Bioresource Technology 203 (2016) 259–266

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Influence of the gas composition on the efficiency of ammonia stripping of biogas digestate

J. Bousek [a,*], D. Scroccaro [a], Jan Sima [a], Norbert Weissenbacher [b], W. Fuchs [a]

[a] Institute for Environmental Biotechnology, IFA-Tulln, University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz Straße 20, 3430 Tulln, Austria
[b] Institute of Sanitary Engineering and Water Pollution Control, University of Natural Resources and Life Sciences, Vienna, Muthgasse 18, 1190 Wien, Austria

HIGHLIGHTS

- Different options of NH_3 side stream stripping of digestate were investigated.
- Efficiency of alternative strip (biogas and CHP flue gas) gases was compared to air stripping.
- CO_2 levels $\geqslant$40% have a strong negative influence on the stripping performance.
- CHP flue gas is a suitable alternative to air in ammonia stripping.

ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form 14 December 2015
Accepted 15 December 2015
Available online 19 December 2015

Keywords:
Side stream stripping
Ammonia removal
Anaerobic digestion
Biogas
Flue gas

ABSTRACT

Impact of strip gas composition on side stream ammonia stripping, a technology aiming at the reduction of high ammonia levels in anaerobic reactors, was investigated. Evaluation of the effect of oxygen contact during air stripping showed a distinct, though lower than perceived, inhibition of anaerobic microflora. To circumvent, the feasibility and possible constraints of biogas and flue gas as alternatives in side stream stripping were studied. Experiments, with ammonia bicarbonate model solution and digestate, were conducted. It was demonstrated that the stripping performance is negatively correlated to the CO_2 level in the strip gas with a progressive performance loss towards higher concentrations. In contrast to biogas with its high CO_2 content, the efficiency reduction observed for flue gas was significantly less pronounced. The later provides the additional benefit that its high thermal energy can be re-utilized in the stripping unit and it is therefore considered a viable alternative for air.

1. Introduction

Anaerobic digestion (AD) has become a primary process for the treatment of agricultural wastes and food residues (Chen et al., 2008; Hansen et al., 1998; Wäger et al., 2009). AD has several advantages such as waste reduction in combination with energy production, however, certain hurdles exist. One such problem is ammonia inhibition which can occur during digestion of animal manure or highly proteinaceous wastes e.g. from slaughterhouses (Chen et al., 2008; Serna-Maza et al., 2014). In aqueous solution ammonia nitrogen is present in two forms, ammonium ions and free ammonia (FA), depending on pH and temperature. FA is believed to be the main cause of inhibition since it is freely membrane-permeable and may diffuse passively into the cell, causing proton imbalance, and/or potassium deficiency (Gallert et al., 1998). The inhibitory concentrations of total ammonia nitrogen reported are in the range of 0.76–4 g N/l. Only few publications report the corresponding FAN levels but generally it is believed that concentrations above 100 mg/l cause process inhibition (Ortner et al., 2014).

Various means to reduce the ammonia inhibition in AD have been investigated as comprehensively reviewed in Yadvika et al. (2004) and Chen et al. (2008). One option is to remove ammonia by stripping. Stripping is a process in which a liquid, in this case biogas reactor content, is percolated with gas. Dissolved gases present in the liquid phase are released and carried away. The released components are removed from the total gas stream through a scrubber (Huang and Shang, 2006). Currently, full scale ammonia stripping is almost exclusively established as a post treatment process for the treatment of sludge return liquor derived from sludge digesters in wastewater treatment (Jardin et al., 2006). However, side stream stripping, a process were the ammonia-depleted digestate is recycled into the biogas reactor, could be applied to lower ammonia concentration in the reactor itself. This has been

---

* Corresponding author. Tel.: +43 2272 66 280 555.
E-mail address: johannes.bousek@boku.ac.at (J. Bousek).

http://dx.doi.org/10.1016/j.biortech.2015.12.046
0960-8524/

demonstrated on the laboratory scale (Hansen et al., 1998; Serna-Maza et al., 2014; Walker et al., 2011).

Air is frequently used as strip gas in ammonia stripping (Huang and Shang, 2006; Wäger et al., 2009). In a side stream configuration, the disadvantage is that oxygen may have a deteriorating effect on the anaerobic microbial consortium. It is commonly perceived that oxygen acts as a strongly inhibitory/toxic agent (Chu et al., 2005; Kato et al., 1993; Shen and Guiot, 1996; Zitomer and Shrout, 1998; Zitomer, 1998) in AD due to the involvement of strictly anaerobic microorganism groups of acetogens and methanogens (Whitman et al., 2006). Impact of free oxygen towards anaerobic organisms present in biogas plants have been investigated by a number of authors (Hungate, 1969; Scott et al., 1983; Whitman et al., 2006). The generation of highly reactive oxidizing agents such as peroxides and superoxides in the liquid medium causes not only functional inhibition but also rapid cell lysis (Gottschalk and Peinemann, 1992) of obligatory anaerobic species. However, as demonstrated by other researchers oxygen inhibition is less severe as generally expected. One major reason for that is that mixed anaerobic communities comprise also many facultative anaerobic strains. Especially among those species involved in acidogenesis. These microorganisms rapidly eliminate dissolved oxygen and thereby protect obligate anaerobic strains. (Gerritse, 1990; Kumar et al., 2015). Botheju and Bakke (2010) found that rigorous initial aeration of an anaerobic inoculum resulted in a three times longer lag period before gas generation started but also noted a certain reversibility of the inhibition. While details of the reversibility of oxygen inhibition of methanogens remains unknown such an effect was also observed by Gerritse (1990). Zitomer (1998), who conducted experiments under limited oxygenation conditions, reported that the activity was inhibited for a short period (30 min) but methanogens were not irretrievable damaged.

