PHYSICAL - ANAEROBIC - CHEMICAL PROCESS FOR TREATMENT OF DAIRY CATTLE MANURE

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Abstract

An overall treatment process for the removal of nitrogen, methane production and obtention of valuable fertilizers from dairy manure has been investigated in laboratory scale. Solid and liquid fractions were separated by flocculation and screening. The solid fraction contained 81.6%, 84.4%, 58.6% and 85.2% of TS, VS, TKN-N and P_T originally present in manure. Batch anaerobic digestion of this solid fraction at 50ºC resulted in methane production of 29.0 L CH_4/kg. The liquid fraction, free of suspended solids, was satisfactorily treated at 35ºC in an upflow anaerobic sludge blanket reactor operating stably at an organic loading rate of 40.8 g COD/(L·d) reaching a methane production of 10.3 L CH_4/(L·d). Accumulation of volatile fatty acids did not occur. This volumetric methane production is much higher than that of conventional complete mix reactors treating dairy manure. Ammonia nitrogen concentration in the anaerobic effluent fluctuated between 850-1170 mg NH_4^+-N/L and was reduced to values less than 100 mg NH_4^+-N/L by struvite precipitation.

Keywords: Dairy manure; liquid fraction; UASB reactor; methane; struvite.

1. Introduction

Dairy manure is one of the most polluting agro-industrial wastewaters. Intensive dairy farming produces large amounts of manure which, when not properly managed due to its high organic matter, nitrogen and phosphorous concentrations, can cause severe environmental problems such as eutrophication of water bodies (Carpenter et al., 1998), groundwater contamination (Hao and Chang, 2002), air pollution by volatilization of ammonia and other compounds (Ryden et al., 1987) and soil degradation when manure is applied in excess. High concentrations of hazardous heavy metals such as Cu^{2+}, Zn^{2+} and Pb^{2+} are not usually present in dairy manure (Nicholson et al., 1999).

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 et al., 2009). In areas with a higher dairy cattle number than available agricultural land for a correctly disposal of dairy cattle manure (one hectare for two milk cattle), another strategy will be necessary, such as treatment processes before deposition in the land. When the weather is rainy, and the ground shows pronounced slopes, as it happens in Cantabria, a region in Northern Spain with a bovine population of around 280,000 livestock units (mainly milk), the liquid fraction of dairy manure is a big problem due to run-off, facilitating grow pollution in near ecosystems.

Anaerobic digestion of dairy manure has been demonstrated to be an attractive treatment that provides benefits such as pollution control, odour and pathogen level reduction, nutrient recovery and energy production (Amon et al., 2007; Hartmann and Ahring, 2005; Karim et al., 2005; Umetsu et al., 2006). Dairy manure, which has too much suspended solids (SS) content, presents low anaerobic biodegradability. The hydrolytic stage has been identified as the rate-limiting step in the anaerobic digestion of organic particulate slurries such as dairy manure (Gossett and Belser, 1982;

Pavlostathis and Giraldo-Gomez, 1991; Vavilin et al., 2002; Veeken et al., 2000). Separation of liquid (LF) and solid (SF) fractions of the waste is a desirable upstream operation in the treatment process. The separated LF, with much less SS content, will require lower temperatures and hydraulic retention times (HRT). However, screened manure presents merely a little more anaerobic biodegradability because only SS larger than mesh openings have been removed (Kalyuzhnyi et al., 1999). Since the SS content in the LF from screening is still high and only a small fraction of its COD is in soluble form, additional treatments must be performed on screened dairy manure to produce a LF suitable for handling by a high load anaerobic reactor (i.e. in this case HRT could be lower than 1 day). Rico et al. (2007) developed a procedure to obtain a LF from dairy manure to which the major possible quantity of organic matter was transferred, with high anaerobic biodegradability (84%) and free of SS. García et al. (2008) satisfactorily treated this LF in a high load anaerobic reactor (UASB), improving biomass retention into the reactor.

