

1 **Volatile fatty acids (VFAs) production from swine manure through short-term**
2 **dry anaerobic digestion and its separation from nitrogen and phosphorus**
3 **resources in the digestate**

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Abstract

The sustainability of an agricultural system depends highly upon the recycling of all useful substances from agricultural wastes. This study explored the feasibility of comprehensive utilization of C, N and P resources in swine manure (SM) through short-term dry anaerobic digestion (AD) followed by dry ammonia stripping, aiming at achieving (1) effective total volatile fatty acids (VFAs) production and separation; (2) ammonia recovery from the digestate; and (3) preservation of high P bioavailability in the solid residue for further applications. Specifically, two ammonia stripping strategies were applied and compared in this work: (I) ammonia stripping was directly performed with the digestate from dry AD of SM (i.e. dry ammonia stripping); and (II) wet ammonia stripping was conducted by using the resultant filtrate from solid-liquid separation of the mixture of digestate and added water. Results showed that dry AD of the tested SM at 55 °C, 20% TS and unadjusted initial pH (8.6) for 8 days produced relatively high concentrations of total VFAs (94.4 mg-COD/g-VS) and ammonia-N (20.0 mg/g-VS) with high potentially bioavailable P (10.6 mg/g-TS) remained in the digestate, which was considered optimal in this study. In addition, high ammonia removal efficiencies of 96.2% and 99.7% were achieved through 3 hours' dry and wet stripping (at 55 °C and initial pH 11.0), respectively, while the total VFAs concentration in the digestate/filtrate remained favorably unchanged. All experimental data from the two stripping processes well fitted to the pseudo first-order kinetic model ($R^2 = 0.9916-0.9997$) with comparable theoretical maximum ammonia removal efficiencies ($A_{eq} > 90\%$) being obtained under the tested

dry and wet stripping conditions, implying that the former was more advantageous due to its much higher volumetric total ammonia-N removal rate thus much smaller reactor volume, less energy/chemicals consumption and no foaming problems. After 8 days' dry AD and 3 hours' dry ammonia stripping, the separated liquid containing VFAs and the recovered ammonia were both marketable products, and the solid residues with averagely higher C/N ratios of 25.7 than those of raw SM (18.0) meanwhile maintaining a relatively high bioavailable P content of 8.1 mg/g-TS can serve as better feedstock for methane fermentation.

Keywords: Swine manure; Dry anaerobic digestion; Volatile fatty acids; Dry ammonia stripping; Phosphorus fractionation

1. Introduction

Intensive livestock industry annually produces staggering amounts of animal manure in China. Generally, manure wastes are generated in two forms, i.e. liquid manure (animal excrement) flushed by water which runs through a sloping concrete floor, and solid manure (a mixture of manure and urine with bedding materials). These manure wastes represent a huge burden to the environment. According to a report published by MEP China (2014), the livestock husbandry in China annually releases 10.7 million tons of chemical oxygen demand (COD) and 0.6 million tons of ammonia-N, resulting in serious environmental issues. For this reason, appropriate methods for manure treatment and management are demanding for the sustainability of our society.

Anaerobic digestion (AD) has been recognized as a promising practice for animal manure stabilization due to its potentials for bioenergy production through organic matters decomposition, reduction in greenhouse gas emission and deactivation of pathogens (Abbasi et al., 2012; Massé et al., 2011). Traditionally, AD is performed in wet state with total solids (TS) content $< 15\%$ (always $\leq 10\%$ TS), and a large volume of water is required to achieve such a low TS condition. Despite its efficacy for biogas production, wet AD has some shortcomings such as large reactor volume, high construction cost, and discharge of large volume of digestate with high contents of organics and nutrients (mainly N and P), posing a serious threat to the surrounding water bodies. On the other hand, although this digestate can be re-utilized and applied on farmlands, a large proportion of N in the liquid digestate occurs as

ammonia-N which can easily lose and release during storage and land spreading, leading to insufficient nutrients utilization and air pollution. What's more, ammonia-N can be further nitrified in soil environment into nitrate, a highly movable form through the soil matrix to the aquifer, contributing to groundwater contamination (Alburquerque et al., 2012).

To optimize the economic efficiency for AD of livestock manure and to avoid the production of large quantities of liquid digestate, dry AD ($TS \geq 20\%$) can be adopted for the treatment of solid manure fraction obtained through solid-liquid separation, meanwhile the liquid fraction can be treated separately. Operation of AD in dry conditions contributes to smaller biogas facilities, easy handling of the digestate and minimal loss of nutrients that can be fully recovered and utilized as fertilizers (Karthikeyan and Visvanathan, 2013). Rico et al. (2015) reported a high methane yield of 265 ml/g-VS from thermophilic dry AD of dairy manure using percolate recirculation technology. High rate psychrophilic (20 °C) dry AD of dairy manure at 35% TS has been proven to be possible when sufficient quantity of well acclimatized inocula was used (Saady and Massé, 2015). Chen et al. (2015) further justified the technical and economic feasibility of a continuous plug-flow dry AD reactor operated at ambient temperature for swine manure treatment. Although being advantageous in size and costs of required facilities, dry AD of livestock manure frequently encounters ammonia inhibition and volatile fatty acids (VFAs) buildups which would to a greater extent exert inhibition effect on methanogenic activity, hindering its full application to treat livestock manure in practice. During dry AD of swine manure, noticeable

inhibition to methane production was observed when ammonia-N concentration exceeded 3000 mg/L (Chen et al., 2015). In a solid-phase AD system developed for dairy manure treatment, high concentration of accumulated VFAs also brought about decrease in organics degradation rate and daily methane yield (Rico et al., 2015). Hence, it is important to timely remove and recover these useful while inhibitory substances to guarantee high efficiencies of a dry AD system. Up to now, however, little information is available as per this aspect.

This study sought to maximize the utilization of the three major resources (C, N and P) in the manure so as to reduce its risk to the environment, aiming at realizing the specific goals outlined as follows: (1) VFAs production from short-term dry AD of animal manure and its separation; (2) ammonia recovery from the digestate by stripping; and (3) preservation of high bioavailable P in the solid residue for further application (as solid fertilizer or feedstock for composting and/or methane fermentation). Swine manure (SM) was chosen as an example of livestock manure in this study.

In order to obtain separated VFAs solutions and ammonia-N resource from SM, a two-step process involving dry AD followed by ammonia stripping was adopted as illustrated in Fig. 1a. For ammonia stripping and final acquisition of the VFAs solutions, two strategies were tested in this study: (I) stripping of ammonia directly from the digestate in dry state followed by water dilution, mixing and solid-liquid separation (i.e. dry ammonia stripping); and (II) addition of water to the digestate, then solid-liquid separation, and finally ammonia stripping from the filtrate (i.e. wet

ammonia stripping). Both the ammonia recovered from the digestate and the final liquid extract containing VFAs have market values. To the best of our knowledge, the feasibility of ammonia stripping from the digestate at $TS \geq 20\%$ has not yet been documented.

In this study, VFAs production efficiency was investigated under different dry AD conditions, and the fractionations of P before and after dry AD were revealed. Much attention was paid to the performance of ammonia stripping through the two proposed strategies, which was further compared in terms of technical and economic feasibility. Finally, the availability of VFAs, N and P resources in the liquid extract and solid residue obtained after the two-step treatment process was evaluated. Results from this study are expected to provide new concepts and useful information for the integral and comprehensive utilization of manure wastes in practice.

2. Materials and methods

2.1. Swine manure

Raw swine manure (RSM) was collected from a pig farm in Ibaraki, Japan. Chopped straw was used as bedding materials in the pig house. Solid RSM containing straw was sampled directly from the floor of pig house. The obtained RSM was mixed thoroughly and stored at 4 °C before experimental analyses, and its main characteristics are presented in Table 1 based on five tests in parallel.

