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Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types

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ABSTRACT

Air stripping at alkaline pH was carried out to remove ammonia from the piggery wastewater, and its effects on subsequent anaerobic digestion were investigated in semi-continuous experiments. In ammonia stripping process, three alkalis (NaOH, KOH and CaO) were used for pH adjustment. When using NaOH and KOH, the methane production rate increased more than two folds as compared to the control (no ammonia stripped), but cation toxicity exerted by sodium and potassium ions was observed. When using lime, on the contrary, it was found that volumetric methane production rates (1040–1130 mL CH_4/L day) and yields (262.3–258.9 mL CH_4/g of COD_{added}) were significantly higher than others. In addition, the organic removal efficiencies (54.2–59.5% of volatile solid, 59.6–64.0% of total COD, 72.1–81.9% of soluble COD and 89.3–98.9% of volatile fatty acid) were also high. Batch toxicity test results confirmed that cations of Na^+, K^+ were strong methanogenic inhibitors as compared to Ca^{2+}. From these observations, it was concluded that ammonia stripping at alkaline pH is important for anaerobic digestion of piggery wastewater and the alkali types should be chosen cautiously to avoid cation toxicity.

1. Introduction

As the demand of pork is increasing, enormous amounts of piggery wastes are generated worldwide. For example, in Korea, piggery waste production was about $5 \times 10^7\,m^3$ in 2006 [1]. Therefore, piggery waste management has become a serious environmental issue not only because of the contamination of water bodies, but also emission of odor and greenhouse gas (GHG) [2]. Recently, the outbreak of swine flu makes the hygienization of piggery waste become a more urgent issue. Anaerobic digestion has been recommended as a treatment process for piggery waste due to the waste reduction, nutrient conservation in liquid fraction, renewable energy production (biogas) and the mitigation of pollutant emissions in the closed system (odor, GHG and animal pathogens) [2–4].

However, process imbalances and limitations have often been reported in the biogas plants in which animal manure is the main substrate [5]. Anaerobic digestion of animal manure can be inhibited by different compounds such as ammonia (NH_3) and hydrogen sulfide (H_2S) [6,7]. The former is generated by the fermentation of organic nitrogen (urea and proteins) and the latter by sulfate reduction. Because of high nitrogen concentration in the animal manure and high pH, free ammonia is considered as the main inhibitor. Many researchers [7,8] reported that an "inhibited steady state", which is characterized by a stable process operation with a low methane yield and a high volatile fatty acid (VFA) level in the effluent, could be established in anaerobic digestion of piggery wastewater due to high ammonia concentration. In order to avoid VFA accumulation, lowering organic loading rate (OLR) or increasing the biomass retention time were the frequently adopted strategies, which would decrease the methane productivity thus damaging the economic feasibility.

The other way for enhanced methanization of nitrogen-bearing feeds was through the removal of ammonia [9]. Ammonia removal as a pretreatment method of anaerobic digestion could not only enhance its performance by decreasing the ammonia concentration in the feed but also maintain the ammonia concentration of the effluent in a range that is safe for subsequent biological processes [10]. Several different physical, chemical and biological methods, such as zeolite adsorption [11], ammonia stripping [12–15], chemical precipitation [10,16–18], microwave radiation [19] and a biological A/O (anoxic/oxic) process [20] have been proposed for ammonia removal or recovery. Among these processes, the ammonia stripping method seems to be the most practical as this method generates less extra sludge and is associated with modest reagent cost and an easy operation [20].

In the ammonia stripping process, pH control is a critical step. Liao et al. [13] and Bonmatí and Flotats [12] studied ammonia stripping from piggery slurry at room temperature (22 °C) and

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at a high temperature (80 °C). At room temperature, a high pH (10.5–11.5) was required to achieve high ammonia removal efficiency. When fresh piggery slurry was used, a high initial pH (11.5) was required for complete ammonia removal even at 80 °C. In order to obtain a high pH (10–12), a large amount of alkali is needed in the ammonia stripping process. The resulting high concentration of cations might readily affect the activity of microbes and interfere with their metabolism in the subsequent biological processes. For example, sodium ion concentrations of 5, 10, and 14 g/L led to inhibition by 10%, 50% and 100%, respectively, with respect to the inhibition of methanogens in an anaerobic granular biomass at mesophilic temperature and neutral pH [21]. Therefore, during ammonia pretreatment, not only ammonia removal efficiency, but also the effects of cations which are introduced for enhancing efficiency of ammonia stripping are needed to be evaluated.

In this study, we used three different alkalis for ammonia stripping and compared their effects on subsequent anaerobic digestion of piggery wastewater. Additionally, the toxicity of cations contained in alkalis was also examined.

2. Materials and methods

2.1. Piggery wastewater and inoculum

The piggery wastewater used in this study was obtained from storage tanks, which contained the feces, urine, and tap water which was used for cleaning pig pens, on a swine farm located in Yongin, Republic of Korea. After arriving at the laboratory, the wastewater was filtered through a 2 mm mesh to remove the coarse particles, and then stored at 4 °C until used. The composition of the raw piggery wastewater is presented in Table 1.

The anaerobic seed culture was obtained from a 20-L bench scale anaerobic digester which had been used to treat 2 folds diluted piggery wastewater for longer than two years. The seed sludge was considered as a well acclimated inoculum to high level ammonia, as the digestate contained around 4.4 g/L of NH_3-N. Volatile suspended solids (VSS) concentration of the seed culture was approximately 15 g/L.