To circumvent a potential oxygen inhibition, it might be advisable to use other gaseous stripping media available on AD plants, i.e. biogas and flue gas from the CHP (combined heat and power plant employed for conversion of biogas into electricity and thermal energy). The use of biogas for ammonia stripping has been suggested by several authors (De la Rubia et al., 2010; Serna-Maza et al., 2014, 2015) whereas the application of flue gas has not been discussed in literature yet. Beside potential advantages these gases feature may also entail certain drawbacks. They feature an elevated CO_2 content, which might be of mayor impact on the stripping performance. It is well known that the concurrent CO_2 removal influences the carbonate buffer system (alkalinity) in the course of stripping and leads to improved ammonia stripping due to the pH raise (Budzianowski and Koziol, 2005; Ni, 1999). Change of alkalinity as a major parameter of influence was monitored in many studies on ammonia stripping (Bonmatí and Flotats, 2003; De la Rubia et al., 2010; Wäger et al., 2009). It can be generally perceived that higher CO_2 concentration provide less efficient CO_2 stripping. However, no reports quantifying the effect of CO_2 rich strip gases on the course of alkalinity during ammonia stripping are found.

The work presented here was carried out in the frame of the EC project “ManureEcoMine – Green fertilizer upcycling from manure”. The overall goal of the project is to demonstrate the technical feasibility of a treatment cascade, including side stream ammonia stripping as one of the major process components, to efficiently recover nutrients from digestate. The study aimed to evaluate different configurations of the stripping process for subsequent implementation in the pilot plant. One aspect of interest was to judge the effect of the initially selected stripping conditions (air stripping at 65 °C). To investigate, a series of biogas potential tests were conducted to obtain information on the residual biogas production capacity of the treated digestate. The second issue addressed was the suitability of the mentioned alternative strip gases. To gain a principle understanding of the influence of CO_2 on the stripping performance, experiments with a model solution employing increasing CO_2 concentrations in the strip gas were conducted. Further on experiments using simulated CHP flue gas and biogas using the model solution as well as real digestate samples were performed.

2. Methods

2.1. Stripped media

2.1.1. Model solution used for stripping

Ammonia bicarbonate (99.0% pure, Alfa Aesar, USA) was used as model solution. The reason for this choice was as follows: bicarbonate alkalinity is produced by the destruction of nitrogen containing substrate and the reaction of the released ammonia-nitrogen with the CO_2 produced within the reaction (Grady et al., 1999). According to the chemical reaction ($NH_3 + H_2O + CO_2 > NH_4^+ + HCO_3^-$) the formation of bicarbonate and ammonium occurs in equal molarities (Tchobanoglous et al., 2003). Part of the alkalinity might be consumed by the formation of VFAs (volatile fatty acids). On the other hand several other matrix components within digestate feature buffer capacity and can therefore provide counterions to permanently dissolve these volatile substances. Calculation of the NH_4^+:HCO_3^- ratio from data on digestate composition from several literature sources provided typically a range of 0.83–1.86 (with some extreme values from 0.36 to 2.70). With respect to that, it was assumed that a 1:1 ratio is a reasonable approximation of the real conditions. Moreover, at the given ratio the pH of the model solution corresponded very well to the pH of the sludge sample (pH ~ 7.8). A similar solution (although in slightly different in NH_4^+:HCO_3^- ratio) was used as a reference for stripping experiments reported by Bonmatí and Flotats (2003).

The set NH_4-N concentration was 6000 mg/l (430 mM NH_4), a level where considerable ammonia inhibition in biogas plants can be observed (Chen et al., 2008; Hansen et al., 1998).

2.1.2. Digestate

Sieved (1 mm) digestate, a 1:1 mixture of the reactor content of two mesophilic biogas plants, was used for the stripping experiments. One was a large scale plant treating pig manure and maize silage. The second plant, a pilot scale experimental reactor, was run on sugar and pig fodder. Blending was conducted to reduce the fiber content.

Sludge was characterized by repeated measurements during the duration of the experiments. The averaged results (±standard deviation) are: pH 7.8 ± 0.3; COD 45.1 ± 5.0 g/kg sludge; dry matter content (DM) 4.43 ± 0.24% and organic dry matter (ODM) 2.97 ± 0.20%, corresponding to 67 ± 0.2% of the DM; total Kjeldahl nitrogen (TKN) 5590 ± 140 mg/kg sludge. Ammonia concentration was artificially increased to reach concentrations of ammonia inhibition. The native NH_4-N concentration (2670 ± 180 mg/l) was spiked with ammonia bicarbonate to 6000 mg/l. The bicarbonate alkalinity (226 mM carbonate) was thereby increased to 436 mM. Total concentration of volatile fatty acids (VFAs) was 1710 ± 45 mg/l.

2.2. Stripping plant

The lab scale stripping plant (Fig. 1.) was constructed from glass elements. The stripper consisted of a 1 l round bottom flask, the working volume was 0.5 l. To provide sufficient volume for foaming a 1 l glass was installed on top with a foam destruction device,

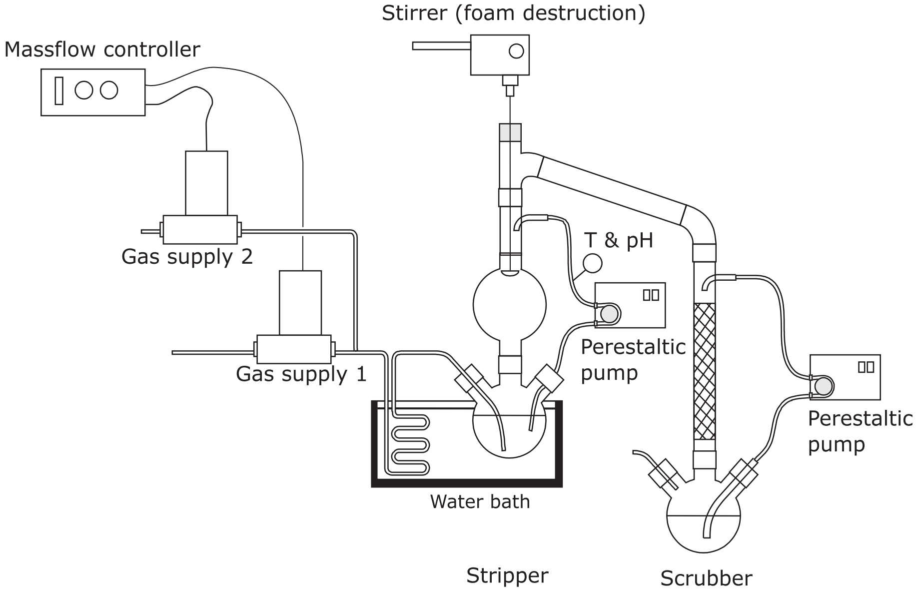

Fig. 1. Schematics of the lab scale batch strip plant.

