E C O L O G I C A L  C H E M I S T R Y  A N D  E N G I N E E R I N G  A

Vol. 17, No. 12 2010

Mariusz KUGLARZ[1] and Jolanta BOHDZIEWICZ[2]

# MESOPHILIC ANAEROBIC DIGESTION OF PIG MANURE FOR BIOGAS PRODUCTION

## FERMENTACJA METANOWA GNOJOWICY ŚWIŃSKIEJ W WARUNKACH MEZOFILNYCH

**Abstract:** The aim of the research was to establish the most appropriate technological parameters of anaerobic digestion treating non-straw-bedded pig manure. The digesters were maintained at a constant temperature of 36 °C (±0.5). The process was carried out at the following hydraulic retention times (HRT): 15, 18, 20, 23, 25, 30, 35 and 40 days. The applied range of HRT corresponds to the OLR value of between 1.18 and 3.13 kg VS/($m^3 \cdot$ d). Both analyses of fermentation digestate, including the susceptibility to dewatering, as well as quantitative and qualitative biogas generated were carried out during the experiment. The criteria taken into account while assessing the applied HRT values included: biogas production rate, biogas yield, organic matter decomposition (VS and COD reduction) as well as stability indices (VFA; VFA/TA). It was established that anaerobic digestion of the analysed manure in conditions of high ammonia concentration (5760–6390 mg $NH_4^+$/$dm^3$) turned out to be stable and effective for the HRT value of between 25 and 35 days. When the HRT was reduced to below 25 days, a significant decrease in biogas production and deterioration in organic matter decomposition was noticed. Moreover, the VFA/alkalinity ratio exceeded 0.4; ie a value which is believed to cause instability in methanogens activity. The capillary section time (CST) measurement showed that the digestion process impacted the dewatering properties of the digested manure in a positive way.

**Keywords:** methane fermentation, renewable energy, biogas, animal by-products, swine manure

Animal breeding is strictly connected with generation of waste and by-products impacting on the natural environment. Animal rearing is either straw-bedded or non-straw-bedded, which determines the consistence and chemical composition of by-products generated. In the former case, the by-products are stall waste and liquid manure. Stall waste consists of animal faeces mixed with bedding material and a limited amount of urine. While liquid manure contains urine with a limited amount of water and stall waste leachate. Agricultural intensive production favours non-straw-bedded method.

[1] Institute of Engineering and Environmental Protection, University of Bielsko-Biala, ul. Willowa 2, 43–309 Bielsko-Biała, Poland, email: mkuglarz@ath.bielsko.pl

[2] Institute of Water and Wastewater Engineering, Silesian University of Technology, ul. Konarskiego 18, 44–100 Gliwice, Poland, email: jolanta.bohdziewicz@polsl.pl

In this case, by-products constitute semi-liquid straw-bedded manure containing faeces, urine and fodder leftovers. Animal by-products, just like straw and harvest leftovers are treated as natural fertilizers and should be used predominantly for this purpose. Farms rearing animals on the massive scale (> 2000 animal standings for pigs weighted more than 30 kg or 750 standings for sows) are obliged to use at least 70 % of the manure generated as a natural fertilizers in their own arable land. The rest can be sold proving that it would also be used agriculturally. The manure which is not directly used as natural fertilizers is treated as waste and has to be neutralized [1, 2].

Natural fertilizers, including liquid animal by-products should be applied in the way which does not negatively affect the environment. According to the law [2, 3], maximum permissible dosages (45 $m^3$/ha) and application periods (1st March–30th November) should be strictly observed. Moreover, agrotechnical requirements and storage conditions should be met. Liquid manures should be stored in leak-proof containers with the capacity sufficient to keep the manure generated over a period of at least 4 months [3]. During storing animal excrements undergo natural biodegradation, which leads to the release of gases, mainly $NH_3$, $CH_4$, $CO_2$ and $NO_x$ [4, 5]. Especially, ammonia released during excretion and storage is associated with agricultural activity. The ammonia release depends mainly on the amount of albumin compounds in fodder, pH, humidity as well as temperature [4, 6, 7]. It is estimated that in areas with high-intensity animal production about 70–80 % of the ammonia released comes from farming [4, 8]. Apart from releasing ammonia into the atmosphere, liquid manures leakages from storage tanks, may cause soil as well as surface and groundwaters degradation [4, 8, 9].