2.2. Ammonia stripping

For ammonia stripping experiments, six identical reactors with working volumes of 0.5 L were prepared. According to the previously optimized conditions for ammonia stripping [22], two pH values (pH 9.5 and 10) under the conditions of aeration rate of 0.5 L/min and aeration time of 24 h were chosen. Forced air (37 °C) was introduced directly into the liquid phase of the reactor via an aquatic air stone at the aeration rate of 0.5 L/min for 24 h. In order to increase ammonia removal efficiency, three types of alkali (NaOH, KOH and lime) were used to adjust the pH to pH 9.5 and pH 10 prior to air stripping. In order to compensate water loss during air stripping, distilled water (DW) was added up to the original volume. pH was also readjusted to pH 7.8 using 6.0 M HCl after ammonia stripping was finished. The resulting piggery wastewaters were stored at 4 °C prior to anaerobic digestion. The characteristics and features of air-stripped wastewaters are summarized in Table 2.

Table 1
Characteristics of piggery wastewaters used in this study and reported in literatures.

Parameter (unit)	Ahn et al. [26]	Hansen et al. [6,7]	This study
pH	6.37 ± 0.10	7.62 ± 0.02	6.64
Total solid (TS) (wt%)	6.18 ± 0.04	–	5.95
Volatile solid (VS) (wt%)	4.45 ± 0.02	4.5 ± 0.1	3.89
VS/TS ratio	0.72	–	0.65
TCOD (g/L)	130.8 ± 3.0	–	94.2
SCOD (g/L)	59.7 ± 0.9	–	54.2
TKN (g/L)	7.3 ± 0.1	6.6	7.6
Ammonia-N (g/L)	4.8 ± 0.1	5.3 ± 0.1	4.95
Protein (g/L)[a]	15.8 ± 0.9	8.13	16.6
Lipid (g/L)	20.1 ± 0.1	4.86	2.30
Acetate (g/L)	11.1 ± 0.2	–	14.23
Propionate (g/L)	4.2 ± 0.1	–	4.35
iso-Butyrate (g/L)	–	–	1.53
n-Butyrate (g/L)	6.4 ± 0.1	–	4.88
iso-Valerate (g/L)	–	–	1.70
n-Valerate (g/L)	–	–	0.75
Total VFA as acetate (g/L)	36.7 ± 0.1	11.0 ± 0.5	27.44

–, Data not available.
[a] Protein content = (TKN-ammonia nitrogen) × 6.25 [26].

2.3. Semi-continuous experiments

Semi-continuous experiments were carried out in a 500-mL Schott Duran bottle with a 200-mL working volume. Seven bottles were incubated by feeding different substrates, which were the control, Na9.5, Na10, K9.5, K10 and Ca9.5 and Ca10 as indicated in Table 2. Each bottle was set up by filling 190 mL of seed sludge and 10 mL of substrate. The hydraulic retention time (HRT) was kept at 20 days by manually withdrawing and feeding 10 mL of the substrates once a day. All the operations were made under nitrogen atmosphere to avoid contacting oxygen. Then, the bottles were placed in a thermostatic shaking incubator at 37 °C and 140 rpm. In order to ensure sufficient acclimation and to achieve a steady state,

Table 2
Characteristics of feeding substrates in semi-continuous experiments.

Parameter (unit)	Raw wastewater[a]	Ammonia stripped using NaOH		Ammonia stripped using KOH		Ammonia stripped using CaO	
RUN	Control	pH 9.5 Na9.5	pH 10.0 Na10	pH 9.5 K9.5	pH 10.0 K10	pH 9.5 Ca9.5	pH 10.0 Ca10
TCOD (g/L)	94.2	87.9	86.0	82.4	85.9	85.9	80.4
SCOD (g/L)	54.2	51.6	53.3	48.8	50.0	46.1	42.5
Acetate (g/L)	14.23	12.99	12.72	10.19	10.86	11.50	11.34
Propionate (g/L)	4.35	4.28	4.23	3.54	3.62	3.89	3.53
n-Butyrate (g/L)	1.53	1.52	1.52	1.36	1.34	1.44	1.29
iso-Butyrate (g/L)	4.88	4.55	4.73	3.80	4.04	4.00	3.97
n-Valerate (g/L)	1.70	1.64	1.52	1.49	1.40	1.41	1.42
iso-Valerate (g/L)	0.75	0.67	0.94	0.66	0.69	0.65	0.61
Total VFAs (g/L)	27.44	25.66	25.65	21.04	21.96	22.89	22.16
pH	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Ammonium-N (g/L)	4.95	2.51	1.46	2.95	1.42	3.44	2.52
Cation conc. (g/L)[b]	0	4.49 (Na^+)	6.44 (Na^+)	4.05 (K^+)	7.43 (K^+)	3.63 (Ca^{2+})	5.07 (Ca^{2+})

[a] After pH adjustment to pH 7.8.
[b] Externally added cations as alkalis.

the experiment had been conducted for 53 days. Steady-state conditions were assumed to be achieved when the methane production rate remained practically constant throughout the time. During the steady state period, the total solid (TS), volatile solid (VS), chemical oxygen demand (COD), VFA and ammonia were measured.

2.4. Batch experiment

Batch anaerobic digestion in a 160-mL serum bottle with a working volume of 50 mL was carried out with 30% (v/v) piggery wastewater and 70% (v/v) seed sludge. Before starting incubation, the bottle was flushed with pure nitrogen for 5 min in order to remove the oxygen. Then, the bottles were placed in a thermostatic shaking incubator under the conditions of 37 °C and 140 rpm. To examine the effects of different cations (Na^+, K^+ and Ca^{2+}) on anaerobic digestion of piggery wastewater, different amounts of NaCl, KCl and $CaCl_2$ were added to the mixture of seed sludge and raw piggery wastewater. Since the cumulative methane production was linear with the reaction time in the early stage of incubation, the methane production rate referred to the initial slope of the cumulative methane production curve as described elsewhere [23]. The relative methanogenic activity was calculated by comparing the methane production rate of a cation added case to that of the control (without cation addition).

