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A pilot scale study on synergistic effects of co-digestion of pig manure and grass silage

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Abstract

This study aimed to assess the system stability and synergistic effects of co-digesting pig manure (PM) and grass silage (GS) in a pilot-scale study. Anaerobic digestion of PM alone and co-digestion of PM with GS was carried out in a 480-litre continuously stirred tank reactor. The experiment consisted of two phases. In Phase I, PM was digested at an organic loading rate (OLR) of 0.87 kg volatile solid (VS) $m^{-3}\cdot d^{-1}$, and in Phase II, PM and GS were co-digested at 1:1 on a VS basis at an OLR of 1.74 kg $VS\cdot m^{-3}\cdot d^{-1}$. The pilot-scale anaerobic digestion system was stable in both phases. At the steady state, average pH and free ammonia concentrations were 7.99 and 233.0 $mg\cdot l^{-1}$ in Phase I and were 7.77 and 158.3 $mg\cdot l^{-1}$ in Phase II, respectively. The specific methane yields increased from 154 ml CH_4/g VS added in Phase I to 251 ml CH_4/g VS added in Phase II. On average, soluble COD and VS removal efficiencies increased from 81.4% and 41.4% in Phase I to 87.8% and 53.9% in Phase II, respectively. Further evaluation of synergism suggests that co-digestion of PM and GS can improve system stability and biogas yields despite marginal synergistic effects at pilot-scale.

Keywords: Anaerobic co-digestion; Bioenergy recovery, Organic waste, Pilot-scale evaluation; Synergistic effects.

1. INTRODUCTION

Globally, pig production is one of the main animal agricultural enterprises from which large volumes of high nutrient content manure is produced. Pig manure (PM) has the potential to be environmentally harmful if handled in an inappropriate manner. Historically PM has been land-spread as an organic fertilizer for growing grass and other crops. However, application rates of PM have recently been curtailed primarily due to regulations. For example, the EU Nitrates Directive has limited the amount of organic nitrogen applied to grasslands and tillage lands to 170 kg N/hectare/year (S.I. No. 610, 2010). This has resulted in an increase in land area required for PM application in the EU, and a consequent drive to find alternative treatment and disposal methods for PM. In addition, many countries have agreed to reduce GHG emissions from agriculture and increase production of renewable energy. Ireland, for example, has agreed to reduce GHG emissions by 20% of 2005 levels by 2020 (as part of the EU 2020 growth strategy), and is required to generate 16% of gross final consumed energy through renewable means by 2020 (under the 2009 Renewable Energy Directive (2009/28/EC)). Therefore, there is a need to explore and develop alternative non land-spread options for PM management which can reduce GHG emissions and generate renewable energy.

Anaerobic digestion (AD) is an environmentally friendly technology for the PM management (Dennehy et al., 2017a). AD of PM can help reduce odor, pathogens levels and greenhouse gas emissions in addition to producing a valuable bioenergy source in the form of methane-rich biogas (Chae et al., 2008). The resulting digestate can also be a valuable fertilizer because it typically contains higher concentrations of biologically available nitrogen than raw manure (Kaparaju and Rintala, 2011). In this regard, AD has been recognised worldwide as a valuable technology. A large number of large-scale agricultural or centralized biogas plants for treating animal manures, agricultural crops, wastewater and organic waste solids have been constructed in Europe and Asia-Pacific Region (Angelidaki & Ellegaard, 2003; Clarke et al., 2016; Nghiem et al., 2017; Pantaleo et al., 2013).

Climatically suited to the production of grass, the agricultural area is predominately grassland with 4.3 million ha compared to only 0.28 million ha of arable land in Ireland (Hamelinck et al., 2004). Grass is normally utilized by grazing animals and is conserved as grass silage (GS) for feeding to ruminants over the winter months (Xie et al., 2011). Therefore, GS could be readily available for anaerobic co-digestion with PM. Studies have shown the beneficial effects of co-digesting manures with a range of agricultural residues. For example, Kaparaju and Rintala (2005) in a study of the co-digestion of PM with potato tubers found that co-digestion improved specific methane yields and increased process stability. Similar results were found when co-digesting a range of different manures (cattle manure and PM) and agricultural/food residues (such as whey, GS, sugar beet tops, energy crops, quinoa residues and herbal extract residues) as substrates (Alvarez and Lidén, 2008; Gelegenis et al.,2007; Lehtomaki et al.,2007; Li et al.,2011). Compared to AD of PM alone, co-digestion with agricultural residues can enhance the process performance by: (i) overcoming ammonia inhibition which is sometimes a feature in digestion of pure manure (Xie et al., 2012); and (ii) optimising the carbon to nitrogen (C/N) ratio in the feedstock for the AD (Wu et al., 2017).

Laboratory-scale research has shown that it is feasible to co-digest PM and GS, and that the optimum PM to GS ratio in the feedstock for process stability and biogas production when co-digesting GS and PM was 1:1 on a volatile solid (VS) basis (Xie et al., 2011). Similar results have been found by Dechrugsa et al. (2013) in laboratory scale batch experiments on co-digestion of grass and PM. It has been calculated that by employing co-digestion of PM and GS at a 3:2 mix ratio on a VS basis, a 654-sow pig unit could generate 371 MWh/a electricity and 530 MWh/a heat, compared with 268 MWh/a electricity and 383 mWh/a heat at a 4:1 mix ratio; a much lower electricity and heat generation can be expected during mono-digestion of PM alone (Xie et al., 2012). However, it remains unknown if pilot scale studies can demonstrate that co-digestion of PM and GS at optimal operating conditions derived from lab scale studies can generate the methane yields underlying these energy yield estimates at full scale, taking into account the variations in mass transfer efficiencies and substrate properties and composition at varied scales of studies. In addition, scientific results from pilot-scale studies can further contribute towards the establishment of mathematical tools to guide the operation of on-farm anaerobic co-digestion systems (Xie et al., 2016).

In this study, anaerobic co-digestion of PM with GS was investigated in a pilot-scale anaerobic digester to examine (1) process stability in terms of pH, oxidation reduction potential (ORP) and concentrations of ammonium nitrogen and free ammonia; (2) the effect of anaerobic co-digestion of PM and GS on biogas productivity and removal of soluble chemical oxygen demand and volatile solids.