a fast rotating pedal (approx. 1000 rpm) at the upper end. To counter heat loss the stripping device was insulated. The lower end was immersed into a water bath to heat the stripping liquid (stripping temperature 65 ± 1 °C). The water bath also served to pre-heat the stripping gas, which was passed through a coiled metal tube. The stripper was connected to the scrubber unit via a horizontal lab glass tube (30 cm length, 3.2 cm diameter). The scrubber column (Vigreux column, 40 cm length, 3.2 cm diameter) and a 1 l round bottom flask, was operated in parallel current mode using 1 M H_2SO_4 as scrubbing media. The total volume was approximately 1.3 l with a working volume of 0.5 l. Liquid phases, in stripper and scrubber, were recirculated by peristaltic pumps (Watson Marlow 520U, UK). pH and temperature (WTW 340i and Sentix 41, Germany) were continuously monitored in the stripper recirculation loop. Collected data were transmitted and stored on a PC. Fraction collectors (FARC 100 and RediFARC, Amersham Biosciences, Sweden) served for automatic periodic sampling from the stripping and the scrubbing liquid.

Air was supplied through the in-house compressed air system. For experiments with increasing percentage of CO_2 (5–40%), bottled CO_2 (technical grade) was mixed into the air stream. Alternative gases were simulated by mixing their main components. Artificial biogas was composed of 60% methane (3.5) and 40% carbon dioxide, flue gas contained 82% nitrogen (5.0) and 18% carbon dioxide. Composition of the dry flue gas was stoichiometrically calculated from complete combustion of biogas with air. Gas flow control to the stripper as well as the blending of the different gases was achieved by mass flow controllers (Modell 5850TR, Brooks, USA). Duration of the experiments on the influence of CO_2 were made dependent on the ammonia removal rate. Operation times were 4, 6, 8, 10 and 24 h for CO_2 concentrations of 5%, 10%, 20%, 30% and 40%, respectively. Experiments using the alternative strip gases were operated for a fixed period of 4 h. All tested conditions were run in duplicates.

2.3. Choice of stripping conditions

Efficient ammonia stripping is dependent on the already discussed equilibrium between ammonia and ammonium ions, with the effort to push the equilibrium towards the side of free strippable ammonia by the application of high pH and elevated temperature. Theory of ammonia stripping is well studied and relevant information is available in many textbooks as well as comprehensive scientific papers (e.g. Budzianowski and Koziol, 2005; Huang and Shang, 2006). However, stripping of digestate is confined by specific boundary conditions. Moreover, the application of routinely utilized packed bed columns is not possible due to the high solids content, which causes clogging or scaling. Stripping conditions applied here were selected based on information provided by an industrial cooperation partner. Stripping temperature was set to 65 °C. Necessity to apply a temperature of ~65 °C or higher for efficient stripping was already pointed out by other authors (De la Rubia et al., 2010; Serna-Maza et al., 2014), but is limited by the thermal energy available on-site. According to the industrial partner, the chosen temperature level can be effectively obtained from the excess heat of the combined heat and power plant. The pH of the stripping was not increased to comply with the idea of side stream stripping. This makes stripping less effective (Huang and Shang, 2006; Liao et al., 1995), on the other hand it avoids additional stress on the biogas reactor due to the recirculation of the stripped sludge with higher pH.

The gas flow was 300 l per liter stripping liquid and hour (total gas flow 1200 l/l within a 4 h stripping experiment). This gas flow was at the upper limit suggested by the partner ($75 - 300\,\mathrm{l}/(\mathrm{l} * h)$). In preliminary experiments, it was found to be most suitable for parameter comparison in the lab scale stripping plant. For comparison, in other lab scale stripping experiments a wide range of gas flow rates was applied: from $3.75 - 7.5\,\mathrm{l}/(\mathrm{l} * h)$ (Serna-Maza et al., 2015) up to $60 - 600\,\mathrm{l}/(\mathrm{l} * h)$ (Zhang et al., 2012) or $270 - 540\,\mathrm{l}/(\mathrm{l} * h)$ (Liao et al., 1995).

2.4. Analytical methods

pH was measured with a WTW 340i using a Sentix 41 ph probe (WTW, Germany). DM and oDM were determined by differential weighing after drying at 105 °C over night and by subsequent incineration at 550 °C, respectively. For substrate characterization TKN and the NH_4-N concentration were analyzed using a Büchi distillation/titration unit (K370, Büchi, Switzerland). In the stripping experiments the NH_4-N concentration was determined in a different manner based on indophenol formation with sodium salicylate. The method follows the protocol described in the German standard methods (DIN 38406/5) but was downsized to the ml scale to allow the use of 24 well microtiter plates (Falcon, USA) and photometric analyses in a plate reader (Infinite M200 Pro, Tecan, Switzerland). Digestate samples were centrifuged (12,500 rpm 15 min; CS-15 Beckman Coulter, USA), the supernatant was used for further analysis. Samples from the scrubber were analyzed directly without pretreatment. Each sample was diluted in three different ratios, the average of values within the calibration range was taken as result.

Bicarbonate alkalinity was measured by titration (autotitrator Metrohm Titrino 721 NET, Switzerland) with 0.1 M HCl to the pH end point 5.0 following a protocol provided by the manufacturer. The applied method is a routine analysis for biogas plants to determine the so called FOS/TAC value. The FOS value corresponds to the volatile fatty acids content and the TAC value is an estimation of the carbonate buffer of the sample.

