Gas analysis reveals novel aerobic deammonification in thermophilic aerobic digestion

Y.-S. Yi, S. Kim, S. An, S.I. Choi, E. Choi and Z. Yun

Dept. of Environmental Engineering, Korea University, Jochiwon, Choong Nam 339-800, Korea
(E-mail: *envzyun@korea.ac.kr*)

Abstract A laboratory-scale thermophilic aerobic digester was operated with piggery wastewater. The operating temperature varied from 50–70°C. It has been found that excessive nitrogen removal occurred in the laboratory-scale thermophilic system at various HRTs. Nitrite and nitrate were not observed in the effluent. Gas measurement reveals the presence of significant amount of N_2O along with NH_3 gas. The rational production of N_2O gas in accordance with temperature and HRT suggests that biologically mediated deammonification processes significantly contribute to the N removal. Although further microbiological investigation is required to clarify the exact nitrogen removal mechanism, the large production of N_2O gas seems to be a result of the existence of a rapid growing heterotrophic deammonification process in the thermophilic system.

Keywords Aerobic deammonification; N_2O; nitrogen removal; piggery wastewater; thermophilic aerobic digestion

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Introduction

In Korea, piggery wastewater is considered the major source of environmental pollution in the rural area. Typical characteristics of piggery wastewater is both high in organic and nitrogen (N) contents. In addition, annual usage of N fertilizer in this country is 423,000 tons. With chemical N fertilizer, 8.4 million hogs discharge significant amounts of N to the limited farming land in this country. Thus, N overload problem is an oncoming environmental issue in this country.

The treatment alternatives for piggery wastewater are limited by the characteristics of both high organic and nitrogen contents. An application of the anaerobic digestion for piggery wastewater is hampered by various factors including the ammonium antagonism due to high NH_4 content. In order to investigate an efficient N removal alternative for strong nitrogenous wastewater, the thermophilic aerobic digestion process was examined in this paper.

From the early study of Sürücü *et al*. (1976) to the recent study by Kelly and Warren (1997), previous work has shown that maintaining the self-sustained thermophilic aerobic digestion system was possible. The thermophilic aerobic digestion (TAD) requires the reactor configuration with an energy-preserving closed system. Although the TAD has a clear disadvantage of higher energy costs, an increasing demand for the sanitization of sludge solids, as well as the rapid reaction, enables future usage. If the TAD system can be combined with the anaerobic digestion system, the combination would be an attractive alternative for sludge treatment. However, efficient removal of NH_4 becomes a key for the successful operation since most of the biological slurries including piggery waste usually exhibit high nitrogenous content.

The TAD system was not studied in detail because of the experimental difficulties associated with it, not only to maintain the high temperature but also the limited information on the thermophilic organism itself. A variety of thermophilic and hyperthermophilic organisms have been discovered in recent years (Stetter, 1996). The optimum temperature for most of thermophilic organisms is in the range of 45–70°C. As a rule, hyperthermophilic bacteria grow fastest in between 80–100°C. However, variety of hyperthermophilic species could grow at a temperature as low as 60°C. Unfortunately, the engineering significance of thermophilic and hyperthermophilic microbiology is still largely unexplored. It is known that the thermophilic organisms found in the aerobic digester were mostly *Bacillus* or *Bacillus*-like organisms (Sürücü *et al.*, 1976). The dispersed growth pattern is primary characteristic of the thermophilic organism (Lapara and Alleman, 1999; Reily and Forster, 2001). Because of the dispersed growth pattern and high temperature, foaming is a general characteristic of thermophilic sludge that may cause a serious operating problem.