2.2. Dry AD for VFAs production

The SM was anaerobically incubated at controlled experimental conditions, i.e. temperature ranging from 25 °C to 55 °C, TS content from 20% to 35%, and initial pH from 7.0-12.0, respectively. The initial system pH was adjusted with 6 M HCl solution or solid $\text{Ca}(\text{OH})_2$. In this section, $\text{Ca}(\text{OH})_2$ was used due to its low cost, wide availability, and better performance for VFAs production than other alkalis like NaOH, KOH, and CaO according to our preliminary tests (Fig. S1, Supporting Information). For the dry AD trials, 12 identical cylindrical reactors (4.4 cm in diameter, 7 cm in height) with working volume of 100 ml were used. The manure was first added with water and mixed thoroughly to achieve a designed TS content, and 90 g of the mixture was loaded into each reactor. The reactors were then flushed with N_2 for 2 min, and sealed with silicone stoppers before being placed in a temperature-controlled water bath and incubated at the designed temperature for 8 days. During the incubation three of them were sacrificed for determination of related parameters every other day.

To get sufficient amount of VFAs and ammonia enriched digestate for the stripping experiments (Fig. 1b), an anaerobic reactor (18.8 cm in diameter, 14.5 cm in height) with a working volume of 4 L was operated for 8 days without mixing under the optimal conditions determined in the above trials. The digestate was then homogenized and stored at 4 °C before used for ammonia stripping experiments.

2.3. Ammonia stripping

Ammonia stripping from the solid digestate was conducted in an enclosed

system as illustrated in Fig. 1b. For dry ammonia stripping, 130 g digestate was loaded into a 500 ml glass vessel equipped with motor-driven propeller. As for wet ammonia stripping, 130 g liquid was introduced into a bubbling reactor with a working volume of 500 ml and a buffer tank was followed to prevent the foams from entering the acid solution bottle. Air was firstly pumped into a vessel containing water to pre-warm the gas and to compensate the moisture loss from the stripping reactor. It was then flushed into the digestate containing vessel through a circular tube with small openings ($\phi 2$) at the bottom or purged into the bubbling reactor and carried the volatile ammonia into the HCl absorption bottles (500 ml \times 2, 1.5 M) for entrapment. The gas was circulated among the vessels and acid solutions at a gas flow rate of 216 ml/min. Temperature and pH were tested respectively at two levels (35 °C, 55 °C and initial pH of 10.0 and 11.0) for a stripping duration of 3 hours. NaOH was applied for pH adjustment in the ammonia stripping experiments due to its efficacy and retention of P availability. Concentrations of ammonia and total volatile fatty acids (TVFAs) in the solid digestate/liquid filtrate were detected every 30 min during the stripping process.

For solid-liquid separation, the mixture of water and digestate was centrifuged at 9000 rpm for 20 min and then filtered by filter papers. Characteristics of the VFAs containing solution and the final solid residue obtained through the two proposed strategies (Fig. 1a) under their optimal stripping conditions were also tested.

2.4. Analytical methods

TS content was measured by drying the manure sample at 105 °C till constant weight, and volatile solids (VS) content was determined by igniting the dried manure at 600 °C for 3 hours. C/N ratio of the manure was measured using an organic element analyzer (Perkin-Elmer 2004 CHN, USA). The manure pH was measured with a semi-solid pH meter (Testo 206, Germany). Total Kjeldahl nitrogen (TKN) was determined by adding known amount of deionized water into 1 g solid manure and then analyzing the mixture in accordance with standard method (APHA, 2012). Total organic nitrogen (TON) was calculated as the difference between TKN and total ammonia nitrogen (TAN).

For analysis of soluble products, 4 g manure sample (wet weight) was diluted with 40 ml deionized water. The mixture was centrifuged at 9000 rpm for 20 min and then filtered through a 0.45 µm microfiber filter. Measurements of TAN, ortho-P and soluble chemical oxygen demand (SCOD) were conducted in accordance with standard method (APHA, 2012). The filtrate was acidified by 3% phosphoric acid solution to pH around 4.0 before VFAs analysis by a Shimadzu GC-14B/FID packed with Unisole F-200 30/60 column. The column and the injector temperatures were set at 150 °C and 180 °C, respectively. The pressure of N₂ carrier gas was maintained at 200 Kpa. In this study, the concentrations of VFAs were presented as equivalent COD values calculated from the theoretical formula of each VFA component.

To reveal the dynamic change of P species in SM before and after dry AD, fractionation of P was conducted according to Standards, Measurements and Testing (SMT) Programme extraction protocol (Medeiros et al., 2005; Ruban et al., 1999).

Details of P fractionation are illustrated in Fig. S2 (Supporting Information). P in the solid SM was classified into 2 categories: organic phosphorus (OP) and inorganic phosphorus (IP). Two main forms of IP were fractionated, i.e. bio-available non-apatite inorganic phosphorus (NAIP) loosely bound on exchange sites or associated with Al, Fe and Mn oxide, and Ca-bound apatite phosphorus (AP) which is not able to be utilized by most microorganisms and plants (Manning et al., 1984; Ruban et al., 1999). Total phosphorus (TP) was the sum of OP and IP. The fractions of P that can be potentially released and utilized by microorganisms and plants were termed potentially bioavailable P (i.e. OP and NAIP).

2.5. Kinetics of ammonia stripping process

Pseudo first-order kinetic model expressed as Eq. (1) was applied for process analysis in order to disclose the mechanisms of ammonia stripping at dry or wet state.

$$A_t = A_{eq} (1 - e^{-kt}) \quad (1)$$

where t (min) is the stripping duration, and k (min^{-1}) the TAN removal rate constant.

A_{eq} and A_t (%) represent the TAN removal efficiency at equilibrium and time t , respectively.

In addition to TAN removal efficiency, effective TAN removal duration (τ_e , min) defined as the stripping duration for achieving 80% TAN removal was used to indicate the performance of the stripping process.

2.6. Statistical analysis

One-way analysis of variance (ANOVA) was used to analyze the statistical difference among the experimental scenarios by using Microsoft Office Excel 2010. Significance was assumed if $p < 0.05$.

3. Results and discussion

3.1. VFAs production from swine manure during 8 days' dry AD

3.1.1. Effect of temperature

The effect of temperature on net VFAs yield at 25% TS without initial pH adjustment (pH~8.6) is shown in Fig. 2a. It is clear that an increase in temperature favored the production of VFAs. After 8 days' dry AD, a low TVFAs yield of 5.5 mg-COD/g-VS was obtained at 25 °C. In comparison, the final TVFAs yield was increased by 1.3 and 5.8 times at 35 °C and 55 °C, about 12.6 and 37.2 mg-COD/g-VS, respectively. The VFAs detectable during dry AD of SM were mainly short-chain fatty acids with 2-5 C atoms, including acetic, propionic, iso-butyric, n-butyric, iso-valeric and trace of n-valeric acids. Acetic acid (HAc) was the dominant VFAs product at all tested temperatures, accounting for 71.7%, 62.9% and 56.6% of the TVFAs produced after 8 days' dry AD of SM at 25 °C, 35 °C and 55 °C, respectively. Propionic acid (HPr) was the second most prevalent VFAs product at 25 °C and 35 °C, respectively accounting for 11.9% and 16.4% of the TVFAs generated at the end of fermentation, whereas iso-valeric acid (iso-HVa) was the second major VFAs at higher temperature of 55 °C, and its percentage in the produced TVFAs remained pretty stable between 22.2-24.2% ($p = 0.3962 > 0.05$) throughout the whole dry AD

process at this thermophilic temperature. In view of VFAs production efficiency, 55 °C was considered to be the most favorable among the three tested temperatures.

3.1.2. Effect of TS content

In this section, dry AD of SM was performed at 55 °C and different TS contents (without initial pH adjustment), and the profiles of VFAs yield are shown in Fig. 2b. At 20% TS, the TVFAs yield increased with fermentation time and reached a maximum of 66.4 mg-COD/g-VS on day 6. After that, obvious VFAs consumption was observed, leading to decreased final TVFAs yield to 55.3 mg-COD/g-VS at the end of fermentation. As for TS contents of 25%, 30% and 35%, the highest TVFAs yields were recorded as 39.6 mg-COD/g-VS on day 8, 38.5 mg-COD/g-VS on day 8, and 30.7 mg-COD/g-VS on day 6, respectively. During the dry AD of SM at 55 °C, HAc was the most abundant VFAs product at all tested TS levels, followed by iso-HVa.