Determination of VFA concentration was done following the method described in Ortner et al. (2014) by HPLC (Agilent 1100 Series, refractive index and multiple wavelength detector, column: Transgenomic CARBOSep CORGEL): operating temperature 65 °C, carrier liquid 0.005 mol/l H_2SO_4, column flow 0.9 ml/min. For sample preparation, the liquid samples were centrifuged (12,500 rpm, 15 min). 200 μl supernatant were acidified with 760 μl 0.025 M H_2SO_4 and Carrez precipitation was done by adding 20 μl each of potassium ferrocyanide (10.6 g per 100 ml osmotic water) and zinc sulfate (28.8 g/100 ml) solution. After the precipitation the centrifuged (12,500 rpm, 15 min) samples were filtered (0.45 μm membrane). The sample injection volume was 40 μl.

2.5. Biogas potential tests

Batch tests followed the protocol for determination of biomethane potential (BMP-tests) described in VDI 4630. The approach is to mix an organic substrate with an anaerobic inoculum, at defined conditions the gas evolved is quantified by displacement of water. A batch test comprises a reactor vessel connected to a displacement bottle filled with acidified water and a collecting bottle. 1000 ml Schott bottles (reactors) were filled with 400 ml pretreated sludge and 1.5 g glucose was added as substrate. Incubation had lasted for 28 days at constant temperature (37 ± 1 °C). Gas volume was measured daily and corrected to standard conditions. After each measurement the reactor was gently stirred by hand.

Before the batch tests were started pH of pretreated sludge was measured and if necessary adjusted (0.1 M HCl) to the original pH-value. During the test pH was measured on days 4 and 16 and again at day 28.

All tests were conducted in duplicate. Blank tests (untreated sludge with glucose) served as control.

3. Results and discussion

3.1. Impact of stripping on anaerobic activity

To assess the influence of the stripping process on the anaerobic consortium both inhibitory effects (temperature increase and contact with oxygen) were studied. Three different pretreatment conditions were chosen: (i) aeration with $75\ \mathrm{l}/(\mathrm{l} * h)$ at ambient temperature, (ii) heating to 65 °C, (iii) aeration and heating. To study the influence of exposure time, samples from the pretreatment test were taken after different time periods: 30, 90 and 180 min, respectively. All pretreatment options resulted in an inhibition of the biogas production. The Fig. 2a–c shows the averaged cumulative biogas production over 28 days. The strongest effect was observed for the actual stripping conditions (combined aeration and heating). With regard to the individual effects, the inhibition caused by heating to 65 °C was more pronounced than the impact of aeration. Similar to the observations reported by several authors (Botheju and Bakke, 2010; Gerritse, 1990; Zitomer and Shrout, 1998) a certain degree of recovery of activity was observed. A more detailed analysis of parameters (data not shown) revealed that low biogas production was linked to accumulation of VFAs that only later on were converted to biogas.

The extent to which implementation of side stream air stripping influences the biogas production capability of an anaerobic reactor is controversially discussed. It obviously depends on the recirculation rate as well as on the general operational conditions. Certain hesitations were already raised by Walker et al. (2011) and by Bonmatí and Flotats (2003). On the other hand Serna-Maza et al. (2014) claim that side-stream stripping of ammonia using thermal

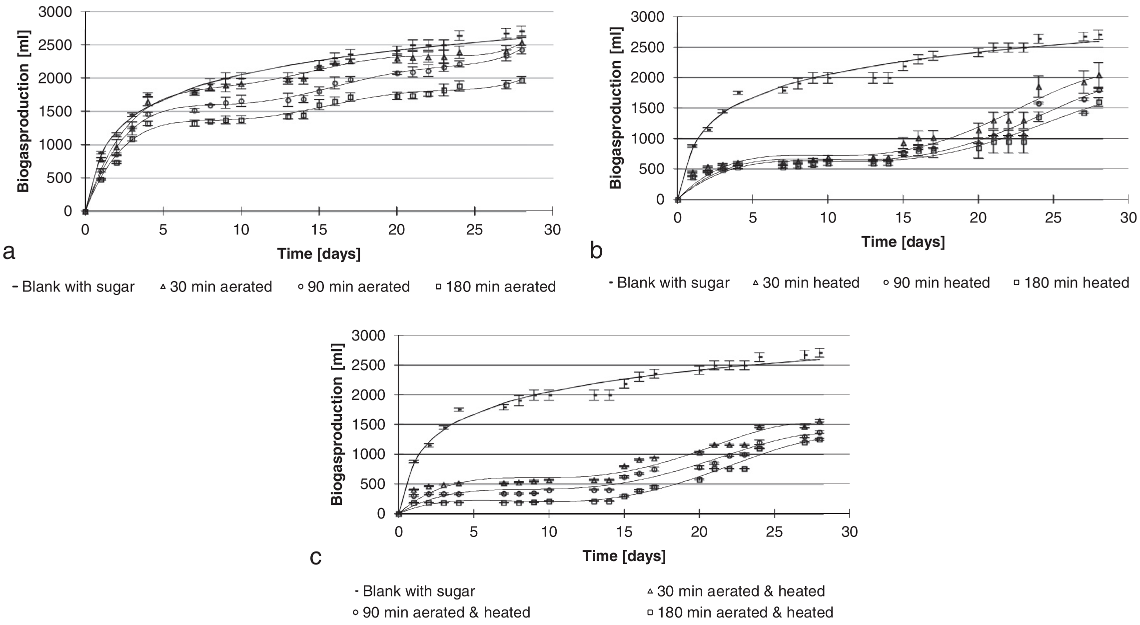

Fig. 2. Cumulative biogas production (a) aerated sludge, (b) heated sludge, (c) aerated and heated sludge, individual curves in each graph represent different exposure times.

