



# Progress in inhibition mechanisms and process control of intermediates and by-products in sewage sludge anaerobic digestion



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## ABSTRACT

Anaerobic digestion is an effective waste treatment method both for the pollution control and energy recovery, such as treating many agricultural and industrial wastes which contain high level of easily biodegradable substances. However, there are also many problems to be resolved, such as low methane yield, long retention time and process instability, preventing this technique from being widely applied. Variety of inhibitory substances and intermediate products are the primary cause of anaerobic digester upset or failure, including free ammonia (FA), volatile fatty acids (VFAs) and sulfide/sulfate, though they are essential nutrients for bacterial growth and anaerobic digestion process. Many researches have been conducted to investigate the inhibition mechanisms and the controlling factors during the overall anaerobic digestion process. In this paper, a detailed summary of the researches was discussed on the inhibition of the anaerobic digestion process. Furthermore, the controlling and recovery of the inhibitors as valuable products were also reviewed in detail. Co-digestion with other wastes, acclimation of microorganisms, and incorporation of methods could significantly improve the efficiency of sewage sludge anaerobic digestion.

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## 1. Introduction

Anaerobic digestion (AD) is considered as one of the oldest and well-studied sustainable biological treatment technologies for stabilization and reduction of organic wastes [1–3], including fruit

and vegetable processing wastes, packinghouse wastes, industrial organic wastes and agricultural wastes [4,5], especially the sewage sludge. Among the treatment technologies available for treating organic solid wastes, AD is very welcome for large scale wastewater treatment plant (WWTP) because of its limited environmental harmful impacts [6–9] and high potential for bioenergy recovery [6,7,10].

Nowadays, waste activated sludge (WAS) produced from municipal WWTP is a critical problem because of its huge production,

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potentially environmental risk and high cost for disposal accounting for up to 30–50% of the total wastewater treatment expense [11,12]. AD is considered to be the most energy efficient method for reducing and stabilizing WAS and methane by-product as a form of fuel which may reduce treatment cost [13,14].

Anaerobic digestion experienced an important growth after the first energy crisis in the 1970s, and now it has been proved to be a mature technology [15,16]. AD includes the degradation and stabilization of organic materials under anaerobic conditions by anaerobes, leading to the formation of biogas (a mixture of carbon dioxide, methane and other gas), microbial biomass [2,17] and an effluent fertilizer for application on agricultural and garden fields for nutrient recovery [5,17,18]. Biogas from anaerobic degradation of wastewater biosolids may be beneficially used in boilers or dryers for process heat, or could be used in micro-turbines or internal combustion engines for generating electricity [19,20]. Besides, anaerobic digestion also presents numerous other significant advantages, such as low sludge production, low energy requirement, easy operation and green energy recovery [21–24]. Not only does this technology have a positive net energy production but also the biogas production can replace fossil fuel. Therefore, it has a direct positive effect on the greenhouse gas reduction. In spite of these benefits, poor operational stability still prevents AD process from being widely industrialized [25,26].

AD is a biological process for biodegrading organic matters (substrate) in the absence of free molecular oxygen ( $O_2$ ) through four main steps, including hydrolysis, acidogenesis, acetogenesis and methanogenesis [27]. The hydrolysis step is generally considered as the rate-limiting step for complex organic substrates degradation reported by most researchers [28–43], resulting from the formation of toxic by-products (complex heterocyclic compounds) or non-desirable volatile fatty acids (VFAs) during the hydrolysis step [44,45]. However, methanogenesis was regarded as the rate-limiting step for easily biodegradable substrates [44,46–48]. Extensive researches have been conducted on pretreatment methods to accelerate the hydrolysis step [49–54] and to obtain suitable by-products from this step [45], as well as to improve the quality of useful components like nitrogen and phosphorus to be recycled [55,56].

However, inhibitory substances produced in the AD process including by-products and intermediates are often found to be the leading cause of anaerobic reactor upset and failure which are considered to be vital to affect the AD process performance and stability, specifically the free ammonia (FA), volatile fatty acids (VFAs) and sulfide/sulfate concentrations. Sewage sludge is characterized by low organic loads and relative high nitrogen concentrations, which may inhibit methanogens. Most of these problems could be solved by addition of a co-substrate in [57], such as fat, oil, and grease collected from the food service industry [58–63]. Recently, a wide variety of substances have been reported to show inhibition during the AD process by an adverse shift in the microbial population or inhibition of bacterial growth presented in the form of the decrease of the steady-state rate of methane gas production and accumulation of organic acids [64].