It is noteworthy that under the same operational conditions (55 °C, TS 25%, and initial pH~8.6), the results of VFAs yield and its composition obtained in these experiments were slightly different from those presented in section 3.1.1. A similar phenomenon was also noticed for ammonia production and P fractionation, most probably attributable to the complexity of dry AD process and heterogeneous nature of the SM investigated. Considering the efficiency of VFAs production, 20% TS was applied in the following tests.

3.1.3. Effect of initial pH

The effect of different initial pH on VFAs production at 55 °C and 20% TS is demonstrated in Fig. 2c. As shown, the highest yields of TVFAs were detected on day 8 at all tested initial pH levels, which followed a descending order as pH 11.0 (79.1 mg-COD/g-VS) > pH 10.0 (75.7 mg-COD/g-VS) > pH 9.0 (60.0 mg-COD/g-VS) > pH 7.0 (54.0 mg-COD/g-VS) > pH 8.0 (50.5 mg-COD/g-VS) > pH 12.0 (11.5 mg-COD/g-VS). Obviously, initial pHs of 11.0 and 10.0 were beneficial for VFAs accumulation. Despite a slightly higher TVFAs yield was obtained at initial pH 11.0 than that at pH 10.0, their difference was statistically insignificant ($p = 0.4589 > 0.05$). After 8 days' dry AD at 55 °C, 20% TS and initial pH 8.0-10.0, high volumetric TVFAs production rate of 979.7 to 1468.6 mg-COD/L/d was achieved in this study.

After 8 days' fermentation, the proportion of HAc yield to TVFAs yield was in the following order: pH 12.0 (80.4%) > pH 10.0 (63.2%) > pH 11.0 (60.5%) > pH 9.0 (55.8%) > pH 8.0 (38.0%) > pH 7.0 (33.3%). It is apparently that the proportion of HAc increased almost linearly with the increase of initial pH, suggesting that HAc production pathway is more dominant and robust than the production of other VFAs under alkaline dry AD conditions.

As pointed out by Lin et al. (2013), initial pH adjustment could alter the microbial communities in SM thus affecting its hydrolysis and acidification processes. It is interesting to notice that, when operated at 55 °C, 20% TS and similar initial pHs of 8.0 (adjusted with HCl), 8.6 (unadjusted) and 9.0 (adjusted with $\text{Ca}(\text{OH})_2$), the patterns of VFAs accumulation were quite different (Figs. 2b and 2c). At adjusted initial pHs 8.0 and 9.0, the TVFAs yield increased gradually during the dry AD

process and reached a maximum on day 8 although impermanent stagnation seemed to occur during days 2-4 and days 4-6, respectively. In comparison, quicker TVFAs accumulation was observed at unadjusted initial pH 8.6 with higher maximum TVFAs yield on day 6. This observation was most probably brought about by the disturbance of chemical (HCl or Ca(OH)₂) addition on the microbial communities localized in SM, that is, some adaptation or acclimation was necessary for the fermentation bacteria to accommodate to the resultant microenvironment like elevated ionic strength or free ammonia.

3.2. Ammonia recovery by stripping

During dry AD of SM, substantial amount of ammonia-N was released gradually through organic matters decomposition. Fig. S3 (Supporting Information) illustrates the effects of different temperature, TS content and initial pH on ammonia production after the 8 days' dry AD trials. Similar to the production of VFAs, thermophilic temperature (55 °C), lower TS (20%) and moderate alkaline initial pH (8.0-10.0) were beneficial for the production of ammonia. Despite a higher TAN yield obtained after dry AD at initial pH 10.0, ANOVA analysis indicated statistically insignificant difference in the final TAN yield among initial pH 8.0-10.0 (including the scenario of initial pH 8.6, i.e. without initial pH adjustment).

For the purpose of maximizing the utilization of C, N and P resources in the digestate as well as minimizing chemicals consumption (detailed discussion was given in section 3.3), ammonia stripping was conducted with the digestate obtained

after 8 days' dry AD at 55 °C, 20% TS and unadjusted initial pH. Table 2 lists the main resources available in the digestate after dry AD under 4 typical experimental conditions in this study.

3.2.1. Dry ammonia stripping

Fig. 3a displays the removal efficiencies of TAN from the solid digestate under different stripping conditions. An increase in both initial pH and temperature gave rise to higher concentrations of free ammonia nitrogen (FAN) (Hansen et al., 1998), contributing to higher removal efficiencies of TAN from the digestate. The highest TAN removal efficiency of 96.2% was achieved at 55 °C and initial pH 11.0 after 3 hours' stripping. Quantitative analysis of the amount of TAN entrapped by acid solution or water and that escaped from the digestate revealed a high TAN recovery efficiency $\geq 95.5\%$ under all stripping conditions.

As illustrated in Fig. 3b, most probably as a consequence of ammonia removal the digestate pH dropped in all circumstances, from 10.0 to 8.9 and 8.5, and from 11.0 to 9.6 and 9.1 when the stripping was conducted at 35 °C and 55 °C, respectively. On the other hand, the concentration of TVFAs in the digestate remained pretty stable throughout the whole stripping process. As it is known, VFAs are volatile under acidic conditions while they become stable and exist as ionic forms in alkaline solutions. In the stripping systems, due to the fact that pH was maintained at $\text{pH} > 7.0$, the escaped TVFAs from the reactor were considered insignificant. In these trials, averagely 92.5% of the TVFAs were successfully retained in the digestate after 3 hours'

stripping at 55 °C and initial pH 11.0. Only 4.7% and 2.1% of TVFAs were averagely detected in the scrubbing solutions and the water containing bottle (vessel 3 in Fig. 1b), respectively. And the loss of TVFAs from the stripping system was most probably brought about by measurement errors. Based on the experimental results (Fig. 3a), the effective TAN removal duration (τ_e), about 60 min and 90 min, was obtained for the stripping process at initial pH 11.0 and pH 10.0 (55 °C), respectively. The former (55 °C and initial pH 11.0) was considered to be the optimal dry ammonia stripping condition in this study.

3.2.2. *Wet ammonia stripping*

The removal efficiencies of TAN during wet ammonia stripping are shown in Fig. 3c. At the end of stripping (the 3rd h), the removal efficiencies of TAN were detected to be 79.1% at 35 °C and initial pH 10.0, 91.5% at 55 °C and initial pH 10.0, and 95.0% at 35 °C and initial pH 11.0, respectively. The highest TAN removal efficiency was achieved at 55 °C and initial pH 11.0, which increased rapidly to 98.7% after stripping for 2 hours, and then climbed slowly to 99.7% after 3 hours' stripping. TAN balance analysis again revealed good performance of TAN recovery by using the stripping/absorption processes. Greater than 94.0% of the stripped TAN from the filtrate was able to be entrapped by the acid solution and water in all cases studied.

As shown in Fig. 3d, the filtrate pH declined during the process of stripping from 10.0 to 8.8 (35 °C) and 8.4 (55 °C), and from 11.0 to 9.7 (35 °C) and 9.1 (55 °C),

respectively. On the other hand, the decrease of TVFAs in the filtrate was found to be less than 11% in all the tested scenarios. For instance, an average decrease of 6.3% after stripping was detected when the stripping was conducted at 55 °C and initial pH 11.0. Moreover, to a great extent the lost TVFAs could be re-entrapped by the scrubbing solutions (~ 61%) and water containing vessel 3 (~ 32%, Fig. 1b). Again, based on Fig. 3c, the effective TAN removal duration (τ_e) was determined to be around 65 min and 85 min, respectively for wet stripping at initial pH 11.0 and pH 10.0 (55 °C), which was almost similar to that of dry ammonia stripping process (Fig. 3a).

