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Volatile fatty acids (VFAs) production from swine manure through short-term dry anaerobic digestion and its separation from nitrogen and phosphorus 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 ℃ 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 ≤ 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 ≥ 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 ºC) 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

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

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

111 In order to obtain separated VFAs solutions and ammonia-N resource from SM, a
112 two-step process involving dry AD followed by ammonia stripping was adopted as
113 illustrated in Fig.1a. For ammonia stripping and final acquisition of the VFAs
114 solutions, two strategies were tested in this study: (I) stripping of ammonia directly
115 from the digestate in dry state followed by water dilution, mixing and solid-liquid
116 separation (i.e. dry ammonia stripping); and (II) addition of water to the digestate,
117 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 ≥ 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

140 The SM was anaerobically incubated at controlled experimental conditions, i.e.
141 temperature ranging from 25 °C to 55 °C, TS content from 20% to 35%, and initial
142 pH from 7.0-12.0, respectively. The initial system pH was adjusted with 6 M HCl
143 solution or solid $Ca(OH)_2$. In this section, $Ca(OH)_2$ was used due to its low cost, wide
144 availability, and better performance for VFAs production than other alkalis like
145 NaOH, KOH, and CaO according to our preliminary tests (Fig. S1, Supporting
146 Information). For the dry AD trials, 12 identical cylindrical reactors (4.4 cm in
147 diameter, 7 cm in height) with working volume of 100 ml were used. The manure was
148 first added with water and mixed thoroughly to achieve a designed TS content, and 90
149 g of the mixture was loaded into each reactor. The reactors were then flushed with N_2
150 for 2 min, and sealed with silicone stoppers before being placed in a temperature-
151 controlled water bath and incubated at the designed temperature for 8 days. During
152 the incubation three of them were sacrificed for determination of related parameters
153 every other day.
154 To get sufficient amount of VFAs and ammonia enriched digestate for the
155 stripping experiments (Fig. 1b), an anaerobic reactor (18.8 cm in diameter, 14.5 cm in
156 height) with a working volume of 4 L was operated for 8 days without mixing under
157 the optimal conditions determined in the above trials. The digestate was then
158 homogenized and stored at 4 °C before used for ammonia stripping experiments.
159
160 *2.3. Ammonia stripping*
161 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 (ϕ2) at the bottom or purged into the bubbling reactor and carried the volatile ammonia into the HCl absorption bottles (500 ml×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

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

193 For analysis of soluble products, 4 g manure sample (wet weight) was diluted
194 with 40 ml deionized water. The mixture was centrifuged at 9000 rpm for 20 min and
195 then filtered through a 0.45 μm microfiber filter. Measurements of TAN, ortho-P and
196 soluble chemical oxygen demand (SCOD) were conducted in accordance with
197 standard method (APHA, 2012). The filtrate was acidified by 3% phosphoric acid
198 solution to pH around 4.0 before VFAs analysis by a Shimadzu GC-14B/FID packed
199 with Unisole F-200 30/60 column. The column and the injector temperatures were set
200 at 150 °C and 180 °C, respectively. The pressure of N_2 carrier gas was maintained at
201 200 Kpa. In this study, the concentrations of VFAs were presented as equivalent COD
202 values calculated from the theoretical formula of each VFA component.

203 To reveal the dynamic change of P species in SM before and after dry AD,
204 fractionation of P was conducted according to Standards, Measurements and Testing
205 (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 ℃ 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

273 The effect of different initial pH on VFAs production at 55 °C and 20% TS is
274 demonstrated in Fig. 2c. As shown, the highest yields of TVFAs were detected on day
275 8 at all tested initial pH levels, which followed a descending order as pH 11.0 (79.1
276 mg-COD/g-VS) > pH 10.0 (75.7 mg-COD/g-VS) > pH 9.0 (60.0 mg-COD/g-VS) >
277 pH 7.0 (54.0 mg-COD/g-VS) > pH 8.0 (50.5 mg-COD/g-VS) > pH 12.0 (11.5 mg-
278 COD/g-VS). Obviously, initial pHs of 11.0 and 10.0 were beneficial for VFAs
279 accumulation. Despite a slightly higher TVFAs yield was obtained at initial pH 11.0
280 than that at pH 10.0, their difference was statistically insignificant (p = 0.4589 >
281 0.05). After 8 days' dry AD at 55 °C, 20% TS and initial pH 8.0-10.0, high volumetric
282 TVFAs production rate of 979.7 to 1468.6 mg-COD/L/d was achieved in this study.
283 After 8 days' fermentation, the proportion of HAc yield to TVFAs yield was in
284 the following order: pH 12.0 (80.4%) > pH 10.0 (63.2%) > pH 11.0 (60.5%) > pH 9.0
285 (55.8%) > pH 8.0 (38.0%) > pH 7.0 (33.3%). It is apparently that the proportion of
286 HAc increased almost linearly with the increase of initial pH, suggesting that HAc
287 production pathway is more dominant and robust than the production of other VFAs
288 under alkaline dry AD conditions.
289 As pointed out by Lin et al. (2013), initial pH adjustment could alter the
290 microbial communities in SM thus affecting its hydrolysis and acidification processes.
291 It is interesting to notice that, when operated at 55 °C, 20% TS and similar initial pHs
292 of 8.0 (adjusted with HCl), 8.6 (unadjusted) and 9.0 (adjusted with $Ca(OH)_2$), the
293 patterns of VFAs accumulation were quite different (Figs. 2b and 2c). At adjusted
294 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 ℃), 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

