Comparative Study of Enhanced Biogasification from Ammonia-Rich Swine Manure by Wheat-Rice-Stone Addition and Ammonia Stripping

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Abstract

Anaerobic digestion as an attractive waste treatment method for renewable energy production has been received considerable attention worldwide. However, when using anaerobic digestion to treat ammonia-rich substrate, ammonia will be released and accumulated during the process. Due to the high ammonia concentration, it is difficult to anaerobically digest ammonia-rich waste for high energy recovery in practice. In order to avoid the inhibition of ammonia, development of ammonia removal method for higher biogas production is in an urgent need. In this study wheat-rice-stone (WRS) addition and air stripping were used for mitigating ammonia inhibition to anaerobic process, aiming at realizing enhanced biogas production.

This research investigated the effect of WRS addition on mesophilic anaerobic fermentation for methane production from swine manure under high ammonia nitrogen level (5,145 mg-N/L) in addition to exploring its possible mechanisms involved. Results show that addition of WRS could not only effectively increase methane production by 72% from 82.8 (control) to 142.7 ml/g-VS but also remarkably shorten the effective biogasification period from 40 (control) to 20 days. In addition, WRS addition could promote the degradation of n-HBu and slow down the accumulation of other VFAs species, achieving much faster volatile fatty acids (VFA) utilization rate and better pH maintaining capability. More specifically, the existing and released ions especially Ca^{2+}, Mg^{2+}, and $Fe^{3+/2+}$ were supposed to form precipitates (like struvite and Fe-precipitates) with NH_4^+ and PO_4^{3-} rich in the fermentation liquor, probably contributing a lot to the decreased ammonia concentration and enhanced biogasification under WRS addition.

In addition, the feasibility of ammonia stripping as a pretreatment method for dry anaerobic digestion of swine wastes (SW) was investigated, including the effect of pH level on ammonia stripping under dry condition (total solid >35%), and the effect of different ammonia stripping conditions on subsequent dry anaerobic digestion. The results indicated

that ammonia stripping at 10.2 resulted in the highest ammonia removal (90.1%), and 85.0% of ammonia removal was achieved at pH8.8. However, adjusting the pH to 10.2 brought about a decrease of VFAs. After ammonia stripping pretreatment, the subsequent dry anaerobic digestion (at total solid of 20%) of air stripped SW was carried out. All stripped SW showed a higher biogas production potential than the raw SW. Especially after ammonia stripped at pH8.8, the biogas yield was 74.8 ml/g-VS, which was almost the same with that obtained after air stripping at pH10.2 (71.0 ml/g-VS). The two yields were 172% and 158% higher respectively than the control (27.5 ml/g-VS).

Finally, a comparison of the performance and efficiency between WRS addition and ammonia stripping as a pretreatment method for anaerobic digestion of ammonia-rich swine wastes was carried out. The result showed that WRS addition and air stripping digestion system significantly increased both biogas yields and volumetric biogas productivity compared to the control. The highest biogas yield of 269 ml/g-VS was obtained after WRS addition, and the highest volumetric biogas productivity of 12,150 L/m^3 estimated after air stripping.

Based on the above results, both WRS addition and air stripping could improve the biogas production from ammonia-rich SW. The mechanism of WRS addition under high ammonia level anaerobic digestion which was investigated in the study provided the important information on mechanism of material addition method for anaerobic digestion. Furthermore, the study proved air stripping was a possible solution for ammonia removal and recovery from SW for dry anaerobic digestion of ammonia-rich SW.

Keywords: ammonia-rich waste, wheat-rice-stone, air stripping, anaerobic digestion, ammonia inhibition

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1. Introduction

1.1. Environmental problems caused by swine wastes and applicable technologies

In Japan, annual livestock manure production is about 82.95 million tons, in which swine manure accounts for about 27% (MAFF, 2013). These abundant swine wastes (SW) brought out severe environmental problems such as odor problems, attraction of insects, rodent and other pests, release of animal pathogens, contamination of surface and groundwater, deterioration of biological structure of the earth and catastrophic spills (Nasir et al., 2012).

Nowadays, anaerobic digestion as an attractive waste treatment method for renewable energy production has been received considerable attention worldwide. This biotechnology has been successfully applied in the treatment of various organic wastes. The renewable energy produced from anaerobic digestion, namely biogas, is regarded as a promising candidate for fossil fuels. However, when using anaerobic digestion to treat ammonia-rich substrate, ammonia nitrogen released during this process will be accumulated (Abouelenien et al., 2010). The ammonia-rich organic matters, such as manures and some food wastes, with large amount of annual output are urgently needed to be disposed (Jiang et al., 2013). Due to the high ammonia accumulated, it is difficult to treat ammonia-rich waste by using anaerobic digestion for high energy recovery in practice (Procházka et al., 2012). Liu and Sung (2002) reported that a low ammonia concentration range of 50 – 200 mg/L was favorable for microbial activity in the investigated anaerobic degradation processes. Rajagopal et al. (2013) also suggested an optimal ammonia concentration could enhance the buffer capacity of methanogenic medium in anaerobic digestion and thus increased stability of the digestion process. It is noteworthy that a high concentration of ammonia will lead to inhibited microbial activity and low biogas production, ultimately resulting in failure of anaerobic digestion. In addition, compared with ionized form of ammonium, a large amount of unionized free ammonia is more toxic to microorganisms since it diffuses more rapidly

through cell membrane of the microorganisms (Ho and Ho, 2012).

Therefore, in order to alleviate the ammonia inhibition, development of ammonia removal methods for higher biogas production is in an urgent need. Numerous attempts have been tried to decrease or remove ammonia during anaerobic digestion process, such as dilution with water, acclimation of microbial consortia, or by using adsorption, membrane, air stripping and chemical precipitation approaches, etc(Bi et al., 2014; Kotsopoulos et al., 2008; Laureni et al., 2013; Molino et al., 2013; Niu et al., 2013; Zhang and Jahng, 2010).

1.2. Ammonia inhibition in anaerobic digestion of swine wastes

Anaerobic digestion can be divided into four steps: hydrolysis, acidogenesis, acetogenesis, methanogenesis (Fig 1.1) (Batstone et al., 2002). In the first step, solid complexes are decomposed into soluble substrates (e.g. carbohydrates, lipids and proteins). In the second step, proteins, lipids, and carbohydrates are hydrolyzed to amino acids, long-chain fatty acids, and sugars, respectively. Then, amino acids and sugars are fermented to produce volatile fatty acids (VFAs), hydrogen and carbon dioxide in acetogensis. In the final step, methane can be produced in the methanogenesis. During the anaerobic process, ammonia is mostly produced through the degradation of proteins and amino acids. The anaerobic process is often limited by slow hydrolysis rate mainly due to the high level of ammonia in the fermentation liquor when using anaerobic digestion to treat ammonia-rich substrate. Ammonia is originated from the decomposition of proteins and urea, leading to lower biogas yield (Batstone et al., 2002). Methanogens are reported to be sensitive to ammonia. A concentration of total ammonia nitrogen (TAN) around 1,700 – 1,800 mg/L could result in failure of a high rate digester, and partial inhibition has also been discerned in anaerobic digestion of swine manure at TAN of 3,000 mg/L (Chen et al., 2008; Yenigun and Demirel, 2013). Procházka et al. (2012) claimed that the activity of methanogens ceased when ammonia nitrogen concentration was about 4,200 mg/L.

Free ammonia is considered as the main component which could inhibit methanogenesis (Chen et al., 2008). Hansen et al. (1998) investigated the effect of ammonia on anaerobic digestion of swine manure. The results indicated when the free ammonia concentration was more than 1.1g-N/L, the anaerobic digestion was inhibited. In addition, the mechanism of ammonia inhibition was attributed to the elevated ammonia levels resulting in the change of intracellular pH, increase in maintenance energy requirement, depletion of intracellular potassium, and inhibition of specific enzyme reactions (Wittmann et al., 1995). It has been pointed out that aceticlastic methanogens are more sensitive to ammonia compared with hydrogenotrophic methanogens (Fotidis et al., 2013). The influence of ammonia concentration on the methanogenic pathway and on the methanogenic composition should be further examined.

Chen et al. (2008) extensively summarized various inhibition of anaerobic digestion process with ammonia as an inhibitor. Yenigün and Demirel (2013) reviewed the research works of ammonia inhibition on anaerobic processes including effect of digestion temperature, microbiology, and energy recovery, etc. In addition, Rajinikanth et al. (2013) discussed not only the ammonia inhibition of anaerobic processes but also their mitigating strategies. Regarding ammonia inhibition in anaerobic digestion, however, limited information is available on reviewing the corresponding removal methods. As it is known, the removal of ammonia from anaerobic feedstock is very important for achieving high biogas yield. On the other hand, compared with the mitigating strategies, the recovery of ammonia as available resource is possible through ammonia removal.

1.3. Efficient methods for ammonia removal in anaerobic digestion

Various techniques have been investigated to remove and/or recover ammonium from nitrogen-rich waste such as air stripping, chemical precipitation, ion exchange or adsorption, electrodialysis, membrane and microbial fuel cells, etc (Lei et al., 2007; Marti, 2008; Tada et

al., 2005; Meabe et al., 2013; Kuntke et al., 2012; Desloover et al., 2012). In recent studies, the main approaches for ammonia removal in anaerobic digestion are associated with ammonia stripping, chemical precipitation, adsorption and membrane technology.

1.3.1. Membrane

Membrane technology has been widely used for ammonia removal in wastewater treatment. This technology allows a gaseous transfer between two liquid phases. The microporous hydrophobic membrane separates an ammonia-rich feed and an acidic absorption solution to achieve this mass transfer. The gas filled pores of the membrane are the actual transfer area. The difference in NH_3 partial pressure between the two liquid phases is the driving force for the mass transfer (Hasanoğlu et al., 2010). Waeger and Fuchs (2012) applied hollow fiber membrane contactors for ammonia removal from anaerobic digestate. The membrane fibers were simply submerged into the digestate and the performance was evaluated at temperatures ranging from 20 to 40℃ and pH of 8.6 - 10.0. The results suggested this method could be applied efficiently for the treatment of particle rich solutions at a high ammonia level of 3,000 - 3,500 mg/L, with removal rates from 80% up to 98.5%. However, up to now, there are only a few studies applied the membrane technique to counteracting ammonia inhibition for biogas production. Lauterböck et al. (2012) tested the feasibility of membrane contactors for continuous ammonia removal in anaerobic digestion of slaughterhouse wastewater (6,700 - 7,300 mg/L of ammonia) and to alleviate ammonia inhibition. Additionally, Lauterböck et al. (2014) successfully used the submerged membrane contactor for continuous ammonia extraction from a digester treating slaughterhouse wastewater at different organic loading rates (OLR). This leads to an enhanced methane yield, less VFAs accumulation, improved COD degradation and a more diverse microbial community. This is also true under higher organic loading rates and increased sulfide concentrations. Due to the sulfuric acid absorption solution used in membrane contactor, it is

possible to recover ammonia from ammonium sulfate ($(NH_4)_2SO_4$).

1.3.2. Adsorption

Compared with some complicated systems, adding materials with high adsorption capacity such as zeolite, activated carbon and mordenite into anaerobic reactors seems a simple method to alleviate related inhibitory compounds for enhanced biogas production (Wang et al., 2011; Akram and Stuckey, 2008; Tada et al., 2005).

Among these adding materials, zeolite addition has been reported to be an effective way to mitigate ammonium inhibition due to its high adsorption capacity and selectivity for ammonium during the digestion process (Ho and Ho, 2012; Montalvo et al., 2005). Meanwhile, zeolite has a great capacity for metal adsorption and this property can be useful for removing toxic materials that inhibit the microorganisms (Montalvo et al., 2012). Attributed to the above-mentioned properties, zeolite addition could enhance biogasification performance. In addition, several studies has claimed that natural zeolite is favorable for the immobilization of microorganisms in different reactor configurations (Wang et al., 2011; Umaña et al., 2008; Weiß et al., 2013). Wang et al. (2011) used a fixed zeolite bioreactor to enhance anaerobic digestion of ammonium-rich SW (NH_4^+-N = 3,770 mg/L). It was found that the bioreactor significantly shortened startup time, and obtained methane yield more than 2-fold than the reactor without zeolite or with sunken zeolite. Furthermore, ammonium concentration was indeed reduced during the anaerobic digestion. Lin et al. (2013) investigated VFAs evolution, cation variation, and related microbial diversity during anaerobic digestion of swine manure under 60 g/L of natural zeolite addition. Results showed that zeolite addition had a faster start-up and better performance, especially under high ammonium concentrations, achieving 20% increased biogas yield (356 mL/g VS_{added}).

Tada et al. (2005) investigated the effect of different inorganic additives (including natural and synthetic zeolites like mordenite, clinoptilolite, zeolite 3A and zeolite 4A, and

other additives like manganese oxides such as hollandite and birnessite) on batch anaerobic digesters of ammonium rich organic sludge (4,500 mg N/L). Noteworthily, the addition of zeolites resulted in significant ammonium (NH_4^+) removal from the organic sludge. Natural mordenite also enhanced methane production by 1.7-fold. The released Ca^{2+} from mordenite enhanced the methane production through a Ca^{2+}/NH_4^+ exchange at high ammonia concentration, which is effective for the mitigation of ammonia inhibition against methane production. Halim et al. (2010) made some attempt on the combination of activated carbon and zeolite as a natural ion exchanger in composite media which provided both hydrophobic and hydrophilic surfaces for organic and inorganic substances removal, especially ammonia removal. Their results showed that ammonia adsorption was the best on composite media (24.39 mg/g), followed by zeolite (17.45 mg/g) and activated carbon (6.08 mg/g).

1.3.3. Chemical precipitation

One of the proposed solutions for ammonia removal is to recover nitrogen by using crystallization (chemical precipitation), e.g. magnesium ammonium phosphate (MAP) precipitation ($MgNH_4PO_4 \cdot 6H_2O$) (Huang et al., 2011). Generally, MAP known as struvite is a kind of slow-release valuable fertilizer (Uludag-Demirer et al., 2005; Batstone et al., 2002). Additionally, controlled precipitation and recovery of struvite could also decrease maintenance costs of wastewater treatment systems by eliminating undesirable struvite precipitation in pipes and pumps (Doyle and Parson, 2002). Ammonia recovery as struvite from anaerobic digester could be interpreted by the following chemical reactions (Türker and Celen, 2007; Yetilmezsoy and Sapci-Zengin, 2009):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4\ 6H_2O \downarrow$$

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4\ 6H_2O \downarrow + H^+$$

The above reactions reveal that the success of MAP precipitation depends on two main factors: the pH of the solution and Mg^{2+}: NH_4^+-N: PO_4^{3-}-P ratio. Regarding the optimum pH

range for MAP precipitation, many researches have made efforts on it, and the optimum range of pH was considered between 8.5 and 10.5 for MAP precipitation (Altinbas et al., 2002; Booker et al., 1999; Nelson et al., 2003; Ohlinger et al., 1998; Ryu et al., 2008; Stratful et al., 2001; Wilsenach et al., 2007; Zhang, et al., 2009). On the other hand, the amount of magnesium and phosphate in waste streams, like in pig manure, is usually insufficient to remove ammonia. Thus, in order to ensure the formation of MAP precipitation, it is necessary to add magnesium and phosphate (Chimenos et al., 2003; Romero- Güiza et al., 2014). Yetilmezsoy and Sapci-Zengin (2009) investigated the Mg^{2+}: NH_4^+-N: PO_4^{3-}-P stoichiometric ratio for recovery of high ammonium nitrogen (NH_4^+-N = 1,318 mg/L) from UASB effluent. It was found that the maximum NH_4^+-N removal (85.4%) was achieved at a pH of 9.0 with the addition of magnesium and phosphate at the ratio (Mg^{2+}: NH_4^+-N: PO_4^{3-}-P) of 1:1:1. Meanwhile, the maximum removal efficiencies of about 54% for COD and about 50% for residual color were obtained under the same experimental conditions. Although above-mentioned studies have successfully obtained a high ammonia removal efficiency via adding magnesium and phosphate to form MAP precipitation for the treatment of poultry manure wastewater, coking wastewater and landfill leachate respectively (Yetilmezsoy and Sapci-Zengin, 2009; Zhang et al., 2009; Huang et al, 2014), in practice, the high cost of magnesium salts and phosphate consumption is a barrier for application of the kind of chemical precipitation.

Therefore, the cost-effective chemical precipitation and recycle technology for ammonia was investigated in recent studies (Quan et al., 2010; Rahman et al., 2014). In a lab-scale study, Zhang et al. (2009) found that MAP pyrolysate could be formed under the specified conditions with a hydroxyl to ammonium molar ratio of 2:1 at 110℃ for 3 h. Magnesium sodium phosphate ($MgNaPO_4$) was the main component of the above-mentioned pyrolysate. In addition, at pH of 9.5, the pyrolysate could be recovered as a magnesium and phosphate source. Huang et al. (2014) removed ammonia from landfill

leachate by MAP precipitation by using cheap phosphate and magnesium sources. 83% of ammonia removal was achieved by using magnesium oxide with an Mg:N:P molar ratio of 3:1:1. Additionally, the results indicated that compared to pure chemicals, using cheap magnesium oxide and waste phosphoric acid could save 68% of chemical costs. Furthermore, Romero-Güiza et al. (2014) achieved an improved anaerobic digestion of pig manure by adding a stabilizing agent formulated with low-grade magnesium oxide into the same reactor. The results indicated that compared with the reference digester, the addition of 5 and 30 kg/m^3 of stabilizing agent resulted in a 25% - 40% increase in methane production.