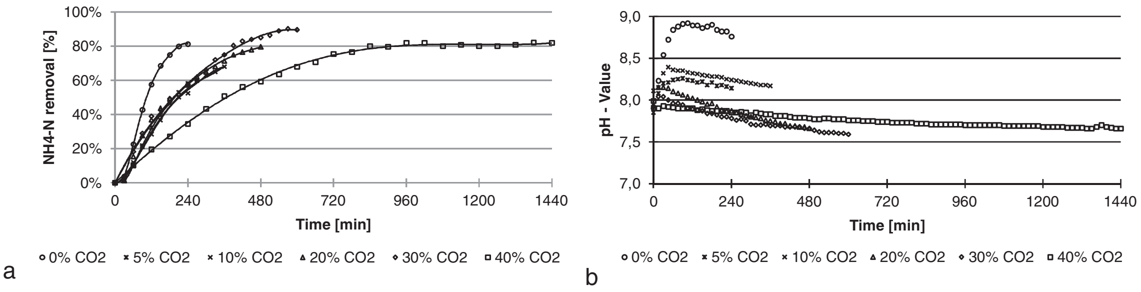

Fig. 3. CO_2 influence experiments (a) NH_4-N removal [%]. (b) pH-value during the stripping runs.

Table 1
Comparative overview of the stripping efficiency (% NH_4-N removal) and the pH-value of all conducted stripping experiments.

Sampling time	Stripping efficiency [% NH_4-N removal]			pH-value			
	2 h	4 h	8 h	0 h	2 h	4 h	8 h
Stripping experiment							
Model solution							
0% CO_2	58 ± 2.7	81 ± 2.7	–	7.9 ± 0.2	8.9 ± 0.2	8.8 ± 0.2	–
5% CO_2	32 ± 2.0	58 ± 1.6	–	7.9 ± 0.0	8.2 ± 0.1	8.2 ± 0.1	–
10% CO_2	29 ± 3.8	52 ± 2.4	–	8.0 ± 0.0	8.3 ± 0.2	8.2 ± 0.1	–
20% CO_2	37 ± 1.2	57 ± 1.3	80 ± 1.2	7.9 ± 0.1	8.0 ± 0.1	7.9 ± 0.1	7.7 ± 0.1
30% CO_2	39 ± 2.8	58 ± 3.4	85 ± 2.6	7.9 ± 0.2	7.9 ± 0.1	7.8 ± 0.1	7.7 ± 0.2
40% CO_2	20 ± 2.0	34 ± 0.0	59 ± 0.3	8.0 ± 0.1	7.9 ± 0.1	7.8 ± 0.0	7.8 ± 0.2
Air	51 ± 0.5	86 ± 0.8	–	7.8 ± 0.2	8.8 ± 0.0	8.7 ± 0.0	–
Flue gas	35 ± 0.2	45 ± 0.2	–	7.8 ± 0.1	8.3 ± 0.0	8.2 ± 0.1	–
Biogas	11 ± 2.1	16 ± 2.0	–	7.8 ± 0.1	8.0 ± 0.1	8.0 ± 0.1	–
Sludge							
Air	81 ± 0.7	96 ± 2.7	–	7.7 ± 0.2	8.8 ± 0.1	8.7 ± 0.0	–
Flue gas	68 ± 3.5	86 ± 1.7	–	7.9 ± 0.1	8.1 ± 0.1	7.9 ± 0.2	–
Biogas	25 ± 2.4	47 ± 1.3	–	7.8 ± 0.1	7.8 ± 0.1	7.8 ± 0.1	–

The values are the mean of the repeated stripping runs ± the standard deviation.

alkaline treatment (70 °C, pH 10) had no adverse effect on performance or stability of the digestion process at the given bleed rate (up to 3.5% per day). It was even stated that thermal hydrolyses contributes to an improved substrate utilization.

In the context of our investigations, it was concluded that the extent of inhibition, in particular with respect to oxygen impact, was much lower than initially suspected. However, it must be also considered that extensive oxygen carry over to the anaerobic reactor leads to enhanced oxidative degradation of the substrate, which decreases the attainable methane yield. Therefore, still alternatives to air stripping were sought to optimize the benefits of side stream ammonia removal.

3.2. Impact of carbon dioxide concentration on a model solution for stripping

The well known effect that during digestate stripping an pH increment occurs which enhances the speed of ammonia removal has been already mentioned. The underlying reactions involve the simultaneous mass transfer of two gases, NH_3 and CO_2 accompanied by parallel reversible chemical reactions (Budzianowski and Koziol, 2005). In simplified terms: CO_2 stripping corresponds to the removal of carbonic acid and consequently in an increase of pH, the higher pH shifts the NH_4^+/NH_3 ratio towards free strippable ammonia. The desorption rate of a certain component from liquid to gas is related to the partial pressure difference of the two phases. Accordingly, elevated CO_2 concentrations in the gas should lower stripping efficiency. The achieved stripping degrees (percentage of NH_4-N removal at a given sampling time) are presented in Fig. 3a. As expected, the stripping efficiency declined with the presence of CO_2. However, in a range between 5% and 30% CO_2 the stripping performances were relatively similar to each other. In contrast, application of the highest CO_2 concentration, 40%, significantly further reduced performance. In Fig. 3b, the corresponding pH in the course of the experiments is shown. It is clearly visible that CO_2 removal occurs very rapidly resulting in an initial pH increase whereas later on the pH decreases again when ammonia stripping becomes predominant. The lower the initial CO_2 concentration in the gas the more pronounced is the observed pH increase.

The impact of the increasing CO_2 concentrations in the stripping gas can be illustrated by the percentage of ammonia removal reached within 4 h. The reference run using plain air reached a stripping degree of 81%, with CO_2 concentrations between 5% and 30% the ammonia-nitrogen removal rate was 52–58% and at 40% CO_2 only a 34% stripping degree was obtained.

These findings are not only of interest with respect to the potential distinct performance loss applying biogas as stripping media. Increased CO_2 levels in the stripping also result from recirculation of stripping gas after ammonia scrubbing. The practical reason is the high energy demand for fresh air. Firstly, it needs to be heated up to the stripping temperature. Even more important is the fact that significant extra thermal energy is consumed for the water saturation of the gas during stripping due to evaporation. To illustrate: it takes 45.3 kJ/kg to increase the temperature of dry air from 20 to 65 °C, whereas the energy difference between air at 20 °C having a relative humidity of 60% and water saturated air at 65 °C is ~560 kJ/kg. The obtained data provide also useful information on the applicable recirculation rate bearing in mind that to high CO_2 concentrations may lead to a sudden decline in efficiency.