3.2.3. Comparative analysis

Two ammonia stripping strategies (dry or wet) were employed for ammonia recovery from the digestate, which were further compared in terms of technical and economic aspects. According to the results of kinetic analysis presented in Table 3, the experimental data from both dry and wet ammonia stripping processes fitted well to the pseudo first-order kinetic model ($R^2 = 0.9916-0.9997$). Interestingly, when operated under the same temperature and initial pH conditions, almost similar A_{eq} values were obtained by either dry or wet ammonia stripping. This observation indicated that TS content could only affect the kinetics of TAN removal since similar A_{eq} values were achieved under both dry and wet stripping conditions while a higher TAN removal rate constant (k) for wet stripping process. Results indicated that the extent to which ammonia stripping could proceed was driven by the substrate

FAN/TAN ratio closely related to system pH and temperature, whereas the ammonia removal rate was largely affected not only by the effective contact between gas and substrate, but also the influencing factors like gas distribution and existing form, viscosity and fluidity of the substrate. Among all the tested scenarios, 55 °C, the optimal temperature for VFAs production, was also found to be the optimal temperature for both dry and wet ammonia stripping in this study. In addition, for these two stripping strategies, about 60-65 min and 85-90 min were necessary for achieving 80% of TAN removal from the digestate or filtrate when ammonia stripping was conducted at 55 °C with initial pH 11.0 and pH 10.0, respectively (Table 3).

In the stripping system developed in this study, the gas was circulated among the vessels and acid absorption solutions in a close loop, to a great extent avoiding unnecessary ammonia loss and OH⁻ consumption resulted from the reaction between NaOH and CO₂ in the air. From this work, dry ammonia stripping possesses the following advantages compared to traditional wet stripping. Firstly, dry ammonia stripping can avoid the foaming problems which always occur in wet systems. Secondly, much higher volumetric TAN removal rates (0.75-0.99 g/L-digestate/h) were obtained in the dry ammonia stripping systems operated at 20% TS, in comparison to those (0.14-0.17 g/L-filtrate/h) of wet ammonia stripping systems. In addition, processing of the digestate in semi-solid state requires much smaller reactor and thus less construction investment. And thirdly, the consumptions of energy for heating as well as chemicals (i.e. both alkalis applied to raise digestate/filtrate pH during ammonia stripping and acids used for re-neutralization of the ammonia-

stripped digestate/filtrate before being further processed) are considerably saved.

Zhang and Chen (2009) stated that it's feasible to use struvite precipitation for simultaneous recovery of ammonia-N and soluble ortho-P from sludge fermentation liquor. This process, however, is less beneficial for the liquid extract from fermented manure mainly due to the following two considerations. (1) Numerous organic compounds and inorganic ions co-existing in the liquid would definitely affect the purity of struvite precipitates. (2) The theoretical molecular ratio of N:P in struvite is 1:1, while the molecular ratio of TAN to ortho-P in the liquid extract was close to 13:1. The concentration of water extractable ortho-P (~90 mg/L) in the fermented manure was disproportionally lower than that of TAN (~540 mg/L) due to the fact that most P was fixed in biomass or formed precipitates with the co-existing metallic ions like $\text{Fe}^{2+/3+}$ and Ca^{2+} (Huang et al., 2015). In this context, dry ammonia stripping offers a promising alternative for direct separation and recovery of ammonia-N from the dry AD digestate.

3.3. Changes in P bioavailability in the digestate

3.3.1. During VFAs fermentation

Fig. 4a depicts the analytical results of P fractions and pH variations in RSM and the digestates obtained from the 8 days' dry AD at different temperatures. As shown, TP remained stable at around 18.0 mg/g-TS in all tested manure samples. The increase in temperature, however, has some positive effect on the conversion of OP to IP. Generally, the P group in OP compounds is bound to C by an ester bond. Thus OP

is mineralized as a byproduct of the C cycle, during which enzymatic hydrolysis is an essential step for the degradation of OP to IP (Tiessen, 2011). Various enzymes such as nucleases, phytase, phospholipase, and phosphatases are involved in this enzymatic hydrolysis process, and the activity of each enzyme depends highly upon system temperature and pH (Tiessen, 2011; Turner et al., 2005). After the 8 days' dry AD process, the proportion of potentially bioavailable P decreased slightly from 61.3% (RSM) to 59.8%-58.6%. This is to some extent consistent with the finding of G ng r and karthikeyan (2008) who declared that AD of dairy manure was capable of reducing the immediately available P in the solid phases. On the other hand, the system pH dropped from 8.6 to 8.0, 7.8 and 7.7 after dry AD at 25  C, 35  C and 55  C, respectively, most probably resulting from VFAs accumulation (Fig. 2a).

Results of P fractionation and pH in RSM and the digestates after the 8 days' dry AD at 55  C and different TS contents are displayed in Fig. 4b. It was observed that at the end of experiments, the conversion efficiency of OP increased from 18.4% to 47.4% with TS increased from 20% to 35%. This observation might be partially explained by the increase in their final pHs from 7.7 at 20% TS to 8.3 at 35% TS. A strong correlation relationship was found between the OP conversion efficiency and the final pH of the digestate by using linear regression analysis ($R^2 = 0.9960$). Unlike the production of VFAs, TS content was not the limiting factor dictating the conversion efficiency of OP to IP. Instead, system pH played a more important role in OP mineralization. A proper increase in the system pH might be beneficial for the microbial degradation of OP. In this work a greater extent of OP mineralization

seemed to be accompanied by a slightly higher final pH (like 35% TS).

Fig. 4c displays the effects of initial system pH on P speciation after the 8 days' dry AD at 55 °C and 20% TS. An increase in initial pH from 7.0 to 10.0 contributed to an increased OP conversion efficiency from 15.8% to 68.4%. Further increase of system pH to 11.0 or 12.0, however, led to a decline in OP conversion efficiency. On the other hand, a larger proportion of AP in IP was detected in the digestate when dry AD was conducted at higher initial pHs. This phenomenon was due to the fact that in this study $\text{Ca}(\text{OH})_2$ was employed to adjust the initial pH of SM to alkaline conditions under which Ca^{2+} and PO_4^{3-} could react with OH^- to form apatite (Van Kemenade and De Bruyn, 1987), contributing to a higher amount of AP in the digestate. The lowest potentially bioavailable P was detected to be 1.7 mg/g-TS at initial pH of 10.0, accounting for 9.5% of TP in the digestate.

3.3.2. During ammonia stripping

Table 2 also lists the availabilities of TVFAs, TAN and P species in the digestate after dry AD under 4 typical conditions. In spite of the highest TVFAs and TAN yields obtained in the digestate from dry AD at 55 °C, 20% TS and initial pH 10.0, its bioavailable P (OP + NAIP) was very low. In contrast, after 8 days' dry AD at 55 °C, 20% TS and no adjustment of initial pH, relatively high concentrations of TVFAs, TAN and bioavailable P in the digestate were obtained simultaneously. In order to optimize the costs relating to chemicals consumption and to meet the requirements of multipurpose utilization of the digestate, the optimal dry AD condition was

determined as 55 °C, 20% TS and unadjusted initial pH. The digestate obtained after 8 days' dry AD under the optimal conditions underwent dry or wet ammonia stripping; thereafter the availability of C, N and P in the separated liquid solution and solid residue were explored.

Table 4 presents the main characteristics of the liquid and solid phases obtained by strategies I and II, respectively, at stripping conditions of 55 °C and initial pH 11.0. As it can be seen, the final concentration of TVFAs was almost same in the liquid phase by using both stripping processes, around 2250 mg-COD/L. As for P availability, slightly higher concentration of soluble ortho-P was detected in the liquid after dry ammonia stripping, possibly due to thermal-alkaline hydrolysis of the organic solids during the stripping process. As expected, a slightly lower concentration of OP was detected in the solid residue after strategy I, about 2.4 mg/g-TS in comparison to 3.1 mg/g-TS of OP in the solid residue acquired with strategy II. AP and NAIP concentrations were almost similar regardless of different stripping strategies applied. In summary, the potentially bioavailable P in the solid residue was able to be maintained at a relatively high level of 8.1-8.4 mg/g-TS (51.6%-53.5% of TP) after ammonia stripping and solid-liquid separation through both strategies. Most notably, the C/N ratios in the solid residues after strategies I and II were detected to be 25.7 and 21.9, respectively, both higher than that of RSM (C/N=18.0, Table 1) and falling within the optimal C/N range (20-30) for biomethane production (Esposito et al., 2012).

