

Enhanced anaerobic digestion of livestock waste by ultrasonication: A tool for ammonia removal and solubilization

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Abstract—Ultrasonication was applied to lower the ammonia level in livestock waste to enhance the anaerobic digestion performance. In simulated waste tests, in spite of an identical temperature increase, a higher ammonia removal rate was observed at lower frequency. This could be explained by the existence of athermal effects, accounting for 64% of the total ammonia removal rate. These effects originated from various convections (micro-streaming, micro-convection, shock-waves, and micro-jets), possibly caused by stable bubbles, and this indigenous mixing ability led to a negligible effect of aeration in the ultrasound assisted ammonia stripping process. In actual waste tests, an ammonia removal rate of up to 55% was achieved with a 0.77 h^{-1} mass transfer rate coefficient. After ultrasonication (28 kHz, pH 11, 15 min) of livestock waste, 58% higher CH_4 yield was achieved due to the decrease of ammonia concentration (28%) and enhanced solubilization (51%).

Keywords: Ammonia Inhibition, Ultrasonication, Stable Bubble, Livestock Wastewater, Anaerobic Digestion

INTRODUCTION

Livestock waste is a high-strength organic waste that contains non-biodegradable substances and highly-concentrated ammonia, and so is considered a troublesome pollutant. At 169,000 tons per day, the production of livestock waste in Korea is immense, accounting for up to 80% of total organic waste production. Most livestock waste is currently converted into fertilizer after aerobic treatment [1]. However, the aerobic process consumes huge amounts of energy, and the quality of the final product is often unsuitable for market sale. Meanwhile, anaerobic digestion (AD) is economical and environmentally benign owing to advantages such as a reduction of waste volume, generation of energy-rich gas in the form of methane (CH_4), and a nutrient-containing final product [2,3].

Numerous studies have been conducted on AD of livestock waste, but the performance of the developed approaches has often been limited, owing to several reasons, including in particular the presence of highly-concentrated ammonia, ranging from 2,000–6,000 mg $\text{NH}_4\text{-N/L}$ [4,5]. Ammonia can be present in either ion form (NH_4^+) or molecular form (NH_3), but the latter is known as the main inhibition trigger, since hydrophobic free ammonia can be passively diffused into cells, leading to proton imbalance and potassium deficiency. Generally, inhibition starts to occur at ammonia concentrations of 1,500–3,000 mg $\text{NH}_4\text{-N/L}$ [6]. However, while some studies have reported that continuous exposure of microorganisms to higher am-

monia levels could increase ammonia tolerance, CH_4 production yield and microbial growth have been found to be limited [7,8].

Hence, lowering the ammonia level is important, and various methods such as ammonia-stripping, chemical precipitation, and electrochemical conversion have been applied. Among them, ammonia stripping, based on the transition of the NH_4^+ form to NH_3 , has been the most frequently used. This process proceeds under high pH and temperature conditions since it favors ammonia volatilization by driving the equilibrium between NH_4^+ and NH_3 to molecular ammonia. Air is also purged to promote the mass transfer of NH_3 , from the liquid phase to the gas phase [9].

Recently, ultrasonication technology, which has generally been applied for extracting enzymes and enhancing hydrolysis, has been employed in ammonia removal. Matouq and Al-Anber [10] observed a 32% rate of ammonia removal from simulated industrial wastewater containing 50 g $\text{NH}_4\text{-N/L}$ by ultrasonication at 2.4 MHz for two hours. The mechanism of ammonia removal by ultrasonication is believed to be the temperature increase caused by rupturing of a “cavitation bubble,” which was generated in the rarefaction region. The temperature and pressure can rise up to 5,000 °C and 500 bar, respectively, at a lifetime of a few microseconds [11]. Wang et al. [12] reported a much higher ammonia removal rate of 96%, achieved in treating landfill leachate containing 680 mg $\text{NH}_4\text{-N/L}$ after 180 min of ultrasonication at 20 kHz [13].

