Journal of Hazardous Materials 199–200 (2012) 36–42

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Ammonia stripping for enhanced biomethanization of piggery wastewater

Lei Zhang[a,b,1], Yong-Woo Lee[c], Deokjin Jahng[b,*]

[a] Key Laboratory of Industrial Ecology and Environmental Engineering, School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, PR China
[b] Department of Environmental Engineering and Biotechnology, Myongji University, San 38-2, Namdong, Cheoin-Gu, Yongin, Gyeonggi-Do, 449-728, Republic of Korea
[c] Major in Chemistry & Applied Chemistry, College of Science and Technology, Hanyang University, 1271 Sa-3 Dong, Sangnok-Gu, Ansan, Gyeonggi-Do 426-791, Republic of Korea

ARTICLE INFO

Article history:
Received 9 May 2011
Received in revised form 14 October 2011
Accepted 14 October 2011
Available online 20 October 2011

Keywords:
Ammonia stripping
Ammonia inhibition
Anaerobic digestion
Piggery wastewater
Sodium inhibition

ABSTRACT

In this study, the effects of ammonia removal by air stripping as a pretreatment on the anaerobic digestion of piggery wastewater were investigated. Ammonia stripping results indicated that ammonia removal was strongly dependent on pH and aeration rate, and the ammonia removal rate followed the pseudo-first-order kinetics. A significant enhancement of biomethanization was observed for wastewaters of which ammonia was air-stripped at pH 9.5 and pH 10.0. The methane productivity increased from 0.23 ± 0.08 L CH_4/L d of the control (raw piggery wastewater) to 0.75 ± 0.11 L CH_4/L d (ammonia-stripped at pH 9.5) and 0.57 ± 0.04 L CH_4/L d (ammonia-stripped at pH 10.0). However, the improvement of methane production from the piggery wastewater pretreated at pH 11.0 was negligible compared to the control, which was thought to be due to the high concentration of sodium ions supplied from sodium hydroxide for pH adjustment. From these results, it was concluded that ammonia removal through air stripping at the alkaline pH could be a viable option for preventing the failure of anaerobic digestion of the raw piggery wastewater. Additionally, it was also found that a high concentration of sodium ion originated from sodium hydroxide for pH adjustment inhibited methane production.

1. Introduction

Anaerobic digestion has been recommended as a primary process for treating piggery wastewater, because through which waste reduction, energy production (biogas) and mitigation of pollutant emissions (odor, greenhouse gases and animal pathogens) can be accomplished [1,2]. For example, many farm digesters running in European countries (most of them with animal manure as the main substrate) indicate that anaerobic digestion is applicable in the field. However, the economic feasibility of anaerobic digester treating animal manure was often reported low because biogas production was not satisfactory. One reason might be due to the characteristics of feeding substrates. In many cases, the organic matter is diluted with cleaning water and the fraction of inert materials in the animal manure is high. The high ammonia concentration (3.0–6.0 g NH_4^+–N/L) has often been identified as another important technical reason for the low level of biogas production and unstable system operation [3]. Furthermore, the high ammonia concentration in the effluent of anaerobic digestion also hinders the performance of subsequent biological processes, such as the conventional activated sludge system and the biological A/O (anoxic/oxic) process [4].

In order to mitigate the ammonia inhibition without changing the ammonia level, addition of mineral materials and lowering the temperature from thermophilic to mesophilic conditions were attempted [5]. Decreasing the ammonia concentration was another way to avoid ammonia inhibition. In order to lower the concentration of ammonia, many methods have been practiced. For example, the dilution of the wastewater with fresh water was found to be effective [5,6]. However, this dilution method worsens the economic feasibility of the anaerobic digestion of piggery wastewater due to reduced mass retention time and gas production efficiency as well as the increased dewatering cost. Several different physical, chemical and biological methods, including zeolite adsorption [7], ammonia stripping [8–10], chemical precipitation [11] and a biological A/O process [12] have been investigated for ammonia removal or recovery.

Among these processes, the ammonia stripping method is thought to be the most applicable, especially for wastewaters containing high concentrations of ammonia, such as SSFW (source sorted food waste) digestate [10], chicken manure [13] and poultry litter leachate [14], because this method generates no extra sludge and is associated with modest reagent costs and an easy operation. In this process, the free ammonia is stripped out of the wastewater and enters the gas phase. The efficiency of ammonia stripping is

* Corresponding author. Tel.: +82 31 330 6690; fax: +82 31 336 6336.
E-mail addresses: wxzyfx@yahoo.com (L. Zhang), djahng@mju.ac.kr (D. Jahng).
[1] Tel.: +86 411 84707 669; fax: +86 411 84707448.

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.10.049

strongly dependent on two thermodynamic equilibria, the Henry's law equilibrium (Eq. (1)) and the ammonia dissociation equilibrium (Eqs. (2) and (3)) [8].

$$p = K_c c \quad (1)$$

$$NH_4^+ \leftrightarrows NH_3 + H^+ \quad (2)$$

$$\frac{[NH_3]}{[TNH_3]} = \left(1 + \frac{10^{-pH}}{10-(0.09018+2729.92/T(K))}\right) \quad (3)$$

Here, p is the partial pressure of the ammonia gas, c is its molar concentration in the liquid phase, and K_c is the Henry's law constant. $[NH_3]$ and $[TNH_3]$ represent the concentrations of free ammonia and the sum of free ammonia and ammonium ion, respectively. T (K) is the Kelvin temperature. As shown in Eq. (3), the free ammonia concentration in the aqueous phase depends on the pH and temperature. Higher pH and temperature lead to a higher free ammonia fraction. Liao et al. [9] and Bonmatí and Flotats [8] found that alkaline pH (10.5–11.5) and high temperature (80 °C) were required to achieve high ammonia removal efficiency from piggery slurry. Mass transfer rate of ammonia was also controlled by air flow rate. In biogas stripping of SSFW (source-sorted food waste) digestate, 4.5-fold increase in the ammonia removal rate was observed when the flow rate increased from 0.125 to 0.375 $L_{biogas}\ L_{digestate}^{-1}\ min^{-1}$ [10].