2. MATERIALS AND METHODS

2.1 Feedstock

Pig manure was collected from a local pig farm and GS was sourced from a conserved pit on an Irish farm. PM was stored in two 1 m^3 intermediate bulk containers (IBCs) and was fed into the digester with a water submersible pump (FTS 1100A1, Florabest). The precision chopped GS had an average chop length of 5 cm and was mixed to ensure a homogenous feedstock. It was then stored in individual plastic bags sized for each day's feeding in a freezer room (-17 °C) to prevent biological decom position during the study. Prior to the daily feeding, the frozen GS in the individual bag was transferred to a cold room (4 °C) for one day and placed at room temperature for one hour. The characteristics of fresh PM and GS are given in Table 1.

[Table 1]

2.2 Pilot-scale anaerobic digester

The pilot-scale anaerobic digester was designed to allow remote control. The system consisted of four components: (a) the digester, (b) feeding system, (c) control panel and (d) biogas storage system. The schematic of the digester is shown in Figure 1. The digester was cylindrical and constructed from 316-stainless steel. It had a total volume of 480 l and a working volume of which 360 l. Two propellers fabricated from 316 stainless steel were installed for continuously homogenizing the feedstock and rotation (30 - 60 rpm) was controlled by an electric three-phase motor (380 V) operated by an inverter (Hitachi SJ200, Japan) through the control panel. A Tiger 80 submersible vortex chopper pump (Arven S.R.L., Italy) with a capacity of about 250 l/ min was placed inside the digester to circulate the digestate after each feeding and before each discharge so as to avoid the build-up of GS and fibre at the surface of liquid digestate. The external surface of the digester was wrapped with a water jacket, to maintain a constant temperature of 37 °C, and fully enclosed with insulating material to minimize heat loss. Two air operated valves with an inner diameter of 10.16 cm (4 inches) on the bottom of the digester allowed the removal of the digestate and permitted collection of the samples for subsequent chemical analysis.

[Figure 1]

The feeding system was located at the top of the reactor. The GS feeding system was comprised of a pipe and two chambers controlled using two compressed-air operated valves. These valves allowed the feeding of GS into the reactor tank through the removable cover, while preventing air from entering the digester by opening the top and bottom valves consecutively. Pig manure was fed into the digester via a 1 litre chamber where both ends were connected with 3.8 cm (1.5 inches) diameter pipes; one pipe was connected to the inlet of a submersible pump (FTS 1100A1, Florabest) placed in the PM storage IBCs, and the other was submerged in the IBCs. Recirculation of the PM prior to feeding helped ensure a uniform feedstock in the IBCs. The PM feeding chamber was controlled using a compressed-air operated valve, thereby preventing air from entering the digester.

The movement of all mechanical devices and the operation sequence was controlled through a control panel situated within a protecting and closed box. For the functioning of the digester, all the electric systems were controlled by Allen Bradley MicroLogix 1200 programmable logic controllers (Rockwell Automation, Inc. Milwaukee, WI, USA), which were located within the control panel box. In the upper part two LCD monitors were mounted (Thermo Scientific Alpha transmitter), one connected to a pH probe (Hamiltion electro-chemical sensors, Esslab, UK) and the other connected to an ORP probe (Hamiltion electro-chemical sensors, Esslab, UK), both located in the midsection of the digester body.

The biogas collection (from the top of the digester), storage and measurement system consisted of biogas piping, a biogas bag with a 3 m^3 capacity (Puxin, China) and a biogas flow meter. The mass (volume) of biogas produced in the digester was measured by a mass and volumetric flow meter (FMA-1620A, Omega, UK) with 0.48 cm (3/16 inch) tubing (Tygon, USA). An in-line water trap element was installed at the upper part of the tubing to prevent water vapour collection with the biogas.

2.3 Operation of pilot-scale anaerobic digester

The digester was loaded semi continuously (12 times per day) with PM and once daily with GS. One day before the commencement of the operation, the reactor was filled with 360 litres of sludge seed (inoculum) sourced from an anaerobic digester treating PM in Ireland.

From Day 1 to Day 61 (Phase I), one litre of PM was fed into the digester 12 times a day resulting in a daily volumetric load of 12 litres/day and a hydraulic retention time (HRT) of 30 days. The organic loading rate (OLR) was 0.87 kg $VS \cdot m^{-3} \cdot d^{-1}$, on average. From Day 62 to Day 109 (Phase II), in addition to the feeding of PM as described above, approximately 991 g GS was added into the digester once a day at a PM to GS VS ratio of 1:1. The OLR was increased immediately to 1.74 kg $VS \cdot m^{-3} \cdot d^{-1}$ on Day 62. The digestate was discharged (12 litres/day) once daily to ensure a constant working volume in the digester thereby ensuring a constant HRT.

2.4 Calculations

2.5.1 VS removal

VS removal was calculated using the mass balance equation, which uses VS concentrations (VS_{conc}) in the feedstock and the digestate, expressed in Eq. 1:

$$\text{VS removals (\%)} = \frac{VS_{conc,in} - VS_{conc,out}}{VS_{conc,in}} \qquad \text{Eq. 1}$$

where $VS_{conc,in}$ is the VS concentration of the feedstock and $VS_{conc,out}$ is the VS concentration of the digestate.

2.4.2 Soluble COD removal

Soluble COD removal efficiency was determined according to Eq. 2:

$$\text{Soluble COD removals (\%)} = \frac{sCOD_{conc,in} - sCOD_{conc,out}}{sCOD_{conc,in}} \qquad \text{Eq. 2}$$

where $sCOD_{conc,in}$ is the soluble COD concentration of the feedstock and $sCOD_{conc,out}$ is the soluble COD concentration of the digestate.

2.5 Analytical methods

Digestate samples were collected in 100-ml containers from a thoroughly mixed 12 litres discharge. After the immediate pH measurement, the samples were firstly centrifuged at 3,900 rpm for 10 min and then at 18,000 rpm for 20 min at 4 °C. The supernatants were measured for the soluble COD and NH_4^+-N concentrations.