In the present work, ultrasonication was applied to the treatment of livestock waste for the first time, to the best of our knowledge, with the aim of lowering the ammonia level and enhancing subsequent AD efficiency. Experiments were conducted at different pH (10–12) and two fixed ultrasonication frequencies (28 and 40 kHz);

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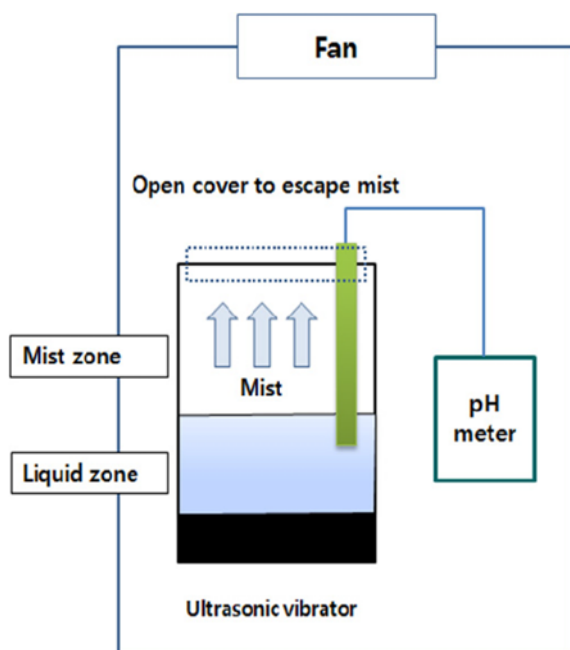


Fig. 1. Schematic diagram of experimental setup for the ultrasound treatment.

ammonia removal rate was monitored with time and the mass transfer coefficient was calculated. Additional experiments were conducted to investigate the mechanisms of ammonia removal by ultrasonication. Finally, enhanced AD performance of livestock waste by ultrasonication was confirmed.

MATERIALS AND METHODS

1. Ammonia Nitrogen

Ammonium sulfate (99.0%, Samchun Chemicals, Korea) was used as the ammonia nitrogen source for the experiment. For the feasibility test using simulated waste, the concentration of ammonia nitrogen was adjusted to 7,000 mg $\text{NH}_4\text{-N/L}$ with distilled water. Actual livestock waste containing 5,000 mg $\text{NH}_4\text{-N/L}$ was obtained from a local farm located in D city.

2. Ultrasonication

Fig. 1 is the schematic of the experimental set-up. The initial pH (10–12) was adjusted by 6 N KOH (Samchun Chemicals, Korea), then 4 L of sample was treated for 5 min to one hour by two different bath-type ultrasounds to investigate the effect of frequency on ammonia removal rate (28 kHz and 40 kHz, Doo-In, Korea). Then, the effect of air purging and temperature on ammonia removal rate was investigated using the best condition observed in the previous test. Air was purged by blower at 1 L/min of flow rate. To investigate the non-thermal effect, an ice pack was used to keep the temperature below 15 °C.

3. Mass Transfer Coefficient

Mass transfer in a batch ammonia stripping experiment can be modeled by expanding the “two film theory” [14]. In the two film theory, each film implies a resistance to mass transfer; however, concentrations in the two fluids at the interface are in equilibrium [15]. Based on the two film theory, ammonia mass transfer rate has been derived as follows [16].

$$F_A = Q_G \times C_{L,A} \times H_A \times \left[1 - \exp\left(-\frac{K_L \times a \times V_L}{Q_G \times H_A}\right) \right] \quad (1)$$

where F_A is the ammonia mass transfer rate, g/h; Q_G is the gas flow rate, m^3/h ; $C_{L,A}$ is the liquid phase concentration of ammonia, g/m^3 ; H_A is the dimensionless Henry’s constant; K_L is the overall liquid mass transfer coefficient, h^{-1} ; a is the interfacial area per unit volume of liquid, m^2/m^3 ; and V_L is the total volume of liquid, m^3 . If the stripping process only happened in the batch reactor, an ammonia mass balance could be calculated as

$$V_L \times \frac{dC_{L,A}}{dt} = F_A \quad (2)$$

Eqs. (1) and (2) are combined to obtain the equation shown below:

$$\frac{dC_{L,A}}{C_{L,A}} = \frac{1}{V_L} \times Q_G \times H_A \times \left[1 - \exp\left(-\frac{K_L \times a \times V_L}{Q_G \times H_A}\right) \right] dt \quad (3)$$

Integrating the Eq. (3) at initial conditions $C_{L,A} = C_{L,A0}$ at $t=0$ yields Eq. (4).

$$-\ln \frac{C_{L,A}}{C_{L,A0}} = \frac{Q_G \times H_A}{V_L} \times \left[1 - \exp\left(-\frac{K_L \times a \times V_L}{Q_G \times H_A}\right) \right] \times t \quad (4)$$

This equation can be used to determine overall mass transfer coefficient ($K_L \times a$) and plot of $-\ln(C_{L,A}/C_{L,A0})$ versus time.

