EFFECT OF ANAEROBIC SLUDGE COMPOSITION ON A BIOGAS PRODUCTION

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ABSTRACT

The laboratory tests indicated the significant differences in gas production during anaerobic digestion of sludge from Jasło municipal WWTP. The doses 200 and 500 mg Cr(III)/L caused decrease of a methane production of 20%, increase of inhibiting compound dose up to Cr(III) 1500 and 2000 mg Cr(III)/L and concentration of Cr(III) equal to 3000 mg/L led to 45% and 47 % decrease of methane production respectively. The inhibitory effect of trivalent chromium was determined as decrease of a reaction rate and also as change in real time necessary for stabilization of inhibitor containing sludge. Period of maximum gas production can be assessed with the use of presented method and the same biomass efficiency can be measured.

KEYWORDS

Anaerobic sludge, digestion, gas production, trivalent chromium, inhibition.

INTRODUCTION

The main aims of anaerobic sludge disposal are: biological sludge stabilization and recovery of highly energetic methane gas. Operational disadvantages of raw wastewater sludge are their hydrophilic character, high viscosity, odour emission and risk of biohazard. Anaerobic stabilization process is converting sludge to biologically stable product for ultimate disposal, safe storage and utilization. Stabilization also reduces the odours, bacteria levels and amount of solids present in sludge. Besides it is possible to recover energy - thermal and/or electrical when applying anaerobic process. During the methane fermentation approximately 50% of total organic matter present in sludge is decomposed producing a biogas. The biogas is a mixture is varying depending mostly on sludge content. Gas composition is influenced by degradable matter content while amount of gas produced depends mostly on a content of organic matter to be mineralised.

This paper summarises a preliminary stage of tests on finding proper tool for design and operation of mesophilic digestion process for adequate stabilisation of sludge with a special emphasis on energy recovery.

Anaerobic degradation

The microbial decomposition of complex organic substrates provides a source of energy and building materials to the bacterial cells, which convert the organic material to carbon dioxide and methane. The anaerobic degradation of organic material has been described as a multi-step conversion of many, parallel, and biochemical reactions. Numerous groups of anaerobic bacteria are involved in this process.

Four main stages of this degradation can be distinguished:

I - hydrolysis of complex organic materials to soluble products (hydrolytic fermentative bacteria)

II - acidogenesis – generation of intermediary products such as short-chain fatty acids, (hydrogen producing and acetogenic organisms)

III - acetogenesis – acetate production (hydrogen-producing, hydrogen-consuming acetogenic organisms)

IV - methanogenesis – methane production (methane-forming bacteria)

The nature and chemical composition of the substrates used in anaerobic digestion determine the type and amount of the products. In case the chemical composition of the organic matter is known, the stoichiometric equation according to McCarty (Pavlostathis et al., 1991) can be used for the description of organic matter conversion to methane:

$$C_nH_aO_bN_c + (2n + c - b - 9sd/20 - ed/4)\ H_2O \rightarrow de/8\ CH_4 + (n - c\ sd/5 - de/8)\ CO_2 + sd/20\ C_5H_7O_2N + (c - sd/20)\ NH_4^+ + (c - sd/20)\ HCO_3^-$$

where: d = 4n + a - 2b - 3c,

s = fraction of waste converted to cells,

e = fraction of waste converted to methane for energy (s + e = 1),

$C_nH_aO_bN$ = empirical formula of waste being digested,

$C_5H_7O_2N$ = empirical formula of bacterial dry mass (VSS).

The production of intermediates can also be described by stoichiometric equations. Based on thermodynamic and bioenergetics principles the estimation of microbial yields and specific substrate utilisation rates is possible.

All biochemical processes taking place within a living cell cause chemical structural changes accompanied by an energetic effects. These effects are strictly related to change of chemical potential of reacting substances. So two main types of such reaction can be recognised:

- exergonic which progress spontaneously causing decrease of total chemical potential of the system
- endergonic which causes increase of total chemical potential within the system so this type of reactions require to be supplemented by energy from outside of the system.

Methane production

Methane production is a final stage of organic matter decomposition that performs in anaerobic conditions. As a result of its chemical structure: four valences of a carbon atom are saturated with four hydrogen atoms, methane gas is most stable product of this process.

Various bacteria species are specialised in methane production from different compounds (Ferry, 1993, Cimochowicz-Rybicka, 1999). Some of these species utilise substrates to cell growth and reproduction both as an energy source and as the sole carbon source. The catabolic pathways of methanogens are very complicated. They can be divided into three groups: CO_2-reducing, methylotrophic and aceticlastic pathways as it were detailed in references (Ferry, 1993).