2.5. Analytical methods

TS, VS and calcium ion were measured according to the Standard Methods [24]. The pH was determined using a pH meter (Orion, Model 370). Chemical oxygen demand (COD) measurements were made using COD ampoules (Hach Chemical) with a spectrophotometer (DR/2010, Hach). Soluble COD was measured for the supernatant of a sample after centrifugation (Micro 17R centrifuge, Hanil Science Industrial Co., Ltd., Korea) at 14,000 × *g* for 10 min. 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. The free ammonia was calculated based on total ammonium concentration, pH, and temperature according to Eq. (1) as suggested by El-Mashad et al. [25].

$$NH_3\text{-}N = (NH_4^+\text{-}N) \times \left[1 + \frac{10^{-pH}}{10^{-(0.1075+(2725/T))}}\right]^{-1} \quad (1)$$

where NH_3-N and NH_4^+-N represent the concentrations of free ammonia and the sum of free ammonia and ionized ammonium, respectively, and T is the absolute temperature in the range of 273–373 K. The protein content was estimated by multiplying the organic nitrogen value (TKN subtracted by total ammonia nitrogen) by 6.25 [26]. Lipid was gravimetrically measured [27].

The biogas composition (N_2, CH_4 and CO_2) was determined using a gas chromatograph (GC) (Hewlett Packard 6890, PA, USA) equipped with a thermal conductivity detector (TCD) and an HP-PLOT Q (Agilent Technologies, USA) capillary column (30 m × 0.32 mm × 20 μm). The operational temperatures at injection port, the column oven and detector were 60, 35 and 200 °C, respectively. Helium was used as a carrier gas at a flow rate of 0.5 mL/min in the splitless mode.

Biogas volume generated was calculated according to the change of molar ratio of CH_4 or CO_2 to N_2 [28]. Before daily wastage, the composition of mixed gas (nitrogen gas and biogas generated) in the headspace was determined. Since the biogas (CO_2 and CH_4) was generated and accumulated in the headspace during each feeding and drawing cycle, the relative molar ratio of CO_2 or CH_4 to N_2 was increased from 0 to a specific value. It was assumed that the volume of nitrogen gas in the headspace was constant due to its inert feature and low solubility in aqueous phase. The generated gas volume of CH_4 or CO_2 was calculated by multiplying the nitrogen gas volume by molar ratio, and corrected to the STP condition (standard temperature and pressure, 298.15 K and 1.0 atm). The validity of the biogas measurement methodology was confirmed by the water displacement method.

The concentrations of volatile fatty acids (including acetate, propionate, n-butyrate, iso-butyrate, n-valerate and iso-valerate) were determined using another gas chromatograph (M600D, Younglin, Korea) equipped with a flame ionization detector (FID) and an HP-INNOWAX (Agilent Technologies, USA) capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as a carrier gas at a flow rate of 20 mL/min with the split ratio of 1:20. The operational temperatures at the injection port and detector were 250 and 300 °C. The initial temperature of oven was 80 °C for 1 min, then increased to 220 °C at the rate of 10 °C/min and maintained for 5 min. Digestates were centrifuged (Micro 17R centrifuge, Hanil Science Industrial Co., Ltd., Korea) at 14,000 × g for 10 min, and 1.0 mL of supernatant was acidified with 0.2 mL of 20 wt% H_3PO_4 to lower the pH below pH 3 to ensure that acids were unionized and volatile. Then 0.2 mL of an internal standard containing 1000 mg/L of 2-ethyl butyric acid was added before injection.

3. Results and discussion

3.1. Characterization of raw and ammonia-stripped piggery wastewaters

As shown in Table 1, TS, VS, total and soluble CODs of the piggery wastewater used in this study were 6.64 wt%, 5.95 wt%, 94.2 g/L and 54.2 g/L, respectively. The 51% of soluble COD were contributed by short chain fatty acids (27.44 g/L as acetate), which were reported as the highly desirable substrates for biomethanization [29]. The piggery wastewater showed a lower VS/TS ratio (0.65) as compared to 0.8–0.95 for food wastes [30]. The piggery wastewater also contained 2.3 g/L of lipid and 16.6 g/L of protein. Another important feature was that the piggery wastewater contained extremely high concentrations of total Kjeldahl nitrogen (TKN) (7.6 g-N/L) and ammonia (4.95 g-N/L).

Since the ammonia concentration was in the inhibitory range [6,7], the ammonia control mechanism was necessary in order to achieve the high biogas production and organic removals in the anaerobic treatment of piggery wastewater. Table 2 shows the characteristics of ammonia-stripped piggery wastewaters under different stripping conditions. The final concentrations of ammonia-nitrogen after air stripping were in the range of 1.42–3.44 g/L, which was significantly lower than that of the raw piggery wastewater (4.95 g/L). The ammonia removal efficiency was strongly dependent on initial pH and alkali type during the pH adjustment process. The higher initial pH caused the higher ammonia removal rate, and the sodium hydroxide and potassium hydroxide were more effective than lime. All the variations of total COD and VFA were less than 20%, which could be explained by stripping out of volatile organic compounds like acetate, and by aerobic biodegradation during the air stripping.