3.4. Implication of this study to practice

After the two-step treatment process under optimal conditions, the obtained liquid rich in VFAs (Table 4) might be utilized as external carbon source to enhance biological nutrients removal after being further processed (like extraction or adsorption) or used for other industrial purposes. The recovered ammonia, on the other hand, is a valuable raw material that can be used for synthesis of chemical fertilizers (e.g. urea), antibacterial agents and many commercial cleaning products. The solid residue with much lower N content while maintaining a relatively high content of bioavailable P can serve as feedstock for dry methane fermentation or composting for solid fertilizer production. In brief, it is practically feasible to achieve maximum utilization of C, N and P resources in livestock manure by combining short-term dry AD and dry ammonia stripping technologies.

To make full use of livestock manure, future research on further enhancement of VFAs production from dry AD of SM and dry methane production of the resultant solid residue should be followed up. Specifically, in addition to cost-effectiveness analysis of the whole system, attentions should also be paid to the preservation and retention of the bioavailable N and P resources in the digestate and utilization of the digestate as high quality fertilizers as well.

4. Conclusions

This paper presented a novel strategy for stabilization and utilization of SM using short-term dry AD followed by dry ammonia stripping, specifically focusing on

the changes in VFAs, TAN and P bioavailability throughout the treatment procedure.

From this work, the following conclusions can be arrived at:

(1) Thermophilic temperature, lower TS of 20% and moderate alkaline initial pH of 8.0-10.0 are beneficial for the accumulation of VFAs and ammonia during short-term dry AD of SM. After 8 days' dry AD under above conditions, high volumetric TVFAs and TAN production rates of 979.7-1468.6 mg-COD/L/d and 181.3-214.0 mg/L/d were achieved, respectively.

(2) In the thermophilic dry AD system, proper increase in system pH (brought about by increasing TS from 20% to 35%) was beneficial for the microbial degradation of OP. Mineralization of OP was found to be significantly enhanced when SM was fermented under 20% TS and 55 °C by using $\text{Ca}(\text{OH})_2$ to adjust initial pH, which lowered the amount of bioavailable P (OP + NAIP). Considering full utilization of C, N and P resources in the SM, the short-term dry AD without initial pH adjustment (pH~8.6) is suggested in practice.

(3) The two-step procedure involving short-term dry AD and dry ammonia stripping not only provides an alternative for the production and separation of VFAs from ammonia and P resources, but also serves as pretreatment to reduce ammonia buildups. Thus the treated SM residue is also expected to have high potential for dry methane fermentation, which has been manifested by our followed-up experiments (data not shown).

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References

Abbasi, T., Tauseef, S.M., Abbasi, S.A., 2012. Anaerobic digestion for global warming control and energy generation—An overview. *Renew. Sust. Energ. Rev.* 16, 3228-3242.

Albuquerque, J.A., de la Fuente, C., Ferrer-Costa, A., Carrasco, L., Cegarra, J., Abad, M., Bernal, M.P., 2012. Assessment of the fertiliser potential of digestates from farm and agroindustrial residues. *Biomass Bioenerg.* 40, 181-189.

APHA, 2012. *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition edited by E.W. Rice, R. B. Baird, A.D. Eaton and L.S. Clesceri. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington, D.C., USA.

Chen, C., Zheng, D., Liu, G., Deng, L., Long, Y., Fan, Z., 2015. Continuous dry fermentation of swine manure for biogas production. *Waste Manage.* 38, 436-442.

Esposito, G., Frunzo, L., Giordano, A., Liotta, F., Panico, A., Pirozzi, F., 2012. Anaerobic co-digestion of organic wastes. *Rev. Environ. Sci. Biotechnol.* 11, 325-341.

Güngör, K., Karthikeyan, K.G., 2008. Phosphorus forms and extractability in dairy

559 manure: A case study for Wisconsin on-farm anaerobic digesters. *Bioresource*
 560 *Technol.* 99, 425-436.

561 Hansen, K.H., Angelidaki, I., Ahring, B.K., 1998. Anaerobic digestion of swine
 562 manure: Inhibition by ammonia. *Water Res.* 32, 5-12.

563 Huang, H., He, L., Lei, Z., Zhang, Z., 2015. Contribution of precipitates formed in
 564 fermentation liquor to the enhanced biogasification of ammonia-rich swine
 565 manure by wheat-rice-stone addition. *Bioresource Technol.* 175, 486-493.

566 Karthikeyan, O.P., Visvanathan, C., 2013. Bio-energy recovery from high-solid
 567 organic substrates by dry anaerobic bio-conversion processes: a review. *Rev.*
 568 *Environ. Sci. Biotechnol.* 12, 257-284.

569 Lin, L., Wan, C., Liu, X., Lee, D.-J., Lei, Z., Zhang, Y., Tay, J. H., 2013. Effect of
 570 initial pH on mesophilic hydrolysis and acidification of swine manure.
 571 *Bioresource Technol.* 136, 302-308

572 Manning, P.G., Birchall, T., Jones, W., 1984. The partitioning of non-apatite inorganic
 573 phosphorus in sediments from lakes Erie and Ontario. *Can. Mineral.* 22, 357-365.

574 Massé, D., Gilbert, Y., Topp, E., 2011. Pathogen removal in farm-scale psychrophilic
 575 anaerobic digesters processing swine manure. *Bioresource Technol.* 102, 641-
 576 646.

577 Medeiros, J.J.G., Cid, B.P., Gómez, E.F., 2005. Analytical phosphorus fractionation in
 578 sewage sludge and sediment samples. *Anal. Bioanal. Chem.* 381, 873-878.

579 MEP China (Ministry of Environmental Protection of the People's Republic of
 580 China), 2014.

581 http://zls.mep.gov.cn/hjtj/nb/2013tjnb/201411/t20141124_291868.htm (accessed
582 on 14th December, 2015).

583 Rico, C., Montes, J.A., Muñoz, N., Rico, J.L., 2015. Thermophilic anaerobic digestion
584 of the screened solid fraction of dairy manure in a solid-phase percolating reactor
585 system. *J. Clean. Prod.* 102, 512-520.

586 Ruban, V., López-Sánchez, J.F., Pardo, P., Rauret, G., Muntau, H., Quevauviller, P.,
587 1999. Selection and evaluation of sequential extraction procedures for the
588 determination of phosphorus forms in lake sediment. *J. Environ. Monit.* 1, 51-56.

589 Saady, N.M.C., Massé, D.I., 2015. High rate psychrophilic anaerobic digestion of
590 high solids (35%) dairy manure in sequence batch reactor. *Bioresource Technol.*
591 186, 74-80.

592 Tiessen, H. 2011. Phosphorus Availability in the Environment. in: eLS, John Wiley &
593 Sons, Chichester. DOI: 10.1002/9780470015902.a0003188.pub2.

594 Turner, B.L., Frossard, E., Baldwin, D.S. 2005. Organic phosphorus in the
595 environment. CABI, Wallingford.

596 Van Kemenade, M.J.J.M., De Bruyn, P.L., 1987. A kinetic study of precipitation from
597 supersaturated calcium phosphate solutions. *J. Colloid and Interface Sci.* 118,
598 564-585.

599 Zhang, C., Chen, Y., 2009. Simultaneous nitrogen and phosphorus recovery from
600 sludge-fermentation liquid mixture and application of the fermentation liquid to
601 enhance municipal wastewater biological nutrient removal. *Environ. Sci.*
602 *Technol.* 43, 6164-6170.

Tables

Table 1. Characteristics of raw swine manure used in the experiments.