317 after 8 days' dry AD at 55 °C, 20% TS and unadjusted initial pH. Table 2 lists the
318 main resources available in the digestate after dry AD under 4 typical experimental
319 conditions in this study.
320
321 *3.2.1. Dry ammonia stripping*
322 Fig. 3a displays the removal efficiencies of TAN from the solid digestate under
323 different stripping conditions. An increase in both initial pH and temperature gave rise
324 to higher concentrations of free ammonia nitrogen (FAN) (Hansen et al., 1998),
325 contributing to higher removal efficiencies of TAN from the digestate. The highest
326 TAN removal efficiency of 96.2% was achieved at 55 °C and initial pH 11.0 after 3
327 hours' stripping. Quantitative analysis of the amount of TAN entrapped by acid
328 solution or water and that escaped from the digestate revealed a high TAN recovery
329 efficiency ≥ 95.5% under all stripping conditions.
330 As illustrated in Fig. 3b, most probably as a consequence of ammonia removal
331 the digestate pH dropped in all circumstances, from 10.0 to 8.9 and 8.5, and from 11.0
332 to 9.6 and 9.1 when the stripping was conducted at 35 °C and 55 °C, respectively. On
333 the other hand, the concentration of TVFAs in the digestate remained pretty stable
334 throughout the whole stripping process. As it is known, VFAs are volatile under acidic
335 conditions while they become stable and exist as ionic forms in alkaline solutions. In
336 the stripping systems, due to the fact that pH was maintained at pH > 7.0, the escaped
337 TVFAs from the reactor were considered insignificant. In these trials, averagely
338 92.5% of the TVFAs were successfully retained in the digestate after 3 hours'

339 stripping at 55 °C and initial pH 11.0. Only 4.7% and 2.1% of TVFAs were averagely
340 detected in the scrubbing solutions and the water containing bottle (vessel 3 in Fig.
341 1b), respectively. And the loss of TVFAs from the stripping system was most probably
342 brought about by measurement errors. Based on the experimental results (Fig. 3a), the
343 effective TAN removal duration (τ_e), about 60 min and 90 min, was obtained for the
344 stripping process at initial pH 11.0 and pH 10.0 (55 °C), respectively. The former
345 (55 °C and initial pH 11.0) was considered to be the optimal dry ammonia stripping
346 condition in this study.
347
348 *3.2.2. Wet ammonia stripping*
349 The removal efficiencies of TAN during wet ammonia stripping are shown in
350 Fig. 3c. At the end of stripping (the 3rd h), the removal efficiencies of TAN were
351 detected to be 79.1% at 35 °C and initial pH 10.0, 91.5% at 55 °C and initial pH 10.0,
352 and 95.0% at 35 °C and initial pH 11.0, respectively. The highest TAN removal
353 efficiency was achieved at 55 °C and initial pH 11.0, which increased rapidly to
354 98.7% after stripping for 2 hours, and then climbed slowly to 99.7% after 3 hours'
355 stripping. TAN balance analysis again revealed good performance of TAN recovery
356 by using the stripping/absorption processes. Greater than 94.0% of the stripped TAN
357 from the filtrate was able to be entrapped by the acid solution and water in all cases
358 studied.
359 As shown in Fig. 3d, the filtrate pH declined during the process of stripping from
360 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),

