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Biogas from Poultry Manure

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Abstract: It is estimated that around 2 billion of waste annually is formed in the European Union (EU), which is deposited-in sanitary and industrial dumps, and it is recorded continuous increasing in the production of organic waste. Biodegradability of organic substances enables the emission of CH_4 (biomethane) that has 25 times higher the greenhouse potential than CO_2 as a predominant greenhouse gas in the atmosphere. The treatment of organic waste through anaerobic digestion flourished in the 20th century, thus opening the way to the environmental remediation of manure, as one of the most influential source of methane emissions. This study research the production of methane in poultry manure, as one of the most usual animal fertilizers in Bosnia and Herzegovina. The research activities are comprised of waste characterization and testing the biodegradability of waste using Biomethan Potential Test BMP The temperature range of the study was 37 ± 1°C (mesophilic process). The research topic is manure of laying hens, without bed. The conducted research activities have shown the existence of possibilities for the production of biogas by using anaerobic biological treatment of poultry manure. The yield of biogas in the amount of 5752 mL was achieved with a methane content of 53.19% for the treatment of the substrate with 15% total solid (TS). By treating the substrate with 17% total solid (TS) less biogas is obtained, in the amount of 2337.50 mL of biogas but with a higher content of methane, in the amount of 56.36%. Physico-chemical analysis revealed a deviation ratio of C(COD):N:P:S from the optimal ratio for substrate and digestate, which caused disturbances in the performance of the anaerobic digestion process. Inadequate ratio is expressed with low carbon content and a high content of nitrogen and sulfur. The course of the study has proven to be extremely useful for testing the possibilities of biogas production in combination with other organic waste, which opens up opportunities for further research.

INTRODUCTION

Manure from all types of farms, is a potential polluter of the environment, due to the natural content and gas emission and with greenhouse effect. Also, manure is abundant with natural content of anaerobic microorganisms that produce methane (CH_4), which has 25 times higher the greenhouse effect than CO_2, which is the most abundant gas with greenhouse effect in the atmosphere. Among all of the manures, most intense emission of methane has bovine manure.

The utilization of the anaerobic digestion (AD) process has been recognized since ancient times, but it flourished in the 20th century. The treatment of organic waste, from which energy can be obtained in the form of methane, is carried out indoors at a temperature that corresponds to anaerobic microorganisms (mesophilic or thermophilic).

As the manure is naturally rich with anaerobic microorganisms and nutrients, it is suitable material for biological treatment, where as final products biogas and digestate are formed. It can be treated alone or in combination with other organic waste (co-digestion), such as waste from the harvest, straw, corn silage, organic communal waste, etc., which are the most common. The energy value of biogas is chemically related to methane and increases according to the increasing content of methane in it. The average energy value of biogas is of 20 to 30 MJ/m^3 with a methane content of 55% to 70%. Biogas can be used for the simultaneous production of electricity and heat in cogeneration plants, it can be placed in the system of gas distribution network or used as a fuel for vehicles. The use of biogas depends on its quality.

Digest is the decomposition of anaerobic digestion, cleaned of pathogenic microorganisms and enriched with easily accessible and high-quality nutrients for plants. It is an excellent replacement for natural fertilizer. The amount of biogas and energy from manure depends on the type, weight and age of the animal. Organic waste of older animals has better biogas potential due to intensive metabolism and the formation of larger amounts of waste. Today, there are several million biogas plants for anaerobic digestion of various organic wastes, and in the European countries, the most of them are installed in Sweden, Germany, Finland, Latvia, etc. In 2013 the energy derived from biomass covered 10% of the global primary energy consumption in the amount of 56.6 EJ of energy.

MATERIALS AND METHODS

In the realization of experimental activities, as a substrate was used a manure from the poultry complex (meat industry) Brovis LLC, Donje Moštre, Visoko. Experimental activities are carried out in two parts: the physical and chemical analysis and using BMP test.