Parameters	Raw swine manure (RSM)
Total solids (TS)	37.1 (± 0.2) %
Volatile solids (VS, TS based)	77.6 (± 0.2) %
Total ammonia nitrogen (TAN)	10.6 (± 0.3) mg/g-VS
Total organic nitrogen (TON)	19.3 (± 1.1) mg/g-VS
Organic phosphorus (OP)	3.8 (± 0.3) mg/g-TS
Apatite phosphorus (AP)	7.0 (± 0.5) mg/g-TS
Non-apatite inorganic phosphorus (NAIP)	7.3 (± 0.5) mg/g-TS
Total volatile fatty acids (TVFAs)	39.1 (± 1.1) mg-COD/g-VS
C/N	18.0 (± 0.5)
pH	8.6 (± 0.1)

The data are expressed as mean (\pm SD).

Table 2. Availability of nutrient elements and total volatile fatty acids in the digestate under 4 typical experimental conditions after 8 days' dry AD.

No.	Fermentation conditions			Compositions of nutrient elements and TVFAs in the digestate						
	Temperature	TS	Initial pH	TVFAs	TAN	TON	OP	NAIP	AP	P bioavailability ^b
	(°C)	(%)	(chemical used)	(mg-COD/g-VS)	(mg/g-VS)	(mg/g-VS)	(mg/g-TS)	(mg/g-TS)	(mg/g-TS)	(%)
1	55	20	8.6 ^a	94.4	20.0	9.7	3.1	7.5	7.4	58.9
2	55	35	8.6 ^a	67.4	16.2	13.7	2.0	8.5	7.8	57.3
3	55	20	8.0 (HCl)	89.6	19.9	9.9	2.9	7.1	7.9	55.9
4	55	20	10.0 (Ca(OH) ₂)	114.8	21.3	8.3	1.2	0.5	16.2	9.5

^aNo initial pH adjustment. ^bP bioavailability (%)=100 × (OP + NAIP)/TP.

AP-apatite phosphorus, NAIP-non-apatite inorganic phosphorus, OP-organic phosphorus, TAN-total ammonia nitrogen, TON-total organic nitrogen, TS-total solids, TVFAs-total volatile fatty acids, VS-volatile solids.

Table 3. Stripping rate constants associated with the pseudo first-order kinetic model and effective TAN removal durations under different stripping conditions.

Strategy	Stripping conditions		Pseudo first-order kinetic model			τ_e (min)
	Temperature (°C)	Initial pH	A_{eq} (%)	k (min ⁻¹)	R^2	
I: Dry stripping	35	10.0	83.4	0.0117	0.9916	278.5
	55	10.0	90.6	0.0238	0.9970	90.2
	35	11.0	95.2	0.0154	0.9974	119.1
	55	11.0	97.3	0.0280	0.9958	61.7
II: Wet stripping	35	10.0	83.9	0.0165	0.9996	186.0
	55	10.0	91.9	0.0242	0.9997	84.5
	35	11.0	96.4	0.0176	0.9984	100.6
	55	11.0	99.9	0.0251	0.9977	64.3

Table 4. Main characteristics of the final liquid solutions and solid residues obtained from the two operation strategies under their corresponding optimal stripping conditions (both at 55 °C and initial pH 11.0).

	Parameters	Unit	Strategy I	Strategy II
			(Dry stripping)	(Wet stripping)
Liquid phase	Total ammonia nitrogen (TAN)	mg/L	19.5 (±3.3)	1.6 (±1.1)
	Soluble ortho-P	mg/L	93.1 (±4.6)	86.7 (±6.7)
	Total volatile fatty acids (TVFAs)	mg-COD/L	2247.3 (±114.2)	2261.2 (±125.0)
	Soluble chemical oxygen demand (SCOD)	mg/L	3926.6 (±163.6)	3728.5 (±177.9)
	pH	—	9.2 (±0.3)	9.1 (±0.2)
Solid phase	Total solids (TS)	%	17.5 (±1.6)	16.4 (±1.6)
	Volatile solids (VS, TS based)	%	76.3 (±1.0)	77.0 (±1.5)
	Total ammonia nitrogen (TAN)	mg/g-VS	0.5 (±0.0)	4.0 (±0.3)
	Total organic nitrogen (TON)	mg/g-VS	9.1 (±0.3)	9.5 (±0.5)
	Organic phosphorus (OP)	mg/g-TS	2.4 (±0.3)	3.1 (±0.3)
	Apatite phosphorus (AP)	mg/g-TS	7.6 (±0.8)	7.3 (±0.6)
	Non-apatite inorganic phosphorus (NAIP)	mg/g-TS	5.7 (±0.3)	5.3 (±0.2)
	C/N	—	25.7 (±0.6)	21.9 (±0.5)
	pH	—	8.4 (±0.2)	7.6 (±0.3)

The data are expressed as mean (±SD).

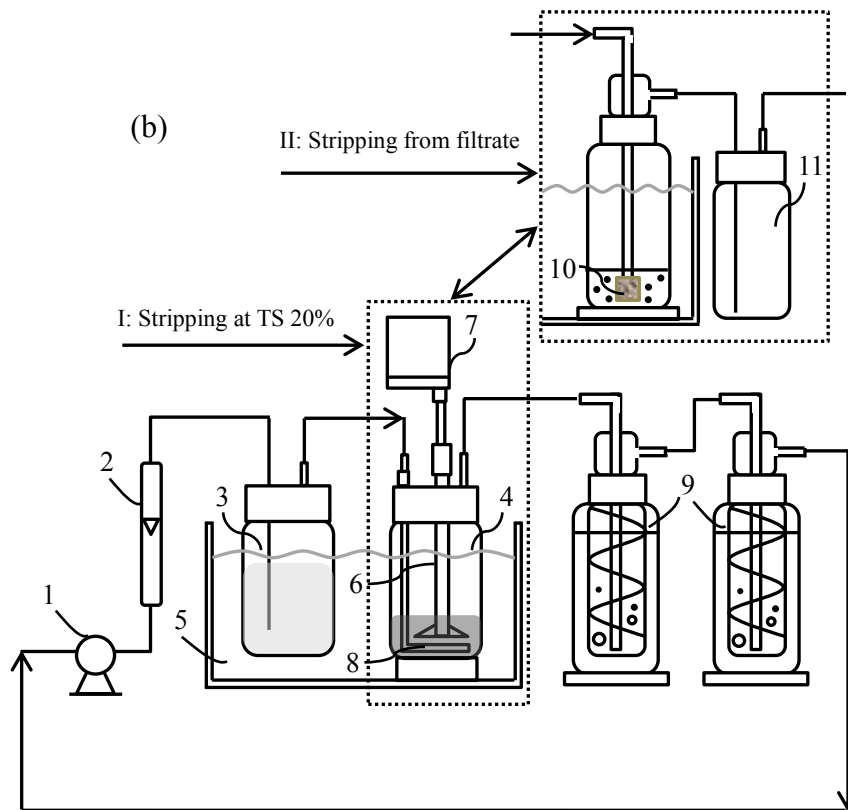
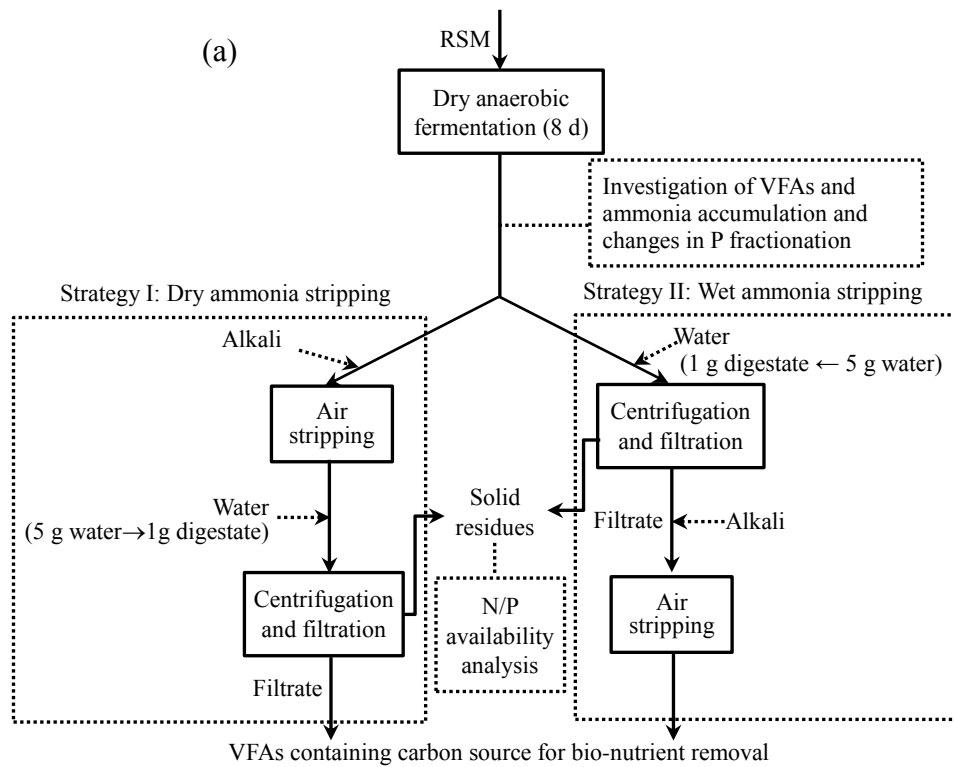