3.2. Semi-continuous anaerobic digestion of raw and ammonia-stripped piggery wastewaters

3.2.1. Biogas profile

Fig. 1 shows the daily methane production rate and methane content of the raw piggery wastewater (control) and the ammonia-stripped piggery wastewaters. During the start-up period, the daily methane productions for all cases gradually increased by more than two folds during days 0–14, which might be attributed to the accli-

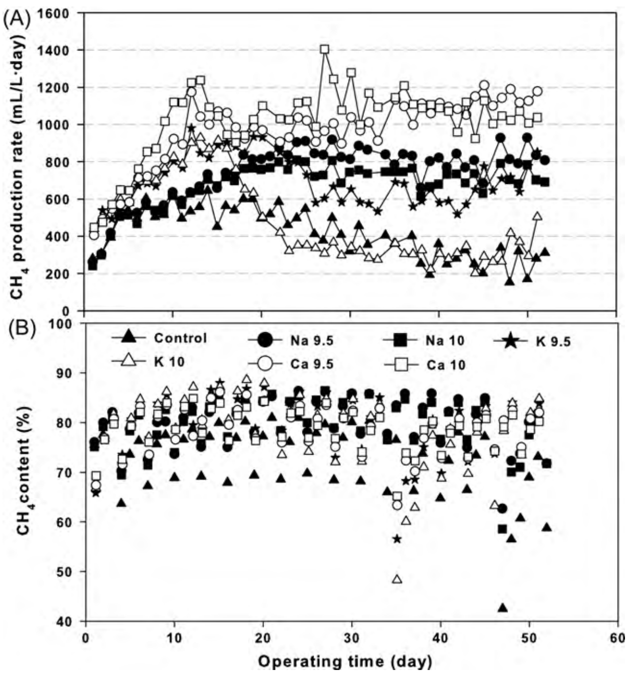

Fig. 1. Effects of different alkalis for ammonia stripping on methane production rates as compared to the control (no pretreatment) in semi-continuous experiments. Each setup (control, Na9.5–Ca10) is given in Table 2.

mation and the increased organic loading rate. However, as the original inoculum was gradually replaced by the raw or ammonia-stripped piggery wastewaters, methane production rates from days 15 to days 53 were markedly affected by the feeding substrates.

In the control reactor, where raw piggery wastewater was used as a substrate, the daily methane production rates decreased from the highest rate of 645 mL CH_4/L d on day 14 to 262.0 ± 63.5 mL CH_4/L d in the steady state (days 41–53). This declining pattern could be explained by the increase of ammonia concentration. From days 0 to 14, the ammonia concentration gradually increased from 4.4 to 5.5 g/L of NH_3-N. Considering that the seed biomass had well been acclimated to 4.4 g/L of NH_3-N in a 20-L bench scale reactor, the methanogenic biomass was thought to adapt to the increased ammonia concentrations from 4.4 to 5.5 g/L of NH_3-N. Subsequently, a further increase of the ammonia concentration to 7.25 ± 0.49 g/L of NH_3-N resulted in significant ammonia inhibition. This result again supported the idea that ammonia control strategy was needed to improve process stability and efficiency of anaerobic digestion of piggery wastewater.

When ammonia stripped piggery wastewaters were used as feeding substrates, in most cases (Na9.5, Na10, K9.5, Ca9.5 and Ca10), the more stable and higher methane production rates were observed during the prolonged operation period (days 15–53) than that of the control (Fig. 1A). Volumetric methane production rate, which is defined as the produced methane volume per reactor volume, is known to be an important performance parameter to determine the process economic feasibility [4]. As shown in Fig. 2, the volumetric methane production rates increased from 262.0 ± 63.5 mL/L day for the control reactor to 716.1 ± 46.4 mL/L day for Na9.5 reactor and 668.9 ± 99.9 mL/L day for Na10 reactor, indicating that the process economic feasibility was greatly improved by ammonia stripping pretreatment. For K9.5 reactor, the volumetric methane production rate was 668.9 ± 99.9 mL/L day, which was similar to those of Na9.5 and Na10 reactors. Superior process performance was observed in Ca9.5 and Ca10 reactors, where lime was used for ammonia stripping process, and the volumetric methane production rates were 1130 ± 47

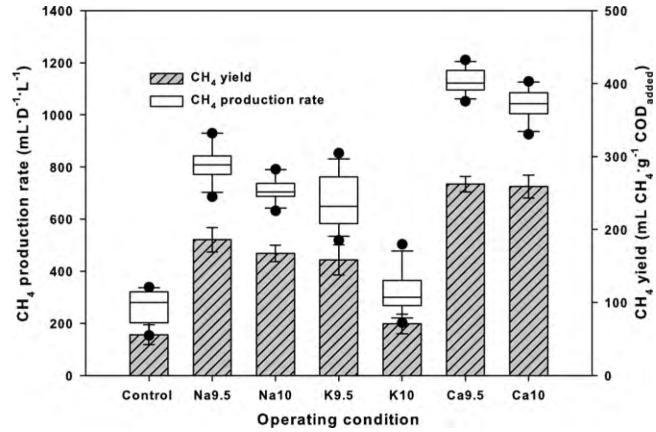

Fig. 2. Steady state volumetric methane production rate and yield. Vertical bars indicate the standard deviations.

and 1040 ± 61 mL/L day for Ca9.5 reactor and Ca10 reactor, respectively.

