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Impacts of ammonia nitrogen on autothermal thermophilic micro-aerobic digestion for sewage sludge treatment

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HIGHLIGHTS

- TAN was a suitable indicator to characterize ammonia inhibition for ATMAD system.
- TAN adversely affected sludge digestion as it reached 1000 mg L^{-1} apprximately
- Three pathways are closely related to ammonia inhibition.
- High TAN resulted in the deficiencies of K^+ and Mg^{2+} in the cells.
- ROS produced under micro-aerobic condition caused oxidative stress on thermophiles.

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ABSTRACT

The concentration of ammonia nitrogen is relatively high during autothermal thermophilic micro-aerobic digestion (ATMAD), which could significantly affect the sludge stabilization. This paper aims to investigate the impacts of ammonia nitrogen on ATMAD process, batch experiments were carried out with dosage of certain amount of NH_4HCO_3 into digestion system. The total ammonia nitrogen (TAN) was considered as a suitable indicator to characterize the ammonia inhibition. As the TAN reached to approximately 1000 mg L^{-1}, the sludge digester presented a relatively low removal of volatile solids, due to adverse effects of ammonia nitrogen on sludge digestion. Three pathways that closely related to ammonia inhibition were investigated in this research. Digestion system could be inhibited by high TAN due to K^+ deficiency of the cells and the decline of Mg^{2+} in the cytoplasm, and the accumulations of reactive oxygen species lead to oxidative stress for the microbes. Ammonia inhibition can be mitigated by the increase of oxidative enzyme.

1. Introduction

For medium- and small-sized wastewater treatment plants, autothermal thermophilic micro-aerobic digestion (ATMAD) is a promising technology for sewage sludge stabilization, due to its advantages such as efficient pathogen inactivation, good biomass degradation, and low oxygen demand (Liu et al., 2012a; USEPA, 1990). Though the ATMAD process attracted much attention, there were still many problems in its practical application, such as the production of foam and high ammonia nitrogen (Layden et al., 2007; Liu et al., 2012b).

In ATMAD digestion system, the less temperature-tolerant strains in the un-treated sewage sludge lysed and surpassed by the more temperature-tolerant strains, the cellular destruction could produce nitrogen in the form of ammonia due to the high temperature could inhibit the nitrification and denitrification (Liu et al., 2012a; Yenigün and Demirel, 2013). In a large-scale ATMAD digester, the total ammonia nitrogen (TAN) was up to 1241 mg L^{-1} during batch-mode operation, and it could still remain steady at about 1150 mg L^{-1} even when the most of the organic matter has been stabilized at the end of the digestion period (Liu et al., 2011). If the digestion temperature remained at 65 °C, the highest concentration of ammonia nitrogen reached 1173 mg L^{-1}, and the average TAN was 998 mg L^{-1} from 7 to 23 days, however the VS removal was less than 25% at the 23rd day, far below the other digester with low ammonia nitrogen (Liu et al., 2012b). As a certain amount of $MgCl_2$ and NaH_2PO_4 were added to ATMAD digester at different digestion time, the concentration of ammonia nitrogen declined sharply, and the VS removal in the 2nd day dosing digester was

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38.3% at 12 day, which was 9 days earlier to achieve stabilization than the non-dosing digester (Xu et al., 2013). It was evident that sludge stabilization was significantly affected by the removal of ammonium nitrogen during ATMAD process.

For anaerobic digestion, the inhibition of ammonia nitrogen has been reported by many of researches. Free ammonia (FA) can pass through cell membrane, which is considered to be an internal factor leading to the inhibition of ammonia nitrogen (Kayhanian, 1998; Yuan and Zhu, 2016). Gallert and Winter (1997) reported that free NH_3 of 560–568 mg L^{-1} caused a 50% inhibition of methanogenesis under thermophilic condition, and the inhibition increased follow the rising of temperature due to the fact that thermophilic cultures are more susceptible to ammonia than mesophilic ones (Ozturk et al., 2003; Poggi-Varaldo et al., 1997). However, other researchers insisted that both free NH_3 and ionized NH_4^+ can affect the biogas fermentation process (Niu et al., 2013). TAN is a combination of free NH_3 and ionized NH_4^+, and the early literature also found that process inhibition is dependent on TAN concentration, methanogenic activity decreased by about 75% at the TAN concentration of 759 mgL^{-1} (Kayhanian, 1998). Katunuma et al. (1966) investigated the biochemical and enzymatic fundamentals of ammonia toxicity, and the results indicated that tricarboxylic acid (TCA) cycle could be inhibited by ammonia. Some studies were conducted with pure cultures, indicating that ammonia may affect methanogenic bacteria in two ways: (1) ionized NH_4^+ may inhibit the methane synthesizing enzyme directly; (2) the hydrophobic ammonia molecule may diffuse passively into the cell and cause proton imbalance and potassium deficiency.