Total solids (TS), VS and soluble COD were measured according to standard methods (APHA, 1995). The NH_4^+-N concentration in the supernatants was analysed by a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland). The volume of biogas was measured using a mass and volumetric flow meter (FMA-1620A, Omega, UK), and the value obtained was corrected to standard temperature and pressure conditions of 0 °C and 1 atmosphere. The CH_4 and CO_2 contents in biogas were measured daily using a portable biogas analyser (BM2K2-E000, Geotechnical Instruments Ltd, UK) on site. All measurements were conducted in duplicate, and the results presented are the mean value. Statistical analysis was performed using SPSS 18.0 for Windows (IBM Corp., Armonk, NY, USA).

3. RESULTS AND DISCUSSION

3.1 Process stability

3.1.1 pH

In Phase I, pH decreased rapidly after the commencement of the experiment from 7.99 to 7.78 on Day 12 (Figure 2). The decrease in pH may indicate the on-set of hydrolysis and acidogenesis as the population of methanogens had not yet stabilised to maturity. Then, pH rose and stabalised at 7.99 after 33 days of operation, coinciding with pseudo steady state biogas production. In Phase II, the increase in the OLR from 0.87 to 1.74 $VS{\cdot}m^{-3}{\cdot}d^{-1}$ resulted in the decrease of pH to an average value of 7.77 (Day 80 - Day 109). It is noteworthy that GS had low pH values and underwent a longer hydrolysis stage than PM (Xie et al., 2011); thus the increased OLR resulted in a slight increase in the concentrations of VFAs (up to 300 mg·l^{-1}) within the reactor.

[Figure 2]

3.1.2 Oxidation reduction potential (ORP)

ORP has been employed successfully as a control and monitoring indicator in several anaerobic treatment systems, primarily due to the degradation of organic material by enzyme catalysed redox reactions under anaerobic conditions (Khanal & Huang, 2003; Nghiem et al., 2014). Typical ORP for a stable AD system is lower than -280 mV, and methane production can drop appreciably at elevated ORPs (Khanal & Huang, 2003). In this study, under the pseudo steady state, ORP was -361 mV, on average in Phase I. It decreased further to an average of -389 mV in Phase II, indicating a likely more stable co-digestion process. Consistently uniform ORP profiles obtained in Phase II in this study corresponded to the steady daily methane production and further verified the stability of the complex anaerobic co-digestion system (refer to section 3.2 for methane generation performance). It is noteworthy that dissolved and gaseous sulfides can hardly be removed at this ORP level (Nghiem et al., 2014). Nevertheless, no significant sulfide toxicity that can result in the severe inhibition of methanogenesis was observed based on the methane production rates.

3.1.3 Ammonium/free ammonia

The ammonium nitrogen (NH_4^+-N) concentrations in the digestate at steady state in Phase I and Phase II were increased from the average of 2,323 mg·l^{-1} (Day 34 - Day 61) to 2,541 mg·l^{-1} (Day 80 - Day 109) as shown in Figure 3. This suggests that co-digestion of GS with PM can enhance the hydrolysis of solids from PM and GS releasing more NH_4^+-N compared with AD of PM alone. It is well known that the concentration of NH_4^+-N and free ammonia can cause digester failure due to inhibition of methanogenesis. For example, as NH_4^+-N concentrations rose from 2.5 to 11 g·l^{-1}, up to 50% reductions in methane production have been observed (Yenigün & Demirel, 2013). Free ammonia (NH_3) is extremely dependent on pH, as follows in Eq. 3 (Anthonisen et al., 1976):

$$NH_3 = \frac{[NH_4^+]10^{pH}}{10^{pH} + e^{6344/(273+t)}} \quad \text{Eq. 3}$$

where, t is temperature, °C.

High concentrations of free ammonia and NH_4^+-N can cause a certain level of inhibition on AD, and it can be reversible (Xie et al., 2016; Bayrakdar et al., 2017). Wu. et al. (2009) found that methanogens were notably inhibited by free ammonia at concentrations greater than 400 mg·l^{-1} during anaerobic co-digestion of meat and bone meal. Nevertheless, the reversible inhibition was observed when the free ammonia concentration reached up to 998 mg·l^{-1}. The varying inhibition concentrations of free ammonia and NH_4^+-N can be attributed to the differences in properties and composition of substrates and inocula, environmental conditions (e.g. temperature, pH), and acclimation stages (Rajagopal et al., 2013). The average free ammonia concentrations in the pseudo steady state decreased from 233.0 mg·l^{-1} in Phase I (Day 34 - Day 61) to 158.3 mg·l^{-1} in Phase II (Day 80 - Day 109) (Figure 3). This may have been due to the lower average pH value in the digester (Figure 2) despite higher NH_4^+-N concentrations in the digestate. It can therefore be speculated that there would have been less inhibition in Phase II due to the lower free ammonia concentrations. The metaproteomic approach would be beneficial for future research to reveal the underpinning mechanisms associated with anaerobic co-digestion at the presence of inhibitory intermediate compounds (e.g. free ammonia) (Lin et al., 2016).

[Figure 3]

3.2 Methane generation performance of the pilot-scale anaerobic digester

The performance of the pilot-scale digester in terms of the biogas yield and biogas composition is summarised in Table 2 and Figure 4. Daily biogas production, CH_4 and CO_2 contents in biogas during the experiment are presented in Figure 4. The daily biogas production increased from an average of 84 $l \cdot d^{-1}$ in Phase I (Day 34 - Day 61) to 254 $l \cdot d^{-1}$ in Phase II (Day 80 – Day 109). The methane contents in biogas in Phase I and Phase II were up to an average of 58% and 62%, respectively at steady state (Day 34 - Day 61 in Phase I and Day 80 - Day 109 in Phase II). The mass balance analysis shows that the specific methane yields (SMY) at steady state in Phase I and Phase II were 154 ± 8 and 251 ± 13 ml CH_4/g VS added, respectively (Table 2). It should be noted that during an early stage in Phase I (Day 15 - Day 25), the biogas analyser underwent recalibration and the digester had essential maintenance (e.g. recalibration of probes, PLC reprogramming) completed. This resulted in some variation in measured biogas composition, as highlighted in Figure 4. However, the average biogas composition and production rates during steady state were not affected. Indeed, the volumetric methane yield in the steady state increased more than threefold from 0.134 ± 0.007 m^3 $CH_4 \cdot m^{-3}$ reactor$\cdot d^{-1}$ to 0.437 ± 0.022 m^3 $CH_4 \cdot m^{-3}$ reactor$\cdot d^{-1}$ (Table 2).