With regard to methane production as a function of initial COD, the methane yields were calculated and plotted in Fig. 2. Ammonia stripping increased methane yield from 50.7 ± 15.9 mL CH_4/g COD_{added} for the control reactor to 165.7 ± 11.1, 155.3 ± 20.2, and 155.3 ± 20.2 mL CH_4/g COD_{added} for Na9.5, Na10 and K9.5 reactors, respectively. When lime was employed in ammonia stripping process, 262.3 ± 12.0, and 258.9 ± 17.3 mL CH_4/g COD_{added} were obtained for Ca9.5 reactor and Ca10 reactor, respectively. The values were compatible with 270 mL CH_4/g COD_{added} [31] and 249–277 mL CH_4/g COD_{added} [32], where batch and extended incubation was adopted for anaerobic digestion of the piggery wastewater.

The biogas quality (methane percentage) was also monitored, and the results are shown in Fig. 1B. The methane contents of the biogas from the ammonia stripped setups were around 79% except for the control (72.5%). The difference might be due to that the carbon dioxide was stripped out during ammonia stripping process. The methane percentage obtained in this study was much higher than that of anaerobic digestion of other substrates (around 65%) [28]. This was probably the result of the high pH values of the digestate (8.00–8.49) that increased the solubilization of carbon dioxide, thus promoting the autotrophic methanogenic microorganisms. Another reason might be attributed to efficient hydrolysis and acidogenesis of feeding substrates which were reflected by the high VFA content. The carbon dioxide is the main gas byproduct during hydrolysis and acidogenesis steps, which would decrease the methane content. In addition, the characteristics of feeding substrates also affected the methane content. For example, the high concentration of proteins in piggery wastewater might cause the high methane content.

3.2.2. VFA profile

Fig. 3 shows the VFA profile of different substrates during days 28–53. In the control reactor, where raw piggery wastewater was used as a substrate, a high level VFA (21.46 ± 2.20 g/L) was accumulated in the system, which was slight lower than that of unfermented raw piggery wastewater (27.44 g/L). Among the accumulated VFAs, acetate was the major component, which comprised of almost 60.0% of total VFAs. The high level VFA in the effluent, together with the extremely low methane production rate and methane yield, indicated that the anaerobic digestion of raw piggery wastewater was severely inhibited by the presence of inhibitors or toxic substances. The inhibition was thought to be due to the high level of ammonia concentration in the raw piggery wastewater. Similar results were also reported by Angelidaki and

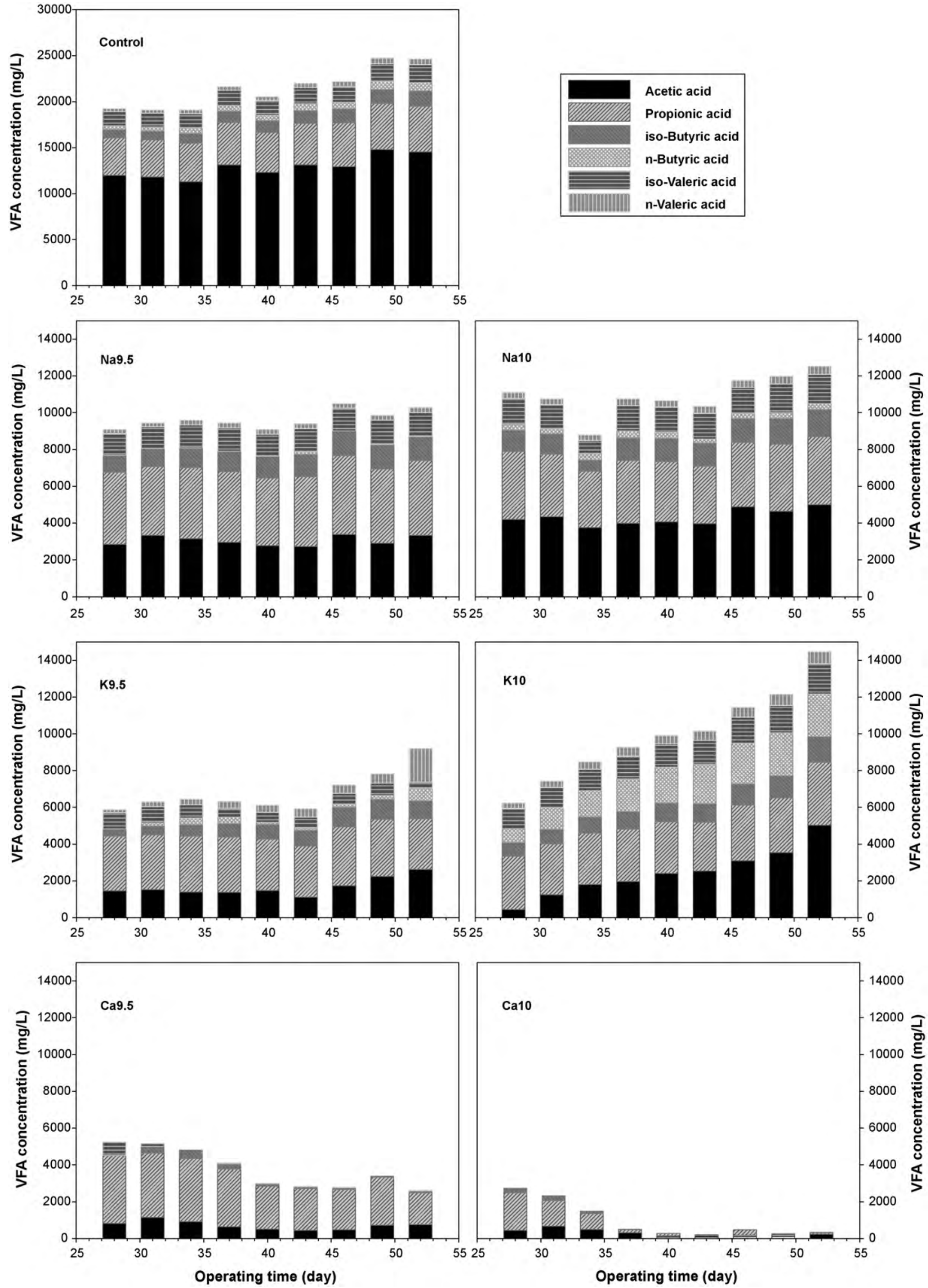

Fig. 3. Variation of VFAs during anaerobic digestion of different substrates.