The aim of this review is to present a detailed comparative summary of the previous and current researches on the inhibition mechanisms and process control by intermediates and by-products from anaerobic digestion.

## 2. An overview of intermediates and by-products effect on anaerobic digestion process

### 2.1. Ammonia (free ammonia nitrogen)

Despite numerous advantages of the AD process, instability is a most probable problem that can lead to complete failure of the

reactor because of the accumulation of VFAs. They can overcome the digester buffer capacity, leading to the acidification and failure of the system. During the hydrolysis and fermentation stages of AD, there is a consumption of alkalinity, while alkalinity is produced and acidification is compensated during the methanogenic stage. Most of the nitrogen organic compounds were converted to ammonia nitrogen ( $NH_3$  and  $NH_4^+$ ) during the anaerobic digestion process. The ammonia nitrogen concentration in the anaerobic digestion system is gradually increasing. The total ammoniacal nitrogen (TAN) in the anaerobic reactors plays a significant and multiple roles. On the one hand, ammonia nitrogen is the nutrient substance of anaerobic microorganism, providing the partial alkalinity of the anaerobic digestion system. On the other hand, the ammonia nitrogen concentration exceeding after a certain value will have a strong inhibition of the anaerobic digestion system, even leading to the instability of the anaerobic treatment system, especially in the thermophilic digestion system. Furthermore, ammonia is the end-product of anaerobic digestion of proteins, urea and nucleic acids [65–67] during the hydrolysis process. Due to most of the organic nitrogen in the raw material of the anaerobic digestion and the reduction and removal of the nitrogen reacts to produce ammonia, resulting in an increase in the content of ammonia nitrogen concentration. Optimal ammonia concentration ensures sufficient buffer capacity of methanogenic medium in AD, increasing the stability of the anaerobic digestion process, while not inhibiting the process.

The effect of TAN on the AD process depends on the temperature and pH, and so on. The AD bioreactors performed best at TAN concentrations of 600–800 mg/L (at pH=7.2–7.5 and mesophilic condition) [68,69]. However, some studies reported that low concentrations of ammonia (below 200 mg/L) are beneficial to the AD process [70], because low ammonia nitrogen concentration (such as 500 mg/L) caused low methane yield, loss of biomass (as VSS) and loss of the aceticlastic methanogenic activity. Otherwise, the negative effect of low FAN concentration on biomass was caused not only by low buffer capacity but also by insufficiency of nitrogen as nutrient [68]. The instability of AD process with a concurrent decrease in biogas production was resulted from a high ammonia nitrogen concentration with its levels up to 1500–7000 mg/L at thermophilic temperature and high waste concentration [71–73]. The methanogenic activity in a high solid sludge digestion process decreased with an increase in ammonia nitrogen, dropped 10% at an ammonia nitrogen concentration of 170–3720 mg/L, dropped 50% at 4090–5550 mg/L, and losing its activity at about 6000 mg/L [73]. 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 [5]. In general, earlier research reported that a TAN concentration of 1700–2000 mgTAN/L is toxic to unacclimated microbes, whereas the 50% inhibition for acclimated methanogens could reach up to 12,000–14,000 mg TAN/L, thus co-digestion and the adjustment of the initial pH (pH=7.5) has been considered as an effective approach [74,75]. However, McCarty [72] investigated that when TAN concentration exceeded 3000 mg  $NH_4^+$ -N/L, the AD process would be inhibited at any pH values. Hobson and Shaw [76] also reported that TAN concentration reaching up to 2500 mg  $NH_4^+$ -N/L showed some inhibition to methane production, while a concentration of 3300 mg  $NH_4^+$ -N/L inhibited methanogenesis completely. On the contrary, Wang et al. [77] found that the highest methane yield was obtained at a TAN concentration of 2500 mg/kg (based on total weight) during the anaerobic digestion process, with a 50% reduction at a concentration of 6000 mg/kg. In addition, reduction of reaction rates and microbial activities for hydrolysis of cellulose and methanogenesis from acetate were observed at TAN concentrations higher than 4300 mg/kg. The different results may be

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