[Table 2]

[Figure 4]

Table 3 compares the SMYs for the mono-digestion of PM measured in this pilot study with values obtained in other bench scale studies. Despite the ammonia inhibition observed during the experiment, Hansen et al. (1998) reported a relatively high SMY calculated as 188 ml CH_4/g VS added. In addition, Zhang et al. (2011) suggested that the low SMY measured in their study (187 ml CH_4/g VS added) was due to the inherently low biochemical methane potential of PM (242.3 ml CH_4/g VS added), but did not rule out the potential effect of ammonia inhibition on SMYs. When compared to these findings, it would appear that this pilot scale study achieved similar SMYs as those reported by Li et al. (2011), but higher SMYs compared to those reported by Molinuevo-Salces et al. (2012) (Table 3). Nevertheless, the biochemical methane yield of PM achieved in batch trials exhibited the relatively high SMYs (260 ml CH_4/g VS added) as reported by Dennehy et al. (2016), reflecting its ultimate methane potential at the optimal conditions (Table 3). Thus, the likelihood of ammonia inhibition and the inherent biochemical methane yield of PM largely govern the SMYs in this study. It is noteworthy that TS and VS concentrations of the PM used in this study were lower than those used in other studies by continuous digesters, however, the difference in TS and VS concentration did not have a significant effect on SMYs.

[Table 3]

Table 4 compares SMYs measured in studies where PM was digested with a range of grass and silage substrates at mesophilic conditions. The SMY found in this study was similar to values found in bench scale studies (Li et al., 2011; Xie et al., 2012). Bułkowska et al. (2012) obtained higher SMYs when different types of silage were used as feedstocks. Their study utilized a longer HRT, a far lower proportion of PM in the feedstock and a slightly higher temperature which might have led to higher SMYs (Dennehy et al., 2017b). It is noteworthy that given the varied SMYs of grass and silage substrates, it becomes difficult to compare the SMYs amongst these studies, as none of them have quantified the synergistic or antagonistic effects during co-digestion as discussed below.

[Table 4]

Synergistic effects can be quantified using a combined kinetics modelling and COD balance approach during batch anaerobic co-digestion of sewage sludge and organic wastes (Xie et al., 2017a). In this study, a universal equation was adopted to qualitatively illustrate the synergism as follows (Xie et al., 2017b):

$$\alpha = \frac{SMY_{pm} \cdot A + SMY_{gs} \cdot B}{(A+B) \cdot SMY_{co}} \qquad \text{Eq. 4}$$

where SMY_{co}, SMY_{pm}, *and* SMY_{gs} are the SMYs of the feedstock mix, PM and GS, respectively (ml CH_4/g VS added); A and B are corresponding mass of VS fraction in the feedstock daily (g); α is the synergism coefficient. α less than 1 indicates a synergistic effect, while α greater than 1 suggests an antagonistic effect during co-digestion.

In this study, assuming that (1) SMY_{pm} during mono-digestion of PM alone in Phase I was 154 ml CH_4/g VS added (Table 2), (2) SMY_{gs} was 330 ml CH_4/g VS added previously tested using the same source of silage from a conserved pit on an Irish farm (Xie et al., 2012), and (3) SMY_{co} during co-digestion was 251 ml CH_4/g VS added (Table 2), the synergism coefficient α, calculated based on the 50% VS contribution of GS addition to the feedstock mix, was 0.96. However, given the variations in SMYs from the feedstock (Table 2), it is likely that the observed slightly synergistic effect based on Eq. 4 is not notable (Kim et al., 2017). Alternatively, assuming that the SMY_{gs} used in Phase II was equal to its maximum methane potential (i.e. biochemical methane potentials), meaning that 100% of degradable organic matter in GS would be used for methane production, the amount of CH_4 yield contributed by PM in Phase II was 172 ml CH_4/g VS added. This was 12% greater than the value of SMY_{pm} measured in Phase I (154 ml CH_4/g VS added), indicating the possible increase in extent of degradation in PM due to the synergistic metabolism. Hence, in this study co-digestion of PM and GS exhibited likely synergistic effects, and consequently improved the digester performance. Likewise, Callaghan *et al.* (2002) observed that by increasing the proportion of fruit and vegetable wastes from 36% to 69% on a VS basis during co-digesting with cattle slurry, SMYs improved from 230 to 450 ml CH_4/g VS added. Astals et al. (2012) found that biogas yields increased by 400% when PM was digested with 4% glycerol at mesophilic conditions; a SMY increase from 450 ml biogas/g VS added to 740 ml biogas/g VS added was observed. The authors attributed this increase to the high biodegradability of glycerol and the synergism between the substrates. However, the marginal synergistic effects observed in this pilot-scale study may be attributed to differences in mass transfer efficiencies and methanogenic activities facilitated by a more vigorous and thorough mixing compared to laboratory studies (Dennehy et al., 2016; Vavilin and Angelidaki, 2005; Xie et al., 2012). Thus, future research on the development of mathematical model to distinguish the effect of mixing intensity and its impact on methanogenic activities during anaerobic co-digestion underpinning synergistic effects is needed for full scale implementation.

Nevertheless, one possible reason for the marginally improved SMY of VS added for PM during co-digestion observed in this study was the C/N ratio (Xie et al., 2017). GS has been found to have C/N ratios of more than 20/1 (Huang *et al.*, 2004; Koch *et al.*, 2009). The ideal C/N ratio for AD has been reported to be in the region of 20/1- to 30/1 (Parkin and Owen, 1986). Inappropriate (too high or too low) C/N ratios in the feedstock (e.g. PM used in this study) could result in a release of excessive ammonia or an accumulation of VFAs in the digester, which are potential inhibitors in the AD process and would decrease the activity of methanogens and eventually terminate the AD process (Dennehy et al., 2017b). As demonstrated in this study, co-digesting PM that has a low C/N ratio of less than 12/1 along with a substrate with low levels of nitrogen (e.g. GS) represents a more stable operation and a higher methane yield than AD of manure alone.