In a pilot-scale experiment, Song et al. (2011) applied MAP precipitation accumulation devices in a sequencing batch reactor (SBR) and a continuous-flow reactor, and achieved nutrients removal and recovery from anaerobically digested swine wastewater. This process was carried out through CO_2 stripping for pH increase and without any alkali and Mg^{2+} addition. The results showed that in the two reactors, during the long-term operation of 247d, 85% of phosphorus was removed and recovered.

1.3.4. Ammonia stripping

Air stripping has been successfully used for the purification of groundwater and wastewater containing volatile compounds (FRTR, 2014). In addition, air stripping has been reported as an economical and efficient chemical engineering technology for removing ammonia from poultry litter leachate (Bonmatí and Flotats, 2003). During the air stripping, the chemical equilibrium of ammonia and dissolved nitrogen was involved as the following:

$$NH_4^+ \leftrightharpoons NH_3\uparrow + H^+$$

When pH $<$ 7, all the ammonia will be soluble ammonium ions. Above pH12, all the ammonia will be present as a dissolved gas. When the pH is in the range of 7 - 12, both ammonium ions and dissolved gas exist together. The content of dissolved gas increases with the increase in temperature and pH. Higher temperature and pH is favorable for

ammonia removal from solution. In order to maintain a stable stripping system, the pH and temperature should be controlled at constant (Zhang et al., 2012). The process could not be affected by toxic compounds which may disrupt the performance of a biological system (De la Rubia et al., 2010). Guštin and Marinšek-Logar (2011) applied a continuous ammonia stripping system to treat the anaerobic digestion effluent. It was reported that pH level, temperature, and amount of air had significant effects on the ammonia removal efficiency: Increased pH (lower than 10) would promote ammonium removal; Higher temperature and amount of air is beneficial for the removal efficiency; and the increase of air to liquid ratio also promotes ammonium removal, but only up to the ratio of 2,000.

Compared with air stripping, recently some trials have been attempted on using biogas for stripping, which is thought to be a promising method for direct integration with an anaerobic digestion plant. Abouelenien et al. (2009) successfully removed ammonia from thermophilic anaerobically digested chicken manure through recycling of biogas. By using this method, 80% total nitrogen of chicken manure was converted to ammonia and 82% of the produced ammonia was removed. Walker et al. (2011) investigated ammonia removal in batch anaerobic digestion of source segregated food waste by biogas stripping. The results showed that either increasing temperature, initial pH or biogas flow rate could enhance the ammonia removal rates. On the other hand, several studies used another type of stripping: sidestream stripping process for ammonia removal (Serna-Maza et al., 2014; Siegrist et al., 2005). Through this process, nitrogen can be recycled as ammonium sulphate for fertilization, meanwhile, the biogas was enhanced during the anaerobic digestion. Siegrist et al. (2005) used the process for free ammonia removal from slaughterhouse wastes after membrane separation at temperatures below 65 ℃ and pH 8.5 - 9 with NaOH addition. Serna-Maza et al. (2014) used sidestream stripping process with biogas as the stripping medium for ammonia removal in the reactors used for food waste anaerobic digestion which were operated under different conditions of temperature (55, 70, 85 ℃), pH (unadjusted and

pH 10), and retention time (2 - 5 days). They suggested an appropriate condition (a temperature ⩾70 ℃ and a pH of 10) were needed for ammonia removal. In addition, during 138 days` anaerobic digestion, 48% of the TAN was removed without any negative effects. By means of these techniques various ammonia-rich materials including food waste, animal manures and slaughter waste can be used as the candidate feedstocks for anaerobic digestion as a single substrate.

Although ammonia stripping has been proven to be technically feasible for ammonia removal, it needs to integrate a stripping operation combined with acid absorption, and re-adjust pH of the treated effluent for further applications (Jiang et al., 2014). Optimization of stripping conditions including pH, temperature, air flow, etc. is necessary for cost reduction. Raising the pH of dairy anaerobic digestion effluent to 11.0 requires 63% of more alkali than to 10.0 because of the abundance of bicarbonates in the digestate. The ammonia stripping temperature and pH were economically optimized by combining the ammonia stripping efficiency with the titration correlation.

1.3.5. Problem and challenge

Indeed, some of the above-mentioned methods exhibited high efficiency of alleviating ammonia inhibition to anaerobic fermentation. However, these methods are expensive to be applied in practice. Moreover, little research work can be found on the effect of higher level of ammonia (> 5,000 mg-N/L) on anaerobic process, which will be encountered if further increasing organic loading rate or total solids content so as to achieve high rate or high solids anaerobic fermentation of swine manure. Compared with the above-mentioned methods, a few researchers tried the addition of wheat-rice-stone (WRS), namely porphyritic andesite into anaerobic reactors, to enhance the biogasification performance (Kao et al., 2003; Li et al., 2009; Wang et al., 2012). WRS with porous structure is an abundant material in Asia, possessing excellent adsorption ability and bioactivity by cation dissociation (Kao et

al., 2003). Li et al. (2009) reported that WRS could adsorb VFAs, elevate pH level, and accelerate organics degradation during anaerobic digestion of soybean residue. Results from our previous research (Wang et al., 2012) indicated that modified WRS could effectively mitigate ammonium inhibition (3,550 mg/L), possibly due to its high adsorption capacity and selectivity for ammonium. Addition of WRS into anaerobic reactors has the following advantages like low cost, non-chemicals addition and handleability. Up to now, however, whether this WRS application is feasible for coping with higher ammonia conditions or not remains unknown. Furthermore, due to the complexity of anaerobic process and variety of feedstocks, the real mechanisms involved in the enhancement of biogasification by WRS addition are still unclear.

On the other hand, although ammonia stripping has been proven to be favorable for ammonia removal from animal manure, few research works could be found on the feasibility ammonia stripping as a pretreatment method for dry anaerobic digestion (DAD) of SW. Up to now, only Abouelenien et al. (2009) performed ammonia stripping under high solid content (TS 25%). In order to improve the efficiency of ammonia stripping, they paved a layer of chicken manure which was 1 cm thick, and the ammonia removal was 85.5% for 1 day, before DAD.

1.4. Objectives and originality of this study

As it is known, ammonia removal is very important to obtain high biogas yield in anaerobic digestion. Compared to the mitigating strategies, the recovery of ammonia as available resource is prospective through ammonia removal. Therefore, the major objectives of this study are: (1) to test the effect of wheat-rice-stone (WRS) addition on biogasification of swine manure at ammonia nitrogen > 5,000 mg/L (5,145 mg- N/L) by using batch experiments. The variations of biogas production, pH, ammonia concentration, soluble chemical oxygen demand (SCOD), and VFAs were monitored during the whole anaerobic

process. In addition, the major cations and anions were determined in order to estimate the possibility of precipitation reactions between/among them; (2) to investigate the feasibility of ammonia stripping as a pretreatment method for dry anaerobic digestion of swine wastes: including the effect of pH level on ammonia stripping under dry condition (TS > 35%); and effects of different ammonia stripping conditions on subsequent dry anaerobic digestion; (3) to compare the two methods for anaerobic digestion of swine wastes. A detailed comparative summary of both anaerobic digestion performance, ammonia mitigation or removal efficiency and feasibility of ammonia recovery is also included.

The originalities of this study are: (1) In this study, much higher ammonia nitrogen level (> 5,000 mg/L) was investigated under the addition of WRS. Compared to previous research works, much attention was paid in this study to the precipitates possibly formed in the fermentation liquor, with expectation of shedding light on the mechanisms of enhanced biogasification involved in the complex anaerobic process brought about by WRS addition. (2) Compared to previous studies which used air stripping at low solid content for ammonia removal, feasibility of ammonia stripping as a pretreatment method for high-solid swine wastes was evaluated. In addition, this study compared wet and dry anaerobic digestion processes with respect to the alleviation of ammonia inhibition. Up to now, little information could be found on the above mentioned two aspects.

1.5. Structure of this study

The main contents of this study were divided into three parts as follows (Fig. 1.2):

In Chapter 2, the effect of wheat-rice-stone (WRS) addition on mesophilic anaerobic fermentation for methane production from swine manure under high ammonia nitrogen level (5,145 mg- N/L) was investigated in addition to exploring its possible mechanisms involved. The variations of biogas production, pH, ammonia concentration, SCOD, and VFAs were monitored during the whole anaerobic process. In addition, the major cations and anions

were determined in order to estimate the possibility of precipitation reactions between/among them.

In Chapter 3, the feasibility of ammonia stripping as a pretreatment method for dry anaerobic digestion of swine wastes was investigated, including the effect of pH level on ammonia stripping under dry condition (TS > 35%), and the effects of different ammonia stripping conditions on subsequent dry anaerobic digestion.

In Chapter 4, a comparison of the performance and efficiency between WRS addition and ammonia stripping as a pretreatment method for anaerobic digestion of ammonia-rich swine wastes was carried out.

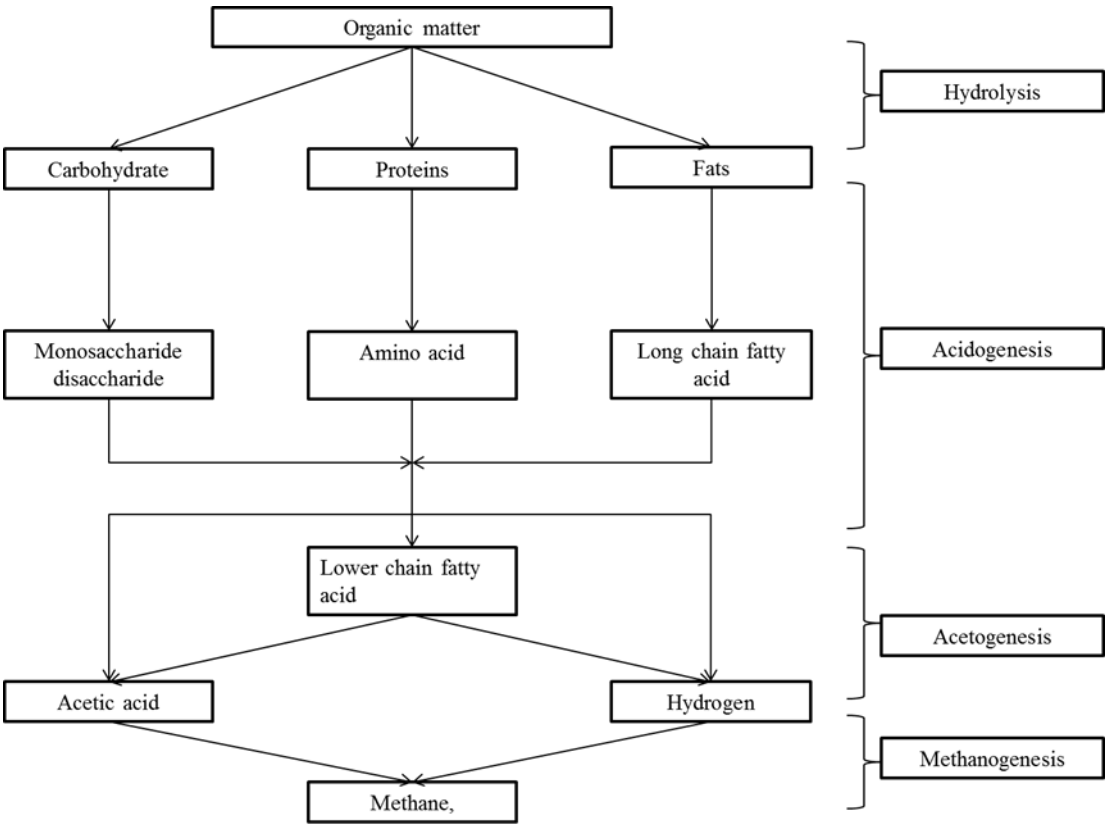


Figure 1.1 The degradation pathway of the organic matter in anaerobic digestion (Batstone et al., 2002)

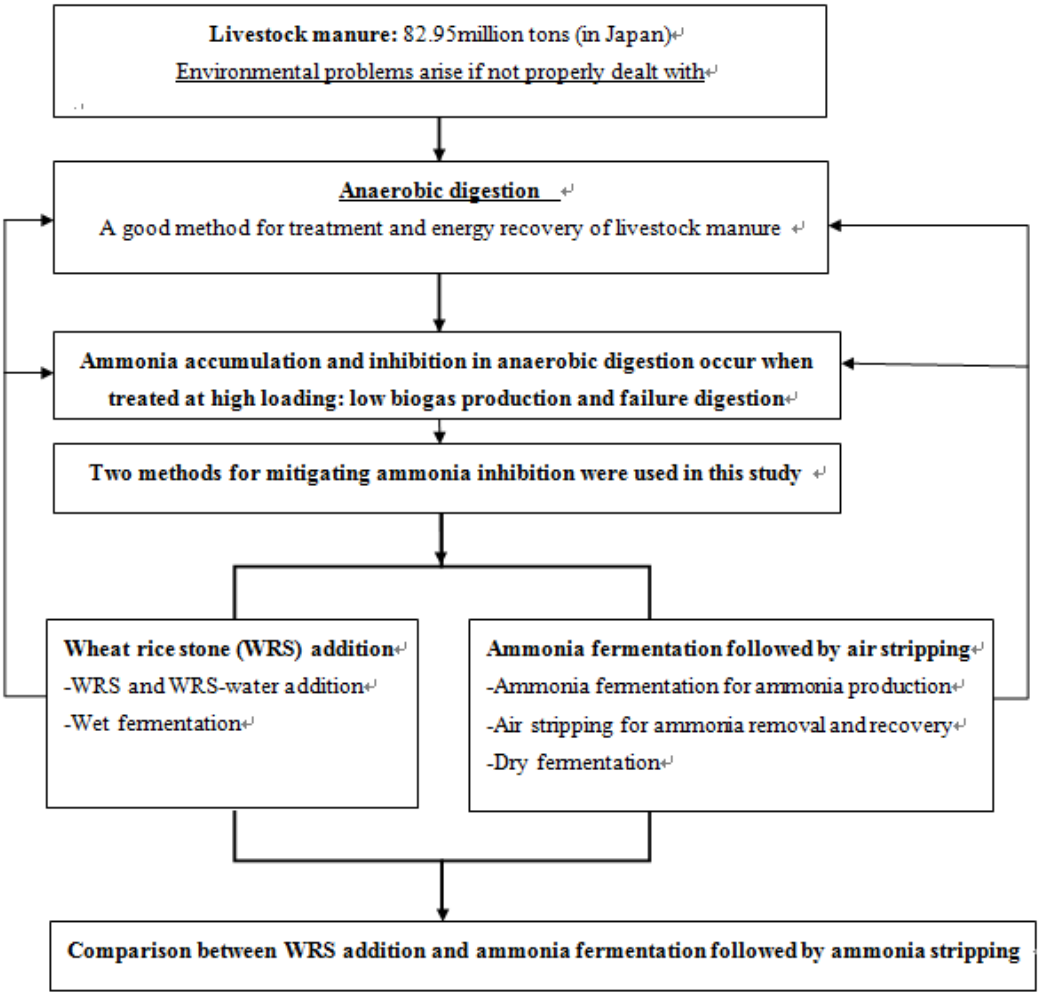


Figure1.2 The structure of this study

2. Enhanced biogasification of ammonia-rich swine manure by wheat-rice-stone addition

2.1. Introduction

The anaerobic process of swine manure is often limited by slow hydrolysis rate mainly due to the high level of ammonia in fermentation liquor, which is originated from the decomposition of proteins and urea, leading to lower biogas yield(Batstone et al., 2002).

This study tested the effect of WRS addition on biogasification of swine manure at ammonia nitrogen > 5,000 mg/L (5,145 mg-N/L) by using batch experiments. The variations of biogas production, pH, ammonia concentration, SCOD, and VFAs were monitored during the whole anaerobic process. In addition, the major cations and anions were determined in order to estimate the possibility of precipitation reactions between/among them. Due to the fact that many cations could be released from WRS during anaerobic process (Wang et al., 2012), batch anaerobic fermentation experiments with addition of WRS soaked water (WRS-water) was also conducted in parallel with WRS addition condition. Compared to previous research works, much attention was paid in this study to the precipitates possibly formed in the fermentation liquor, with expectation of shedding light on the mechanisms of enhanced biogasification involved in the complex anaerobic process brought about by WRS addition.