361 respectively. On the other hand, the decrease of TVFAs in the filtrate was found to be
362 less than 11% in all the tested scenarios. For instance, an average decrease of 6.3%
363 after stripping was detected when the stripping was conducted at 55 °C and initial pH
364 11.0. Moreover, to a great extent the lost TVFAs could be re-entrapped by the
365 scrubbing solutions (~ 61%) and water containing vessel 3 (~ 32%, Fig. 1b). Again,
366 based on Fig. 3c, the effective TAN removal duration (τ_e) was determined to be
367 around 65 min and 85 min, respectively for wet stripping at initial pH 11.0 and pH
368 10.0 (55 °C), which was almost similar to that of dry ammonia stripping process (Fig.
369 3a).
370
371 *3.2.3. Comparative analysis*
372 Two ammonia stripping strategies (dry or wet) were employed for ammonia
373 recovery from the digestate, which were further compared in terms of technical and
374 economic aspects. According to the results of kinetic analysis presented in Table 3,
375 the experimental data from both dry and wet ammonia stripping processes fitted well
376 to the pseudo first-order kinetic model (R^2 = 0.9916-0.9997). Interestingly, when
377 operated under the same temperature and initial pH conditions, almost similar A_{eq}
378 values were obtained by either dry or wet ammonia stripping. This observation
379 indicated that TS content could only affect the kinetics of TAN removal since similar
380 A_{eq} values were achieved under both dry and wet stripping conditions while a higher
381 TAN removal rate constant (k) for wet stripping process. Results indicated that the
382 extent to which ammonia stripping could proceed was driven by the substrate

383 FAN/TAN ratio closely related to system pH and temperature, whereas the ammonia
384 removal rate was largely affected not only by the effective contact between gas and
385 substrate, but also the influencing factors like gas distribution and existing form,
386 viscosity and fluidity of the substrate. Among all the tested scenarios, 55 °C, the
387 optimal temperature for VFAs production, was also found to be the optimal
388 temperature for both dry and wet ammonia stripping in this study. In addition, for
389 these two stripping strategies, about 60-65 min and 85-90 min were necessary for
390 achieving 80% of TAN removal from the digestate or filtrate when ammonia stripping
391 was conducted at 55 °C with initial pH 11.0 and pH 10.0, respectively (Table 3).
392 In the stripping system developed in this study, the gas was circulated among the
393 vessels and acid absorption solutions in a close loop, to a great extent avoiding
394 unnecessary ammonia loss and OH^- consumption resulted from the reaction between
395 NaOH and CO_2 in the air. From this work, dry ammonia stripping possesses the
396 following advantages compared to traditional wet stripping. Firstly, dry ammonia
397 stripping can avoid the foaming problems which always occur in wet systems.
398 Secondly, much higher volumetric TAN removal rates (0.75-0.99 g/L-digestate/h)
399 were obtained in the dry ammonia stripping systems operated at 20% TS, in
400 comparison to those (0.14-0.17 g/L-filtrate/h) of wet ammonia stripping systems. In
401 addition, processing of the digestate in semi-solid state requires much smaller reactor
402 and thus less construction investment. And thirdly, the consumptions of energy for
403 heating as well as chemicals (i.e. both alkalis applied to raise digestate/filtrate pH
404 during ammonia stripping and acids used for re-neutralization of the ammonia-

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

406 Zhang and Chen (2009) stated that it's feasible to use struvite precipitation for
407 simultaneous recovery of ammonia-N and soluble ortho-P from sludge fermentation
408 liquor. This process, however, is less beneficial for the liquid extract from fermented
409 manure mainly due to the following two considerations. (1) Numerous organic
410 compounds and inorganic ions co-existing in the liquid would definitely affect the
411 purity of struvite precipitates. (2) The theoretical molecular ratio of N:P in struvite is
412 1:1, while the molecular ratio of TAN to ortho-P in the liquid extract was close to
413 13:1. The concentration of water extractable ortho-P (~90 mg/L) in the fermented
414 manure was disproportionally lower than that of TAN (~540 mg/L) due to the fact that
415 most P was fixed in biomass or formed precipitates with the co-existing metallic ions
416 like $Fe^{2+/3+}$ and Ca^{2+} (Huang et al., 2015). In this context, dry ammonia stripping
417 offers a promising alternative for direct separation and recovery of ammonia-N from
418 the dry AD digestate.