Yang et al. [15] reported that the swine wastewater pretreated in an ammonia stripping process resulted in enhanced acidogenesis. In comparison to the control (4.0 g NH_4^+–N/L), a maximum of 4.7 folds higher acidification was achieved for the ammonia-stripped piggery wastewater (0.8 g NH_4^+–N/L). However, Bonmatí and Flotats [8] concluded that ammonia stripping, as a pretreatment method, was not feasible. They ascribed the infeasibility to the high concentration of remaining free ammonia, the extra cost to neutralize the high pH (8.5–9.9) and the presence of heavy metals, which would be concentrated by air stripping. Considering the conflicting results of ammonia removal on anaerobic process, therefore, it is necessary to evaluate the effect of the ammonia stripping of piggery wastewater on its anaerobic digestion.

In this study, the feasibility of ammonia stripping as a pretreatment method for the anaerobic digestion of piggery wastewater was systematically evaluated. First, the buffering capacity of piggery wastewater and the effects of the operational parameters for ammonia stripping (dosage of sodium hydroxide, pH and aeration rate) on ammonia removal were examined. Secondly, the effects of ammonia removal on the anaerobic digestion of piggery wastewater were investigated in batch experiments. Finally, the feasibility of different ammonia stripping conditions on subsequent anaerobic digestion was carefully monitored in semi-continuous experiments.

2. Materials and methods

2.1. Piggery wastewater and seed sludge

The raw piggery wastewater used in this study was obtained from a farm near the Yongin Wastewater Treatment Plant in Yongin, Republic of Korea, and was stored at 4 °C. The unacclimated inoculum (about 25 g/L of VSS) was obtained from a domestic anaerobic sludge digester at the Yongin Wastewater Treatment Plant, and the inoculum (approximately 15 g/L of VSS) acclimated to a high concentration of ammonia was obtained from the 20-L bench scale digester treating 2-fold diluted piggery wastewater containing approximately 4.0 g NH_4^+–N/L for more than a year.

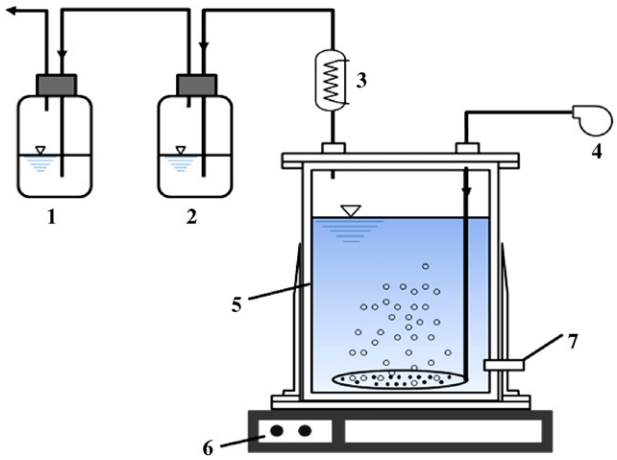

Fig. 1. Schematic diagram of the ammonia stripping reactor of piggery wastewater. (1) 20% NaOH solution, (2) 50% H_2SO_4 solution, (3) condenser, (4) air pump, (5) main reactor vessel, (6) temperature controller, (7) effluent port.

2.2. Measurement of buffering capacity

While being magnetically stirred, a 40% (w/w) sodium hydroxide solution was gradually added through a volumetric burette to 500 mL piggery wastewater or mixed liquor (7000 mg/L of VSS) from an MBR (membrane bioreactor) treating domestic wastewater. When the pH was stabilized, the cumulative volume of added sodium hydroxide solution and the corresponding pH values were recorded. The sodium ion concentration was calculated from the added amount of sodium hydroxide.

2.3. Experimental setup and procedure

2.3.1. Ammonia stripping experiments

Ammonia stripping of the piggery wastewater was conducted in a 1.0 L reactor (ID 80 mm × H 200 mm) with a working volume of 0.5 L as shown in Fig. 1. Air was introduced into the liquid phase via an aquatic air stone. The air flow rate was controlled at 1.0, 2.0, 4.0 or 10.0 $L\ L^{-1}\ min^{-1}$ by a flow meter, and the pH of the wastewater was adjusted to pH 9.0, pH 9.5, pH 10.0 or pH 11.0 using a 40% (w/w) sodium hydroxide solution. Considering volume changes by pH adjustment and water evaporation, the real ammonia concentrations in each set of experiment were experimentally determined. The ammonia stripping reactor was kept at 37 °C. The exhaust gas was passed through solutions of 50% (w/w) H_2SO_4 and 20% (w/w) sodium hydroxide to prevent release of ammonia and other volatile compounds into atmosphere.

2.3.2. Batch biomethanization of ammonia-stripped piggery wastewater

Batch anaerobic digestion was performed in a 160-mL serum bottle with the working volume of 50 mL. The main focus of this section was to show the kinetics of biogas generation during the first day rather than to obtain the ultimate methane yield. The unacclimated sludge was used as an inoculum, and raw piggery wastewater and ammonia-stripped piggery wastewaters were used as substrates. Each bottle contained 0.53 g COD of biomass as an inoculum. The control reactor contained 1.24 g COD per bottle as a substrate (raw piggery wastewater). The bottles receiving pH 7.2, pH 9.0, pH 10.0, and pH 11.0 air-stripped piggery wastewater contained 1.09, 1.15, 1.15, and 1.16 g COD per bottle as substrate, respectively. Likewise, the bottles receiving 0 $L\ L\ min^{-1}$, 1.0 $L\ L\ min^{-1}$, 2.0 $L\ L\ min^{-1}$, 4.0 $L\ L\ min^{-1}$, and 10.0 $L\ L\ min^{-1}$ air-stripped piggery wastewater contained 1.22, 1.07, 1.00, 0.83, and 0.63 g COD per bottle as substrate, respectively. Finally, distilled