The anaerobic digested LF still presents a high ammonia nitrogen concentration which must be diminished when land area of farm is lower than necessary according to current nitrogen limits under EU regulations (170 kg TKN / (Ha·yr)). Castrillón et al. (2009) achieved a removal efficiency of 75% for total Nitrogen by centrifugation of the liquid fraction of cattle manure followed by a two step biological treatment. Qureshi et al. (2008) reported that nitrifying systems treating high strength animal manure can possibly lead to unacceptably high levels of effluent nitrate and nitrite nitrogen.

One simple and rapid process to remove and recover nitrogen is its crystallization in the form of struvite (magnesium ammonium phosphate, or $MgNH_4PO_4 \cdot 6H_2O$), which may be utilized as a valuable source of slow release fertilizer due to its solubility characteristics (Nelson et al., 2003). The struvite precipitation technique has been applied to various wastewaters, such as swine waste, agro-industrial effluents, landfill leachate, calf manure, coke manufacturing, leather tanning and anaerobic digester sidestreams (Pastor et al., 2008, 2010; Uludag-Demirer and Othman, 2009; Uludag-Demirer et al., 2005). Depending on wastewater composition, struvite precipitation can be used to recover either ammonia nitrogen, phosphorus or both.

The separated SF from dairy manure, after a dry anaerobic digestion and optional composting processes, could be transported to agricultural zones that are deficient in organic matter and nutrients, to be used as fertilizer or land conditioner. Transport cost, since digested solid fraction is dewatered, will be lower than that for digested dairy manure.

This study evaluates the separation process of dairy manure in solid and liquid fractions, its treatment by anaerobic process and ammonia nitrogen removal from anaerobic digested liquid fraction by struvite precipitation. The organic matter, nitrogen and phosphorous distribution in liquid and solid fractions were obtained. The performance of a UASB reactor treating the liquid fraction of dairy manure as the removed percentage of organic matter removal and methane volumetric production was studied. The effect of pH and Mg^{2+}/PO_4^{3-} molar ratio on the performance of struvite precipitation and ammonia nitrogen removal was evaluated. The specific methane production by anaerobic digestion of solid fraction was determined.

2. Materials and Methods

2.1. Collection and storage of manure

Fresh manure was taken directly from a dairy cow house of a farm located in Cantabria, on Spain’s northern coast. The manure was kept at indoor ambient temperature (18-20ºC) for 4 weeks, in order to allow the hydrolytic and acidogenic stages to take place but preventing, as far as possible, the methanogenic (Rico et al., 2009). Vessels of 25 litres were employed as controlled dung pits and were provided with hydraulic closing systems in order to avoid the entrance of air, to prevent volatile fatty acids (VFA) oxidation, and to allow the release of generated gas, to prevent an excessive increase in pressure. After this time, by a flocculation and screening process, solid and liquid fractions of dairy manure were separated. Fig. 1 represents the experimental set up scheme.

2.2. Preparation of polymer and solid-liquid separation

A prepared polyacrylamide solution (PPS) with concentration 3 g/L of commercial polyacrylamide emulsion (CPE), known as Praestol K144L, was employed in the separation of SF and LF of dairy manure. Details of the separation process carried out at laboratory scale are described in García et al. (2008).

2.3. Analytical Techniques

VFA were determined using a HP6890 GC 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 following the Standard Methods for the Analysis of Waters and Wastewaters. Determination of methanogenic activity was performed according to the method described by Field et al. (1988).

2.4. Experimental equipment

A continuous liquid fraction operation was performed employing a lab-scale UASB reactor containing a total usable volume of 1.0 litre. The reactor was cylindrical, made of plexiglass and divided into three zones joined by clamps. The feed came into the lower zone, the middle area was jacketed and a temperature of 35ºC 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. 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 production measurements are expressed at 0ºC and standard pressure of 760 mm Hg (NCTP). Details of experimental equipment are described in García et al. (2008). The separated solid fraction was stabilized, by anaerobic dry digestion in batch conditions, at 35ºC and 50ºC in cylindrical reactors made of PVC of 2.5 and 2.0 of total and useful volume, respectively.