419

420 *3.3. Changes in P bioavailability in the digestate*

421 *3.3.1. During VFAs fermentation*

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

427 is mineralized as a byproduct of the C cycle, during which enzymatic hydrolysis is an
428 essential step for the degradation of OP to IP (Tiessen, 2011). Various enzymes such
429 as nucleases, phytase, phospholipase, and phosphatases are involved in this enzymatic
430 hydrolysis process, and the activity of each enzyme depends highly upon system
431 temperature and pH (Tiessen, 2011; Turner et al., 2005). After the 8 days' dry AD
432 process, the proportion of potentially bioavailable P decreased slightly from 61.3%
433 (RSM) to 59.8%-58.6%. This is to some extent consistent with the finding of Güngör
434 and karthikeyan (2008) who declared that AD of dairy manure was capable of
435 reducing the immediately available P in the solid phases. On the other hand, the
436 system pH dropped from 8.6 to 8.0, 7.8 and 7.7 after dry AD at 25 °C, 35 °C and
437 55 °C, respectively, most probably resulting from VFAs accumulation (Fig. 2a).
438 Results of P fractionation and pH in RSM and the digestates after the 8 days' dry
439 AD at 55 °C and different TS contents are displayed in Fig. 4b. It was observed that at
440 the end of experiments, the conversion efficiency of OP increased from 18.4% to
441 47.4% with TS increased from 20% to 35%. This observation might be partially
442 explained by the increase in their final pHs from 7.7 at 20% TS to 8.3 at 35% TS. A
443 strong correlation relationship was found between the OP conversion efficiency and
444 the final pH of the digestate by using linear regression analysis ($R^2 = 0.9960$). Unlike
445 the production of VFAs, TS content was not the limiting factor dictating the
446 conversion efficiency of OP to IP. Instead, system pH played a more important role in
447 OP mineralization. A proper increase in the system pH might be beneficial for the
448 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 $Ca(OH)_2$ 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

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

475 Table 4 presents the main characteristics of the liquid and solid phases obtained
476 by strategies I and II, respectively, at stripping conditions of 55 °C and initial pH 11.0.
477 As it can be seen, the final concentration of TVFAs was almost same in the liquid
478 phase by using both stripping processes, around 2250 mg-COD/L. As for P
479 availability, slightly higher concentration of soluble ortho-P was detected in the liquid
480 after dry ammonia stripping, possibly due to thermal-alkaline hydrolysis of the
481 organic solids during the stripping process. As expected, a slightly lower
482 concentration of OP was detected in the solid residue after strategy I, about 2.4 mg/g-
483 TS in comparison to 3.1 mg/g-TS of OP in the solid residue acquired with strategy II.
484 AP and NAIP concentrations were almost similar regardless of different stripping
485 strategies applied. In summary, the potentially bioavailable P in the solid residue was
486 able to be maintained at a relatively high level of 8.1-8.4 mg/g-TS (51.6%-53.5% of
487 TP) after ammonia stripping and solid-liquid separation through both strategies. Most
488 notably, the C/N ratios in the solid residues after strategies I and II were detected to be
489 25.7 and 21.9, respectively, both higher than that of RSM (C/N=18.0, Table 1) and
490 falling within the optimal C/N range (20-30) for biomethane production (Esposito et
491 al., 2012).
492

493 *3.4. Implication of this study to practice*

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

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

511

512 **4. Conclusions**

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

515 the changes in VFAs, TAN and P bioavailability throughout the treatment procedure.
516 From this work, the following conclusions can be arrived at:
517 (1) Thermophilic temperature, lower TS of 20% and moderate alkaline initial pH
518 of 8.0-10.0 are beneficial for the accumulation of VFAs and ammonia during short-
519 term dry AD of SM. After 8 days' dry AD under above conditions, high volumetric
520 TVFAs and TAN production rates of 979.7-1468.6 mg-COD/L/d and 181.3-214.0
521 mg/L/d were achieved, respectively.
522 (2) In the thermophilic dry AD system, proper increase in system pH (brought
523 about by increasing TS from 20% to 35%) was beneficial for the microbial
524 degradation of OP. Mineralization of OP was found to be significantly enhanced when
525 SM was fermented under 20% TS and 55 °C by using $Ca(OH)_2$ to adjust initial pH,
526 which lowered the amount of bioavailable P (OP + NAIP). Considering full
527 utilization of C, N and P resources in the SM, the short-term dry AD without initial
528 pH adjustment (pH~8.6) is suggested in practice.
529 (3) The two-step procedure involving short-term dry AD and dry ammonia
530 stripping not only provides an alternative for the production and separation of VFAs
531 from ammonia and P resources, but also serves as pretreatment to reduce ammonia
532 buildups. Thus the treated SM residue is also expected to have high potential for dry
533 methane fermentation, which has been manifested by our followed-up experiments
534 (data not shown).
535
536 **Acknowledgements**

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603

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 (±SD).

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

611 AD.

	Fermentation conditions			Compositions of nutrient elements and TVFAs in the digestate						
No.	Temperature (°C)	TS (%)	Initial pH (chemical used)	TVFAs (mg-COD/g-VS)	TAN (mg/g-VS)	TON (mg/g-VS)	OP (mg/g-TS)	NAIP (mg/g-TS)	AP (mg/g-TS)	P bioavailability [b] (%)
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

612 [a]No initial pH adjustment. [b]P bioavailability (%)=100 × (OP + NAIP)/TP.

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

615 Table 3. Stripping rate constants associated with the pseudo first-order kinetic model

616 and effective TAN removal durations under different stripping conditions.