water was added up to 50 mL. The ISR (inoculum substrate ratio) was 0.53 ± 0.13. Different amounts of NH_4Cl were added to adjust the ammonia concentrations until they were equal to the level of the substrates (0.36–4.8 g NH_4^+–N/L, as shown in the table inset of Fig. 4C. Before incubation, the pH of the ammonia-stripped and raw piggery wastewaters was adjusted to pH 7.7–7.8 using 6.0 M hydrochloric acid. Since small volume of the acid solution (<0.2 mL) was added, volume change was regarded as negligible. The bottle was flushed with nitrogen gas for 3 min, closed with a rubber stopper and sealed with an aluminum crimp. It was then incubated in a shaking incubator at 37 °C and 140 rpm. The bottle containing the inoculum without any added substrate was run as the seed control. The produced biogas (mainly containing methane and CO_2) was stored in the headspace of each reactor (serum bottle). Since the headspace of reactor was filled with known amount of inert nitrogen gas, the composition of mixed gas (biogas plus nitrogen gas) changed with incubation time. The mixed gas composition was determined by GC, which detected nitrogen, methane and CO_2. According to the change of gas composition, the amount of methane and CO_2 was calculated as described by Angelidaki and Sanders [16] and Zhang and Jahng [17]. The methane production from the seed controls was subtracted. All experiments were run in duplicate.

2.3.3. Semi-continuous biomethanization of ammonia-stripped piggery wastewater

Semi-continuous anaerobic digestion was carried out in a 500-mL Schott Duran bottle with the 200 mL working volume. Initially, the bottles were filled with 190 mL acclimated seed and the 10 mL substrate (raw or piggery wastewaters air-stripped at pH 9.0, pH 10.0 and pH 11.0). The bottles were flushed with nitrogen gas for 3 min and incubated in a shaking incubator at 37 °C and 140 rpm. On the second and third days, the bottles were fed with 10 mL substrate using a 20 mL syringe. On the fourth day, the gas in the headspace was released, and the stopper was opened. The 30 mL solution in the bottle was then withdrawn, and 10 mL fresh substrate was added. All operations were preformed under nitrogen atmosphere. By repeating this 4-day cycle, the HRT/SRT was approximately 20 days. Similarly to batch experiments, the produced biogas during each withdrawing-feeding cycle was also stored in the headspace of each reactor. The gas composition was analyzed every day before feeding the substrate or opening the stopper. The daily methane production rate was calculated according to the change of the ratio between methane and nitrogen [17]. In order to ensure sufficient acclimation and to achieve a steady state, the experiment was conducted for nearly 90 days.

2.4. Analytical methods

Total suspended solids (TSS), volatile suspended solids (VSS) were measured following the procedures listed in the Standard Methods [18]. The pH values of the samples were determined using a pH meter (Orion, Model 370). Total Kjeldahl nitrogen (TKN) was analyzed using a Kjeldahl apparatus (Kjeltec 2100, Foss, Sweden), and total ammonium content was determined by the Kjeldahl method without the destruction step [17]. Lipid was gravimetrically measured [19]. The protein content was estimated by multiplying the organic nitrogen value (TKN subtracted by total ammonia nitrogen) by 6.25 [17]. The biogas composition (CH_4 and CO_2) was determined using a HP-6890 gas chromatograph (GC) (Hewlett Packard 6890, PA, USA) with a thermal conductivity detector (TCD) and a HP-Plot Q column (30 m × 0.32 mm × 20 μm) [17]. VFAs were determined using another GC (M600D, Younglin, Korea) with a flame ionization detector (FID) and a HP-INNOWAX (30 m × 0.25 mm × 0.25 μm) column [17]. Metal analysis was carried out using an ion coupled plasma-atomic emission spectrometer (ICP-AES) (OPTIMA 4300DV, PerkinElmer, USA) or an inductively coupled plasma-mass spectrometer (ICP-MS) (ELAN6100, PerkinElmer SCIEX, USA) [17].

Table 1
Characteristics of the raw piggery wastewater used in this study.

General feature (g/L)	
pH	6.64
Total solid	59.5
Volatile solid	38.9
TCOD	94.2
SCOD	54.2
Alkalinity as $CaCO_3$	7.0
TKN	7.6
NH_4^+–N	4.95
Proteins	16.6
Lipids	2.30
Acetate	14.23
Propionate	4.35
iso-Butyrate	1.53
n-Butyrate	4.88
iso-Valerate	1.70
n-Valerate	0.75
Total VFA	23.57
Metal element (mg/L)	
Na	606.65
K	3956.82
Ca	1775.03
Mg	672.15
Ag	0.017
Cd	0.014
Co	0.119
Cr	0.169
Cu	39.18
Mn	24.93
Mo	0.420
Ni	0.454
Zn	154.54
Fe	98.91
Al	41.28

3. Results and discussion

3.1. Characterization of piggery wastewater

3.1.1. General feature

As shown in Table 1, TS, VS, total and soluble COD's of the piggery wastewater used in this study were 59.5 g/L, 38.9 g/L, 94.2 g/L and 54.2 g/L, respectively. About half of soluble COD was contributed by short chain fatty acids (27.44 g/L), which were reported as readily utilizable substrates for biomethanization. The piggery wastewater also contained 2.3 g/L lipid and 16.6 g/L protein. Other important features of the piggery wastewater were extremely high concentrations of TKN (7.6 g-N/L) and ammonia (4.95 g-N/L). As for metal elements, the piggery wastewater contained high concentrations of light metals, such as Na, K, Ca, and Mg, and trace elements, such as Co, Mo, Ni, and Fe, which could play essential roles in anaerobic digestion [20].

