Bioresource Technology 143 (2013) 632–641

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

A critical review on inhibition of anaerobic digestion process by excess ammonia

Rajinikanth Rajagopal, Daniel I. Massé *, Gursharan Singh

Dairy and Swine Research and Development Center, Agriculture and Agri-Food Canada, Sherbrooke, Quebec J1M 0C8, Canada

HIGHLIGHTS

- First detailed review on inhibition of anaerobic digestion (AD) process by ammonia.
- Organic substrates with elevated ammonia concentrations are given priority.
- AD process is more susceptible to inhibition by free ammonia nitrogen.
- Discussed various strategies for controlling ammonia inhibition.
- More profound knowledge on parameters influencing ammonia inhibition is needed.

ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form 3 June 2013
Accepted 10 June 2013
Available online 17 June 2013

Keywords:
Anaerobic digestion
Ammonia
Inhibition
Methanogens
Nitrogen

ABSTRACT

Ammonia plays a vital role in the performance and stability of anaerobic digestion (AD) of N-rich organic-feedstock. Several research works were carried-out to study the effect of ammonia on the efficiency of AD of agro-food, industrial and livestock wastes/wastewater. However, excess ammonia remains a critical hitch in AD process. The mechanism of ammonia-inhibition has also been studied and there is no simple strategy available to mitigate ammonia-toxicity, when it exceeds threshold inhibition-level. For successful operation of AD systems at higher ammonia-level, adequate choice of temperature, control of pH and C/N ratio, and utilization of acclimatized-microflora to higher ammonia concentrations may ensure a stable and undisturbed digestion. This review provides a critical summary of earlier and recent research conducted on ammonia-inhibition during the anaerobic degradation of organic substrates, especially, at high ammonia concentrations. This article emphasizes that more profound knowledge on parameters influencing ammonia-inhibition is needed to apply appropriate control strategies.

1. Introduction

Bioenergy production from anaerobic digestion (AD) of organic wastes is a promising climate change mitigation option and considered as a sustainable treatment technology (Pantaleo et al., 2013). Recently, AD of animal wastes has been encouraged in order to overcome the uncontrolled emissions of methane during storage. AD process involves the degradation and stabilization of organic materials by microorganisms in the absence of oxygen. AD leads to the formation of a biogas (mixture of methane and carbon dioxide), microbial biomass and an effluent fertilizer for application on agricultural fields for nutrient recovery (Chen et al., 2008; Kelleher et al., 2002; Rajagopal et al., 2011). AD offers numerous significant advantages, such as low sludge production, low energy requirement and green energy recovery (Massé et al., 2010; Xia et al., 2012). Not only does this technology has a positive net energy production but the biogas produced can also replace fossil fuel, therefore, has a direct positive effect on greenhouse gas reduction. In spite of these benefits, however poor operational stability still prevents AD process from being widely commercialized (Dupla et al., 2004; Shanmugam and Horan, 2009). Several factors affect the AD process performance and stability; among them feed compositions and more specifically the ammonia concentrations are considered to be vital.

Optimal ammonia concentration ensures sufficient buffer capacity of methanogenic medium in AD thus increasing the stability of the digestion process. However, high ammonia is regularly reported as the primary cause of digester failure because of its direct inhibition of microbial activity (Chen et al., 2008; Hejnfelt and Angelidaki, 2009; Sung and Liu, 2003). Early literature related the inhibition of AD process to total ammonia nitrogen (TAN) concentration (Hansen et al., 1998; Nakakubo et al., 2008; Procházka et al., 2012), which is a combination of free [unionized] ammonia nitrogen (FAN) and ionized ammonium nitrogen (NH_4^+). There are