3.3 Soluble COD and VS removals

Soluble COD concentrations reflect the quality of digestate after AD, while VS removals can affect the process efficiency (Marcato et al., 2009; Xie et al., 2016). In this study, soluble COD removal rates increased from 81.4% in Phase I to 87.8% in Phase II (p<0.05). VS removal rates in this study improved from 41.4% in Phase I to 53.9% in Phase II (p<0.05) (Table 5). Thus, less monetary cost can be expected during the downstream processes of the digestate in terms of digestate dewaterability and biosolids production (Almomani et al., 2017; Jensen et al., 2014; Nghiem et al., 2017). AD of GS has resulted in VS removals in the range 37%-67% (Cirne *et al.*, 2007; Lehtomaki *et al.*, 2008; Lehtomaki and Bjornsson, 2006; Yu *et al.*, 2002), depending on operating conditions (e.g. the reactor configuration, temperature), properties and composition of the substrate (e.g. type of GS), and pre-treatment methods. The VS removals for AD of PM alone or co-digestion with various agro-industrial wastes range from 42% to 88% (Bułkowska et al., 2012; Monou *et al.*, 2009). It is noteworthy that as the feedstocks quoted varied greatly in terms of their properties and composition, the variations in terms of VS removals and SMYs are expected.

[Table 5]

4. CONCLUSIONS

The anaerobic co-digestion of GS and PM on a VS basis of 1:1 was successful in this pilot-scale study. The study demonstrated that co-digestion of PM with GS offered several advantages over mono-digestion of PM, including a higher methane content in biogas, a higher SMY of PM, and higher VS and soluble COD removals. The superior performance of the systems with regard to higher system stability and particularly the improved SMY during co-digestion of PM and GS can be largely attributed to the synergistic effects, likely associated with lower free ammonia inhibition and appropriate C/N ratio in the feedstock mixture compared with mono-digestion of PM alone. It is therefore recommended that anaerobic co-digestion of PM and GS be applied in practice for the demand driven biogas production despite the marginal synergistic effects. Future research on the optimisation of operating envelope underpinning synergistic effects is needed for full scale implementation.

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REFERENCES

Almomani F., Shawaqfah M., Bhosale R.R., Kumar A., Khraisheh M.A.M. 2017. Intermediate ozonation to enhance biogas production in batch and continuous systems using animal dung and agricultural waste. International Biodeterioration & Biodegradation, 119, 176-187.

Alvarez R., Lidén G. 2008. Anaerobic co-digestion of aquatic flora and quinoa with manures from Bolivian Altiplano. Waste Management, 28, 1933-1940.

Angelidaki I., Ellegaard L. 2003. Co-digestionof manure and organic wastes in centralized biogas plants. Applied Biochemistry and Biotechnology, 109(1-3), 95-105.

Anthonisen A. C., Loehr R. C., Prakasam T. B. S., Srinath E. G. 1976. Inhibition of nitrification by ammonia and nitrous acid. Journal (Water Pollution Control Federation), 835-852.

APHA. 1995. Standard methods for the examination of water and wastewater. 19th. Edition. American Public Health Association. Washington, DC.

Astals S., Nolla-Ardevol V., Mata-Alvarez J. 2012. Anaerobic co-digestion of pig manure and crude glycerol at mesophilic conditions: biogas and digestate. Bioresource Technology, 110, 63-70.

Bayrakdar A., Molaey R., Sürmeli R.Ö., Sahinkaya E., Çalli B. 2017. Biogas production from chicken manure: Co-digestion with spent poppy straw. International Biodeterioration & Biodegradation, 119, 205-10

Bułkowska K., Pokój T., Klimiuk E., Gusiatin Z.M. 2012. Optimization of anaerobic digestion of a mixture of Zea mays and Miscanthus sacchariflorus silages with various pig manure dosages. Bioresource Technology, 125, 208-216.

Callaghan F.J., Wase D.A.J., Thayanithy K., Forster C.F. 2002. Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure. Biomass Bioenergy, 27, 71–77.

Chae K.J., Jang A., Yim S.K., Kim, I.S. 2008. The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure. Bioresource Technology, 99(1), 1-6.

Cirne D.G., Lehtomäki A., Björnsson L., Blackall L.L. 2007. Hydrolysis and microbial community analyses in two-stage AD of energy crops. Journal of Applied Microbiology, 103, 516-527.

Clarke W.P., Xie S., Patel M. 2016. Rapid digestion of shredded MSW by sequentially flooding and draining small landfill cells. Waste Management, 55, 12-21.

Dechrugsa S., Kantachote D., Chaiprapat S. 2013. Effects of inoculum to substrate ratio, substrate mix ratio and inoculum source on batch co-digestion of grass and pig manure. Bioresource Technology, 146(0), 101-108.

Dennehy C., Lawlor P.G., Croize T., Jiang Y., Morrison L., Gardiner G.E., Zhan X. 2016. Synergism and effect of high initial volatile fatty acid concentrations during food waste and pig manure anaerobic co-digestion. Waste Management, 56, 173-180.

Dennehy C., Lawlor P. G., Gardiner G. E., Jiang Y., Cormican P., McCabe M.S., Zhan X. 2017b. Process stability and microbial community composition in pig manure and food waste anaerobic co-digesters operated at low HRTs. Frontiers of Environmental Science & Engineering, 11(3), 4.

Dennehy C., Lawlor P.G., Jiang Y., Gardiner G.E., Xie S., Nghiem L.D., Zhan X. 2017a. Greenhouse gas emissions from different pig manure management techniques: a critical analysis. Frontiers of Environmental Science & Engineering, 11(3), 11.

Gelegenis J., Georgakakis D., Angelidaki I., Mavris V. 2007. Optimization of biogas production by co-digesting whey with diluted poultry manure. Renewable Energy, 32, 2147-2160.

Hamelinck C., van den Broek R., Rice B., Gilbert A., Ragwitz M., Toro F. 2004. Liquid biofuel strategy for Ireland, Sustainable Energy Ireland, Glasnevin, Dublin 9, Ireland, December, 2004.

Hansen K.H., Angelidaki I., Ahring B.K. 1998. Anaerobic digestion of swine manure: inhibition by ammonia. Water Research, 32, 5–12.