3.1.2. Buffering capacity of piggery wastewater

The relationships among the pH, sodium hydroxide dosage and salinity as Na^+ were examined before the ammonia stripping of the piggery wastewater, because these parameters can influence the ammonia removal efficiency, reagent cost and biological treatability. As shown in Fig. 2, the pH followed different paths for different wastewaters (piggery wastewater and mixed liquor of MBR) when sodium hydroxide was added. For example, the amounts of sodium hydroxide needed to increase the pH of the wastewaters to pH 11.0 were 0.845 g/L and 14.21 g/L for the mixed liquor of MBR and the piggery wastewater, respectively. The different pH responses to the addition of sodium hydroxide was mainly due to the different

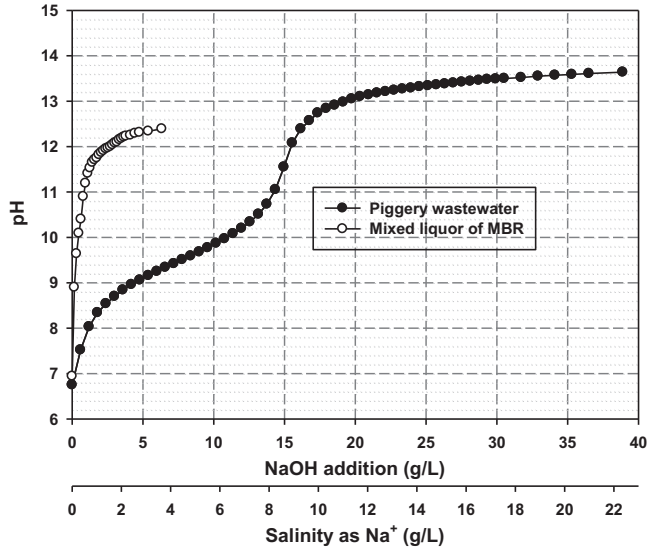

Fig. 2. Relationships among pH, NaOH dosage and salinity.

levels of alkalinity, as determined by the concentrations of the hydroxides, carbonates, and bicarbonate salts of calcium, magnesium, sodium, potassium and ammonia. It has been known that the piggery wastewater contains higher alkalinity (7.0 g/L as $CaCO_3$) than other types of wastewaters [21] as seen in Fig. 2. When the pH was adjusted to pH 9.0, pH 9.5, pH 10.0 and pH 11.0 for the piggery wastewater used in this study, the resulting salinities as Na^+ were 2.67, 4.44, 6.29 and 8.18 g/L, respectively, due to a high buffering capacity of the piggery wastewater. Yang et al. [15] also reported that the final Na^+ concentration in the wastewater was 4.3 g/L, when the pH of the raw piggery wastewater was adjusted to pH 10.25 using 6.0 M sodium hydroxide. This level of sodium ions was higher than that of typical food waste [20].

3.2. Optimization of ammonia stripping conditions

For the ammonia stripping of the piggery wastewater, the plot of the natural logarithm of ammonia concentration vs. aeration time yielded reasonably straight lines (Fig. 3). To compare ammonia removal rates, the obtained data were fitted to a general first-order expression as shown in Eq. (4), and the value of a pseudo-first-order rate constant k was estimated (Table 2).

$$\frac{d[NH_3\text{–N}]}{dt} = -k[NH_3\text{–N}] \quad (4)$$

Fig. 3A shows that ammonia removal increased as the initial pH increased because of the shift in the equilibrium between ammonia (NH_3) and ammonium ions (NH_4^+). As shown in Table 2, the

Table 2
Estimated pseudo-first-order rate constant (k) of ammonia removal kinetics by batch ammonia stripping under different conditions.

Ammonia stripping condition		k (h^{-1})	R^a
pH (aeration rate = 1.0 L L^{-1} min^{-1})	pH 7.2	0.00677	0.9963
	pH 9.0	0.01369	0.9831
	pH 10.0	0.03352	0.9888
	pH 11.0	0.04524	0.9726
Aeration rate (initial pH = 9.0)	1.0 L L^{-1} min^{-1}	0.01266	0.9698
	2.0 L L^{-1} min^{-1}	0.02040	0.9721
	4.0 L L^{-1} min^{-1}	0.03020	0.9543
	10.0 L L^{-1} min^{-1}	0.16562	0.9714

[a] R is the linear regression coefficient for the plot of $\ln(C/C_0)$ vs. the reaction time (h) shown in Fig. 3.

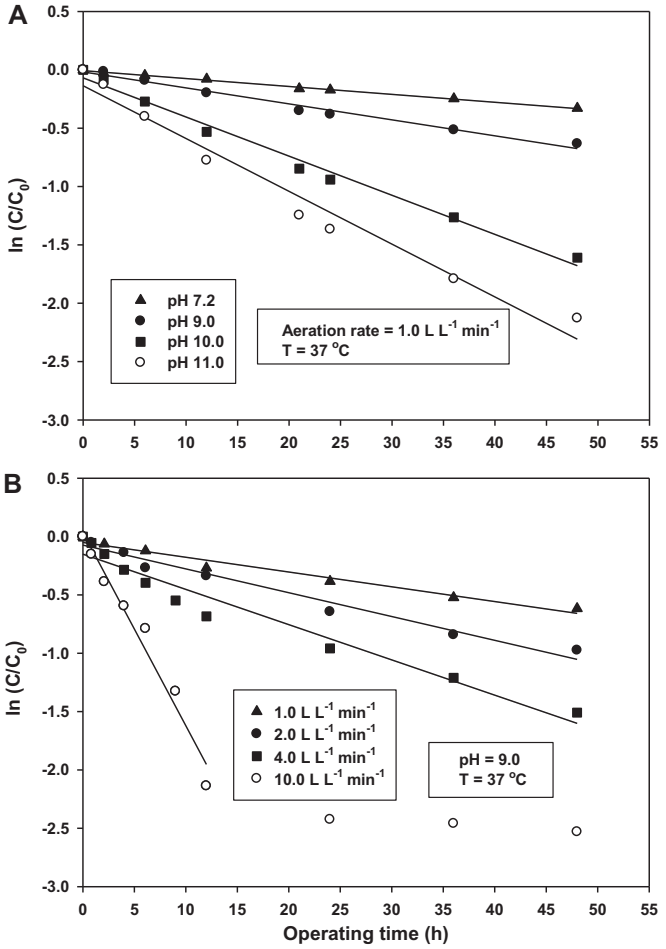

Fig. 3. Ammonia removal kinetics by air stripping at various initial pH values (A) and aeration rates (B). Initial ammonia concentrations ranged from 3.91–4.55 g NH_4^+–N/L. C_0 and C represent the ammonia concentrations at time 0 and t, respectively.

rate constant k for ammonia removal increased nearly 8-fold (from 0.00677 h^{-1} to 0.04524 h^{-1}) when the initial pH increased from pH 7.2 to pH 11.0. After 48 h of air stripping, the ammonia removal at pH 7.2, pH 9.0, pH 10.0 and pH 11.0 were 28.0%, 47.0%, 80.0% and 88.1%, respectively. At pH 10.0 and pH 11.0, the final concentrations of ammonia were 838 and 465 mg NH_4^+–N/L, respectively.