A very rapid rate of organic degradation is considered the obvious advantage of the aerobic thermophilic system. However, the maintenance of sufficient oxygen supply is a technical tradeoff. In addition, ordinary methods to measure the dissolved oxygen (DO) content may not be applicable to the high temperature systems (Vogelaar *et al.*, 2000; Urban and Gulliver, 2000), since a very rapid consumption rate of DO, as well as lower DO saturation concentration at high temperature coupled with foaming characteristic, create a unique operational problem. Furthermore, the basic operating parameters such as pH and alkalinity were not rationalized in detail. Thermophilic application of strong nitrogenous wastes generally exhibited an increase in pH resulting in a possible role of ammonia stripping for N removal. Although the system pH was not considered as a critical operating parameter in thermophilic system according to EPA (1990), the relation with pH and alkalinity must be recognized in order to establish the nitrogen balance.

This paper aims to determine the nitrogen balance in the thermophilic system with piggery wastewater. The relation of pH and alkalinity was also examined in order to establish the effect of ammonia stripping on N removal. In addition, the gaseous form of nitrogenous compounds such as NH_3, N_2O and NO were also monitored to establish the N balance. Nitrous oxide and nitric oxide are intermediates of biological nitrogen conversion whereas NH_3 usually produced from physico–chemical interaction. Thus, the gas measurement would be the essential tool to establish the N balance in the thermophilic system.

Material and methods

Laboratory reactor

Figure 1 shows the schematic diagram of the laboratory-scale aerobic thermophilic digester. The total reactor volume was 25 L including 10 L of reaction volume and 15 L of overhead space to control the foam. A turbine-type foam-cutter was installed on the top of the reactor in order to provide partial mixing and to reduce the foam. The mechanical defoamer worked efficiently throughout the experimental period of 12 months. Aeration was achieved by an air compressor (Cole-Parmer Cat. #05053-10) and diffusers. A sealed internal air recycle pump (10 W) was also installed not only to aerate the sludge but also to preserve energy in the system. The reactor was placed in a heated-water bath to control the reaction temperature. A Masterflex pump (Cole-Parmer L/S 77521-40) with controller was used to add piggery wastewater with a semi-continuous feeding pattern. The effluent from the reactor was collected and analyzed daily.

Wastewater

The piggery wastewater from a small livestock farm was periodically taken to the laboratory and stored in a refrigerator (at 4°C). The appropriate amount of wastewater warmed to the room temperature of 25°C before being injected into the reactor. TCOD and TKN concentrations averaged to 34,900 mg/L and 4,680 mg/L, respectively, indicating that the piggery waste was a typical slurry-type wastewater in this country.

Operating conditions

The laboratory reactor was continuously operated for 12 months with various operating conditions. Table 1 shows the operating conditions of the laboratory reactor. The operating temperature of the reactor varied from 50–70°C. The operating temperature was controlled within a variation of ± 0.5°C. At each operating temperature, the reactor HRT varied from 0.5–3.0 days. The air supply rate including internal air recycle was kept constantly for 0.5 M^3 of air/min/M^3 of reactor throughout the experimental period. Sufficient mixing and aerobic conditions were maintained in the laboratory reactor since the DO level was about 2–3 mg/L at 50°C of operating temperature. The reactor pH and alkalinity were not controlled during the experiment.

Sampling and analysis

The sludge samples were analyzed on a daily basis during the steady state operating condition. The steady-state condition was justified on the basis of the measurement of daily effluent concentration as well as washout time. All water quality parameters were measured in accordance with *Standard Methods* (1998). A gas chromatography (Donam Instrument Co., DS 6200, Porapack 80/100 mesh column) with a TCD detector was used to analyze the gas samples taken from the gas outlet of the reactor.

