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ON THE EFFECT OF AQUEOUS AMMONIA SOAKING PRETREATMENT ON CONTINUOUS ANAEROBIC DIGESTION OF DIGESTED SWINE MANURE FIBERS

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SUMMARY: The continuously increasing demand for renewable energy sources renders anaerobic digestion to one of the most promising technologies for renewable energy production. Due to the animal production intensification, manure is being used as the primary feedstock for most of the biogas plants. Thus, their economical profitable operation relies on increasing the methane yield from manure, and especially of its solid fraction which is not so easily degradable. Aqueous Ammonia Soaking (AAS) has been successfully applied on digested fibers separated from the effluent of a manure-fed, full-scale anaerobic digester to enhance their methane productivity in batch experiments. In the present study, continuous experiments at a mesophilic (38°C) CSTR-type anaerobic digester fed with swine manure first and a mixture of manure with AAS-treated digested fibers in the sequel, were performed. The methane yield of AAS-treated digested fibers under continuous operation was even higher than that calculated in batch experiments (0,238 compared to 141-160 l CH_4 / g TS, respectively). Anaerobic Digestion Model 1 (ADM1) previously fitted on manure fed digester was used in order to assess the effect of the addition of AAS-pretreated digested manure fibers on the kinetics of anaerobic digestion process. It was found that AAS treatment had a profound effect mainly on the hydrolysis rate of particulate carbohydrates.

1. INTRODUCTION

Anaerobic digestion is one of the most promising renewable energy technologies, as it provides a solution to both environmental and energy considerations. Some of the benefits of this technology are that it reduces the odour, minimizes the size of the organic wastes, contributes to the reduction of the GHG emissions and produces a high value fertilizer as well as a renewable energy gas. Anaerobic digestion of swine manure has been a wide matter of discussion and it has been proved a promising approach for renewable energy production in the form of methane. In fact, twenty-two (22) large-scale biogas plants are currently under operation in Denmark using manure as primary feedstock but their economical profitable operation relies on increasing the methane yield from manure. New separation technologies for being applied before anaerobic digestion have been tested during the last few years (Hjorth et al., 2010). Thus, manure liquid fraction could be used as fertilizer in the farms while the solid fraction could be transported to centralized biogas plants for methane production (Jurado et al., 2010). However, the fibers present in the solid fraction of manure are not easily degraded mainly due to their lignocellulosic nature. It has been shown that Aqueous Ammonia Soaking (AAS) pretreatment combined with subsequent removal of ammonia (which also gives the possibility for being recycled in a full-scale plant) could be very effectively applied for increasing the methane yield from raw manure fibers (Jurado et al, 2012a) as well as already anaerobically digested manure fibers (Mirtsou-Xanthopoulou et al., 2012). Postreatment of digested fibers focuses only on hardly biodegradable biomass compared to raw fibers where easily biodegradable material is also present. Therefore, the mass of fibers to be treated is expected to be significantly lower in case of digested fibers leading thus to a more economical process.

In the present study, continuous experiments at a mesophilic (38°C) CSTR-type anaerobic digester fed with swine manure first and a mixture of manure with AAS-treated digested fibers in the sequel, were performed in order to verify the experimental data obtained from batch experiments. Anaerobic Digestion Model 1 (ADM1) (Batstone, 2002) was used in order to assess the effect of the addition of AAS-pretreated digested manure fibers on the kinetics of anaerobic digestion process.

2. MATERIALS AND METHODS

2.1 Feedstock

Digested manure fibers were kindly provided by Morsø BioEnergi and stored at -20°C until used.