The aeration rate was another decisive parameter for ammonia removal. As shown in Fig. 3B, the ammonia removal rate increased as the aeration rate increased. As shown in Table 2, the pseudo-first-order rate constant (k) for ammonia removal increased from 0.01266 h^{-1} at 1.0 L L^{-1} min^{-1} to 0.16562 h^{-1} at 10.0 L L^{-1} min^{-1}. After 48 h of air stripping, the ammonia removals were 46.0%, 62.2%, 77.9% and 92.0% for 1.0, 2.0, 4.0 and 10.0 L L^{-1} min^{-1}, respectively. At 4.0 L L^{-1} min^{-1} and 10.0 L L^{-1} min^{-1}, the residual ammonia concentrations were 997 and 359 mg NH_4^+–N/L, respectively. At 10.0 L L^{-1} min^{-1}, the ammonia was rapidly removed, and the ammonia removal reached 88.2% after 12 h of air stripping. However, the high aeration rate was known to cause problems such as water evaporation as well as the foaming and cooling of the wastewater [9,10]. It was also observed that organic matters were degraded during ammonia stripping. The TCOD and SCOD decreased when the pH was near neutral at 1.0 L L^{-1} min^{-1} or when aeration rate was higher than 4.0 L L^{-1} min^{-1} at pH 9.0. This was explained by the aerobic biological degradation and the stripping out of volatile compounds such as volatile fatty acids.

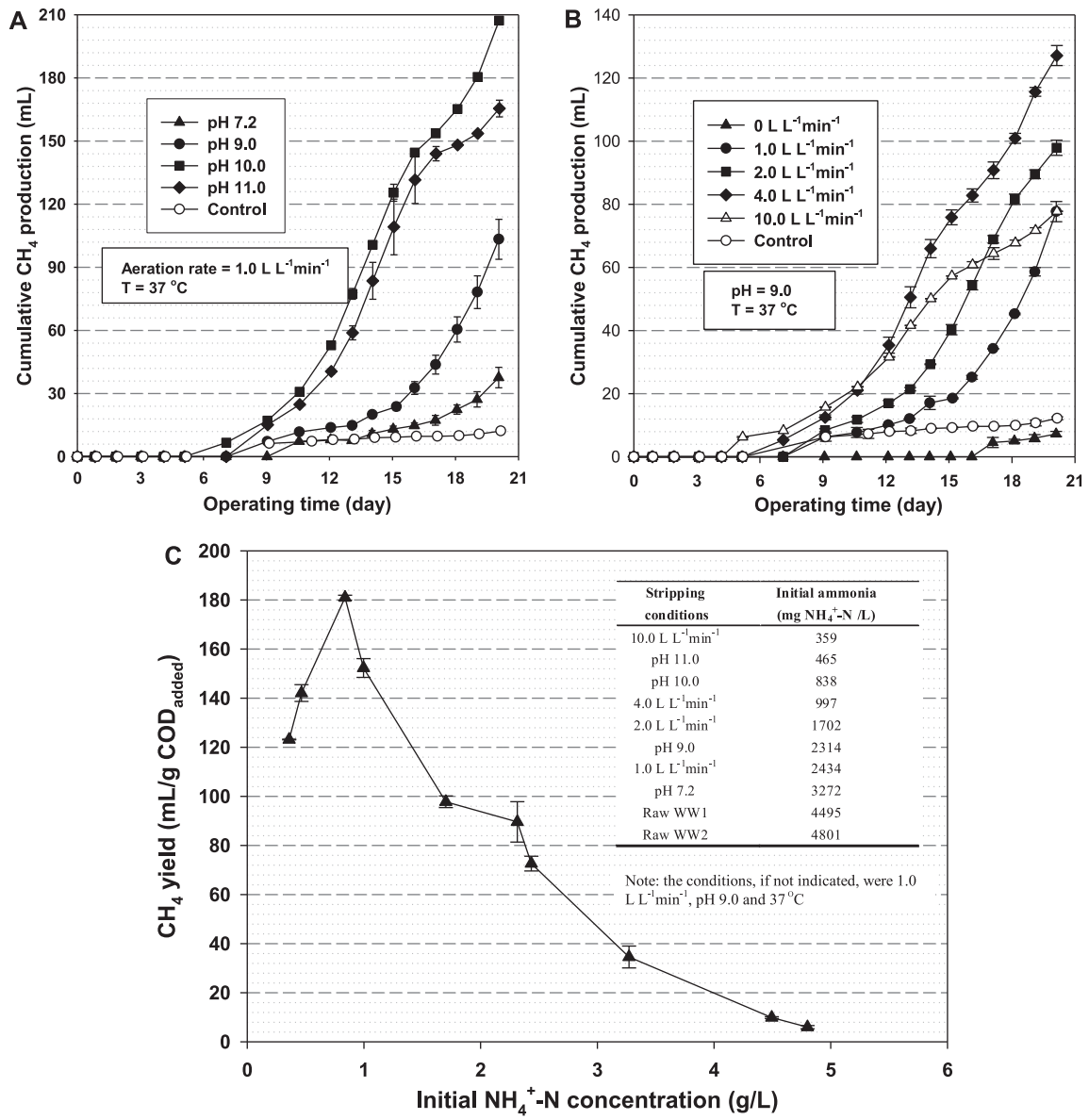

Fig. 4. Batch anaerobic digestion of piggery wastewaters treated at different air stripping conditions: different initial pH (A), different aeration rate (B), the relationship between the 20-day methane yield and the initial ammonia concentration (*C*). Anaerobic digestion was carried out using an unacclimated seed sludge.

