Anaerobic digestion of the liquid fraction of dairy manure separated by screw-pressing and centrifugation in a UASB reactor at 25°C.

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Abstract

Anaerobic digestion of the liquid fraction of dairy manure was studied in lab scale in a high load anaerobic reactor (UASB) operated at 25°C. The liquid fraction was obtained by a separation process in a pilot plant consisting of screw pressing and centrifugation enhanced by flocculation in a pilot plant. The separation process produced a liquid fraction free of suspended solids, whose supernatant chemical oxygen demand (COD) and COD due to volatile fatty acids (VFA) were 93.7% and 71.6% of the total COD respectively, with an anaerobic biodegradability of 84%. The UASB reactor processing the liquid fraction exhibited a significantly higher volumetric methane production than conventional complete mixing reactors treating manure since UASB reactor required low hydraulic retention time (HRT) due to the characteristics of the liquid fraction. At HRTs between 1 and 2 days, COD removal efficiencies higher than 80% were achieved without VFA accumulation in the effluent. A minimum HRT of 0.65 day was performed with a corresponding organic loading rate of 34.8 g [COD] l\textsuperscript{-1} d\textsuperscript{-1}, reaching a volumetric methane production of 8.41 [CH\textsubscript{4}] l\textsuperscript{-1} d\textsuperscript{-1}.

Keywords: UASB; Liquid fraction; Dairy manure; Methane yield; Organic loading rate.

1. Introduction

Dairy cattle manure has traditionally been used as a fertiliser, but the growth of livestock industry has led to a surplus of plant nutrients relative to crop requirements facilitating grow pollution in near ecosystems such as surface and ground water.
contamination, odours and ammonia emissions. Land application, the traditional dairy
manure management strategy, is nowadays conditioned not only by nutrient
requirements of the crops, amount and season, but also by the vulnerability of the near
ecosystems and the energy cost for its application (Flotats, Bonmatí, Fernández, Magrí,
2009). Requirements for nutrient management plans, manure solids disposal, and odour
control make it necessary that new manure management approaches be considered.
Regarding rational recycling of nutrients, in the origin of the problem some research
activities focus on reducing the nitrogen surplus of cow diets (Arriaga, Salcedo,
Casalmiglia, Merino, 2010).

Free stalls are currently the most popular method for housing large dairy herds in
Cantabria, a region in Northern Spain with a bovine population of around 280,000
livestock units (mainly milk). Most of the intensive farming is operated on the coastal
flatlands, which are tourism areas. Free stall housing provides a means for collecting
essentially all of the manure but storage capacity is limited and there is not enough land
available for its disposal by direct application during those periods when the soil
benefits from nutrient additions, which leads to environmental damage. In addition the
liquid fraction of dairy manure is a big problem due to run-off, which facilitates
growing pollution in near ecosystems.

Anaerobic digestion is a consolidated technology mainly used for green energy
production but that also provides other environmental benefits such as pollution control,
odour and pathogen level reduction and enhancement in agronomic properties of
digested materials (Lee & Han, 2012; Clemens, Trimborn, Weiland, Amon, 2006).
Manure, if managed properly, can be a valuable resource for energy production and can
be used to provide nutrients for crops and to improve soil properties through accretion
The main limitation of anaerobic digestion of manure is that the process does not
remove nitrogen. For this reason, in livestock production areas, anaerobic digestion
alone does not solve the nutrient issues since digested materials have to be managed
according to current nitrogen limits under EU regulations (170 kg [N] ha\(^{-1}\) year\(^{-1}\)).

Separation of manure in liquid and solid fractions is a treatment option that
complements the anaerobic digestion. Separation can be used as a pre-treatment to
obtain concentrated solid fractions with higher methane yields per digested mass or as
post-treatment to obtain a nutrient-rich solid fraction that lowers the cost of
transportation, facilitating the export and redistribution of nutrients from areas with
excess of manure to others in need of nutrients (Holm-Nielsen, Al Seadi, Oleskowicz-Popiel, 2009).