2.2 Analytical methods

Total (TS) and volatile (VS) solids and N-Kjendahl were measured according to standard methods (APHA, 2005). Inorganic phosphorus analysis was carried out by applying ascorbic acid photometric determination (APHA, 2005). Total and soluble Chemical Oxygen Demand (COD) was determined using Hach Lange kits LCK_914 (5-60 g L-1 range) and LCK_514 (100-2000 mg L-1 range), respectively. Analysis of ammonium nitrogen (NH_4-N) was performed with Hach Lange kit LCK_305 (1-12 mg L-1 range). Two groups of carbohydrates were determined in the samples of manure and manure fibers: the first group was the total carbohydrates, including those bound in the lignocellulosic biomass and the second group was the simple sugars (Haagensen et al., 2009). Analysis of the two groups of carbohydrates was carried out based on the NREL analytical procedures (Sluite et al., 2008). Detection and quantification of sugar monomers (glucose, xylose and arabinose) was made with HPLC-RI equipped with an Aminex HPX-87H column (BioRad) at 60°C. A solution of 4 mmol L-1 H_2SO_4 was used as eluent at a flow rate of 0.6 mL min-1. Samples for HPLC analysis were acidified with a 10% w/w solution of H_2SO_4, centrifuged at 10000 rpm for 10 min and finally filtered through a 0.45μm membrane filter. For the quantification of VFA, 1ml of sample was acidified with 17% H_3PO_4 and filtered through minisart high flow filter (pore size 0,5μm). VFA were analyzed on a gas chromatograph (PerkinElmer Clarus 400) with a flame ionization detector and a capillary column (Agilent HP-FFAP column, 30m long and 0,53mm inner diameter). Biogas composition in methane was measured with a gas chromatograph (SRI GC model 310) equipped with a thermal conductivity detector and a packed column (Porapak-Q, length 6ft and inner diameter 2.1 mm). The temperature for injector, column and detector was set to 80°C. The volume of methane produced in sealed vials during methane potential tests was calculated by multiplying the biogas composition in methane with the headspace volume.

2.3 Ammonia pretreatment

Samples of manure fibers were soaked in ammonia reagent (32% w/w in ammonia) at a ratio of 10 mL reagent per g TS. The treatment was performed in closed glass flasks to avoid ammonia evaporation. After the completion of the treatment, water was added at a ratio of 10 mL per g TS to facilitate the subsequent ammonia distillation step. Distillation was performed using a rotary evaporator (Buchi RII Rotavapor) with a vertical condenser.

2.4 Experimental procedure

2.4.1 Feedstock characterisation

AAS-treated digested manure fibers were characterized in terms of total and soluble COD, total carbohydrates and free sugars, total and soluble Kjendahl nitrogen and NH_3-N, volatile fatty acids (valeric, butyric, propionic and acetic acids), inorganic phosphorus and inorganic carbon. Particulate and soluble inerts were determined as the residual COD after three months of batch anaerobic digestion. Particulate carbohydrates and proteins were calculated as the difference between total and free carbohydrates/sugars and total and soluble Kjendahl nitrogen, respectively. Aminoacids were calculated as the difference between soluble Kjendahl nitrogen and NH_3-N. Calculation of particulate lipids was based on the difference between non-soluble COD (total – soluble COD) and the sum of particulate carbohydrates, proteins and inerts, while long chain fatty acids were calculated as the difference between soluble COD and all measured soluble components (sugars, aminoacids, volatile fatty acids and soluble inerts).

2.4.2 Continuous experiments

One mesophilic (38°C) CSTR-type digester of 3 l useful volume was started-up and fed with swine manure at a hydraulic retention time of approximately 25 d. After the digester reached steady-state, the influent was changed to a mixture of swine manure and AAS-treated digested manure fibers (at a ratio of 0.52:0.48 on Total Solids basis). The feeding was intermittent and repeated once a day.

Daily monitoring of the digester included biogas production and composition in methane, pH, volatile fatty acids and soluble COD concentration. When the digester reached the second steady state while fed with the mixture of manure and fibers, complete characterisation was performed in terms of almost all measurable components of ADM1. Subsequently, the digester was subjected to impulse disturbances of acetic, propionic and butyric acids and soluble influent fraction in order to study the dynamics of the processes. The responce of the bioreactor to these impulses was monitored mainly through measurements of biogas production and composition in methane, pH and VFA concentration until all components approach their levels before the impulse.

2.4.3 Modeling

Anaerobic Digestion Model No1 (ADM1) was used to simulate the anaerobic digestion process and to assess the effect that the addition of AAS pretreated digested fibers had on the kinetic parameters. At the study of Jurado et al. (2012b), the IWA anaerobic digestion model (ADM1) had been fitted to the experimental data obtained from a manure-fed digester different than the one used in this study and hydrolysis constants of carbohydrates (khydr_ch), proteins (khydr_pr) and lipids (khydr_li) and maximum uptake rates of long chain fatty acids (Km_fa) and volatile fatty acids (km_c4, km_pro and km_ac for butyric, propionic and acetic acid, respectively) had been calculated. That model was used to simulate the first steady state of the reactor (with manure as influent). Subsequently, the model was fitted to the experimental data obtained throughout the experiment with the mixture of manure and fibers as influent and new hydrolysis constants had been obtained. The software used was Aquasim 2.1 g and the secant method was applied.

