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Short Communication

Anaerobic co-digestion of dairy cattle manure and pear waste

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HIGHLIGHTS

- The synergetic effect of pear waste and dairy cow slurry was clearly illustrated.
- Storage of pear waste did not compromise its use as substrate for anaerobic digestion.
- Co-digestion of 75% PLF:25% LCM (v:v) gave the best process performance results.
- Process flexibility was shown as inversion of substrates' ratio did not compromise performance.
- Co-digestion of manure and pear waste is an interesting approach for energy production.

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ABSTRACT

Anaerobic co-digestion of pre-treated dairy cattle manure (LCM) with pear waste after a storage period (PLF) was tested at four inclusion levels: 0%, 25%, 75% and 100%. Inclusion levels consisted in the replacement of the volatile solids (VS) from the LCM with the VS from PLF keeping the organic loading rate around 1.1 ± 0.4 g SV L^{-1} d^{-1}. The introduction of the co-substrate clearly enhanced methane production rate (MPR) in comparison to single substrate (phase I) as phases II and III, respectively, achieving values 1.3 and 2.8 times higher than phase I. The overall performance was optimized for the mixture 25:75 (LCM:PLF; v:v). Moreover, storage of pear waste did not compromise its use in AD. This fact is important once it can improve waste management from pear production through its valorisation as co-substrate in AD process.

1. Introduction

The large amount of waste produced along the food chain (from agriculture, to industrial processing, retail and household consumption) leads to the need of finding alternative valorisation options, namely extraction of valuable compounds or its use as substrate for energy production. Mirabella et al. (2014) extensively review the options for the valorisation of food processing waste.

Fruit waste (FW) is very rich in organic matter and has a tendency to undergo fermentation what can complicate its management. The most common treatment for FW is composting but several authors have studied the feasibility of using FW as a substrate for anaerobic digestion (AD) (Arhoun et al., 2013; Bouallagui et al., 2003, 2005, 2009; Coalla et al., 2009; Garcia-Peña et al., 2011; Hamelin et al., 2014; Scano et al., 2014; Shen et al., 2013; Sitorus et al., 2013).

Nevertheless, the high biodegradability of FW leads to the production of volatile fatty acids (VFA) resulting in a rapid decrease in pH that inhibits the methanogenic activity (Jiang et al., 2012). Anaerobic co-digestion technology provides simultaneous digestion of different solid and liquid wastes, and can be an interesting strategy to avoid system acidification. This technology allows achieving more appropriate carbon to nutrient ratio (C/N/P) by co-digesting nutrient-rich and highly chemical oxygen demand (COD) concentrated wastes contributing to pH regulation and avoiding possible ammonia inhibition problems.

An example of substrates with high buffering capacity (alkalinity) is livestock manure. Although the common practice for manure management is landspreading, normally there is a surplus, which can be used in anaerobic digestion. This way, decentralized co-digestion of manure and FW seams as an interesting approach as a farm scale energy production and as a waste treatment solution.

Several studies have reported the advantages of anaerobic co-digestion of manure and FW, showing that experimental methane yields obtained for the mixtures resulted in higher values than those obtained from single substrates (Estevez et al., 2012; Giuliano et al., 2013; Molinuevo-Salces et al., 2013). Lin et al. (2012) investigated batch anaerobic co-digestion of pulp and paper sludge and FW at different mixture ratios. The authors reported

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higher methane yield and organics removal efficiency and also more buffering capacity for the co-digestion scenario than for single-substrate digestion.

On another hand, it is known that solubilisation of particulate COD can be a critical aspect in AD, as the microbial consortia requires organic matter in soluble form. Several treatments have been applied to FW (e.g. thermal, enzymatic, mechanical, etc.) with the aim of maximizing COD solubilisation (Graunke and Wilkie, 2014).

The purpose of the present work was to study the co-digestion of pear waste (non-marketable pears) with dairy cattle manure, under mesophilic conditions in a completely mixed stirring tank reactor (CSTR). The effect of substrate type and inclusion level on gas production rate (GPR) and methane production rate (MPR) was evaluated.