Most of the methane produced in nature originates from acetate. However, the some amounts of methane produced from the methyl group of acetate or reduction of CO_2 can vary depending on the presence of other metabolic groups of anaerobes and the environment (Ferry, 1993).

Tests performed by numerous authors (Cimochowicz-Rybicka, 1999) proved that acetic acid decomposition could be described by following equation:

$$CH_3COOH \rightarrow CO_2 + CH_4 \qquad \Delta G^{o'} = -36\ kJ/mol\ CH_4$$

Although acetate is a major substrate for methane production, only two genera of methanogenic acetotrophs - *Methanosarcina* and *Methanothrix* and a few species have been described. The acetate-utilising anaerobes cleave acetyl-CoA followed by oxidation of the carboxyl groups to CO_2 and reduction of methyl group to methane. Methanogenesis from acetate has the smallest free energy $\Delta G^{o'}$ value of all methanogenic substrates. The reactions involved in the conversion of acetate to CH_4 and CO_2 are presented in Table 1.

Table 1. Reactions involved in the fermentation of acetate by *Methanosarcina* and *Methanothrix* (Ferry, 1993)

	Reaction	$\Delta G^{o'}$ [kJ/mol]
1.	$CH_3COO^- + ATP \rightarrow CH_3CO_2PO_3^{2-} + ADP$	+13
2.	$CH_3CO_2PO_3^{2-} + CoA \rightarrow CH_3COSCoA + P_i$	-9
3.	$CH_3COO^- + CoA + ATP \rightarrow CH_3COSCoA + AMP + PP_i$	-
4.	$CH_3CO\text{-}S\text{-}CoA + H_4SPT \rightarrow CO + CH_3\text{-}H_4SPT + CoA$	+62
5.	$CH_3\text{-}H_4SPT + HS\text{-}CoA \rightarrow CH_3\text{-}S\text{-}CoM + H_4SPT$	-29
6.	$CH_3\text{-}S\text{-}CoM + HS\text{-}HTP \rightarrow CH_4 + CoM\text{-}S\text{-}S\text{-}HTP$	-43
7.	$CO + H_2O \rightarrow CO_2 + H_2$	-20
8.	$CoM\text{-}S\text{-}S\text{-}HTP + H_2 \rightarrow HS\text{-}CoM + HS\text{-}HTP$	-42
9.	$ADP + P_i \rightarrow ATP$	+32
10.	$AMP + ATP \rightarrow 2ADP$	0
11.	$PP_i \rightarrow 2P_i$	-22
12.	$2ADP + 2P_i \rightarrow 2ATP$	+64
13.	$CH_3OO^- + H \rightarrow CH_4 + CO_2$	-36

Gas composition and its technological feature

Specific volume of a gas can be obtained from each substrate. The amount and characteristic of gas produced during anaerobic digestion are presented in Table 2.

Table 2. The amount and gas composition produced in anaerobic digestion (Heidrich , 1999)

Substrate	Gas amount [L/kg VSS]	Gas composition
Carbohydrates	790	50 % CH_4
		50 % CO_2
Lipids	1250	68 % CH_4
		32 % CO_2
Proteins	700	71 % CH_4
		29 % CO_2

Gas production rates range from 750 - 1000 L of gas produced per kg of volatile solids removed (WEF, 1992). Biogas production in relation to COD is about 0.5 m^3/kg COD removed, corresponding to a methane production of 0.35 m^3 CH_4 per kg of COD removed (Grady, et al. (1999).

Gas composition varies with sludge characteristics. Gas components include methane, carbon dioxide, hydrogen sulphide, nitrogen and hydrogen. The characteristic of digestion gas is presented in Table 3.

Table 3. Typical characteristic of anaerobic digester gas (WEF, 1992)

Constituent	Constituent fraction, %
Methane	55 - 75
Carbon dioxide	25 - 45
Hydrogen sulphide	0.01 - 1
Nitrogen	2 - 6
Hydrogen	0.1 - 2

Methane determines the heating value of the gas; carbon dioxide represents the stabilized carbon; hydrogen sulphide determines the corrosivity and odour potential of the gas.