3.3. Batch biomethanization of ammonia-stripped piggery wastewater

Fig. 4 shows the performance of batch biomethanization of the piggery wastewater air-stripped at different conditions using an unacclimated inoculum. The methane production was strongly affected by air stripping conditions. In the controls (anaerobic digestion of the raw piggery wastewater), only negligible amount of methane was generated during 20 days of experimental period. By contrast, the ammonia stripping significantly enhanced the methanization of piggery wastewaters. Shorter lag phase and faster methane production were observed for the air stripping conditions of higher initial pHs (pH 9.0, 10.0 and 11.0) (Fig. 4A). Similarly, the higher aeration rates also facilitated the faster methane evolution (Fig. 4B). However, the excess aeration ($10.0\,L\,L^{-1}\,min^{-1}$) resulted in a lower and slower methane production, which was mainly due to the aerobic degradation and organics loss by air stripping. Fig. 4C summarizes the relationship of methane yield and initial ammonia concentration. The methane yield decreased as the ammonia concentration increased, but the maximum yield was observed at ammonia concentration of 838 mg NH_4^+–N/L. Masoud [6] also found that a high-solid anaerobic digester performed the best when operated in the narrow range of 600–800 mg NH_4^+–N/L. Since ammonia serves as a nutrient, there must be an optimal concentration for the growth of microorganisms. However, different inocula exhibited different sensitivities to ammonia. It was reported that acclimation to ammonia effectively mitigated the extent of ammonia inhibition [6]. In our study, a higher IC_{50} (50% inhibition concentration) value (4.03 NH_4^+–N/L) for the acclimated inoculum was observed, which was a 1.8-fold higher than that (2.22 g NH_4^+–N/L) of the unacclimated inoculum (data not shown). However, regardless of which inoculum was used, strong ammonia inhibition was observed for the ammonia concentrations between 3.0 and 6.0 g NH_4^+–N/L. This result was in agreement with findings of Hansen et al. [3].

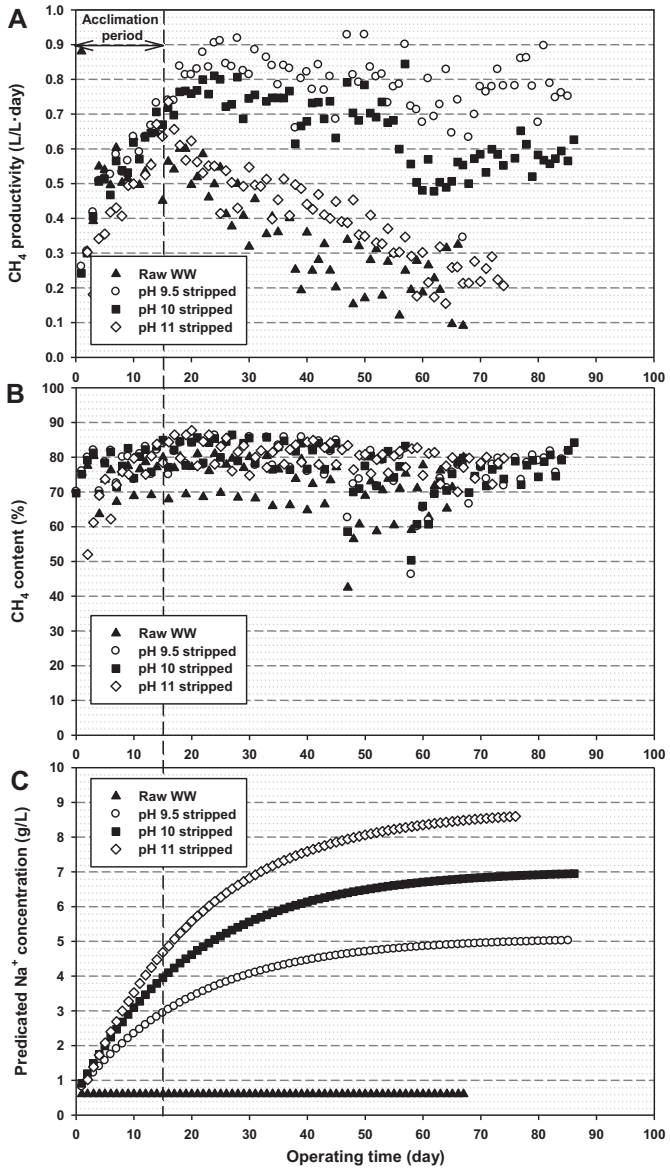

Fig. 5. Performance of semi-continuous biomethanization of ammonia-stripped piggery wastewater compared to the control (raw piggery wastewater). The aeration rate, temperature and aeration time were 4.0 L L^{-1} min^{-1}, 37 °C and 24 h, respectively.

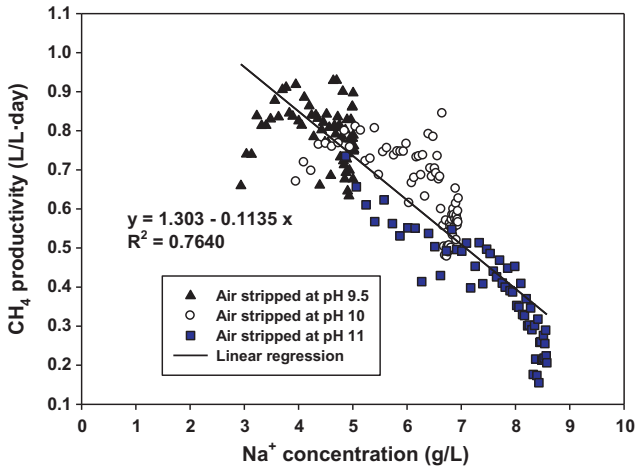

Fig. 6. Relationship between methane productivity and Na^+ concentration during semi-continuous anaerobic digestion (The data were extracted from Fig. 6 after acclimation period of 2 weeks).