2.2. Methods

2.2.1. Swine manure and seed sludge

Swine manure and seed sludge (anaerobically digested sludge) in this study were collected from a pig farm located in Tokyo and the Shimodate Wastewater Treatment Plant (Ibaraki, Japan), respectively. The main physical and chemical characteristics are listed in Table 2.1. In order to elevate the ammonia nitrogen level higher than 5,000 mg-N/L after dilution of the swine manure in the following fermentation experiments, a certain amount of

NH_4Cl was added into the raw swine manure. After being mixed thoroughly, the prepared swine manure and the seed sludge were stored at 4℃ and used within one month.

2.2.2. WRS and WRS-water

WRS were obtained from Henan Province, China. Table 2.2 shows the main elements analysis by EDX on the surface of WRS. The WRS particles with size between 3 - 4 mm were used in this study. 50 gram of WRS were immersed in 1,000 ml distilled water at 35℃ for 60 days and the resultant supernatant was labeled as WRS-water in this study.

2.2.3. Experimental conditions for batch anaerobic fermentation

Batch anaerobic fermentation trials were conducted in 500 ml glass bottles with working volume of 400 ml. The effect of WRS addition on biogasification was assessed under high ammonia nitrogen level (> 5,000 mg-N/L in this study). These reactors were grouped into three kinds, namely Control, Reactor 1 (R1) and Reactor 2 (R2), respectively. All the fermentation tests started from the same initial conditions of total solids (TS), volatile solids (VS), total ammonia nitrogen (TAN), and chemical oxygen demand (COD) concentrations by diluting the swine manure with distilled water or WRS-water, about 2.1%, 1.8%, 5,145 mg-N/L and 35,945 mg/L, respectively. Each reactor was inoculated with 20% (v/v) of the seed sludge, and all the initial pH values in the reactors were adjusted to 7.0 with 1N HCl or NaOH. The differences among the three group reactors were as follows: (1) only swine manure (diluted with distilled water) in the Control, (2)swine manure thoroughly mixed with the designated amount of WRS (50 g/L) and diluted with distilled water in R1, and (3)swine manure diluted with WRS-water in R2 reactors, respectively. All these reactors were placed in a temperature-controlled water bath (35 ±2℃). Every day the reactors were manually shaken for 2 min twice at fixed time points, and the fermentation process lasted for 60 days based on our preliminary experiments. These batch experiments were conducted in

duplicate and average values were taken for performance assessment.

2.2.4. Analysis and calculation

Determinations of TS, VS, soluble COD (SCOD), TAN and phosphorus (PO_4-P) were in accordance with the Standard Methods (APHA, 2005). Total phosphorus (TP) was determined after the sample being digested with a mixture of HNO_3 and $HClO_4$ (1:1, v/v). Free ammonia nitrogen (FAN) concentration was estimated by using Eq. (2-1) based on the measured TAN concentration and pH value (Anthonisen et al., 1976).

$$[FAN](mg\text{-}N/L)/[TAN](mg\text{-}N/L)=10^{pH}/(10^{pH} + e^{6344(273+T)}) \quad (2\text{-}1)$$

where T is the temperature in degree Celsius (35℃ in this study).

pH was measured with a pH meter B-211 (HORIBA, Japan). Volatile fatty acids (VFAs) were quantified by gas chromatography (Shimadzu GC-14B) equipped with a flame ionization detector and a Unisole F-200 30/60 column (3.0 mm in diameter and 2.0 m in length). 1 μl of sample was injected with the carrier gas N_2. The injector, detector and column temperatures were kept at 200 ℃, 200 ℃ and 160 ℃, respectively. For determining the concentrations of metals in solid and liquid fractions, the sample was digested with HNO_3 and H_2O_2 according to the method proposed by USEPA (1996), and then the filtrate was used for quantification of metals by using ICP-OES (Optima-7300 V, Perkin Elmer) and ICP-MS (ELAN DRC-e, PerkinElmer).

Biogas produced from each reactor was collected using a 50ml plastic syringe, and the volume was read directly from the scale on the syringe. Biogas composition was analyzed by means of gas chromatography (GC-8A, SHIMADZU, Japan) with nitrogen as carrier gas, which was equipped with a thermal conductivity detector (80℃) and a Porapak Q column(60℃).

In this study, besides biogas or methane yield, effective biogasification period (τ_e, day) and averagely effective biogas production rate (r_e, ml/g-VS·d) are also used to indicate the

performance of each reactor, which can be used for reactor design in practical application and are calculated as Eqs. (2-2) and (2-3), respectively.

Effective biogasification period (τ_e, day) $=N_{80}^{th}$ (day) – S_0^{th} (day) (2-2)

Effective biogas production rate (r_e, ml/g-VS·d)=Total biogas yield (ml/g-VS) /τ_e(day) (2-3)

in which the N_{80}^{th} day is the day when the accumulative biogas production amounts to 80% of the total biogas production during the operation, and the S_0^{th} day refers to the duration of lag phase period or the day when biogas starts to produce from the reactor.

2.3. Results and discussion

2.3.1. Overall performance of biogasification

Figs. 2.1 - 2.3 shows the changes in daily biogas production, percentage of accumulative biogas production to the total amount, and methane content in the reactors during 60 days' operation. Seen from Figs. 2.1 and 2.2, to some extent the microorganisms in the seed sludge could be acclimated to high level of ammonia (5,145 mg-N/L in this study) after about 12 days (lag phase). No significant difference was found among the three group reactors in regard of biogasification during this period. Although very little biogas was detected from each reactor before day 12, most probably due to the inhibition of high ammonia level, the anaerobic bacteria in the reactors seemed to be alive from day 12 on. During the subsequent operation period, the three group reactors behaved much differently in the advancement of biogasification. In the Control reactors, biogas production increased gradually before day 40 and increased quickly to its maximum daily biogas production rate, averagely 19.9 ml/g-VS·d around day 42, and then declined till the end of experiment. In contrast to the Control reactors, R1 and R2 reached their maximum daily biogas production much earlier, around day 18 and day 30, about 20.6 and 21.9 ml/g-VS·d in average, respectively (Fig. 2.1). Much difference was also observed in the effective biogasification

period (τ_e, time duration needed for producing 80% of total biogas yield, Fig. 2.2): about 40, 20, and 30 days for the Control, R1 and R2, respectively. In addition, R1 and R2 yielded 269 and 252 ml/g-VS of biogas during the 60 days' trials, increased by 15% and 8% respectively compared with the biogas yields from the Control (233 ml/g-VS). Furthermore, the effective biogas production rates in R1 and R2 were respectively 13.4 ml/g-VS·d and 8.4 ml/g-VS·d, increased by 131% and 45% in comparison to the Control reactors (5.8 ml/g-VS·d).

As for methane content in the biogas, R1 and R2 achieved 60% on day 29 and day 31, respectively, and from then on the methane content in these reactors kept between 60 - 62% and 60 - 74%, respectively. The methane content of the Control reactors, however, reached 60% on day 44. The methane yields were 82.8, 142.7, and 147.2 ml/g-VS for Control, R1 and R2 reactors, respectively.

The above results show that R1 (with WRS addition) exhibited much better performance than the Control reactors in terms of biogas and methane production, achieving higher and faster biogasification even under > 5,000 mg-N/L of ammonia conditions. Specifically, WRS addition shortened the effective biogasification period from 40 days (Control) to 20 days (R1), greatly reducing the reactor volume when using anaerobic digestion to treat the same amount of swine manure.

2.3.2. Changes in ammonium and pH

Ammonia nitrogen is present either as free ammonia or/and as ammonium ion in wastewater depending on pH and temperature of the wastewater. As shown in Fig.2.4, TAN concentration fluctuated in a similar way in the reactors, especially in the Control and R2: slightly increased during the initial 10 days and then decreased gradually to some extent. The lowest ammonia concentrations in the Control and R2 were 4,040 and 3,930 mg-N/L, respectively on day 50. Compared to the Control and R2, R1 showed a faster decrease trend in ammonia concentration during the initial 30 days and reached the lowest value of 4,070

mg-N/L on day 28.

On the other hand, FAN increased from 60 to 150 mg-N/L in the Control during the initial 15 days, and then decreased to 20 mg-N/L on day 34. After that, the FAN increased gradually in the Control and reached to 200 mg-N/L at the end of experiment. In R1 and R2, although TAN decreased to some extent, FAN showed an increase trend along with the operation from initial 57 mg-N/L to 254 mg-N/L and 311 mg-N/L, respectively. This observation was most probably attributable to the gradual increase of pH in these reactors, from initial 7.0 to 7.7 and to 7.8, respectively (Fig. 2.5). FAN of > 150mg-N/L was reported to cause methanogenic growth inhibition to unacclimated microorganisms (Braun et al., 1981). However, as indicated by Eq. 1, FAN concentration is directly related with the pH value of substrate when temperature is constant: lower pH value would result in a lower concentration of free ammonia (Anthonisen et al., 1976; Rajagopal et al., 2013). Although FAN in the Control was always lower than those in R1 and R2 after day 20, its higher TAN concentration still seemed to inhibit the methane production (Fig. 2.4 and Fig. 2.3). Restated, the variation of FAN is coincident with the changes of pH in the reactors.

The above results imply that WRS addition favors the maintaining of pH and prevents excessive acidification in the reactors (Fig. 2.5), which is in agreement with the finding of Cheng et al. (2010) who claimed that WRS addition was beneficial for VFA adsorption and elevation of pH level during hydrolysis and acidogenesis of solid food waste. In addition, R2 (with WRS-water addition) also exhibited better performance for maintaining pH value than the Control. The real reason for this phenomenon needs further investigation, which may closely relate to the ions released from WRS resulting in a better balance between acidogenesis and methanogenesis processes.

2.3.3. Effect of WRS addition on VFAs evolution and SCOD degradation during anaerobic digestion

Biogas production accompanies with the formation of VFAs throughout the anaerobic digestion of swine manure. High concentration of VFAs may cause microbial stress and low pH, ultimately leading to failure of the digester. Therefore, concentration of VFAs can be used as an important indicator of the performance of anaerobic digester (Wang et al., 1999).

Figure 2.6 shows the variation of VFAs including acetic acid (HAc), propionic acid (HPr), n-butyric acid (n-HBu), isobutyric acid (i-HBu), n-valeric acid (n-HVa), and isovaleric acid (i-HVa). Clearly, much difference was found in VFAs evolution in the reactors during anaerobic digestion under the tested high ammonia level condition.

In the Control, all the VFAs were detected to accumulate and increase to their maximum concentrations around days 20 - 30 with total VFAs being 11,000 - 12,000 mg-COD/L, much higher than those in R1 (about 9,600 mg- COD/L in total,) possibly due to the inhibition of high ammonia level to methanogens and thus lower VFAs utilization rate. In contrast to the Control, all the VFAs in R1 exhibited similar trends during the anaerobic process except HPr: firstly increased and accumulated during the initial 12 days, and then declined substantially after the biogas peak on day 18. The highest amount of total VFAs occurred on day 12 (9,600 mg- COD/L, Fig.2.6) when biogasification process started to accelerate (Figs. 2.1 and 2.2). In R2, HAc and HPr were firstly observed to decrease or utilize by the microorganisms during the initial 10-12 days, and then advanced rapidly to about 2,820 and 1,240 mg- COD/L, respectively before the appearance of biogas peak. Along with the digestion process going on, these VFAs were decreased to a great extent and totally about 440 mg- COD/L around day 40, the end of effective biogasification period for R2.

In this study, HBu (especially n-HBu) was found to be the dominant VFA species in all the reactors before the biogas peaks approached, *i.e.* day 42, day 18, and day 30 in the

Control, R1 and R2, accounting for 46 - 72%, 64 - 76%, 43 - 74%, respectively. Correspondingly, HAc, the dominant VFA usually produced from anaerobic digestion of swine manure (Lin et al., 2013), was about 10 - 33%, 8 - 11%, and 4 - 34% of the total VFAs, respectively. In addition, compared with HAc and HBu, the concentrations of HPr and n/i-HVa were relatively very low and their changes were less obvious in all the reactors.

The above results reveal that WRS addition can promote the degradation of n-HBu and slow down the accumulation of other VFAs species. On the other hand, VFAs were also found to decrease to some extent with increased biogas yield in R2 (with WRS-water addition), signaling that the ionic environment of R2 might be more favorable for methanogens to utilize VFAs than that of the Control.

It is well known that biodegradable organic substances can be reduced through conversion into methane and carbon dioxide during the anaerobic digestion, resulting in SCOD decrease in the digester. In this study, during the effective biogasification period (τ_e), the proportions of total VFAs to SCOD were 60 - 100%, 40 - 55%, and 30 - 85% in the Control, R1 and R2 reactors, respectively, probably attributable to their different VFAs utilization rates of methanogens under the tested high ammonia level condition (5,145 mg-N/L in this study). Compared with the initial SCOD concentration (about 18,700 mg/L), the final SCODs in the Control, R1 and R2 were about 4,800, 2,400, and 3,800 mg/L, namely, decreasing by 74%, 87%, and 80% after 60 days' anaerobic digestion, respectively. In fact, R1 and R2 already achieved the above-mentioned SCOD reduction performance after 30 - 32 days' operation, while during the same period of anaerobic fermentation only about 38% of SCOD reduction was obtained in the Control. The variation of SCOD in the reactors (Fig. 2.7) to a certain extent agrees with the changes in biogas production from the reactors (Fig.2.1). This observation indicate that WRS addition (R1) or some elements released from WRS (containing in WRS-water, R2) might have positive effect on the anaerobic degradation of biodegradable organic substances.

Restated, R1 exhibited the best and the fastest utilization of VFAs produced during anaerobic digestion of swine manure. According to the changes in pH, ammonia, VFAs and SCOD in the fermentation liquor of the Control, R1 and R2, this observation could be mainly contributed by the following aspects: (1) Better H^+ balance and pH maintaining ability due to improved ionic environment resulted from WRS addition; (2) Lower ammonia concentration possibly resulted from its precipitation with other cations or anions like Ca^{2+}, Mg^{2+} and PO_4^{3-} which are abundant in swine manure (Table 2.1); (3) Lower VFAs in the fermentation liquor due to their adsorption onto WRS and thus mitigated inhibition to methanogens; (4) Other factors such as metal ions contained in the swine manure or released from WRS may add some positive effects to this enhancement performance.

2.3.4 Cations profile and possible mechanisms involved in the enhanced anaerobic digestion of swine manure under high level of ammonia

According to our preliminary experiment, many cations can be released from WRS, including Mg, Ca, Fe, and Ni in addition to more than 20 trace elements (data not shown), which are necessary for microbial growth and also antagonistic to ammonium inhibition (Braun et al., 1981). In this study the prepared WRS-water mainly contained (mg/L) Na (4.7±0.3), K (3.2±0.7), Ca (50.7±6.9), Mg (10.6±2.2), Fe (33.1±0.4), Ni (0.5±0.1), and Co (0.1±0.0). As shown in Table 2.1, metals like Ca, Mg, Fe, etc were also detected in the swine manure to a certain level, which would influence the existing forms of NH_4^+ and PO_4^{3-} in the fermentation liquor (Möller and Müller, 2012).

The variation of cations and anions in the fermentation liquor was mainly dependent on three processes involved: uptake by the microorganisms for better growth, dissolution from the solid-state substances (swine manure, seed sludge and/or WRS) because of hydrolysis or dissociation and precipitation between/among the existing or produced ions due to oversaturation under the tested ionic and pH conditions. In this study, the concentrations of

main cations, i.e. Ca, Mg, Fe and Ni were observed to vary obviously during the anaerobic process as shown in Fig. 2.8.

During the lag phase period (before day 12), less variance was found in Ca and Mg contents in all the reactors. Specifically, in the Control and R2 reactors, Ca and Mg contents seemed to have a similar variation trend: decreased at first from 290 - 330 mg/L (Ca) and 60 - 75 mg/L (Mg) respectively to some extent before day 20, then increased till the appearance of biogas peak (around day 30), and thereafter decreased substantially. Compared to the Control and R2, R1 exhibited a different variation trend in Ca and Mg contents which substantially decreased near the biogas peak period (around days 15 - 20). Although some changes in concentration were detected for these two cations during the anaerobic process, the levels of Ca and Mg in the reactors kept relatively stable after biogas peaks: about 45-50 mg/L of Ca in R1 and R2, 200 mg/L of Ca in the Control and about 20 mg/L of Mg in all the reactors. That is, a larger decrease in Ca content occurred in R1 and R2 than in the Control, possibly due to that Ca is more advantageous for methanogenesis while Mg favored acidogenesis under high level of ammonia condition. This observation partially agrees with the finding of Lin et al. (2013).

Previous research revealed that Fe, Co and Ni ions were important for improving the biological activity of methanogens to avoid acidification (Karlsson et al., 2012). Among them, Ni plays an important role in the growth of methanogens and methane formation (Demirel and Scherer, 2011). Meanwhile, VFAs could be degraded effectively in presence of a certain concentration of Ni (Karlsson et al., 2012). Fig. 2.8d shows that Ni content almost varied in a similar way in these reactors: firstly increased possibly due to hydrolysis; after the lag phase, the Ni content greatly decreased because of recovered microbial activity, signaling that Ni plays a positive role in biogasification in agreement with previous studies. The highest Ni level was detected in R1, about 3.6 mg/L, probably resulting in the enhanced biogasification performance of R1 under the high ammonia concentration condition (5,145

mg-N/L). This observation could also partly contribute to the accelerated hydrolysis and VFAs degradation under WRS addition (Fig. 2.6).