3. RESULTS AND DISCUSSION

3.1 Influent characterisation

The characteristics of manure and AAS-treated digested manure fibers are shown in Table 1. As anticipated, the AAS-treated fibers consisted mainly of particulate organic matter with carbohydrates being a substantial fraction while manure was also rich in soluble organic matter.

Table 1. Characteristics of manure and AAS-pretreated raw manure fibers

Characteristics, particulate matter	Manure	AAS-pretreated digested fibers
COD, kg / 100 kgTS	79.11	75.34
Carbohydrates, kg COD/ 100 kg TS	6.10	32.75
Proteins, kg COD/ 100 kg TS	28.00	21.41
Lipids, kg COD/ 100 kg TS	32.65	1.10
Inerts, kg COD/ 100 kg TS	12.37	20.08
Characteristics, soluble matter		
COD, kg / 100 kgTS	91.83	23.7
Sugars, kg COD/ 100 kg TS	0	0
Aminoacids, kg COD/ 100 kg TS	18.92	1.02
Long chain fatty acids, kg COD/ 100 kg TS	21.25	19.49
Valeric acid, kg COD/ 100 kg TS	0	0.66
Butyric acid, kg COD/ 100 kg TS	3.98	0.00
Propionic acid, kg COD/ 100 kg TS	8.46	0.34
Acetic acid, kg COD/ 100 kg TS	34.75	2.07
Inerts, kg COD/ 100 kg TS	4.46	0
Inorganic carbon, kmole / 100 kg TS	0.53	0.05
Inorganic phosphorus, kmole / 100 kg TS	9.59×10^{-3}	6.52×10^{-3}
Inorganic nitrogen (NH_3-N), kmole / 100 kg TS	0.73	4.28×10^{-2}

3.2 Continuous experiments

Figure 1 shows the volumetric and the organic loading rate of the digester throughout the continuous experiment. Operating conditions and steady state characteristics of the anaerobic digester fed with manure and a mixture of manure and AAS-pretreated digested manure fibers are summarised in Table 2. Despite the fact that manure fibers were characterised by a much lower content in soluble organic material (Table 1) the biogas production of the second steady state (with manure and fibers as influent) was 11% higher than that of the first (with only manure as influent). The methane yield was calculated as 0,303 l CH_4 / g TS during the first steady state with manure as influent and 0,272 l CH_4 / g TS during the second steady state when the digester was being fed with mixture of manure and AAS-treated digested fibers. Given that the TS ratio of manure:fibers in the influent of the digester was 0.52:0:48 and assuming that the methane yield due to the manure fraction was 0,303 l CH_4 / g TS also during the second steady state, then the methane yield of AAS-treated digested fibers was calculated to be 0,238 l CH_4 / g TS. In previous studies, the methane yield from AAS-pretreated digested fibers was measured in the range of 141-160 l CH_4 / g TS in batch experiments (compared to a methane yield of 76 l CH_4 / g TS from non-treated digested fibers) (Mirtsou-Xanthopoulou et al., 2012). Consequently, the continuous experiments verified what it was observed in batch experiments, namely, that AAS pretreatment results to a significant increase of methane yield of digested fibers. The even higher methane yield obtained from the continuous experiment was most probably due to the adaptation of the mixed microbial culture on the different feedstock since the batch experiments were performed with inoculum which was adapted to manure only, where actually no hydrolysis was taken place (Jurado et al., 2012b).

