High-solids Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste: From Experimental Setup to Model Development

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Abstract

Objective

The objective of this study was to design and operate batch and semi-continuous experiments to understand the effects of increasing the total solid (TS) content in high-solids anaerobic digestion (HS-AD) of the organic fraction of municipal solid waste (OFMSW). Simultaneously, the development and calibration of a HS-AD model based on the Anaerobic Digestion Model No.1 (ADM1) aimed to condense the knowledge gathered from the HS-AD experiments.

Methods

OFMSW was used as a main substrate, while beech sawdust was used in some cases as a co-substrate to simulate green waste. Batch experiments were performed at different initial TS (i.e. 10-33 %) and inoculum-to-substrate ratio (i.e. 0.5-1.5 g VS/g VS). Semi-continuous experiments were performed in draw-and-fill mode from 'wet' AD (i.e. TS < 10 %) to HS-AD (i.e. TS ≥ 10 %). The HS-AD model accounted for the biogas production as a crucial mechanism implying the modification of the reactor content mass/volume.

Results

The experimental setups highlighted the importance of the increasing TS content to exacerbate NH_3 inhibition, and the need to reduce the effluent regarding the influent in semi-continuous HS-AD for OFMSW treatment. Similarly, the HS-AD model implementation verification required the reduction of the effluent regarding the influent to maintain the HS-AD reactor volume constant, while the TS dynamics were adequately simulated.

Conclusions

The HS-AD model might be useful to enhance the OFMSW treatment performance by providing insight about the most important mechanisms triggering HS-AD inhibition/acidification.

Keywords: High-solids Anaerobic Digestion; Organic Fraction of Municipal Solid Waste; Batch and Semi-Continuous Experiments; ADM1.

1. Introduction

Nowadays, the uncontrolled greenhouse gases (GHG) emissions from landfills receiving the organic fraction of municipal solid waste (OFMSW) rise up to 5 % of the global anthropogenic GHG emissions [1]. Therefore, important legislative efforts are being implemented worldwide to divert OFMSW from landfills as, for example, the European Waste Framework Directive (Directive 2008/98/EC) targeting the reuse and recycling, including biochemical treatments, of at least 50 % of the produced OFMSW by 2020. OFMSW includes both household and food waste, while different proportions of green/lignocellulosic wastes might be also added depending on many factors as, for example, the season and/or the municipality waste management strategies [2-4].

Anaerobic digestion (AD) is a well-suited biotechnology for OFMSW treatment, allowing the recovery of a high-methane-content biogas as source of renewable energy, and an organic effluent (digestate) rich in nutrients (i.e. nitrogen, phosphorous and trace elements) with potential applications as soil amendment [5,6]. AD is a biochemical process occurring in absence of oxidative species (i.e. O_2, NO_3^- and SO_4^{2-}) by consortia of anaerobic microorganisms, being responsible for the hydrolysis, acidogenesis, acetogenesis and methanogenesis of organic substances [7]. However, some setbacks limit the applicability of AD for OFMSW treatment as, for example, the difficulties to successfully start the AD process at industrial scale, and the risk of accumulation of inhibitory substances mainly originating from the organic substrate decomposition [8,9]. For example, the free ammonia nitrogen (NH_3) is one of the most important inhibitory substances in AD of OFMSW, since the degradation of proteins and amino acids contained in the organic waste might lead to intolerable NH_3 levels for the acetoclastic and/or hydrogenotrophic methanogenic biomass [10,11]. The presence of undesirable levels of inhibitors (i.e. NH_3, H_2S or free ions) might lead to volatile fatty acids (VFA) and/or hydrogen (H_2) accumulation in AD, requiring the implementation of counteracting measurements to avoid the complete reactor acidification (i.e. pH $\leq$ 6.0) [12].

'High-solids' anaerobic digestion (HS-AD) is a particular AD operation at a total solid (TS) content $\geq$ 10 %, enhancing the overall system economy, in contrast to 'wet' AD (i.e. TS < 10 %). Thus, HS-AD permits the use of a smaller reactor volume, while reducing the need for water addition and digestate dewatering [5,13]. However, HS-AD is subjected to an even greater risk of acidification by substrate overload than 'wet' AD due to the higher organic content used, while bioprocess inhibition (i.e. by NH_3) might be exacerbated due to the lower amount of water available to dilute inhibitory compounds [14,15]. Therefore, understanding the practical limitations of HS-AD becomes crucial to foster the advantages, while enhancing the overall economy of the organic waste treatment process.

Batch experiments are normally used to extract valuable information about the main operative parameters of AD (i.e. optimal TS, treatment length and temperature). For example, the biomethane potential (BMP) test assesses the maximum methane yield of an organic substrate under anaerobic conditions [16,17]. Among the most important operative parameters in HS-AD batch experiments fed with OFMSW, the initial TS content and the inoculum-to-substrate ratio (ISR) are of major interest, as these parameters might be a preliminary estimation of the operational values to be used in industrial reactors. The initial TS content is related to the TS balance, while the ISR (i.e. g VS/g VS) relates to the VS balance of the inoculum-substrate mixture in batch experiments. In general, the TS content needs to be maximized, while the ISR – reuse of inoculum – needs to be minimized, aiming to enhance the specific biogas yield (i.e. $mL/L_{Reactor\ Content}$) of HS-AD reactors [3,18]. In order to optimize the TS-ISR pair in batch experiments, different strategies are followed as, for example, drying the substrate and/or centrifuging the inoculum to reduce the presence of water in the system, as well as using different co-digestion ratios with high-TS-content co-substrates (i.e. green/lignocellulosic waste) [18-20]. However, the increasing TS content has been mentioned to affect/reduce the methane yield of organic substrates (i.e. OFMSW and cardboard) in HS-AD batch experiments [14,21], potentially compromising the global economy of industrial HS-AD. Therefore, an adequate trade-off must be found between maximizing the TS and fostering the HS-AD efficiency.