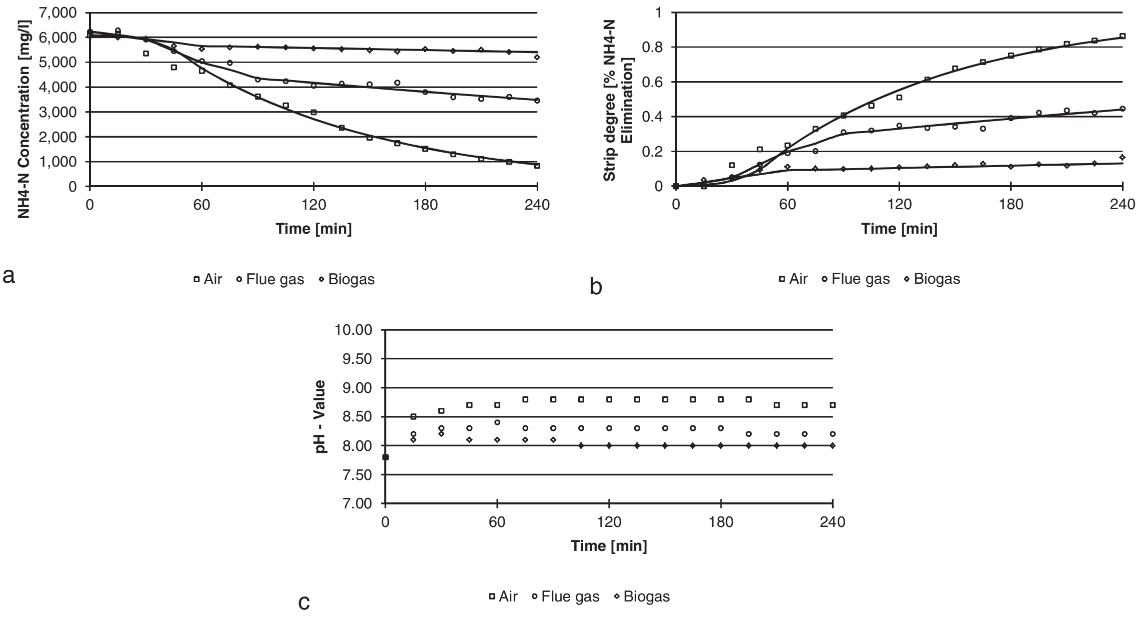

Fig. 4. Model ammonia stripping solution experiments comparing air, flue gas and biogas. (a) NH_4-N concentration. (b) NH_4-N removal [%]. (c) Trend of the pH.

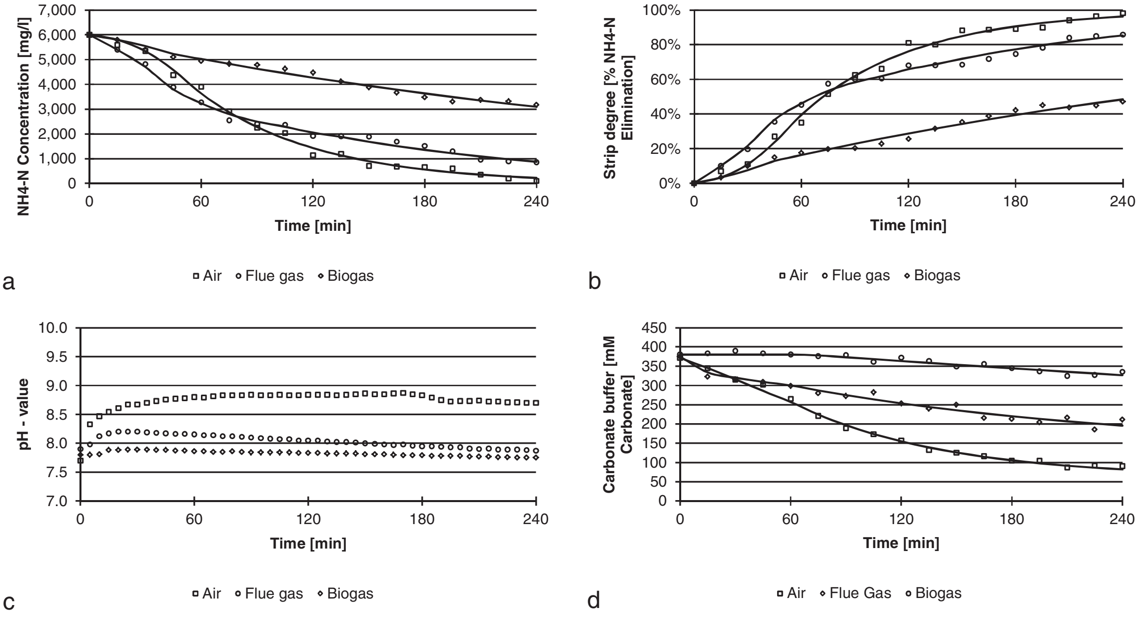

Fig. 5. Sludge ammonia stripping experiments comparing air, flue gas and biogas. (a) NH_4-N concentration. (b) NH_4-N removal [%]. (c) Trend of the pH. (d) Carbonate buffer.

3.3. Impact of alternative stripping gases

To verify the results above biogas and flue gas were compared to air stripping (Table 1). As outlined, both types of gases investigated have a certain CO_2 content. Biogas has a typical CO_2 concentration in the range of 35–55 (Risberg et al., 2013). Typical CO_2 levels in flue gas are around 14–18% (Gaj et al., 2009; Li et al., 2003). At first glance the lower CO_2 content seems to be surprising, but it must be considered that the air used for combustion has a 79% share of nitrogen and that stoichiometrically 2 mol (equivalent to volume) of oxygen are required per mol CH_4. The direct conversion of biogas into electricity and thermal energy by a CHP (the source of flue gas) is the most widely used practice (Rutz, 2012). Real flue gas is not totally oxygen free (up to 7%, (Gaj et al., 2009; Li et al., 2003)), since an excess amount of air is used to ensure the total combustion of the biogas. However, an important advantage of flue gas is that it allows direct use of waste heat in the stripping device without the need for a heat exchange unit.

