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METHANE PRODUCTION FROM COW MANURE IN THE PRESENCE OF Bi(III) COMPLEX OF SULFAMIC ACID

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ABSTRACT

The present study examines the process of biomethanization of cow manure in an anaerobic environment, in the presence of small amounts of Bi(III) complex of sulfamic acid. Since this complex has good antimicrobial activity, the purpose of adding the complex is to determine its effect on biogas and methane production.

The reference samples (cow manure only) and mixtures of cow manure + 10 mg and cow manure + 20 mg of bismuth complex with a composition $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ *are subjected to biodegradation under the following conditions – duration of 33 days, nitrogen atmosphere and temperature of 34.5 ± 1°C. During the process, the volume of biogas and the percentage content of methane in biogas are measured in 2 - 3 days as well.*

The analyses performed reveal that until the 10th day, the amount of biogas produced increases constantly and is comparable both for the control samples and for the mixtures. Further, until the end of the experiment, a significant and constant increase in the volume of biogas produced by the mixtures is observed compared to the control samples.

Regarding the percentage of methane produced by the reference samples and the mixtures, comparable relative amounts are found by the 7th day. From the 8th day to the 33rd day, the percentage of methane released by the mixtures is visibly greater than that by the reference samples.

Keywords: Bi(III) complex, cow manure, anaerobic fermentation, biogas, methane.

INTRODUCTION

During the last few decades, methane has dominated as one of the most important and most used fuels for production of heat and electricity, in chemical industry, metallurgy as well as in transport and household. Its wide use as a fuel is also determined by the fact that during its combustion, only carbon dioxide is emitted as a harmful product, compared to all other hydrocarbon fuels [1]. In addition, methane is a very valuable, even key raw material for the fabrication of important organic and inorganic products, such as methanol, halogenated alkanes, acetylene, nitromethane, formaldehyde, hydrogen, ammonia as well as in production of automobile tires and many others [2].

The main sources of methane are natural gas and renewable biogas. While natural gas contains about 98 % CH_4, the amount of methane in biogas is between 50 % and 75 %. The other components of biogas are CO_2, H_2O, H_2S, O_2, H_2, etc. [3, 4].

Biogas is a product of the acidity-driven anaerobic digestion of biological wastes, as in particular the production of methane (methanogenesis) takes place under the influence of methane-producing bacteria [5]. Methanogenesis is the last, third and most important stage, in which a complete biodegradation process occurs within 2 - 3 weeks and it is strongly dependent on pH of the environment [5].

The classic and at the same time renewable raw materials for obtaining biogas are cow manure, industrial and household organic waste, fruit, and vegetable waste, etc., and their mixtures in different ratios have been widely applied for several decades, mostly to increase methane production [4]. In this regard, one of the most modern approaches to increase methane content in biogas is the addition of small amounts of biologically active substances with antimicrobial properties that act synergistically on the main processes of methanogenesis [6 - 8].

There is no data in the literature (except [7]) about the effect of bismuth-containing substances on the processes leading to biogas and methane production. In this sense, the aim of the present work is to investigate the influence of a new antibacterial substance – bismuth complex of sulfamic acid, $[Bi_6O_4(OH)_4](NH_2SO_3)_6$, mixed in two different quantities with cow manure, in order to increase the production of biogas and methane [9-10].

EXPERIMENTAL

Laboratory installation

A laboratory installation presented in Fig. 1 was set up for all experiments. It comprised the following components: a thermostated water bath, magnetic stirrer, three anaerobic bioreactors along with three gas collectors, as each of them was connected to a gas analyser, which registers the methane percentage. Hermetic and chemically inert polypropylene bottles of 500 cm^3 volume were used as bioreactors, connected by silicone hoses and one-way gas valves to the biogas collectors of 2000 cm^3 volume.

Light impervious bioreactors above described, ensured area where bio-fermentation processes took place, as the period for their realization was 33 days at constant temperature of 34.5 ± 1°C and under an inert nitrogen atmosphere.

pH of the reference samples and mixtures was measured before and after bio-fermentation by means of Hanna instrument pH 211, 0 - 14 pH units and accuracy pH of ± 0.01, working in temperature range 0 - 100°C.