Semi-continuous experiments might bring also important information about the optimum operational parameters to be used in (semi-)continuous HS-AD industrial reactors for OFMSW treatment, as the maximum organic loading rate (OLR) and minimum hydraulic retention time (HRT). Thus, the OLR and HRT are mainly a function of the substrate TS, VS and anaerobic biodegradability, while these operational parameters need to ensure an adequate waste treatment and minimize the HS-AD treatment costs. Moreover, semi-continuous experiments could be also used to assess the effect of increasing TS in HS-AD by dynamically modifying the TS during the process. Importantly, in HS-AD of OFMSW an important TS removal might occur as a consequence of biogas production. For example, HS-AD of OFMSW might yield between 30 to 80 % TS removal, depending on the OFMSW characteristics (i.e. biodegradability and/or presence of inert materials), the reactor design and/or the operational parameters used (i.e. OLR and HRT) [3,22]. Therefore, the reactor content mass/volume might be considerably reduced in HS-AD of OFMSW, while the mass/volumetric effluent of (semi-)continuous reactors might need to be relative lower than the influent to maintain the reactor content mass/volume constant [23].

Alongside HS-AD batch and semi-continuous experiments, a mathematical model is still required for HS-AD development and process optimization, similarly to the multiple applications for 'wet' AD of the Anaerobic Digestion Model No. 1 (ADM1) [24-26]. ADM1 gathers together the main biochemical and physical-chemical processes in AD, including the disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis of organic substrates, the ionic equilibrium of VFA, inorganic carbon (i.e. HCO_3^-) and inorganic nitrogen (i.e. NH_4^+), and the liquid-gas transfer of CH_4, CO_2 and H_2. However, the continuously stirred tank reactor (CSTR) implementation of ADM1 was primarily conceived for 'wet' AD (i.e. wastewater sludge treatment), where the reactor volume could be assumed constant [27]. Moreover, ADM1 did not include/consider the effects of a high TS content on the HS-AD bio-physical-chemistry. Therefore, potential model modifications are required in ADM1 to address the main bio-physical-chemical processes occurring in HS-AD of OFMSW, with the aim to enhance the efficiency and applicability of HS-AD for OFMSW treatment.

The objective of this study was to design and operate HS-AD batch and semi-continuous experiments to understand the effects of increasing the TS content in HS-AD of OFMSW. Meanwhile, the gathered knowledge could provide adequate feedback regarding the development and calibration of a HS-AD model based on ADM1. Thus, the HS-AD model development and HS-AD experiments were conducted in parallel to benefit simultaneously from both approaches. The joint development of HS-AD model and experiments might bring important insights about potential inhibitory mechanisms in HS-AD of OFMSW, as the NH_3 build-up and the risk of reactor acidification.

2. Material and Methods

2.1. Substrates and Inoculum

In this study, OFMSW consisting in different proportions of household waste, restaurant waste, spent coffee and green waste was used. All the wastes were collected during a month timespan while stored at 4ºC. Subsequently, the wastes were mixed together, ground with the aid of an industrial meat mincer, fully homogenized and stored in sealed buckets at -4ºC until required to fed the batch or semi-continuous experiments. In some cases, OFMSW was dried at 55ºC during 7-10 days to increase the TS content of batch experiments, being further ground by mortar and pestle. Goldspan® beech sawdust with a particle size of 1.0-2.8 mm was used in some co-digestion experiments to simulate the addition of green/lignocellulosic waste in OFMSW.

Thermophilic (55ºC) inoculum was obtained from a 30 L methanogenic reactor fed with water-diluted OFMSW, along different periods for each batch/semi-continuous experiment. Therefore, the inoculum was slightly different in each experiment, despite they were collected from the same source reactor. All inoculums were filtered through a 1 mm sieve. In some cases, the inoculum was centrifuged at 6000 rpm for 10 min to increase the TS content of batch experiments, before being fully homogenized manually. Macro- and micro-nutrients were added to each experimental setup as recommended by Angelidaki and Sanders [16].

2.2. Batch Experiments Setup

Batch experiments were performed in 160 or 250 mL serum bottles using centrifuged inoculum and 55ºC-dried OFMSW. Depending on the setup requirements, distilled water and/or beech sawdust were also included. All the bottles were sealed with butyl rubber stoppers and aluminium crimps, prior to being flushed with inert gas (i.e. He or N_2) and incubated within a thermophilic (55ºC) oven.

Batch experiments consisted in equally-spaced TS contents ranging from 10 up to a maximum 33 % TS, by optimizing the maximum TS content with the ISR – TS and VS balances, respectively. In this study, six batch experiments were used at different TS, ISR and/or co-digestion ratios, including two sacrifice tests. In sacrifice tests, a bottle was open periodically and the content analysed for the main physical-chemical variables (i.e. TS and VFA). A summary of the batch experiments operated in this study is shown in Table 1. TS contents lower than the maximum in each experiment included different amounts of distilled water to reach the desired TS. Therefore, different TS contents within the same family of batch experiments yielded different medium volumes. All the batch experiments were conducted in triplicate, with the exception of sacrifice tests where 15 replicates were used.