The impact on stripping observed using those alternative gases (Fig. 4a) could be well explained by their CO_2 content. The final stripping degrees after 4 h (Fig. 4b) were 45% and 16% for flue gas and biogas, respectively, whereas 86% ammonia-nitrogen removal was achieved through air stripping. The pH increase (Fig. 4c) during the beginning of a stripping run was lowered at higher CO_2 concentration in the gas stream leveling to 8.8 (air), 8.3 (flue gas) and 8.0 (biogas stripping).

3.4. Efficiency of alternative strip gases on digestate samples

Subsequently the experiments were repeated using digestate samples. Anaerobic sludge contains several components that act as a buffer system, e.g. short chained fatty acids or humic compounds, and that may circumvent the above discussed impact on pH. The trend of these sludge experiments (Fig. 5a), was comparable to the model solution (Table 1). However, the achieved performance was generally better. The course of pH (sludge versus model solution, Figs. 4c and 5c) was relatively similar and does not explain this difference in removal performance. It is presumed that foaming, which only occurred with anaerobic sludge, leads to a higher exchange surface and hence enhanced NH_4-N stripping rates. The NH_4-N removal rates (Fig. 5b) achieved within 4 h were 86% (flue gas) and 47% (biogas). An additional parameter, the carbonate buffer (CO_2^{2+}, HCO_3^- and dissolved CO_2) in the stripped sludge, was measured during these experiments (Fig. 5d). These data underline the CO_2 concentration's impact in the strip gas on the CO_2 stripping efficiency.

Nevertheless, in the experiments with sludge the difference between the performance of air and flue gas was less pronounced than in ammonia bicarbonate (Table 1). The exact reason for this observation is not clear and generally attributed to matrix effects. Despite that, flue gas is still considered strongly preferable to biogas with respect to optimization of the side stream stripping process.

4. Conclusion

Side stream air stripping is a promising approach to reduce high NH_4-N levels during AD but may have adverse impact on anaerobic microflora. Inhibition due to oxygen exposure was lower than perceived but still clearly observable. Experiments with alternative stripping gases revealed a significant jump in loss of stripping performance at elevated CO_2 concentrations. Hence biogas is less appropriate as a substitute for air. For flue gas the observed impact was much lower. This slight disadvantage is compensated by distinct benefits (low O_2 carry over, heat recovery). Consequently, the use of flue gas is considered a highly viable option.

Acknowledgements

The presented work was carried out in the frame of the EC-FP7 project "ManureEcoMine – Green fertilizer upcycling from manure". ManureEcoMine is co-funded by the European Community's Framework Program (FP7/2007–2013) under Grant Agreement n° 603744. The authors would like to thank all project partners for the excellent cooperation within the project. Special thanks go to Colsen Adviesburo voor Milieutechniek BV (NL), for advice and discussion of operational parameters of the stripping unit.

References

Bonmatí, A., Flotats, X., 2003. Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. Waste Manage. 23, 261–272. http://dx.doi.org/10.1016/S0956-053X(02)00144-7.

Botheju, D., Bakke, R., 2010. Bio-gasification under partially aerated conditions; results from batch experiments. Linnaeus Eco-Tech'10, The 7th International Conference on the Establishment of Cooperation between Companies in the Nordic Countries, the Baltic Sea Region and the World, Kalmar, Sweden.

Budzianowski, W., Koziol, A., 2005. Stripping of ammonia from aqueous solutions in the presence of carbon dioxide. Chem. Eng. Res. Des. 83, 196–204. http://dx.doi.org/10.1205/cherd.03289.

Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresour. Technol. 99, 4044–4064. http://dx.doi.org/10.1016/j.biortech.2007.01.057.

Chu, L.-B., Zhang, X.-W., Li, X., Yang, F.-L., 2005. Simultaneous removal of organic substances and nitrogen using a membrane bioreactor seeded with anaerobic granular sludge under oxygen-limited conditions. Desalination 172, 271–280. http://dx.doi.org/10.1016/j.desal.2004.07.040.

De la Rubia, M.Á., Walker, M., Heaven, S., Banks, C.J., Borja, R., 2010. Preliminary trials of *in situ* ammonia stripping from source segregated domestic food waste digestate using biogas: effect of temperature and flow rate. Bioresour. Technol. 101, 9486–9492. http://dx.doi.org/10.1016/j.biortech.2010.07.096.

Gaj, K., Knop, F., Trzepierczynska, I., 2009. Technological and environmental issues of biogas combustion at municipal sewage treatment plant. Environ. Prot. Eng. 35, 73–79.

Gallert, C., Bauer, S., Winter, J., 1998. Effect of ammonia on the anaerobic degradation of protein by a mesophilic and thermophilic biowaste population. Appl. Microbiol. Biotechnol. 50, 495–501. http://dx.doi.org/10.1007/s002530051326.

Gerritse, J., 1990. Mixed chemostat cultures of obligately aerobic and fermentative or methanogenic bacteria grown under oxygen-limiting conditions. FEMS Microbiol. Lett. 66, 87–93. http://dx.doi.org/10.1016/0378-1097(90)90263-P.

Gottschalk, G., Peinemann, S., 1992. The anaerobic way of life. In: Balows, A., Trüper, H.G., Dworkin, M., Harder, W., Schleifer, K.-H. (Eds.), The Prokaryotes: A Handbook on the Biology of Bacteria. Springer-Verlag, New York, NY, pp. 300–311.

Grady, L.C.P., Daigger, G.T., Lim, H.C., 1999. Biological Wastewater Treatment, second ed. Marcel Dekker, New York, NY.

Hansen, K.H., Angelidaki, I., Ahring, B.K., 1998. Anaerobic digestion of swine manure: inhibition by ammonia. Water Res. 32, 5–12. http://dx.doi.org/10.1016/S0043-1354(97)00201-7.