Every 48 or 72 hours one measured total biogas volumes accumulated in the gas collectors, as for the purpose a glass-made graduated gas-sampling syringe

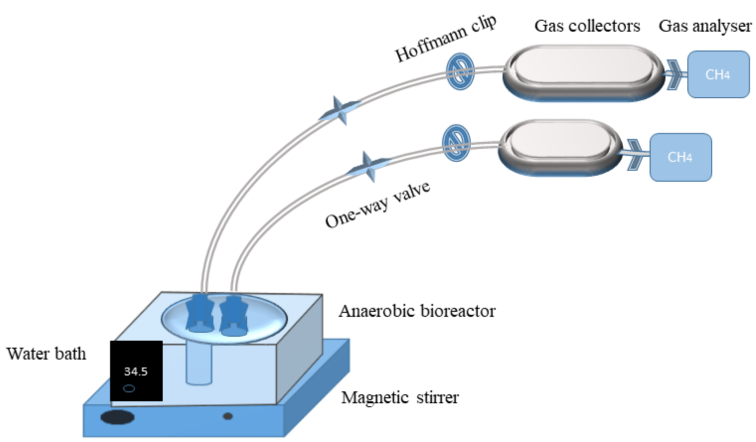

Fig. 1. Scheme of laboratory installation.

was used for biogas volumes determination. At the same time, along with the biogas volume measurement, the gas was transferred into a supporting gas container, aimed at measurement of methane relative amount.

Gas analyzer MS104K Diffusion Type, having IR sensor and operating within -40°C to 70°C, was implemented for measuring the volume percentage (% vol.) of methane in biogas.

Mixtures preparation

The mixtures under investigation were prepared using fresh cow manure biomass (Vrana cow farm, Sofia, Bulgaria), which was leached through 0.5 mm strainer and vigorously stirred until a homogeneous suspension [5]. The reference samples (CM1) prepared, comprised equal quantities of pure manure and distilled water forming a total volume of 400 cm^3, while working mixtures (CM2 and CM3) were of the same total volume and had the same composition as the reference ones plus 10 mg and 20 mg bismuth complex of sulfamic acid with a composition $[Bi_6O_4(OH)_4](NH_2SO_3)_6$, respectively.

The reference samples and working mixtures (CM1, CM2, CM3) were sampled for determination of the following parameters - total solid (TS), moisture content, volatile solid (VS) and pH, as these parameters were ascertained both before and after the anaerobic digestion processes. TS, VS, as well as moisture content of three mixtures, were determined using methods according to BDS EN25934, EN15935 and BDS EN ISO 18134-1, respectively.

RESULTS AND DISCUSSION

It is obvious from Table 1, that TS value before anaerobic fermentation processes of the control sample (CM1) is 6.59 %, for the mixture CM2 containing 10 mg from the complex $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ is 7.10 %, while for CM3 comprising 20 mg of the same complex the TS value is 7.22 %. It occurs that all three values of total solid mentioned above do not prevail 10.00 %, which according to [5] means that the reference samples CM1 and mixtures CM2 and CM3, belong to "conventional wet" anaerobic decomposition technology. It is known from the literature [5] that with the progress of anaerobic digestion processes, volatile solid content decreases while at the same time moisture content increases. Such relations are visible within the data presented in Table 1 and Table 2. In the beginning moisture content is between 92 - 94 % while at the end of experiments it is 95 - 99 %.

Table 1. Operating parameters of mixtures before anaerobic fermentation.

Abbreviation	Assignment	Total solid (TS), %	Moisture content, %	Volatile solid (VS), %	pH
CM1	Reference sample	6.59	93.41	82.64	7.23
CM2	Mixture 1	7.10	92.10	82.59	7.21
CM3	Mixture 2	7.22	92.40	82.61	7.19

Table 2. Operating parameters of mixtures after anaerobic fermentation.