Each individual experiment included a blank assay also in triplicate. In blank assays, no substrate was used, while further distilled water was added to compensate for the absence of substrate, usually up to the lowest TS content of each particular experiment (i.e. 10 % TS). Batch bottles were manually agitated only on those days when the gas production was measured. Batch experiments lasted until biogas production was negligible. All the initial batch configurations were designed to be porosity free (i.e. $\varepsilon = 0$).

Table 1 *High-solids anaerobic digestion batch experiments for high-solids anaerobic digestion (HS-AD) of the organic fraction of municipal solid waste (OFMSW), at different inoculum-to-substrate ratio (ISR) and initial total solids (TS), including in some cases beech sawdust as a co-substrate*

No.	Test	Substrate	ISR (g VS/g VS)	Operational TS (%)
1	TS Increase	Dried OFMSW	0.5	10.2, 12.6, 15.6, 19.2, 23.3, 28.3 & 33.6
2			1.0	9.5, 13.6, 18.4 & 24.0
3			1.5	10.8, 13.4, 16.4 & 19.6
4		Dried OFMSW + Sawdust	0.2	10.0, 15.0, 20.0, 24.7 & 30.2
5	Sacrifice	Dried OFMSW	1.0	15.0
6		Dried OFMSW + Sawdust	0.6	19.4
-	BMP	OFMSW	2.0	2.9
-		Sawdust	1.0	4.1

2.3. Semi-continuous Experiments Setup

Semi-continuous experiments for mono-digestion of OFMSW and co-digestion of OFMSW and beech sawdust were performed in 5 L PET bottles with a modified PVC head allowing the introduction and removal of high-solids materials (i.e. substrate/digestate). All the semi-continuous reactors were kept in a thermophilic (55ºC) oven and manually operated for a maximum of five days per week. Before and after each discharge operation, the reactors were weighed in a ± 0.01 kg precision scale. The influents and effluents were weighed in a ± 0.01 g precision scale. The semi-continuous reactors were manually agitated only during the feeding days.

The semi-continuous experiments were started at TS < 5 % using 'wet' AD inoculum and were progressively loaded to increase the TS content up to HS-AD conditions (i.e. TS ≥ 10 %). With the aim to reduce the influence of substrate overload, the effluent mass was reduced in comparison to the influent mass to maintain a constant reactor mass. This strategy permitted also to extend relatively the mass retention time (MRT) as a potential strategy to favour methanogenesis adaptation along stressful conditions (i.e. NH_3 inhibition) [7,10]. As the reactors showed VFA accumulation due to the high OLR used, the reactor feeding was diluted and/or stopped to recover methanogenesis activity. Semi-continuous reactors were fed until reactor failure occurred by acidification (i.e. pH ≤ 6.0).

2.4. HS-AD Model Development

HS-AD batch and semi-continuous experiments allowed the development of a mathematical model based on ADM1, but particularly adapted to homogenized (i.e. completely mixed) HS-AD conditions. In the CSTR implementation of ADM1, the TS dynamics as well as the effects of TS on the biochemical processes were not considered [24]. Therefore, the mass balances needed to be readapted both to simulate the TS (and VS) and the effect of mass/volume modification in soluble and particulate components of the ADM1 biochemistry. To reduce the complexity of the HS-AD model, four main hypotheses were used: the specific weight (ρ_s) of solids and solvents was considered constant, transport processes (i.e. diffusion) were considered negligible, porosity (ε) was disregarded and the main bio-physical-chemical reactions were assumed to occur predominantly in water. These hypotheses were based on a reasoned assessment of the experimental results showed in sections 3.2 and 3.3, in order to keep the model as simple as needed, but also as informative as possible, regarding the effects of TS in HS-AD for OFMSW.

The proposed HS-AD model accounts for the biogas production as a crucial mechanism implying the modification of the reactor content mass/volume. In this line, the global, solids and inert mass balances were implemented as a function of the biogas outflow, to simulate adequately the soluble and particulate substances in the biochemical framework of ADM1, but also the TS and VS dynamics. Meanwhile, the reactor volume was simulated as a function of the reactor content specific weight. In this scheme, the soluble compounds in the HS-

AD model were associated to the concentration effect of the high-TS-content matrix, since the main bio-physical-chemical reactions were assumed to take place mainly in presence of water.

With these modifications, the HS-AD model could be used to simulate indistinctly high-solids and 'wet' AD applications and/or the transition between these two operational regimes, for example, when using co-digestion strategies. The HS-AD model implementation was verified for continuous 200-days 'wet' AD and HS-AD operation. The HS-AD model was verified for 'wet' AD according to Rosén and Jeppsson [28]. In HS-AD simulations, a continuous 25 % TS influent was used. In these influents the organic content mainly associated to carbohydrates and inert compounds – to avoid NH_3 inhibition and VFA accumulation in high-TS-content simulations. In HS-AD simulations, a proportional controller was used to reduce the volumetric effluent ($Q_{Effluent}$), regarding the volumetric influent ($Q_{Influent}$) with the aim to stabilize the reactor volume and HRT. Meanwhile, a preliminary HS-AD model calibration simulated the sacrifice test for mono-digestion of OFMSW (i.e. TS = 15 %).