* Corresponding author. Tel.: +1 819 780 7128; fax: +1 819 564 5507.
E-mail addresses: rajinikanth.rajagopal@agr.gc.ca (R. Rajagopal), daniel.masse@agr.gc.ca (D.I. Massé).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.06.030

numerous possible remediation techniques have been reported for the control of ammonia inhibition in AD process such as struvite precipitation (Nelson et al., 2003), anammox (Egli, 2003), use of zeolite and carbon fiber textiles [CFT] (Sasaki et al., 2011; Sawayama et al., 2004), but these are expensive to implement at a large scale. Acclimation of methanogenic consortia to high ammonia levels or raising ammonia tolerance capacity is a proven useful and economical method for improving the AD process and production of methane from different types of wastes (Abouelenien et al., 2009; Angenent et al., 2002). The relatively high N content, often excludes the possibility of treating animal by-products in their original undiluted form.

It is also reported that feedstock C:N ratio, pH control and low temperature operating conditions were considered as feasible options to reduce the ammonia toxicity in AD (Kayhanian, 1999; Massé et al., 2003). This paper provides detailed review of the research conducted on (i) inhibition of anaerobic processes by ammonia and (ii) its controlling strategies. Special focus was put on the effect of elevated ammonia nitrogen concentrations on the anaerobic fermentation of different organic wastes (animal wastes/wastewater in particular).

2. An overview of ammonia inhibition of AD process

Ammonia is the end-product of anaerobic digestion of proteins, urea and nucleic acids (González-Fernández and García-Encina, 2009). Unlike the importance of ammonia for bacterial growth at lower concentration, high concentration of ammonia may cause a severe disturbance in the anaerobic process performance i.e. cause an important decrease of microbial activities (Liu and Sung, 2002; Zhang et al., 2011). Inhibition of the AD process is usually indicated by the decrease in the steady state methane production rates and increase in the intermediate digestion products like volatile fatty acid (VFA) concentrations. Toxicity is manifested by a total cessation of methanogenic activity (Calli et al., 2005; Sung and Liu, 2003). An anaerobic digester has some similarities with the rumen of cattle. In the rumen absorption of ammonia through the rumen wall seems to prevent the occurrence of inhibitory concentrations (Chaucheyras-Durand et al., 2008). The stability of an anaerobic process depends upon the maintenance of a delicate biochemical balance between the acidogenic and methanogenic microorganisms. AD instability can be due to the accumulation of VFA concentrations with a concurrent decrease in methane gas production. Such an unstable situation may happen as a result of TAN levels up to 1500–7000 mg/L (Hejnfelt and Angelidaki, 2009; McCarty, 1964). This wide range of inhibiting ammonia concentrations is probably due to the differences in nature of substrates, inocula, environmental conditions (temperature, pH) and acclimation periods (Chen et al., 2008). However, in particular, McCarty (1964) indicated that when TAN concentration exceeds 3000 mg NH_4–N/L, the AD processes are inhibited at any pH. In a similar study, Hobson and Shaw (1976) reported that TAN concentration of 2500 mg NH_4–N/L resulted in some inhibition of methane production, while a concentration of 3300 mg NH_4–N/L inhibited methanogenesis completely. For an adapted process, Angelidaki and Ahring (1993) showed that an ammonia nitrogen tolerance of up to 3000–4000 mg NH_4–N/L. These results are in accordance with the studies reported by Sung and Liu (2003) and Procházka et al. (2012), where they have demonstrated that higher TAN concentrations (>4000 mg/L) could cause obvious inhibition of methanogenesis. Whereas, Sawayama et al. (2004) and Lauterböck et al. (2012) observed the inhibition when the TAN concentration exceeds 6000 mg NH_4–N/L. While, low ammonia nitrogen concentration (500 mg/L) can cause low methane yield, loss of biomass (as VSS) and loss of the aceticlastic methanogenic activity (Procházka et al., 2012). They mentioned that negative influence of low ammonia nitrogen concentration on biomass is caused not only by low buffer capacity but also by deficiency of nitrogen as nutrient. Table 1 summarizes the concentrations at which ammonia are beneficial, inhibitory or toxic to the AD process.