The methane fermentation generates a renewable energy in the form of biogas and digested manure in the form of stabilized natural fertilizer. Besides, the process ensures odour neutralization and has a positive impact on the separation of manure into liquid and solid fraction. The former can be utilized directly on the farm, while the latter can be easier transported into areas deficient in natural fertilizers [10, 11].

The aim of the research project was to establish the most appropriate technological parameters of anaerobic digestion of non-straw-bedded pig manure. The mesophilic digestion for biogas production was conducted at the *hydraulic retention times* (HRT) ranging from 15 to 40 days. The criteria taken into account while assessing the applied HRT values included: biogas production rate, biogas yield, organic matter biodegradation (VS and COD reduction) as well as process stability indices. Moreover, the influence of the digestion process on the dewatering properties of the digested manure was evaluated.

## Materials and methods

In this experiment, pig liquid manure from a non-straw bedded rearing farm was used as a digestion feedstock. The samples were collected at the outlet of the pipe connecting animal standings with manure storage tanks. Table 1 presents the physical and chemical properties of the raw manure used.

Table 1

Characteristics of the digestion feedstock

| Parameter | Unit | Raw manure | |
|---|---|---|---|
| | | Range of variation | Average value |
| pH | — | 6.62–7.32 | 6.89 |
| ORP | mV | -90–-255 | –170 |
| $BOD_5$ | g $O_2/dm^3$ | 23.5–26.0 | 24.4 |
| COD | g $O_2/dm^3$ | 26.6–37.0 | 30.7 |
| $BOD_5$/COD | — | 0.70–0.88 | 0.79 |
| Ammonia | g $NH_4^+/dm^3$ | 4.5–5.7 | 5.41 |
| Phosphates | g $PO_4/dm^3$ | 1.32–1.57 | 1.49 |
| Total solids (TS) | % | 5.72–6.25 | 5.90 |
| Volatile solids (VS) | % | 4.58–4.92 | 4.71 |

The digestion was conducted in a bioreactor with a working volume of 3 $dm^3$. The digester was maintained at a constant temperature of 36 $^oC$ (±0.5). The process was carried out at the following hydraulic retention times (HRT): 15, 18, 20, 23, 25, 30, 35 and 40 days. The applied range of HRT corresponds to the *organic loading rate* (OLR) value of between 1.18 and 3.13 kg VS/($m^3$ · d). The digesters contents were mixed periodically – 5 minutes in every 3 hours. Both analyses of the biogas produced as well as digested manure were carried out during the experiment. Chemical composition of the biogas produced was also periodically determined. The scope of the analyses conducted encompassed: pH value and ORP potential measurement as well as *total solids* (TS), *volatile solids* (VS), *chemical oxygen demand* (COD), *biochemical oxygen demand* ($BOD_5$), phosphates ($PO_4^{3-}$), *total volatile fatty acids* (VFA), *total alkalinit*y (TA) and ammonium-nitrogen ($NH_4^+$) determinations. The susceptibility of the digested manure to separation into solid and liquid fraction was based on the *capillarity section time* (CST) [12–14].

## Results and discussion

The process of methane fermentation was conducted under high ammonia concentration (5790–6390 mg $NH_4^+/dm^3$). The hydraulic retention time (HRT) of the manure in the bioreactor was gradually increased. Physical and chemical characteristics of the digested manure are presented in Table 2.

Firstly, the influence of the particular HRTs on the degrees of organic matter decomposition was taken into consideration. The process was initially adopted by the application of the shortest HRT value, ie 15 days, which was tantamount to 1.18 kg VS/($m^3$ · d) of bioreactor *organic loading rate* (OLR). Anaerobic digestion for biogas production is a multi-step biochemical process, whereby macromolecular substances are converted into simpler compounds. The organic matter conversion can be expressed as a degree of volatile matter (VS) reduction or COD reduction – dissolved in supernatant, which is presented in Fig. 1. Under those conditions, the low reduction of VS, ie 25.2 %