Strategy	Stripping conditions		Pseudo first-order kinetic model			τ_e
	Temperature (°C)	Initial pH	A_{eq} (%)	k (min^{-1})	R^2	(min)
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

617

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

	Parameters	Unit	Strategy I (Dry stripping)	Strategy II (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)

621 The data are expressed as mean (±SD).
622

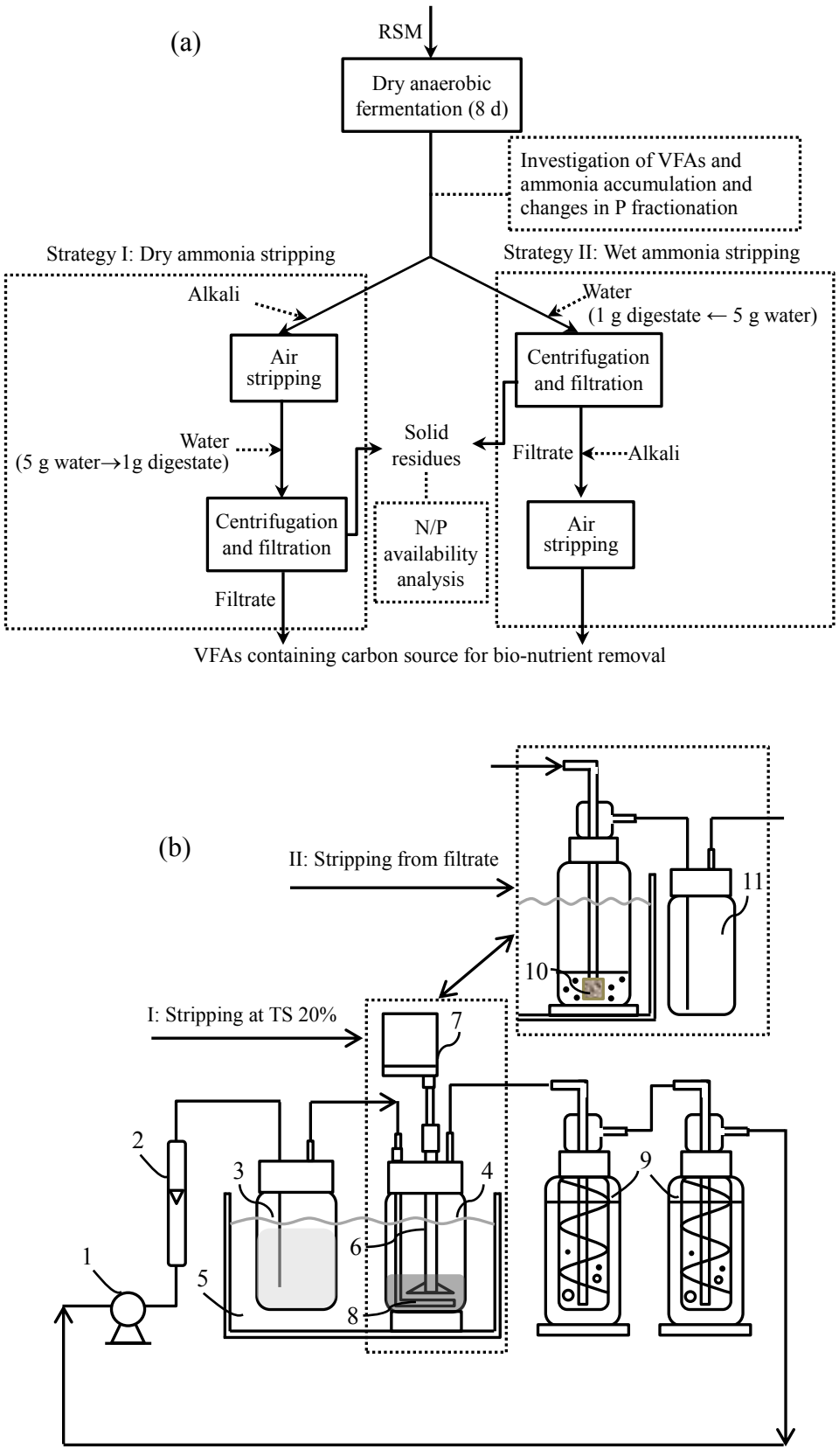

Fig. 1 - Schematics of (a) the procedure for VFAs separation from the fermented swine manure; and (b) the recirculating system for ammonia stripping and recovery.