Fig. 1 - Schematics of (a) the procedure for VFAs separation from the fermented swine manure; and (b) the recirculating system for ammonia stripping and recovery.

667 1-gas pump, 2-gas flow meter, 3-vessel with water, 4-vessel with digestate, 5-
668 temperature controlled thermostat, 6-propeller, 7-motor, 8-circular hollow tube with
669 openings at the bottom, 9-acid absorption bottles, 10-porous ceramic head, 11-buffer
670 bottle.
671

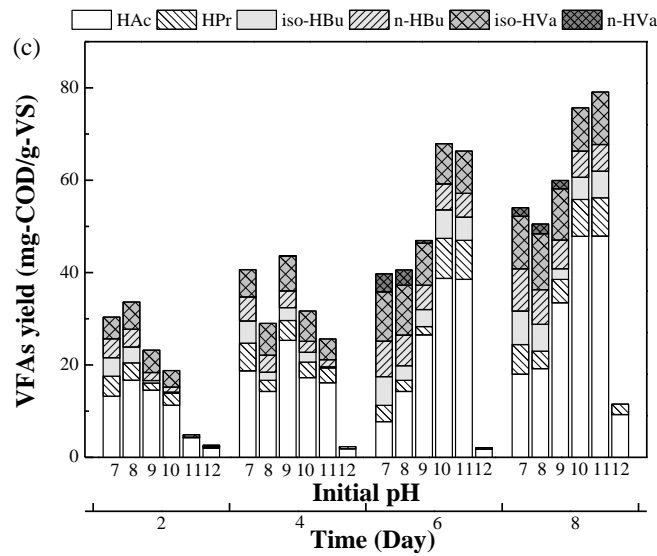
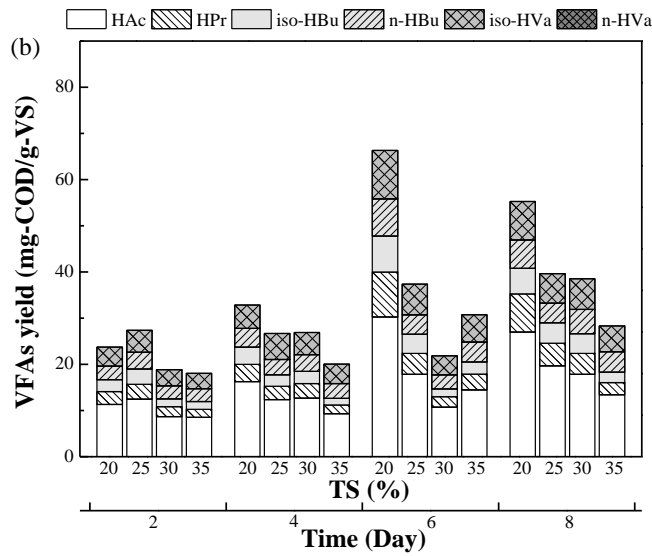
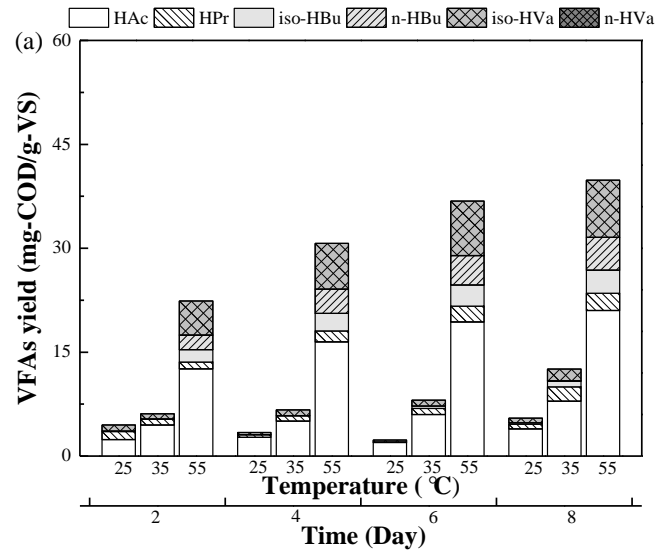
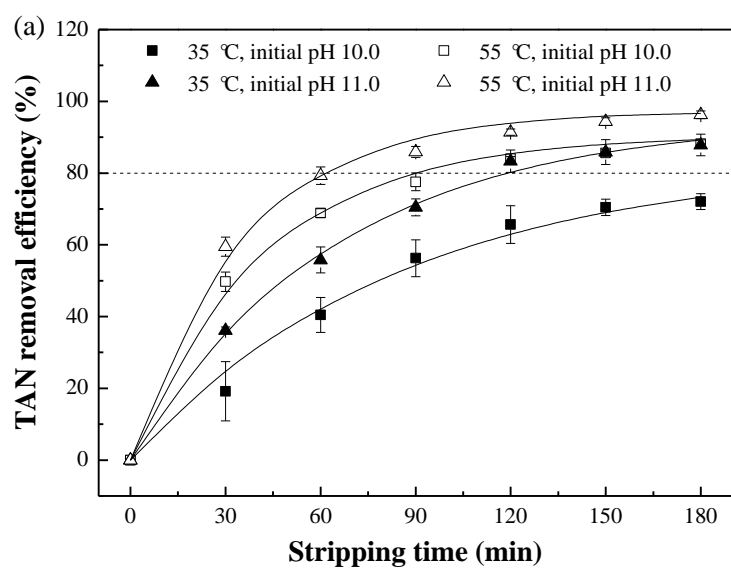
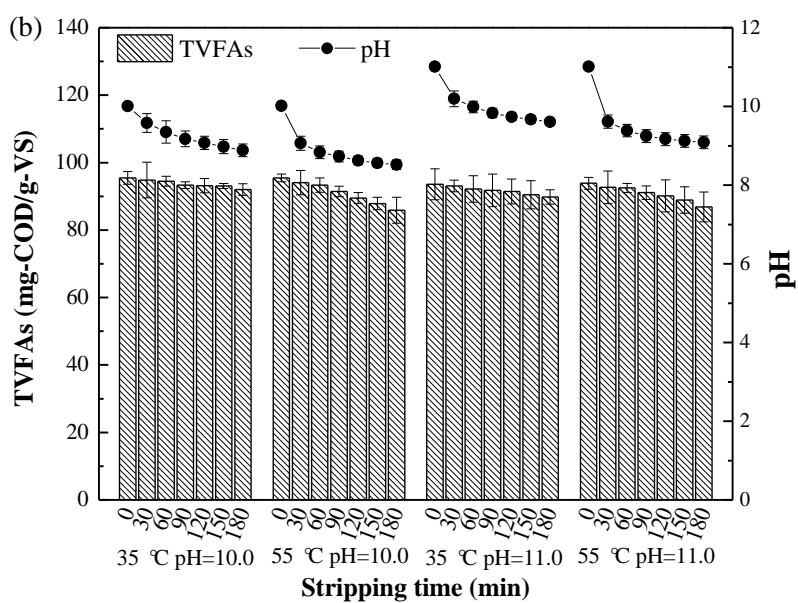


