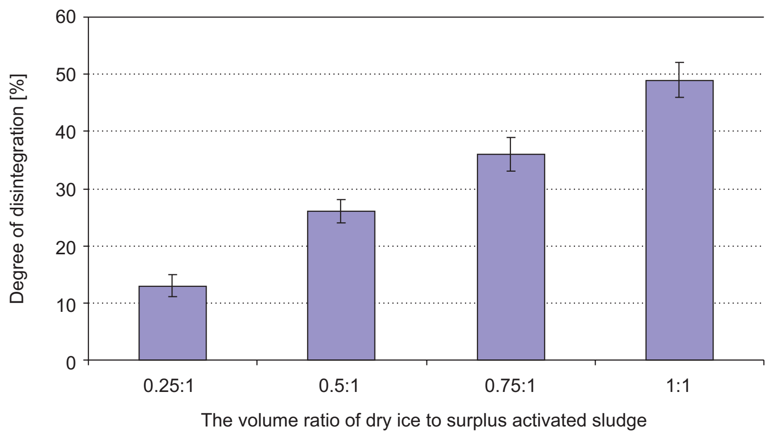

Fig. 2. Degree of surplus activated sludge disintegration by dry ice

Within the range of dry ice volume, between 0.25:1 to 1:1, the degree of disintegration increased most rapidly. The achieved degree of sludge disintegration was about 49 % (Fig. 2).

The effectiveness of the dry ice disintegration effect of these relations by volume of sludge to dry ice were as follows:

– for the volume ratio of dry ice to sludge 0.25:1, DD was 13 % (Fig. 2),

– for the volume ratio of dry ice to sludge 0.5:1, DD was 26 % (Fig. 2),

– for the volume ratio of dry ice to sludge 0.75:1, DD was 36 % (Fig. 2),

– for the volume ratio of dry ice to sludge 1:1, DD was 49 % (Fig. 2).

The disintegration of raw sludge resulted in the release of proteins. The increase of proteins concentration were associated with the destructive effects of dry ice in the cells, which resulted in the release of organic matter into the liquid phase. The proteins and carbohydrates concentration in untreated surplus activated sludge supernatant was 39 mg/dm^3 and 15 mg/dm^3, respectively. These concentrations increase with volume of dry ice (Fig. 3).

Freezing/thawing disintegration by dry ice accelerates the biological degradation of sludge. The cell liquid contains components, which upon being released, can be easily assimilated. The released organic substances (expressed here, as SCOD) as a result of

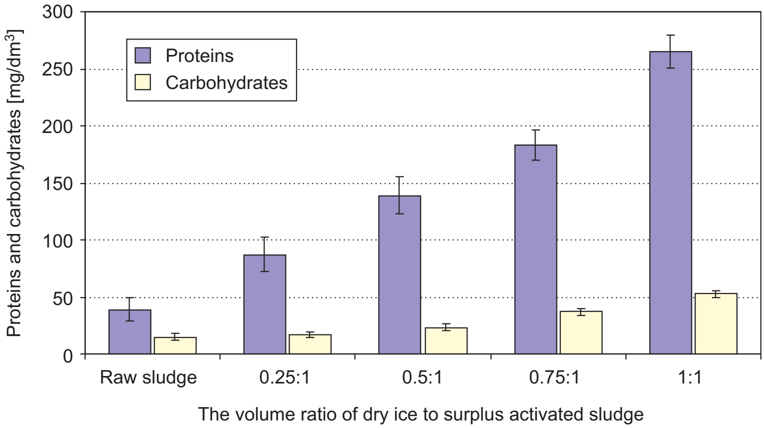

Fig. 3. Changes proteins and carbohydrates concentration before and after disintegration of dry ice

surplus activated sludge flocs disintegration, lead to a substantial increase of biogas production in the subsequent anaerobic sludge digestion process (Fig. 4).