4. Batch Anaerobic Digestion Test

Biochemical methane potential (BMP) tests were performed to determine the effect of ultrasonication. 150 mL of anaerobic digester sludge taken from a local waste water treatment plant (WWTP) was placed with 50 mL of ultrasonicated livestock wastewater in a 300 mL serum bottle. Initially, pH was adjusted to 7.5 and then an anaerobic medium solution was added. Each liter of anaerobic medium solution contained 0.53 g of NH_4Cl , 0.27 g of KH_2PO_4 , 0.35 g of K_2HPO_4 , 1.20 g of NaHCO_3 , 0.075 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.10 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.02 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.05 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.05 g of H_3BO_3 , 0.05 g of ZnCl_2 , 0.03 g of CuCl_2 , 0.01 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.50 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.05 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.05 g of Na_2SeO_3 . All the bottles were purged with N_2 gas to provide anaerobic conditions. The bottles were incubated in a shaking incubator at 35 °C, and all tests were conducted in duplicate.

5. Measurement and Analysis

The concentrations of ammonia, chemical oxygen demand (COD), total solids (TS) and volatile solids (VS) were measured according to Standard Methods [17], and total nitrogen concentration was determined with a Hach DR2010 portable instrument (Hach, USA). Measured biogas production was adjusted to standard temperature (0 °C) and pressure (760 mmHg) (STP). The CH_4 gas content was analyzed with a gas chromatographer (GC, Gow Mac Series 580) equipped with a thermal conductivity detector (TCD) and a 2 m × 2 mm stainless-steel column packed with a Porapak Q mesh (80/100) with helium as a carrier gas at a flow rate of 40 mL/min. The temperatures of injector, detector, and column were kept at 80, 90, and 50 °C, respectively.

RESULTS AND DISCUSSION

1. Effect of pH and Ultrasonication Frequency

As can be seen in Fig. 2, the pH effect was crucial on ammonia

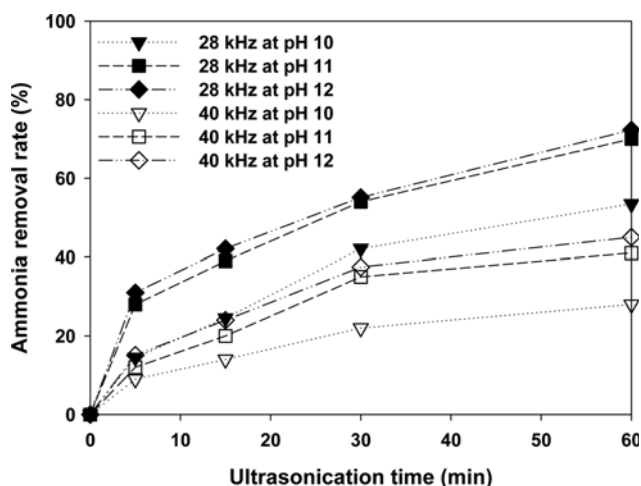


Fig. 2. Effect of pH and frequency on the ammonia removal rate.

Table 1. Calculated mass transfer coefficient at different conditions

Conditions		Mass transfer coefficient (h^{-1})
28 kHz	pH 10	0.79
	pH 11	1.22
	pH 12	1.24
40 kHz	pH 10	0.32
	pH 11	0.47
	pH 12	0.53

removal. Generally, a higher ammonia removal rate was observed with higher pH and the rate increased with greater ultrasonication time. As previously mentioned, only NH_3 can be stripped, and high pH conditions drive the equilibrium between NH_3 and NH_4^+ to NH_3 [18]. The calculated mass transfer coefficient increased from 0.32 h^{-1} to 1.24 h^{-1} , as summarized in Table 1.

The highest removal rate (73%) was achieved with pH 12 at 28 kHz. However, as there was not a very large increase (less than 3%) compared to pH 11, pH 11 at 28 kHz was chosen for the subsequent experiment due to economical considerations. At a lower frequency, a higher ammonia removal rate was observed, which could be attributed to the difference in cavitation size. According to Laborde et al. [19], cavitation size is inversely proportional to the frequency of sound waves. With greater cavitation size, accordingly higher energy release will take place when the cavitation bubble ruptures, thereby facilitating ammonia removal. However, contrary to the expectations of higher energy release, interestingly, the temperature increase after ultrasonication was almost the same at identical ultrasonication time (5 min: 31–34 °C (28 kHz), 32–34 °C (40 kHz); 15 min: 49–50 °C (28 kHz), 50 °C (40 kHz); 30 min: 60–62 °C (28 kHz), 61–63 °C (40 kHz); 60 min: 69–71 °C (28 kHz), 69–72 °C (40 kHz)), even though a higher ammonia removal rate was achieved with a lower frequency at the same pH. The experimental results suggested the existence of other mechanisms for ammonia stripping by ultrasonication excluding the temperature increase.