2.5. Seed sludge

The UASB reactor was seeded with dairy cattle manure that had been taken from the bottom of the dung pit of the farm. The dairy manure was sieved (20 mm mesh) to remove any straw, grass and large particles, and then was anaerobically digested in a CSTR laboratory scale reactor at 35ºC .The digested dairy manure was then treated with a PPS (dose of 20 mg CPE $\cdot g^{-1}$ TS) to obtain the SF employed as biomass. García et al. (2008) reported that a UASB reactor with flocculated biomass treating the same kind of LF as that employed in the current study, showed better behaviour both in biomass retention and organic load removal than a similar UASB reactor whose biomass had not been flocculated, especially at low hydraulic retention times. In this study, 600 g of the flocculated SF of digested dairy manure, 47.29 g VSS/kg, were added to the UASB reactor.

2.6. Setup of UASB reactor

As the characteristics of the separated LF fluctuated a bit during the experiment, the UASB reactor was operated at different constant HRT. During start-up period for the seed biomass the HRT was 1.5 days, till biogas productions were stable ± 10%. For all the successive HRT, operating 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 UASB reactor was operated at that HRT until data for six days were obtained. This UASB reactor was operated with eight different HRTs from of 1.3 to 0.22 days, so organic loading rate (OLR) was increased from 12.3 up to 72.5 g COD/(L·d).

2.7. Struvite precipitation

Struvite precipitation from effluent anaerobically digested LF was performed at batch systems. The experiment was carried out at effluent pH value of 8.3 and also at pH of 9.8 adjusted by NaOH addition. To identify the optimal conditions for struvite precipitation, several molar relationships $Mg^{2+}:PO_4^{3-}$ from 0.75:1 to 1.2:1 were tested at constant molar relationship $Mg^{2+}:NH_4^+$ 1.2:1 at both pH values. $MgCl_2 \cdot 6H_2O$ and $K_2HPO_4 \cdot 3H_2O$ were used as chemical reagents. The calculated amount of chemical reactives were added in 50 ml of samples, for both pH values. Then stirring was started for 5 minutes. After this time, the contents were allowed to settle for 10 minutes. Experiments were carried out by triplicate.

2.8. Methane productivity tests

To measure the methane productivity of manure, liquid and solid fractions, five cylindrical reactors, made of PVC, of 2.5 L total volume (2.0 L useful volume), were used. Reactors were placed in thermostatic baths and kept at the temperature selected. Seed biomass acclimatised to temperature tests was employed. No stirring was applied. Gas production was measured during 35 days by means of a displacement system using an alkaline solution to absorb the CO_2 produced. All the measurements are expressed at 20ºC and standard pressure of 760 mmHg (NCTP).

3. Results and discussion

3.1. Characteristics of liquid fraction and solid fractions

Distribution of TS, VS, TKN-N and P_T for the lab scale separation process of dairy manure by flocculation and screening is shown in Table 1. TKN transferred to SF was 58.6%, whereas for TS, VS and P_T the percentage transferred to SF was comprehended between 81 and 85%. The relation VS/TS increased in the SF and diminished in the LF, which indicates mineralization of the latter. The mean characteristics of the LF from dairy manure employed as feeding of the UASB reactor are shown in Table 2.