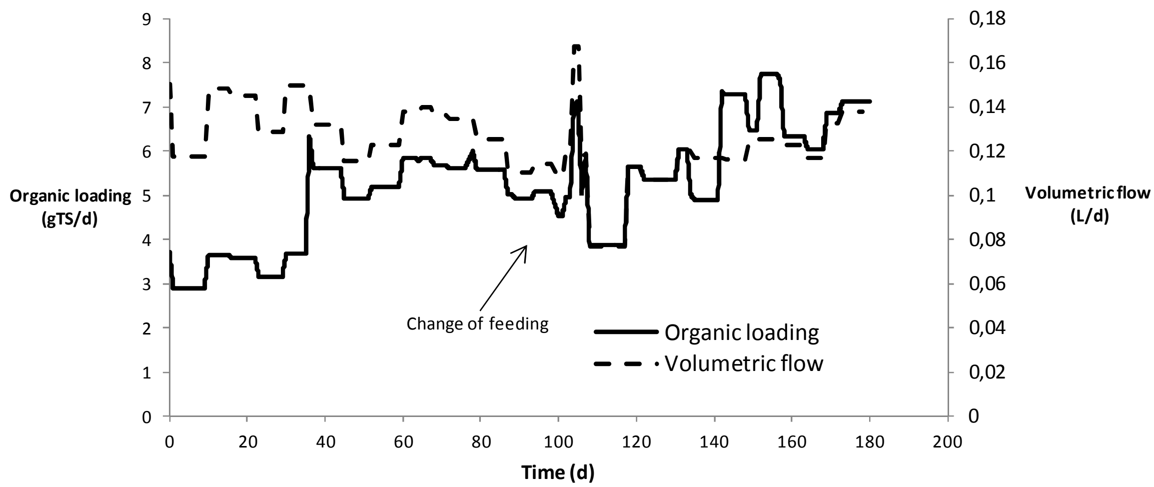

Figure 1. Volumetric and organic loading rate of the digester during the continuous experiment.

Table 2. Operating conditions and steady state characteristics of the anaerobic digester fed with manure and a mixture of manure and AAS-pretreated digested manure fibers

Operating conditions	Manure	Mixture of manure and AAS-treated digested fibers
HRT, d	24-25	24-25
Flow rate, ml/d	114-134	117-125
Organic loading rate (OLR), g COD/l/d	2,83-3,53	2,30-3,65
Soluble OLR, g soluble COD/l/d	1,52-1,90	1,00-1,58
Characteristics at steady state		
Biogas productivity, l/l/d	0,85 ± 0,07	0,94 ± 0,06
Methane, %	67 ± 0,023	65 ± 0,008
Methane productivity, l/l/d	0,57 ± 0,08	0,62 ± 0,08
Methane yield, l/g COD	0,18	0,20
Methane yield, l/g TS	0,303	0,272
Volatile fatty acids, mg/l	190	160
pH	8,2 ± 0,1	8,1 ± 0,1
Soluble COD, g/l	4,77 ± 0,15	4,84 ± 0,11

Model predictions for the steady state on manure as well as experimental measurements are shown in Table 3. It is noticeable that the model, which was developed in another digester fed with manure, was able to accurately predict the steady state reached in the present study.

Table 3. Model predictions and experimental measurements for the steady states on manure and mixture of manure and AAS-treated digested fibers.

Steady state characteristics	Manure		Mixture of manure and AAS-treated digested fibers	
	Experimental	Model	Experimental	Model
Methane, %	67,6 ± 2,1	64,2 ± 8,3	66,6 ± 1,8	67,0 ± 7,6
Biogas production, m^3/d	$2{,}32 \times 10^{-3} \pm 0{,}2 \times 10^{-3}$	$2{,}65 \times 10^{-3} \pm 0{,}1 \times 10^{-3}$	$2{,}70 \times 10^{-3} \pm 0{,}3 \times 10^{-3}$	$2{,}9 \times 10^{-3} \pm 0{,}2 \times 10^{-3}$
pH	8,2	8,1	8,1	8,0
Acetic acid, $kgCOD/m^3$	0,159 ± 0,055	0,087 ± 0,013	0,208 ± 0,146	0,081 ± 0,018
Propionic acid, $kgCOD/m^3$	0,031 ± 0,013	0,018 ± 0,002	0,045 ± 0,003	0,019 ± 0,002
Butyric acid, $kgCOD/m^3$	0,033 ± 0,011	0,011 ± 0,001	0,005 ± 0,001	0,012 ± 0,001

During the second time period, where the digester was fed with the mixture of manure and AAS-pretreated digested fibers, the only kinetic parameters, which were mostly affected, were those of carbohydrates and proteins hydrolysis. Hydrolytic kinetic constants for carbohydrates and proteins in manure had been calculated as 0 and 2.8×10^{-3} d^{-1}, respectively (Jurado et al., 2012b), while for the mixture were increased to 6.8×10^{-2} and 7.0×10^{-3} d^{-1}. Kinetics of volatile fatty acids uptake seemed to be unaffected as the behaviour of the digester under the impulse disturbances was satisfactorily simulated by the model without any further change in the kinetic parameters. The latter is depicted in Figure 2 where the experimental and predicted by the model acetic acid concentration is presented. Similar results have been obtained for the propionic and butyric acids (data not shown here). Figure 3 shows the experimental and theoretical biogas production throughout the duration of the experiment.