Pressurised filtration (e.g. screw press) and centrifugation with or without chemical addition are the most common techniques used for separation of animal manure (Hjorth, Christensen, Christensen, Sommer, 2010). Screw pressing is only efficient in removing dry matter (DM), but not in removing nutrients (Møller, Lund, Sommer, 2000; Møller, Sommer, Ahring, 2002; Rico, Rico, Tejero, Muñoz, Gómez, 2011). Centrifugation, improved by chemical addition promotes nutrient removal (Hjorth, Christensen, Christensen, 2008) and allows liquid fractions with very little suspended solids (SS) content to be obtained. For example, a liquid fraction of dairy manure was obtained by flocculation with an anaerobic biodegradability of 83.7% and specific methane production 0.604 l [CH₄] g⁻¹ [VS] (Rico, García, Rico, Tejero, 2007). These characteristics allow the treatment of this liquid fraction as a wastewater rather than slurry. For instance, this liquid fraction is suitable to be treated in high-load anaerobic reactors, such as UASB. A review of UASB reactor process can be found in Latif, Ghufran, Wahid, and Ahmad (2011). One of the main advantages of the UASB reactor is the capacity to retain biomass so that biomass retention and liquid retention are uncoupled (Lettinga, van Velseo, Hobma, de Zeeuw, 1980). High-load anaerobic reactors have a high treatment capacity which implies lower size compared to conventional CSTR digesters. Used as a pre-treatment, centrifugation enhanced with flocculants would produce a nutrient rich concentrated solid fraction and a liquid fraction that could be processed as a wastewater. Solid fraction may be shipped for redistribution of nutrients or transported to centralised biogas plants demanding concentrated biomass (Xie, Wu, Lawlor, Frost, Zhan, 2010).

By comparison with conventional dairy manure based biogas plants, where dairy manure is first digested and then separated, the main novelty of the proposed system is the separation of dairy manure before anaerobic digestion. If the separation method allows the treatment of the liquid fraction as a wastewater in high load anaerobic reactors, the main advantages of this method are the shorter HRT and lower temperatures required for its anaerobic digestion compared to anaerobic digestion of dairy manure slurry. In addition, high load anaerobic systems do not require mechanical stirrers which also implies saving in costs. For the solid fraction, the dry batch anaerobic digestion is an option to recover its methane potential. Dry batch anaerobic digestion can also be performed without mechanical stirrers (Weiland, 2006). The main
The drawback of this method is the cost of the separation process since it requires a screw-press and a decanter centrifuge with the use of chemical reagents. However, the stabilised solid fraction could be marketed as an organo-mineral fertiliser thus compensating the pre-treatment cost. In addition, in areas with high stocking density, manure separation or shipment to other zones is necessary which also represents an operational cost.

The present study evaluates the treatment of the liquid fraction separated by screw pressing and centrifugation enhanced by chemical reagents in a UASB reactor at 25°C. The performance of a UASB reactor treating the liquid fraction of dairy manure has been studied in terms of reactor stability, removal percentage of organic matter and methane yield.

2. Materials and methods

2.1. Liquid fraction

Liquid fraction was collected from a dairy manure Research and Development pilot plant located in Heras, Cantabria, Spain. Details of the pilot installation can be found in Rico, Rico, Tejero, Muñoz, Gómez, 2011. Raw manure was first screened with a Doda (Buscoldo, Mantova, Italy) screw press separator, model MS5CE (mesh size 0.8 mm). Then, the screened liquid fraction was centrifuged. A Perialisi (Jesi, Ancona, Italy) decanter centrifuge, model Baby 2, operating at 5200 rpm, was used to obtain the liquid fraction used in the present work. Before processing by the decanter centrifuge, the screened liquid manure was mixed with a cationic polyacrylamide in a labyrinth-pipe section adapted as a static mixer. The polymer used was a polyacrylamide (PAM) with the commercial name of Praestol K144L®, Ashland Chemicals (Covington, KY, USA). It is a copolymer of acrylamide (medium cationic PAM). Commercial PAM was supplied in solid form and was prepared as a solution in a 1000 litre tank equipped with a mixing impeller. The PAM solution was used with a concentration of 4 g l⁻¹. Polymer dose was 2% in a total solid base (20 g of solid polymer per kg TS in the screened manure). A schematic diagram of the separation process in the pilot plant is shown in Fig. 1.
2.2. UASB reactor