As it can be observed in Table 2, the supernatant chemical oxygen demand (COD_{sup}) was 92.6% of total COD (COD_T), whereas COD due to volatile fatty acids (COD_{VFA}) reached 77.3% of the COD_{sup}. The predominant VFA was acetic (AcH), with a concentration of 5009 ± 491 mg/L. Propionic acid (PrH) had the second highest concentration (1555 ± 223 mg/L) and butyric (BuH), the third (863 ± 224 mg/L). The rest of the VFAs had mean values lower than 200 mg/L. Patni and Jui (1985) and Rico et al., (2009) reported similar VFA distribution in dairy manure supernatant. With regards to nutrients content, the LF contained between 35-45% of the TKN initially present in the dairy manure. These are low values compared to those shown in Møller et al. (2002), who reported that LF separated from dairy manure by centrifugation or screw press contained TKN values of 51-73% and 92-96%, respectively. 78.2% of TKN was as ammonia nitrogen. Most part of total phosphorus ended up in the SF; the LF contained between 12-18% of the phosphorus present in dairy manure. These values are also low compared to those shown in Møller et al. (2002), who reported a transfer of P_T to the liquid fraction of dairy cattle manure of 18-22%, when the separation was by centrifuge, and 85-92%, when the separation was by screw press. The differences between the results found in this work and those reported by Møller et al. (2002) have to be due to the employment of a flocculant agent and to that the separation process was carried out with a lab stationary sieve, which implies that the separated SF had lower solids content than the one that could be obtained by means of an industrial screw press separator.

3.2. Operation of UASB reactor

Table 3 presents the mean values for removal efficiencies and methane yields obtained for all HRT. At an HRT of 1.3 days, COD reduction of 83.6% and methane production of 3.37 L $CH_4/(L\cdot d)$ were achieved. By lowering the HRT, higher methane production rates were obtained, although COD removal efficiency tended to minimally decrease due to the higher OLR applied, in particular at HRTs lower than 0.74 days. A stable operation was performed at 0.35 days HRT (40.8 g $COD/(L\cdot d)$ OLR) without VFA accumulation and COD removal percentage of 73.9%, reaching a volumetric methane production of 10.3 L $CH_4/(L\cdot d)$. HRTs lower than 0.35 days resulted in higher methane production rates but significant decrease in COD removal efficiency and high VFA accumulation in the effluent. The greatest drop in this percentage corresponds to the change to a HRT of 0.22 days. In this case, the increase in the OLR was the greatest, due also to a greater affluent COD value, as shown in Table 3. As indicated in Fig. 2, the OLR removed increased with the OLR affluent, although for the 0.22 days HRT, linearity was lost. This indicates that the highest value for removed organic loading rate in the UASB reactor had been reached. The Table 3 presents, as well, the mean values of COD, solids and VFA of affluent and effluent. The percentages of the COD_{sup} removed were similar to that of the COD, though slightly superior for the shortest HRT. At 0.58 days HRT, the COD_{VFA} in the effluent was 385 mg/L due to the fact that the methanogenic activity of the biomass had not yet reached a high level. At HRTs of 0.50 and 0.35 days, COD_{VFA} concentrations dropped to values slightly higher than 100 mg/L, being AcH and PrH the only VFAs present at concentrations of 60 and 30 mg/L, respectively. For the HRT of 0.26 days, AcH and PrH concentrations increased up to 300 mg/L. As shown in Fig. 3, PrH was predominant initially. However AcH later became the VFA with the highest concentration. VFA concentrations continued rising, and small concentrations of isobutyric (iBuH) and isovaleric (iVaH) appeared. For the HRT 0.22 days, at day 138, the COD_{VFA} reached a value of almost 4000 mg/L. At day 139, the affluent flow into the reactor was halted and changed over to recirculate the effluent. At day 140, the COD_{VFA} in the effluent was 59 mg/L, with a concentration of 25 and 14 mg/L of AcH and PrH, respectively. With an HRT of 0.22 days, once the maximum capacity for the elimination of organic matter was reached, the experimentation with the UASB reactor was concluded. At the end of the operating period, there was 43.66 g VSS in the UASB reactor. At this point, the methanogenic activity of the biomass present in the UASB reactor was tested and reached a value of 1.03 g COD/(g VSS·d). This value is a bit higher than the calculated taking into account the organic removal rate and the biomass content into the UASB reactor for the last HRT.

