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Full Length Article

Removal of nitrogen from chicken manure anaerobic digestion for enhanced biomethanization

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ARTICLE INFO	A B S T R A C T
A R T I C L E I N F O Keywords: Ammonia removal Side-stream stripping Anaerobic digestion Chicken manure Ammonia inhibition	The effects of side-stream ammonia stripping as a pre- and post-treatment on the anaerobic mono-digestion of chicken manure were investigated in laboratory-scale continuous stirred tank reactors. Ammonia stripping columns were operated at pH 10 but different temperatures (35, 55, 70 °C). Results showed that digestate stripping at 70 °C and pH 10 got the highest ammonia removing rate (18.2–45.2%), and under these conditions, the methane yield at OLR of 9 g VS $L^{-1} d^{-1}$ reached 0.199 $L g^{-1} VS_{added}$ which was significantly higher than that of other digesters (0.01–0.03 $L g^{-1} VS_{added}$), although no improvement of methane yield was observed at OLR 3 and 6 g VS $L^{-1} d^{-1}$. The microbial community analysis revealed that hydrolytic and fermentative bacteria dominated all bacterial communities. Methanogenic pathway of feedstock stripping digester was predominant by hydrogenotrophic <i>Methanimicroccus</i> , while hydrogenotrophic/aceticlastic <i>Methanoscarcina</i> was dominant in the archaeal structures of the rest digesters. However, a shift from <i>Methanosarcina</i> to <i>Methanoculleus</i> was observed in R3 (digestate stripping at 70 °C/pH 10) when dominant species were inhibited and decreased in other digesters, indicating that the high methanogenic activity in R3 was maintained by shifting to methanogens with high tolerance to inhibitors.

1. Introduction

Poultry breeding industries became more centralised and mechanized along with the raising consumption. In 2013, as a result, about 0.146 billion tons of chicken manure (CM) was generated in China. This vast amount of CM is a potential pollution source causing many environment problems. Traditional utilizations of CM include composting as fertilizer, combustion for energy and methane production. Unfortunately, when spreading as fertilizer, composted CM can release malodor significantly threating air quality [1]. The heavy metal elements and pathogens in CM also make it difficult to recycle back to agricultural land for food production. Besides, its high water content was not appropriate to recover energy through thermal treatment. Therefore, CM has been targeted for biogas generation because of its high biogas potential and high fraction of biodegradable organic components. Indeed, nitrogen content of CM was generally higher than other animal manures [2]. Excessive ammonia was produced from the hydrolysis of uric acid, urea and proteinaceous nitrogen materials in poultry manure, which exerts negative effect on methanogen activity and leads to process upset.

According to Niu et al. [3], biogas production and methane content of sole CM fermentation decreased when total ammonia nitrogen (TAN) concentration reached 6000 mg L^{-1} . Large amount of water has to be used to dilute and wash the reactor for recovering from inhibition, and this method is obviously cost-expensive. Recent work by Li et al. [4] has shown that improved performance was found in co-digestion of CM with corn stover. The carbon to nitrogen ratio was adjusted to alleviate ammonia inhibition, while this method was not always effective and the low nitrogen co-substrate might be site-specific or seasonable. Another approach is to supply trace element so as to simulate the synthesis of essential coenzymes or cofactors involved in anaerobic microbial growth and metabolism, especially methane formation [5]. But the addition of trace element may cause heavy metals pollution and was not able to overcome the toxicity of high ammonia concentrations [6]. For example, Zhang [7] reported that the organic loading rate (OLR) of Fe supplemented digester feeding CM could be raised to $5 g VS L^{-1} d^{-1}$. When OLR further improved to $6 \text{ g VS L}^{-1} \text{ d}^{-1}$, specific methane production (SMP) decreased dramatically from $314.3 \text{ mLg}^{-1} \text{ VS}_{added}$ to $230.5 \text{ mL g}^{-1} \text{ VS}_{added}$. Although methane yield was recovered after the addition of Ni, the high-strength concentrations of TAN and free

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ammonia (FA), as much as 8500 mg L^{-1} and 966 mg L^{-1} , were still a potential risk for leading to ammonia inhibition.

As mentioned above, unless ammonia concentration in digestate was reduced, it is hard for the CM to be digested as a single substrate. However, the referred typical methods might be not available for digestate containing high concentrations of ammonia. The process of ammonia stripping combined with absorption has been investigated by several researchers and seems to be a feasible method for removing and recovering ammonia from chicken slurry and digestate. In this process, free ammonia is transferred from the waste stream into the gas phase and is captured by absorber. Existing methods for ammonia stripping are based on adjusting temperature or pH to force the ammonia dissociation equilibrium of NH_4^+/NH_3 to favor in the formation of free NH₃. pH of substrate has higher effect on FA formation than temperature [8], but large mount of alkalis (NaOH, KOH, CaOH) have to be added to increase the pH, which exerts negative effect on methanogenesis caused by the toxicity of residual ions [9]. Increasing temperature seems to be a potential choice, especially when a cheap thermal energy source is available.

Ammonia stripping has been tested under a range of temperatures for variety materials. For example, stripping temperature in ranges of 6–55 °C and 80 °C has been tested for swine wastewaters [10,11]; and 35–85 °C with and without pH adjustment for food waste [12]. Increased ammonia removal efficiency was found at higher temperature and alkalinities [13]. In the studies below, however, this law may not always be the case. According to Fatma et al. [14], 82% ammonia was removed when CM stripped after 4 days anaerobically digesting at 55 °C and pH of 8–9, while Hong et al. [15] found that liquid fraction of CM digestate with an initial pH of 9 stripped around 80 °C and 450 mbar vacuum pressure leading to 72% TAN removal rate, although lower pressure was also favorable for higher TAN removal rates. Considering the limited and conflicting results of ammonia removal studies on CM digestate, further investigation was necessary to evaluate the effects of temperature on ammonia stripping from CM.