The methane-forming bacteria control the anaerobic degradation process. Methane formers are very sensitive to environmental factors: temperature, pH, toxic substances.
Temperature. The performance of anaerobic processes is significantly affected by operating temperature. The rates of biochemical reactions increase as temperature increase. Each group of methane-forming bacteria has an optimum temperature for growth. The digestion process can be performed in the one of the three ranges of temperature: psychrophilic 20^{o}C - 25^{o}C, mesophilic 30^{o}C - 40^{o}C, thermophilic 50^{o}C - 60^{o}C.
pH. Anaerobic bacteria, especially the methane formers, are very sensitive to pH deviates. A pH range of 6.8 to 7.4 generally provides optimum conditions for the methanogens. pH can also affect the activity of the acidogenic microorganisms but the effect is less significant. A decrease in pH value increases the production of un-ionized volatile acids that become toxic to methanogenic bacteria but in case of pH above 8 the dissolved ammonia becomes toxic to these microorganisms.
Toxic substances. Anaerobic biodegradation process can be inhibited by two groups of chemicals:
⇒ substances that are produced as process intermediates: e.g. volatile fatty acids;
⇒ contaminations present in wastewater: light metal cations, heavy metals, ammonia, sulphide, oxygen, salt and organic compounds.

In this paper influence of one of heavy metals - trivalent chromium - on methane production is presented. The batch test method has been chosen by author of this paper to determine the amount of digestion gas.

MATERIALS AND METHODS

Assumptions for batch system investigation.

Temperature: 35^{o}C.
pH: 7 to 7.4.
Experimental system: a mechanically stirred system
Substrate and biomass concentration: substrate: a volatile fatty acids (VFA) mixture - main component: acetic acid; range of biomass concentration: 2 to 5 gVSS/l
Source of sludge: digestion sludge from Jas³o municipal wastewater treatment plant
Mineral nutrient composition: standards for methane-forming bacteria (Cimochowicz-Rybicka, Rybicki, 1999)
Concentration of toxicant: range of Cr(III) from 200 to 3000 mg/L
Volume of samples: 500 mL vessels
Gas measured system: anaerobic respirometer ANR-100
Period of experiment: 12 days (each series).

Experimental methods

The measurements of the amount of methane produced during the fermentation process was conducted from reaction vessels filled with:
- anaerobic biomass, VFA substrates, mineral nutrients - as a control sample and
- anaerobic biomass, VFA substrates, mineral nutrients, various dosage of Cr(III) - as a treatment samples (Cimochowicz-Rybicka, Rybicki, 1999).
The investigations included three test series with following doses of Cr(III): 200 mg/L, 500 mg/L, 1500 mg/L, 2000 mg/L, 3000 mg/L.

Experimental procedure

The 500 mL reaction vessels filled with anaerobic biomass, desired amount of substrate, mineral nutrients, yeast extract in control sample and toxicant added in treatment sample, were closed and sealed then placed in water bath at 35^{o}C. A magnetic stirrer mixed the samples during the entire test period. At the beginning of the test, all vessels were saturated with nitrogen. The methane produced during the anaerobic process was transported by pipes through a respirometer system and was recorded by the computer system. A chromatographic analysis of gas quality was carried out for each sample separately. A control analysis of samples for COD, VFA, VSS and pH were performed as well.

Calculations

Based on the amount of the gas produced during the batch methanogenic test and chromatography analyses of methane content, cumulative methane production curves were plotted (Fig. 1). Using those curves, the maximum methane production was determined.

RESULTS AND DISCUSSION

During the research significant differences in gas production were observed. Basing on the results of methane production obtained from 3 series carried out with Cr(III) concentration from 200 to 3000 mg/L, cumulative gas production curves were plotted. The curves were drawn for control samples and samples with toxicant in the batch tests (Fig.1). According to gas chromatographic analyses the amount of methane produced from samples during the test period was quite high: 80% and 70-74% for control and toxic samples respectively.