Results and discussion

Operating results

The laboratory thermophilic aerobic digester was operated with various temperature and HRTs without serious operating problems. The turbine type foam-cutter worked

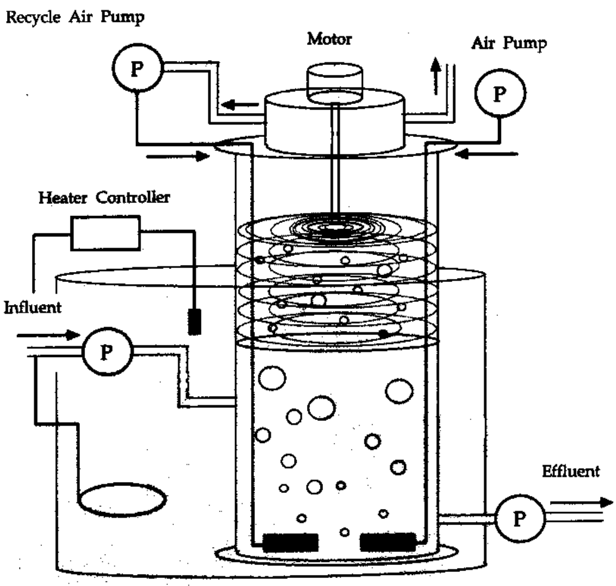

Figure 1 A schematic diagram of laboratory-scale thermophilic aerobic digester

Table 1 Operating conditions for lab reactors

Temperature (°C)	HRT (d)			Air supply (m^3 air/min/m^3 reactor)
50	N/O	1.0	3.0	0.5
60	0.5	1.0	3.0	0.5
70	N/O	1,0	3.0	0.5

N/O = Not operated

effectively throughout the experimental period. The overall operational results are shown in Table 2. The results indicate that relatively high removal of both total and soluble portion of COD could be achieved with longer HRTs. The solids portion in piggery wastewater was not converted to a great extent during the digestion. A significant removal of nitrogenous compounds in piggery wastewater was observed at the operating conditions of higher temperature and longer HRTs, especially for the ammonium portion of nitrogen. At an HRT of 3 days and operating temperature of 70°C, up to 91% of NH_4 removal efficiency was achieved as shown in Table 3. The TKN and NH_4 removal decreased with low temperature as well as short HRT. In the run with HRT of 0.5 day, NH_4 removal efficiency decreased to 40%.

It seems that the conventional biological nitrification was not associated with the nitrogen conversion process since nitrate and nitrite were not observed throughout the experimental period. Although alkalinity was removed in significant amounts, the reduction of alkalinity was probably caused by other biochemical reasons than nitrification. The observed alkalinity reduction was far smaller than the stoichiometric alkalinity requirement of 7.14 gAlk/gNH_4-N for nitrification. Overall, the experimental results indicate that the thermophilic aerobic digestion system is an efficient alternative to reduce both organics and nitrogenous compounds in piggery wastewater compare to conventional anaerobic processes.

Relation between pH and alkalinity

In the thermophilic aerobic system, the pH process was not considered as a limiting parameter for system operation. According to the manual of autothermal aerobic digestion from EPA (1990), the process pH does not have to be controlled by special design considerations. The manual reasoned that pH depression could not occur since the nitrifying environment may not be experienced in the thermophilic environment.

Table 2 Average influent and effluent concentration according to various HRTs and operating temperature in laboratory reactor

Parameters	Influent conc. (mg/L)*	Average effluent concentration (mg/L)*						
		HRT = 3 days			HRT = 1 day		HRT* = 0.5 days	
		50°C	60°C	70°C	50°C	60°C	70°C	60°C
TCOD	34,935	20,060	17,970	18,370	22,240	23,030	23,240	24,460
SCOD	25,447	11,970	12,460	12,060	13,890	14,080	14,950	17,900
TS	18,031	15,490	14,310	16,534	16,230	16,410	16,030	16,769
VS	9,513	7,565	7,096	7,800	8,276	7,896	8,086	8,657
TKN	4,679	1,804	1,640	1,354	2,873	2,381	1,877	3,170
NH_4-N	3,653	857	662	329	1,884	1,501	1,020	2,192
pH	7.9	9.2	9.4	9.4	9.1	9.4	9.5	9.5
Alkalinity	12,133	4,910	4,410	3,500	8,220	7,050	5,150	8,614