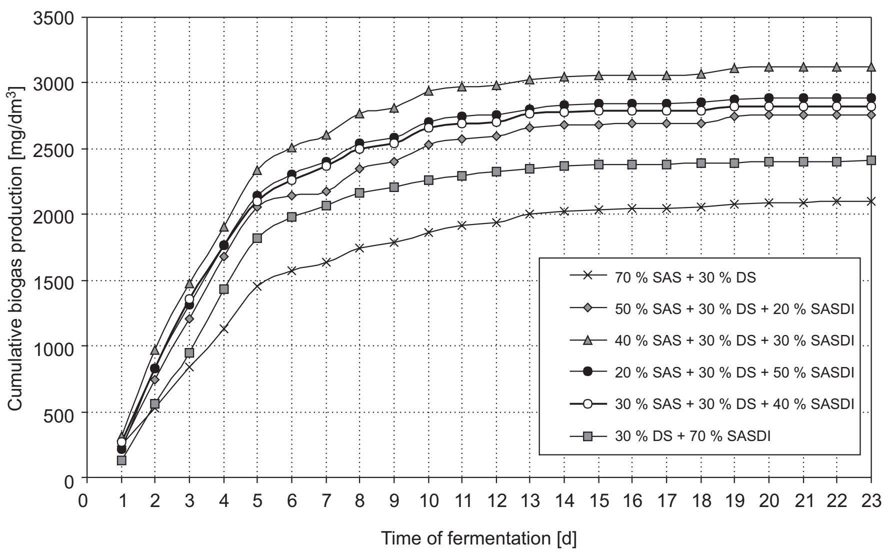

Fig. 4. Changes of cumulative biogas production during anaerobic digestion

Significantly higher amounts of biogas were produced in the fermenters feed with disintegrated activated sludge (20 %, 30 %, 40 %, 50 % or 70 % volume of fermenter). The gas production during sludge digestion depends on volatile solids, degree of disintegration (expressed as COD) and fermentation time.

Figure 4 shows the development of biogas production after 23 days of fermentation. Comparing the results it can be concluded that in the case of sample with addition disintegrated sludge in volume of 70 %, there was a smaller production of biogas (2 408 cm^3/dm^3) than in sample involving 40 % (2826 cm^3/dm^3) and 50 % (2890 cm^3/dm^3) of volume of surplus activated sludge after thermal destruction. Low biogas production is probably due to too high load of organic matter introduced into the digester. The samples with 30 % of volume of disintegrated surplus activated sludge produced 3 124 cm^3/dm^3 of biogas, which gives a 49 % more of biogas in comparison to the blank sample (70 % SAS + 30 % DS) (Fig. 4).

The organic matter transferred by dry ice treatment from the sludge solids into the liquid phase was readily biodegradable. Surplus activated sludge consists mainly of heterotrophic bacteria. The gradual break–up of the bacterial cell walls limits the degradation process. By applying freezing/thawing disintegration the lysis of cells occurs in minutes instead of days. The intracellular and extracellular components are set free and are immediately available for biological degradation which leads to an improvement of the subsequent anaerobic process. In Fig. 4, this is shown by comparing the increase of biogas production in the anaerobic digestion, post thermal disintegration. A calculation of energy consumption and cost shows that the disintegration by dry ice is an economically viable process. The surplus gas can be used for power and heat production. This energy yield can be used for the thermal disintegration of surplus activated sludge. The reduced cost of the sludge disposal, enhanced fermentation rates and acceleration of biogas production should lead to the practical use of disintegration by dry ice as a new technology.

Conclusions

The experiments have clearly demonstrated that thermal disintegration is a suitable method to destroy surplus activated sludge micro-organisms. In this study, the addition of disintegrated by dry ice raw sludge was examined in order to improve the anaerobic digestion process. The most important conclusions are:

– The disintegration by dry ice surplus activated sludge destroys the flocs structure of sludge and ruptures the cells of the micro-organisms. As a result of sludge disintegration, organic matter is transferred from the sludge, solid phase into the liquid phase (expressed as SCOD). SCOD increased from 63 mg/dm^3 to 583 mg/dm^3 in direct proportion with the time needed for disintegration.

– With increasing doses of dry ice, the degree of disintegration and increased volume ratio of the excess sludge to a dry ice 1:1 was 49 %.

– As a result of disintegration of surplus activated sludge dry ice, the destruction of cell structures of microorganisms and thereby increasing the concentration of proteins. In the settlement is not subjected to excessive disintegration of the dry ice, the concentration of protein amounted to 39 mg/dm^3, and the volume ratio of dry ice to precipitate 1:1, protein concentration was 265 mg/dm^3.