Abbreviation	Assignment	Total solid (TS), %	Moisture content, %	Volatile solid (VS), %	pH
CM1	Reference sample	1.26	98.70	61.38	7.80
CM2	Mixture 1	3.46	96.54	72.33	7.23
CM3	Mixture 2	4.23	95.77	75.95	7.25

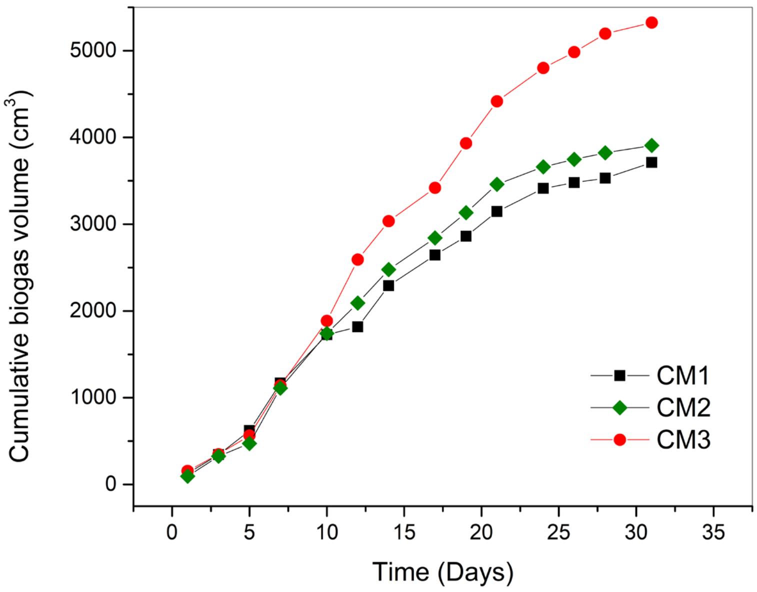

Fig. 2. Cumulative biogas volume (cm^3) of reference samples (CM1) as well as mixtures (CM2 - cow manure + 10 mg $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ and CM3 - cow manure + 20 mg $[Bi_6O_4(OH)_4](NH_2SO_3)_6$) investigated, measured within 1 - 33 days.

Table 1 and Table 2 depict that TS content for CM3 mixtures is the highest both at the start and at the end of digestion, which according to [5] is related to elevated biogas production. This tendency is observable concerning Fig. 2, where CM3 (20 mg bismuth complex) demonstrates the largest biogas production. It is noteworthy, that CM2 (10 mg bismuth complex) produces second in quantity biogas.

Concerning volatile solid values (Tables 1 and Table 2), the tendency of biogas production remains the same as that observed for total solid content. For CM3 and CM2 mixtures, VS values are higher than the control samples CM1, hence the biogas production (Fig. 2) registered for CM3 is the highest followed by CM2 and the least biogas amounts correspond to CM1 samples.

Production of biogas and methane from investigated mixtures

In Fig. 2 data recorded about cumulative biogas volumes of the reference samples and mixtures, measured for a period from the 1st to 33rd day of the experiment are presented. As could be seen from this figure, from the start of biodegradation to 10th day, the amount of biogas produced increases constantly and is comparable for the reference samples (CM1) and for the two mixtures (CM2 and CM3). It is noteworthy, that after the period considered, a completely new tendency appears of a significant and constant increase in the volume of biogas produced by the mixtures CM3 compared to this one by control samples. This tendency remains the same until the end of the experiment as between 25th and 30th day the difference in biogas volumes is most significant (Fig. 2). Concerning CM2, there is a slight increase in biogas production after 10th day, compared to reference samples CM1.