Ahring [8] and Hansen et al. [6,7], where the low methane yield and high level VFA in the effluent were also found.

When ammonia-stripped piggery wastewaters were fed, Na9.5, Na10, K9.5 and K10 reactors showed the lower VFA level in the effluent compared to the control reactor. The VFA profiles were coincided with the methane production profile (Fig. 1A), as indicated by the high methane production rate together with high VFA conversion rate. For example, in the K10 reactor, the increasing trend of VFA in the effluent coincided with the declining methane production rate as shown in Fig. 1A. Although the VFA level and removals were enhanced by ammonia stripping in Na 9.5, Na10, K9.5 and K10 reactors, high concentrations of remaining VFA (6.81–10.96 g/L) suggested that some inhibition other than ammonia inhibition occurred. Interestingly, in Ca9.5 and Ca10 reactors, significantly lower VFA levels were observed. Especially for Ca10, almost all the VFA was consumed, which was well matched with the higher methane production rates in Figs. 1 and 2.

Interestingly, the levels of the propionic acid in Na9.5, Na10, K9.5 and K10 were almost the same as that of the control, for which no significant degradation was observed. Ammonia was found to influence propionate degradation when ammonia concentration was in the range of 4.05–5.73 g/L [33]. Wang et al. [29] showed that propionic acid degradation was inhibited when acetic acid concentration was higher than 1400 mg/L. The propionate concentrations in the Ca9.5 and particularly Ca10 reactors were much lower than others (Fig. 3), which indicated that calcium addition might be essential to propionate degraders with unknown reasons.

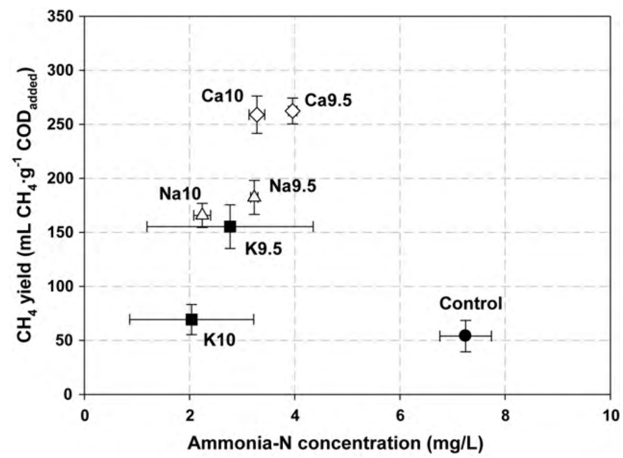

Fig. 4. Relationship between methane yield and ammonia concentration in the steady state of continuous experiments.

3.2.3. Comprehensive comparison

The organic matter (TS, VS, COD and VFA) removals and biogas production parameters were calculated and listed in Table 3. In terms of VS removals, no significant differences were observed among the control reactor, Na9.5, Na10, K9.5 and K10 reactors, all the values were in the range of 38.7–46.7%. TCOD removal efficiencies in the reactors where NaOH and KOH were used for pH adjustment were in the range of 33.0–44.7%, which were significantly higher than that of the control reactor (23.0 ± 3.4%). As mentioned, the differences of VS removals were less significant than those of TCOD removals to explain the differences of methane generation rates. These small differences of VS removals can be attributed to the VS measurement methodology. For VS measurement, a weighed sample is dried at 105 °C to determine the dry matter content and then is ignited at 550 °C to determine the fixed residue. The VS content is the difference between these two values [24]. It should be noted that the volatile compounds like short chain fatty acids can evaporate during drying at 105 °C, which generates errors on VS value. Particularly, the VFA content in the effluent of the control reactor was much higher than others, so that measured VS values became lower than real values, which resulted in exaggerated VS removals. This type of error in VS measurement had also been observed by other researchers [34,35]. Compared to VS removal, it was thought that TCOD removal more accurately reflected the biomethanization performance in anaerobic digestion of piggery wastewater. In Ca9.5 and Ca10 reactors, the TCOD removal efficiencies were 59.6 ± 0.7% and 64.0 ± 0.3%, respectively. The SCOD removal also increased from 19.5 ± 6.5% for the control reactor to 81.9 ± 0.6% for the Ca10 reactor. The higher removals of VS, TCOD, SCOD and VFA in Ca9.5 and Ca10 indicated that ammonia stripping using lime as an alkali for pH adjustment greatly enhanced anaerobic digestion of piggery wastewater, and no significant inhibition was observed.

It was observed in Table 3 that ammonia concentrations in the digestate and biogas production capability were not correlated well. For example, methane production rate of the K10 reactor (320.6 ± 79.4 mL/L day) was lower than those of Ca9.5 (1130 ± 47 mL/L day) and Ca10 (1040 ± 61 mL/L day), although K10 contained a lower concentration of ammonia (1.42 g/L of ammonia-N) than Ca9.5 (3.44 g/L of ammonia-N) reactor and Ca10 reactor (2.52 g/L of ammonia-N). As shown in Fig. 4, methane yields of the control and ammonia stripped piggery wastewaters were not correlated with ammonia concentrations. This suggested that there must be additional factors besides the ammonia concentration that influence biogas production. And hence it has been noticed that cations added to the system as a form of alkali probably caused unforeseen results in anaerobic digestion.