As mentioned above, the change in the concentrations of cations and anions in the fermentation liquor is also closely associated with the precipitation reactions occurred between/among the existing or released ions due to oversaturation under the tested ionic and pH conditions. Taking the variation of the major ions involved in the anaerobic process in this study, namely NH_4^+, H^+(pH), Ca^{2+}, Mg^{2+}, Fe^{3+} or Fe^{2+}, and PO_4^{3-} (Figs. 2.4 and 2.8) into consideration, it was assumed that some precipitates might be formed under the tested conditions (CO_3^{2-} concentration was estimated based on charge balance in the fermentation liquor). In this study, Saturation Index (SI) was adopted to estimate the possibility of mineral precipitation by using the Minteq.v3.1 database (PHREEQC software): a positive SI signals the mineral can precipitate while negative values indicate dissolution conditions (Montastruc et al., 2003; Barat et al., 2011).

Fig. 2.9 illustrates the changes of SI for the possible precipitates formed in the anaerobic reactors along with the progress of the anaerobic fermentation. Some precipitates were found to be easily formed under the tested conditions because of their highly positive SI values, especially the followings: (1) Ca- precipitates like $CaCO_3$ (less possibility than the other two due to much lower SI values), $Ca_3(PO_4)_2$, and hydroxyapatitie (Ca_5 $(OH)(PO_4)_3$); (2)Ca/Mg- precipitates including dolomite ($CaMg(CO_3)_2$), an anhydrous carbonate mineral formed under anaerobic conditions (Vasconcelos et al., 1995); and (3)various Fe-precipitates such as ferrihydrite ($Fe_2O_3 \cdot H_2O$), goethite (α-FeO(OH)), hematite (Fe_2O_3), lepidocrocite (γ-FeO(OH), maghemite (γ-Fe_2O_3), and strengite ($FePO_4 \cdot 2H_2O$). Mg was also found to possibly form precipitates with other cations like NH_4^+ (struvite, $NH_4MgPO_4 \cdot 6H_2O$) and Fe^{3+} (magnesioferrite, $MgFe_2O_4$). More specifically, the formation of two kinds of precipitates, struvite and Fe-precipitates might contribute to the decrease in ammonia concentration in the reactors during fermentation (Fig. 2.4), especially in R1 and

R2 with more stable positive SI values (Fig. 2.9). Struvite formation might be one of the major reasons for pH variation and NH_4^+ decrease in the fermentation liquor of the reactors (Uludag-Demirer et al., 2008; Le Corre et al., 2009; Möller and Müller, 2012). In addition, among the Fe- precipites ferrihydrite is reported to be nanoporous mineral with a high specific surface areas of about 180 m^2/g capable of adsorbing cations and pH_{pzc} (the pH at which surface charge density is zero) of 7.9 (Davis and Leckie, 1978), partially in agreement with the phenomenon observed in this study (Figs. 2.5 and 2.9). Surface element analysis results of the solids from the three group reactors after 60 days' anaerobic fermentation and the large increase in Fe content was also detected on the surface of WRS, partially coinciding with the above precipitation assumption (Table 2.2). Restated, the formation of Fe-precipitates may contribute a lot to the large decrease in ammonia concentration and enhanced biogasification in R1 due to their larger quantity and stably higher SI values (Figs. 2.8 and 2.9), which provides a new method for mitigating inhibition of high ammonia level to anaerobic fermentation. Detailed investigation is still on-going for exploring the nature of the above phenomenon.

2.4. Summary

This study reveals that: (1) WRS addition systems could effectively ameliorate ammonia inhibition to anaerobic fermentation of swine manure under high ammonia level (5,145 mg- N/L), achieving better stability and much smaller volume to treat the same amount of ammonia-rich wastes. (2) Based on this work, the ionic environment in fermentation liquor is crucial for maintaining the balance between acidogenesis and methanogenesis processes, especially under high ammonia levels. (3) Two kinds of precipitates, struvite and Fe-precipitates, likely formed during the fermentation process, probably contribute a lot to the decrease in ammonia concentration in the fermentation liquor.

Table 2.1 Physical and chemical characteristics of raw swine manure and seed sludge used in the experiments.

Items	Unit	SW	Seed sludge
Total solid (TS)	%	18.9 ±0.1	1.15 ±0.01
Volatile solid/Total solid (VS/TS)	%	76.4 ±0.1	70.05 ±0.02
Chemical oxygen demand (COD)	g/L	210.0 ±48.0	6.7 ±0.4
Total ammonia nitrogen (TAN)	mg/L	22506.0 ±1052.1	1806.0 ±16.2
Total phosphorus (TP)	mg/L	2758.6 ±87.2	534.5 ±2.8
Orthophosphate phosphorus (Ortho-P)	mg/L	1525.0 ±59.8	335.3 ±4.0
Main metals in the swine manure and seed sludge			
Na	mg/L	1414.8 ±21.6	41.3 ±0.3
K	mg/L	3808.0 ±41.0	166.2 ±3.5
Mg	mg/L	376.0 ±8.0	23.9 ±0.1
Ca	mg/L	2032.0 ±9.0	68.5 ±2.2
Fe	mg/L	106.0 ±3.9	45.0 ±2.8
Co	mg/L	0.4 ±0.1	N.D.
Ni	mg/L	1.6 ±0.1	N.D.

N.D., non-detectable

Table 2.2 Main elements analysis by EDX on the surface of solids from the three group reactors after 60 days' anaerobic fermentation and on the surface of WRS samples before and after being immersed in distilled water and anaerobic fermentation (in average, wt%).

Element	Solids after fermentation			WRS		
	Control	R1*	R2	Raw	After immersed	After fermentation
O	28.52	27.78	25.02	39.77	40.86	39.94
Na	2.62	2.85	4.08	7.50	7.50	6.15
Mg	4.43	4.40	3.91	0.38	0.85	1.06
Al	2.3	2.07	2.51	11.36	13.12	12.90
Si	4.38	4.53	5.43	34.43	32.99	32.04
P	14.62	13.68	10.13	0.00	0.37	0.38
Cl	6.67	9.22	12.67	0.00	0.10	0.23
K	5.09	4.98	9.32	1.43	0.92	1.87
Ca	24.94	25.48	18.64	0.37	1.89	1.39
Fe	4.03	3.01	3.51	4.76	0.94	3.27
Others	2.39	1.98	4.77	0.00	0.46	0.77

*The solids after WRS being removed.

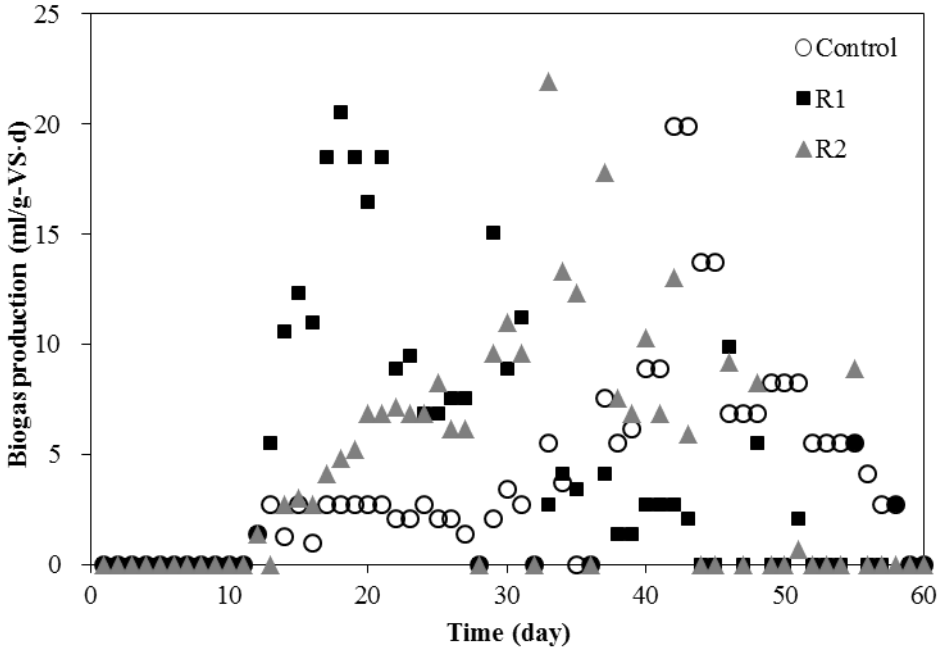


Figure 2.3 Daily biogas production during anaerobic digestion.

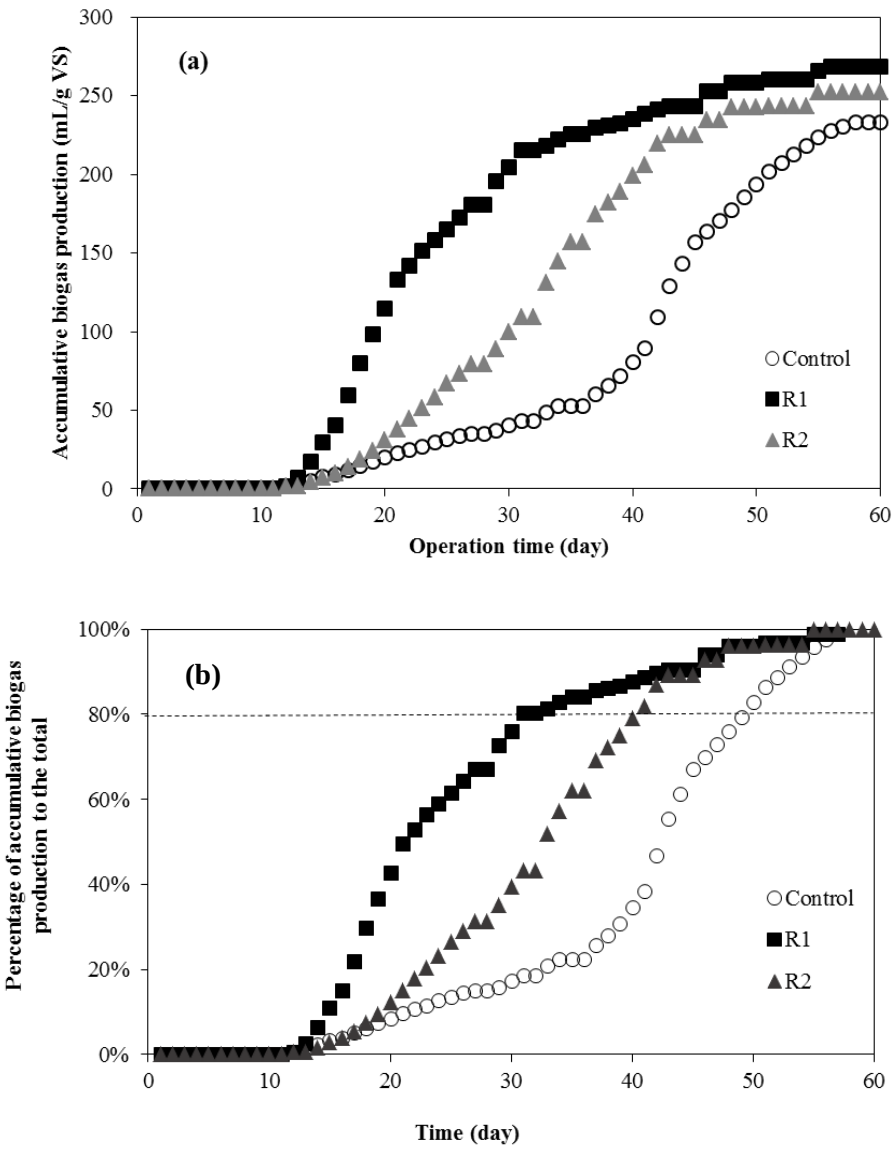


Figure 2.4 Accumulative biogas production (a) and percentage of accumulative biogas production to the total biogas yield (b).

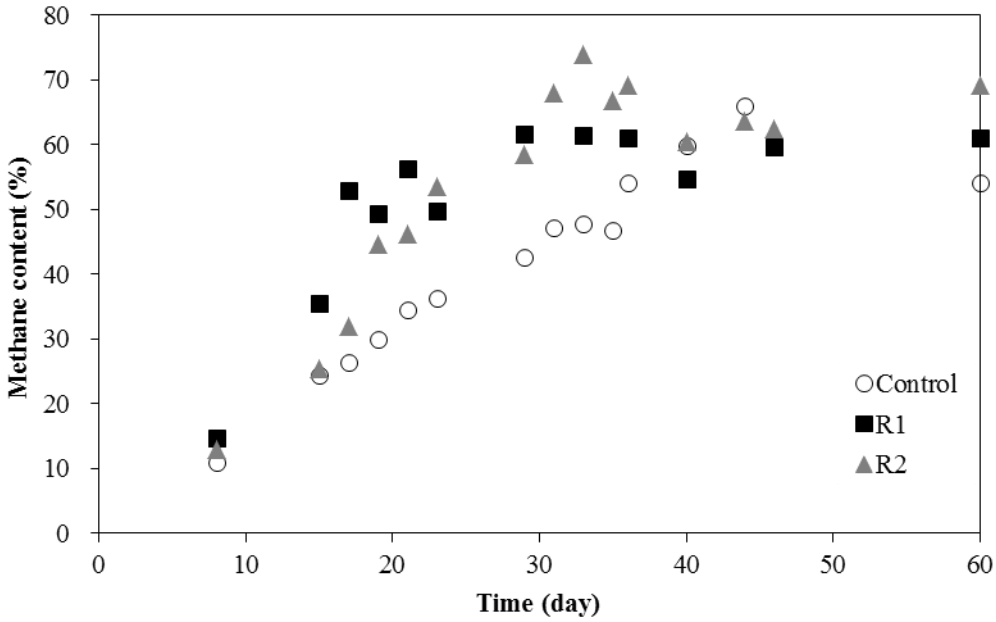


Figure 2.5 Changes in methane content during anaerobic digestion.

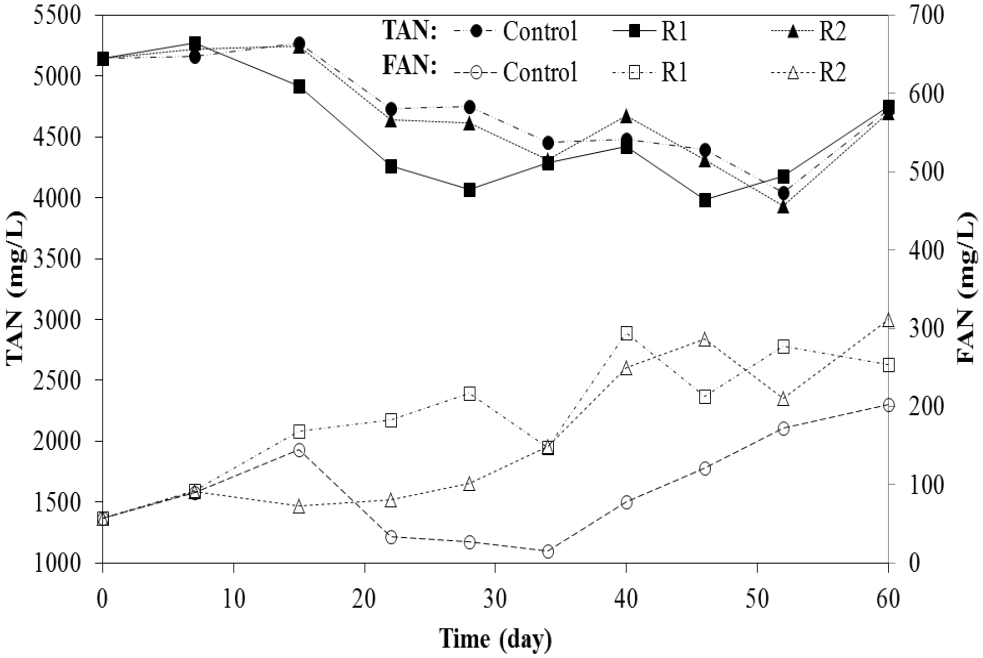


Figure 2.6 Variations in total ammonia nitrogen (TAN) and free ammonia nitrogen (FAN) concentrations during anaerobic digestion.