3.4. Semi-continuous biomethanization of ammonia-stripped piggery wastewater

Fig. 5 and Table 3 show the methane production and other performance parameters for the anaerobic digestion of the raw piggery wastewater as compared to the ammonia-removed piggery wastewaters by air stripping at pH 9.5, pH 10.0 and pH 11.0. As shown in Fig. 5, for all cases the daily methane production gradually increased by more than 2 folds (from 0.24–0.28 L/L d to 0.64–0.73 L/L d) during days 0–14. This increase of the methane production was attributed to the acclimation of microorganisms to the ammonia and the increased organic loading rate (2.8 g COD/L d vs. 3.28–4.71 g COD/L d). From days 15, however, the methane production was significantly affected by the conditions of ammonia stripping (Fig. 5).

In the anaerobic digestion of the raw piggery wastewater, the methane productivity decreased from 0.45 L CH_4/L d at days 15 to 0.09 L CH_4/L d at days 67. The average methane yield was 49.2 ± 16.6 mL CH_4/g COD_{added}, which was significantly lower than the theoretical value (350 mL CH_4/g COD_{added}) [22]. This declining pattern was explained by the increase of the ammonia concentration, because the ammonia concentration gradually increased from 4.4 to 5.5 g NH_4^+–N/L from days 0–14. Considering that the seed had well been acclimated at 4.4 g NH_4^+–N/L in a bench scale reactor, the methanogens were thought to adapt to the increased ammonia concentrations from 4.4 to 5.5 g NH_4^+–N/L. A further increase of the ammonia concentration to 6.30 g NH_4^+–N/L resulted in significant ammonia inhibition. In addition to the lower methane productivity and yield, reduction of removal rates of TCOD and SCOD (approximately 20% and 13%, respectively) were also observed (Table 3). The level of VFA in the effluent was extremely high (21.15 g/L), which was only slightly lower than that of the influent. This poor performance strongly suggested that the anaerobic digestion of the raw piggery wastewater containing a high ammonia concentration was not feasible without ammonia removal. In contrast, enhanced methane production and removal of organics were achieved by appropriate ammonia removal through air stripping. As shown in Fig. 5, the methane productivity of 0.75 ± 0.11 L CH_4/L d and 0.57 ± 0.04 L CH_4/L d for the cases of ammonia-stripped piggery wastewaters at pH 9.5 and pH 10.0, respectively, were achieved after a digestion period of 87 days. The methane content increased from 67.9% for the control to around 77% for the wastewaters with air stripping at pH 9.5 and pH 10.0 (Table 3), indicating that the biogas quality was greatly improved. About 20% more TCOD and SCOD were removed compared to the control. In addition, more than 50% VFA was converted to biogas. In summary, these results clearly showed positive impacts of air stripping on the anaerobic digestion of piggery wastewater.

Interestingly, the methane productivity (0.75 ± 0.11 L CH_4/L d), yield (170.3 ± 26.0 mL CH_4/COD_{added}) and TCOD and SCOD removals of the ammonia-stripped piggery wastewater at pH 9.5 were statistically ($p < 0.05$) higher than those (0.57 ± 0.04 L CH_4/L d and 132.6 ± 8.6 mL CH_4/COD_{added}) of the pH 10.0 ammonia-stripped wastewater, despite the fact that the ammonia concentration of the pH 9.5 ammonia-stripped wastewater (2.93 g NH_4^+–N/L) was higher than that of the pH 10.0 stripped wastewater (1.85 g NH_4^+–N/L). This was thought to be caused by higher sodium ion concentration in the digestate fed with the ammonia-stripped wastewater at pH 10.0 compared to that with the ammonia-stripped wastewater at pH 9.5 (6.88 g/L of Na^+ vs. 4.97 g/L of Na^+). In other words, the positive influence by ammonia removal was masked by the increase of the sodium ion concentration. The

Table 3
Performance of the semi-continuous anaerobic digestion of raw and ammonia-stripped piggery wastewaters at steady states.

Parameter	Unit	Semi-continuous mode of anaerobic digestion			
		Reactor 1 (control)	Reactor 2 (pH 9.5)	Reactor 3 (pH 10.0)	Reactor 4 (pH 11.0)
Daily loading rate	g COD/L d	4.71	4.40	4.30	3.28
Retention time	d	20	20	20	20
CH_4 productivity	L CH_4/L d	0.23 ± 0.08	0.75 ± 0.11	0.57 ± 0.04	0.26 ± 0.06
CH_4 content	%	67.9 ± 9.2	76.8 ± 3.9	77.0 ± 3.6	78.1 ± 3.6
Specific CH_4 yield	mL CH_4/g COD_{added}	49.2 ± 16.6	170.3 ± 26.0	132.6 ± 8.6	78.9 ± 17.9
TCOD	g/L	72.53 ± 3.22	48.60 ± 0.20	50.82 ± 0.80	48.20 ± 2.65
SCOD	g/L	43.65 ± 3.53	25.67 ± 0.33	28.30 ± 0.46	28.06 ± 0.54
Acetate	g/L	14.08 ± 0.99	3.20 ± 0.26	4.84 ± 0.18	6.87
Propionate	g/L	4.93 ± 0.14	4.12 ± 0.14	3.62 ± 0.10	2.23
n-Butyrate	g/L	0.79 ± 0.11	0	0.30 ± 0.03	0.39
iso-Butyrate	g/L	1.59 ± 0.07	1.33 ± 0.02	1.41 ± 0.09	1.01
n-Valerate	g/L	0.58 ± 0.06	0.27 ± 0.02	0.41 ± 0.03	0.23
iso-Valerate	g/L	1.89 ± 0.11	1.29 ± 0.03	1.51 ± 0.08	1.08
Total VFAs as HAc	g/L	21.15 ± 1.33	8.37 ± 0.42	10.07 ± 0.41	10.40
pH	–	8.0 ± 0.2	8.0 ± 0.2	8.0 ± 0.2	8.2 ± 0.2
NH_4^+–N	mg/L	6304 ± 45	2932 ± 54	1848 ± 72	864 ± 61
Salinity as Na^+	g/L	0.61	4.97 ± 0.04	6.88 ± 0.05	8.40 ± 0.13
TCOD removal	%	23.0 ± 3.4	44.7 ± 0.23	40.9 ± 0.93	26.6 ± 4.03
SCOD removal	%	19.5 ± 6.5	50.3 ± 0.63	45.2 ± 0.90	21.9 ± 1.48
TVFAs removal	%	10.3 ± 4.8	56.8 ± 1.17	49.6 ± 1.43	31.7

