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Comparison of anaerobic digestion characteristics and kinetics of four livestock manures with different substrate concentrations

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HIGHLIGHTS

- This work compared the AD characteristics of four livestock manures.
- Negative correlations were found between initial manure substrate concentrations and CMY.
- Percentages of methane in final biogas volume decreased when loading rate increased from 8 g VS/L to 64 g VS/L.
- Cone model fitted the experiment data better than first order model and transfer function model.

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ABSTRACT

Anaerobic digestions of pig manure (PM), dairy manure (DM), chicken manure (CM) and rabbit manure (RM) at initial volatile solid loading (VSL) of 8 g VS/L, 16 g VS/L, 32 g VS/L, 64 g VS/L were investigated under mesophilic conditions. The maximum methane yields of 410, 270, 377 and 323 mL CH_4/g VS_{added} for PM, DM, CM and RM were all obtained at initial VSL of 8 g VS/L, respectively. The improvement of substrate concentration to 64 g VS/L not only decreased the methane yield and biodegradability both by 22.4%, 37.3%, 49.1% and 34.6% for PM, DM, CM and RM respectively, but also reduced the methane content in final biogas production. The Cone model (R^2: 0.9910–0.9974) showed a better fit to the experiment data and the calculated parameters indicated that anaerobic digestion of manures at higher loading has longer lag phase and lower hydrolysis rate.

1. Introduction

Huge amount of livestock manures were annually produced in China, and the uncontrolled decomposition of manure could result in the degradation of atmosphere quality and the pollution of water resources. On the other hand, animal manures as an excellent substrate for anaerobic digestion (AD) have already received considerable attention due to its characteristics of high moisture, buffering capacity, organic matter and wide variety of nutrients. Anaerobic digestion is doubtlessly a more suitable method to treat and dispose animal wastes, for it bridges organic wastes and bioenergy and solves the problem of manure contamination and energy shortage at the same time. To improve the AD performance of manure, extensive research about anaerobic digestion of manure have been conducted. It was founded that the methane potential and biodegradation rate of manure can be affected by its composition which is varied with animal species (Wang et al., 2014).

Actually, the composition of manures from different animal types is highly dependent on some animal factors as well as the feeding patterns. Specifically, the different components of manures excreted by livestock could be originated from different diet composition, nutrient digestibility and intestinal microorganisms (Farnworth et al., 1995). And various feed formulas have to be adopted to match the animals' physiological and nutritional requirements (Garcia-Launay et al., 2014). On the other hand, for the yard raised livestock or poultry could not be cleaned immediately, food residues, bed materials and feathers were frequently found in raw manures. These variability in the composition of livestock manures has great influences on the biodegradation and methane production characteristics of manure. Additionally, the usage of mineral elements and antibiotics in feed for animal growth and therapeutic purposes lead to antibiotic and heavy metal residues in manure (Ji et al., 2012), and the inhibited influence of which to biogas process has been reported in several studies (Guo et al., 2012).

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Besides components of substrate, concentration of substrate is another significant operational factor for the stability and methane productivity of biogas process. It has been stated that increasing substrate concentrations could initially enhance methane fermentation efficiency. But an excessive substrate concentration could produce inhibition to biogas process caused by accumulation of total ammonia (TAN), free ammonia (FAN) and volatile fatty acids (VFA). Fernandez et al. (2008) observed in a batch experiment of municipal solid waste that the methane yield of 30% total solids content was 17% lower than that of 20% TS. Sanchez et al. (2001) showed that the optimal concentration for the anaerobic methane digestion of piggery waste at mesophilic and ambient temperatures is 19.3 g COD/L, and too high or too low substrate concentrations could decrease methane production. In addition, some studies have reported the negative relationship between initial substrate concentration and methane content in final biogas volume (Alzate et al., 2012).

Therefore, the objectives of this research was to investigate the anaerobic digestion characteristics of manures from four normal livestock (pig, chicken, dairy, rabbit) whose diet and digestive system was quite different from each other. Firstly, methane production rate and cumulative methane yield of four substrates at various concentrations were determined under mesophilic temperature and the difference between theoretical methane yield and measured methane yield were compared. Secondly, kinetic model was used to describe methane production of these substrates. Four kinetic models were compared to find the optimum model for each sample and the kinetic model parameters of all batch experiments were analyzed.

2. Methods

2.1. Substrates and inoculum

The fresh pig manure, cow feces, chicken manure and rabbit manure were collected from farms located in the Fengxian county of Shanghai city, China. Stones and grass were picked away from manure and then the manures were stored in a refrigerator at −20 °C. The anaerobically digested sewage sludge obtained from a wastewater treatment plant in Shanghai, China, was used as inoculum. The inoculum was mixed thoroughly and filtered through 0.85 mm pore size screen. All the substrates were collected in half month before the experiment and the inoculum was got no more than one day before the experiment. The properties and characteristics of substrates and inoculums are analyzed in triplicates and the results are showed in Table 1.