The objectives of this study were to analyze systematically the efficiency of side-stream ammonia stripping in terms of the effects of temperature and to study the feasibility of the stripping process as a pre- or post-treatment for semi-continuous AD of CM. At present, in semi-continuous anaerobic fermentation of chicken manure, the extent to which the ammonia stripping treatment can improve the organic loading capacity of the system has been rarely reported. Furthermore, high-throughput sequencing method was used to determine the dynamic changes in microbial community structure during digestion process and reveal the links between AD reactor performance and the structure of its microbial community. To the best of our knowledge, few reports studied the dynamic changes in microbial groups in OLR increasing AD reactors which were coupled to stripping columns. Therefore, insights gained from this trial would enhance the comprehension of microorganisms involved in partly stripped digestate as well as the factors that influence the performance and stability of anaerobic digester.

2. Materials and methods

2.1. Origin of inoculum and feedstock

The semi-continuous digesters were inoculated with anaerobically digested sewage sludge from a West Wastewater Treatment Plant in Shanghai, P. R. China which was then acclimated to high nitrogen substrates by feeding CM over a period of 37 days at an OLR of $2 g VS L^{-1} d^{-1}$. Before use, the digestate was first sieved through a 0.85 mm pore size screen to remove large particles.

The fresh chicken manure, with total solids (TS) of 20.1%, was collected from farms located in the Fengxian county of Shanghai, P. R. China. Any non-biodegradable contaminants like stones were removed. Then the manures were homogenized, packed into 4 L plastic storage

Table 1		
Properties and characteristics of inoculums	chicken	manures.

Characteristics	Sewage sludge	Chicken manure
TS (% FW)	4.43 ± 0.24	20.06 ± 0.04
VS (% FW)	2.17 ± 0.11	14.03 ± 0.08
VS (% TS)	49.21 ± 1.15	69.94 ± 0.35
pH	7.50 ± 0.01	8.64 ± 0.02
TAN (mg kg ^{-1} FW)	1525.2 ± 23.7	4646.5.0 ± 23.8
TN (mg kg ^{-1} FW)	3668 ± 127.6	9276.0 ± 44.7
VFAs (mg L ⁻¹ FW)	22.5 ± 2.2	7327.4 ± 32.2
C (%TS)	23.43 ± 0.03	34.48 ± 0.02
N (%TS)	2.55 ± 0.00	2.70 ± 0.00
H (%TS)	3.46 ± 0.05	4.83 ± 0.01
S (%TS)	0.87 ± 0.02	0.90 ± 0.00
O (%TS)	20.98 ± 0.44	31.68 ± 0.03
C/N	9.20	12.78

Values are presented as mean and data afterwards are standard deviations (n = 3).

FW:fresh weight; TS: total solids; VS: volatile solid; TAN: total ammonia nitrogen; TN: total nitrogen; VFA: total volatile fatty acid; NA: none analysis.

boxes, and frozen in a refrigerator at -20 °C. The properties and characteristics of inoculum, chicken manure are showed in Table 1.

When used, the feedstock was thawed. CM was ground with deionized water to designed TS content using a laboratory grinder (HD2010W, Shanghai SILE Instruments Co., LTD., Shanghai, China) at 800 rpm. The CM slurry, hereafter called raw CM, was used as the feedstock of digestate stripping digesters (R1, R2, R3) and control digesters (R5). The CM slurry stripped ammonia by stripping column, hereafter called ammonia stripped CM, was used as the feedstock of feedstock ammonia stripping digester (R4). The main differences between raw CM and ammonia stripping CM were in total nitrogen (TN) and TAN content. The TN contents of stripped CM used as feedstock at three loading rates were 4086.94, 4872.41, 6484.77 mg kg⁻¹, respectively, much lower than raw CM slurry with TN of 6774.01, 6113.10 and 8861.27 mg kg⁻¹. Ammonia concentration has a similar trend. The TS and volatile solid (VS) were also analyzed to present substrate properties. The characteristics of chicken manure slurry and ammonia stripped chicken manure slurry in different batches are shown in Table 2.

2.2. Digesters and ammonia stripping columns

Five 2.5 L capacity semi-continuous digesters were used, constructed of PVC pipe with airtight top and bottom. The top was sealed with water and incorporated a feed port as well as a gas outlet. Drainage port was fitted on the bottom. A stirrer connected to a motor was inserted through the top plate to allow mixing at 20 rpm. Temperature of 36 ± 1 °C in digesters was controlled by recirculating water from a thermostatical water bath. The biogas production was daily collected by gas-impermeable bags, and was corrected to standard temperature and pressure (0°C, 101.325 kPa) after measured. Biogas composition was determined every one or two week.

The stripping columns were constructed of stainless steel tubes (40 cm height \times 3.5 cm internal diameter). Temperature was maintained by using externally intelligent digital thermostatically-controlled electrical heating mats (YL-2600/6400, Shanghai YaTai instruments, China). Nitrogen used as stripping gas was recirculated through the columns using a peristaltic pump (FAY4002, Chengdu Xinweicheng Technology, China). The flow was set to $0.15 \, L \, min^{-1} \, L_{digestate}^{-1}$. Stripping gas was firstly drawn from top of the stripping column, and then bubbled through ammonia trap which consisted of conical flasks containing $0.25 \, N \, H_2 SO_4$ to removal ammonia. The gas entered the column from bottom after passing through a sintered-glass diffuser. The stripping gas stored in gas-impermeable bags and the gas bags were incorporated into the gas circulation loop, acting as gas reservoir to

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