* Average concentrations during the steady state operating conditions

Table 3 Average removal efficiencies at various operating conditions

Parameters	Removal efficiencies (%)						
	HRT = 3 days			HRT = 1 day		HRT = 0.5 days	
	50°C	60°C	70°C	50°C	60°C	70°C	60°C
TCOD	42.6	48.6	47.4	36.3	34.1	33.5	30.0
SCOD	53.0	51.0	52.6	45.4	44.7	41.3	29.0
TKN	61.4	64.9	71.0	38.6	49.1	60.0	32.3
NH_4-N	76.5	81.9	91.0	48.4	58.9	72.1	40.0

It is interesting to note that the reactor pH of this experiment increased up to 9.5 depending on operating conditions without pH control as shown in Figure 2. The alkalinity concentration, however, decreased with HRT and temperature. The increase of reactor pH is an important aspect in order to analyze the nitrogen mass balance since NH_3 stripping would be a considerable part of NH_4 removal. The increased reactor pH in aerobic thermophilic system was not clearly understood in relation to reactor alkalinity. A recent thermophilic study by Tripathi and Grant Allen (1999) with pulp craft mill effluent suggested that pH increase was due to the formation of basic chemical compounds and/or removal of organic acids in the influent. On the other hand, the aerobic thermophilic experiments with fish farm sludge (Skjelhaugen, 1999) indicated that the reactor input pH of 6.2 had been increased to 8.7. Skjelhaugen (1999) further suggested the increase of reactor pH in the thermophilic system could be related with ammonia.

The N profiles of influent and effluent in our laboratory experiments are plotted as shown in Figure 3. The nitrogen removal in a conventional biological system treating strong nitrogenous wastewater is a result of various factors, including nitrogen assimilation to cell synthesis, nitrogen removal via nitrification–denitrification, and gaseous conversion of NH_4 to NH_3. Conventional nitrification may not be associated in the thermophilic system since no nitrate was observed in the effluent. However, ammonia stripping seems an important consideration in high temperature and strong nitrogenous system. With a simple aeration of piggery wastewater, Liao *et al.* (1995) have shown that up to 80% of NH_4 could be removed via ammonia stripping at pH 9.3 and 20°C. On the other hand, the thermophilic

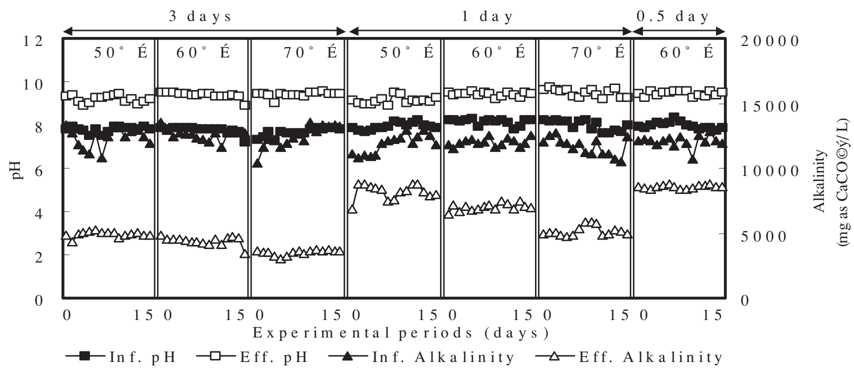

Figure 2 Variation of pH and alkalinity in various operating temperatures and HRTs (the steady state operating data for 15 days at each operating temperature are shown)

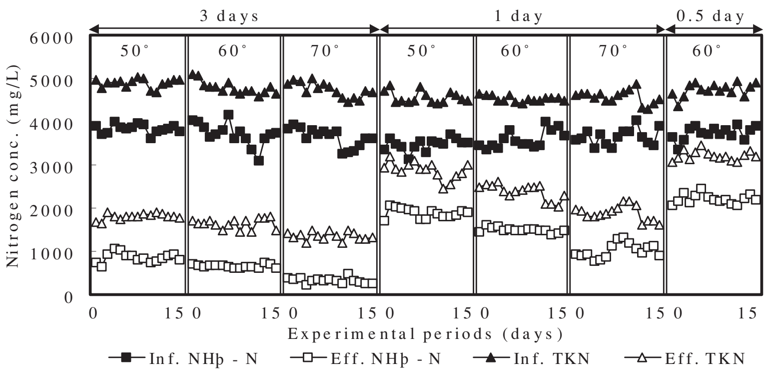

Figure 3 Concentration profiles of TKN and NH_4-N in various operating temperatures and HRTs (nitrate and nitrite were not detected). The experimental periods corresponded to Figure 2