Table 2

Physical and chemical properties of the digested manure

| Parameter | Unit | HRT [days] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 15 | 18 | 20 | 23 | 25 | 30 | 35 | 40 |
| pH | — | 7.44 | 7.51 | 7.59 | 7.60 | 7.85 | 7.90 | 7.93 | 7.95 |
| TS | % | 4.58 | 4.42 | 4.12 | 4.01 | 3.93 | 3.60 | 3.69 | 3.70 |
| VS | % | 3.52 | 3.41 | 3.14 | 2.96 | 2.88 | 2.58 | 2.72 | 2.71 |
| COD | g $O_2/dm^3$ | 28.5 | 26.2 | 24.4 | 22.0 | 14.3 | 13.0 | 12.9 | 14.3 |
| Ammonia | g $NH_4^+/dm^3$ | 6.39 | 6.21 | 5.94 | 5.88 | 5.79 | 5.81 | 5.92 | 5.89 |
| VFA | g $CH_3COOH/dm^3$ | 7.54 | 7.38 | 7.25 | 5.17 | 3.80 | 3.15 | 3.47 | 3.79 |
| TA | g $CaCO_3/dm^3$ | 12.3 | 12.4 | 12.3 | 12.0 | 12.2 | 13.7 | 13.6 | 14.3 |

as well as COD, ie 24.0 % was recorded. The HRT value was subsequently extended and the corresponding changes in VS and COD reduction recorded. The VS reduction increased gradually for the HRT ranging from 18 to 30 days. The maximal reduction of the VS – 45.2 % was achieved when the HRT was extended to 30 days, which was associated with an increase in OLR value to 1.57 kg /($m^3 \cdot$ d). Further increase in HRT (35 days) did not have a positive impact on the parameter.

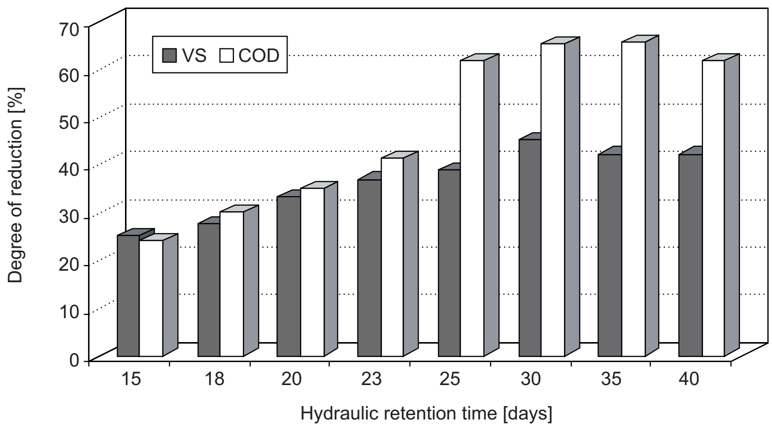


Fig. 1. The influence of hydraulic retention time (HRT) on the degree of organic matter decomposition

Just as in case of VS reduction, the degree of COD reduction increased up to the point where the HRT reached the level of 30 days. What is more, the most significant enhancement of the parameter occurred at the HRT of 25 days. In this case, the COD reduction amounted to 61.9 %. The maximum value of the parameter fluctuated around 65 % (65.3–65.6 %) and was recorded for the HRT in the range of 30–35 days. The application of the highest value of HRT (40 days) did not affect the organic matter bioconversion, expressed either in VS or COD reduction.

Secondly, the biogas production as well as methane content in the biogas generated was recorded. Figure 2 shows the amount of biogas produced for various HRT values, expressed in terms of daily production and biogas yield. Conducting the process for the HRT in the range of between 15–18 days, a relatively low daily biogas production (0.38–42 $dm^3/dm^3 \cdot d$) as well as biogas yield (0.16–0.18 $dm^3/g\ VS_{removed}$) was achieved. As the hydraulic retention time was extended (20–25 days), the daily biogas production (0.59–0.81 $dm^3/dm^3 \cdot d$) and biogas yield (0.26–0.37 $dm^3/g\ VS_{removed}$) increased gradually. When the HRT was increased to 30 days, the highest daily biogas production, ie 0,86 ($dm^3/dm^3 \cdot d$) was achieved, which is more than twice as in case of the amount of biogas generated for the initial range of HRT. Under those conditions, the biogas yield reached the value of 0.41 $dm^3/g\ VS_{removed.}$ The maximum value of biogas yield, ie 0.46 $dm^3/g\ VS_{removed}$ was received for the HRT of 35 days. Whilst the daily biogas production decreased slightly in those conditions (0.78 $dm^3/dm^3 \cdot d$). Similarly to the organic matter decomposition, the application of the highest HRT (40 days) did not play a positive influence on both biogas production indices.