The percentages of VS eliminated were lower than those expected based on the COD and COD_{sup} for all the HRTs. This can be explained by the fact that VS determination includes drying (105ºC) and incineration (550ºC). According to Derix et al. (1994), depending on the pH of the sample, during the drying phase, up to 75% of the VFA in the samples can be lost. In the affluents, the concentration of VFAs was high, and for this reason the VS found values were lower than the real values. Meanwhile, for the effluents, in which VFA levels were very low, this loss in the determined values did not occur. For this reason, the values obtained for percentages of VS removed were lower than those expected from calculations based on removed COD values. The mean ratio VS/TS in LF affluent was only 58.9% in current study.

The volumetric production of methane, values shown in Table 3, increased with increasing OLR. As seen in Fig. 2, there was a linear relationship for all HRT except for 0.22 days. The value of the methane volumetric production value according to the slope of the regression line was 0.230 L CH_4/g COD affluent. As for the volumetric production of methane with respect to the removed organic rate (g COD_{rem}/L·d), there was a linear relationship for all HRTs. The equation of the regression line was $y = 0.343 x -0.0285$, with $R^2 = 0.997$, indicating a specific production in the range of 0.343 L CH_4/g COD_{rem}. The values of methane volumetric production for all HRTs, were significantly higher than the nearly 1 L CH_4/L·d produced with unscreened or screened dairy manure in a conventional type CSTR digester. This fact is especially remarkable for 0.22 days HRT when a maximum value of 14.1 L CH_4/L·d was reached. The mean percentage of methane in the biogas for each HRT of operation remained between 80.6 and 84.6%. Due to the limitation of CO_2 solubility in the liquid phase, the percentage of CO_2 was higher, and that of CH_4 was lower, in the biogas when OLR increased.

Methane production of the UASB reactor in the current study was notably higher than that reported in other works. Typical methane yields ranging from 0.075 to 0.223 L CH_4/g VS have been reported for dairy manure with up to 7% TS in various digester configurations (Ogejo and Li, 2010). Table 4 summarizes the results of past studies reporting methane production from dairy manure employing conventional CSTR reactors and a UASB reactor. Dugba and Zhang (1999) obtained a maximum of 0.82 L CH_4/L·d when treating screened dairy manure with two-stage (thermophilic-mesophilic) anaerobic sequencing reactor systems. Karim et al. (2005) reported methane production rates of 0.45 L CH_4/L·d in the digestion of dairy manure slurry at mesophilic conditions in CSTR lab scale reactor. The removal percentage of COD_T was 50%, also lower than the one obtained in this work. Demirer and Chen (2005) reported a maximum methane production of 1.2 L CH_4/L·d in two-phase anaerobic digestion of unscreened dairy manure under extreme conditions of OLR (12.6 g VS/L day). Wen et al. (2007) reported 0.88 L CH_4/L·d for the anaerobic digestion of liquid dairy manure using a sequential CSTR system. Kavacik and Topaloglu (2010) obtained 0.60 L CH_4/L·d in the mesophilic co-digestion of a mixture of dairy manure and cheese whey in CSTR reactors. With regards to the performance of UASB reactors, diluted decanted cattle manure (4-6 g VS/L) was successfully treated in a UASB reactor by Kalyuzhnyi et al. (1999). The maximum OLR applied was 6 g COD/L·d at an HRT of 1 day. The total COD reduction was a mere 41.5% and methane production was 0.70 L CH_4/L·d.

The mean value of TKN concentration in the affluent for all HRT was 1140 mg/L, being the mean percentage as ammonia nitrogen of 78.2%. In the effluent, the TKN mean concentration value was 1044 mg/L, 100 mg/L lower than that for the corresponding affluent. In the effluent, ammonia nitrogen mean concentration was 906 mg NH_4^+-N/L, 86.8% of TKN. This change is due to ammonification process, ammonia nitrogen use in cellular synthesis processes, struvite precipitation and gaseous emissions of ammonia nitrogen due to pH increases. Mean values for P_T present in the affluent and effluent were 86 and 24 mg/L, respectively. The decrease in effluent total phosphorus concentration was caused by the precipitation of various phosphates: magnesium ammonium phosphate (struvite), calcium phosphate. Noticeable difficulties in the UASB reactor performance, such as excessive foaming or sludge flotation were not observed.