Physical and chemical analysis

Physical and chemical analysis were carried out on a sample of solid to the sludge consistency, so all the methods used for analysis are customized, in order to provide more representative and more accurate results. The analysis was conducted from a solution made of 10 g sample in a metering container of 1 L. In physico-chemical terms, the substrate and digestate (treated substrate) were analyzed. The analysis involved determining the following parameters: total solids (TS), Volatile solids (VTS), pH value, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), volatile fatty acids (VFA), total nitrogen (N), total phosphorus (TP) in the form of orthophosphate and sulphide content (S^{2-}). Phosphorus was determined by spectrophotometry with ammonium molybdate and ascorbic acid (Čoha F., 1990). BPK_5 is analyzed in accordance with ISO 5815: 2003. The organic nitrogen (N) and ammonia (NH_3) were determined according to the Kjeldahl method (APHA, 2012). All other parameters were analyzed according to APHA, 1998.

BMP test

The BMP test was carried out using a volumetric method at the mesophilic temperature zone (37°C ± 1) for a period of 31 days of retention time. The experiments were performed in the so-called "batch" reactors fueled by the use of clogged glass bottles. BMP test apparatus used in the experimental section is shown in Figure 1.

Figure 1: BMP test apparatus

Analysis of biogas was performed by gas chromatography (SICK GMS 810).

RESULTS AND DISCUSSION

The efficiency of the anaerobic digestion depends on several key factors, and it is very important to ensure optimal conditions in the system of anaerobic microorganisms. BMP test was intended to examine the production of biogas with normal activity of anaerobic microorganisms in the substrate. The following samples were examined using BMP test:

- O1 - Substrate with 15% total solid
- O2 - Substrate with 17% total solid
- M1 - Inokulum1 (muddy consistency emerged AD settings O1) + O1
- M2 - Inokulum2 (muddy consistency emerged AD settings O2) + O2
- The content of examined mixture used in BMP test, was determined by calculating. For preparation the sample O1 was used 98.55 g substrate per100 mL water, and for the sample O2 was used 131.41 g per 100 mL water. Preparation the samples M1 and M2 was done the same like the samples O1 and O2 but on formed muddy consistency. With the realization of samples O1 and O2, a rich anaerobic environment is tried to be developed, to be used as inoculum for the realization of samples M1 and M2.

The results of physico-chemical analysis

Aims of physico-chemical analysis of substrate and digestate were monitoring of changes of the defined parameters during the anaerobic digestion process and their mutual impact. The results of physical-chemical analysis of substrate and digestate are listed in Table 1.

Analyzing the substrate, pH value of 7 was determined, which represents the optimal conditions for the operation and growth of microorganisms and correction of pH value with acid / base or the addition of buffer is not necessary. pH value of all digests did not exceed 8, which gives an indication of weakly alkaline environment and partly a stable process that can stabilize over time. Variation of the pH environment was affected by the concentration of substances contained in the substrate, which are usually prone to change of the concentration of ammonia and VFA, and which have an inhibiting effect on the process in specific concentrations. Sulfur and heavy metals concentrations have inhibitory effect, in smaller cases. The inhibitory concentration of NH_3 is 600 mg/L, for the VFA it is 2000 mg/L (Al Seadi T. and al., 2008), while for the sulfur in the sulfide form it is 200 mg/L (Dodić J. and al., 2013).

The analysis revealed that contents of these substances in the substrate and digestate are not in the form of inhibitory concentrations.

Table 1. The results of physical-chemical analysis of substrate and digests

Parameter	Substrate	O1	O2	M1	M2
ST (%)	30,44	14,11	17,26	16,29	11,49
Humidity (%)	69,56	85,89	82,74	83,71	88,51
VTS (%)	74,53	65,89	67,12	65,90	60,59
Ash (%)	25,47	34,11	32,88	34,10	39,41
pH value	7,00	8,00	8,00	8,00	8,00
HPK (mg/g)	73,56	32,60	50,91	33,63	42,27
BPK_5 (mg/g)	19,84	-	-	13,00	27,23
VFA (mg/g)	30,01	14,36	19,96	3,59	4,31
Organic Nitrogen-N (mg/g)	9,10	-	-	0,96	1,06
Ammonia-NH_3 (mg/g)	2,74	-	-	6,00	8,50
Sulphides (mgS^{2-}/g)	0,740	0,240	0,400	0,470	0,460
Orthophosphate-P (mg/g)	0,150	0,118	0,122	0,116	0,118