2.5. Physical-Chemical Analyses and Calculations

The total (TS) and volatile (VS) solids, total Kjeldahl (TKN) and ammonia (TAN) nitrogen, pH and specific weight (ρ_s) physical-chemical analyses were performed according to the standard methods [29-31]. The free ammonia nitrogen (FAN, NH_3) was approximated as shown by Angelidaki and Ahring [32]. The carbonate (ALK_P) and intermediate (ALK_I) alkalinity was evaluated as described by Lahav et al. [33]. VFA were analysed via high pressure liquid chromatography (HPLC) coupled to a 210 nm UV detector, using diluted H_2SO_4 as eluent. The density (ρ) – containing air/liquid-based porosity (ε) – was approximated by using a calibrated cylinder and a ± 0.01 g precision scale. ε was obtained as $1 - \rho/\rho_s$. The methane production was evaluated with a 2-recipient water displacement system, containing the first recipient a 4 M NaOH solution to capture the CO_2 in the biogas, and the second recipient distilled water to be 'displaced'. After measuring the methane production, the reactor gas space was sampled with a pressure-lock syringe and analysed via gas chromatography (GC) for CH_4, CO_2 and H_2. The carrier gas was argon.

A BMP for OFMSW and a BMP for sawdust were performed as described in section 2.2 [Table 1], by using an ISR of 2.0 g VS/g VS in 250 mL bottles for OFMSW and an ISR of 1.0 g VS/g VS in 160 mL bottles for sawdust [16,17]. Both BMP used 'wet' inoculum (i.e. TS < 5 %). Distilled water was added only to the BMP of OFMSW to dilute potential inhibitors contained in the substrate (i.e. NH_3). To evaluate the substrate BMP, the endogenous methane production of the inoculum – blank assay – was subtracted to the methane production of the substrate/inoculum mixture, being the substrate methane production normalized (P = 1bar T = 0 ºC) and expressed per unit of substrate VS (VS_{subs}). The methane yield of batch experiments was evaluated as mentioned for the BMP. To evaluate the chemical oxygen demand (COD) conversion at the end of batch experiments, the overall methane and/or hydrogen production and the accumulated VFA were expressed in COD units, per unit of VS added in terms of substrate and inoculum (VS_{added}). The OLR of semi-continuous reactors was evaluated as the daily VS influent per unit of reactor mass. Since the semi-continuous reactors were operated a maximum of five days per week, a 7-days moving average was calculated.

3. Results and Discussion

3.1. Bio-Physical-Chemical Characterization of Substrates and Inoculum

An average composition of the organic substrates used is shown in Table 2. OFMSW showed a TS content of 26 %, a TKN of 6.5 g N/kg and a BMP of 457 NmL CH_4/g VS_{subs}, in agreement with reported values [2,4]. The high VS/TS ratio (i.e. > 0.9 g VS/g TS) of OFMSW suggested a reduced presence of inert materials [22]. The 55ºC-dried OFMSW showed a TS content of 92 % and a TKN content of 25.5 g N/kg. Meanwhile, the COD/TKN (i.e. 50-60 g O_2/g N) and VS/TS ratios (i.e. 92-93 g VS/g TS) were relatively maintained between the raw and dried OFMSW. Therefore, drying at 55ºC for short periods (i.e. 10 days) might be considered an adequate strategy to increase the TS content of HS-AD batch experiments, as the macroscopic composition of OFMSW was maintained approximately constant. The beech sawdust showed a TS content of 94 % and a BMP of 148 NmL CH_4/g VS_{subs}, in agreement with the TS and BMP of green/lignocellulosic wastes [18,34], suggesting that beech sawdust could be used to simulate the green waste inclusion in OFMSW. Noteworthy, the BMP of sawdust was considerably lower than the BMP of OFMSW, implying a much lower biodegradability of sawdust than OFMSW under anaerobic conditions.

Table 2 *Physical-chemical characterization of organic wastes and inoculum: Total (TS) and volatile (VS) solids, total Kjeldahl (TKN) and ammonia (TAN) nitrogen, pH, partial (ALK_P) and intermediate (ALK_I) alkalinity*

	Organic Substrates			**Inoculum**	
	OFMSW	**Dried OFMSW**	**Sawdust**	**'Wet'**	**Centrifuged**
TS_0 (%)	26.3 ± 0.1	92.2 ± 1.7	93.6 ± 0.6	2.8 ± 1.1	15.6 ± 2.0
VS_0 (%)	24.1 ± 0.4	85.7 ± 1.7	92.9 ± 0.3	1.9 ± 0.8	12.4 ± 1.4
TAN (g N/kg)	1.29 ± 0.06	3.45 ± 0.09	0.11 ± 0.00	3.23 ± 0.60	3.24 ± 0.65
TKN (g N/kg)	6.50 ± 1.50	25.45 ± 1.12	0.67 ± 0.45	4.13 ± 0.84	8.66 ± 1.35
pH	4.4 ± 0.1	4.4 ± 0.2	5.6 ± 0.1	8.4 ± 0.2	8.4 ± 0.5
ALK_P (g $CaCO_3$/kg)	-	-	-	11.4 ± 0.8	8.7 ± 2.4
ALK_I (g Acetic/kg)	0.8 ± 0.7	0.7 ± 0.6	2.2 ± 0.7	7.7 ± 1.3	3.5 ± 1.5

The average composition of the 'wet' and centrifuged inoculums is shown in Table 2. The TS of 'wet' and centrifuged inoculum were 3 and 16 %, respectively. On the other hand, centrifugation increased the particulate characteristics of the inoculum (i.e. TKN), while reduced the soluble compounds (i.e. ALK_P and TAN) regarding the 'wet' inoculum composition. Inoculum centrifugation to increase the TS content of HS-AD batch experiments was also used by Brown and Li [18], since both TS and VS mass balances need to be fulfilled to increase simultaneously the TS content and ISR of HS-AD batch experiments, minimizing the chances of reactor acidification. Drying at 105ºC or filtering the anaerobic inoculum have been also reported as inoculum conditioning strategies to increase the TS of HS-AD experiments [19,35].