3.3. Ammonia nitrogen removal by struvite precipitation

Experiments were carried out by triplicate. Struvite precipitation was conducted at UASB effluent pH value (8.3) and also at a pH of 9.8 adjusted by NaOH addition. Due to thefact that the concentration values of NH_4^+-N and PO_4^{3-}-P of anaerobic effluent were $6.47\cdot10^{-2}$ M and $7.75\cdot10^{-4}$ M, respectively, to force the formation of struvite Mg^{2+} and PO_4^{3-} ions were added by using $MgCl_2\cdot6H_2O$ and $KH_2PO_4\cdot3H_2O$. Fig. 4 shows the removal percentage of ammonia nitrogen at a constant molar ratio Mg^{2+}:NH_4^+ of 1.2:1 and a molar ratio Mg^{2+}:PO_4^{3-} from 0.75:1 to 1.2:1. When PO_4^{3-}:NH_4^+ was higher than 1, the removal efficiency of NH_4^+ by struvite precipitation increased but PO_4^{3-}-P concentration in the supernatant obtained after the precipitation also increased. There was a sudden decrease in the pH of solution after addition of chemicals ($MgCl_2\cdot6H_2O$ and $KH_2PO_4\cdot3H_2O$) at the beginning of each experiment as it was reported by Uludag-Demirer et al. (2005). This decrease can be due to the release of H^+ cations from $H_2PO_4^-$, HPO_4^{2-} and Cl^- originated in the precipitation of struvite. For the samples whose pH was not adjusted, pH decreased from 8.3 to 7.8 and for the other samples, initial pH of 9.8 decreased down to 8.6. In all the experiments stirring was maintained for five minutes after reactives addition, and then it was allowed to settle for another ten minutes. Afterwards, pH maintained the values reached after chemicals addition. Under these conditions of pH it can be assumed that the majority of the ammonia nitrogen removed was due to struvite precipitation. When pH values were adjusted to 9.8, the percentage of N-NH_4^+ removed was higher than that for the same molar rate

Mg^{2+}:PO_4^{3-} at pH 8.3. When the molar ratio Mg^{2+}:PO_4^{3-} increased from 0.75:1 to 1.2:1, for the non-pH-adjusted samples, the removal percentage of NH_4^+ decreased from 82.6% to 70.8%, whereas for the pH-adjusted samples, the removal percentage of NH_4^+ decreased from 92.7% to 80.2%.

During all the operating conditions of UASB reactor, the effluent ratio NH_4^+-N/TKN-N ranged between 0.82 and 0.94 and decreased with lowering HRT. When the effluent contained 1170 mg NH_4^+-N/L, the NH_4^+-N/TKN ratio was 0.87. After struvite precipitation, the ammonia nitrogen concentration decreased down to 87 mg NH_4^+-N/L. The characteristics of the solid containing struvite obtained for a molar ratio Mg^{2+}:NH_4^+:$PO4^{3-}$ 1:1:1 are presented in Table 5. In this case, struvite was not the only compound that precipitated; due to the use of K_2HPO_4 as source of phosphorus, it also precipitated $MgKPO_4 \cdot 6H_2O$, known as potassium struvite (Pastor et al., 2010). Besides struvite and potassium struvite other phosphates and magnesium and calcium carbonates precipitate (Uludag-Demirer and Othman, 2009). The experimental processes employed enabled us to reduce the TKN concentration of over 4500 mg TKN-N/L, found in dairy manure, to a value of less than 200 mg TKN-N/L in the final liquid fraction effluent. The significance of this is that the land required to apply the final LF effluent from the processing line, in accordance with Directive 91/676/CEE, would be reduced to an area 20 times smaller. Thus, intensive dairy farms would have enough land to handle the TKN disposal needs in the LF after struvite precipitation.