It also established that substrate contained 27.60 mg/L of ammonia concentration, 300.11 mg/L of VFA, and 7.7 mg/L of sulfur in the form of the sulfide. Organic nitrogen in the amount of 92.61 mg/L (9.10 mg/g) came from the proteins present in the substrate. For digestate sample the following concentrations were determined: VFA in the amount of 143.60 mg/L and the sulfide in the amount of 2.42 mg/L. For digestate sample O2 the following concentrations were determined: VFA in the amount of 196.63 mg/L and the sulfide in the amount of 4.04 mg/L. Ammonia and organic nitrogen were not analyzed in samples O1 and O2. These samples were intended for the adaptation and development of micro-organisms, namely for the creation of anaerobic environments to be used as inoculum for M1 and M2. For digestate sample M1, the following concentrations were determined: ammonia in the amount of 62.72 mg/L, VFA in the amount of 35.95 mg/L and the sulfide in the amount of 4.73 mg/L. For digestate sample M2, the following concentrations were determined:ammonia in an amount up to 89.60 mg/L, VFA in the amount of 43.15 mg/L and the sulfide in the amount of 4.65 mg/L. Low phosphorus content is explained by the fact that it was determined in the form of orthophosphate, total phosphorus was not determined.

The most important assessment of the quality of the substrate and of the monitoring of anaerobic digestion is the ratio C(COD):N:P:S.

The optimal ratio of C(COD):N:P:S is 600:15:5:1 (Al Seadi T. and al., 2008, Imamović N., 2014). In this study through the physico-chemical analysis it is possible to determine the ratio of C(COD):N:P:S for M1 and M2 substrate and digestate samples. The analysis determined the relation C(COD):N:P:S -598.30:74.01:1.22:6.00 for substrates, 594.32:140.67:0.24:8.31 for digestate sample M1 and 598.23:135.30:0.20:6.51 for digestate sample M2. The deviation from the optimal ratio resulted because of the low carbon content in relation to the nitrogen and sulfur. According to the ratio, nitrogen deviates 4.9 and sulfur 6 times more in the substrate, nitrogen by 9.4 and sulfur 8.3 times more in digestate sample M1, while in the digestate sample M2 nitrogen deviates by 9.02 and sulfur 6.51 times more. Unbalanced ratio C(COD):N:P:S can lead to increased production of NH_3, H_2S, increasing the partial pressure of hydrogen (H_2) and reducing the production of VFA, which results in slowing or stopping the process.

Variations of those components cause changes in the pH environment and increase the sensitivity of bacteria in the methanogenic stage. The optimum ratio of the pH value for the operation of microorganisms is 7-7.5, while the deviation of pH value leads to disturbances for the process of anaerobic digestion. Great amount of NH_3 observed in digestate M1 and M2 encourages the conversion of undesirable amino acids in NH_3 instead of in acetate. Although none of the digestates did not contain inhibitory concentration of NH_3 in the amount of 600 mg/L, the increased concentration of NH_3 had a braking effect on the implementation anaerobic digestion phase. The impact expected of undesirable proteins conversion is less production of biogas and methane content.

The impact of free NH_3 was sought to avoid with the dilution method of substrate in assay mixture, which reduced the total solid (ST) content and provided contact of anaerobic environment with substrate nutrients. However, due to the low content of organic carbon, anaerobic organisms spent more organic matter for the the formation of NH_3, H_2S, CO_2, NO_x and H_2, than for the formation of VFA. The formation of these gases led to a slowing of the process of anaerobic digestion. In phase of acetogenesis, homoacetogenic bacteria consume H_2 and CO_2 to form acetate to maintain a stable condition of low partial pressure of H_2 required for the process (Kukkonen T., 2014). The activity of these bacteria could not come to the fore due to the excessive accumulation of these gases and low-carbon content. The variation of TS and VTS results in digestate determined by physical and chemical analysis, originate from different activities of anaerobic microorganisms in phases of anaerobic digestion process.

The results of the analysis of digestate substrate inoculum in samples M1 and M2 revealed low amount of VFA which leads to the consumption of VFA in acetogenesis and methanogenesis processes. However due to a deviation of C(COD):N:P:S substrate ratio from the optimal, it is possible that there has been a brake in the formation of VFA influenced by unwanted gaseous products formed in phases of acidogenesis and of acetogenesis.

The aforementioned settings revealed increased ash content, which gives an indication that nutrients were not adequately spent in microbial food chain. Increased ash content came from the the formation of salts of heavy metals with sulfur and phosphorus.