In Fig. 3 considering methane content in the reference samples CM1 and in the two mixtures - CM2 and CM3, comparable relative amounts are registered from the start of experiment to 7th day. From 8th day to 33rd day, the methane content produced by the mixtures CM3 is obviously the greatest, followed by CM2 mixtures, and least amount is released by CM1. It is worth to mention that from 25th to 30th day the difference in methane percentage is most clearly rendered between CM1 and CM3. These results could be explained on one hand by the variation of pH within a slightly alkaline

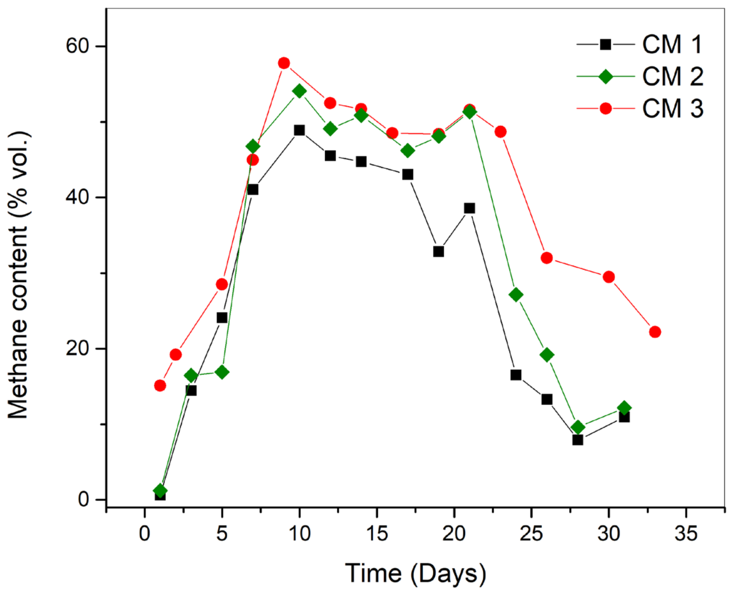

Fig. 3. Methane content (% vol.) in biogas of reference samples (CM1) as well as mixtures (CM2 - cow manure + 10 mg $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ and CM3 - cow manure + 20 mg $[Bi_6O_4(OH)_4](NH_2SO_3)_6$) investigated, measured within 1 - 33 days.

region (from 7.25 to 7.23, Table 2), which strongly favours the methanogenesis process, requiring pH values between 6.5 and 8 [5]. On the other hand, the increased methane production, especially for mixtures CM3, after 10^{th} day (Fig. 3) could be explained by the presence of twofold greater quantity of bismuth complex, compared to CM2.

It could be seen from Fig. 3 that mixtures containing the bismuth complex $[Bi_6O_4(OH)_4](NH_2SO_3)_6$ (CM2 and CM3) release higher relative volumes of methane, which would be explained by powerful antimicrobial properties of the sulfamic acid bismuth complex, mixed with fresh cow manure biomass. According to literature data [9], this complex ascertains significant activity towards *Staphylococcus aureus* (ATCC 29213), which is much higher than that of ampicillin and is comparable to kanamycin as well as moderate activity against two strains of *Escherichia coli* (ATCC 47093 and ATCC 25922) tested. Moreover, it is of interest to note that the complex under consideration is insoluble in a neutral (pH 7) aqueous environment, but it has good solubility in acidic aqueous solutions. In this regard, it is found out [5] that throughout the second stage of anaerobic digestion (acidogenesis), there is substantial decrease of mixture pH, because of accumulation of fatty carboxylic acids. Therefore, it could be expected that the bismuth complex considered would be dissolved successfully in such acidic environment. This probable explanation correlates well with the data in Fig. 2 and Fig. 3, where during the first few days of this experiment, the biogas and methane production from CM1, CM2 and CM3 is comparable. The observable difference in parameters measured between the reference samples and the two mixtures, becomes substantial after 10^{th} day when the bismuth complex used would be completely dissolved.

CONCLUSIONS

The results of the study presented could be summarized in the following conclusions. First of all, the largest biogas quantity as well as the highest methane percentage, from 10^{th} day to the end of experiment, is produced from mixtures CM3, containing 20 mg bismuth complex $[Bi_6O_4(OH)_4](NH_2SO_3)_6$. Moreover, concerning the same period of measurements, the mixtures CM2, containing 10 mg of the same complex, produce both second in quantity biogas and methane percentage as at the same time these amounts are higher than those generated from the reference samples.

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