Huang, J., Shang, C., 2006. Air stripping. In: Lawrence, K.W., Yung-Tse, H., Nazih, K.S. (Eds.), Advanced Physicochemical Treatment Processes, pp. 47–79.

Hungate, R.E., 1969. Chapter IV: a roll tube method for cultivation of strict anaerobes. Methods Microbiol. 3, 117–132. http://dx.doi.org/10.1016/S0580-9517(08)70503-8.

Jardin, N., Thöle, D., Wett, B., 2006. Treatment of sludge return liquors: experiences from the operation of full-scale plants. Proceedings of the Water Environment Federation, WEFTEC, pp. 5237–5255.

Kato, M.T., Field, J.A., Lettinga, G., 1993. High tolerance of methanogens in granular sludge to oxygen. Biotechnol. Bioeng. 42, 1360–1366. http://dx.doi.org/10.1002/bit.260421113.

Kumar, G., Bakonyi, P., Sivagurunathan, P., Kim, S.-H., Nemestóthy, N., Bélafi-Bakó, K., Lin, C.-Y., 2015. Enhanced biohydrogen production from beverage industrial wastewater using external nitrogen sources and bioaugmentation with facultative anaerobic strains. J. Biosci. Bioeng. 120, 155–160. http://dx.doi.org/10.1016/j.jbiosc.2014.12.011.

Li, X., Hagaman, E., Tsouris, C., Lee, J.W., 2003. Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase. Energy Fuels 17, 69–74.

Liao, P.H., Chen, A., Lo, K.V., 1995. Removal of nitrogen from swine manure wastewaters by ammonia stripping. Bioresour. Technol. 54, 17–20.

Ni, J., 1999. Mechanistic models of ammonia release from liquid manure: a review. J. Agric. Eng. Res. 72, 1–17. http://dx.doi.org/10.1006/jaer.1998.0342.

Ortner, M., Leitzinger, K., Skupien, S., Bochmann, G., Fuchs, W., 2014. Efficient anaerobic mono-digestion of N-rich slaughterhouse waste: influence of ammonia, temperature and trace elements. Bioresour. Technol. 174, 222–232. http://dx.doi.org/10.1016/j.biortech.2014.10.023.

Risberg, K., Sun, L., Levén, L., Horn, S.J., Schnürer, A., 2013. Biogas production from wheat straw and manure – impact of pretreatment and process operating parameters. Bioresour. Technol. 149, 232–237. http://dx.doi.org/10.1016/j.biortech.2013.09.054.

Rutz, D., 2012. Sustainable Heat Use of Biogas Plants. A Handbook. WIP Renewable Energies, Munich, Germany.

Scott, R.I., Williams, T.N., Lloyd, D., 1983. Oxygen sensitivity of methanogenesis in rumen and anaerobic digester populations using mass spectrometry. Biotechnol. Lett. 5, 375–380. http://dx.doi.org/10.1007/BF00131275.

Serna-Maza, A., Heaven, S., Banks, C.J., 2014. Ammonia removal in food waste anaerobic digestion using a side-stream stripping process. Bioresour. Technol. 152, 307–315.

Serna-Maza, A., Heaven, S., Banks, C.J., 2015. Biogas stripping of ammonia from fresh digestate from a food waste digester. Bioresour. Technol. 190, 66–75. http://dx.doi.org/10.1016/j.biortech.2015.04.041.

Shen, C.F., Guiot, S.R., 1996. Long-term impact of dissolved O_2 on the activity of anaerobic granules. Biotechnol. Bioeng. 49, 611–620. http://dx.doi.org/10.1002/(SICI)1097-0290(19960320)49:6<611::AID-BIT2>3.0.CO;2-R.

Tchobanoglous, G., Franklin, B.L., Stensel, D.H., Metcalf, Eddy., 2003. Wastewater Engineering: Treatment and Reuse, fourth ed. McGraw-Hill, Boston.

Wäger, F., Wirthensohn, T., Corcoba, A., Fuchs, W., 2009. Air stripping of ammonia from anaerobic digestate. In: Ashley, K., Mavinic, D., Koch, F. (Eds.), Air Stripping of Ammonia from Anaerobic Digestate, International Conference on Nutrient Recovery From Wastewater Streams, Vancouver, Canada. IWA Publishing, London, pp. 41–52.

Walker, M., Iyer, K., Heaven, S., Banks, C.J., 2011. Ammonia removal in anaerobic digestion by biogas stripping: an evaluation of process alternatives using a first order rate model based on experimental findings. Chem. Eng. J. 178, 138–145. http://dx.doi.org/10.1016/j.cej.2011.10.027.

Whitman, W.B., Bowen, T.L., Boone, D.R., 2006. The methanogenic bacteria. In: Falkow, S., Rosenberg, E., Schleifer, K.-H., Stackebrandt, E. (Eds.), Prokaryotes. A Handbook on the Biology of Bacteria, vol. 3. Springer, New York, NY, pp. 165–207.

Yadvika, Santosh, Sreekrishnan, T.R., Kohli, S., Rana, V., 2004. Enhancement of biogas production from solid substrates using different techniques – a review. Bioresour. Technol. 95, 1–10. http://dx.doi.org/10.1016/j.biortech.2004.02.010.

Zhang, L., Lee, Y.-W., Jahng, D., 2012. Ammonia stripping for enhanced biomethanization of piggery wastewater. J. Hazard. Mater. 199–200, 36–42. http://dx.doi.org/10.1016/j.jhazmat.2011.10.049.

Zitomer, D.H., 1998. Stoichiometry of combined aerobic and methanogenic cod transformation. Water Res. 32, 669–676. http://dx.doi.org/10.1016/S0043-1354(97)00258-3.

Zitomer, D.H., Shrout, J.D., 1998. Feasibility and benefits of methanogenesis under oxygen-limited conditions. Waste Manage. 18, 107–116. http://dx.doi.org/10.1016/S0956-053X(98)00008-7.