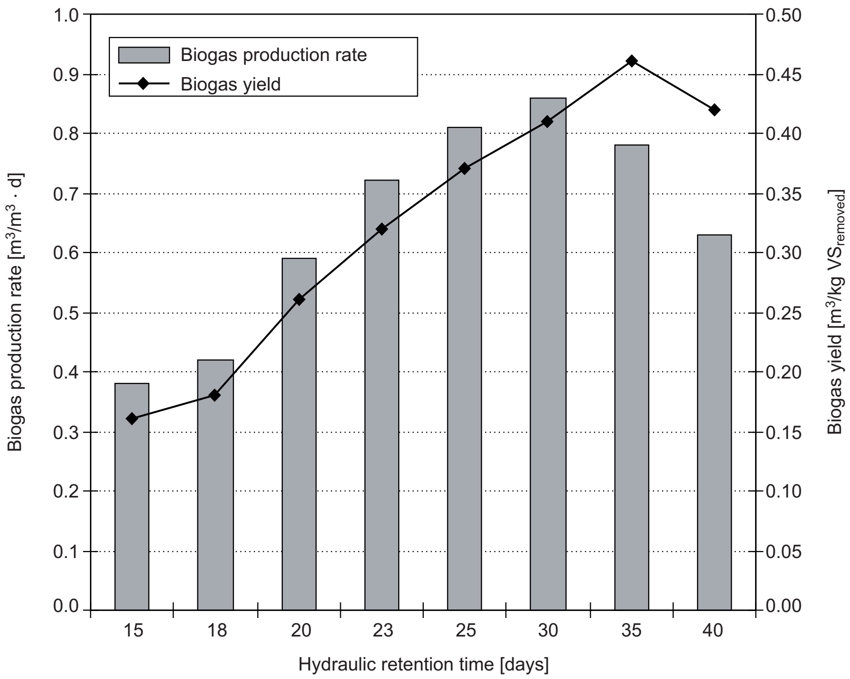


Fig. 2. Biogas production recorded during the experiment

The $CH_4$ concentration as well as several other biogas ingredients were analysed. The average methane content measured in a stable state of the process; for the HRT in the range of 18–40 days; fluctuated between 72 and 76 %. A high content of $CH_4$ was ascribed to the digestion feedstock rich in proteins, which are believed to produce biogas with the highest $CH_4$ content [15–16]. Whilst a relatively lower $CH_4$ content in biogas produced might have been a result of the lowest HRT applied (15 days). It turned out to be insufficient for effective methane fermentation in case of that type of feedstock.

Table 3

Chemical composition of the biogas produced

| Ingredient | Unit | Hydraulic retention time [days] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 15 | 18 | 20 | 23 | 25 | 30 | 35 | 40 |
| $CH_4$ | % vol. | 65 | 72 | 74 | 76 | 74 | 75 | 76 | 75 |
| $CO_2$ | % vol. | 30 | 23 | 22 | 20 | 21 | 20 | 21 | 20 |
| $O_2$ | % vol. | 0.18 | 0.26 | 0.23 | 0.25 | 0.19 | 0.17 | 0.18 | 0.20 |
| $H_2S$ | ppm | 62 | 81 | 12 | 11 | 12 | 10 | 14 | 10 |
| CO | ppm | 18 | 23 | 30 | 28 | 31 | 25 | 20 | 19 |