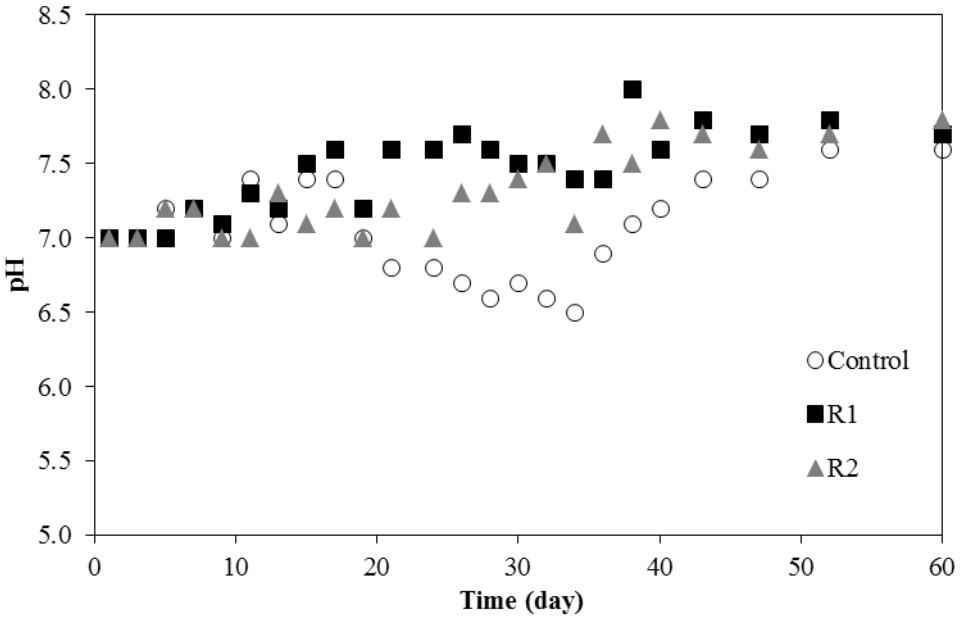


Figure 2.7 Variations in pH during anaerobic digestion.

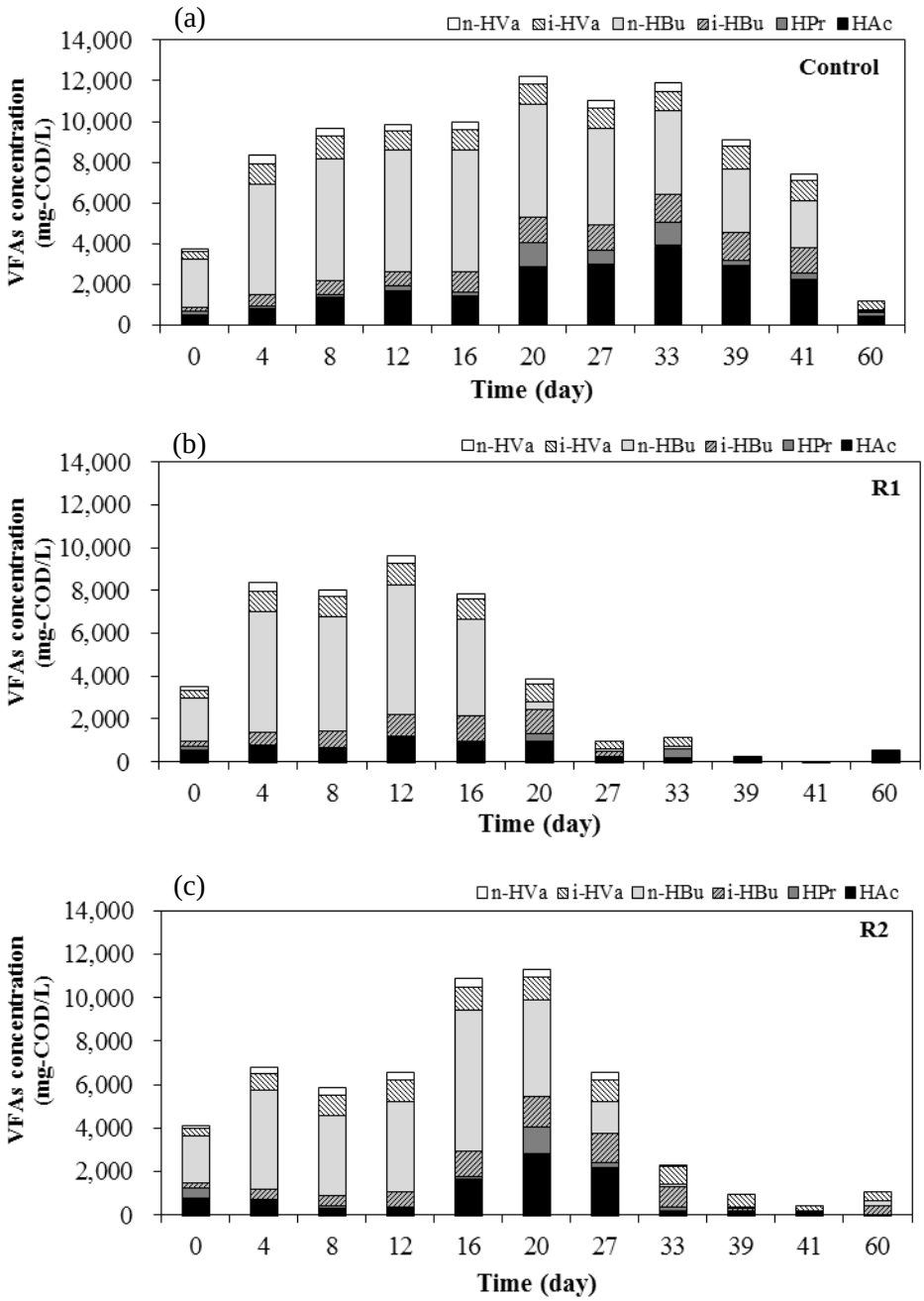


Figure 2.8 Profiles of acetic acid (HAc), propionic acid (HPr), n-butyric acid (n-HBu), isobutyric acid (i-HBu), n-valeric acid (n-HVa), and iso-valeric acid (i-HVa) concentrations in the control reactor (a), WRS-augmentation reactor (R1, b) and WRS-water reactor (R2, c) .

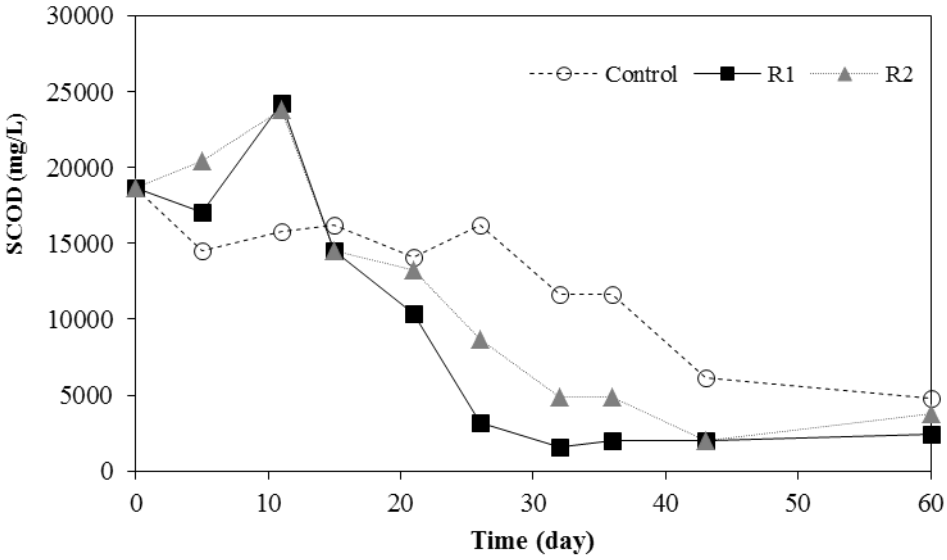
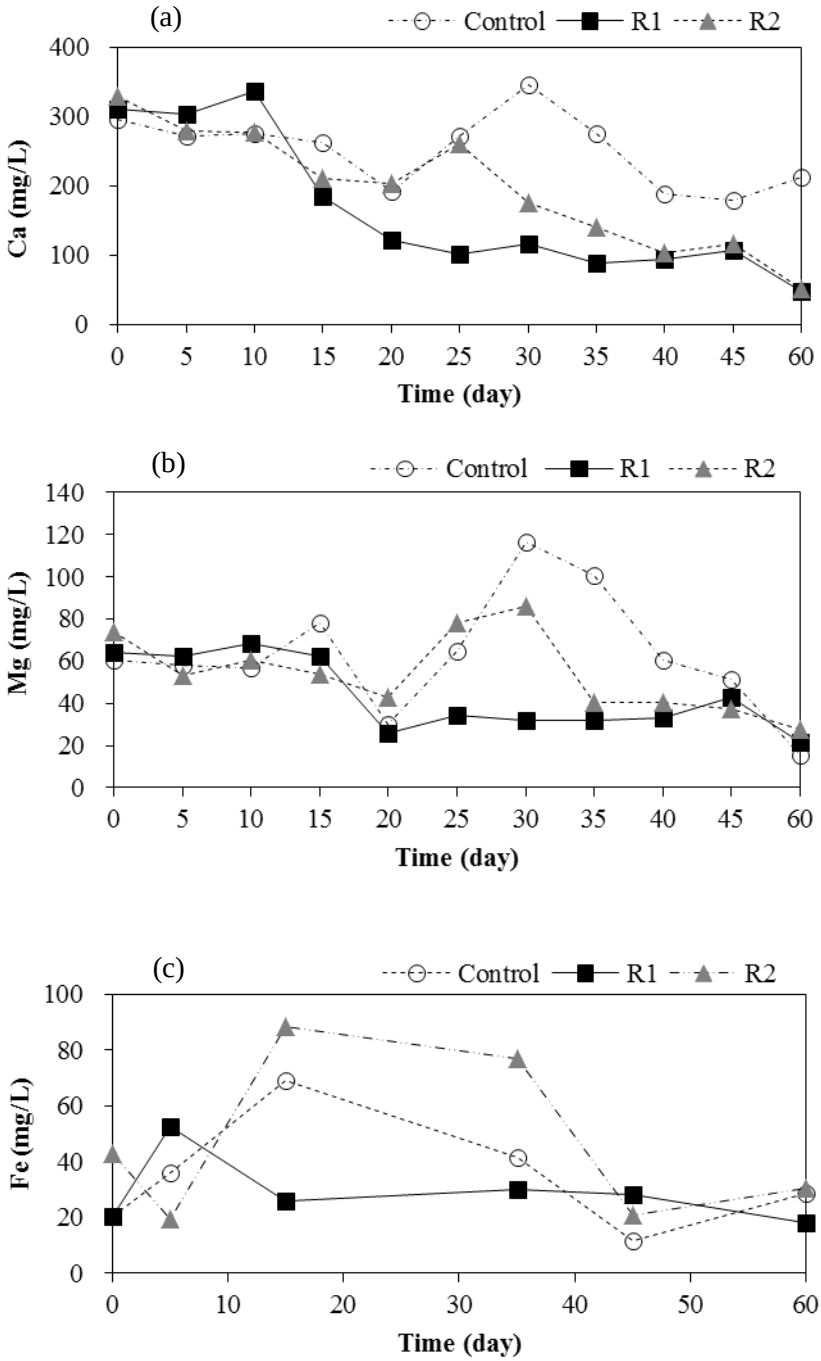


Figure 2.9 Changes in soluble chemical oxygen demand (SCOD) concentration during anaerobic digestion.


(a)
Control
R1
R2
Ca (mg/L)
Time (day)
(b)
Control
R1
R2
Mg (mg/L)
Time (day)
(c)
Control
R1
R2
Fe (mg/L)
Time (day)

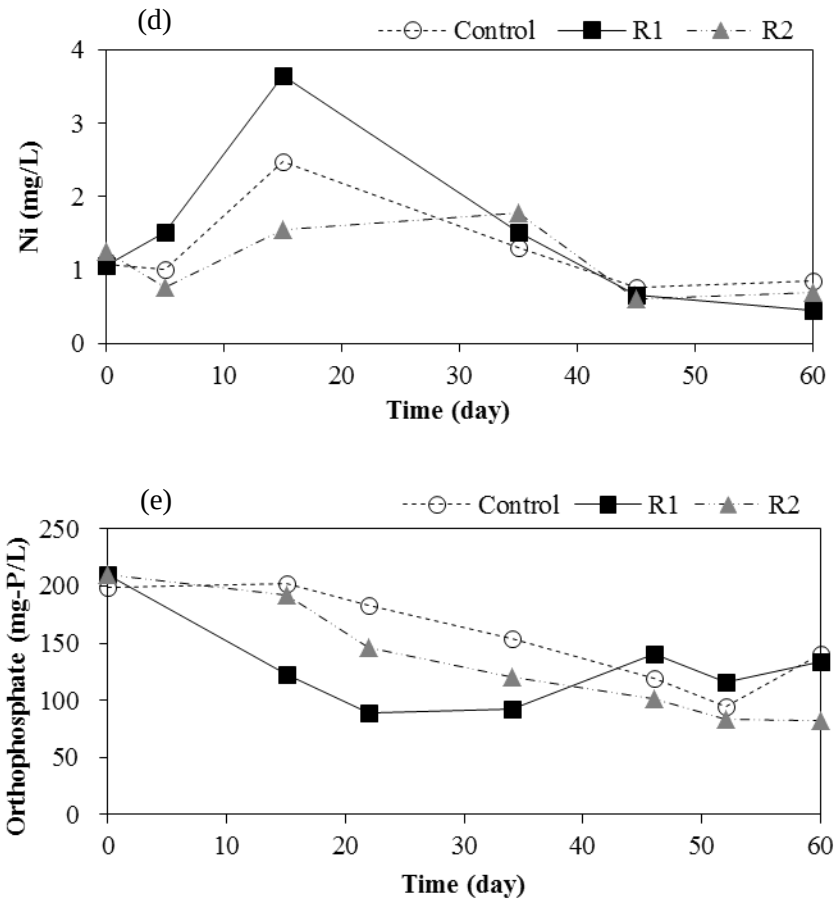


Figure 2.10 Variations of Ca (a), Mg (b), Fe (c), Ni (d) and orthophosphate (e) concentrations in liquid phase of the reactors during anaerobic digestion.

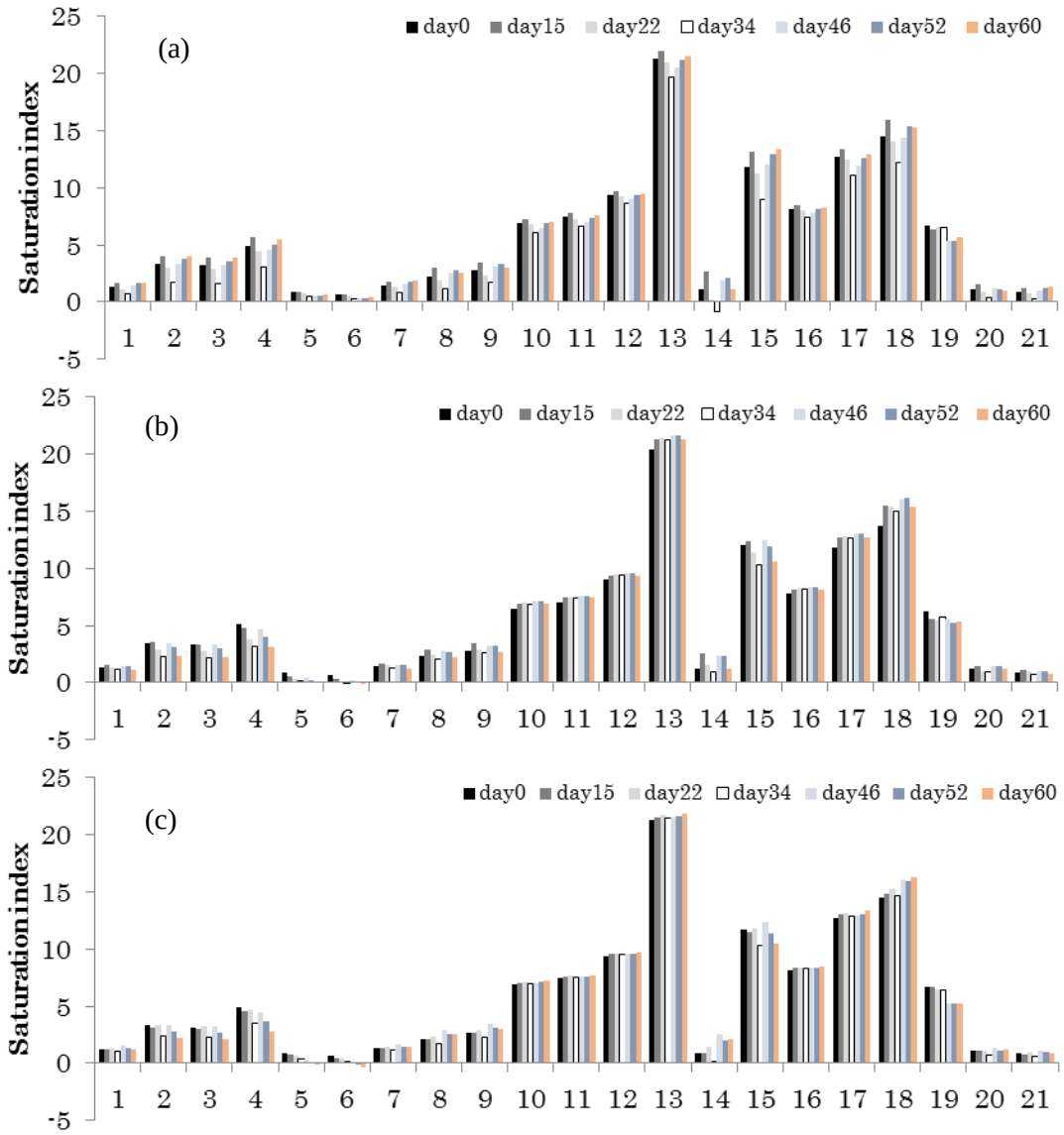


Figure 2.11 Changes in saturation indices (SI) for major oversaturated inorganic components in the Control (a), R1 (b) and R2 (c) reactors during the operation period.