2. Methods

2.1. Materials

2.1.1. Pear waste

Pears from Frutasobreiro, Lda. were harvested in August and kept refrigerated (0 ± 0.2 °C) until October. Non-marketable pears, pear waste (PW), were stored and transported to the laboratory where they were pulped. As pear waste management will probably include a storage period at room temperature, the effect of storage on pulp characteristics was assessed. For that purpose 2 plastic 1 L bottles were filled with 500 mL of pulp and kept closed at room temperature for 180 days. After this period key parameters were measured (characterization before and after the storage period is presented in Table 1). The bioconverted pulps were joined and filtered through a 150 mm filter to separate the liquid and solid fractions. The pear liquid fraction (PLF), representing 60% of the total volume of pear pulp, has been characterized to be used as co-substrate in the AD trial. In order to achieve similar volatile solids amount for both substrates, PLF was diluted with water in the ratio 1:4.

2.1.2. Dairy cattle manure

Cattle manure (CM) was obtained from a 120 dairy cows farm unit, located in a municipality 40 km North of Lisbon, Portugal. CM was sieved to remove coarse materials, obtaining 34% of solid fraction and 66% of liquid fraction (LCM), this last was used as substrate.

Regarding the solid fractions from PW and CM, although they were not comprised in the present study, it was considered that in future work they should be characterized in order to evaluate their potential use in composting process.

2.2. Analytical methods

The following parameters were determined according to standard methods (APHA, 1998): pH, electrical conductivity (EC), total solids (TS), volatile solids (VS), chemical oxygen demand (COD), total Kjeldhal nitrogen (TKN), organic nitrogen (N_{org}), ammonium nitrogen (NH_4^+-N) and total phosphorus (TP). Refractive index (BRIX) was determined using Atago Digital Pocket refractometer. Table 2 summarizes the characteristics of LCM and PLF.

2.3. Pilot-scale anaerobic digestion assays

2.3.1. Feedstock

PLF was mixed with LCM in different percentages (v:v) according to the trial plan: phase I (0% PLF + 100% LCM), phase II (25% PLF + 75% LCM), phase III (75% PLF + 25% LCM), phase IV (100% PLF + 0% LCM). In phase IV, as only PLF was used which is acidic it was necessary to correct pH to a value around 7.0 with NaOH (25%).

2.3.2. Experimental set-up

The completely mixed stirring reactor has an overall volume of 6 L, it is partially insulated with a polymeric layer and equipped with a radial stirrer and an electrical heating system, which guarantees an operating temperature up to 37 ± 2 °C.

The biogas collection system includes a flow meter and a gasholder. The digestate is removed from the reactor gravimetrically and conveyed to the digestate tank.

The pilot plant is controlled by a PLC system that receives signals from the different sensors and drives the main electrical and pneumatic pieces of equipment (pumps, stirrers, heaters, etc.).

2.3.3. Operating procedures and process monitoring

The monitoring period lasted 126 days and included four different phases, in which PLF was tested in co-digestion with LCM at four inclusion levels: 0% (phase I), 25% (phase II), 75% (phase III) and 100% (phase IV). Inclusion levels consisted in the replacement of VS from LCM with VS from PLF. This procedure aimed at identifying the optimum operating parameters of the AD process to achieve the efficient conversion of PLF into biogas.

The reactor was kept in mesophilic conditions (37 ± 0.5 °C) throughout the trial. Phase I lasted 42 days, the reactor was continuously operated for three consecutive hydraulic residence time (HRT) of 14 days to achieve steady state conditions. In phases II–IV the reactor was operated for two consecutive HRT to keep steady-state conditions.

The most important operating parameters, such as: pH, EC, TS, VS, COD, TKN, N-NH_4^+ were monitored, both in feed and digestate, to control the process performance. The operational parameters organic loading rate (OLR), gas production rate (GPR), biogas quality, specific methane production (SMP) and methane production rate (MPR) were determined during the experimental trial. GPR was measured daily using a gas meter (Contigea Schlumberger instruments) and biogas composition in methane (CH_4), carbon dioxide (CO_2) and hydrogen sulphide (H_2S) was determined once

Table 1
Characterization of pear pulp before and after storage for 180 days.