A lab-scale UASB anaerobic reactor, useful volume of 1.0 l, was employed for anaerobic treatment of the liquid fraction of dairy manure. The reactor was cylindrical, made of plexiglass and divided into three zones joined by flanges. The feed came into the lower zone, the middle area was jacketed and a temperature of 25ºC was maintained by recirculation of warm water inside the jacket. In the upper part, there was a gas-liquid-solid separator similar to those described in the literature for UASB reactors. Treated wastewater left the reactor by means of an exit tube at the top of the reactor. A recirculation outlet device was available but not used under this configuration. The biogas generated was gathered by means of a bell placed in the top part and measured by means of a wet gas-meter. All the biogas and methane yields are expressed at 0ºC and 1 atmosphere. A diagram of the UASB reactor can be found in Fig. 2.

2.2.1. Setup of UASB reactor

The UASB reactor was seeded with solid fraction of flocculated and digested dairy cattle manure that previously had been processing the same liquid fraction of dairy manure in a UASB operating at 35ºC. At the start of this treatment the methanogenic activity of the biomass was determined at 35 and 25ºC, reaching 1.03 and 0.50 g [COD] g⁻¹ [VSS] d⁻¹, respectively. Determination of methanogenic activity was performed according to the method described by Field, Sierra, and Lettinga (1988).

The liquid fraction of dairy manure was continuously fed to the UASB reactor. Start-up of the reactor was performed under 2 days HRT. The treatment system was allowed to operate 20 days as adaptation period. Steady state conditions were assumed when the operation conditions were maintained for a minimum of three HRT and biogas production values were stable, then the reactor was operated at that HRT until at least data for six days were obtained. The UASB reactor was then operated with decreasing the HRT. The UASB reactor was operated with six different HRTs from 2.0 to 0.65 days, so organic loading rate (OLR) was increased from 9.2 up to 34.8 g [COD] l⁻¹ d⁻¹. Operation was stopped when a decrease in reactor efficiency was observed supported by the presence of volatile fatty acids in the effluent. The performance of the UASB reactor was monitored by analysing the feed influent, the UASB effluent and methane production.
2.3 Analytical techniques

Volatile fatty acids (VFA) were determined using a Hewlett-Packard (Wilmington, DE, USA) model HP6890 Gas Chromatograph instrument fitted with a 2m x 1/8 in. glass column, liquid phase 10% AT 1000, packed with the solid support Chromosorb W-AW 80/100 mesh. Nitrogen was the carrier gas and a FID detector was installed. Biogas composition was measured on a 2m Poropak T column in a HP 6890 GC System with helium as the carrier gas and a TCD detector. All other analyses (pH, TS, VS, COD, total Kjeldahl nitrogen (TKN-N), ammonia nitrogen (NH$_4^+$-N), and total phosphorous (P$_T$) were performed according to Standard Methods (APHA, 1998). Supernatant of the liquid fraction was obtained by centrifugation at 4000 rpm for 10 min.

3. Results and Discussion

3.1 Mass balance of the separation process

Percentages of TS and VS transferred to the solid fraction after the separation process carried out at the pilot plant were 83.8% and 87.5%, respectively. Distribution of TKN in solid and liquid fractions were 66.6% and 33.4%, respectively. Phosphorous was mainly transferred to the solid fraction. The percentages of phosphorous transferred to solid and liquid fractions were 92.3% and 7.7%, respectively (results not presented).

3.2 Characteristics of the liquid fraction (feed of the UASB reactor)

Mean characteristics of the liquid fraction (LF) from dairy manure employed as feeding of the UASB reactor are shown in Table 1. As it can be observed the supernatant chemical oxygen demand (COD$_{sup}$) was 93.7% of total COD (COD$_T$), whereas COD due to volatile fatty acids (COD$_{VFA}$) reached 76.2% of the COD$_{sup}$. The predominant VFA was acetic (AcH), with a concentration of 6673 ± 678 mg l$^{-1}$. Propionic acid (PrH) had the second highest concentration (2265 ± 205 mg l$^{-1}$) and butyric (BuH), the third (1296 ± 164 mg l$^{-1}$). The rest of the VFAs had mean concentration values lower than 300 mg l$^{-1}$. With regards to nutrients content, the LF contained between 35-45% of the
TKN and 10-18% of the phosphorus initially present in the dairy manure. Nutrients content in the LF were very low compared to those reported by Møller, Sommer, and Ahring (2002) obtained by centrifuging and screw press at industrial scale. The higher nutrients removal efficiencies obtained in the present study can be due to the employ of a flocculant agent.