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

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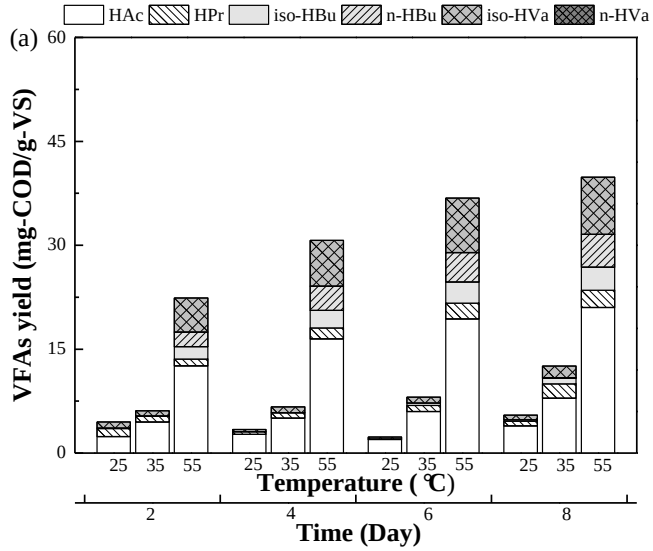

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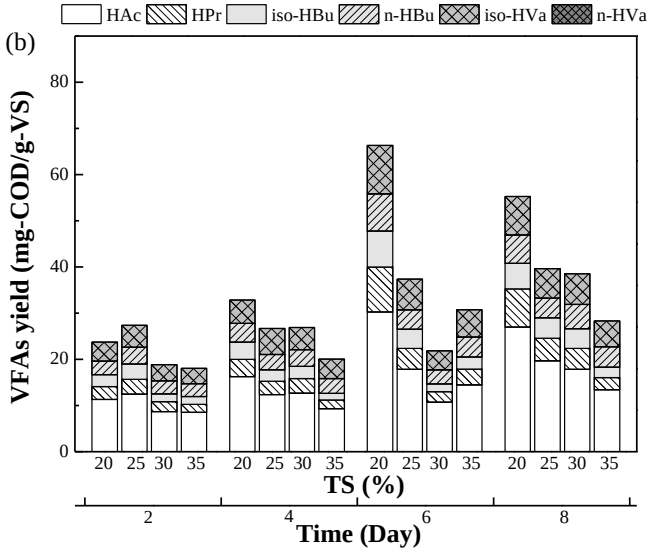

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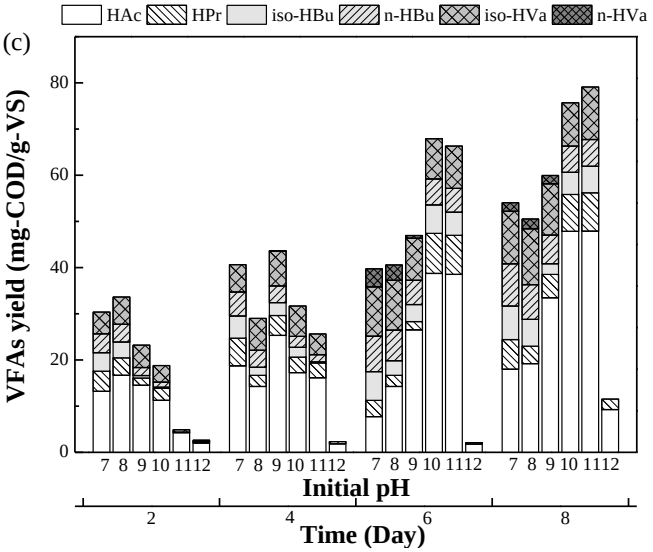