sodium ion inhibition was more clearly observed in the anaerobic digestion of the ammonia-stripped piggery wastewater at pH 11.0. As seen in Fig. 5, the methane production of the ammonia-stripped piggery wastewater at pH 11 increased from 0.22 to 0.64 L CH_4/L d during days 0–15 and then decreased to 0.26 ± 0.06 L CH_4/L d. On day 87, however, the ammonia concentration in the digestate for the ammonia-stripped piggery wastewater at pH 11.0 was 864 mg NH_4^+–N/L, which was believed to be within the optimal range for anaerobic digestion (Fig. 4C). As shown in Fig. 6, the methane productivity appeared inversely linear to the Na^+ concentration in the range of 3.0–8.7 g Na^+/L. Therefore, the observed reduction of methane production from the piggery wastewater pretreated at high pH was thought to be due to sodium ion inhibition.

4. Conclusions

Ammonia stripping at a pH between 10 and 11 effectively removed ammonia with an efficiency higher than 80%. Ammonia stripping enhanced the biomethanization of piggery wastewater from 0.23 ± 0.08 L CH_4/L d for the control to 0.75 ± 0.11 L CH_4/L d (ammonia-stripped at pH 9.5) and 0.57 ± 0.04 L CH_4/L d (ammonia-stripped at pH 10). In addition, 20% more TCOD and SCOD were removed and the VFA level was significantly lower. However, the methane production from the anaerobic digestion of the ammonia-stripped piggery wastewater at pH 11.0 was similar to that of the control due to the excess introduction of sodium ions during pH adjustment for ammonia stripping. Therefore, it is necessary to consider not only ammonia concentration but also Na^+ concentration for improving biogas production from the piggery wastewater.

Acknowledgments

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0022968) and UNITEF (2010).

References

[1] C.J. Banks, A.M. Salter, M. Chesshire, Potential of anaerobic digestion for mitigation of greenhouse gas emissions and production of renewable energy from agriculture: barriers and incentives to widespread adoption in Europe, Water Sci. Technol. 55 (2007) 165–173.
[2] D.P. Chynoweth, A.C. Wilkie, J.M. Owens, Anaerobic processing of piggery wastes: a review, in: ASAE Meeting Presentation, 1998.
[3] K.H. Hansen, I. Angelidaki, B.K. Ahring, Anaerobic digestion of swine manure: inhibition by ammonia, Water Res. 32 (1998) 5–12.
[4] X.Z. Li, Q.L. Zhao, Efficiency of biological treatment affected by high strength of ammonium-nitrogen in leachate and chemical precipitation of ammonium-nitrogen as pretreatment, Chemosphere 44 (2001) 37–43.
[5] H.B. Nielsen, I. Angelidaki, Strategies for optimizing recovery of the biogas process following ammonia inhibition, Bioresour. Technol. 99 (2008) 7995–8001.
[6] K. Masoud, Performance of a high-solids anaerobic digestion process under various ammonia concentrations, J. Chem. Technol. Biotechnol. 59 (1994) 349–352.
[7] Z. Milán, E. Sánchez, P. Weiland, R. Borja, A. Martín, K. Ilangovan, Influence of different natural zeolite concentrations on the anaerobic digestion of piggery waste, Bioresour. Technol. 80 (2001) 37–43.
[8] A. Bonmatí, X. Flotats, Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, Waste Manage. 23 (2003) 261–272.
[9] P.H. Liao, A. Chen, K.V. Lo, Removal of nitrogen from swine manure wastewaters by ammonia stripping, Bioresour. Technol. 54 (1995) 17–20.
[10] M.Á. De la Rubia, M. Walker, S. Heaven, C.J. Banks, R. Borja, Preliminary trials of in situ ammonia stripping from source segregated domestic food waste digestate using biogas: effect of temperature and flow rate, Bioresour. Technol. 101 (2010) 9486–9492.
[11] H.-D. Ryu, S.-I. Lee, Application of struvite precipitation as a pretreatment in treating swine wastewater, Process Biochem. 45 (2010) 563–572.
[12] B.-B. Lind, Z. Ban, S. Bydén, Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite, Bioresour. Technol. 73 (2000) 169–174.
[13] F. Abouelenien, W. Fujiwara, Y. Namba, M. Kosseva, N. Nishio, Y. Nakashimada, Improved methane fermentation of chicken manure via ammonia removal by biogas recycle, Bioresour. Technol. 101 (2010) 6368–6373.
[14] A. Gangagni Rao, T. Sasi Kanth Reddy, S. Surya Prakash, J. Vanajakshi, J. Joseph, A. Jetty, A. Rajashekhara Reddy, P.N. Sarma, Biomethanation of poultry litter leachate in UASB reactor coupled with ammonia stripper for enhancement of overall performance, Bioresour. Technol. 99 (2008) 8679–8684.
[15] K. Yang, C. Oh, S. Hwang, Optimizing volatile fatty acid production in partial acidogenesis of swine wastewater, Water Sci. Technol. 50 (2004) 169–176.
[16] I. Angelidaki, W. Sanders, Assessment of the anaerobic biodegradability of macropollutants, Rev. Environ. Sci. Biotechnol. 3 (2004) 117–129.
[17] L. Zhang, D. Jahng, Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: effects of alkali types, J. Hazard. Mater. 182 (2010) 536–543.
[18] APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington DC, 2005.
[19] E. Bligh, W. Dyer, A rapid method of total lipid extraction, Can. J. Biochem. Physiol. 37 (1959) 11–19.
[20] L. Zhang, Y.-W. Lee, D. Jahng, Anaerobic co-digestion of food waste and piggery wastewater: focusing on the role of trace elements, Bioresour. Technol. 102 (2011) 5048–5059.
[21] G. Tchobanoglous, F. Burton, H. Stensel, Wastewater Engineering: Treatment and Reuse, McGraw-Hill Science/Engineering/Math, 2003.
[22] B.E. Rittmann, P.L. McCarty, Environmental Biotechnology: Principles and Applications, McGraw-Hill, Boston, 2001.