A component which additionally affected breaking of the process is the partial pressure of hydrogen (H_2). This intermediator is a normal product of acidogenesisandacetogenesis phases of production, but due to insufficient carbon content, there was a non-conforming production of VFA in oxidation reactions and consumption of H_2 in respiratory reactions, where additionally,the production of VFA was slowed by NH_3 and H_2S. This is a normal occurrence in bioreactors, which becomes neutralized by adding more substrate rich in carbon, and by waiting for the system to return to a stable state. The lack of experimental activities is the interruption of the process after the 31st day.

The results of BMP test

In theory, the retention time of the mesophilic temperature is between 20 to 40 days (Ward A.J. and al., 2008). According to research of Kukić, S. and associates (2010) biogas production begins after the third day, and the maximum production is achieved on the 15th to the 20th day and reduces by the end of the retention time. The results of volumetric analysis of BMP test are shown in the diagram 1.

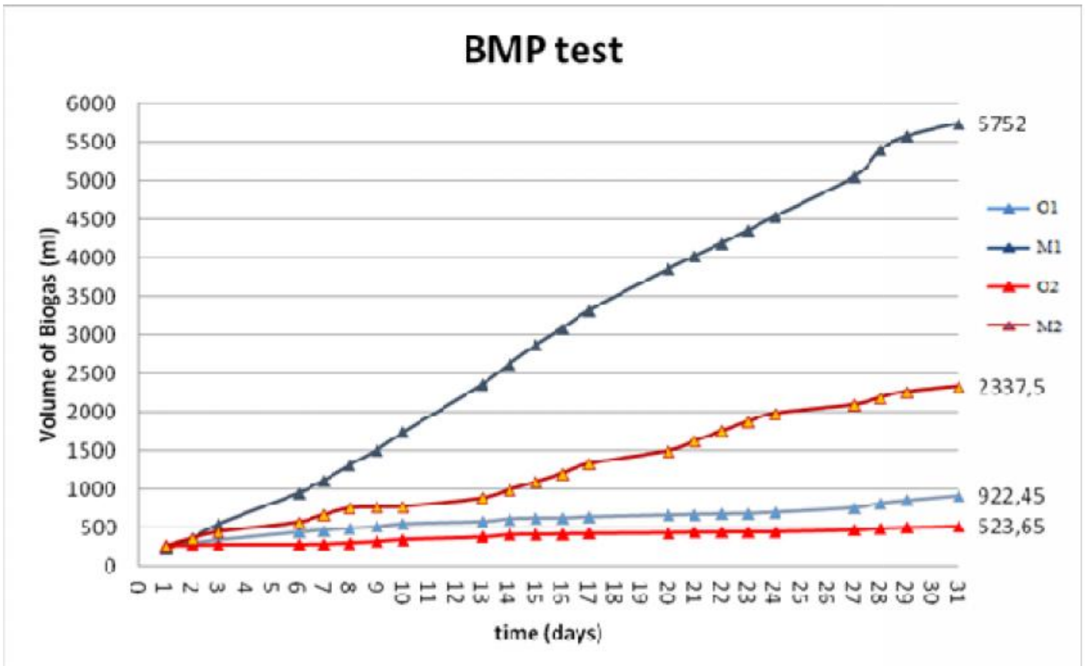

Figure 2. The results of BMP test

Using volumetric analysis of O1 and O2 samples, a slight inclination/slope is noticed to the end of the retention time. Although the daily volumes by the end of the analysis fluctuated, the process was terminated after thirty days. With the addition of new quantities of raw material of the substrate on the muddy consistency as inoculum in the settings of the M1 and M2, there was a remarkable activity of microorganisms and the production of biogas increases. According to physical-chemical analysis, allowable concentrations of influential substances in the substrate were established. However, their relationship which is expressed through optimal ratio C(COD):N:P:S is not satisfactory, because of the low content of organic carbon in relation to other substances. The deviation from the optimum relationship had an impact on the process of anaerobic digestion, where in the already formed biogas there was an increased extrication of NH_3, H_2S, CO_2 and H_2, which inhibited the methane separation. The disturbances in the quality of the production of biogas were already noticed in the settings of O1 and O2 samples, in which the conversion of cumulative production of methane from theoretical amounted only 36.35% for O1 and15.48% for O2. The low conversion was expected because of the sensitivity of anaerobic microorganisms since for their adaptation, a nutritious methanogens base wasn't used. The improvement in the quality of anaerobic digestion process was noticed in the settings of M1 sample, where the conversion of methane production amounted from cumulative to theoretical up to 95.18%, while for the M2 it was only 26.81%. Positive results in setting of the M1 can be seen in the diagram, where they grow without constant flow to the end of the retention time. In both M1 and M2 settings, the constant flow at the end of the retention time was not noticed, which means that AD was not completed until the end.The analysis of biogas on 31st day with gas chromatography revealed methane content in the amount of 53.19% for the sample of biogas settings M1 and 56.36% for the sample of biogas settings M2.