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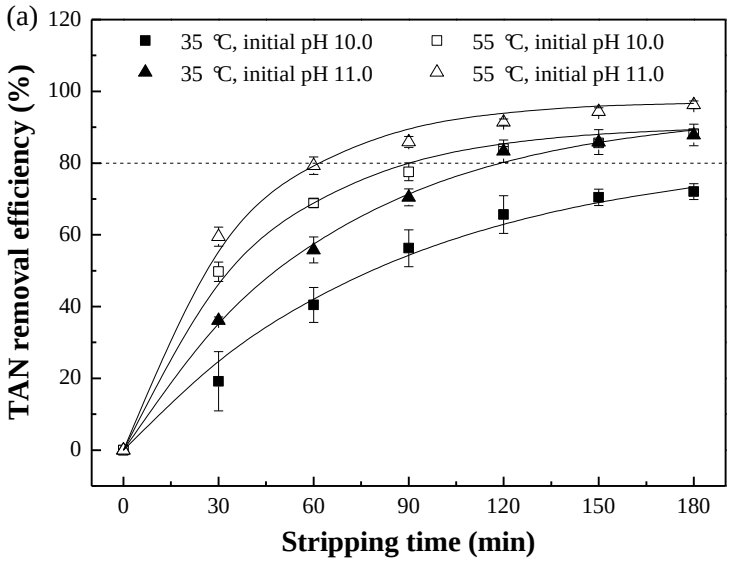
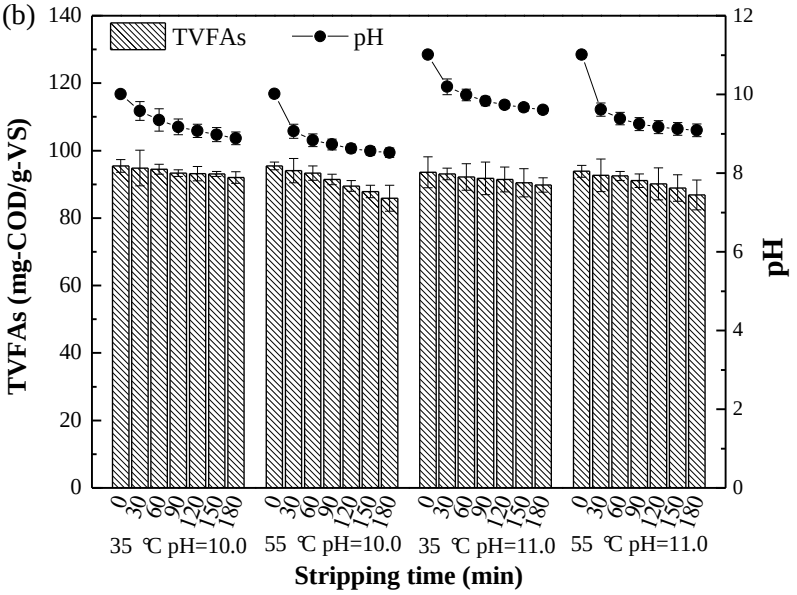
676 **Fig. 2 -** Effects of temperature (a, TS=25% without pH adjustment), TS content (b,

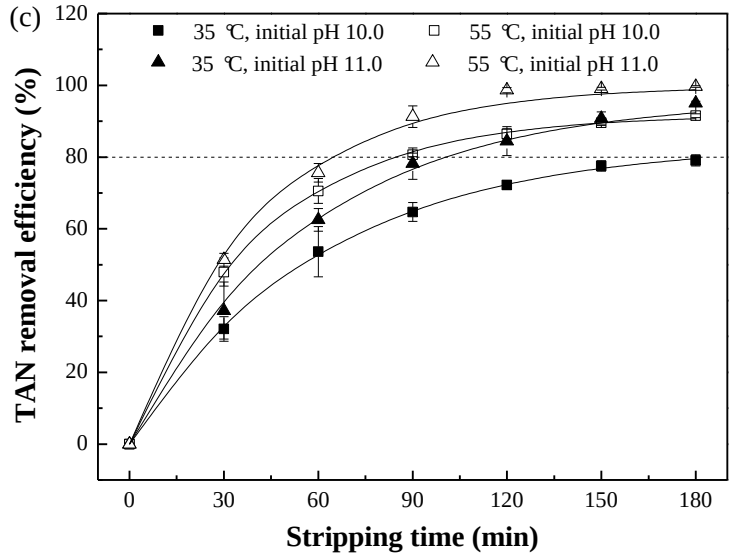
55 °C without pH adjustment) and initial pH (c, 55 °C and 20% TS) on dry AD for the production of VFAs. Acetic acid (HAc), propionic acid (HPr), iso-butyric acid (iso-HBu), n-butyric acid (n-HBu), iso-valeric acid (iso-HVa) and n-valeric acid (n-HVa).


(a)
35 ℃, initial pH 10.0
55 ℃, initial pH 10.0
35 ℃, initial pH 11.0
55 ℃, initial pH 11.0
TAN removal efficiency (%)
Stripping time (min)

682


(b)
TVFAs
pH
TVFAs (mg-COD/g-VS)
pH
35 ℃ pH=10.0
55 ℃ pH=10.0
35 ℃ pH=11.0
55 ℃ pH=11.0
Stripping time (min)

683



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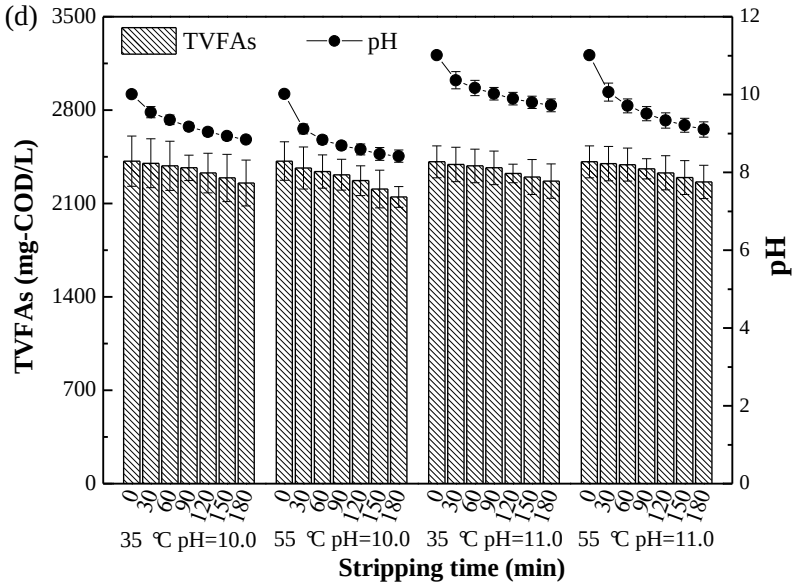