The cycles of cavitation, which are nucleation, growth, and implosive collapse, can induce high intensity convection in a liquid through

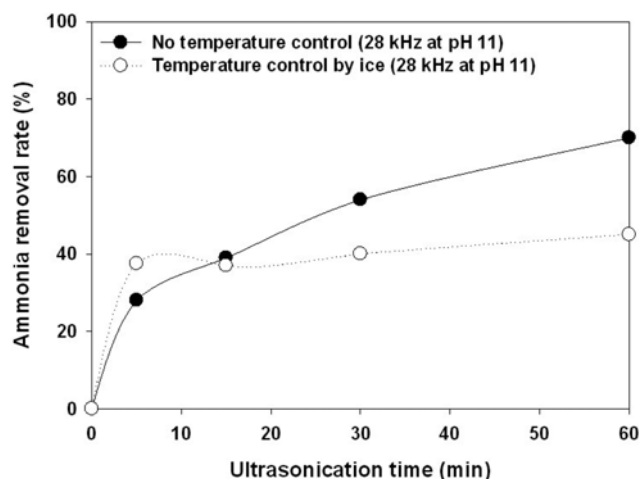


Fig. 3. Effect of temperature control on the ammonia removal rate.

various phenomena such as micro-streaming (oscillatory motion of fluid elements induced by ultrasound), micro-convection (motion of liquid in the vicinity of a gas-liquid interface or a bubble wall induced by radial motion of a bubble), shock waves (waves generated due to reflection of converging liquid at the bubble wall during collapse), and micro-jets (high velocity liquid jet generated due to an uneven pressure gradient around the bubble in the vicinity of an inter-phase boundary) [20]. These various convective phenomena are not directly related to the temperature, and are thus named athermal effects; nevertheless they could play important roles in the ammonia stripping process. Therefore, additional experiments were carried out to investigate the importance of athermal effects in the ammonia stripping process by ultrasonication.

2. Athermal Effects in Ammonia Removal by Ultrasonication

To clarify the important roles of athermal effects in the ultrasound assisted ammonia stripping process, the temperature increase during ultrasonication was suppressed to less than 15 °C using an ice-pack surrounded by a container. As can be seen in Fig. 3, after 60 min of ultrasonication, an approximately 45% ammonia removal rate was observed in spite of the temperature control. Considering that a 70% ammonia removal rate was achieved in the temperature uncontrolled case, it can be calculated that approximately 64% of ammonia removal can be ascribed to athermal mechanisms in the ultrasound assisted ammonia stripping process.

The role of air purging in the conventional ammonia stripping process is to increase mass transfer by promoting internal mixing. Lin et al. [18] and Gustin et al. [21] have shown higher ammonia removal performance with air purging. However, when air purging was applied together with ultrasonication, the additional increase of the ammonia removal rate was negligible, as can be seen in Fig. 4. Until 10 min, a less than 10% higher ammonia removal rate was observed in the air-purged case, but the difference became less, and then negligible after 20 min. This indicates that the effect of air purging found in the conventional ammonia stripping process was counteracted by the athermal effects, that is, various strong convective phenomena, in the ultrasound assisted ammonia stripping process.

The main driving force of ultrasonication is the cavitation bubble, and there are two different types: transient bubbles and stable bubbles [22]. Transient bubbles are generated when acoustic pres-

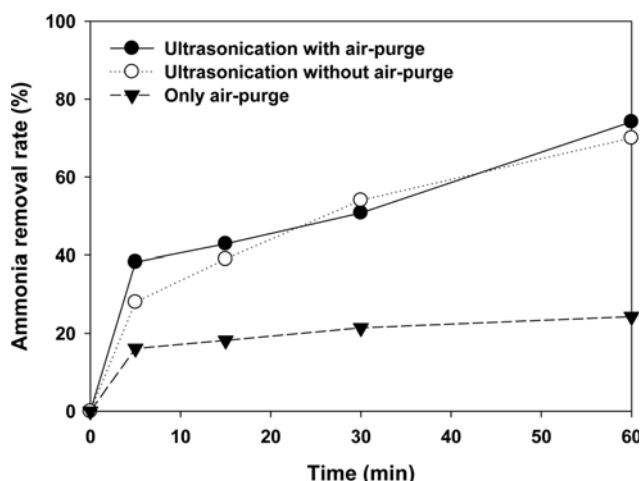


Fig. 4. Effect of air-purge on the ammonia removal rate.