2.2. Batch anaerobic digestion experiments

The batch digestion test was carried out in 250 mL conical flasks. To determine the degradation characteristics of four manures with different initial substrate concentrations, required amounts of four kinds of manures were added to reach concentrations of 8, 16, 32, 64 g VS/L, respectively. The minimum concentration was designed as low as 8 g VS/L mainly in regards of comparing its methane content with that of high substrate concentration. Then add 150 mL inoculum and adjust the working volume to 200 mL with deionized water. Finally, pH was adjusted to 7.0 with 1 M HCl or 1 M NaOH. Anaerobic conditions were ensured by flushing high pure nitrogen gas for 3 min before closing digesters with rubber stoppers. The temperature of each reactor was kept at 37 °C by a water-bath. Biogas produced was collected by gasholders and determined once a day. Digesters only with inoculum and deionized water were also set up to determine the background biogas produced from inoculum and this part in the biogas yield of each digester will be subtracted. All the batch tests were performed in triplicate. The experiments were ceased when no biogas were produced for 15 days. Then open the rubber stoppers and measure total solid (TS), volatile solid (VS), pH, VFA, alkalinity and TAN of the digestate.

2.3. Analytical methods

The pH, TS, VS, soluble chemical oxygen demand (SCOD), TAN, and alkalinity were determined according to standard methods 2450G (APHA, 2005). The concentration of free ammonia (FAN) was calculated by Eq. (1) (Niu et al., 2013).

$$FAN = \frac{TAN}{1 + 10^{(pKa - pH)}} \tag{1}$$

$$pKa = 0.09018 + \frac{2729.92}{T + 273.15}$$

VFA C_2–C_5 were quantified using gas chromatography (Agilent-7890A) equipped with a flame ionization detector and a 30 m × 530 μm capillary column. The temperatures of the

Table 1
Properties and characteristics of manures and inoculums.

Characteristics	PM	DM	CM	RM	Sewage sludge
TS (% FW)	47.45 (0.63)	19.41 (0.08)	41.90 (0.79)	27.84 (1.62)	12.66 (0.78)
VS (% FW)	36.49 (0.31)	18.07 (0.37)	35.38 (0.02)	24.49 (1.56)	1.62 (0.77)
VS (% TS)	77.27 (0.38)	93.11 (2.15)	84.46 (1.56)	87.94 (0.48)	12.76 (1.14)
pH	7.29 (0.03)	8.27 (0.01)	6.63 (0.01)	7.83 (0.02)	6.99 (0.01)
TAN (mg/kg FW)	12510 (37.3)	3640 (114)	9940 (68.5)	2610 (51.3)	422.76 (35.0)
FAN (mg/kg FW)	143.29 (5.50)	5.43 (0.33)	24.60 (2.64)	104.30 (21.44)	2.28 (0.19)
SCOD (mg/kg FW)	35300 (1114)	23700 (460)	27147 (2101)	15400 (4432)	10318 (2456)
Alkalinity (mg $CaCO_3$/kg FW)	44398 (968)	16762 (1216)	38425 (423)	7771 (1589)	6034 (641)
VFAs (mg CH3COOH/kg FW)	95502 (254)	1023 (34)	111495 (122)	1817 (57)	NA
Cellulose (% TS)	15.86	23.51	4	11.72	NA
Hemi-cellulose (% TS)	16.69	12.82	11.84	20.63	NA
Lignin (% TS)	1.83	7.95	1.7	6.97	NA
C (% TS)	39.14 (0.04)	39.18 (0.09)	33.61 (0.03)	37.65 (0.14)	23.79 (0.16)
N (% TS)	3.92 (0.02)	2.46 (0.06)	8.95 (0.04)	2.11 (0.00)	2.99 (0.01)
H (% TS)	5.27 (0.27)	5.93 (0.00)	4.80 (0.12)	5.65 (0.00)	3.46 (0.18)
S (% TS)	0.79 (0.01)	0.42 (0.00)	0.94 (0.00)	0.31 (0.01)	3.39 (0.03)
O (% TS)	32.47 (0.39)	35.34 (0.25)	40.05 (0.06)	37.70 (0.23)	NA
C/N	10.0	15.9	3.8	17.9	7.9

Values are presented as mean and data in parentheses are standard deviations ($n = 3$).
FW: fresh weight: TS: total solid; VS volatile solid; FAN: free ammonia; SCOD: soluble chemical oxygen demand:
NA: none analysis.