Maximal methane potential of different animal manures collected in northwest region of China

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Abstract: Maximum methane potential (B_0) is an important parameter used in assessing suitability of a substrate for biogas production. This study examined maximum methane potential of different manures generated from three major Chinese livestock, namely chicken, hog and cattle, and evaluated the important factors that affect the maximum methane potential of a substrate. The livestock manures collected from the local farms were incubated under a thermophilic anaerobic condition (55°C). The results showed that the maximum methane potential (B_0) of cattle, hog and chicken manures were 292.0 mL/g VS, 272.0 mL/g VS and 266.4 mL/g VS, respectively. The B_0 value decreases with increasing contents of crude protein and crude fat, while increases with increasing the contents of carbohydrates and crude fiber in manures. The content of NH_4^+-N in chicken manure was significantly higher during the digestion period, reached as high as 1962.5 mg/L by the end of incubation period. Heavy metals of Cu and Zn in the manure also affect the B_0. Empirical relationships that describe the B_0 decrease in response to increase of Zn and Cu contents in manure were developed and used as a simple tool to assess the effects of these metals on the B_0. It was concluded that the protein, Cu and Zn contents of manure are most important chemical compositions that negatively affect maximum methane potential. Based on the three experimental manures, the maximum methane potential was limited by either ammonium content or Cu and Zn content in the manure. For a commercial biogas production facility using these manures as main feedstock, one should consider to add co-substrate or co-substrates to reduce concentration of these chemicals to maximize biogas production.

Keywords: anaerobic digestion, manure compositions, biomethane potential, volatile solid degradation
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1 Introduction

With rapid development of livestock industry in China, animal manure has become an important pollution source for environment[1-4]. Manure contains high concentration of nutrients, large amount of volatile substances, and enriched microorganisms[5-8]. Inappropriate dispose of manure would cause fish kills, algal blooms, drinking water contaminates, nauseating

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odors and disease transmission, resulting in a serious environmental issue[9-11]. Extraction of the plant nutrients from bulk manure for reuse is not economically feasible, however, inherent energy of manure could make it valuable via a microbiological process[12-13]. Combining energy extraction with the creation of value-added products from manure could turn manure into a resource rather than a pollutant. Anaerobic digestion process is one of promising technologies to achieve this goal.

Anaerobic digestion is a biochemical process where organic substrates are decomposed into methane and CO_2 along with some trace gases such as H_2S and NH_3, referred as biogas, through a microbial driven reaction under free-oxygen conditions. Biogas typically contains about 60%-70% methane, depending on the nature of the substrate and digestion conditions[14-15]. Maximum methane potential, B_0, is defined as the maximum methane generated from a unit of substrate in the presence of methanogenic microorganisms at given sufficient time or t->∞. It is a critical parameter to determine the economic viability of manure for biogas production using a substrate[16-17]. The B_0 is directly related to organic or inorganic compositions of manure. The proportions of carbohydrate, protein and fat in manure could alter the metabolic pathways of microbial consortium and its associated methane production during anaerobic digestion process[18-20]. Feed additives for Chinese livestock often resulted in higher heavy metal content, such as Cu and Zn[21-22]. Understanding the effect of manure compositions as digesting substrate for biogas production is critical for successfully designing and operating a biogas facility. The purpose of this laboratory-based study was to examine the biomethane potential of livestock manure derived from the northern-west region of China, and evaluate the effect of manure composition of biomethane production.

2 Materials and methods

2.1 Samples and inoculum

Hog, dairy and poultry are major food livestock sectors in Shanxi province, northern-west region of China. This study focuses on hog, dairy, chicken manure and corn straw. Chicken manure was taken from a chicken farm in Xinzhou, located in the north central of the Shanxi Province; hog manure from Xu Ming concentrated breeder; dairy manure from the livestock farms of Shanxi Agricultural University; corn straw from the resources and environment experiment station of Shanxi Agricultural University. The samples were air-dried and stored in a refrigerator (–20°C) until testing. Heavy metal elements (Cu and Zn) were determined using an atomic absorption spectrophotometry after HNO_3-$HClO_4$ digestion. Inoculums of anaerobic fermentation (containing total solids 6%) were obtained from a rural anaerobic digester in the City of Gaoping, located in the east of Shanxi.