Huang G.F., Wong J.W.C., Wu Q.T., Nagar B.B. 2004. Effect of C/N on composting of pig manure with sawdust. Waste Management, 24(8), 805-813.

Jensen P.D., Astals S., Lu Y., Devadas M., Batstone D.J. 2014. Anaerobic codigestion of sewage sludge and glycerol, focusing on process kinetics, microbial dynamics and sludge dewaterability. Water Research, 67, 355-366.

Kaparaju P., Rintala J. 2005. Anaerobic co-digestion of potato tuber and its industrial by-products with pig manure. Resources, Conservation and Recycling, 43, 175-188.

Kaparaju P., Rintala J. 2011. Mitigation of greenhouse gas emissions by adopting anaerobic digestion technology on dairy, sow and pig farms in Finland. Renewable Energy, 36(1), 31-41.

Khanal S.K., Huang J.C. 2003. ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater. Water Research, 37(9), 2053-2062.

Kim M., Chowdhury M.M.I., Nakhla G., Keleman M. 2017. Synergism of co-digestion of food wastes with municipal wastewater treatment biosolids. Waste Management, 61, 473-483.

Koch K., Wichern M., Lübken M., Horn H. 2009. Mono fermentation of grass silage by means of loop reactors. Bioresource Technology, 100(23), 5934-5940.

Lehtomaki A., Björnsson L. 2006. Two-stage AD of energy crops: methane production, nitrogen mineralisation and heavy metal mobilisation. Environmental Technology, 27, 209-218.

Lehtomäki A., Huttunen S., Rintala J.A. 2007. Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio. Resources, Conservation and Recycling, 51 (3), 591-609.

Lehtomäki A., Huttunena S., Lehtinena T.M., Rintalaa J.A. 2008. AD of grass silage in batch leach bed processes for methane production. Bioresource Technology, 99, 3267-3278.

Li Y., Yan X.L., Fan J.P., Zhu J.H., Zhou W.B. 2011. Feasibility of biogas production from anaerobic co-digestion of herbal-extraction residues with swine manure. Bioresource Technology, 102(11), 6458-6463.

Lin Y.W., Tuan N.N., Huang S.L. 2016. Metaproteomic analysis of the microbial community present in a thermophilic swine manure digester to allow functional characterization: a case study. International Biodeterioration & Biodegradation, 115, 64-73.

Marcato C.E., Mohtar R., Revel J.C., Pouech P., Hafidi M., Guiresse M. 2009. Impact of anaerobic digestion on organic matter quality in pig slurry. International Biodeterioration & Biodegradation, 63(3), 260-266.

Molinuevo-Salces B., González-Fernández C., Gómez X., García-González M.C., Morán A. 2012. Vegetable processing wastes addition to improve swine manure anaerobic digestion: Evaluation in terms of methane yield and SEM characterization. Applied Energy, 91(1), 36-42.

Monou M., Kythreotou N., Fatta D., Smith S.R. 2009. Rapid screening procedure to optimise the anaerobic co-digestion of industrial biowastes and agricultural livestock wastes in Cyprus. Waste Management, 29, 712–720.

Nghiem L.D., Koch K., Bolzonella D., Drewes J.E. 2017. Full scale co-digestion of wastewater sludge and food waste: Bottlenecks and possibilities. Renewable and Sustainable Energy

Reviews, 72, 354-362.

Nghiem L.D., Manassa P., Dawson M., Fitzgerald S.K. 2014. Oxidation reduction potential as a parameter to regulate micro-oxygen injection into anaerobic digester for reducing hydrogen sulphide concentration in biogas. Bioresource Technology, 173, 443-447.

Pantaleo A., Gennaro B.D., Shah N. 2013. Assessment of optimal size of anaerobic co-digestion plants: An application to cattle farms in the province of Bari (Italy). Renewable and Sustainable Energy Reviews, 20(0), 57-70.

Parkin G. F., Owen W. F. 1986. Fundamentals of anaerobic digestion of wastewater sludges. Journal of Environmental Engineering, 112(5), 867-920.

Rajagopal R., Masse D.I., Singh G. 2013. A critical review on inhibition of anaerobic digestion process by excess ammonia. Bioresource Technology, 143, 632-41.

S.I. No. 610, 2010. European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010. The Stationary Office Dublin, Ireland. http://www.environ.ie/en/Legislation/Environment/Water/FileDownload,25133,en.pdf. (accessed on 01.02.2017).

Vavilin V.A., Angelidaki I. 2005. Anaerobic degradation of solid material: importance of initiation centers for methanogenesis, mixing intensity, and 2D distributed model. Biotechnology and bioengineering, 89(1), 113-122.

Wu G., Healy M. G., Zhan X. 2009. Effect of the solid content on anaerobic digestion of meat and bone meal. Bioresource Technology, 100 (19), 4326-4331.

Wu S., Shen Z., Yang C., Zhou Y., Li X., Zeng G., Ai S., He H. 2017. Effects of C/N ratio and bulking agent on speciation of Zn and Cu and enzymatic activity during pig manure composting. International Biodeterioration & Biodegradation, 119, 429-36.

Xie S., Lawlor P.G., Frost J.P., Hu Z., Zhan X. 2011. Effect of pig manure to grass silage ratio on methane production in batch anaerobic co-digestion of concentrated pig manure and grass silage. Bioresource Technology, 102(10), 5728-33.

Xie S., Wu G., Lawlor P.G., Frost J.P., Zhan X. 2012. Methane production from anaerobic co-digestion of the separated solid fraction of pig manure with dried grass silage. Bioresource Technology, 104, 289-297.

Xie S., Lawlor P.G., Frost J.P., Wu G., Zhan X. 2012. Hydrolysis and acidification of grass silage in leaching bed reactors. Bioresource Technology, 114, 406-413.

Xie S., Hai F.I., Zhan X., Guo W., Ngo H.H., Price W.E., Nghiem L.D. 2016. Anaerobic co-digestion: a critical review of mathematical modelling for performance optimization. Bioresource Technology, 222, 498–512.

Xie S., Wickham R., Nghiem L.D. 2017a. Synergistic effect from anaerobic co-digestion of sewage sludge and organic wastes. International Biodeterioration & Biodegradation, 116, 191-197.