3.4 Methane productivity of manure and liquid and solid fractions.

Determination of methane production of dairy manure and its fractions was carried out in batch reactors at 50ºC and 35ºC. For manure, methane productivity at 50ºC was a bit higher than at 35ºC. At day 35 methane productions were 19.3 and 17.7 L CH_4/kg dairy manure, at 50 and 35ºC, respectively. From data in Table 1 it can be calculated a specific methane production of 212 cm^3 CH_4/g VS at 50ºC. Møller et al. (2004) estimated a specific methane production of 190 cm^3 CH_4/g VS for dairy manure. Higher methane production at 50ºC is due to the fact that hydrolysis is the rate-limiting step in anaerobic digestion of waste slurries such as dairy manure and higher temperatures improve hydrolysis stage. However, for dairy manure no big differences were observed between digestion at 35ºC and 50ºC. For the separated LF, methane production at 35ºC finished at day 15, being 4.92 L CH_4/kg dairy manure (4.38 L CH_4/kg LF).

In Fig. 5 the evolution of methane production at 35 and 50ºC for the SF is represented. At day 35, methane production for the SF was 15.2 and 14.2 L CH_4/kg dairy manure, at 50ºC and 35ºC, respectively (29.0 and 27.1 L CH_4/kg SF). That is in accordance with Møller et al. (2004), who reported that the separation of manure was a way to produce manure solid fractions with higher gas potentials based on volume, since solid fractions present higher VS concentration. For the SF, temperature had more influence on methane production kinetics, showing a faster rate of methane production at 50ºC, since at day 15 at 50ºC 90.7% of the final methane production had been reached, but at 35ºC only 56.1%. For the solid fraction the higher temperature promoted the hydrolysis stage, due to the high solids content (19.0% DM) which resulted in higher methane productivity.

Separated digestion of solid and liquid fractions at 50ºC and 35ºC respectively, would allow a better energetic balance and lower digester size, although two digesters would be needed. Taking into account the conventional HRTs employed in the anaerobic digestion of dairy manure and solid fractions of manure (20-30 days) and that of the liquid fraction in this work (0.35 days), a global reactor volume size reduction of 45% could be achieved. The digested SF, due to high content in organic matter and nutrients, could be exported to other agricultural lands with a deficit in them. The cost of transport will be cheaper due to its low humidity content.

4. Conclusions

The results from the present study demonstrated that the anaerobic digestion of liquid and solid fractions of dairy manure separated by flocculation and screening allows reducing digester size requirements. This is possible because of the low HRT required for the anaerobic digestion in UASB reactors of the highly biodegradable separated liquid fraction. A stable operation was performed at 0.35 days HRT (40.8 g COD/(L·d) OLR) without VFA accumulation and COD removal percentage of 73.9%, reaching a volumetric methane production of 10.3 L CH_4/(L·d). HRTs lower than 0.35 days resulted in higher methane production rates but significant decrease in COD removal efficiency and high VFA accumulation in the effluent. UASB effluent was subjected to a precipitation process to remove NH_4^+ by formation of struvite. Better NH_4^+ removal efficiencies were obtained at an adjusted pH of 9.8 rather than at pH of the UASB effluent, 8.3. The best results in terms of NH_4^+ removal efficiency were achieved at a molar ratio Mg:N:P of 1.2:1:1.6, 82.6% and 92.7% for the samples at pH 8.3 and 9.8, respectively. The final liquid effluent presented such a low nutrients content (NKT-N <

200 mg/L; $P_T < 25$ mg/L) that would only need twenty times less farming land than dairy manure to its application. Thermophilic anaerobic digestion of the solid fraction separated by flocculation and screening showed higher methane yield and faster kinetics than that at mesophilic conditions, 29.0 L CH_4/kg SF at 50ºC. Solid fraction, after digested, will be an appreciated fertilizer due to its stabilized organic matter and nutrients content and together with the precipitate containing struvite could be exported to other agricultural lands with a deficit in nutrients.

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