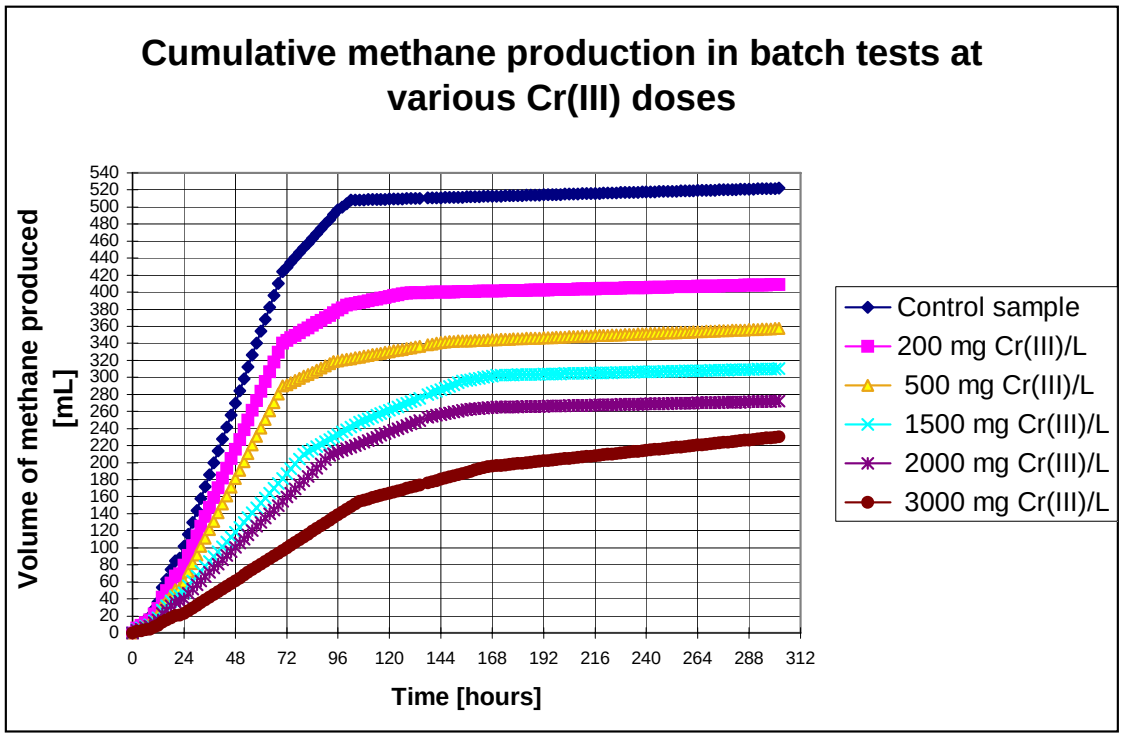

Figure 1. Cumulative methane production in batch tests at various Cr (III) doses.

Total methane amount (expressed in volumetric units) produced during 12 days test period has been presented in Table 4. Methane production under inhibitory conditions was expressed in relation to a reference sample that was inhibitor free.

Table 4. Total volume of CH_4 in tests with various doses of inhibitory substance in relation to non-inhibited methanogenesis

Cr(III) dosage [mg/L]	CH_4 [%]
control	100
200	80
500	80
1500	55
2000	55
3000	53

It can be stated that doses 200 and 500 mg Cr(III)/L[1] caused decrease of a methane production of 20% as compared to the reference sample. Increase of inhibiting compound dose up to Cr(III) 1500 i 2000 mg Cr(III)/L led to 45% decrease of methane production. The concentration of Cr(III) equal to 3000 mg/L caused a 47 % decrease of methane production .

However, methane is produced until entire organic matter is converted its reaction rate tends to decrease as the concentration of substrates drops being consumed by microorganisms. After certain period of time an amount of methane produced is relatively small, and from energetic point of view energy required for

[1] 1 mg/L equals to 1 ppm

facility operation becomes higher than amount of energy recoverable from a biogas. That is why for technical purposes, like digestion tanks design and/or operation optimisation SRT in digestion tanks, estimation of length of period of maximum production rate is a crucial point. It is important to note that decrease of methanogenesis rate is a sign of stabilisation, showing that large part of organic matter has been decomposed into stable by-products. It means that end of maximum gas production is an end of stabilisation. Length of period of maximum methane production can be estimated basing on summarisation curves plotted for each of Cr(III) doses as shown in Table 5.

Table 5. Period of maximum methane production at various Cr(III) doses

Cr(III) dosage [mg/L]	Time of max CH4 production [hours]
control	approx. 96
200	120 - 144
500	144 - 168
1500	approx. 168
2000	to be repeated
3000	exceeds test period

It is visible that volume of methane decreases as the inhibitory dose rises, on the other hand a length of maximum productivity period extends with doses.

CONCLUSIONS

1. The methane production is inhibited at 200 mg Cr(III)/L and significantly decreases at above 1500 mg Cr(III)/L.
2. Results of tests showed an inhibitory effect not only as decrease of a reaction rate but also as change in real time necessary for stabilization of inhibitor containing sludge.
3. Observed changes may lead to more precise explanation of an inhibitory effect of Cr(III) on a methanogenesis. This testing method can be applied for examination of possible inhibition of a methanogenesis by various heavy metals.
4. Data obtained may be applied for design purposes in dimensioning of heated digesters at the municipal wastewater treatment plants. Period of maximum gas production can be assessed with the use of this method and by the same biomass efficiency can be measured.
5. During the batch test period, a high amount of methane was recorded in relation to the total fermentation gas production from all samples. This could prove the proper course of methanogenic process in the tested samples.

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