study by Skjelhaugen (1999) suggested that nitrogen removal with gaseous release of NH_3 was less than 0.8% of total nitrogen input depending on organic wastes.

The alkalinity and pH relation in the thermophilic aerobic system can be simplified as shown in Figure 4. Since the piggery wastewater is nitrogenous waste with a high alkalinity content, ammonia can be formed from NH_4 ´ NH_3 equilibrium at high pH. Liberated proton ions from the ammonia conversion are then neutralized by the available alkalinity resulting a decrease in alkalinity. At the same time, the reactor pH increases with intense aeration since CO_2 in the sludge would be stripped out to the gas phase, although exact calculation with carbonic acid equilibrium cannot easily be made because of the complex biological reactions. Because of this fact, the nitrogen balance in the thermophilic aerobic system must consider the exact measurement of pH and NH_3 production in gas phase. However, the amount of ammonia stripping cannot easily be computed with equilibrium equations because of the complex nature of the stripping system.

Nitrogen balance

Figure 5 shows the results of the nitrogen mass balance at various reactor HRTs and temperature. Both influent and effluent nitrogen consist of the ammonium portion of N and organic N. The gaseous form of nitrogen in the flue gas from the reactor was measured by gas chromatography. The measured gaseous form of N in the gas sample was converted to nitrogen mass in g/day and represented in N in the effluent. The amount of nitrogen utilization for cell synthesis was computed by the COD reduction. In addition, N loss due to analytical error was added to this portion.

NH_3 was the major constituent of the gas sample at a reactor HRT of 3 days as shown in Figure 5. At 60°C, ammonia production increased with longer HRT. However, the ammonia production was not clearly proportional to the operating temperature. The amount of NH_3 that was stripped out from the thermophilic reactor cannot easily be computed from equilibrium equations since volatile amounts of NH_3 critically depend on various factors including operating temperature, pH, aeration intensity, fluid viscosity, and so on. Since the reactor pH is not as high as optimum pH for stripping, small changes of physico–chemical factors greatly affect the stripping process.

The inconsistency of amount of ammonia stripping was overwhelmed by the presence of N_2O in the gas sample, especially for an operating temperature of 60°C. In addition to NH_3, we consistently observed a significant amount of N_2O gas in the gas samples. In general, higher N_2O production was observed at high temperature as shown in Figure 5. With an HRT of 3 days (Figure 5b–1), 37% of influent N (or 58% of removed N) was converted to