– An additional effect of the destructive action of dry ice on microorganisms excessive sludge was released into the supernatant fluid concentrations of organic matter expressed carbohydrates. With the increasing volume of dry ice to precipitate obtained significantly increasing the concentration of carbohydrates. For the ratio of the volume of dry ice to precipitate 1:1 carbohydrate concentration increased by 38 mg/dm^3.

– The thermal disintegration of surplus activated sludge leads to a higher degree of degradation and higher biogas production. Addition of disintegrated sludge (30 % volume of fermenter) to the anaerobic digestion stage resulted in increased biogas production, about 49 %.

References

[1] Wett B, Phothilangka P, Eladawy A. Waste Management. 2010;30:1057-1062. DOI: 10.1016/j.wasman.2009.12.011.

[2] Barjenbruch M, Kopplow O. Adv Environ Research. 2003;7:715-720. DOI: 10.1016/S1093-0191(02)00032-1.

[3] Young-Khee O, Ki-Ryong L, Kwang-Baik K, Ick-Tae Y. Water Research. 2007;41:2665-2671. DOI: 10.1016/j.watres.2007.02.028.

[4] Tiehm A, Nickel K, Zellhorn M, Neis U. Water Research. 2001; 35:2003-2009. DOI: 10.1016/S0043-1354(00)00468-1.

[5] Panyue Z, Guangming Z, Wei W. Bioresource Technol. 2007;98:207-210. DOI: 10.1016/j.biortech.2005.12.002.

[6] Dong-Hoon K, Emma J, Sae-Eun O, Hang-Sik S. Water Research. 2010;44:3093-3100. DOI: 10.1016/j.watres.2010.02.032.

[7] Guangming Z, Jing Y, Huanzhi L, Jie Z. Bioresource Technol. 2009;100:1505-1509. DOI: 10.1016/j.biortech.2008.08.041.

[8] Tak-Hyun K, Sang-Ryul L, Youn-Ku N, Jeongmok Y, Chulhwan P, Myunjoo L. Desalination. 2009;246:275-284. DOI: 10.1016/j.desal.2008.06.023.

[9] Barjenbruch M, Kopplow O. Adv Environ Research. 2003;7:715-720. DOI: 10.1016/S1093-0191(02)00032-1.

[10] Guang-Hui Y, Pin-Jing H, Li-Ming S, Yi-Shu Z. Water Research. 2008;42:1925-1934. DOI: 10.1016/j.watres.2007.11.022.

[11] Azize A, Ayse F, Diclehan S, Ersan K. J Environ Sci Health, Part A: Toxic/Hazardous Subst Environ Eng. 2008;43:1528-1535. DOI: 10.1080/10934520802293685.

[12] Stabnikova O, Liu XY, Wang, JY. Elsevier Science. 2008;28:1654-1659. DOI: 10.1016/j.wasman.2007.05.021.

[13] Saktaywin W, Tsuno H, Nagare H, Soyama T, Weerapakkaroon J. Water Research. 2005;39:902-910. DOI: 10.1016/j.watres.2004.11.035.

[14] Montusiewicz A, Lebiocka M, Rożej A, Zacharska E, Pawłowski L. Bioresource Technol. 2010;101:3466-3473. DOI: 10.1016/j.biortech.2009.12.125.

[15] Jean DS, Lee DJ, Chang CY. Direct sludge freezing using dry ice. Adv Environ Research. 2001;5:145-50.

[16] Vesilind PA, Martel CJ. J Environ Eng. 1990;116:854–862. DOI: 10.1061/(ASCE)0733-9372(1990)116:5(854).

[17] Örmeci B, Vesilind AP. Water Research. 2001;35:4299-4306. DOI: 10.1016/S0043-1354(01)00174-9.

[18] Jean DS, Chu CP, Lee DJ. Water Research. 2000;34:1577-1583. DOI: 10.1016/S0043-1354(99)00303-6.

[19] Wang Q, Fujisaki K, Ohsumi Y, Ogawa IH. J Environ Sci Health, Part A: Toxic/Hazardous Subst Environ Eng. 2001;36:1361-1371. DOI: 10.1081/ESE-100104884.