Xie T., Xie S., Sivakumar M., Nghiem L.D. 2017b. Relationship between the synergistic/antagonistic effect of anaerobic co-digestion and organic loading. International Biodeterioration & Biodegradation, in press.

Yenigün O., Demirel B. 2013. Ammonia inhibition in anaerobic digestion: A review. Process Biochemistry, 48(5-6), 901-911.

Yu H.W., Samani H.W., Hanson A., Smith G. 2002. Energy recovery from grass using two-phase AD. Waste Management, 22, 1-5.

Zhang L., Lee Y.W., Jahng D. 2011. Anaerobic co-digestion of food waste and piggery wastewater: focusing on the role of trace elements. Bioresource Technology, 102(8), 5048-59.

Figure Captions

Figure 1: The schematic of the pilot-scale anaerobic digester

Figure 2: pH profile during the mono-digestion of PM and co-digestion PM and GS

Figure 3: Ammonium nitrogen and free ammonia concentration profiles during the experiment

Figure 4: Daily biogas production (a) and CH_4 and CO_2 content in biogas (b) during the experiment

Table 1: Characteristics of raw PM, GS and inoculum

Characteristics	GS	PM	Inoculum
DM (% of FW)	34.50	3.71	1.56
VS (% of FW)	31.60	2.61	0.79
Ash (% of FW)	2.90	1.1	0.77
NDF (% of DM)	61.51	-	-
ADF (% of DM)	39.62	-	-
pH	4.47	7.90	8.00
Lactic acid (% of DM)	10.49	-	-
VFA (% of DM)	3.36	-	-
CP (% of DM)	14.71	-	-
WSC(% of DM)	2.76	-	-
DMD (% of DM)	68.50	-	-
sCOD ($g \cdot l^{-1}$)	-	24.41	6.70
tCOD ($g \cdot l^{-1}$)	-	128.90	36.64
sCOD (% of DM)	24.64	-	-
NH_4^+-N ($mg \cdot l^{-1}$)	-	1640	2387

Note: FW: fresh weight, DM: dry matter; VS: volatile solids; NDF: neutral detergent fiber; ADF: acid detergent fiber; VFA: volatile fatty acid; CP: crude protein; WSC: water soluble carbohydrate; DMD: dry matter digestibility; sCOD: soluble COD

Table 2: Performance of pilot-scale anaerobic digester at the steady state

Parameters	Phase I	Phase II
Duration (d)	0 - 61	62 - 109
pH	7.99 ± 0.05	7.77 ± 0.05
NH_4^+-N ($mg \cdot l^{-1}$)	2323 ± 24	2541 ± 34
Free NH_3 ($mg \cdot l^{-1}$)	233.0 ± 7.3	158.3 ± 7.9
SMY (ml CH_4/g VS added)	154 ± 8	251 ± 13
Volumetric methane yield (m^3 $CH_4 \cdot m^{-3}$ reactor$\cdot d^{-1}$)	0.134 ± 0.007	0.437 ± 0.022

Table 3: SMYs measured in the mesophilic AD of PM

Study	Molinuevo-Salces et al. (2012)		Hansen et al. (1998)	Zhang et al. (2011)	Li et al. (2011)	Dennehy et al. (2016)	Present Study
SMYs measured (ml CH_4/gVS added)	90	201	188	187	151	260	154
TS (%)	12.5	12.5	nd	5.64	nd	0.8	3.71
CH_4 (%)	49	69	71	50	57	nd	58
HRT (d)	25	15	15	20-40	30	batch trials	30
Temperature (°C)	37	37	37	37	35	37	37

Table 4: SMYs measured in the mesophilic co-digestion of PM and GS

Study	Bułkowska et al. (2012)	Li et al (2011)	Xie et al. (2012)	Present Study
Substrates	PM and silage comprised of Z. mays L. and M. sacchariflorus on a 7.5: 92.5 VS basis	PM and herbal extract residues on a 1:1 VS basis	PM and GS on a 3:2 VS basis	PM and GS on a 1:1 VS Basis
SMYs measured (ml CH_4/g VS added)	350-400	220	271	251
CH_4 (%)	43.50	63.8	54	62
HRT (d)	45	30	30	30
Temperature (°C)	39	35.2	37	37

Table 5: VS and soluble COD removals at the steady state

Parameters	Phase I	Phase II
$VS_{conc,in}$ (%)	2.61	5.22
$VS_{conc,out}$ (%)	1.52	2.41
VS removals (%)	41.4	53.9
$sCOD_{conc,in}$ ($g \cdot l^{-1}$)	24.41	31.42
$sCOD_{conc,out}$ ($g \cdot l^{-1}$)	4.53	3.84
Soluble COD removals (%)	81.4	87.8

Figure 1:

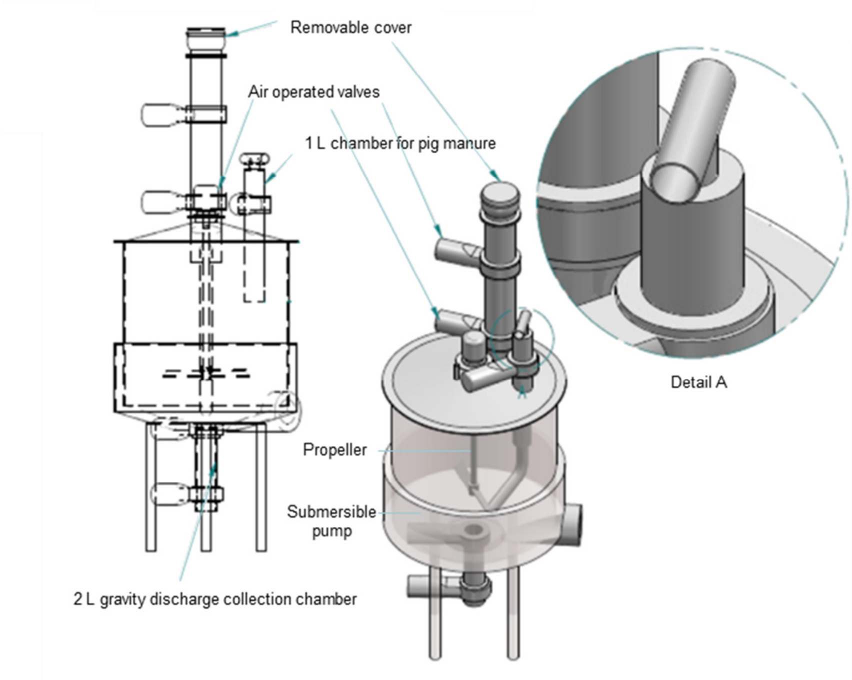

Removable cover
Air operated valves
1 L chamber for pig manure
Detail A
Propeller
Submersible
pump
2 L gravity discharge collection chamber