CONCLUSION

Animal manure is naturally abundant with anaerobic microorganisms which in the process of aerobic digestion consume nutrients from the manure and produce gases with greenhouse effect that accumulate in the atmosphere. The aim of the study was to examine the treatment of anaerobic digestion of one of the most usual aminal waste in Bosnia and Herzegovina, poultry manure, which is currently used as fertilizer for arable land. This study, testing the quality of the substrate determined deviation of C(COD):N:P:S ratio from optimal, but it did not prevent the process of anaerobic digestion to continue with a certain production of biogas and methane content.

The ratio C(COD):N:P:S for the substrate is 598.30:74.01:1.22:6.00, 594.32:140.67:0.24:8.31 for the digestate sample M1 598.23:135.30:0.20:6.51 for the digestate sample M2. Regardless of disturbances, the positive results were recorded in the settings of M1 and M2 samples, where the addition of a new quantity of nutrients has led to improvements in the quality of anaerobic digestion process. The poultry manure has a rather low methane potenthial with variation of substances necessary for the anaerobic digestion process. The analysis of biogas sample O1 found methane content in the amount of 33.80% and in the O2 biogas sample it amounted to 29.48%. To improve the quality of the substrate it must be combined with waste rich in oxygen. With the addition of new quantities of nutrients, an improvement in the production of biogas was visible, with an increase of a methane content by 1.5 times in M1 (53.19%) and 1.9 times in M2 (59.36%). The same substrate was used for co-digestion, but it would be useful to examine the co-digestion with another type of organic waste (sawdust, straw, agricultural waste, municipal organic waste). Combining different types of biomass should be tested in order to eliminate the negative impact on the efficiency of the entire process.

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Summary/Sažetak

U zemljama Europske Unije (EU) procjenjuje se da godišnje nastane oko 2 biliona otpada koji se odlaže na sanitarnim i industrijskim deponijama, a zabilježen je kontinuirani porast nastajanja organskog otpada. Biorazgradivost organskih tvari omogućava emisiju CH_4 (biometan) koji ima 25 puta veći staklenički potencijal od CO_2 kao najzastupljenijeg stakleničkog plina u atmosferi. Tretman organskog otpada anaerobnom digestijom doživljava procvat u 20 vijeku čime otvara puteve ekološke sanacije stajskog gnojiva kao jednog od najuticajnijih izvora emisije metana. U radu ispitana je produkcija bioplina i sadržaja metana iz peradarskog đubriva, kao jednog od najzastupljenijeg animalnog otpada u Bosni i Hercegovini. Istraživačke aktivnosti su se sastojale od karakterizacije otpada i ispitivanja biorazgradivosti otpada putem BMP testa. Temperaturni opseg istraživanja je bio 37 ± 1°C (mezofilni proces) u trajanju od 31 dan. Predmet istraživanja je svjež gnoj nesilica, bez postelje. BMP testom ostvaren je prinos bioplina u iznosi od 5752 ml bioplina sa sadržajem metana od 53,19% za tretman supstrata sa 15% suhe tvari. Tretiranjem supstrata sa 17% suhe tvari dobiveno je manje bioplina, u iznosu od 2337,50 ml, ali sa većim sadržajem metana, u iznosu od 56,36 %. Fizičko-hemijskom analizom utvrđen je odstupanje omjera C(HPK):N:P:S od optimalnog, kod supstrata i digestata, što je prouzrokovalo smetnje u odvijanju procesa anaerobne digestije. Neadekvatan omjer izražen je niskim sadržajem ugljika, a visokim sadržajem azota i sumpora. Tok istraživanja pokazao se izuzetno korisnim za potrebe ispitivanja mogućnosti proizvodnje bioplina u kombinaciji sa drugim organskim otpadom, što otvara mogućnosti daljeg istraživanja.