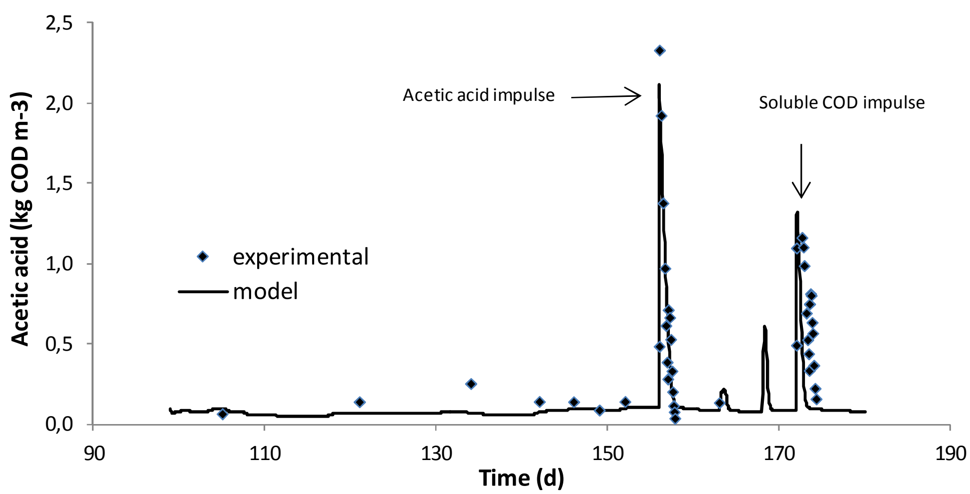

Figure 2: Experimental and predicted by the model acetic acid concentration during the experiment with mixture of manure and AAS-treated digested fibers as influent.

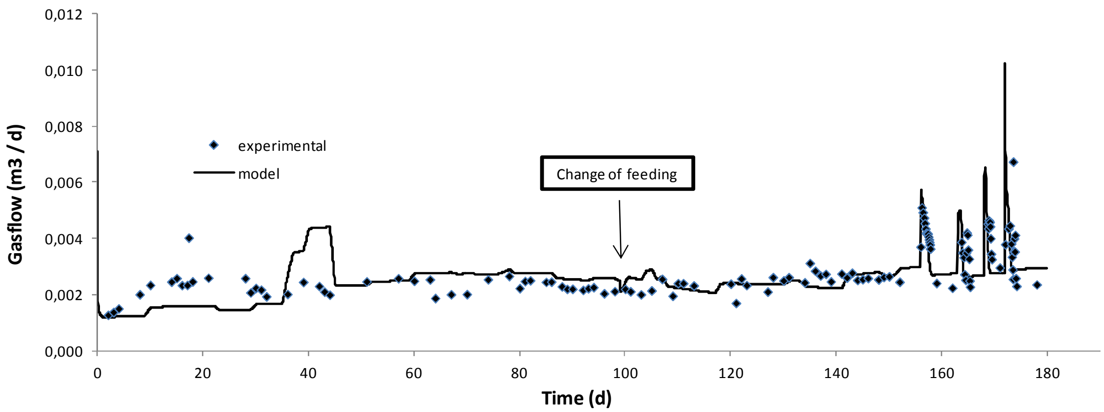

Figure 3. Experimental and theoretical biogas production throughout the duration of the experiment with manure and mixture of manure and AAS-treated digested fibers as influent from t=0-99 days and from t=99 days, respectively.

4. CONCLUSIONS

Recently, Aqueous Ammonia Soaking has been successfully applied on digested fibers separated from the effluent of a manure-fed, full-scale anaerobic digester to enhance their methane productivity in batch experiments. In the present study, continuous experiments at a mesophilic (38°C) CSTR-type anaerobic digester fed with swine manure first and a mixture of manure with AAS-treated digested fibers in the sequel, were performed. The methane yield of AAS-treated digested fibers under continuous operation was even higher than that calculated in batch experiments (0,238 compared to 141-160 l CH_4 / g TS). Anaerobic Digestion Model 1 (ADM1) previously fitted on manure fed digester was used in order to assess the effect of the addition of AAS-pretreated digested manure fibers on the kinetics of anaerobic digestion process. It was found that AAS treatment had a profound effect mainly on the hydrolysis rate of particulate carbohydrates.

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