1- Aragonite, 2- $Ca_3(PO_4)_2$ (am2), 3- $Ca_3(PO_4)_2$ (beta), 4- $Ca_4H(PO_4)_3{:}3H_2O$(s), 5- $CaHPO_4$(s), 6- $CaHPO_4{:}2H_2O$(s), 7- Calcite, 8- Dolomite (disordered), 9- Dolomite (ordered),10- Ferrihydrite, 11- Ferrihydrite (aged), 12- Goethite, 13- Hematite, 14- Huntite, 15- Hydroxyapatite, 16- Lepidocrocite, 17- Maghemite, 18- Magnesioferrite, 19- Strengite, 20- Struvite, 21- Vaterite.

3. Enhanced dry anaerobic digestion of swine wastes by ammonia stripping

3.1. Introduction

In recent years, due to energy crisis and environment problems, anaerobic digestion of agricultural wastes such as livestock manure represents a cost-effective, environmentally-friendly, and societal opportunity to produce renewable energy. The renewable energy produced in anaerobic digestion, namely biogas, is a promising candidate of fossil fuels. Dry anaerobic digestion (DAD) as a technology which is developed for the treatment of waste with high total solids content (TS > 20%) is receiving increasing concern. DAD has many advantages such as reducing reactor size, high volumetric organic loading rate, lower energy consumption for bioprocess heating, and easy handling of digested waste (Li et al., 2011). However, DAD of SW under thermophilic condition is often limited by the high ammonia concentration produced from the decomposition of proteins and urea in the SW resulting in poor biogas potential (Batstone et al., 2002). Especially, free ammonia has been regarded as the main cause of inhibition since it is freely membrane-permeable.

This study aims to test the feasibility of ammonia fermentation of SW followed by air stripping, and using DAD to test the digestibility of pretreated SW: (1) Effect of pH level on ammonia stripping was examined under dry condition (TS > 35%); (2) Effects of different ammonia stripping conditions on subsequent DAD were investigated.

3.2. Methods

3.2.1. SW and anaerobic sludge

SW in this study was collected from a pig farm located in Tsuchiura (Ibaraki, Japan). Anaerobically digested sludge collected from the Shimodate Wastewater Treatment Plant (Ibaraki, Japan) acclimated to SW was used as inoculum after one week of degassing. The main physical and chemical characteristics of raw SW and acclimated seed sludge are listed in Table 3.1.

3.2.2. Ammonia production from SW

Batch ammonia fermentation experiments of SW were carried out in 500 ml glass bottles (400ml of working volume) under anaerobic condition for 7 days. The reactors were placed in a temperature-controlled water bath at 55℃. The characteristics and features of ammonia fermented SW are summarized in Table 3.2. After ammonia fermentation, the SW was labelled as pretreated SW.

3.2.3. Ammonia stripping

After ammonia fermentation, the pretreated SW with initial pH 8.8 (without pH adjustment) and the pretreated SW with initial pH 10.2 were used for ammonia stripping respectively. The pH of SW was adjusted by using $Ca(OH)_2$. Ammonia stripping of the SW was conducted in a 500 ml reactor with a working volume of 200 ml. Air was introduced into the reactor from the bottom of the reactor and the air flow rate was controlled at 50 ml/min indicated by an airflow meter. The stripping was conducted at 55℃ for 24 h. After ammonia stripping, the SW was labelled as stripped SW.

3.2.4. Dry methane fermentation

Batch methane fermentation experiments were carried out in 100 ml glass bottles (80ml of working volume) under anaerobic condition. I/S (Inoculum/Substrate) ratio was controlled at 0.15 (based on VS) for each reactor. The differences among the three group reactors were as follows: (1) only raw SW in the Control reactors, (2) ammonia stripped SW at pH 8.8 was used in $R_{8.8}$ reactors, and (3) ammonia stripped at pH10.2 was in $R_{10.2}$ reactors, respectively. Their TS were averagely 21.1, 21.9 and 22.5%, with VS of 17.7, 16.5 and 16.6% in Control, $R_{8.8}$ and $R_{10.2}$ reactors, respectively. The initial pH of each reactor was adjusted to 7.0 using 4.0 M of hydrochloric acid. All the bottles were sealed with silica gel stoppers, and placed in a temperature-controlled water bath (55℃).

3.2.5. Analytical methods

TS, VS and TAN were determined in accordance with the Standard Methods (APHA, 2005). pH values were determined using TESTO 206-2 pH meter (TESTO, Germany) after the sample being diluted to 20%TS. 3 g of each SW sample (wet basis) was withdrawn to 15 ml plastic tubes, and suspended with 5 ml deionized water. The suspension was centrifuged at 5000 rpm and 4℃ for 10 min, and the resultant supernatant was used for measuring ammonia, VFAs, soluble total organic carbon (STOC). STOC analysis was performed on an automated total organic carbon analyzer (TOC-V CSN, SHIMADZU, Japan). VFAs were measured using a gas chromatograph (GC-14B, SHIMADZU, Japan) equipped with a flame ionization detector and a Unisole F-200 30/60 column (3.0 mm in diameter and 2.0 m in length). 1 μl of sample was injected with the carrier gas N_2. The injector, detector and column temperatures were kept at 200℃, 200℃ and 160℃, respectively. Biogas production was collected using 50 ml plastic syringes, and the volume was read directly according to the scale on the syringes. Biogas composition analysis was carried out by means of a gas-chromatograph (GC-8A, SHIMADZU, Japan) with nitrogen as carrier gas, equipped with a thermal conductivity detector (80℃) and a Porapak Q column(60℃).

3.3. Results and discussion

3.3.1. Effect of ammonia production from SW

As shown in Table 3.1, TS, VS/TS, STOC and ammonia concentration of raw SW used in this study were 36.3%, 77.8%, 23,033 mg/kg-TS and 9,376 mg/kg-TS, respectively. Since its ammonia concentration was in the inhibitory range (Chen et al., 2008), ammonia removal was necessary in order to achieve high biogas production in anaerobic digestion of SW.

In order to enhance the ammonia removal, the ammonia fermentation was carried out under thermophilic condition (55℃) to produce more ammonia in a shorter period before

ammonia stripping. Table 3.2 shows the characteristics of pretreated SW. The final concentrations of TAN after ammonia fermentation were increased to 17,342 mg/kg-TS, which was significantly higher than that of raw SW (9,376 mg/kg-TS).

In addition, by means of ammonia fermentation, not only ammonia produced but also STOC and VFAs were increased, which varied from 23,033 mg/kg-TS and 229 mg-C/kg-TS to 42311 mg/kg-TS and 8,187 mg/kg-TS, respectively. The main VFA species was HAc (2,671 mg/kg-TS), and pH marginally increased from 8.4 to 8.8. The $C_{(VFAs)}$/STOC ratio was increased from 0.068 to 0.144, suggesting that particulate organics or long chain fatty acids were hydrolyzed or decomposed to short chain fatty acids. The produced VFAs and STOC can be readily utilized to produce methane by methanogen. However, after ammonia fermentation, ammonia removal was necessary before methane production, due to ammonia inhibition to methanogen at high ammonia level (17,342 mg/kg-TS after ammonia fermentation).

3.3.2. Effect of air stripping on ammonia fermented SW

pH and temperature have the most important effects on ammonia stripping, and higher temperature and pH can promote ammonia removal. In previous studies, air stripping has been usually used to remove ammonia from substrate with low total solid content (TS < 10%) (Jiang et al., 2014; Bonmatí and Flotats, 2003). In this study, in view of economic benefits, and ammonia stripping was performed under dry condition at TS of 34 ~ 36%.

The physical and chemical characteristics of air stripped SW are summarized in Table 3.2. Compared with the pretreated SW, significant difference was detected in the ammonia concentration of SW before and after air stripped. The ammonia concentration was significantly decreased from 17,342 mg/kg-TS to 2,602 and 1,719 mg/kg-TS in $R_{8.8}$ and $R_{10.2}$ after air stripped, correspondingly to ammonia removals of 85.0% and 90.1%, respectively. Although high pH is beneficial for ammonia removal, $R_{8.8}$ (without pH adjustment) achieved

85.0% of ammonia removal.

STOC was detected to decrease from 42,311 mg/kg-TS to 30,869 and 18,234 mg/kg-TS in $R_{8.8}$ and $R_{10.2}$ reactors, respectively. On the other hand, VFAs was found to increase from 8,187 mg-C/kg-TS to 11,108 mg-C/kg-TS in $R_{8.8}$, while decreased to 6,775 mg-C/kg-TS in $R_{10.2}$. About 40.0% and 37.2% of STOC were contributed by VFAs which were reported to be readily utilizable for biogasification.

3.3.3. Performance of dry methane fermentation

Figs. 3.2 - 3.4 show the daily biogas production, accumulative biogas production and methane content during 35 days' operation. Significant difference was observed in terms of biogas production under different treatment conditions. In the Control, in which the raw SW was used as substrate, very less biogas (27.5 ml/kg-VS) was detected. On the contrary, when ammonia stripped SW were used as substrates, much higher biogas production were detected during the same operation period. Especially, the SW with ammonia stripped at pH 10.2 exhibited the highest biogas production rate. Its maximum daily biogas production occurred 5 days earlier than that for stripped SW at pH 8.8. The biogas yields of 74.8 ml/g-VS and 71.0 ml/g-VS were obtained respectively after ammonia stripping (at pH 8.8 and pH 10.2) of SW, which was 172% and 158% higher than the Control (27.5 ml/g-VS). In addition, when ammonia fermented SW was directly used as substrate, no biogas production was observed (date not shown), most probably due to its high ammonia concentration (4,059 mg/kg).

Methane contents in the biogas from $R_{8.8}$ and $R_{10.2}$ achieved 50% on day 7 and day 2 respectively, and afterwards kept around 55 - 65% and 52 - 60%, respectively. However, the methane content in the biogas from the Control reactors increased gradually and reached 50% until day 22. The average methane yields were 11.3, 40.6 and 39.0 ml/kg-VS for the Control, $R_{8.8}$ and $R_{10.2}$, respectively. And their pH gradually increased from 7.0 to 8.2, 7.9 and 7.7 in the Control, $R_{8.8}$ and $R_{10.2}$ reactors, respectively (Fig 3.5). The results showed that the

ammonia stripped SW exhibited better biogasification performance than raw SW even under high solid condition.

Fig 3.6 shows the changes in average ammonia concentration of the three group reactors. The initial ammonia concentrations in the Control, $R_{8.8}$ and $R_{10.2}$ were 2,354, 1,161 and 724 mg/kg, respectively. After 5 days' anaerobic digestion, the ammonia concentration quickly increased to 3,419 mg/kg in the Control, which was significantly higher than those of ammonia stripped SW. Then the ammonia concentration in the Control reactors kept between 3,400 - 4,000 mg/kg possibly resulting in completely inhibited biogasification. Owing to the high efficiency of ammonia stripping, the initial ammonia concentrations in $R_{8.8}$ and $R_{10.2}$ were at low levels (1,161 and 724 mg/kg, respectively), which kept at 1,600 - 1,800 and 1,100 - 1,500 mg/kg during the subsequent DAD, respectively. Most probably due to the lowest initial ammonia concentration (724 mg/kg) in $R_{10.2}$, the methane production was increased quickly in $R_{10.2}$ resulting in the occurrence of maximum daily biogas production rate of 13.1ml/g-VS·d on day 4. Compared to $R_{10.2}$, slightly higher initial ammonia concentration was detected in $R_{8.8}$ attributing to its slower increased biogas production, and its maximum daily biogas production rate of 8.5mL/g-VS·d occurred on day 10.

Biogas production is always accompanied with the formation of VFAs throughout the anaerobic digestion of organic matter. High concentration of VFAs may cause microbial stress and low pH, ultimately resulting in failure of the digester. Therefore, concentration of VFAs is considered as an important indicator for good performance of anaerobic digester (Wang et al., 1999). Fig 3.7 shows the variation of VFAs including acetic acid (HAc), propionic acid (HPr), isobutyric acid (i-HBu), n-butyric acid (n-HBu) and isovaleric acid(i-HVa). There were significant difference in total VFAs concentrations in the three reactors during DAD.

In the Control reactors, all the VFAs were detected to increase quickly on day 5 and accumulated up to 3,000 mg/kg, much higher than those in $R_{8.8}$ and $R_{10.2}$. More than 50% of the total VFAs was HAc in the Control, signaling HAc is the dominant VFA produced from

anaerobic digestion of SW.

Possibly due to the inhibition of high ammonia level to methanogens, lower VFAs utilization rate was detected in the Control. In $R_{10.2}$, little VFAs were accumulated, which was below 1000 mg/kg during the whole anaerobic digestion period. In $R_{8.8}$, very less VFAs accumulation was detected except on day 5 and day 15, about 1,024 and 1,542 mg-C/kg VFAs, respectively. This observation most probably attributes to its higher ammonia concentration in $R_{8.8}$ compared to that in $R_{10.2}$. Similarly, after day 15, almost no VFAs were produced and the biogas was decreased in $R_{8.8}$ and $R_{10.2}$. In contrast, much higher concentration of VFAs was accumulated in the Control reactors.

Biodegradable organic substances can be removed through conversion into methane and carbon dioxide during the anaerobic digestion, resulting in STOC decrease in the digester. Fig 3.8 shows the variation of STOC concentration in the three group reactors. The initial STOC concentration was 4,276, 5,112 and 3,810 mg/kg in the Control, $R_{8.8}$ and $R_{10.2}$, respectively. STOC concentration of $R_{8.8}$ and $R_{10.2}$ decreased gradually along with the progress of DAD. While STOC concentration in the Control reactors increased quickly during the initial 5 days and reached to the maximum 8,127 mg/kg on day 20 and then the STOC concentration decreased gradually. Compared to the initial STOC concentration, the final concentrations in the Control, $R_{8.8}$ and $R_{10.2}$ were about 6,300, 3,376 and 2,611 mg/kg after 35 days' anaerobic digestion, which were increased by 32% and decreased by 34 and 31%, respectively. In addition, Carbon $_{(VFAs)}$/STOC ratio increased from 0.02 to 0.53 in the Control reactors after anaerobic digestion.

3.4. Summary

The feasibility of ammonia stripping as a pretreatment method for DAD of swine wastes was investigated, which included the effect of pH level on ammonia stripping under dry condition (TS>35%), and the effect of different ammonia stripping conditions on subsequent

DAD. The results indicated that: (1) Ammonia stripping at pH 10.2 achieved the highest ammonia removal (90.1%), meanwhile 85.0% of ammonia removal could be reached in $R_{8.8}$. And adjusting pH to 10.2 resulted in decrease of VFAs. (2) Through the subsequent anaerobic digestion, air stripping after ammonia fermentation was proven as a promising pretreatment for DAD of ammonia-rich SW. (3) All stripped SW sample showed better biogas production potential than the raw SW. Especially, ammonia stripping at pH8.8 achieved a biogas yield of 74.8 ml/g-VS comparable to $R_{10.2}$ (71.0 ml/g-VS). When compared to the Control (27.5 ml/g-VS), 172% and 158% higher biogas production were obtained in $R_{8.8}$ and $R_{10.2}$, respectively.

Table 3.3 Characteristics of raw SW and seed sludge.

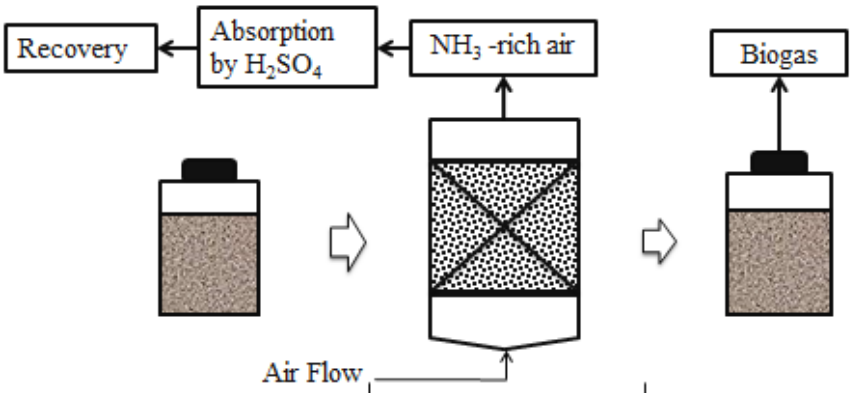
Items	Unit	Raw SW	Acclimated seed sludge
TS	%	36.3 ±2.5	5.8 ±0.3
VS/TS	%	77.8 ±2.0	71.2 ±3.3
TAN	mg/kg-TS	9376 ±119	31136 ±278
	mg/kg w.w.*	3418 ±38	1806 ±16
STOC	mg/kg-TS	23033 ±201	54660 ±779
Acetic acid	mg-C/kg-TS	189 ±2.8	1680 ±14
Propionic acid	mg-C/kg-TS	25 ±0.8	1,115 ±27
Isobutyric acid	mg-C/kg-TS	12 ±0.6	501 ±4
Butyric acid	mg-C/kg-TS	0	716 ±6
Valeric acid	mg-C/kg-TS	3 ±0.1	987 ±10
Total VFAs	mg-C/kg-TS	229 ±4	4999 ±33
pH	-	8.4 ±0.1	7.4 ±0.1

*w.w.: wet weight.