However, it should be noted that any likely inhibition by ammonia in the AD process should not only be related directly to the TAN concentration but to the FAN levels as it is considered to be the main cause of inhibition of methanogenic microflora (Fernandes et al., 2012; Ho and Ho, 2012). FAN concentration primarily depends on three parameters such as TAN, pH and temperature. In addition, ionic strength is also considered as a significant parameter especially for concentrated solutions (Hafner and Bisogni, 2009; Nielsen et al., 2008). Fernandes et al. (2012) demonstrated that for the anaerobic digesters operated at pH 7 and 35 °C, FAN represents less than 1% from the total ammonia, while, at the same temperature, but pH 8 the FAN increases to 10% (Fig. 1). In a similar study, Kayhanian (1999) showed that FAN concentration at thermophilic (55 °C) temperatures is expected to be six times higher than under mesophilic conditions at the same pH. An increase in pH from 7 to 8 will lead to an eightfold increase of the free ammonia levels in mesophilic conditions and even more at thermophilic temperatures, because temperature influences the dissociation constant of ammonia nitrogen based on the Eq. (2) (Hansen et al., 1998).

2.1. Inhibition of AD process by FAN (livestock/slaughterhouse waste)

Angelidaki and Ahring (1994) observed the combined effect of FAN and temperature on AD of cattle manure in the continuously stirred tank reactors (CSTRs). FAN concentrations greater than 700 mg/L, inhibited the methane production at thermophilic temperatures (55 and 64 °C) and resulted in a rapid increase in VFA concentrations (5000 mg/L) at pH 7.9. Borja et al. (1996) reported the initial inhibition of AD process of cattle manure occurred at 995 mg/L of FAN (pH 7.9, 55 °C); however, process pH dropped to 7.6 due to an accumulation of VFA (>5000 mg/L), resulting in a FAN concentration of 685 mg/L and a reduction in the growth rates of the aceticlastic methanogens to 18%. Whereas, Nielsen and Angelidaki (2008) observed that AD of cattle manure was inhibited at 55 °C in CSTRs at 1200 mg/L of FAN at a pH of 7.6.

Braun et al. (1981) observed the inhibition of AD of swine manure at 37 °C during the beginning of a new cycle with an addition of fresh manure at pH 8.0 and FAN 316 mg/L. Subsequently, when the pH of the process was adjusted to 7.4, FAN level was then reduced immediately to 86 mg/L and methanogenic utilization of VFAs was re-established. Nakakubo et al. (2008) noticed the 50% inhibition of methane production at 1450 mg/L of FAN, during the co-digestion of swine manure with solid fractions separated from manure (40% manure, 60% solids) at 51 °C, pH >7.6, in CSTRs. However, they have concluded that TAN concentrations are more responsible than FAN levels as free ammonia did not reflect the acute ammonia inhibition considerably. During the AD of swine manure in CSTRs, inhibition by FAN 1600–2600 mg/L was noticed at different temperatures 55 and 60 °C at pH 7.9 and 8.1, respectively. Inhibitory effect of FAN (750 mg/L, pH 8.0) was also observed at 37 °C with an accumulation of 4800 mg/L of acetate (Hansen et al., 1998).

Lauterböck et al. (2012) observed the ammonia inhibition while digesting slaughterhouse waste, especially when the FAN concentration exceeds 1000–1200 mg/L (6000 mg NH_4–N/L) at 38 °C and pH of 8.1. AD of separated or mixed by-products from pigs such as meat and bone flour, fat, blood, hair, meat, ribs, raw waste was investigated at 55 and 37 °C (Hejnfelt and Angelidaki, 2009). They reported that high concentrations of long-chain fatty acids (>5 g lipids/dm^3) and ammonia (>7 g N/dm^3), in the by-products inhibited the AD process. Poultry manure has a higher fraction of