2.2 Sample characterizations

Total solid content (TS) and volatile solid content (VS) were measured using APHA methods 2540B and 2540E[23]. Total organic carbon (TOC) and total nitrogen (TKN) were determined according to Yeomans and Bremner[24] and the Standard Methods[23], respectively. The ratio of carbon to nitrogen (C/N) of the samples was calculated based on values of TOC to TKN, which represents the total nitrogen (organic and inorganic) content of the samples. Crude fiber, fat, protein and carbohydrate content were measured by gravimetric method[25], Soxhlet extraction method[25], semi-micro Kjeldahl digestion method[23] and phenol-sulfuric acid digestion method[26], respectively. Level of ammonium nitrogen (NH_4^+-N) was determined using a continuous flow analyzer (FIAstar™ 5000 Systems, FOSS, America). Cu and Zn in solid phase were analyzed by HNO_3-$HClO_4$ fermentation-atomic absorption spectrophotometry, and in liquid phase were analyzed by HNO_3-H_2O_2 fermentation-atomic absorption spectrophotometry (PinAAcle 900H, PerkinElmer, America). The characteristics of substrates used in the experiment are presented in Table 1.

2.3 Anaerobic digestion experiments

2.3.1 Biogas production of different manures

Anaerobic digestion was conducted using triplicate batch cultures with 6% total solids substrate. After the cultures were prepared, the experimental bottle headspace was purged with ultra-high pure nitrogen (UHP-N_2) to create an anaerobic condition. The cultures were incubated at 55°C in an incubator without lights. The digesters were monitored for biogas production and quality. Bio-methane was measured by passing biogas into a solution 5% NaOH. The NaOH solution absorbed the CO_2 of the biogas and the difference between the volume before and after CO_2 absorption was considered as the volume of produced bio-methane[7]. Fermentation process continued until daily methane production was less than 1% of cumulative methane production (for 30 days in this study). Four hundred grams of the post-digested samples were taken after mixing digestate thoroughly and TS, VS, TOC, TKN, NH_4^+-N, Cu and Zn were analyzed.

2.3.2 Biogas production in responding to the elevated Cu and Zn concentrations

B_0, as a function of Zn or Cu concentration in the digestate, was conducted to determine the effects of these two heavy metals on biogas production potential. The range of concentrations of these two metals was from 1 to 45 mg/L, with five different levels. The concentration range covers the most observed concentration in manures and their related digestate. The different concentrations of Zn in the samples were prepared using chemical Zn salt and wheat straw, where the concentration of Cu was adjusted in less than 1 mg/L. The samples with different concentrations of Cu were prepared in the sample fashion. The same experimental procedure was followed as biogas production of different manure sections (2.3.1).

2.3.3 Maximum methane potential (B_0) calculation

Cumulative methane production was calculated as the sum of methane produced over the incubation period and expressed as liters per kilogram of VS of substrate added to the digestion process. The volume of methane was normalized to the standard temperature and pressure conditions (0°C and 1 atm). The methane production profile was fitted with two non-linear regression models in GraphPad 5.0[17]. The Equation used for the fitting was:

$$B=B_0\,(1-e^{-k\cdot t}) \qquad (1)$$

where, B is the cumulative methane production at time (t); B_0 is the maximum methane production; k is the rate constant, expressed in reciprocal of the X-axis time units (d^{-1}).

2.4 Data analysis

Statistical data analysis was performed with the software SPSS Statistics, version 17. Analysis included descriptive statistics and mean values, standard errors and standard deviations were calculated. Comparisons of the means were performed by using one-way analysis of variance and evaluated by using the least-significant-difference (LSD) test. Readings were considered significant when $p<0.05$.