The mechanism of ammonium inhibition has been studied in anaerobic digestion process, however the knowledge of how ammonia toxicity occurs in thermophilic micro-aerobic digestion system is not well known. Thus, a series of batch experiments were carried out in this research aimed to investigate the impacts of ammonia nitrogen on autothermal thermophilic micro-aerobic digestion, while certain amount of NH_4HCO_3 was respectively added to sludge digestion system. Moreover the VS removals and the variations of other physico-chemical properties, superoxide anion radical and oxidase activity were also determined. The obtained results are beneficial for gaining deeper insight into the mechanism of ammonium inhibition in ATMAD digestion process.

2. Materials and methods

2.1. Sewage sludge sample

Sewage sludge used in this study was collected from the aeration tank of a municipal wastewater treatment plant in Kunming, China. The collected sludge was sieved to remove matter larger than 0.5 mm in diameters, then centrifuged at 2200 g for 3–5 min to obtain a total solid (TS) level between 5% and 6%. The pH value of the obtained sludge was 6.5, and the other parameters were shown in Table 1.

2.2. Startup of the ATMAD digester

A certain amount of NH_4HCO_3 was added to a 2.5-L sludge sample and mixed completely. After the pH of the mixture was regulated to 6.5 with 5M H_2SO_4, 2 L of the mixing sludge was transferred to a 3-L digester, which was placed in a water bath with a constant stirring rate of 50 resolutions per minute. The temperature in water bath was raised from 27.5 °C to 45 °C at rate of 2.5 °C per 6 h, and then kept at 45 °C for 22 days. Continuous aeration was supplied by an air pump with air flow rate of 26–40 mL min^{-1} (Liu et al., 2012a; Xu et al., 2013), ensuring a strict micro-aerobic condition.

In this study, five digesters were set to investigate the effects of ammonia nitrogen on sludge stabilization. The TAN concentrations at the beginning of digestion were 27, 350, 514, 723, and 1008 mg L^{-1} respectively, and the corresponding digesters were named as R_0, R_1, R_2, R_3 and R_4. During the whole digestion process, the sludge was sampled every 2 days to determine the physico-chemical properties as well as the enzyme activities.

2.3. Analytical methods

Total solid (TS) and VS were analyzed by the Standard Methods (APHA et al., 2005) in triplicate, and all of the other indicators were determined twice.

The pH and ORP was measured by a pH meter and an ORP meter, respectively. After the sludge sample was taken from the digester, it was centrifuged for 10 min at 12 000 g, and then filtered through 0.45-μm mixed cellulose ester membrane. The filtrate was collected to measure volatile fatty acid (VFA), total nitrogen (TN), total ammonia nitrogen (TAN). The analysis of TN and TAN were conducted in accordance with the Standard Methods (APHA et al., 2005), then the concentration of free ammonia was calculated according to the following equation (Kayhanian, 1998).

$$NH_3 = \frac{17}{14} \times \frac{TAN \times \frac{Ka}{[H]}}{\frac{Ka}{[H]} + 1} \quad (1)$$

where NH_3 and TAN presented as the concentrations of free ammonia and total ammonia nitrogen (mg L^{-1}) respectively. K_a was a dissociation constant at a specific digestion temperature, and the value of $K_{a,45^\circ C}$ was 2.08×10^{-9}. [H] represented the concentration of hydrogen ion (10^{-pH}).

According to the previous method conducted by this research group (Liu et al., 2012a), VFAs (including acetic, propionic, n-butyric, iso-butyric, n-valeric and iso-valeric acids) in the supernatant were analyzed by using gas chromatography (GC-2010, Shimadzu Corp., Japan) with a flame ionization detector and DB-FFAP column. The measured VFA constituents were expressed in mg L^{-1} COD (e.g. 1 mg L^{-1} acetic acid is 1.07 mg L^{-1} COD, and 1 mg L^{-1} butyric acid is 1.82 mg L^{-1} COD).

The collected sludge was dried at 60 °C for 24 h and then crushed into powder. 1.0 g of the resulting powder was added to a 12-mL concentrated nitric acid, the mixture was heated and refluxed for 15 min (Xi and Sun, 2010). The obtained filtrate and the sludge supernatant were subjected to Inductively Coupled Plasma (ICP) analysis (Iris-Advangtage1000, USA) to determine the content of metal ions such as K^+, Ca^{2+}, and Mg^{2+}.

After the sampling sludge mixture was centrifuged, the collected sediment was sent to analyze the O_2^- content by a modified hydroxylamine oxidation method (Liu et al., 2016). The main testing process and technical conditions were described as follow, the sediments were pretreated to acquire the O_2^- extraction solution, then 0.5 mL extraction solution was taken for testing O_2^- content, adding carbonate buffer solution with pH 10.2 and

Table 1
Physico-chemical properties of the sludge employed for experiments.

Parameter	pH	TS (g L^{-1})	VS (g L^{-1})	SCOD (mg L^{-1})	TN (mg L^{-1})	NH_4^+–N (mg L^{-1})	TP (mg L^{-1})
Value	6.5	58.2	36.6	124	137	27	123