3.2. Batch Experiments – Dealing with Acidification and Ammonia Inhibition

HS-AD batch experiments for mono-digestion of OFMSW using an ISR of 0.5 and 1.0 g VS/g VS, and showing a maximum TS contents of 33.6 and 24.0 %, respectively, resulted in reactor acidification and H_2 production due to substrate overload [36], with the exception of two 28.3 % TS replicates using ISR of 0.5 g VS/g VS. With mono-digestion of OFMSW using an ISR of 1.5 g VS/g VS, all the TS conditions showed methanogenesis, though the maximum TS content was 19.6 %. With co-digestion of OFMSW and sawdust using a ISR of 0.2 g VS/g VS, a maximum TS content of 30.2 % and a OFMSW:sawdust ratio of 0.25 g TS/g TS, methanogenesis succeeded only at TS contents of 10.0 and 15.0 % TS, but also in one replicate at 30.2 % TS. In these batch experiments, the TS did not seem to affect the methane yield, since different initial TS contents yielded very similar methane yields – data not shown. The sacrifice test for mono-digestion of OFMSW using an ISR of 1.0 g VS/g VS and a TS = 15 % resulted in methane production, while the sacrifice test for co-digestion of OFMSW and sawdust using an ISR of 0.6 g VS/g VS, a 20 % TS and a OFMSW:sawdust ratio of 1.1 g TS/g TS resulted in acidification.

These results suggest that the optimum TS-ISR pair in HS-AD of OFMSW depends on the overall set of physical-chemical characteristics of the substrate-inoculum mixture (i.e. ISR, TS and biodegradability). Thus, ISR had to be increased for easily biodegradable substrates (i.e. OFMSW), while ISR could be reduced for relatively slower biodegradable substances (i.e. sawdust). For example, the presence of lignocellulosic substances in high-solids co-digestion experiments using a mixture of OFMSW and sawdust permitted to reduce substantially the ISR in comparison to mono-digestion (i.e. 0.2 vs. 1.5 g VS/g VS, respectively), due to their reduced hydrolysis rates of lignocellulosic materials under anaerobic conditions [18,37]. On the other hand, methanogenesis started in mono-digestion sacrifice but not in the mono-digestion experiment using the same ISR (i.e. 1.0 g VS/g VS). Moreover, co-digestion sacrifice using an ISR of 0.6 g VS/ g VS resulted in acidification in contrast to co-digestion experiment using an ISR of 0.2 g VS/g VS. These last differences in methanogenesis onsets were likely related to the slight differences in the initial ALK_P of batch experiments, as a source of buffering capacity against acidification in AD [7], since the initial ALK_P in the initial mixture was mainly associated to the inoculum contribution [Table 2]. For example, mono-digestion sacrifice showed an ALK_P (i.e. 4.8 g $CaCO_3$/kg) relatively higher than the mono-digestion of OFMSW using an ISR of 1.0 g VS/g VS (i.e. 1.5-3.8 g $CaCO_3$/kg) and the co-digestion sacrifice (i.e. 2.1 g $CaCO_3$/kg). Meanwhile, the methanogenic onset in some HS-AD replicates only at very high TS contents (i.e. 25-30 %) highlighted the importance of mass transfer effects in those cases. For example, the presence of highly differentiated methanogenic/acidogenic centres and/or the increasing importance of diffusion mechanisms in HS-AD might have promoted the resistance against acidification of all the methanogenic centres under overloading conditions, predominantly at very high TS contents (i.e. $\geq$ 25 %) [38].