3 Results

3.1 Methane production in batch test of chicken, hog and cattle

The anaerobic digestion of chicken manure resulted in the highest daily methane production of (22.3±0.4) mL/g VS, which occurred on day 6 (Figure 1), while the maximum daily methane production for hog and cattle manure occurred on day 10 and 15, respectively. This delay may relate to their chemical and biological compositions. Figure 2 shows the cumulative methane production of the chicken, hog and cattle. The cumulative methane production of cattle manure was higher than both chicken and swine manure.

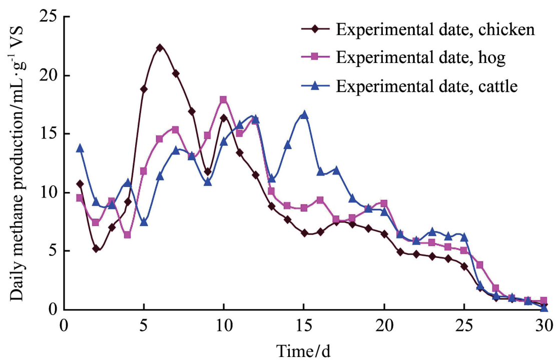

Figure 1 Daily methane production of chicken, hog and cattle

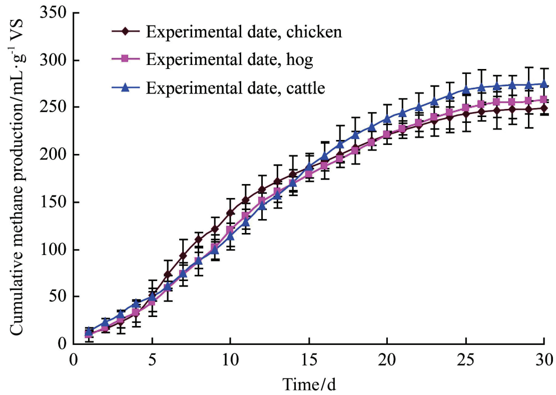

Figure 2 Cumulative methane production of chicken, hog and cattle

3.2 Effects of contents of carbohydrate, protein, fat and fiber of manure on B_0

The characteristics of three animal manures are shown in Table 1. The total carbon content in the cattle manure was higher than that in chicken and hog. The TKN in the chicken manure is the highest while in the cattle manure is the lowest. Therefore, the C/N ratio in the cattle manure is the highest. The carbohydrate content in cattle manure is 2.4 times of chicken manure, and 1.2 times of hog manure, respectively. The crude fiber in cattle manure is 2.3 times of chicken manure, and 1.6 times of hog manure.

Table 1 Characteristics of manures used in the experiments and the B_0

Manure type	chicken		hog		cattle	
	Avg	±SE	Avg	±SE	Avg	±SE
TS/%	90.15	0.19	92.10	0.06	90.61	0.04
VS/%	64.43	0.98	60.49	1.64	74.77	1.48
TOC/g·kg^{-1}	302.83	4.61	284.30	2.85	351.44	6.95
TKN/g·kg^{-1}	20.98	0.01	15.03	0.13	13.64	0.36
C/N	14.44	0.21	18.91	0.27	25.77	0.42
Crude fiber/%	8.92	0.16	12.68	0.20	20.92	0.24
Crude fat/%	2.79	0.09	2.21	0.04	1.94	0.06
Crude protein/%	13.11	0.19	9.39	0.14	8.53	0.12
Carbohydrate/%	16.44	0.85	32.63	1.18	38.90	1.36
Total Cu/mg·L^{-1}	5.38	0.38	24.11	1.18	1.79	0.12
Total Zn/mg·L^{-1}	19.92	0.27	35.23	1.59	4.29	0.24
B_0/mL·(g VS)$^{-1}$	266.4		272.0		292.0	

The maximum methane potential, B_0, of cattle manure is the highest among the studied manures. B_0 increased with increasing carbohydrate and crude fiber contents while decreased as increasing amounts of crude protein and fat in manure. The concentration of NH_4^+-N in chicken manure during the digestion process increased from (749.1±16.58 mg/L) at the day 0 to (1962.5±53.89) mg/L at the day 30, while that in the cattle and hog manures increased from (489.5±23.01) mg/L and (497.0±19.46) mg/L to (864.2±38.24) mg/L and (871.5±27.50) mg/L, respectively.