Parameter	PW	$PW_{180\ days}$
pH	4.4 ± 0.1	3.5 ± 0.04
EC (mS cm^{-1})	1.4 ± 0.94	2.9 ± 0.6
TS (g kg^{-1})	193.6 ± 21.2	162.9 ± 1.2
VS (g kg^{-1})	190.1 ± 21.3	151.4 ± 1.1
Refractive index (%)	17.2 ± 1.1	7.9 ± 0.8
CQO (g kg^{-1})	203.4 ± 25.3	190.6 ± 19.2
$CQO_{soluble}$ (g kg^{-1})	79.0 ± 8.7	179.0 ± 16.5
TKN-N (mg kg^{-1})	393.4 ± 25.0	354.1 ± 19.3
NH_4^+-N (mg kg^{-1})	33.3 ± 5.6	229.3 ± 9.2
N_{org}-N (mg kg^{-1})	360.1 ± 7.6	124.8 ± 6.6
C/N	279.8 ± 13.7	248.1 ± 11.2

Table 2
Pre-treated dairy cattle manure (LCM) and pear liquid fraction (PLF) characteristics.

Parameter	LCM	PLF (1:4)
pH	7.0 ± 0.3	4.6 ± 1.1
EC (mS cm^{-1})	11.3 ± 0.5	1.8 ± 0.6
TS (g L^{-1})	33.7 ± 5.8	17.6 ± 8.4
VS (g L^{-1})	24.0 ± 4.5	16.5 ± 7.4
VS/TS (%)	71	92
COD (g L^{-1})	40.7 ± 4.8	35.8 ± 5.1
TKN (g L^{-1})	1.2 ± 0.1	0.08 ± 0.02
NH_4^+-N (g L^{-1})	0.8 ± 0.1	0.03 ± 0.02
N_{org} (g L^{-1})	0.3 ± 0.02	0.04 ± 0.01
C (g L^{-1})	13.9 ± 2.6	10.1 ± 4.9
C/N	12	103

a week by portable equipment (GAS DATA Multifunction analyser). To follow the digester performance the parameter specific energy-loading rate (SELR) was calculated after each steady state cycle, according to Panter et al., 2011.

3. Results and discussion

The main characteristics of pear pulp before and after storage for 180 days are presented in Table 1.

Regarding the effect of storage for 180 days on pulp characteristics, results point out to the occurrence of fermentation confirmed by the pH and refractive index decrement, around 20% and 54%, respectively. Total COD showed only a slight decrease (about 6%) not compromising pear pulp use as feedstock for AD process. Another important aspect is that COD soluble fraction increased (2.3 times) with the storage period, what has a positive effect on AD performance as more material is readily available for biodegradation. EC followed the same behaviour, increasing around 50%, what can be explained by the fermentation process during storage. These results are in agreement with Ferreira et al. (2007) that observed microbial conversion of free soluble carbohydrates into acids and ethanol developing a low pH environment suitable to preserving organic material (only 5% of total COD was lost during a 3 months storage period). The results obtained can be very useful for pulp management as they indicate that storage improves organic matter solubilisation what is beneficial for AD process.

As described in Section 2.1 only the liquid fractions of the substrates were used in the feeding mixture and their main characteristics are presented in Table 2.

Analysing the characteristics of the two substrates we can notice their complementarity contributing for the optimization of the AD process, for example the C/N ratio of PLF is about 9 times higher than the LCM's. Regarding LCM, total COD values averaged $40.7 \pm 4.8\ g\ L^{-1}$ and VS $24.0 \pm 4.5\ g\ L^{-1}$, representing 71% of TS. The average values of NH_4^+-N and N_{org} were 0.8 ± 0.1 and $0.3 \pm 0.02\ g\ L^{-1}$, respectively. The PLF had a water content around 82% and an acidic pH (4.6 ± 1.1). Total COD values were in the same range as LCM, averaging $35.8 \pm 5.1\ g\ L^{-1}$, but with different availability to the co-digestion process. VS presented average values of $16.5 \pm 8.4\ g\ L^{-1}$ (92% of TS). Nitrogen was present in both organic and ammonium forms, 0.04 ± 0.01 and $0.03 \pm 0.023\ g\ L^{-1}$, respectively.

Table 3 shows the variation of feedstock mixture throughout the AD trial phases, VS from PLF gradually replaces VS from LCM.

Table 4 summarizes the behaviour of performance parameters along the four AD phases.

As it can be seen from Table 4, the maximum GPR was achieved in phase III, where the OLR also had its maximum value. Clear improvement was observed in MPR with the introduction of the co-substrate, phase II and III had values, respectively, 1.3 and 2.8 times higher than phase I.

The best result obtained for phase III may be related to feed mixture C/N ratio, that for this phase was 25 (considered the optimum value), whereas for the other phases it was either lower or higher than the recommended value (Sitorus et al., 2013).