Figure 2

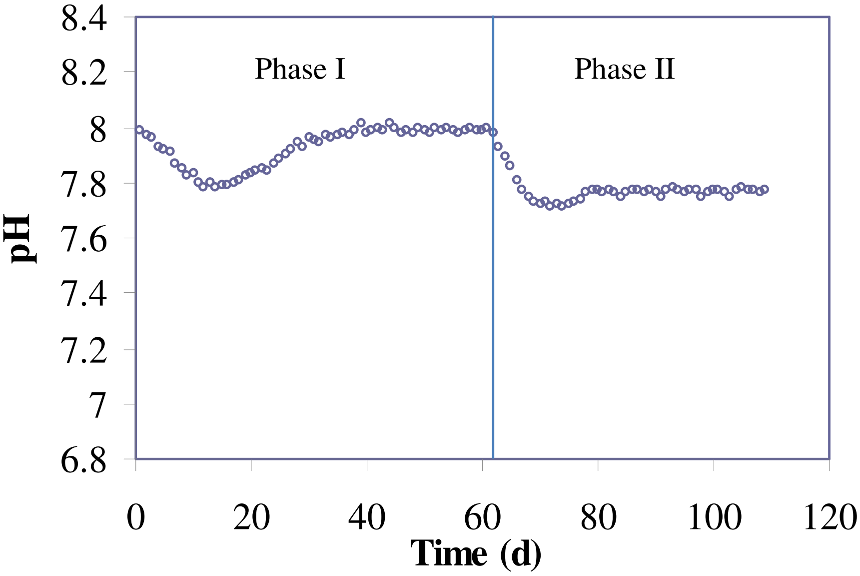
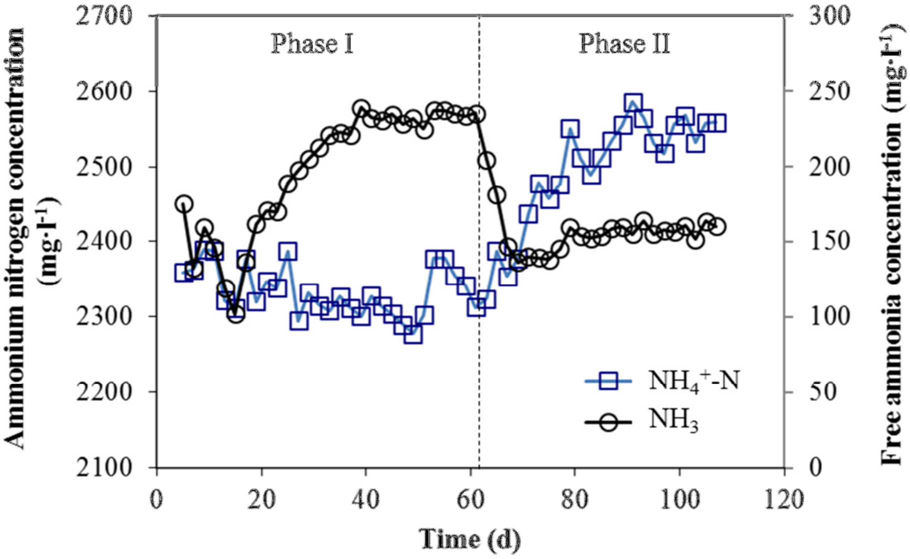
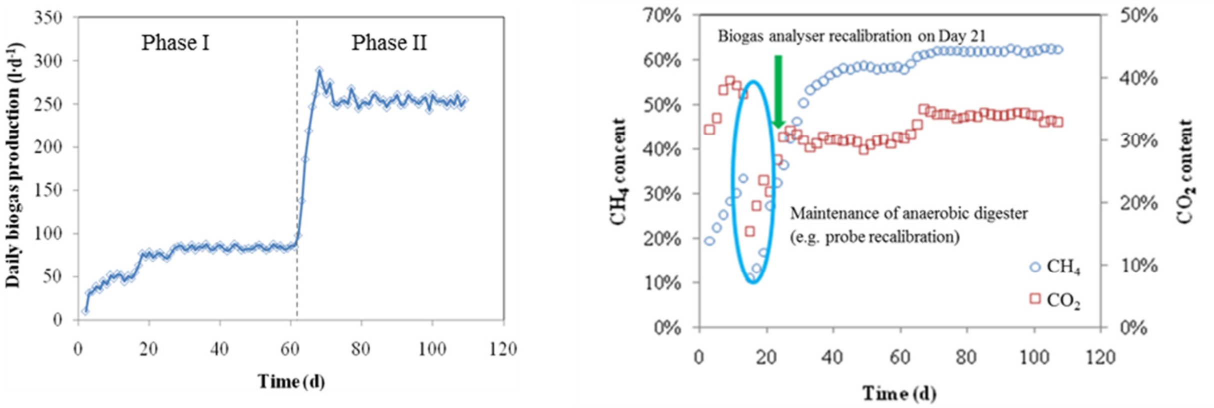

8.4
8.2
8
7.8
7.6
7.4
7.2
7
6.8
pH
Phase I
Phase II
0
20
40
60
80
100
120
Time (d)

Figure 3



Phase I
Phase II
Ammonium nitrogen concentration (mg·l-1)
Free ammonia concentration (mg·l-1)
Time (d)
2700
2600
2500
2400
2300
2200
2100
300
250
200
150
100
50
0
0
20
40
60
80
100
120
NH4+-N
NH3

Figure 4



Phase I
Phase II
Daily biogas production (l·d⁻¹)
Time (d)
Biogas analyser recalibration on Day 21
Maintenance of anaerobic digester
(e.g. probe recalibration)
CH4 concent
CO2 content
CH4
CO2
Time (d)