3.3. Operation of UASB reactor

3.3.1. Organic matter removal

Table 2 presents the performance data of the UASB reactor. Operation started at 2 days HRT corresponding to an average OLR of 9.17 g [COD] l⁻¹ d⁻¹. At 2 days HRT, COD removal percentage was higher than 80%, concretely 81.9%. With regards to COD supernatant (CODₘₚ), it was slightly higher, 83.7%, whereas VS removal percentage reached 67.9%. As can be observed in Table 2, OLR was progressively increased by decreasing HRT. For HRT between 1 and 2 days, the UASB maintained its efficiency. In spite of OLR increased up to 20.7 g [COD] l⁻¹ d⁻¹ at 1 day HRT, COD removal percentage maintained over 80% whereas CODₘₚ and VS removal percentages obtained similar values than those obtained with the previous and longer HRT. Reactor efficiency started to decrease when HRT was set at 0.80 days. At that point the OLR reached 26.4 g [COD] l⁻¹ d⁻¹ and the removal percentage of COD decreased down to 74.7%. CODₘₚ removal percentage also decreased (75.8%) as well as VS removal percentage which was 61.5%. For the last HRT tested, 0.65 days with a corresponding OLR of 34.8 g COD l⁻¹ d⁻¹, reactor efficiency continued to decline: the removal percentage of COD and VS decreased down to 69.8% and 58.6% respectively. The percentages of VS removed (between 67.9% and 58.6%) were lower than those expected based on the values obtained for COD and CODₘₚ. Derikx, Willer, and Ten Have (1994) pointed that during drying at 105°C for VS determination up to 75% of the VFA in the samples can be lost. In the influents, the concentration of VFAs was high; however the values for the effluents were very low, except for two last HRT. For this reason, the values obtained for percentages of VS removed were lower than the real ones. In the current study the mean ratio VS/TS and VS/COD in LF influent were 0.61 and 1.7, respectively.
In Fig. 3, daily COD concentration of influents and effluents versus OLR are represented for all the experimental period. It can be observed that effluent COD values increased at OLR higher than the 25 g [COD] l⁻¹ d⁻¹, values that corresponded with HRTs of 0.80 and 0.65 days. At HRTs lower than 1 day COD removal efficiencies started to decrease indicating that microorganisms present into the reactor were not able to process all the incoming substrate. The mean COD removal efficiency decreased from 81.1% at an HRT of 1 day to 74.7% and 69.8% at 0.80 and 0.65 days HRT respectively.

3.3.2. Methane production rates and methane content of biogas

Specific methane production yields and volumetric methane production rates can be found in Table 2. With regards to specific methane yield in terms of COD, for HRTs between 1 and 2 days, mean values of 0.28 l [CH₄] g⁻¹ [COD] were observed. At 0.80 and 0.65 days HRT, specific methane yield diminished to 0.26 and 0.24 l [CH₄] g⁻¹ [COD], respectively, corroborating the decline observed for COD removal for the shortest HRTs. In Fig. 4, the volumetric methane production rate and the organic removal rate (OLR removed) are plotted against OLR. The volumetric methane production rate ranged from 2.57 l [CH₄] l⁻¹ d⁻¹ at 2 days HRT (OLR 9.17 g [COD] l⁻¹ d⁻¹) to 8.36 l [CH₄] l⁻¹ d⁻¹ at 0.65 days HRT (OLR 34.8 g [COD] l⁻¹ d⁻¹). In Fig. 4, it can be observed that the organic removal rate (OLR removed) increased with the OLR applied and a linear relation was maintained for all the experimental conditions. Although the linear correlation maintained throughout all the experimental period it must be taken into account that, as can be observed in Fig. 3, for the long HRTs (1.5 and 2 days) feed influent had the lowest organic load and this is the cause of linearity in spite of the slight loss in reactor efficiency.