Table 3
Feedstock mixture throughout the AD trial phases.

	Phase I	Phase II	Phase III	Phase IV
Mixture LCM:PLF (% v/v)	100:0	75:25	25:75	0:100
Feed VS ($g\ VS\ d^{-1}$)	4.6	4.3	5.2	3.0
% of VS from PLF	0	21	78	100
C/N	12	14	25	103

Table 4
Behaviour of performance parameters during the four AD phases.

Parameter	Phase I	Phase II	Phase III	Phase IV
OLR ($g\ VS\ L^{-1}d^{-1}$)	1.14 ± 0.3	1.09 ± 0.5	1.3 ± 0.6	0.8 ± 0.2
VS fed ($g\ d^{-1}$)	4.55 ± 0.4	4.35 ± 0.3	5.2 ± 0.2	3.0 ± 0.5
GPR ($mL\ d^{-1}$)	800 ± 120	1700 ± 100	3000 ± 300	2900 ± 200
Biogas quality (% CH_4)	64.0 ± 0.2	71.3 ± 0.3	66.7 ± 0.4	65.5 ± 0.5
SMP ($mL\ g^{-1}$ VS)	112.5 ± 3.1	164.0 ± 1.4	390.0 ± 2.0	472.0 ± 1.3
MPR ($LL^{-1}\ dia^{-1}$)	0.13 ± 0.02	0.30 ± 0.02	0.50 ± 0.05	0.47 ± 0.04
VS reduction (%)	41.5	48.0	60.0	62.0
SELR (d^{-1})	0.11 ± 0.04	0.15 ± 0.02	0.20 ± 0.01	0.25 ± 0.02

Regarding SMP, the increase of PLF percentage as co-substrate leads to 1.5, 2.5 and 3 times higher values, respectively for phases II, III and IV, than for single substrate (phase I). Although the highest SMP was achieved in phase IV ($472.0 \pm 1.3\ mL\ g^{-1}$ VS), considering GPR, biogas quality and MPR trend along the trial phases, the overall performance was optimized in phase III. Furthermore, digestate's pH profile along the trial phases showed a decreasing tendency: 8.60 ± 0.15 (phase I), 7.31 ± 0.21 (phase II), 7.03 ± 0.20 (phase III) and 6.44 ± 0.38 (phase IV), indicating that under the conditions used in phase IV acidification will take place leading to reactor failure. On the contrary, for phase III, the alkaline components of LCM enhanced the buffer capacity and stability of the anaerobic system. Furthermore, addition of LCM increased the total organic nitrogen in the system, resulting in higher concentration of ammonia that may have neutralized the formed VFA avoiding acidification. Therefore, we considered phase III to be the best one because it clearly illustrated the synergetic effect of both substrates.

The SELR values were always below the value recommended by Panter et al. (2011) ($0.4\ d^{-1}$) so it can be said that the capacity of the methanogenesis was never exceed pointing out the possibility of increasing the feeding load without the risk of digester instability or failure.

Another interesting aspect is the effect of inverting the propotion between PLF and LCM, as hapened from phase II (25% PLF + 75% LCM) to III (75% PLF + 25% LCM), leading to an improvement in reactor efficiency, shown by an increase of 2.4 and 1.25 times, respectively in SMP and VS removal efficiency.

Comparing the results obtained with the reported by Scano et al. (2014) for an AD study using fruit and vegetable wastes (SMP of $0.43\ N\ m^3\ kg^{-1}$ VS for a OLR 2.5–3.0 $kg\ VS\ m^{-3}\ d^{-1}$), we can see that in phase III it was possible to achieve a SMP in the same order ($0.42\ N\ m^3\ kg^{-1}$) with an OLR almost 2 times lower.

4. Conclusions

Methane production from co-digestion of PLF with LCM is feasible. Phase III (75% PLF + 25% LCM), clearly illustrated the synergetic effect, avoiding the need of pH correction due to LCM buffering capacity, leading to a SMP of $390.0 \pm 2.0\ mL\ g^{-1}$ VS and a VS removal of 60%.

Moreover, storage of pear waste did not compromise its use in AD, what is important as pear production is seasonal and because it will simplify its management. Overall, co-digestion of LCM and PLF seams an interesting approach for energy production and as waste treatment solution.

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