Fig. 2 - Effects of temperature (a, TS=25% without pH adjustment), TS content (b,

677 55 °C without pH adjustment) and initial pH (c, 55 °C and 20% TS) on dry AD for the
678 production of VFAs. Acetic acid (HAc), propionic acid (HPr), iso-butyric acid (iso-
679 HBu), n-butyric acid (n-HBu), iso-valeric acid (iso-HVa) and n-valeric acid (n-HVa).
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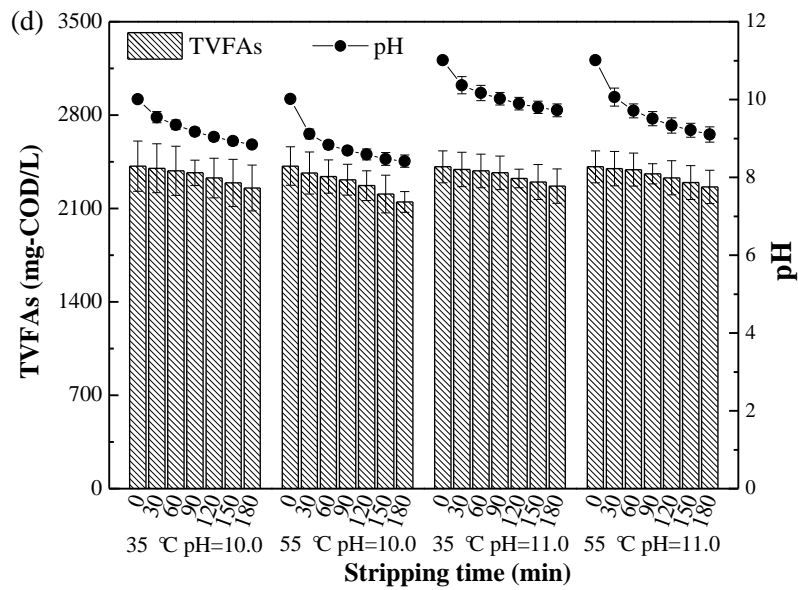
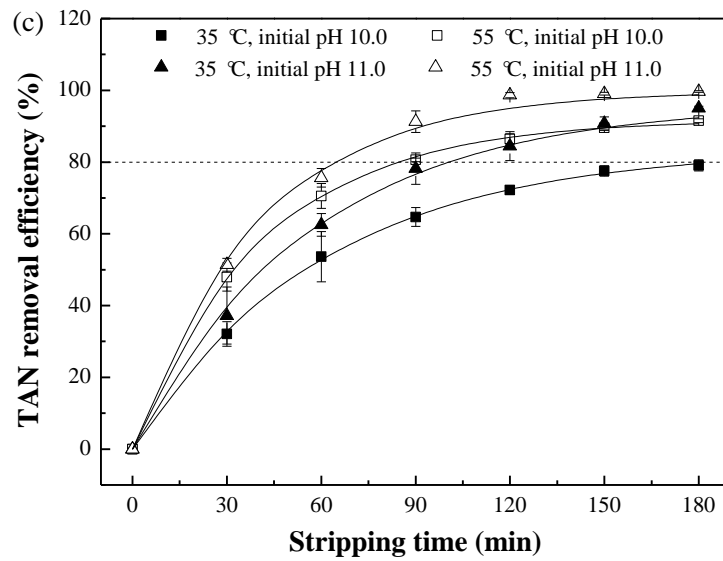


Fig. 3 - Effects of different operational conditions on (a) ammonia removal efficiency and (b) variations of pH and TVFAs during dry ammonia stripping, and those of different stripping conditions on (c) ammonia removal efficiency and (d) changes of pH and TVFAs during wet ammonia stripping.

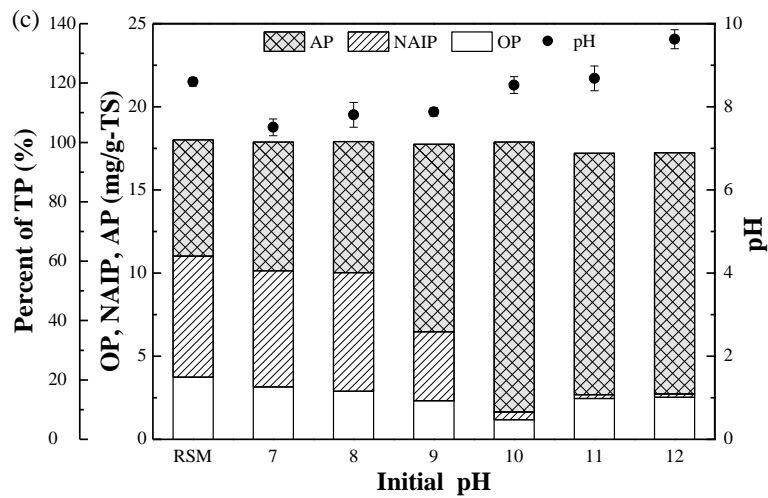
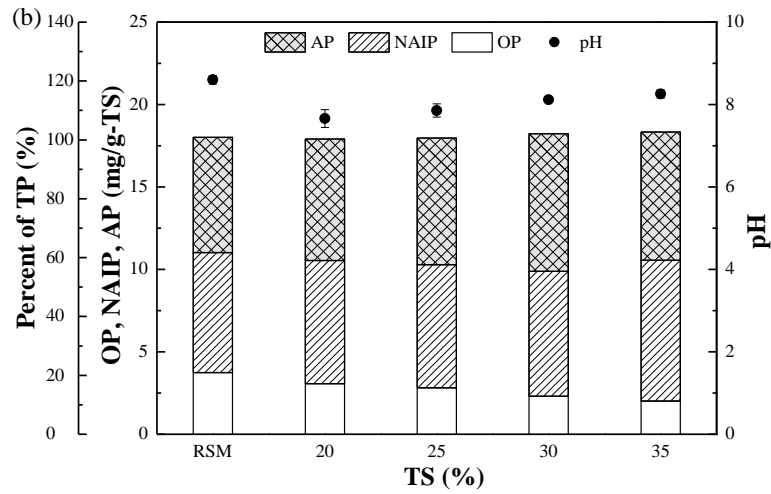
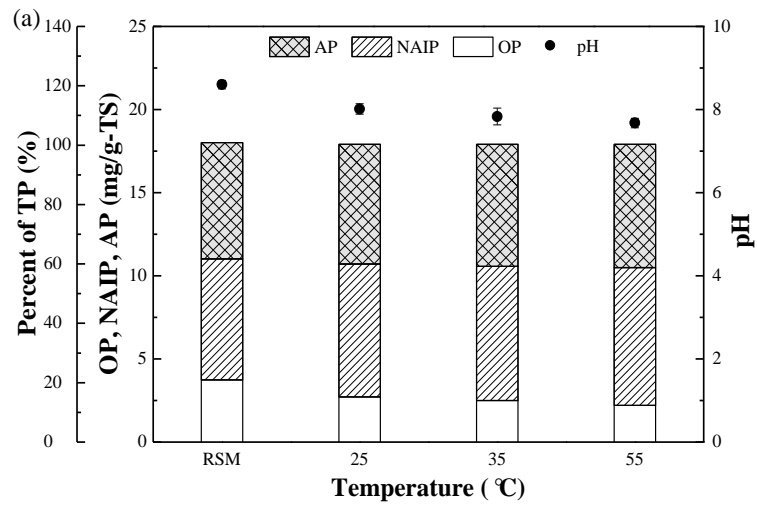


Fig. 4 - Profiles of pH and P fractionation in raw swine manure (RSM) and the digestate under different dry AD conditions tested: (a) operation temperature at 25 °C,

697 35 °C and 55 °C (25% TS and no initial pH adjustment); (b) TS content of 20-35% (at
698 55 °C without pH adjustment); and (c) initial pH varied from 7.0 to 12.0 (at 55 °C and
699 20% TS), respectively.
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701