Methane content of biogas always ranged between 82.8% and 83.9%. Due to the limitation of CO₂ solubility in the liquid phase, the percentage of CO₂ in the biogas should be higher, and that of CH₄ lower, when OLR increased. However, in view of these results, OLR did not seem to affect methane content in biogas.

3.3.3. Volatile fatty acids in effluent
VFA in the effluent followed a similar behaviour to that of the COD. As Table 3 shows, COD\textsubscript{VFA} concentration values for HRTs between 1 and 2 days were lower than 111 mg l\textsuperscript{-1}. For the HRT of 0.80 days the mean value of COD\textsubscript{VFA} reached 1013 mg l\textsuperscript{-1}, a value about nine times higher than that for the previous HRT. For the shortest HRT, 0.65 days the mean value of COD\textsubscript{VFA} continued increasing up to 1615 mg l\textsuperscript{-1}. Figure 5 represents the evolution of the AcH, PrH and COD\textsubscript{VFA} in UASB effluent for HRTs of 0.80 and 0.65 days.

At HRTs between 2 and 1 days the only VFA detected in UASB effluent were acetic and propionic, with mean concentrations of 73 and 22 mg l\textsuperscript{-1} for 1 day HRT. At 0.80 days HRT all VFA except hexanoic were present in the effluent. Predominant VFA were acetic and propionic with mean concentrations of 340 and 274 mg l\textsuperscript{-1} respectively. At 0.65 days HRT all VFA, including hexanoic, were detected. Mean concentrations of acetic and propionic were 463 and 485 mg l\textsuperscript{-1}, respectively. Propionic become the majority VFA. Concentration of VFA with 4, 5 and 6 carbon atoms were low. The presence of VFA in the effluent indicated that the capacity of the bacteria present in the reactor to process the incoming substrate had been overcome which corroborates the previously reported decrease in COD removal. Since methanogenic activity of bacteria in the reactor had been overcome at 25\degree C, operation was stopped. Despite VFA accumulation for the two shortest HRTs and that mean ratio bicarbonate / total alkalinity (BA/TA) in the influent was 0.321, the process was stable because of 71% of the COD\textsubscript{T} was due to VFA, which implies that less alkalinity is needed for the stability of the process. At the end of the operating period, there were 53.34 g [VSS] in the UASB reactor. At this point, the methanogenic activity of the biomass present in the UASB reactor was tested at 25\degree C resulting in 0.644 g [COD] g\textsuperscript{-1} [VSS] d\textsuperscript{-1}.

3.3.4. Nutrients

In Table 3 nutrient concentrations in the effluent are shown for all the HRT operated. The mean value of TKN concentration in the influent was 1.53 g l\textsuperscript{-1}, being the mean percentage as ammoniacal nitrogen of 84%. In the effluent, the TKN mean concentration ranged from 1.33 to 1.57 g l\textsuperscript{-1}, whereas ammonia nitrogen mean concentration ranged from 1.25 to 1.42 g l\textsuperscript{-1}. These variations were caused by nitrogen concentration in feed influent. In this process nitrogen changes are due to ammonification process, ammoniacal nitrogen use in cellular synthesis processes,
struvite precipitation and gaseous emissions of ammoniacal nitrogen due to pH increases.

Mean values for total phosphorous present in influents and effluents were 100 and 24 mg l\(^{-1}\), respectively. In this case, the decrease in effluent total phosphorus concentration is mainly caused by the precipitation of various phosphates: magnesium ammonium phosphate (struvite), calcium phosphate.

3.3.5. Performance of UASB reactor and comparison with conventional CSTR systems

Generally, with a same influent feed, when HRT diminishes OLR increases, which would reduce the percentage of COD removed and reactor performance if the methanogenic activity of the biomass involved in the process was the same. However, in this work, at the first HRT tested, methanogenic activity of the biomass in the reactor was the lowest due to the biomass used had been previously operating at 35\(^\circ\)C, and new temperature conditions were now 25\(^\circ\)C. As HRT diminished, biomass seed was acclimatising and increasing its methanogenic activity. The raise in methanogenic activity compensated the increase of the OLR, maintaining the removal percentage of COD until an HRT of 1 day. At HRTs lower than 1 day reactor performance started to decrease indicating that microorganisms present into the reactor were not able to process all the incoming substrate. Noticeable difficulties in the UASB reactor performance, such as excessive foaming or sludge flotation were not observed.