Table 3
Biogas production and removal rates obtained from the semi-continuous anaerobic digestion of raw and ammonia-stripped piggery wastewaters.

Parameter (unit)	Control	Na9.5	Na10	K9.5	K10	Ca9.5	Ca10
Daily organic loading rate (g of COD L^{-1} d^{-1})	4.71	4.40	4.30	4.12	4.30	4.30	4.02
Hydraulic retention time (HRT) (day)	20	20	20	20	20	20	20
Methane production rate (mL CH_4 L^{-1} d^{-1})	262.0 ± 63.8	816.7 ± 69.6	716.1 ± 46.4	668.9 ± 99.9	320.6 ± 79.4	1130 ± 47	1040 ± 61
Methane content (%)	72.5 ± 7.6	79.9 ± 5.0	79.6 ± 5.5	79.3 ± 6.3	78.2 ± 8.2	78.6 ± 4.8	78.6 ± 4.2
Specific methane yield (mL CH_4/g COD)	54.0 ± 14.5	182.3 ± 15.7	165.7 ± 11.1	155.3 ± 20.2	69.3 ± 13.9	262.3 ± 12.0	258.9 ± 17.3
pH	8.34 ± 0.10	8.20 ± 0.09	8.20 ± 0.13	8.30 ± 0.08	8.49 ± 0.15	8.06 ± 0.10	8.00 ± 0.12
Ammonium-N (g/L)	7.25 ± 0.49	3.23 ± 0.07	2.24 ± 0.16	2.77 ± 1.58	2.04 ± 1.18	3.96 ± 0.08	3.28 ± 0.15
Free ammonia-N (mg/L)	877 ± 68	290 ± 35	216 ± 30	347 ± 62	419 ± 44	258 ± 49	185 ± 39
Organic matter removals (%)							
VS	38.7 ± 1.8	39.8 ± 4.4	40.8 ± 2.3	46.7 ± 3.1	39.1 ± 2.8	54.2 ± 3.0	59.5 ± 1.7
TCOD	23.0 ± 3.4	44.7 ± 0.2	40.9 ± 0.9	43.4 ± 0.6	33.0 ± 0.6	59.6 ± 0.7	64.0 ± 0.3
SCOD	19.5 ± 6.5	50.3 ± 0.6	45.2 ± 0.9	55.1 ± 0.5	39.8 ± 2.2	72.1 ± 1.5	81.9 ± 0.6
Acetate	4.9 ± 7.5	78.8 ± 2.2	68.3 ± 3.3	87.1 ± 4.2	76.6 ± 7.4	96.0 ± 1.0	98.8 ± 0.3
Propionate	−8.8 ± 6.6	8.7 ± 5.4	20.8 ± 5.7	32.7 ± 4.8	31.7 ± 6.7	48.6 ± 7.3	97.2 ± 2.3
n-Butyrate	2.2 ± 9.5	16.5 ± 4.7	11.7 ± 6.3	37.0 ± 8.3	23.9 ± 10.6	94.2 ± 1.8	99.0 ± 0.8
iso-Butyrate	85.0 ± 2.7	99.6 ± 1.0	94.2 ± 1.1	94.9 ± 4.8	55.2 ± 3.1	100	100
n-Valerate	−6.0 ± 8.7	25.2 ± 2.6	13.9 ± 5.3	68.1 ± 7.5	16.3 ± 8.7	98.7 ± 0.8	100
iso-Valerate	30.4 ± 12.6	65.2 ± 1.8	47.4 ± 5.1	2.3 ± 83.4	26.9 ± 11.5	98.8 ± 1.1	100
Total VFAs	16.9 ± 6.7	64.2 ± 2.1	58.3 ± 3.3	73.5 ± 4.9	57.7 ± 6.7	89.3 ± 1.0	98.9 ± 0.4

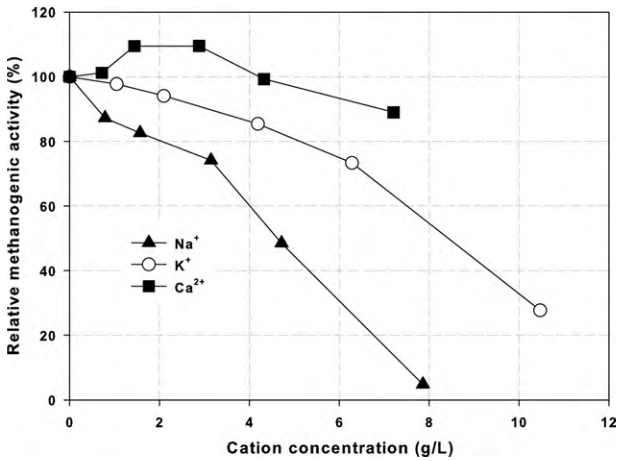

Fig. 5. Relationship between methane production and cation concentrations in batch anaerobic digestion of piggery wastewater containing Na^+, K^+ and Ca^{2+}.