[20] Jean DS, Chu CP, Lee DJ. Separation Sci Technol. 2001;36:2733-2746. DOI: 10.1081/SS-100107222.

[21] Hu K, Jun-Qiu J, Qing-Liang Z, Duu-Jong L, Kun W, Wei Q. Water Research. 2011;45:5969-5976. DOI: 10.1016/j.watres.2011.08.064.

[22] Grübel K, Chrobak E, Rusin A, Machnicka A. Eliminacja *Clostridium perfringens* podczas kondycjonowania osadu czynnego nadmiernego. Inż Ekol. 2013;32:40-47.

[23] Nowicka E, Machnicka A. Ocena skuteczności osadu nadmiernego suchym lodem. Współczesne problemy ochrony środowiska. Gliwice: Archiwum Gospodarki Odpadami i Ochrony Środowiska; 2013.

[24] Jeyasekaran G, Ganesan P, Anandaraj R, Jeya Shakila R, Sukumar D. Food Microbiol. 2006;23:526-533. DOI: 10.1016/j.fm.2005.09.009.
[25] Franceschini O. Dewatering of sludge by freezing. University of Technology. Luleĺ;2010.
[26] Clesceri LS, Greenberg AE, Eaton AD, (eds.). STANDARD METHODS. Standard Methods for the Examination of Water and Wastewater (20th edn.). Washington: American Public Health Association; 1999.
[27] Tchobanoglous G, Burton FL, Stensel HD. Wastewater Engineering: Treatment and Reuse, (4th edition) Metcalf & Eddy, Inc. 2002.
[28] Kunz P, Wagner S. Results and outlooks of investigations of sewage sludge disintegration – Ergebnisse und Perspektive aus Untersuchungen zur Klärschlammdesintegration. Heft 1: AWT Abwassertechnik; 1994.
[29] Müller J. Mechanical disintegration of sewage sludge – Mechanischer Klärschlammaufschluß-, Schriftenereihe "Berichte aus der Verfahrenstechnik" der Fakultät für Maschinenbau und Elektrotechnik der Universität Braunschweig. Germany: Shaker Verlag, Aachen; 1996.
[30] Müller J. Disintegration as key-stop in sewage sludge treatment. Water Sci Technol. 2000;41:123-139.
[31] Bollag DH, Edelstein SJ. Protein Methods. New York: Wiley&Liss; 1992.
[32] Libudzisz Z, Kowal K, Żakowska Z. Mikroorganizmy i środowiska ich występowania. Tom 1. Warszawa: Wyd Nauk PWN; 2007.

DEZINTEGRACJA OSADU CZYNNEGO SUCHYM LODEM W CELU INTENSYFIKACJI FERMENTACJI METANOWEJ

Zakład Mikrobiologii i Biotechnologii Środowiskowej, Instytut Ochrony i Inżynierii Środowiska
Akademia Techniczno-Humanistyczna w Bielsku-Białej

Abstrakt: Jednym z podstawowych problemów występujących w układach przeróbki osadów ściekowych jest zwiększenie dostępności i podatności substancji organicznych na biodegradację, co można osiągnąć poprzez dezintegrację osadu.

W pracy wykorzystano dezintegrację osadu nadmiernego suchym lodem oraz określono jej wpływ na uwalnianie materii organicznej i na efektywność fermentacji metanowej wyrażonej produkcją biogazu.

Zamrażanie/rozmrażanie osadu suchym lodem powodowało wzrost wartości uwolnionego ($UChZT_{Cr}$) o 520 mg O_2/dm^3, a stopień dezintegracji (SD) wyniósł 49 %. W wyniku destrukcji osadu przy pomocy suchego lodu do cieczy nadosadowej zostały również uwolnione proteiny oraz węglowodany, co świadczyło o skuteczności procesu. Stężenia tych parametrów wyniosły odpowiednio 265 mg/dm^3 i 53 mg/dm^3.

Poddanie fermentacji mieszanki: osadu zdezintegrowanego w objętości 30 %, osadu niezdezintegrowanego w objętości 40 % i 30 % osadu przefermentowanego, spowodowało wzrost wydajności produkcji biogazu o 49 %.

Słowa kluczowe: suchy lód, $ChZT_{Cr}$, proteiny, węglowodany, fermentacja metanowa, biogaz