By comparison with the completely stirred tank reactor (CSTR), the conventional treatment technology for the anaerobic digestion of animal manure in biogas plants (Boe & Angelidaki, 2009), some differences arise between both systems. These differences are caused by the substrate characteristics: no presence of suspended solids, high content or organic matter in soluble form and high content in VFA, the precursors of methane. In this case the liquid fraction of manure obtained is more a wastewater than a slurry. These differences can be resumed in two issues, on one hand the higher methane content in biogas, that would enhance biogas purification and conversion into bio-methane and on the other hand the shorter HRT required that results in smaller reactor size and higher volumetric methane productions. In this work, methane yields higher than 0.50 l [CH\(_4\)] g\(^{-1}\) [VS] with methane content in biogas higher than 80% have been obtained under HRT shorter than 2 days. Typical manure based biogas processes
operate at mesophilic or thermophilic temperature range (35°C-55°C) in CSTR systems with HRT between 15 and 30 days, producing average methane yields ranging of 0.20 to 0.25 l [CH₄] g⁻¹ [VS] (Hartmann, Angelidaki, Ahring, 2000). In this kind of system the expected volumetric biogas yield is 1.4 m³ m⁻³ d⁻¹ (Raven & Gregersen, 2007).

Although in the current study operation temperature was 25°C, the OLR and methane production of the UASB reactor were notably higher than that reported in other works. However, it must be said that the results presented in this work are not comparable with the others described above because all these studies used CSTR or similar anaerobic digestion systems for processing manure slurries.

4. Conclusions

This study has shown that the separation of dairy manure by screw pressing and centrifugation enhanced with flocculants offers a new dairy manure management strategy. The separated solid fraction, rich in organic matter and nutrients, may be shipped for redistribution of nutrients or transported to centralised biogas plants demanding concentrated biomass. Due to the characteristics of the separated liquid fraction, it can be processed as a wastewater in high load anaerobic reactors, such as the UASB, with a significantly higher volumetric methane production rate than conventional complete mixing digesters treating manure. The liquid fraction has been satisfactorily treated in a UASB reactor at 25°C. At HRTs between 1 and 2 days with OLR ranging from 9.2 to 20.7 g [COD] l⁻¹ d⁻¹, COD removal efficiencies higher than 80% were achieved, without VFA accumulation and volumetric methane productions from 2.6 to 5.7 l [CH₄] l⁻¹ d⁻¹, respectively. COD removal efficiency was diminished at HRTs lower than 1 day, 74.7% and 69.8% at 0.8 and 0.65 days respectively. Although the reactor worked stably at those HRTs, with OLRs between 26.4 and 34.8 g [COD] l⁻¹ d⁻¹ reaching a maximum volumetric methane production of 8.4 l [CH₄] l⁻¹ d⁻¹, the presence of VFA in the effluent indicated that the capacity of bacteria present in the reactor to process the incoming substrate had been overcome. Under this strategy digester size can be reduced due to shorter HRT requirements and methane content of biogas, higher than 80%, facilitates its upgrading to bio-methane.
REFERENCES


Nomenclature

COD: chemical oxygen demand
CSTR: completely stirred tank reactor
HRT: hydraulic retention time
LF: liquid fraction
OLR: organic loading rate
PAM: Polyacrylamide
SS: suspended solids
TKN: total Kjeldahl nitrogen
TS: total solids
UASB: upflow anaerobic sludge blanket
VFA: volatile fatty acids
VS: volatile solids
VSS: volatile suspended solids
FIGURE CAPTIONS

Fig. 1- Experimental separation scheme.

Fig. 2- Laboratory-scale UASB reactor.

Fig. 3- COD concentration for influent and effluent during experimental period. Black squares represent the influent COD white squares the effluent COD.

Fig. 4- OLR Vs OLR removed and volumetric methane production rate of UASB reactor. Black rhombi represent the organic removal rate and white rhombi the volumetric methane production rate.

Fig. 5- Evolution of VFA concentration in effluent for 0.80 (black) and 0.65 (white) days HRT. Circles represent acetic acid concentration, rhombi propionic acid, triangles butyric acid and squares the COD due to VFA.