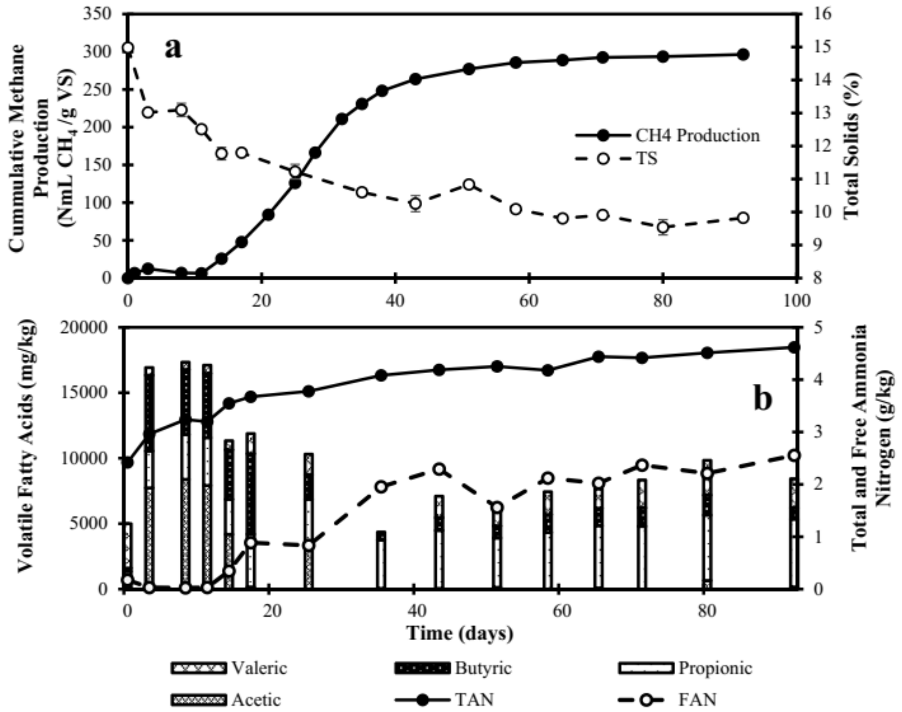

Fig. 1 *Sacrifice test for high-solids anaerobic digestion of the organic fraction of municipal solid waste using an inoculum-to-substrate ratio of 1.0 g VS/g VS: a) Cumulative methane production and total solids (TS); and b) volatile fatty acids and total (TAN) and free (FAN) ammonia nitrogen*

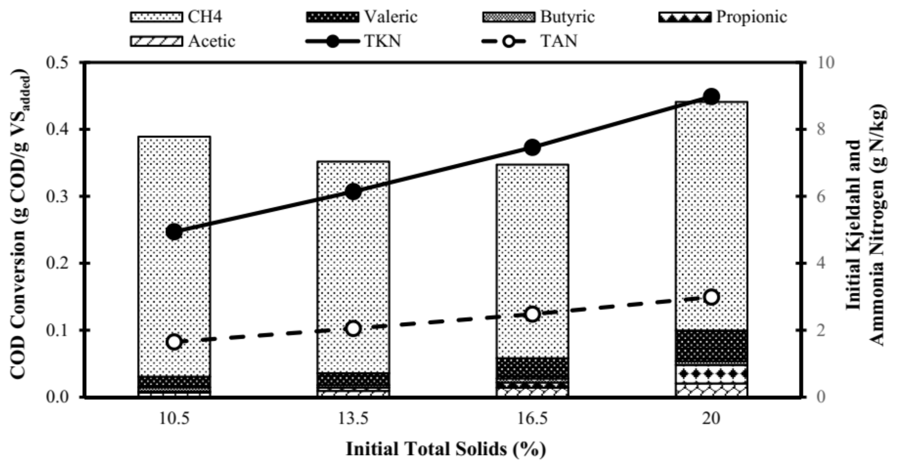

Fig. 2 *Chemical oxygen demand (COD) conversion in high-solids anaerobic digestion of the organic fraction of municipal solid waste using an inoculum-to-substrate ratio of 1.5 g VS/g VS: Volatile fatty acids and overall methane production per unit of substrate-inoculum volatile solids (VS) added, and initial total Kjeldahl (TKN) and ammonia (TAN) nitrogen*

Importantly, the TS removal seemed to slow down in mono-digestion sacrifice as NH_3 built up in the system [Figure 1]. Thus, in spite acetic and butyric acids were practically consumed by day 35, propionic and valeric acids continued to accumulate along the whole experiment, potentially related to NH_3 build-up. NH_3 is a well know inhibitory compound for acetoclastic and hydrogenotrophic methanogens, though the maximum NH_3 threshold might depend on the biomass adaptation and/or some AD operative parameters (i.e. HRT and temperature) [10,11,32]. On the other hand, the valerate and propionate uptakes might be either affected by H_2 and/or NH_3 build-up [24,39], though H_2 was not observed to accumulate in the gas phase of these experiments – data not shown. In the same line, the VFA content in HS-AD experiments for mono-digestion of OFMSW using an ISR of 1.5 g VS/g VS were observed to increase progressively alongside a higher initial TS content [Figure 2]. This last phenomenon was potentially associated also to the NH_3 accumulation, since the initial nitrogen content (i.e. TKN or TAN) was observed to increase progressively at higher TS contents, likely due to the lower amount of free water available in the system. With all the above, HS-AD batch experiments require a compromise between the initial TS content, the ISR, the ALK_P and the nitrogen content to assess the potential feasibility for OFMSW treatment.

3.3. Semi-continuous Experiments – Counterbalancing the TS removal, TAN build-up and VFA accumulation

Semi-continuous experiments showed an important VFA build-up as a consequence of substrate overload and/or the presence of inhibitory compounds (i.e. NH_3) in OFMSW [Figure 3], leading to a progressive drop on the pH and CH_4 content, and the eventual bioprocess failure by acidification (i.e. pH ≤ 6.0) – data not shown. The TS content in semi-continuous mono-digestion of OFMSW started at 2.8 % and reached the lower TS threshold of HS-AD (i.e. 10 %) only under extreme overloading conditions (day 72) [Figure 3a], when total VFA were over the threshold of 10 g Acetic Acid/kg [Figure 3b]. Thus, the rapid biodegradability and high TKN content of OFMSW resulted in a rapid TS removal alongside a rapid TAN build-up and an elevated NH_3 fluctuation in the system, preventing to increase further the TS content in the mono-digestion reactor. Importantly, the weekly-averaged mass effluent was reduced up to 40 % regarding the mass influent in these reactors, permitting to extend relatively the MRT. However, this strategy was not sufficient to counteract both the substrate overloading (i.e. VFA and H_2 accumulation) and/or the high NH_3 levels reached in the reactors (i.e. ≥ 1.0 g N/kg), as two of the main potential inhibition factors for the methanogenic growth.