Table 3.4 Characteristics of ammonia fermented and ammonia stripped SW.

Items	Unit	SW after ammonia fermentation	Ammonia stripped $SW_{8.8}$	Ammonia stripped $SW_{10.2}$
TS	%	35.4 ±1.2	45.3 ±1.1	49.2 ±1.0
VS/TS	%	77.1	76.1	72.8
TAN	mg/kg-TS	17342 ±111	2602 ±242	1719 ±51
	mg/kg w.w.*	6313 ±40	1179 ±109	846 ±25
STOC	mg/kg-TS	42311 ±201	30869 ±351	18234 ±289
Acetic acid	mg-C/kg-TS	2671 ±27	3249 ±23	3043 ±30
Propionic acid	mg-C/kg-TS	1484 ±71	2865 ±28	1523 ±32
Isobutyric acid	mg-C/kg-TS	1086 ±8	1888 ±30	601 ±20
Butyric acid	mg-C/kg-TS	1211 ±54	2665 ±59	880 ±8
Valeric acid	mg-C/kg-TS	1735 ±40	441 ±8	728 ±32
Total VFAs	mg-C/kg-TS	8187	11108	6775
pH	-	8.8 ±0.1	8.4 ±0.1	9.3 ±0.2

*w.w.: wet weight



	Step 1 Ammonia fermentation (pretreatment)	Step 2 Air stripping	Step 3 Methane production
Temperature (℃)	55	55	55
Operation time (d)	7	1	35
Feed stock	Raw SW	Pretreated SW	Stripped SW
TS(%)	34-36	34-36	20-22

Figure3.12 Schematic flowchart of methane fermentation combined with ammonia fermentation followed by ammonia stripping.

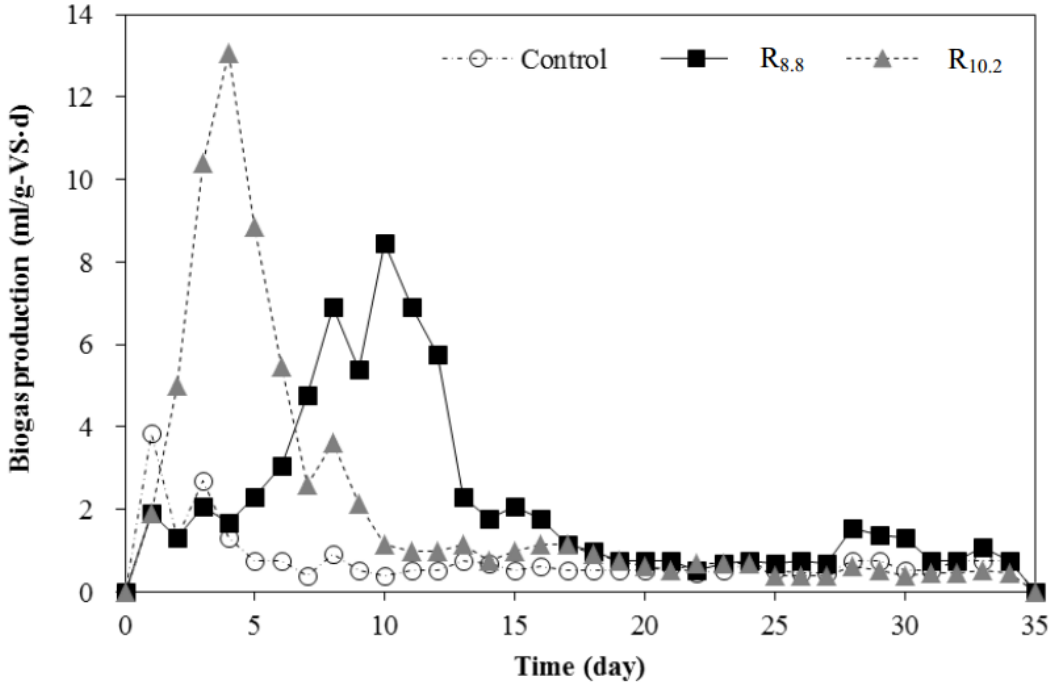


Figure 3.13 Daily biogas production from fermented SW, ammonia stripped SW at pH8.8 ($R_{8.8}$) and ammonia stripped SW at pH10.2 ($R_{10.2}$).

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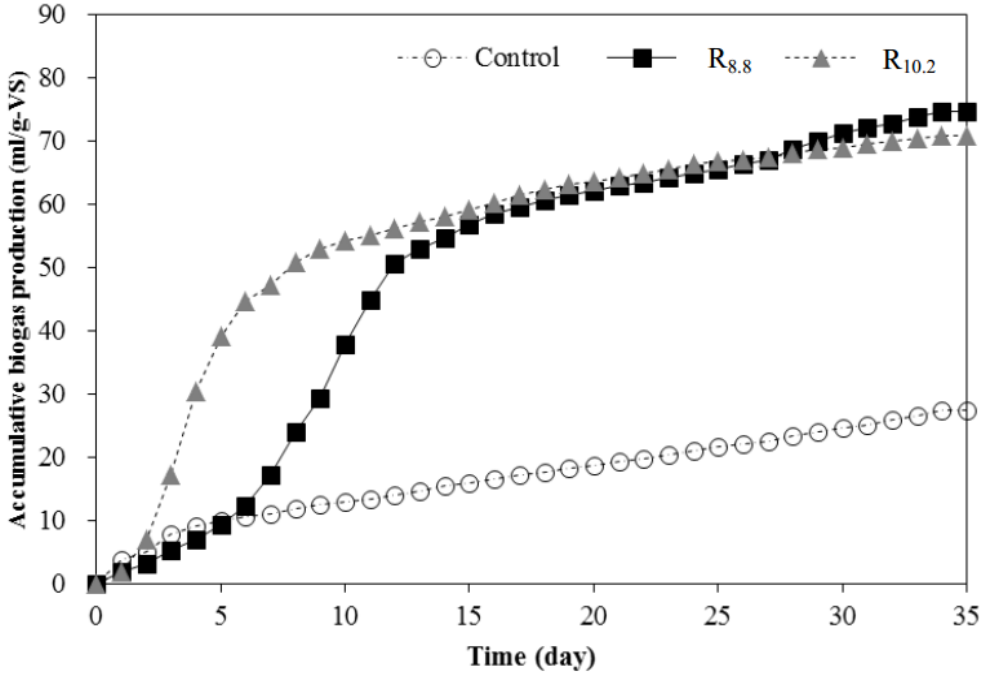

Figure 3.14 Accumulative biogas production from fermented SW, ammonia stripped SW at pH8.8 ($R_{8.8}$) and ammonia stripped SW at pH10.2 ($R_{10.2}$).

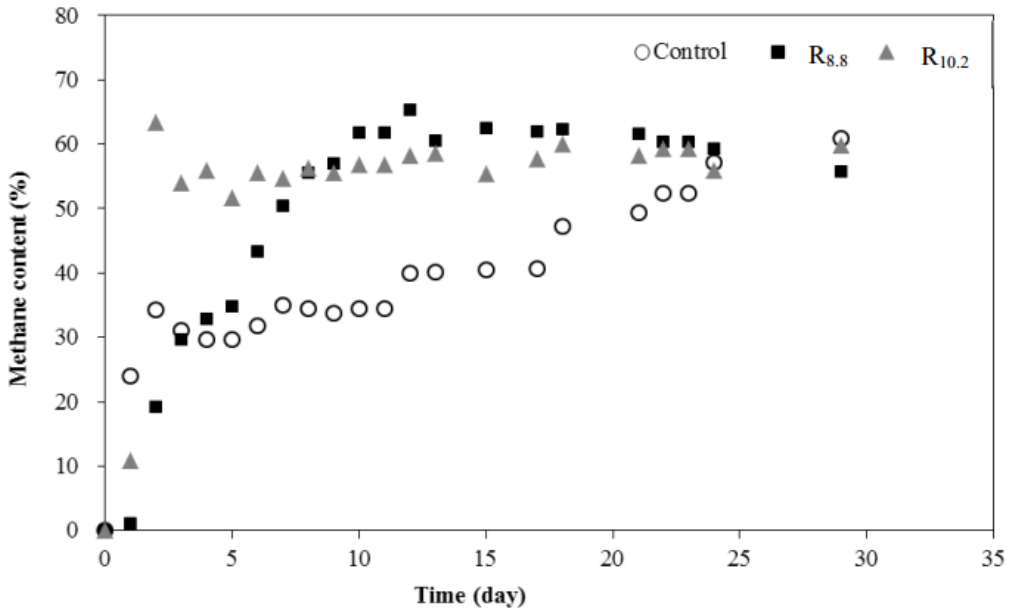

Figure 3.15 Methane content during anaerobic digestion from fermented SW, ammonia stripped SW at pH8.8 ($R_{8.8}$) and ammonia stripped SW at pH10.2 ($R_{10.2}$).

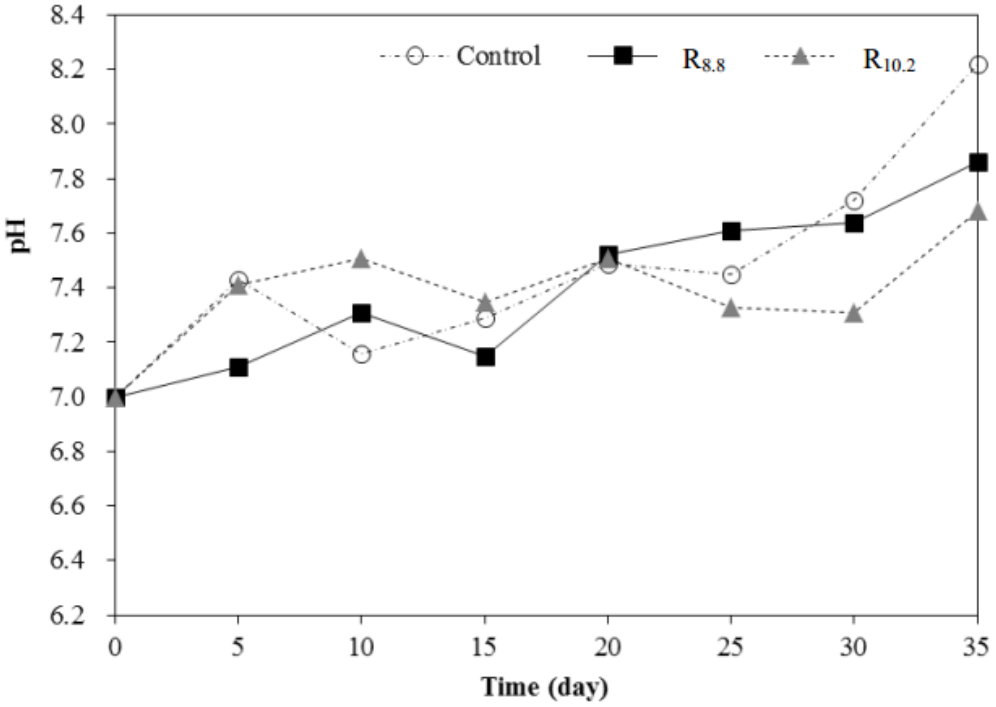

Figure 3.16 Profiles of pH value in the three reactors during dry anaerobic digestion.

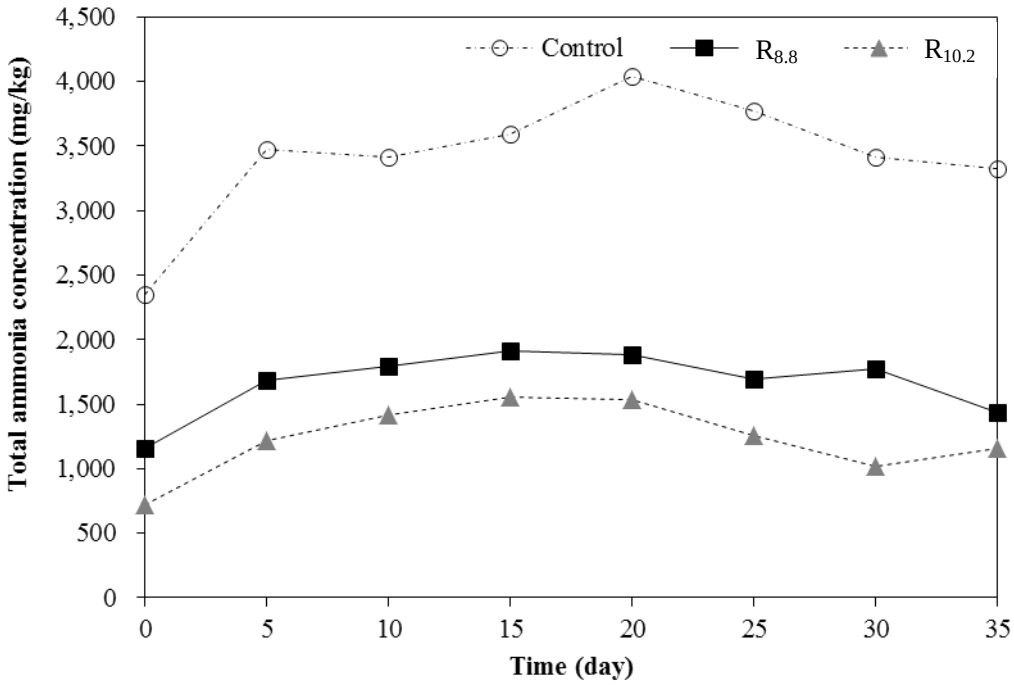

Figure 3.17 Changes of total ammonia nitrogen (TAN) concentration in the three reactors during dry anaerobic digestion.

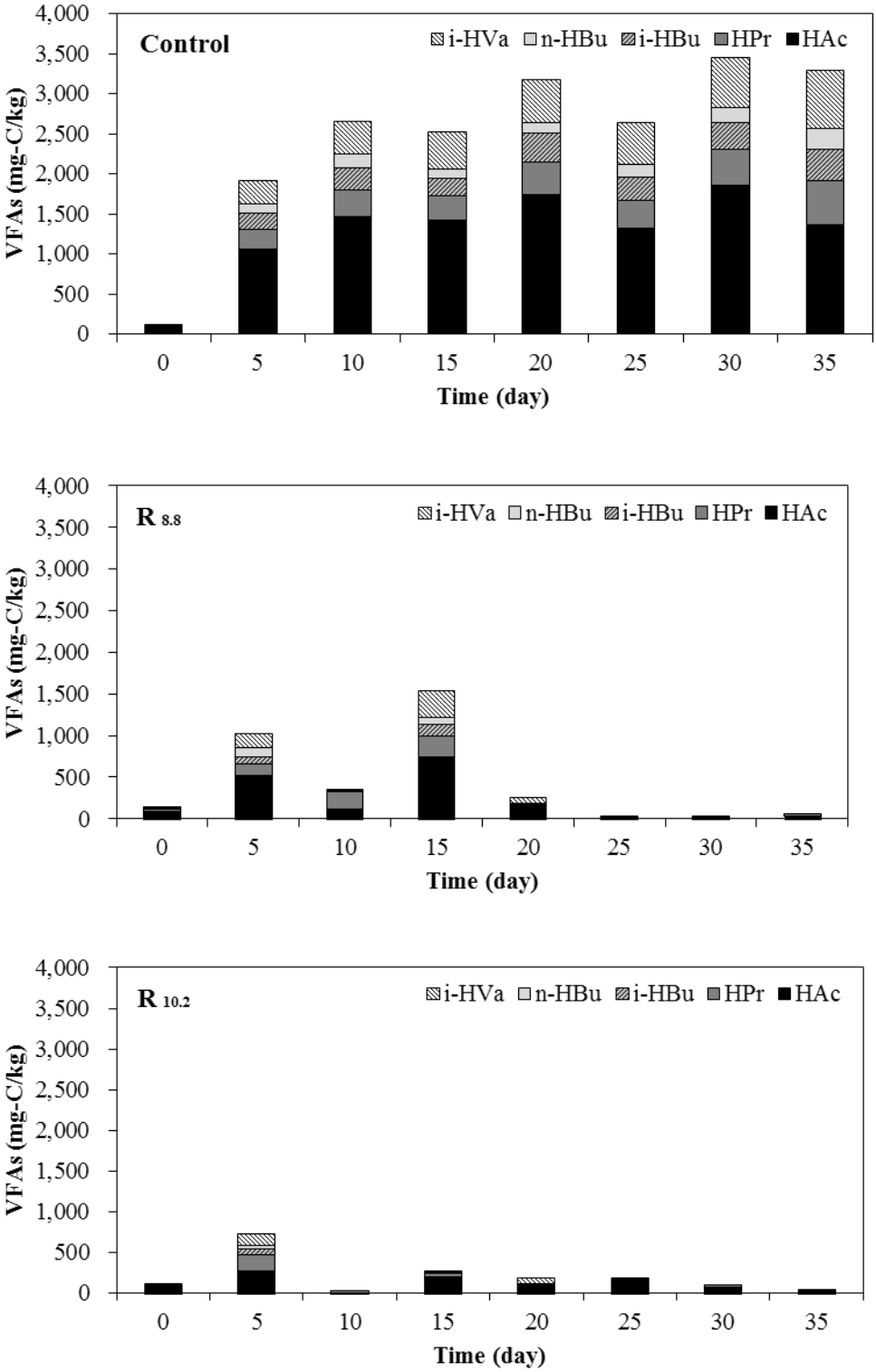

Figure 3.18 Variance of acetic acid (HAc), propionic acid (HPr), n-butyric acid (n-HBu), isobutyric acid (i-HBu) and n-valeric acid (n-HVa) concentration in each reactor.