The concentrations of Cu and Zn in the hog manure were higher than that in chicken and cattle manures.

3.3 Response of B_0 in elevated concentrations of Cu and Zn

The values of B_0 of three manures in response to different concentrations of Cu or Zn, were plotted against to the concentrations of Cu or Zn (Figures 3 and 4). The experimental data were fitted to liner equations. The B_0 value decreased as increasing either Cu or Zn concentration in the digestate. Data from three manures followed a similar pattern for each metal species. The results are shown in Equation (2) for Cu and Equation (3) for Zn:

$$\frac{B_0}{B_{0m}} = 1 - \frac{C}{C_m} \qquad (2)$$

where, B_{0m} is 492.0 mL/ g VS and C_m is 57.9 mg/L. B_{0m} is the value of B_0 when the concentration of Cu in the digestate is approaching to zero and C_m is the concentration of Cu that is too high for biogas production; therefore it is referred as a critical Cu concentration.

$$\left(\frac{B_0}{B_{0m}}\right)^2 = 1 - \left(\frac{C}{C_m}\right)^2 \qquad (3)$$

where, B_{0m} is 456.6 mL/g VS and C_m is 53.3 mg/L. B_{0m} is the value of B_0 when the concentration of Zn in the digestate is approaching to zero and C_m is the concentration of Zn that is too high for biogas production. Same as Cu, this concentration is referred as a critical Zn concentration. Both critical Cu and Zn concentrations were not manure specific.