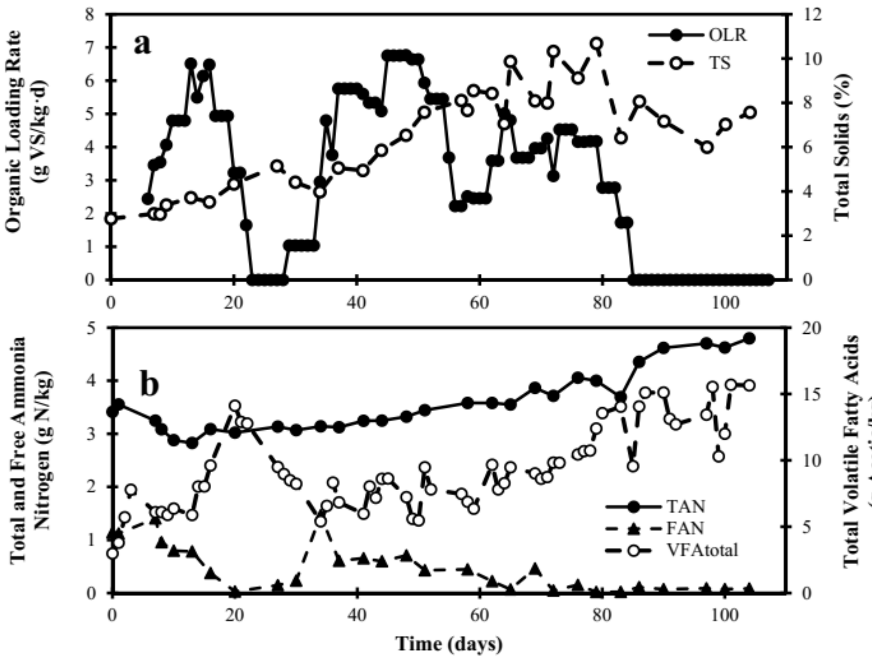

Fig. 3 *Semi-continuous mono-digestion of the organic fraction of municipal solid waste: a) Organic loading rate (OLR) and total solids (TS); and b) total (TAN) and free (FAN) ammonia nitrogen and total volatile fatty acids (VFA)*

Semi-continuous co-digestion of OFMSW and sawdust permitted to increase the TS content over 30 %, being this TS content considerably higher than the HS-AD threshold (i.e. 10 %), before the reactor acidified (day 76) [Figure 4a]. Thus, the lower biodegradability and TKN content of sawdust permitted to use a maximum OLR up to 13 g VS/kg·d, with a OFMSW:sawdust ratio of 0.4-0.5 g TS/g TS. The TAN content was maintained relatively constant at 3 g N/kg, the NH_3 fluctuations were reduced and the VFA release relatively slowed down in comparison to semi-continuous mono-digestion of OFMSW [Figure 4b]. With all the above, the inclusion of lignocellulosic substrates in OFMSW could be considered an adequate strategy to increase the TS content while minimize the risk of NH_3 build-up and VFA accumulation in semi-continuous HS-AD.

Importantly, the maximum TS content in semi-continuous reactors was associated to the acidified (i.e. pH ≤ 6.0) or acidifying conditions (downward trend in pH and/or CH_4 content – data not shown). Therefore, the hydrolysis and/or acidogenesis might have been also affected by the gradual build-up of inhibitory compounds (i.e. VFA, H_2, NH_3) in HS-AD [37,40]. Finally, rising the TS content of co-digestion reactors over 25-30 % approximately, a given degree of porosity (ε) could be observed (though not measured), due to both the low water within the HS-AD reactor and the structuring properties of sawdust as an example of lignocellulosic material.

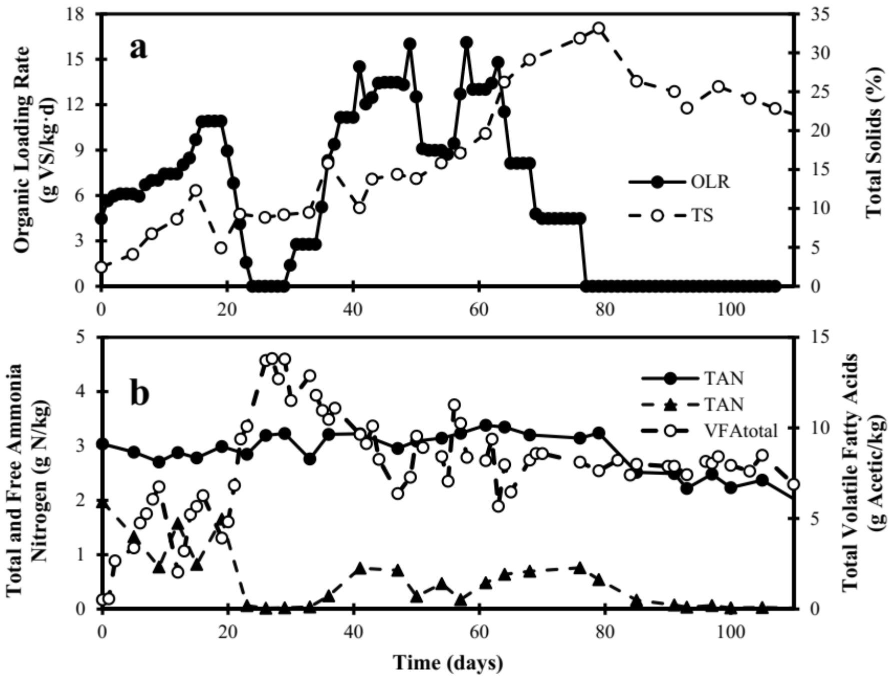

Fig. 4 *Semi-continuous co-digestion of the organic fraction of municipal solid waste and sawdust: a) Organic loading rate (OLR) and total solids (TS); and b) total (TAN) and free (FAN) ammonia nitrogen and total volatile fatty acids (VFA)*