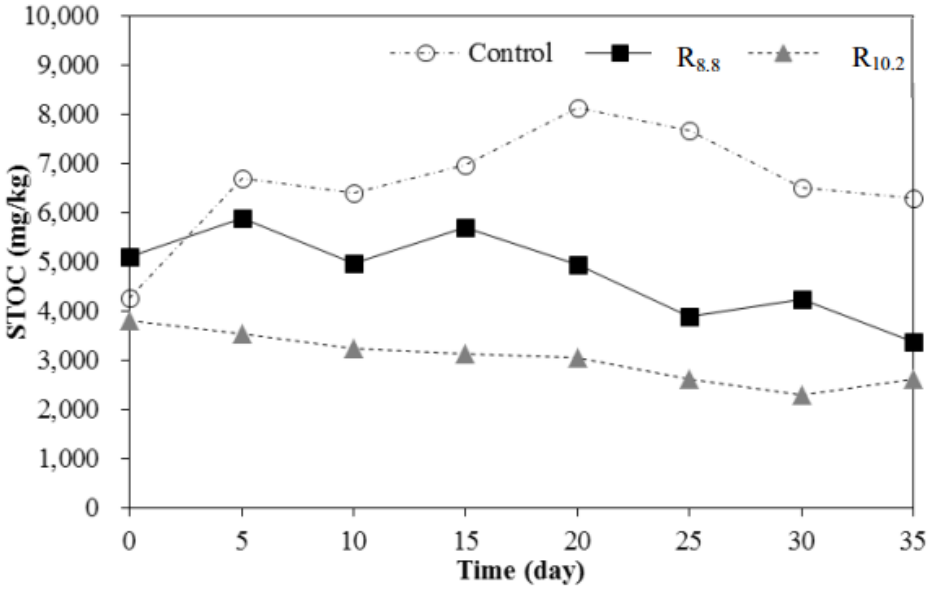

Figure 3.19 Variation of soluble total organic carbon (STOC) concentration during dry anaerobic digestion.

4. Comparison between wheat-rice-stone addition and ammonia stripping for enhanced biogasification from swine wastes

4.1. Introduction

Based on the total solid content (TS), anaerobic digestion is classified into three groups: wet, semi-dry and dry anaerobic digestion. Wet anaerobic digestion systems are typically operated at TS < 10%, semi-solid at 10 - 15% TS, while dry anaerobic digestion is at TS > 15% (Chen et al., 2014; Shi et al., 2013). Wet anaerobic digestion generates low level of sludge, and it is easy to operate and maintain. However, compared to wet anaerobic digestion, dry anaerobic digestion (DAD) has many advantages such as higher volumetric methane productivity, smaller reactor volume, low energy requirements, handleability and positive energy balance (Li et al., 2013). Even though DAD is reported to tolerate high organic loading, low operational stability still hinders its wide application, particularly due to its sensitivity to accumulated VFAs and ammonia under organic overloading.

On the other hand, in order to avoid the inhibition of ammonia in anaerobic digestion of ammonia-rich substrate, development of ammonia removal method for higher biogas production is in an urgent need. There have been increasing attempts to remove ammonia from the digestate during anaerobic digestion process. In Chapters 2 and 3, two methods including WRS addition and ammonia stripping were applied for the high-ammonia anaerobic digestion successfully. WRS addition was applied for wet anaerobic digestion, while ammonia stripping was applied for DAD. Previous studies have compared wet and dry anaerobic digestion, especially the effect of TS levels (Chen et al., 2014; Li et al., 2013). However, little information could be found about the differences in alleviating ammonia inhibition between wet and dry anaerobic digestion processes. No special report addressed the different ammonia removal methods used for anaerobic digestion.

The objective of this study was to compare the performance and efficiency of WRS

addition and ammonia stripping as pretreatment methods for anaerobic digestion of ammonia-rich swine wastes (SW).

4.2. Methods

4.2.1. Calculation assumption

Biogas or methane yield was calculated according to the following Eqs. (4-1) and (4-2). Volumetric biogas or methane productivity was calculated according to Eqs. (4-3) and (4-4). And volumetric biogas or methane production rate was calculated according to Eqs. (4-5) and (4-6), respectively.

$$\text{Biogas yield (ml/g-VS)} = \frac{\text{Total biogas production (ml)}}{\text{VS loaded (g)}} \quad (4\text{-}1)$$

$$\text{Methane yield (ml/g-VS)} = \frac{\text{Total methane production (ml)}}{\text{VS loaded (g)}} \quad (4\text{-}2)$$

$$\text{Volumetric biogas productivity (L/m}^3\text{)} = \frac{\text{Total biogas production (L)}}{\text{Effective volume of reactor (m}^3\text{)}} \quad (4\text{-}3)$$

$$\text{Volumetric methane productivity (L/m}^3\text{)} = \frac{\text{Total methane production (L)}}{\text{Effective volume of reactor (m}^3\text{)}} \quad (4\text{-}4)$$

$$\text{Volumetric biogas production rate (L/m}^3\cdot\text{d)} = \frac{\text{Total biogas production (L)}}{\text{Effective volume (m}^3\text{)}\times\text{Operation time (d)}} \quad (4\text{-}5)$$

$$\text{Volumetric methane production rate (L/m}^3\cdot\text{d)} = \frac{\text{Total methane production (L)}}{\text{Effective volume (m}^3\text{)}\times\text{Operation time (d)}} \quad (4\text{-}6)$$

First-order kinetic model is a simple model applied to anaerobic digestion of complex substrates (Rao and Singh, 2004). In this study, the first-order model was used to compare the performance of each reactor. Biogas production constants k (d^{-1}) and methane production rate constant k_M (d^{-1}) were obtained from linear fitting by transforming the following Eqs. (4 - 7) and (4 - 8) into Eqs. (4 - 9) and (4 - 10), respectively. In addition, G (ml) is the cumulative biogas; G_M (ml) is the methane production; G_T (ml) is the total biogas production; G_{MT} (ml) is the methane production in the anaerobic digestion; and t (d) is the operation time.

$$G = G_T[1-\exp(-kt)] \quad (4\text{-}7)$$

$$G_M = G_{MT}[1-\exp(-k_M t)] \quad (4\text{-}8)$$

$$\ln(1-G/G_T) = -kt \quad (4\text{-}9)$$

$$\ln(1-G_M/G_{MT}) = -k_M t \quad (4\text{-}10)$$

In this study, besides biogas or methane yield, effective biogasification period (τ_e, day) and averagely effective biogas production rate (r_e, ml/g-VS·d) were also used to indicate the performance of each reactor, which can be used for reactor design in practical application and were calculated as Eqs. (4 - 11) and (4 - 12), respectively.

Effective biogasification period (τ_e, day) = N_{80}^{th} (day) – S_0^{th} (day) (4 - 11)

Effective biogas production rate (r_e, ml/g-VS·d) = Total biogas yield (ml/g-VS) /τ_e(day) (4 - 12)

in which the N_{80}^{th} day is the day when the accumulative biogas production amounts to 80% of the total biogas production during the operation, and the S_0^{th} day refers to the duration of lag phase period or the day when biogas starts to produce from the reactor.

4.2.2. Parameters used for comparison

In this study, the above-mentioned parameters including biogas yield (ml/g-VS), methane yield (ml/g-VS), volumetric biogas productivity (L/m^3), volumetric methane productivity (L/m^3), volumetric biogas production rate (L/m^3·d), volumetric methane production rate (L/m^3·d), biogas production constant k (d^{-1}) and methane production rate constant k_M (d^{-1}) were used to compare the performance of the pervious anaerobic digestion.

In addition, since all the experiments were carried out under high-ammonia conditions, the results from this study was expected to provide useful reference for the anaerobic digestion under high ammonia or high solids conditions.

4.3. Results and discussion

4.3.1. Biogas and methane production

Tables 4.1 and 4.2 list the biogas and methane yields, volumetric productivities and production rate in WRS addition and air stripping experiments. It is clear that the biogas yields from the anaerobic digestion systems were 233 (Control), 269 (R1) and 252 (R2) mL/g-VS in WRS addition experiments, respectively, while these values were 28 (Control), 75 ($R_{8.8}$) and 71 (R10.2) ml/g-VS in the air stripping experiments, respectively. Most probably due to the lower organic loading (about 0.30 kg-VS/m^3 • d), higher biogas and methane yields were obtained in wet anaerobic digestion processes (WRS addition). Wet anaerobic digestion could increase the methane production yield per unit mass (Brown et al., 2012). However, due to much higher TS content (20%) in air stripping processes the volumetric biogas and methane productivities was about 2 times higher than those obtained after WRS addition (2% TS). The much higher volumetric biogas productivities and organic loadings (about 4.48 kg-VS/m^3 • d) of dry anaerobic system indicated its advantages over wet anaerobic system, resulting in much smaller reactor volume for the treatment of SW at the same solid loadings. Another possible reason, VFA loss during air stripping and much shorter digestion duration may contribute to the lower biogas or methane yields from stripped SW.

4.3.2. Anaerobic biodegradability

As shown in Table 4.3, methane production could well be explained by the first-order model. The conversion constants (k_M) under WRS addition were 0.077 (R1) and 0.066 (R2), meanwhile for air stripping digestion systems they were 0.114 ($R_{8.8}$) and 0.119 ($R_{10.2}$). Compare to the Control, both two digestion systems had larger k_M values, signaling the increased biodegradability and methane production potential (Li et al., 2013). For the air stripping digestion systems, the highest k_M value of 0.119 L/d was achieved.

4.3.3. Ammonia production and recovery potential

In the anaerobic digestion after WRS addition, the produced ammonia was accumulated in the digestion system with no recovery. However, during air stripping, the NH_3-rich air was collected with NH_3 absorbed by 2N H_2SO_4. From the preliminary trials, when treating 1t SW 14.7 - 15.6 kg ammonia nitrogen could be recovered from SW before dry anaerobic digestion.

4.4. Summary

WRS addition and air stripping significantly increased both biogas yields and volumetric biogas productivity from SW compared to the controls. The results indicated that: (1) The highest biogas yield of 269 ml/g-VS was obtained when WRS was applied to wet anaerobic digestion of SW; (2) the highest volumetric biogas productivity of 12,150 L/m^3 was estimated for the air stripped SW at pH8.8. This research was carried out through batch experiments and continuous or semi-continuous configurations are expected to satisfy the requirement of commercialized ammonia recovery and subsequent DAD system of SW.

Table 0.5 Biogas yields, volumetric biogas productivities and biogas production rates obtained in anaerobic digestion after WRS addition and air stripping.

	Biogas yield (ml/g-VS)	Volumetric biogas productivity (L/m^3)	Biogas production rate (ml/g-VS·d)
WRS addition (Wet anaerobic digestion, 2% TS)			
Control	233	4,258	3.9
R1	269	4,900	4.5
R2	252	4,598	4.2
Air stripping (Dry anaerobic digestion, 20% TS)			
Control	28	4,462	0.8
$R_{8.8}$	75	12,150	2.1
$R_{10.2}$	71	11,538	2.0

Table 0.6 Methane yields, volumetric methane productivities and methane production rates obtained in anaerobic digestion after WRS addition and air stripping.

	Methane yield (ml/g-VS)	Volumetric methane productivity (L/m^3)	Methane production rate (ml/g-VS·d)
WRS addition (Wet anaerobic digestion, 2% TS)			
Control	83	1,510	1.4
R1	143	2,603	2.4
R2	147	2,648	2.5
Air stripping (Dry anaerobic digestion, 20% TS)			
Control	11	1,126	0.2
$R_{8.8}$	41	5,309	0.9
$R_{10.2}$	39	5,635	1.0

Table 0.7 Parameters of first-order model for methane production from different digestion systems.

	k_M	R^2
WRS addition (Wet anaerobic digestion, 2% TS)		
Control	0.047	0.569
R1	0.077	0.927
R2	0.066	0.802
Air stripping (Dry anaerobic digestion, 20% TS)		
Control	0.055	0.609
$R_{8.8}$	0.114	0.932
$R_{10.2}$	0.119	0.958

5. Conclusions

Anaerobic digestion as an attractive waste treatment method for renewable energy production has been received considerable attention worldwide. However, due to the high ammonia concentration, ammonia-rich waste, like SW is difficult to achieve efficient energy recovery in practice.

In this study, the wheat-rice-stone (WRS) addition and air stripping were used for mitigating ammonia inhibition to anaerobic process, aiming at realizing enhanced biogas production. In addition, a comparison of the performance and efficiency was carried out between the two methods for anaerobic digestion of ammonia-rich swine wastes (Fig. 5.1).

In Chapter 2, the effect of wheat-rice-stone (WRS) addition on mesophilic anaerobic fermentation for methane production from swine manure under high ammonia nitrogen level (5,145 mg- N/L) was investigated in addition to exploring its possible mechanisms involved.

The results revealed that WRS addition systems could effectively ameliorate ammonia inhibition to anaerobic fermentation of swine manure under high ammonia level (5,145 mg-N/L), achieving better stability and much smaller volume to treat the same amount of ammonia-rich wastes. Based on this work, the ionic environment in fermentation liquor is crucial for maintaining the balance between acidogenesis and methanogenesis processes, especially under high ammonia levels. Two kinds of precipitates, struvite and Fe-precipitates, likely formed during the fermentation process, probably contribute a lot to the decrease in ammonia concentration in the fermentation liquor.

In Chapter 3, the effect of ammonia stripping on dry anaerobic digestion of SW was investigated: including the effect of pH level on ammonia stripping under dry condition (TS > 35%), and the effect of different ammonia stripping conditions on subsequent dry anaerobic digestion. The results indicated that ammonia stripping at pH 10.2 achieved the highest ammonia removal (90.1%), and about 85.0% of ammonia removal at pH 8.8. Through the subsequent dry anaerobic digestion, ammonia fermentation followed by air stripping was

proven as a pretreatment for dry anaerobic digestion of ammonia-rich SW. All stripped SW showed a better biogas production potential than the raw SW, especially after ammonia stripped at pH8.8, with a biogas yield of 74.8 ml/g-VS comparable to the air stripped SW at pH10.2 (71.0 ml/g-VS). About 172% and 158% higher biogas production were obtained respectively in $R_{8.8}$ and $R_{10.2}$ than the Control (27.5 ml/g-VS).

Chapter 4 compared the performance and efficiency of anaerobic digestion of SW after WRS addition and ammonia stripping. The result showed that WRS addition and air stripping digestion system significantly increased both biogas yields and volumetric biogas productivity compared to the controls. The highest biogas yield of 269 ml/g-VS was obtained after WRS addition, while the highest volumetric biogas productivity of 12,150 L/m^3 was estimated from DAD of SW after being air stripped.

Two methods for mitigating ammonia inhibition

WRS addition	Air stripping
• Methane production: Increased by 72%. • Effective biogasification period: from 40 (control) to 20 days. • Much faster VFAs utilization rate was detected in WRS addition reactors. • Struvite and Fe-precipitates might contribute a lot to the decreased ammonia level	• pH for ammonia stripping was 10.2 resulting in highest ammonia removal (90.1%). • 172% and 158% higher biogas production were obtained respectively at pH8.8 and pH 10.2 than the Control (27.5 ml/g-VS). • The methane yields were 6.9, 32.7 and 34.7ml/g-VS for Control, pH 8.8 and pH10.2 samples, respectively.

Comparison between wheat-rice-stone addition and ammonia stripping

- Two methods significantly increased both biogas yields and volumetric biogas productivity compared to the controls.
- The highest biogas yield of 269 ml/g-VS was obtained at WRS addition R1 reactor. The highest volumetric biogas productivity of 12,150 l/m^3 occurred in air stripping $R_{8.8}$ reactor.

Figure 0.20 Summary of this study.

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