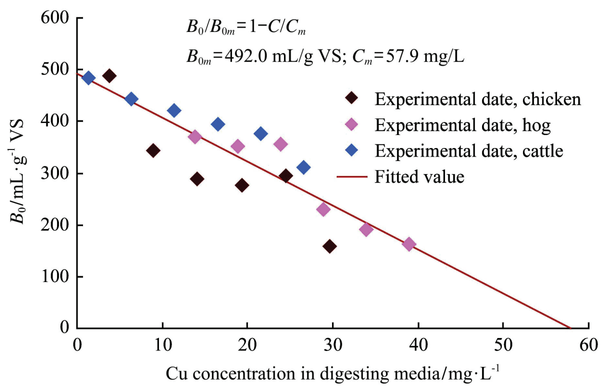

Figure 3 B_0 as function of Cu concentration

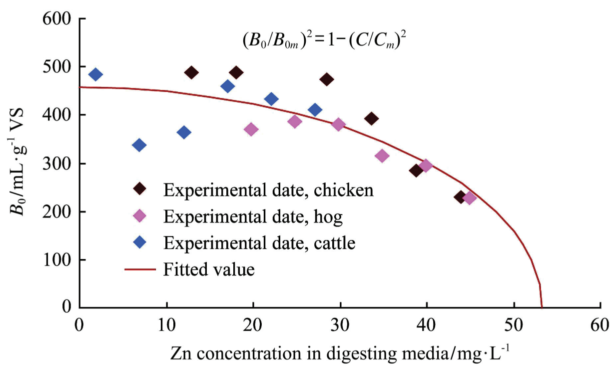

Figure 4 B_0 as function of Zn concentration

4 Discussion

Anaerobic digestion process is carried out by a consortium of microorganisms in the absence of oxygen converting organic materials to CO_2 and CH_4 as end products. Maximum biogas potential, B_0, is defined as the maximum methane generation per unit substrate subject to biological decomposition in the presence of methanogenic microorganisms under anaerobic conditions. The value of B_0 for a specific material depends on its chemical nature. It has been reported that the B_0 value of livestock manure varies as geologic regions, the climate, the variety and quantity of livestock feed additives in 23 provinces of China[27]. Manures in Henan, Sichuan, Hebei, Shandong, Inner Mongolia, Guangdong and Yunnan produced a higher biogas yield[27-29], while manures generated in Beijing, Shanghai, Tianjin, Shanxi, Hainan, Guizhou and Jiangxi areas resulted in a lower biogas yield[27,28-30]. Ye et al.[31] reported that the cumulative methane production of hog manure was 423 mL/g VS in Guangdong. Xiong et al.[32] reported that the cumulative methane production of cattle manure was 324 mL/g VS in Yunnan. Other studies indicated that the cumulative biogas production were much smaller as 200 mL/g VS for hog manure and cattle manure in Jiangxi and Beijing[33-34]. The results of this study are comparable with these literature data.

The levels of carbohydrate, protein and fat in manure affect the metabolic pathways of microbial consortium and therefore affect the methane production during anaerobic digestion process[18-20]. The high level of carbohydrate and fiber in manure could favorite the microbial consortium to switch on acetate oxidation metabolic pathway for methane production. But large amounts of protein and fat contents in manure may inhibit the metabolic pathway. Higher protein value in the materials will result in a higher NH_4^+-N content in the digestate. Once it reached a certain level in digestate, it will inhibit the biogas production[35-36]. Hejnfelt et al.[37] reported that the NH_4^+-N inhibited biogas production when its content in digestate was 1500-7000 mg/L. Hansen et al. [38] reported that when the NH_4^+-N content in the digestate effluent was higher than 1100 mg/L and the pH over 8.0, the biogas production reduced significantly. NH_4^+-N content in the digestate has been recognized as one of critical factors affecting biogas production. The chicken manure used in this study resulted in over 1900 mg/L NH_4-N at the incubation day 30. This is one of major reasons that result in the lowest B_0 for the chicken manure. Therefore the chicken manure is not suitable for producing biogas alone. If it is used for biogas production, it should be mixed with other materials containing higher carbohydrate or fiber, such as straw, to maximum the biogas production.

Heavy metal content is another factor that impacts biogas production[39-40]. Ke et al.[41] reported that when Cu concentration was about 2-6 mg/L, it had a positive effect on gas production, but once the concentration reached 8 mg/L the gas production would be reduced significantly. The concentration of Cu in cattle and chicken manures in this study were relative low. However, Cu concentration in the hog manure was 48 mg/L, this may inhibit the biogas production based on the report by Li et al.[42] This explains the fact that the B_0 value obtained from this study was lower than that the literature reported values. The B_0 value decreases with increasing of Cu or Zn concentration in the digestate for all three manures. However, the decreasing rate differed slightly. This study revealed the critical concentrations of Cu and Zn for three studied livestock manures were 57.9 mg/L and 53.3 mg/L, respectively. These values are similar to the reported values of 48-96 mg/L from the literatures[43]. The empirical relationships presented in the Equations (2) and (3) can be used as indicators for assessing the effect of heavy metals on biogas production potentials when Zn and Cu species as a concern.

5 Conclusions

The values of B_0 from three livestock manure sampled in Shanxi were 292.0 mL/g VS, 272.0 mL/g VS and 259.7 mL/g VS for cattle, hog and chicken, respectively. High protein content in the chicken manure was one of major factor that affects the B_0 value; while the Cu and Zn contents in the hog manure were higher than other two livestock manure resulted in a lower B_0 comparing with the literature values. When the biogas production using these manures as main feedstock, especially for hog and chicken manures, it will be limited by either ammonium build-up or high Zn and Cu concentration, and thus one should consider to add co-substrates to reduce these chemicals for maximizing the biogas production.

The response of B_0 of three livestock manures to increase concentration of Cu and Zn revealed that a critical concentration exists for both Cu and Zn were 57.9 mg/L and 53.3 mg/L, respectively. It can be used as an indicator for assessing heavy metal effect of biogas production for a given substrate.

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