Thirdly, the influence of various HRT applied on the stability of the process was taken into account. One of the primary indicators which influences the biological conversion and microorganisms activity is the pH value. Microorganism consortia participating in anaerobic digestion tolerate the pH value in the range of between 5.5 and 8.5, however, the pH value should be maintained around the neutral level in order to ensure the appropriate growth and development of methane generating bacteria. Considering the digestion of animal by-products, the most important factors which determine the pH value and buffering capacity are: volatile fatty acids and ammonia nitrogen [17–19]. Generally, VFAs accumulation is responsible for a pH value drop. In our study, the highest VFAs concentration (5.17–7.54 mg $CH_3COOH/dm^3$) occurred for the HRT of between 15–23 days. When the process was conducted for the HRT above 23 days, the recorded VFAs concentration were more than twice lower (3.15–3.80 mg $CH_3COOH/dm^3$). The accumulation, which occurred was not related to a significant decrease in pH value (Table 2). The fact is not unexpected, mainly due to high concentration of protein in digested manure, which constitutes a potential source of ammonia nitrogen. On one hand, ammonia released counteracts the decrease of pH value caused by VFAs accumulation. On the other hand, if ammonia is released in excessive amounts, it causes the pH to increase above the value tolerated by most methanogens. The increase in pH can seriously depress the biogas generation or even caused it to stop completely. In our study, the concentration of ammonia nitrogen amounted to between 5.79–6.39 g $NH_4^+/dm^3$ (Table 2). A wide range of inhibiting ammonia concentrations has been reported in the literature – the value amounted to between 1.7 and 14 $g/dm^3$ [20]. What is more, methanogens have a tendency to acclimate to high ammonia concentrations.

Taking into account the fact that changes in pH value caused by VFAs accumulation in well-buffered processes; especially those containing high ammonia concentration; are often limited. Moreover, a significant decrease in pH value usually occurs after the collapse of the process and when the acid phase dominates in the bioreactor. A more reliable stability indicator seems to be a volatile fatty acids to total alkalinity, ie VFA/TA ratio. If the latter exceeds the threshold of 0.3–0.4, it is believed to have an inhibitive effect on the process stability [21–22]. The influence of the various HRT values on the VFAs accumulation and the VFA/TA ratio are shown in Fig. 3. On the basis of the above-mentioned ratio, we can figure out that the process exhibited stable conditions for the HRT higher than 23 days.

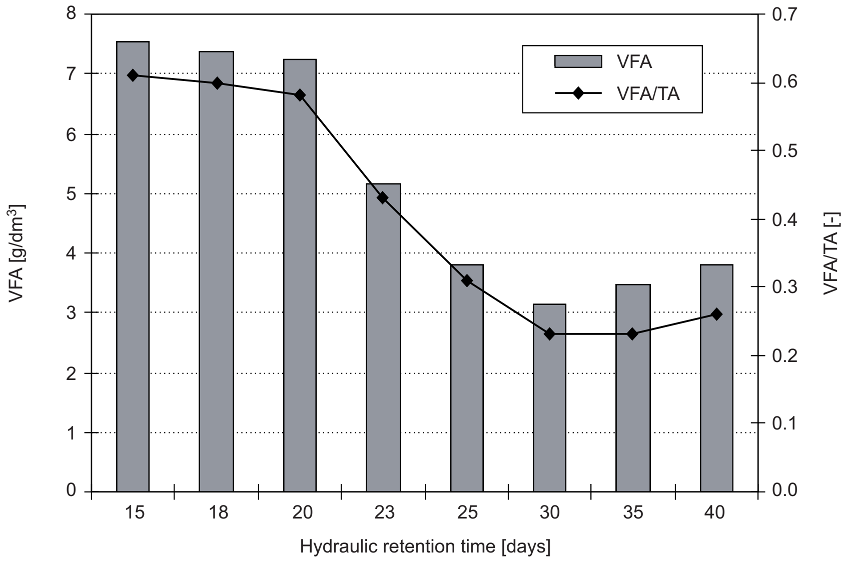


Fig. 3. The influence of various HRTs on the VFAs accumulation and VFA-TA ratio

Finally, the influence of methane fermentation on the dewatering properties of the digested manure was assessed. Digested manure constitutes a valuable natural fertilizer; however, in the areas of concentrated animal production; it is impossible to utilize the