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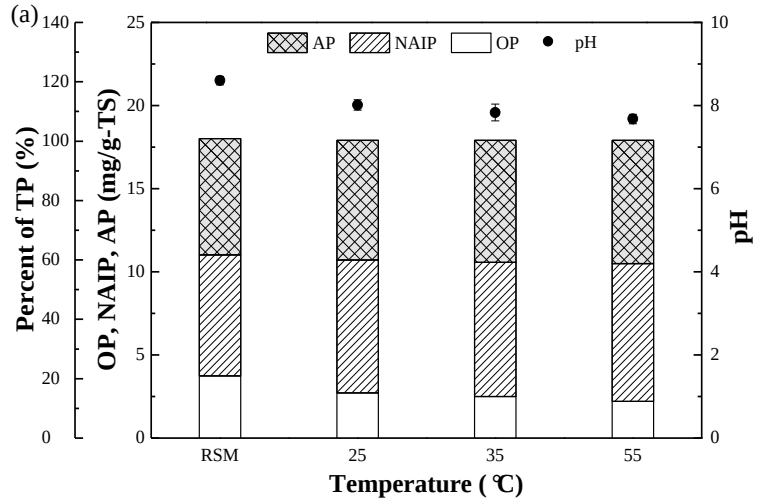
686

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

691



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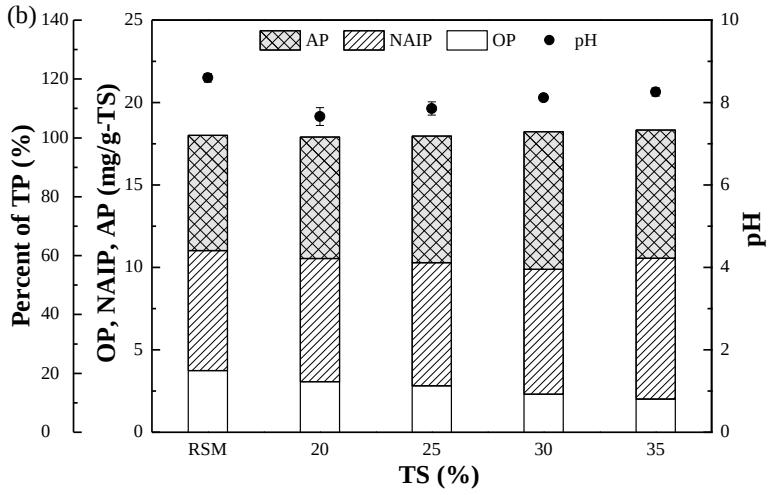

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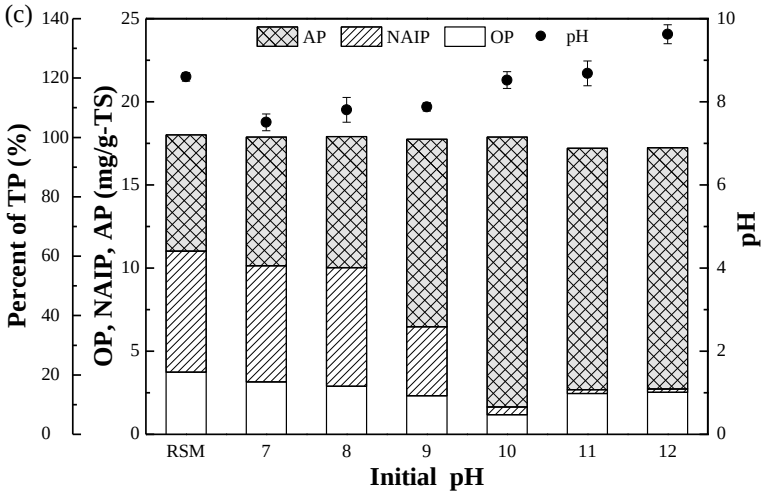

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695 **Fig. 4 -** Profiles of pH and P fractionation in raw swine manure (RSM) and the
696 digestate under different dry AD conditions tested: (a) operation temperature at 25 °C,

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