3.3. *Effect of different cations on anaerobic digestion of piggery wastewater*

In order to determine the effect of cations associated with the alkalis used for pH adjustment during ammonia stripping pretreatment on methane production, batch anaerobic digestion was carried out by adding different amounts of NaCl, KCl and $CaCl_2$ to the raw piggery wastewater. Fig. 5 shows the effects of different alkaline metals (Ca^{2+}, K^+ and Na^+) on the methanization of piggery wastewater. Potassium and sodium demonstrated the similar inhibitory actions with increasing cation concentrations. In terms of IC_{50} (the inhibitory concentration causing 50% reduction in microbial activity), sodium (4.6 g/L of Na^+) was more inhibitory than potassium (8.4 g/L of K^+), which seemed to be contradictory to the above results (Fig. 1A and Table 3) obtained from continuous experiments, where sodium appeared less inhibitory than potassium. The difference might be due to the different operation modes (batch versus continuous). It was often reported that microbial consortia acclimated to high levels of sodium and potassium in the continuous systems [36,37], in which case acclimation behavior could result in different inhibitory levels. Similar inhibitory levels were reported by Feijoo et al. [37], where a sodium concentration higher than 5.0 g/L inhibited anaerobic microbial activity.

As repeatedly mentioned above, the pH of piggery wastewater is recommended to be alkaline for high ammonia removals. Due to the strong buffering capacity of piggery wastewater, a large amount of alkali was needed for increasing pH. For example, for obtaining pH 9.5 and pH 10 of piggery wastewater before air stripping, 4.49 and 6.44 g/L of Na^+, respectively, were added as NaOH. This dosage of NaOH was compatible with Yang et al. [38], where the pH of raw wastewater was adjusted to pH 10.25 using 6 M NaOH, and the final sodium concentration in the wastewater was 4.3 g/L. In the continuous experiment, the daily feeding caused a gradual buildup of cation in the digester. After prolonged operation, the cation concentration in the digestate would approach the level in feeding substrates. According to Fig. 5, 4.49 and 6.44 g/L of Na^+ in Na9.5 reactor and Na10 reactor reduced the methanogenic activity by 47.8% and 75.4%, respectively. Similarly, 4.05 and 7.43 g/L of K^+ were in K9.5 and K10 reactors would decrease the methanogenic activity by 14.0% and 39.2%, respectively. Based on these observations, it was highly probable that the low methane production rate and incomplete organic conversion found in NaOH and KOH added piggery wastewater might, at least, be partially explained by cation toxicity.

This cation toxicity was also observed elsewhere. The addition of $Mg(OH)_2$ or $MgCl_2{\cdot}6H_2O$ and Na_2HPO_4 to the anaerobic reactors resulted in significant reduction in the biogas generation [39]. Li and Zhao [18] also reported that struvite precipitation resulted in a high salinity due to the formation of NaCl as a byproduct, where an equivalent amount of 8.375 g NaCl would be generated to precipitate 1.0 g NH_4^+-N from the leachate if struvite was formed using Na_2HPO_4.

However, calcium ions showed different effects on anaerobic digestion of piggery wastewater (Fig. 5). In a broad range of dosage, calcium ion did not significantly inhibit methanogenic activity. Up to 7.2 g/L of Ca^{2+}, 89.0% of methanogenic activity was maintained, with the optimum activity of 109.5% in the range of 1.44–2.88 g/L of Ca^{2+}. Ahn et al. [26] reported that the addition of 3 g/L of Ca^{2+} yielded the best performance, and the 5–7 g/L of Ca^{2+} showed an inhibitory effect on batch anaerobic digestion of piggery wastewater. On the contrary, Jackson-Moss et al. [40] reported that, in a 9-L upflow anaerobic sludge blanket (UASB) reactor semi-continuously fed with a synthetic waste, a calcium concentration of up to 7.0 g/L had no inhibitory effect on anaerobic digestion. Even though the different inhibitory levels were reported, it seemed clear that Ca^{2+} was less inhibitory than the other two alkaline metal ions, Na^+ and K^+.

In general, the soluble forms of cations are more inhibitory than insoluble form. Detoxification could be made by precipitating the inhibitory cations from aqueous phase. Since the univalent cations of Na^+ and K^+ have high solubilities in the aqueous phase, the soluble cation concentrations may not be changed during ammonia stripping and subsequent anaerobic digestion process. However, the divalent ion like Ca^{2+} could be removed from aqueous phase by precipitation with long chain fatty acids, hydroxide, and carbonate or bicarbonate [26,40]. In our study, when 4.0 g/L of $CaCl_2$ (1.4 g/L of Ca^{2+}) was added to digestate, a heavy and fluffy precipitation was observed, and the soluble Ca^{2+} sharply decreased below 0.1 g/L of Ca^{2+}. In the experiments carried out by Ahn et al. [26], the low levels of soluble calcium (0.08–0.38 g/L of Ca^{2+}) were also found when dosing 1, 3, 5, and 7 g/L of Ca^{2+} using calcium chloride. Ca^{2+} did not significantly cause the precipitation of volatile fatty acid from aqueous phase (data not shown), suggesting that the methane production would not decrease due to the loss of VFA. However, more attentions must be paid due to the fact that additional sludge might be generated from the precipitation of calcium ions with other substances like carbonate.

4. Conclusions

It was observed that anaerobic digestion of piggery wastewater was enhanced by ammonia stripping pretreatment. However, the alkali types and dosage employed in ammonia stripping for pH adjustment had profound impacts on subsequent anaerobic digestion. When using sodium hydroxide or potassium hydroxide for pH adjustment during ammonia stripping process, inhibitory effects on anaerobic digestion of piggery wastewater in semi-continuous mode were noticeably found, as indicated by the low methane yield and high level VFAs in the effluent. This inhibition was attributed to the cation toxicity, as proved by batch anaerobic assay in the presence of NaCl, KCl and $CaCl_2$. However, lime as an alkali for pH adjustment during ammonia stripping process, at tested conditions (pH 9.5 and pH 10), significantly enhanced anaerobic digestion of piggery wastewater without detectable inhibition in terms of methane productivity and yield, and organic removals (VS, COD and VFAs).

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