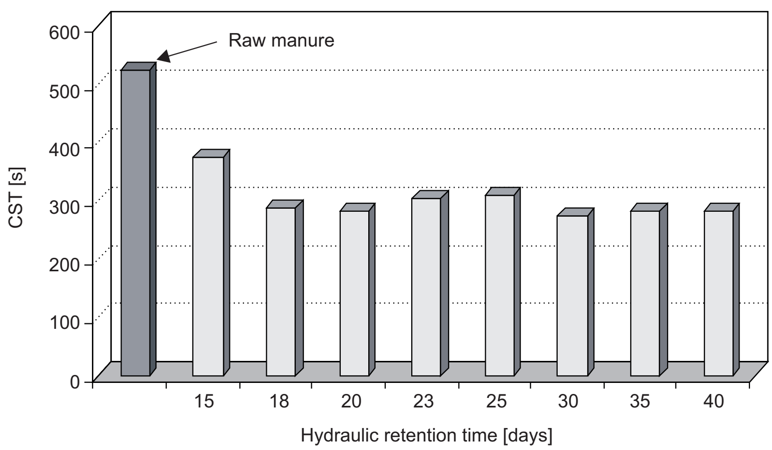


Fig. 4. Capillary suction time (CST) of both raw and digested manure

whole amount of manure generated for agricultural purposes. Therefore, in order to prevent the reverse influence of the unused portion of the manure on the natural environment, a reasonable solution seems to be the separation of the anaerobically digested manure into a solid and liquid fraction. The former can be used on the farm where it was generated, while, the latter can be transported more easily into areas deficient in natural fertilizers. Figure 4 shows the results of CST tests for both raw manure and digested manure. As compared with the raw manure (524 s), the digested manure exhibited a significantly lower value of the parameter (274–375 s). It may be concluded that the anaerobic digestion affects the separation properties of the digested manure in a positive way.

## Conclusions

The research project allows to draw the following conclusions:

1. Taking into account environmental protection as well as the opportunity to produce renewable energy in the form of biogas, controlled anaerobic digestion of liquid animal by-products before its land application seems to be a reasonable solution.

2. The methane fermentation of the manure conducted under high ammonia concentration (5760–6390 mg$NH_4$/$dm^3$) turned out to be stable and effective for the HRT in the range of 25 and 35 days.

3. The highest biogas production (0.78–0.86 $dm^3/(dm^3 \cdot d)$) as well as the most appropriate degree of organic matter bioconversion (VS: 42.3–45.2 %; COD: 65.3–65.6 %) were achieved for the HRT of between 30 and 35 days, which was tantamount to OLR of 1.32–1.57 kg VS/($m^3 \cdot d$).

4. When the process was carried out for the HRT below 25 days, a significant decrease in biogas production as well as organic matter decomposition was recordeed. Moreover, the VFA/TA ratio increased above the critical value indicating instability in the process.

5. The anaerobic digestion affected the dewatering properties of the digested manure in a positive way.

### References

[1] Romaniuk W.: Ekologiczne systemy gospodarki obornikiem i gnojowicą. IMBER, Warszawa 2004.
[2] Ustawa z dnia 10 lipca 2007 roku o nawozach i nawożeniu, DzU 2007, nr 147, poz. 1033.
[3] Załącznik do rozporządzenia Rady Ministrów z dnia 14 kwietnia 2004 roku: Wymagania prowadzania działalności rolniczej z zasadami zwykłej dobrej praktyki rolniczej, DzU 2004, nr 73, poz. 657.
[4] Pawełczyk A. and Muraviev D.: Przem. Chem. 2003, **82**(8–9), 2–4.
[5] Szymańska E.: Wpływ chowu trzody chlewnej na środowisko. Zesz. Nauk. AR Wrocław. 2006, **540**, 531–536.
[6] Van der Stelt B., Temminghoff E.J.M., Van Vliet P.C.J. and Van Riemsdijk W.H.: Biores. Technol. 2007, **98**, 3449–3455.
[7] Hutchings N.J., Sommer S.G., Andersen J.M. and Asman W.A.H.: Atmos. Environ. 2001, **35**, 1959–1968.
[8] Mroczek J.R. and Kostecka J.: *Zagrożenia zrównoważonego rozwoju środowiska obszarów wiejskich spowodowane intensyfikacją produkcji zwierzęcej*. Zesz. Nauk. Pol. Tow. Glebozn. 2008, **10**, 93–100.