sure can expand the resonant radius in half or several acoustic cycles, while stable bubbles are generated under conditions in which the peak sound pressure in the rarefaction cycle is not sufficient to force the bubbles to expand their collapsed radius. It appears that both types of bubbles could result in various convections; however, it can be surmised that stable bubbles are more strongly related to athermal effects in ultrasonication, as they were reported to facilitate pulsation and movement of a bulk liquid, which in turn led to a uniform distribution of ultrasonication energy and heating within a mixed liquor. Meanwhile, the increase of temperature and pressure was previously attributed to the rupture of transient bubbles [23].

3. Application to Actual Livestock Waste and Subsequent AD Performance

Ultrasonication (28 kHz at pH 11) was applied to actual livestock waste to lower the ammonia level and to deliver enhanced AD performance. As can be seen in Fig. 5, an approximately 55% ammonia removal rate was achieved after 60 min of ultrasonication. A mass transfer coefficient of 0.77 h^{-1} (data not shown) was calculated. Considering that a 0.48 h^{-1} mass transfer coefficient was calculated for the treatment of human urine [14], ammonia in livestock waste appears to be easier to strip than that in human urine. In addition to ammonia removal, solubilization of the livestock waste

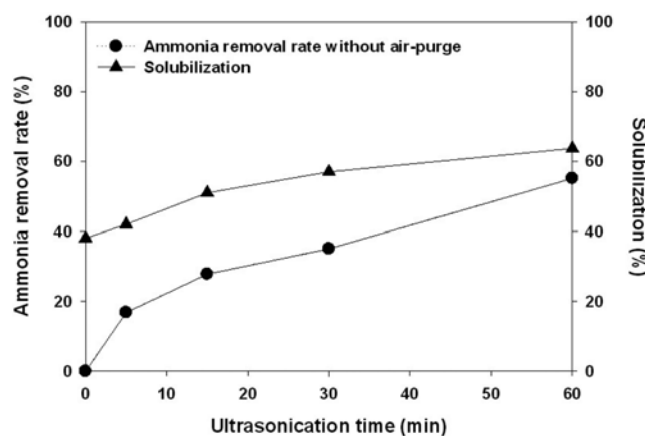


Fig. 5. Effect of modified ammonia stripping process on the livestock wastewater.

increased to over 60%, as shown in Fig. 5. Hydrolysis of solid waste is considered the rate-limiting step of the AD process, and increased solubilization after ultrasonication can therefore increase the CH_4 production potential of livestock waste.

CH_4 production yield increased from 118 to 135, 186, 173, and 164 $\text{mL CH}_4/\text{g COD}_{\text{added}}$ after 5 min, 15 min, 30 min, and 60 min of ultrasonication, respectively (data not shown). The highest CH_4 production yield was obtained after 15 min of ultrasonication, not 60 min, in spite of higher ammonia removal and higher solubilization. It appears that other AD inhibitors such as melanoidines, furfural, and hydroxymethylfurfural are generated during excessive treatment [24,25].

Although the feasibility of the ultrasound assisted ammonia stripping process was verified in the present work, this approach is rarely applied to actual plants due to an insufficient removal rate to meet the effluent regulation. However, it is very promising in terms of application to CH_4 production from livestock waste, since it could result in simultaneous ammonia removal and solubilization. In addition, organic loss could be negligible due to the absence of air-purging, whereas the conventional ammonia stripping process resulted in a decrease of total COD concentration, implying reduced CH_4 potential [26,27].

CONCLUSIONS

We applied ultrasonication to lower the ammonia level in livestock waste to enhance AD performance. In simulated waste tests, a higher ammonia removal rate was observed from higher pH that increased with greater ultrasonication time. In spite of an identical temperature increase, a higher ammonia removal rate was observed at lower frequency. This could be explained by the existence of athermal effects, that is, various convective phenomena, possibly caused by stable bubbles. The athermal effects were the dominant mechanism in the ultrasound assisted ammonia stripping, accounting for 64% of the total ammonia removal rate. In actual waste tests, an ammonia removal rate of up to 55% was achieved with a 0.77 h^{-1} mass transfer rate coefficient. After ultrasonication (28 kHz, pH 11, 15 min) of livestock waste, around 60% higher CH_4 yield, from 118 to 186 $\text{mL CH}_4/\text{g COD}_{\text{added}}$ was observed, and this was achieved by reduction of inhibitor concentration and increased solubilization.

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