3.4. HS-AD Model – Condensing the Lessons Learnt

Batch and semi-continuous experiments highlighted some of the most important aspects to be considered in HS-AD mathematical simulations for OFMSW treatment as, for example, the importance of the organic mass/volume removal as a result of the biogas production, the consequences of NH_3 build-up for HS-AD inhibition, particularly at higher TS contents (i.e. ≥ 15 %), and the overwhelming risk of reactor acidification (i.e. pH ≤ 6.0) by substrate overload. Moreover, both the mass balances (i.e. TS, VS, ρ) and the semi-continuous operation for co-digestion highlighted the effect of porosity (ε) in HS-AD reactors, particularly when working at considerably high TS contents (i.e. ≥ 25-30 %). In this scheme, the correct implementation of mass balances was considered crucial to be used in mathematical simulations of HS-AD, in contrast to 'wet' AD simulations where reactor volume is assumed constant [24,27]. Similarly, understanding the effects of NH_3 inhibition on all the AD biochemical steps (i.e. methanogenesis, acidogenesis) would be essential in HS-AD of OFMSW, in order to operate HS-AD reactors within 'conservative' limits for NH_3 inhibition and/or to design counteracting measures for NH_3 build-up, avoiding the VFA accumulation and risk of reactor acidification.

The HS-AD model implementation was verified for a 200-days continuous 'wet' AD and HS-AD operation. HS-AD simulations using a continuous 25 % TS influent yielded a daily reactor mass content removal of approximately 0.25 %, triggering a progressive OLR increase and HRT decrease when using $Q_{Influent} = Q_{Effluent}$, and eventually leading to reactor acidification – data not shown. However, the HS-AD simulations with $Q_{Effluent}$ control yielded a 5.6 % reduction of the continuous $Q_{Effluent}$ regarding $Q_{Influent}$ in steady-state, while both TS and VS were reduced around 24 % regarding the influent conditions [Figure 5]. On the other hand, preliminary model simulations used for model calibration gathered all the HS-AD dynamics in the mono-digestion sacrifice. Thus, the calibration of a reduced set of biochemical parameters permitted to simulate adequately the TS and VS contents, the VFA accumulation and the NH_3 build-up in HS-AD batch experiments – data not shown. Meanwhile, a thorough sensitivity analysis for the main biochemical parameters and an adequate model calibration strategy are underway with the aim to discern about the effects of a high TS content on the bio-physical-chemistry of HS-AD for OFMSW treatment.

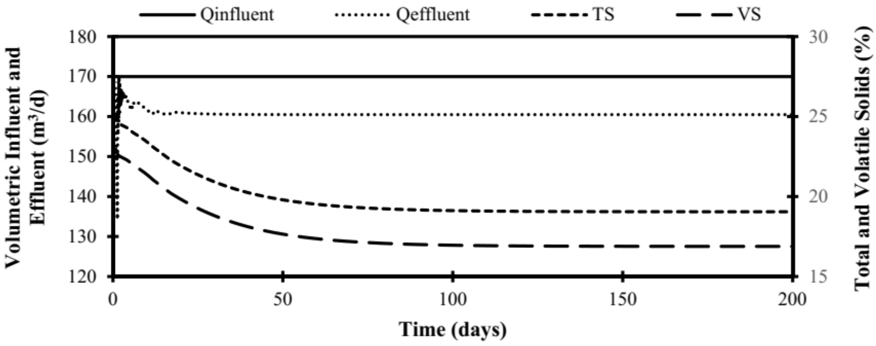

Fig. 5 High-solids anaerobic digestion model verification using a continuous influent at 25% total solids: Volumetric influent ($Q_{Influent}$) and effluent ($Q_{Effluent}$), and total (TS) and volatile (VS) solids contents

4. Conclusions

HS-AD (i.e. TS ≥ 10 %) is a well-suited biotechnology for OFMSW treatment, permitting the enhancement of the overall process economy, though it might be associated to a high risk of NH_3 build-up and/or reactor acidification (i.e. pH ≤ 6.0). In this study, HS-AD batch and semi-continuous experiments were conducted in parallel to the development of a HS-AD model, with the aim to understand the main effects of increasing the TS content in HS-AD of OFMSW. The experimental setups highlighted some of the most important aspects of HS-AD for OFMSW treatment as, for example, the importance of a high TS content to exacerbate NH_3 inhibition in batch bioreactors, and the need to reduce the effluent regarding the influent in semi-continuous bioreactors (i.e. $Q_{Effluent} > Q_{Influent}$). A reduced set of hypotheses was used to minimize the inherent complexity of the HS-AD model, while maintaining the adequacy of the ADM1 biochemical framework for homogenized reactors. The proposed model might be useful to enhance the performance of HS-AD treating OFMSW, by providing insight about the most important mechanisms triggering bioprocess inhibition/acidification. In this line, the HS-AD model might aid in the design and implementation of HS-AD as a source of renewable energy and nutrient recovery from OFMSW.

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