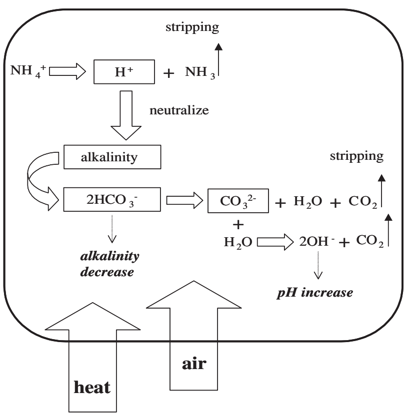

Figure 4 Alkalinity and pH relations in aerobic thermophilic system

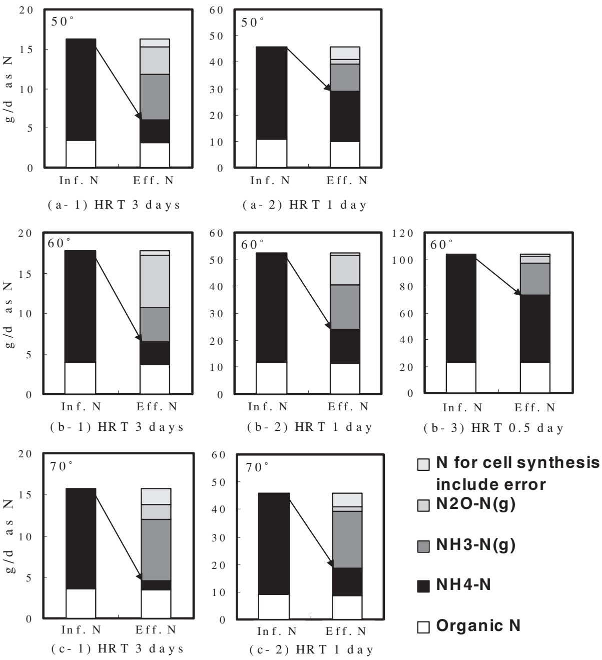

Figure 5 Nitrogen mass balances at various operating temperature and HRTs

N_2O gas in the thermophilic aerobic digester. The formation of N_2O gas could be observed in various biological processes. For instance, N_2O formation along with N_2 gas was observed in typical anoxic denitrifying filter systems (Yun *et al.*, 1997) and a biological nutrient removal system operated with anoxic-oxic conditions for nightsoil treatment (Hanaki *et al.*, 1992). The N_2O production in these systems is considered as the result of either an incomplete reduction of nitrate under the inhibitory denitrifying condition or metabolic change within the nitrifying cell under the low DO condition (Schulthess *et al.*, 1994; Gejlsbjerg *et al.*, 1998). These postulations cannot be applied to this thermophilic aerobic system since nitrite or nitrate was not observed in the effluent.

Hippen *et al.* (1997) suggested two possible ways to remove nitrogen under the aerobic condition: first, direct transformation of ammonium into N_2 gas under the oxygen limiting condition, and secondly, the existence of a denitrifying enzyme system under the aerobic conditions. The direct transformation of ammonium into N_2 or N_2O may require the existence of a specific electron acceptor, such as nitrite, in the medium. However, the increasing evidence on the existence of “true” aerobic denitrifiers have been available in recent years (Robertson *et al.*, 1995; Lukow and Diekmann, 1997; Patureau *et al.*, 2000). In general, the aerobic denitrifier has a capability of simultaneously respiring O_2 and NO_X. Moreover, these bacteria can simultaneously oxidize ammonium to NO_2 and reduce NO_2 to the gaseous form of N_2 and N_2O. Unlike the very slow growing anaerobic ammonium oxidizer in the autotrophic Anammox process (van Dongen *et al.*, 2001), the large production of N_2O gas would be a result of the existence of a rapid growing heterotrophic deammonifier in the thermophilic system. Since the microbiology of thermophilic system was not well understood, the photographic evidence on the existence of such an organism in our laboratory digester could not be made. However, the rational production of N_2O gas in accordance with temperature and HRT suggests that the biologically mediated deammonification process significantly contributed to the N removal in the thermophilic system. As a result, the thermophilic aerobic digestion system operated with HRT as low as

1 day could produce the effluent ammonium concentration suitable to minimize the ammonium antagonism in the anaerobic digestion.

Conclusion

The laboratory-scale thermophilic aerobic digestion system efficiently removed both organics and nitrogenous compounds from piggery wastewater. The experimental results demonstrated that up to 91% of NH_4-N in piggery wastewater could be removed in the thermophilic aerobic digestion with a reactor HRT of 3 days at an operating temperature of 70°C. However, N removal efficiencies decreased at lower HRTs and temperature.

The results of gas analysis indicated that ammonia stripping significantly contributed to the N removal even without pH control. However, production of N_2O gas along with NH_3 indicated that the biologically mediated deammonification process contributed to the removal of ammonium in the piggery wastewater.

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