[9] Macias-Corral M., Samani Z., Hanson A., Smith G., Funk P., Yu H. and Longworth J.: Biores. Technol. 2008, **99**, 8288–8293.
[10] Møller H.B., Lund I. and Sommer S.G.: Biores. Technol. 2000, **74**, 223–229.
[11] Møller H.B., Sommer S.G. and Ahring B.K.: Biores. Technol. 2002, **85**, 189–196.
[12] Eaton A.D., Clesceril S. and Greenberg A.E.: Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington 1995.
[13] Sawyer C.N., McCarty P.L. and Parkin G.F.: Chemistry for environmental engineering and science. McGraw-Hill, New York 2003.
[14] Hermanowicz W., Dojlido J., Dożańska W., Koziorowski E. and Zerbe J.: Fizykochemiczne badanie wody i ścieków. Arkady, Warszawa 1999.
[15] Buraczewski G.: Fermentacja metanowa. PWN, Warszawa 1989.
[16] Podedworna J. and Umiejewska K.: Technologia osadów ściekowych. WPW, Warszawa 2008.
[17] Dymaczewski Z. and Lozański M.: Poradnik eksploatatora oczyszczalni ścieków. PZITS, Poznań 1995.
[18] Miksch K.: Biotechnologia ścieków. Wyd. PŚl., Gliwice 2000.
[19] Boe K.: Online monitoring and control of the biogas process, Technical University of Denmark, Ph.D. Thesis, 2006.
[20] Chen Y., Cheng J.J. and Creamer K.S.: Biores. Technol. 2008, **99**(10), 4044–4064.
[21] Callaghan F.J., Waste D.A.J., Thayanithy K. and Forster C.F.: Biomass Bioener. 2002, **22**(1), 71–77.
[22] Magrel L.: Prognozowanie procesu fermentacji metanowej mieszaniny osadów ściekowych oraz gnojowicy. Wyd. Polit. Białost., Białystok 2004.

## FERMENTACJA METANOWA GNOJOWICY ŚWIŃSKIEJ W WARUNKACH MEZOFILNYCH

[1] Instytut Ochrony i Inżynierii Środowiska
Akademia Techniczno-Humanistyczna w Bielsku-Białej,
[2] Instytut Inżynierii Wody i Ścieków
Politechnika Śląska w Gliwicach

**Abstrakt:** Celem prezentowanych badań było ustalenie najkorzystniejszych parametrów technologicznych fermentacji metanowej gnojowicy świńskiej pochodzącej z hodowli trzody chlewnej. Fermentację prowadzono w warunkach mezofilnych 36 $^{o}$C (±0,5) dla następujących wartości hydraulicznego czasu zatrzymania (HRT): 15, 18, 20, 23, 25, 30, 35 oraz 40 dni. Odpowiadały one obciążeniu komory bioreaktora ładunkiem suchej masy organicznej (s.m.o.) od 1,18 do 3,13 kg s.m.o./(m$^3$ · d). Podczas eksperymentu wykonywano analizy ilościowe i jakościowe generowanego biogazu oraz analizy fizykochemiczne materiału przefermentowanego. Dodatkowo analizowano wpływ fermentacji metanowej na właściwości odwadniające gnojowicy przefermentowanej. Analizując poszczególne wartości hydraulicznego czasu zatrzymania (HRT) gnojowicy w bioreaktorze, w głównej mierze wzięto pod uwagę: dobową oraz jednostkową produkcję biogazu, stopień biokonwersji materii organicznej oraz stabilność procesu (LKT; LKT/zasadowości). Fermentacja metanowa analizowanej gnojowicy prowadzona w warunkach dużego stężenia azotu amonowego (5760–6390 mg $NH_4^+$/dm$^3$) przebiegała stabilnie oraz efektywnie dla wartości HRT od 25 do 35 dni. W przypadku prowadzenia fermentacji metanowej dla wartości HRT poniżej 25, odnotowano znaczne zmniejszenie ilości generowanego biogazu oraz stopnia rozkładu materii organicznej. Stosunek LKT/zasadowości po tym czasie zatrzymania wzrósł powyżej 0,4, co świadczy o niestabilności procesu metanogenezy. Ponadto proces fermentacji metanowej wpłynął korzystnie na właściwości separacyjne przefermentowanej gnojowicy.

**Słowa kluczowe:** fermentacja metanowa, energia odnawialna, biogaz, odpady rolnicze, gnojowica świńska